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Towards power-shaping control of the CSTR: from thermodynamics to the Brayton-Moser formulation of the dynamics [*]

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Abstract: The non-isothermal continuous stirred tank reactor (CSTR) is a classical yet complex case study of nonlinear dynamical systems. Power-shaping control is a recent approach for the control of nonlinear systems based on the physics of the dynamical system and it rests on the formulation of the dynamics in the Brayton-Moser form. The Brayton-Moser formulation of the non-isothermal continuous stirred tank reactor is investigated based on physical considerations on the system.

Keywords: non-isothermal CSTR, power-shaping control, thermodynamics

1. INTRODUCTION

Thermodynamic systems, and among them chemical reaction systems, are usually nonlinear dynamical systems. They can therefore have a complex behaviour and be difficult to analyze and to control. Stability analysis of nonlinear systems requires the use of abstract mathematical tools such as the two Lyapunov methods or the passivity theory. Over the past years, several works have combined those abstract concepts with the underlying physical phenomena giving rise to the dynamical behaviour of the system (see e.g. Eberard et al. (2005, 2006); Favache (2009); Jeltsema et al. (2004); Ortega et al. (2001)). The aim is to use the physical understanding for designing physics-based control systems that specifically act one the physical origins of the undesired behaviour. The non-isothermal continuous stirred tank reactor (CSTR) is a classical study case of nonlinear systems. Indeed the dynamical behaviour exhibits complex features, such as multiple equilibrium points. Up to now no precise physical interpretation of the complex behaviour of the non-isothermal reactor has been found (Favache and Dochain (2009b)).

Power-shaping control (Ortega et al. (2003)) has been developed in the past years as an extension of energy-balancing passivity-based control (Jeltsema et al. (2004); Ortega et al. (2001)). Power-shaping control has been introduced, firstly for the stabilization of nonlinear RLC circuits (Ortega et al. (2003)). The starting point is the Brayton-Moser formulation of the dynamics of electrical circuits (Brayton and Moser (1964)). When writing the dynamics in this particular form a special function, called

the potential function, appears. In the case of electrical circuits the potential function is related to the power dissipated in the resistors and stored in the inductors and capacitors. In the power-shaping control approach, control is achieved by reshaping this potential function by the means of the control input. The power-shaping approach has subsequently been applied to mechanical systems and then to any system, as far as its dynamics can be written in the Brayton-Moser form (García-Canseco et al. (2010)).

In previous work we have already applied the power-shaping approach to the CSTR study case (Favache and Dochain (2009a); Favache (2009)). However in those works, no systematical methodology for applying this approach to general reacting systems has been found and the Brayton-Moser form has not been linked precisely to thermodynamics. In this paper we show how the Brayton-Moser formulation of a general CSTR can be deduced from thermodynamic considerations. We shall first give a brief overview of the power-shaping approach (Section 2). Section 3 presents the dynamical model of the CSTR. Then in Section 4 we shall show how the thermodynamic theory can be used to find the Brayton-Moser representation of a general CSTR. Finally in Section 5 some comments on the previously used assumptions shall be presented.

Notations All vectors (including the gradients) are column vectors. The notation x^t denotes the transpose of the vector or the matrix x.

2. POWER-SHAPING CONTROL

In this section we briefly explain the basic principles of the power-shaping approach. The statements are given without any proof. For more details, the reader can refer

to García-Canseco et al. (2010); Jeltsema and Scherpen (2007); Ortega et al. (2003).

2.1 The Brayton-Moser formulation

Let us consider a dynamic system of dimension N with m inputs. The state of the system is given by the vector $x \in \mathbb{R}^N$ and the input is given by vector $u_c \in \mathbb{R}^m$. As already said, the power-shaping approach rests on on a particular formulation of the dynamics, namely the Brayton-Moser formulation (Brayton and Moser (1964)). The system dynamics are of following form:

$$\boldsymbol{Q}(x) \frac{dx}{dt} = \nabla \mathscr{P}(x) + G(x) u_c \qquad (1)$$

where $\boldsymbol{Q}(x) : \mathbb{R}^N \to \mathbb{R}^N \times \mathbb{R}^N$ is a non-singular square matrix, $\mathscr{P}(x) : \mathbb{R}^N \to \mathbb{R}$ is a scalar function of the state and $G(x) : \mathbb{R}^N \to \mathbb{R}^N \times \mathbb{R}^m$. Additionally the symmetric part of the matrix $\boldsymbol{Q}(x)$ is negative semi-definite, i.e.:

$$\boldsymbol{Q}(x) + \boldsymbol{Q}^t(x) \preceq 0. \qquad (2)$$

The function $\mathscr{P}(x)$ is called the potential function. In electrical and mechanical systems, the potential function has the units of power and is related to the dissipated power in the system. In the first one it is related to the so-called content and co-content of the resistances; in the latter it is related to the Rayleigh dissipation function (Jeltsema and Scherpen (2007); Ortega et al. (2003)).

Let us now assume the system dynamics is given by the following relation:

$$\frac{dx}{dt} = f(x) + g(x) u_c \qquad (3)$$

where $f(x) : \mathbb{R}^N \to \mathbb{R}^N$ and $g(x) : \mathbb{R}^N \to \mathbb{R}^N \times \mathbb{R}^m$. The system (3) can be written in the form (1) if there exists a non-singular matrix $\boldsymbol{Q}(x)$ fulfilling (2) and that solves following partial differential equation [1]:

$$\nabla \left(\boldsymbol{Q}(x) f(x) \right) = \nabla^t \left(\boldsymbol{Q}(x) f(x) \right) \qquad (4)$$

$\mathscr{P}(x)$ is the solution of the following partial differential equation system:

$$\nabla \mathscr{P}(x) = \boldsymbol{Q}(x) f(x) \qquad (5)$$

and the function $G(x)$ is given by $G(x) = \boldsymbol{Q}(x) g(x)$.

2.2 Controller design

Let us assume that the system dynamics can be expressed by using the Brayton-Moser equations presented before. The desired equilibrium state is denoted by x^*. The principle of power-shaping control is to choose the input $u_c(x)$ such that in closed loop the system dynamics are given by the following relation:

$$\frac{dx}{dt} = \nabla \mathscr{P}_d(x) \qquad (6)$$

where $\mathscr{P}_d(x) : \mathbb{R}^N \to \mathbb{R}$ is the re-shaped potential function. The desired equilibrium point x^* must be a local minimum of the potential function $\mathscr{P}_d(x)$ in order to be locally asymptotically stable. The function $\mathscr{P}_d(x)$ can be used as a Lyapunov function for the closed-loop system.

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[1] This condition is equivalent to the existence of the potential function $\mathscr{P}(x)$.

The function $\mathscr{P}_d(x)$ cannot be chosen arbitrarily since the following relation must be fulfilled:

$$g^\perp(x) \boldsymbol{Q}^{-1}(x) \nabla \mathscr{P}_a(x) = 0 \qquad (7)$$

where $\mathscr{P}_a(x) = \mathscr{P}_d(x) - \mathscr{P}(x)$ and

$$g^\perp(x) : \mathbb{R}^N \to \mathbb{R}^{N-m} \times \mathbb{R}^N$$

is a full-rank left annihilator of $g(x)$ (i.e. $g^\perp(x) g(x) = 0$ with rank $\left(g^\perp(x) \right) = N - m$). Under these conditions, a control input $u(x)$ that re-shapes $\mathscr{P}(x)$ into $\mathscr{P}_d(x)$ can be found.

3. THE CSTR DYNAMICAL MODEL

3.1 The dynamical model

We shall use here the dynamic model of the CSTR presented in Favache and Dochain (2009b). This model is more correct from a thermodynamic point of view than the usual model (e.g. Aris and Amundson (1958)). In particular our model has less underlying assumptions such as the constant heat capacity of the mixture. It is derived directly from the mass and internal energy balances. Let us consider a CSTR in which a reaction in a liquid medium takes place and involves two chemical species A and B: $A \rightleftharpoons \nu_B B$ where ν_B is a stoichiometric coefficient. The reactant and the product are dissolved in an inert I. The reactor is connected to a jacket in which a cooling fluid is circulating.

Let us consider the following modelling assumptions.

(1) The reactor is perfectly mixed.
(2) The inlet and outlet volume flow rates are equal.
(3) The concentrations of A and B in the reactor and in the inlet flow are very low compared to the concentration of the inert I so that only the molar volume v_I of I has to be taken into account for the determination of the total volume. The molar volume v_I is constant and in particular it is independent of the quantity of the dissolved species A and B or of the temperature.
(4) The molar constant pressure heat capacity C_{p_i} of each species is constant.
(5) The thermodynamic model considered here is that of an ideal liquid mixture.
(6) The time evolution is a quasi-static process.
(7) The global reaction rate r depends only on the temperature T of the mixture, and on the concentration of the involved species, i.e. A and B. More precisely the reaction rate is in fact composed of two individual reaction rates, one for the forward reaction $(A \rightarrow \nu_B B)$, r_f, and one for the backward reaction $(\nu_B B \rightarrow A)$, r_b. The global reaction rate is given by $r(\cdot) = r_f(\cdot) - r_b(\cdot)$. $r > 0$ if the net reaction is such that A is consumed, whereas $r < 0$ if A is produced. The case $r = 0$ corresponds to the chemical equilibrium. Each reaction rate is a strictly increasing function of the concentration of its reactant, i.e. A for the forward reaction and B for the backward reaction, but it does not depend on the concentration of its respective product. The reaction rates are equal to zero if the concentration of their reactant is equal to zero.

As it can be seen in Favache and Dochain (2009b) and in Favache (2009) these assumptions imply that the volume

and the quantity of I are constant. The reaction rate r is a function of the temperature T and the concentrations of A and B, i.e. $\frac{n_A}{V}$ and $\frac{n_B}{V}$. But the volume is constant and hence the concentrations of A and B are proportional to the quantity of matter n_A and n_B. For the sake of notation simplicity, we shall therefore denote the dependence of the reaction rate as $r\left(T, n_A, n_B\right)\ (= r_f\left(T, n_A\right) - r_b\left(T, n_B\right))$ instead of the usual way that would be $r\left(T, \frac{n_A}{V}, \frac{n_B}{V}\right)$.

This leads to the following dynamical model:

$$
\begin{cases}
\dfrac{dn_A}{dt} = \dfrac{F}{V}\left(C_A^{in} V - n_A\right) - r\left(\hat{T}\left(n_A, n_B, U\right), n_A, n_B\right) V \\[2mm]
\dfrac{dn_B}{dt} = \dfrac{F}{V}\left(C_B^{in} V - n_B\right) \\[1mm]
\qquad\qquad + \nu_B r\left(\hat{T}\left(n_A, n_B, U\right), n_A, n_B\right) V \\[2mm]
\dfrac{dU}{dt} = \dfrac{F}{V}\left(h^{in} V - \hat{H}\left(n_A, n_B, U\right)\right) + \dot{Q}
\end{cases}
$$
$$(8)$$

where n_A, n_B and U stay respectively for the quantity of A, B and for the internal energy of the mixture; F is the volumetric flow rate; C_A^{in}, C_B^{in} and h^{in} are respectively the inlet concentrations of A and B and the volumetric enthalpy of the inlet flow; $\dot{Q}$ is the heat exchange flow rate. $\hat{T}\left(n_A, n_B, U\right)$ and $\hat{H}\left(n_A, n_B, U\right)$ are respectively the temperature and the enthalpy as the function of n_A, n_B and U and are given by the thermodynamic model (here the ideal liquid). In the sequel we shall use the following notation: $\hat{r}\left(n_A, n_B, U\right) = r\left(\hat{T}\left(n_A, n_B, U\right), n_A, n_B\right)$.

Contrary to what has been done in Favache and Dochain (2009b) and in Favache (2009) we shall consider consider two control inputs to our system: the heat exchange flow rate $\dot{Q}$ and the dilution rate $\frac{F}{V}$. This corresponds to the system studied in Ramírez et al. (2009) where the authors considered CSTR model with the usual assumptions for some particular reaction network. However, as the authors mention, they did not manage to extend their result to more general cases. Using the notations of (3) with $u_c = \left[\frac{F}{V}, \dot{Q}\right]^t$, we have:

$$
f\left(n_A, n_B, U\right) = \begin{pmatrix} -\hat{r}\left(n_A, n_B, U\right) V \\ \nu_B \hat{r}\left(n_A, n_B, U\right) V \\ 0 \end{pmatrix} \tag{9}
$$

and

$$
g\left(n_A, n_B, U\right) = \begin{pmatrix} C_A^{in} V - n_A & 0 \\ C_B^{in} V - n_B & 0 \\ \left(h^{in} V - \hat{H}\left(n_A, n_B, U\right)\right) & 1 \end{pmatrix}.
$$

3.2 The unforced system equilibria

For the unforced system ($u_c = 0$), the equilibrium points of (8) are given by the set $\left\{\left(\bar{n}_A, \bar{n}_B, \bar{U}\right)\middle|\hat{r}\left(\bar{n}_A, \bar{n}_B, \bar{U}\right) = 0\right\}$. As a consequence there are an infinity of equilibrium points.

The trajectories are such that:
$$U = U\left(t = 0\right)$$
$$\nu_B n_A + n_B = \nu_B n_A\left(t = 0\right) + n_B\left(t = 0\right).$$
As a consequence, starting from the initial point $\left(n_A^0, n_B^0, U^0\right)$, the only equilibrium points that can be reached are the solution of the following system:

$$
\begin{cases}
\hat{r}\left(\bar{n}_A, \bar{n}_B, \bar{U}\right) = 0 \\
\nu_B \bar{n}_A + \bar{n}_B = \nu_B n_A^0 + n_B^0 \\
\bar{U} = U^0
\end{cases} \tag{10}
$$

Lemma 1. (10) has an equilibrium in the physically admissible domain, i.e. $n_A \geq 0$, $n_B \geq 0$.

