Thermodynamics and chemical systems stability: The CSTR case study revisited

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ABSTRACT

This paper is dedicated to the stability analysis of the Continuous Stirred Tank Reactor (CSTR) model by considering thermodynamics based arguments. Different Lyapunov function candidates related to the thermodynamics, more specifically based on the entropy, the entropy production and the internal energy, are considered. These provide new insight and physical interpretation in the stability/instability of the equilibrium points of the CSTR. This includes in particular extension of the results of Georgakis [C. Georgakis, On the use of extensive variables in process dynamics and control, Chemical Engineering Science 41(6) (1986) 1471–1484] for less restrictive conditions on the system dynamics and thermodynamics, and invariants sets for the stable equilibrium points of the CSTR by considering an internal energy based Lyapunov function.

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1. Introduction

The analysis and design of control algorithms are largely based on system theory tools, and in particular on the stability "à la Lyapunov" which is indeed intrinsically based and justified on energy considerations, e.g. [19]. It is therefore natural to consider the thermodynamics theory for the control design of chemical processes. However, if in many situations it is rather easy to describe the Lyapunov theory in terms of energy for electrical and mechanical systems, this is unfortunately not the case for reaction systems. The link between thermodynamics and system theory has been an active research area over the years starting with the seminal works of Aris and Amundson (see, e.g., [18]) and those of Dammers and Tels [6], Tarbell [17] or Georgakis [11]. More recently, Alonso, Ydstie and coworkers have been quite active in exploring this research area, resulting in very insightful works on the control design of process systems (see, e.g., [1–3,20,21]), while Rouchon and Creff provided important results about the flash dynamics [15].

The objective of this paper is to present several old and new results that aim at linking the thermodynamics and the system theory concepts via the Continuous Stirred Tank Reactor (CSTR) case study. The choice of the CSTR is indeed driven by its simplicity while emphasizing typical important features of reaction system models: it combines energy and mass balances, it is non-linear and is possibly characterized by multiple steady states, the system state variables (concentration, temperature) are non-negative, it is an open system and the balance equations combine kinetics and hydrodynamics. The CSTR has also been largely studied in the literature, yet the way to systematically link thermodynamics and stability theory even for this apparently simple case study remains an open question. The main reason is probably mainly due to the complexity of the chemical thermodynamics and the difficulty to link its concepts with those of system theory. As a matter of example, the notion of entropy is a priori very attractive to analyze the stability of a reaction system (and therefore of the CSTR model) but, as it will be illustrated in the present manuscript, its transcription in terms of Lyapunov based stability is not obvious. It is probably worth noting that the negativeness of the entropy production variation can be emphasized with linear phenomenological laws while no general demonstration is available with non-linear ones (which corresponds indeed to a large class of chemical systems) (e.g. [7, pp. 53–56]). Symptomatically, so far the efforts to take advantage of the positivity of the state variables to consider Lyapunov functions that are not the classical quadratic functions (representative of the energy of mechanical and electrical systems, but not of reactions systems[1]) have produced very limited results, the most illustrative one being the logarithm based function suggested by Feinberg [8] for isothermal reactors. Our objective in the present paper is to clarify as much as possible the reasons that makes the stability analysis with thermodynamical functions so complex. With that respect, the paper of Rouchon and Creff [15] dedicated to the flash case study (i.e. without reaction) provides a good basis for an appropriate explanation: the main difficulty for such a

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[1] For instance, the thermal energy is proportional to the product of the temperature T and of the specific heat C_P, but not, generally speaking, of the square of T.

thermodynamics based stability analysis arise from the reaction terms in the balance models.

The paper is organized as follows. We shall first introduce in Section 2 the modelling assumptions, then derive the dynamical equations for the CSTR from mass and energy balances, as well as the entropy and entropy production equations. For the sake of coherence with thermodynamics, we shall consider a reversible reaction in the CSTR although the classical CSTR model considers an irreversible reaction: this point will further discussed and motivated at the end of Section 2. The core of the paper is concerned with the stability analysis of the CSTR and will be performed by considering first the linearized model of the CSTR and the first method of Lyapunov (Section 3), then using the second method of Lyapunov and the related stability theory results (Section 4). Several thermodynamics based functions will be considered for the stability analysis. We shall indeed successively consider in Section 4 the entropy, the entropy production, and the thermal energy as Lyapunov function candidates, and provide in each case a detailed analysis of the obtained stability results.

