



A REVISIT ON DISSIPATION AND ITS RELATION TO IRREVERSIBLE PROCESSES

Nguyen Chi Thuan, Nguyen Quang Long and Hoang Ngoc Ha

Ho Chi Minh City University of Technology, Vietnam

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ABSTRACT

As usual, industrial process systems operate far from (stable) equilibrium. Under practical operating conditions when putting the system back in equilibrium, this gives rise to the loss of energy (or certain generalized energy). Following the second law of thermodynamics, an irreversible process generates entropy. On the basis of this property, we propose an approach that allows to investigate quantitatively the amount of (generalized) energy lost when the system reaches equilibrium. A liquid phase reactor modelled with the CSTR (continuous stirred tank reactor) in which the acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol subject to steady state multiplicity takes place is used to illustrate the results.

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1 INTRODUCTION

In chemical engineering, thermodynamics plays a central role for studying and evaluating the dynamical evolutions of chemical processes (Callen, 1985; Glansdorff and Prigogine, 1971; Sandler, 1999). The change of states correlates with the change of energy and entropy. The dynamics of thermodynamic system is typically described by Ordinary Differential Equations (ODEs) or Partial Differential Equations (PDEs) (or even, by Differential and Algebraic Equations (DAEs)) on the basis of balanced equations (mass and energy) and possibly momentum equation. The Continuous Stirred Tank Reactors (CSTRs) belong to a large class of nonlinear dynamical systems described by ODEs which proposed by Luyben (1990). Several application of nonlinear control methods to CSTRs can be found in the literature, for example nonlinear feedback control under constraints (Viel *et al.*, 1997), nonlinear PI control (Alvarez-Ramirez and

Morales, 2000), classical Lyapunov based control (Antonelli and Astolfi, 2003), power/energy-shaping control or generalized energy based approach (Favache and Dochain, 2010), port Hamiltonian framework (Hagos *et al.*, 2001; Hudon *et al.*, 2008; Hoang *et al.*, 2011) and recently, stability analysis and control design based on thermodynamically consistent Lyapunov methodology (Ydstie and Alonso, 1997, 2011; Eberard *et al.*; 2007; Ederer *et al.*, 2011; Hoang *et al.*, 2012, 2013a).

This paper focuses on the analysis of reacting systems from an energy-based viewpoint. More precisely, the Van Heerden diagram based analysis via the balance of energy produced and energy consumed shows that the reaction system is subject to steady state multiplicity. In addition, it follows that the practical operation of the reaction system at some stationary equilibrium from any initial operating condition gives rise to the loss of energy (or certain generalized energy) which characterized by

the non-negative property of entropy production rate (i.e., the irreversibility of the reaction system).

2 THE CSTR MODELLING USING THERMODYNAMICS

2.1 The classical model of CSTR

Let us consider a CSTR with one reaction involving n chemical species:

$$\sum_{i=1}^n \nu_i M_i = 0 \quad (1)$$

where ν_i is the signed stoichiometric coefficient of species i .

The following assumptions are made throughout the paper:

(A1) The fluid mixture is ideal, incompressible and under isobaric conditions.

(A2) The heat flow rate coming from the jacket \dot{Q}_j is given by the following expression:

$$\dot{Q}_j = \alpha(T_j - T) \quad (2)$$

with α being the heat exchange coefficient. The jacket temperature is denoted by T_j .

(A3) The specific heat capacities are assumed to be constant.

2.2 Thermodynamic approach

In thermodynamics the system variables are split between extensive variables (such as the internal energy U , the entropy S , the volume V , and the molar number N_i) and intensive ones (such as the temperature T , the pressure p , and the chemical potential μ_i). The variation of the internal energy U (under isobaric conditions, the enthalpy H defined as $H = U + pV$ can then be used instead of the internal energy U) is directly derived from the variation of the extensive variables using the Gibbs' relation (Callen, 1985):

$$dH = TdS + \sum_{i=1}^n \mu_i dN_i \quad (3)$$

As a consequence, the intensive variables are given by:

$$T = \left(\frac{\partial H}{\partial S} \right)_{N_i}, \mu_i = \left(\frac{\partial H}{\partial N_i} \right)_{N_{k, k \neq i}} \quad (4)$$

Since the enthalpy H is also an extensive variable, it is a homogeneous function of degree 1 of (N_1, \dots, N_n, S) . From Euler's theorem, we get (Callen, 1985):

$$H(S, N_i) = TS + \sum_{i=1}^n \mu_i N_i \quad (5)$$

From (3)(5), we have:

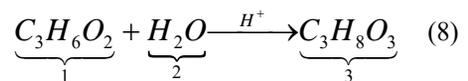
$$dS = \frac{1}{T} dH + \sum_{i=1}^n \frac{-\mu_i}{T} dN_i \quad (6)$$

$$S(H, N_i) = \frac{1}{T} H + \sum_{i=1}^n \frac{-\mu_i}{T} N_i \quad (7)$$

The system with (3)(5) is said to be in energy representation or (6)(7) in entropy representation. In this work, the energy representation will be used to derive the mathematical modeling (i.e., theoretical models), whereas the entropy representation is used to calculate the "energetic" dissipation (i.e., the irreversibility of the system).

3 The liquid phase acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol

A non-isothermal isobaric CSTR involving the liquid phase acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol is considered. For this system, oscillations or unstable behaviors have been experimentally shown (Heemskerk *et al.*, 1980; Rehms *et al.*, 1983; Vleeschhouwer *et al.*, 1988; Vleeschhouwer and Fortuin, 1990). Its stoichiometric equation is as follows:



The rate per mass unit of the reaction (i.e., $\text{mol.kg}^{-1}.\text{s}^{-1}$) is given by:

$$r_m = (k_0 c_{H^+}) e^{-\frac{T_a}{T}} c_1 \quad (9)$$

where c_{H^+} , c_1 , k_0 and T_a stand for the molar concentrations of H^+ and 2-3-epoxy-1-propanol per mass unit, the kinetic constant and the activation temperature, respectively. The system is fed with a mixture of 2-3-epoxy-1-propanol, water and sulfuric acid according to the total mass flow rate q^{in} . The mass fraction of sulfuric acid is assumed to be very low so that its balance equation is neglected.

3.1 System dynamics and steady state multiplicity behavior

The material balances are as follows (Vleeschhouwer *et al.*, 1988; Hoang *et al.*, 2013a):

$$\begin{cases} \frac{dN_1}{dt} = q^{in}c_1^{in} - q^{out}c_1^{out} - r_m M = F_1^{in} - F_1^{out} - r_m M & \text{(a)} \\ \frac{dN_2}{dt} = q^{in}c_2^{in} - q^{out}c_2^{out} - r_m M = F_2^{in} - F_2^{out} - r_m M & \text{(b)} \\ \frac{dN_3}{dt} = -q^{out}c_3^{out} + r_m M = -F_3^{out} + r_m M & \text{(c)} \end{cases} \quad (10)$$

The total mass of the reacting mixture is assumed to be constant (i.e., $M = \sum_i \bar{M}_i N_i = \text{constant}$)

where \bar{M}_i is the molar mass of species i . This condition is satisfied by using an outlet total molar flow regulation so that $\sum_i \bar{M}_i q^{in} c_i^{in} = q^{in} = \sum_i \bar{M}_i q^{out} c_i^{out} = q^{out} = q \text{ (kg.s}^{-1}\text{)}$. The molar fraction of species i given by x_i is expressed as follows:

$$x_i = \frac{N_i}{N} \quad (11)$$

with $N = \sum_i N_i$ the total molar number. We assume that the liquid mixture behaves like an ideal solution¹, the enthalpy and the entropy can be expressed as follows:

$$H = \sum_i N_i h_i \quad (12)$$

$$S = \sum_i N_i s_i \quad (13)$$

The constitutive equations of the partial molar enthalpy, entropy and chemical potential are given as follows (Sandler, 1999):

$$\begin{cases} h_i(P,T) = h_i^*(P,T) = h_i^*(T) = c_{p,i}^*(T - T_{ref}) + h_{ref} & \text{(a)} \\ s_i(P,T) = s_i^*(T) - R \ln\left(\frac{N_i}{N}\right) = c_{p,i}^* \ln\left(\frac{T}{T_{ref}}\right) + s_{ref} - R \ln\left(\frac{N_i}{N}\right) & \text{(b)} \\ \mu_i(T,P,x_i) = \mu_i^*(T,P) + RT \ln\left(\frac{N_i}{N}\right) = h_i^* - T s_i^* + RT \ln\left(\frac{N_i}{N}\right) & \text{(c)} \end{cases} \quad (14)$$

Where the superscript * stands for pure liquid phase component. The model is thermodynamically consistent since it represents thermodynamic

¹ This assumption is usually adopted for the dynamic modeling of liquid phase chemical reactors (Luyben, 1990).

properties of a stable liquid phase mixture. An alternative form of the energy equation written for the temperature variable is given as follows (Vleeschhouwer *et al.*, 1988; Hoang *et al.*, 2013