Proof. An equilibrium point is the solution of (10) only if $\bar{n}_A$ is the solution of the following equation:
$$\tilde{r}\left(\bar{n}_A\right) = \hat{r}\left(\bar{n}_A, \nu_B\left(n_A^0 - n_A\right) + n_B^0, U^0\right) = 0.$$
The solution is located in the physically admissible domain if and only if $\tilde{r}\left(n_A\right)$ has a root in the interval $\left[0; n_A^0 - n_A + \frac{n_B^0}{\nu_B}\right]$. We have $\lim\limits_{n_A \to 0} \tilde{r}\left(n_A\right) = -r_b < 0$ and
$$\lim\limits_{\nu_B n_A \to \nu_B n_A^0 + n_B^0} \tilde{r}\left(n_A\right) = r_f > 0.$$
As a consequence $\tilde{r}\left(n_A\right)$ has at least one root in the interval $\left[0; n_A^0 - n_A + \frac{n_B^0}{\nu_B}\right]$.

4. THE BRAYTON-MOSER FORM OF THE CSTR

4.1 General solution

Our aim is to find the Brayton-Moser formulation of (8). To do this we have to solve the partial differential equation system (4). Using (9) we write:

$$
\boldsymbol{Q}\left(n_A, n_B, U\right) f\left(n_A, n_B, U\right)
$$
$$
= \begin{pmatrix} -q_{11} + q_{12}\nu_B \\ -q_{21} + q_{22}\nu_B \\ -q_{31} + q_{32}\nu_B \end{pmatrix} \hat{r}\left(n_A, n_B, U\right) V
$$

where $q_{ij}\left(n_A, n_B, U\right)$ is the entry in position (i, j) of $\boldsymbol{Q}\left(n_A, n_B, U\right)$. With the following notations (for $i = 1, 2, 3$):
$$a_i\left(n_A, n_B, U\right) = \nu_B q_{i2}\left(n_A, n_B, U\right) - q_{i1}\left(n_A, n_B, U\right)$$
(4) is written as follows (for $i, j = 1, 2, 3$):

$$
\frac{\partial}{\partial x_j}\left[a_i\left(n_A, n_B, U\right)\hat{r}\left(n_A, n_B, U\right) V\right]
$$
$$
= \frac{\partial}{\partial x_i}\left[a_j\left(n_A, n_B, U\right)\hat{r}\left(n_A, n_B, U\right) V\right] \quad (11)
$$

where $x = \left[n_A, n_B, U\right]$. The general form of the solutions is given as follows:

$$a_1\left(n_A, n_B, U\right)\hat{r}\left(n_A, n_B, U\right) V$$
$$= \int \phi\left(n_A, n_B, U\right) dn_B + \psi\left(U, n_A\right)$$
$$a_2\left(n_A, n_B, U\right)\hat{r}\left(n_A, n_B, U\right) V$$
$$= \int \phi\left(U, n_A, n_B\right) dn_A + \varphi\left(U, n_B\right)$$
$$a_3\left(n_A, n_B, U\right)\hat{r}\left(n_A, n_B, U\right) V$$
$$= \int\int \frac{d\phi}{dU} dn_A dn_B + \int \frac{d\psi}{dU} dn_A + \int \frac{\partial\varphi}{\partial U} dn_B + \rho\left(U\right)$$
$$(12)$$

where $\phi\left(n_A, n_B, U\right)$, $\psi\left(n_A, U\right)$, $\varphi\left(n_B, U\right)$ and $\rho\left(U\right)$ are arbitrary real scalar functions. Since these functions are arbitrary, they could have units that are not power-units. The corresponding matrix $\boldsymbol{Q}\left(n_A, n_B, U\right)$ is given by the following expression:

$$\boldsymbol{Q}\left(n_A, n_B, U\right) = \begin{pmatrix} \nu_B q_{12}\left(x\right) - a_1\left(x\right) & q_{12}\left(x\right) & q_{13}\left(x\right) \\ \nu_B q_{22}\left(x\right) - a_2\left(x\right) & q_{22}\left(x\right) & q_{23}\left(x\right) \\ \nu_B q_{32}\left(x\right) - a_3\left(x\right) & q_{32}\left(x\right) & q_{33}\left(x\right) \end{pmatrix}$$
(13)

where $q_{i2}\left(U, n_A, n_B\right)$ and $q_{i3}\left(U, n_A, n_B\right)$ for $i = 1, 2, 3$ can be chosen arbitrarily.

Inserting (12) into (5) we obtain the following expression for the potential function $\mathscr{P}\left(n_A, n_B, U\right)$:

$$\mathscr{P}\left(n_A, n_B, U\right) = \iint \phi\left(n_A, n_B, U\right) \mathrm{d}n_A \mathrm{d}n_B$$
$$+ \int \psi\left(n_A, U\right) \mathrm{d}n_A + \int \varphi\left(n_B, U\right) \mathrm{d}n_B + \int \rho\left(U\right) \mathrm{d}U + \omega$$
(14)

where ω is some real constant.

4.2 Particular solution

In Section 4.1 we have presented the general solution to (4) in the case of a CSTR. This solution is a general solution and nearly any function can be used as the Brayton-Moser potential since $\phi\left(n_A, n_B, U\right)$, $\psi\left(n_A, U\right)$, $\varphi\left(n_B, U\right)$, $\rho\left(U\right)$ and ω can be chosen arbitrarily. However we have only considered the condition (4) and all the choices do not lead to a non-singular matrix $\boldsymbol{Q}\left(n_A, n_B, U\right)$ that fulfills also (2). In this section we shall use thermodynamic considerations to find a non-singular particular solution that fulfills (2).

The two following lemmas shall be helpful in the sequel. Since they are rather trivial, they are given without proof.

Lemma 2. For a non-singular matrix $\boldsymbol{Q}\left(x\right)$, (2) implies that $\frac{d\mathscr{P}}{dt} \leq 0$ when $u_c = 0$.

Lemma 3. For a non-singular matrix $\boldsymbol{Q}\left(x\right)$, (2) implies that $\nabla\mathscr{P}\left(\bar{x}\right) = 0$ at the equilibrium points $\bar{x}$ when $u_c = 0$.

From Lemmas 2 and 3, it is obvious that the particular solution leads to a quantity that is decreasing along the trajectories when the inputs are set to zero and that has a local minimum at the equilibria. From the second principle of thermodynamics, the entropy production is always positive. In our case the unforced system corresponds to a batch reactor, i.e. an isolated system. For such a system, the entropy production is zero at the equilibrium and hence the entropy production has a local minimum. In Glansdorff and Prigogine (1964) a general evolution criterion is given for all macroscopic systems submitted to time independent boundary conditions. For some thermodynamic systems, this criterion implies that the entropy production is decreasing along the trajectories. Therefore we shall use the entropy production σ_S as a candidate for the Brayton-Moser potential.

For an isolated system the entropy production is equal to the entropy variation:

$$\sigma_S = \frac{dS}{dt} = \frac{\partial^t \hat{S}}{\partial x}\frac{dx}{dt} = \left(\frac{\mu_A}{T} - \nu_B \frac{\mu_B}{T}\right)\hat{r}\left(n_A, n_B, U\right)V$$

where $\hat{S}\left(n_A, n_B, U\right)$ is the entropy as a function of n_A, n_B, U and μ_i is the chemical potential of species i. Indeed from thermodynamic theory we have $\frac{\partial \hat{S}}{\partial x} = \left(-\frac{\mu_A}{T}, -\frac{\mu_B}{T}, \frac{1}{T}\right)^t$ (Callen (1985)).

Assumption 1. The reaction kinetics are such that $\Lambda\hat{r}\left(n_A, n_B, U\right) \geq 0$ where $\Lambda = \frac{\mu_A}{T} - \nu_B \frac{\mu_B}{T}$ is the reaction affinity, with equality if and only if both $\Lambda = 0$ and $\hat{r}\left(n_A, n_B, U\right) = 0$.

This assumption is necessary to ensure that the second principle of thermodynamics is fulfilled, namely that the entropy production is always non-negative. It means that the reaction evolves always in the direction of decreasing affinity.

The time variation of the entropy production is given as follows:

$$\frac{d\sigma_S}{dt} = \left(\hat{r}V\right)\left(\nu_B \frac{\partial\sigma_S}{\partial n_B} - \frac{\partial\sigma_S}{\partial n_A}\right)$$
$$= -\left(\hat{r}V\right)^2\left(\frac{d\Lambda}{dn_A} - \frac{d\Lambda}{dn_B}\nu_B\right)$$
$$- \Lambda\hat{r}V\left(\frac{d\left(\hat{r}V\right)}{dn_A} - \frac{d\left(\hat{r}V\right)}{dn_B}\nu_B\right). \quad (15)$$

Let us first consider the term $\frac{d\Lambda}{dn_A} - \frac{d\Lambda}{dn_B}\nu_B$:

$$\frac{d\Lambda}{dn_A} - \frac{d\Lambda}{dn_B}\nu_B = -\begin{pmatrix}\nu_B & -\nu_B^2 & 0\end{pmatrix}\frac{\partial^2\hat{S}}{\partial x^2}\begin{pmatrix}\nu_B \\ -\nu_B^2 \\ 0\end{pmatrix}.$$

A consequence of the second principle of thermodynamics is that the entropy function is concave, i.e. $\frac{\partial^2\hat{S}}{\partial x^2} \preceq 0$ (see e.g. Callen (1985)). As a consequence $\frac{d\Lambda}{dn_A} - \frac{d\Lambda}{dn_B}\nu_B \geq 0$.

However nothing can be said in general about the sign of the second term.

Assumption 2. The reaction kinetics $r\left(T, n_A, n_B\right)$ are such that $\frac{d\sigma_S}{dt} \leq 0$.

Assumption 3. The limit $\lim_{\hat{r}\left(n_A, n_B, U\right) \to 0} \frac{\Lambda}{\hat{r}\left(n_A, n_B, U\right)}$ is defined and finite.

Proposition 4. The following particular solution leads to a matrix $\boldsymbol{Q}\left(n_A, n_B, U\right)$ that fulfills (2) and (4):

$$\boldsymbol{Q}\left(n_A, n_B, U\right) = \begin{pmatrix} \nu_B \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V} - \frac{\partial\sigma_S}{\partial n_A}\frac{1}{\hat{r}V} & \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V} & 0 \\ q_{21} & q_{22} & 0 \\ -\frac{\partial\sigma_S}{\partial U}\frac{1}{\hat{r}V} & 0 & q_{33} \end{pmatrix}$$
(16)

with

$$q_{21} = \frac{4\alpha}{\nu_B}\left(\nu_B \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V} - \frac{\partial\sigma_S}{\partial n_A}\frac{1}{\hat{r}V}\right) - \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V}$$

$$q_{22} = \frac{4\alpha}{\nu_B^2}\left(\nu_B \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V} - \frac{\partial\sigma_S}{\partial n_A}\frac{1}{\hat{r}V}\right)$$

$$q_{33} = \beta\frac{\left(\frac{\partial\sigma_S}{\partial U}\frac{1}{\hat{r}V}\right)^2}{4\left(1 - \alpha\right)\left(\nu_B \frac{\partial\sigma_S}{\partial n_B}\frac{1}{\hat{r}V} - \frac{\partial\sigma_S}{\partial n_A}\frac{1}{\hat{r}V}\right)}$$

where $0 < \alpha < 1$ and $\beta > 1$ are two scalar constants.

Proof. First let us show that (16) fulfills (4). It is sufficient to prove that (16) is a particular choice of (13). By choosing $\psi\left(n_A, U\right) = \varphi\left(n_B, U\right) = \rho\left(U\right) = \omega = 0$ and:

$$\phi\left(n_A, n_B, U\right) = \frac{\partial^2\sigma_S}{\partial n_A \partial n_B}$$

we have for $i = 1, 2, 3$:

$$a_i\left(n_A, n_B, U\right) = \frac{\partial \sigma_S}{\partial x_i} \frac{1}{\hat{r}\left(n_A, n_B, U\right) V}$$
$$= \frac{\partial \Lambda}{\partial x_i} + \frac{\Lambda}{\hat{r}\left(n_A, n_B, U\right) V} \frac{\partial \left(\hat{r} V\right)}{\partial x_i}$$

Assumption 3 guarantees that this quantity is well defined. It is easy to see that (16) is indeed of the form of (13).

Using the principal minors of $\boldsymbol{Q} + \boldsymbol{Q}^t$, $\boldsymbol{Q} + \boldsymbol{Q}^t \prec 0$ if and only if:

$$0 > 2\left(\nu_B \frac{\partial \sigma_S}{\partial n_B} \frac{1}{\hat{r}V} - \frac{\partial \sigma_S}{\partial n_A} \frac{1}{\hat{r}V}\right)$$
$$0 < 4\left(\nu_B \frac{\partial \sigma_S}{\partial n_B} \frac{1}{\hat{r}V} - \frac{\partial \sigma_S}{\partial n_A} \frac{1}{\hat{r}V}\right) q_{22} - \left(\nu_B q_{22}\right)^2$$
$$0 > 2 q_{33} \left[4\left(\nu_B \frac{\partial \sigma_S}{\partial n_B} \frac{1}{\hat{r}V} - \frac{\partial \sigma_S}{\partial n_A} \frac{1}{\hat{r}V}\right) q_{22} - \left(\nu_B q_{22}\right)^2\right]$$
$$- 2 q_{22} \left(\frac{\partial \sigma_S}{\partial U} \frac{1}{\hat{r}V}\right)^2$$

From Assumption 2, these conditions are indeed fulfilled.

Proposition 5. If the kinetics fulfill the Assumptions 1-3, then the system dynamics (8) can be put into the Brayton-Moser form (1) with $\boldsymbol{Q}\left(n_A, n_B, U\right)$ given in (16) and $\mathscr{P}\left(n_A, n_B, U\right) = \sigma_S$.

Proof. This follows directly from Proposition 4 and (14).

In the electrical (mechanical) cases the matrix $\boldsymbol{Q}\left(x\right)$ can also be given a physical interpretation since the elements correspond to the capacitors (springs) and to the inductors (masses) (Jeltsema and Scherpen (2007)). In the case of a chemical system it has not been possible to find a similar interpretation and in this work we have focused on the physical interpretation of the potential function.

5. SOME COMMENTS ABOUT THE ASSUMPTIONS

The matrix proposed in Proposition 4 can be used only if the Assumptions 1 to 3 are fulfilled. Otherwise the matrix could be either not defined at some states or condition (2) may not be fulfilled everywhere. Therefore we shall comment these assumptions with regard to commonly used kinetics. We shall consider here the most simple and usual case, namely mass action law kinetics with Arrhenius type dependence:

$$r\left(T, n_A, n_B\right) = \underbrace{k_f\left(T\right)\left(\frac{n_A}{V}\right)}_{r_f} - \underbrace{k_b\left(T\right)\left(\frac{n_B}{V}\right)^{\nu_B}}_{r_b}$$

with $k_f\left(T\right) = k_{f_0} \exp\left(\frac{E_f}{RT}\right)$ and $k_b\left(T\right) = k_{b_0} \exp\left(\frac{E_b}{RT}\right)$, where k_{f_0}, k_{b_0} are the Arrhenius constants of the forward and backward reaction, respectively, E_f and E_b are the activation energies of the forward and backward reaction, respectively and R is the ideal gas constant.

5.1 Assumption 1

As already said this assumption implies that the reaction evolves always in the direction of decreasing the reaction affinity. In particular we must have:

$$r\left(T, n_A, n_B\right) = 0 \quad \text{if and only if} \quad \Lambda = 0 \qquad (17)$$

For an ideal liquid mixture where A and B are very dilute, the reaction affinity is given by the following expression:

$$\Lambda = RT \ln\left(\frac{\frac{n_A}{CV}}{\left(\frac{n_B}{CV}\right)^{\nu_B}}\right) - T\left(-\Delta_r S\right) + \left(-\Delta_r H\right)$$

where C is the total molar concentration which is constant for dilute mixtures and

$$\left(-\Delta_r H\right) = \left(h_{0_A} - \nu_B h_{0_B}\right) + \left(C_{p_A} - \nu_B C_{p_B}\right) T$$
$$\left(-\Delta_r S\right) = \left(s_{0_A} - \nu_B s_{0_B}\right) - \left(C_{p_A} - \nu_B C_{p_B}\right) \frac{1}{T} \ln\left(\frac{T}{T_0}\right)$$

are the reaction enthalpy and entropy with T_0 the reference temperature, h_{0_i} and s_{0_i} the reference molar enthalpy and molar entropy of species i. When (17) is fulfilled, we have:

$$RT \ln\left(\frac{\frac{n_A}{V}}{\left(\frac{n_B}{V}\right)^{\nu_B}}\right) = T\left(-\Delta_r S\right) - \left(-\Delta_r H\right) - \left(\nu_B - 1\right) \ln C$$
$$= RT \ln\left(\frac{k_b\left(T\right)}{k_f\left(T\right)}\right)$$

This equality can be fulfilled if and only if:

$$E_b - E_f = \left(-\Delta_r H\right) \qquad (18a)$$
$$C_{p_A} - \nu_B C_{p_B} = 0 \qquad (18b)$$
$$\ln\left(\frac{k_{b_0}}{k_{f_0}}\right) = -\frac{s_{0_A} - s_{0_B}}{R} - \left(\nu_B - 1\right) \ln C \qquad (18c)$$

Remark 6. (18a) is a consequence of the van't Hoff relation for ideal mixtures. (18b) expresses the fact that $\left(-\Delta_r H\right)$ and $\left(-\Delta_r S\right)$ are independent of the temperature, which is often the case practically if the temperature range is not too large.

Remark 7. Assumption 1 is necessary for the second principle of thermodynamics to be fulfilled. In a first view, one could therefore think that all reaction kinetics trivially fulfill this assumption. The above considerations show that even the simplest and most usual reaction kinetics do not satisfy this assumption and that the additional conditions (18) are required. This comes from the fact that the kinetics models usually considered in chemical engineering very often do not depend on the affinity: this is indeed due to the fact that kinetics is largely based on experiments.

It can be also seen that if the above relations are fulfilled, then the inequalities of Assumption 1 are also satisfied.

5.2 Assumption 2

As it has been explained in Section 4 this assumption depends on the second term of (15), i.e. $\frac{d(\hat{r}V)}{dn_A} - \frac{d(\hat{r}V)}{dn_B}\nu_B$. This term depends only on the reaction kinetics. A sufficient condition for Assumption 2 to be fulfilled is $\frac{d(\hat{r}V)}{dn_A} - \frac{d(\hat{r}V)}{dn_B}\nu_B \geq 0$. For mass action law kinetics with Arrhenius type dependence and using the relations (18), we have:

$$\frac{\partial\left(\hat{r}V\right)}{\partial n_A} - \frac{\partial\left(\hat{r}V\right)}{\partial n_B}\nu_B$$
$$= \frac{\partial\left(rV\right)}{\partial n_A} - \frac{\partial\left(rV\right)}{\partial n_B}\nu_B - \frac{\partial\left(rV\right)}{\partial T} \frac{\left(-\Delta_r H\right)}{\mathscr{C}_p V}$$
$$= \frac{\partial\left(r_f V\right)}{\partial n_A} + \frac{\partial\left(r_b V\right)}{\partial n_B}\nu_B + \frac{\left(-\Delta_r H\right)^2}{\mathscr{C}_p V R T^2} r_b V$$
$$- \frac{\left(-\Delta_r H\right)}{\mathscr{C}_p V} \frac{E_f}{R T^2} r V$$

where $\mathscr{C}_p$ is the total constant pressure volumetric heat capacity ($\mathscr{C}_p V = \sum_{i=A,B,I} C_{p_i} n_i$). All terms except the last one are clearly positive. The last term can be positive or negative depending on the state. It depends on the numerical values of the parameter if this term can be sufficiently negative such that $\frac{d\sigma_S}{dt} > 0$.

However it can be easily seen that the following set:
$$\{(n_A, n_B, U)|\,(-\Delta_r H)\,\hat{r}\,(n_A, n_B, U)\,V \geq 0\}$$
is an invariant set of the system with $u_c = 0$ since the sets
$$\{(n_A, n_B, U)|\,\hat{r}\,(n_A, n_B, U)\,V \geq 0\}$$
and
$$\{(n_A, n_B, U)|\,\hat{r}\,(n_A, n_B, U)\,V \leq 0\}$$
are invariant sets. Hence it is always possible to restrict the state plane to an invariant set where Assumption 2 is fulfilled.

5.3 Assumption 3

Using (18), it is possible to write the following equality:
$$\frac{\Lambda}{rV} = -\frac{RT}{k_f\,(T)\,n_A}\frac{\ln\left(\frac{k_b(T)}{k_f(T)}\frac{n_B^{\nu_B}}{n_A}V^{1-\nu_B}\right)}{1 - \frac{k_b(T)}{k_f(T)}\frac{n_B^{\nu_B}}{n_A}V^{1-\nu_B}}$$

Using l'Hospital's rule we have:
$$\lim_{\hat{r}(n_A, n_B, U)\to 0}\frac{\Lambda}{rV} = -\frac{RT}{k_f\,(T)\,n_A}$$
Assumption 3 is fulfilled as a consequence of Assumption 1.

6. CONCLUSION

Applying the power-shaping methodology for designing control systems requires first to write the uncontrolled system dynamics in the Brayton-Moser form. This step is often limiting since it requires the solution of a partial differential equation system which can be difficult to solve. In this paper we propose a general solution for this partial differential equation system in the case of a CSTR with control inputs being the heat exchange flow rate and the dilution coefficient. Furthermore we propose a particular solution based on thermodynamic considerations. This particular solution uses the entropy production as the Brayton-Moser potential.

This approach is only valid under some assumptions, among them that the entropy production is decreasing along the system trajectories. These assumptions may be not fulfilled for all reaction kinetics. However we have shown that in the simple case of mass action law kinetics with Arrhenius type dependence these assumptions is fulfilled in at least one invariant subset of the state plane.

Due to the symmetry in dynamics the solution that has been proposed here should be easily extendable to more complex reaction networks. However it could be more difficult to have reaction kinetics that fulfill the assumption of decreasing entropy production.

The next step is of course to use this Brayton-Moser formulation to design control systems based on the power-shaping approach, which in our case is rather an entropy production shaping approach.

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