2. Dynamical model of the CSTR

2.1. Mass and energy balance equations

Let us consider a CSTR in which an exothermic reaction in a liquid medium takes place and involve two chemical species A and B:

$$A \rightleftharpoons \beta B$$

where β is a stoichiometric coefficient. The reactant and the product are dissolved in an inert I. The inlet flow only contains A and I, and the volumetric flowrate is such that the liquid volume in the reactor is kept constant. The reactor is connected to a jacket in which a cooling fluid at temperature T_w is circulating. A schematic view of the reactor is given in Fig. 1.
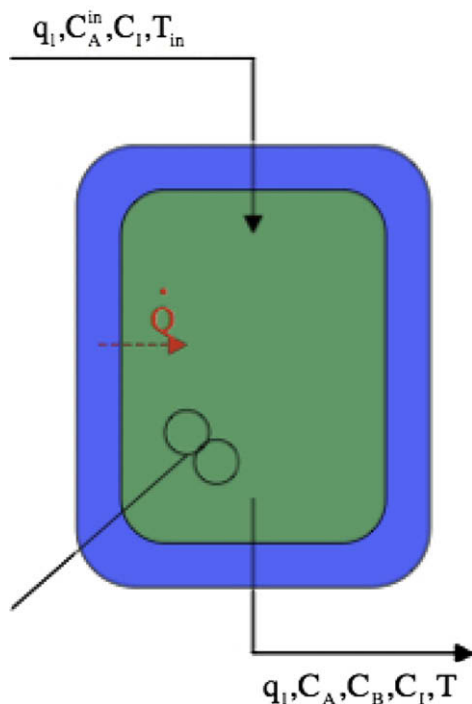

Fig. 1. Schematic view of the CSTR.

Let us consider the following modelling assumptions.

1. The liquid volume V is independent of the dissolved quantities of A and B, and only depends on the number of moles of inert n_I in the mixture ($n_I = C_I V$) with C_I the inert concentration.
2. The inert concentration is constant; the reactor is perfectly mixed.
3. The temperature of the cooling fluid T_w is constant.
4. The thermodynamical model considered here is that of an ideal liquid mixture, the heat exchange is proportional to the temperature difference between the cooling fluid and the liquid in the reactor ($\dot{Q} = h(T - T_w)$ where $\dot{Q}$ is positive if heat is extracted, and with h the heat exchanger coefficient), the time evolution is a quasi-static process, and the molar heat capacity C_v of each species is constant.
5. The reaction rate r is composed of two reaction rates, one for the forward reaction r_f, the other for the backward reaction r_b, with $r = r_f - r_b$. Each reaction rate only depends on the temperature and on the "reactant" concentration, i.e. A for the forward reaction and B for the backward reaction. This means in particular that each individual reaction is non-autocatalytic and without inhibition by the reaction product. For the sake of notation simplicity, since the volume is constant, the concentrations of A and B is proportional to the quantity of matter, and therefore $r(T, n_A, n_B)$ ($= r_f(T, n_A) - r_b(T, n_B)$) can be considered as the reaction rate per unit volume. Each subreaction rate is an increasing of the temperature and of the associated quantity of "reactant" such that it is equal to zero when the associated "reactant" is equal to zero, i.e. $r_f(T, n_A = 0) = 0$, $r_b(T, n_B = 0) = 0$.

Since the CSTR is a simple quasi-static thermodynamical system, its dynamics can be deduced from mass balances on the three involved species, the internal energy balance and the volume balance. Since the volume and the inert concentration are constant, the dynamics of the CSTR are therefore described by the following three balance equations:

$$\frac{dn_A}{dt} = \frac{q}{V}(C_A^{in}V - n_A) - r(T, n_A, n_B)V \tag{1}$$

$$\frac{dn_B}{dt} = -\frac{q}{V}n_B + \beta r(T, n_A, n_B)V \tag{2}$$

$$\frac{dU}{dt} = q\mathscr{C}_v^{in}(T_{in} - T_0) + q(C_A^{in}u_{0_A} + C_I u_{0_I}) - \frac{q}{V}U - h(T - T_w) \tag{3}$$

where q, C_A^{in}, T_{in}, $\mathscr{C}_v^{in}$ ($= C_A^{in}C_{v_A} + C_I C_{v_I}$), u_{0_j} ($j = A, I$), T_0 hold for the volumetric flow rate, the inlet concentration of species A, the inlet temperature, the volumetric heat capacity of the inlet liquid, the reference molar energy of the species j, the reference state temperature, respectively. Note that strictly speaking from a thermodynamical viewpoint, inlet and outlet enthalpies should been considered in the internal energy balance Eq. (3), yet the above writing with the inlet and outlet internal energies is valid under the above assumptions of liquid medium and constant volume. The dynamics of the CSTR are therefore described by the three balance Eqs. (1)–(3).

They have to be completed by a relation linking T, U, n_A and n_B. This is done by considering the thermodynamical model of the ideal liquid for which the internal energy is given by the following relationship (see e.g. [16]):

$$U = \sum_{j=A,B,I} n_j(C_{v_j}(T - T_0) + u_{0_j}) \tag{4}$$

If we note that the global liquid heat capacity $\mathscr{C}_v$ is equal to $\mathscr{C}_v = \sum_{j=A,B,I} n_j C_{v_j}$, the temperature can be expressed as a function of the other variables as follows: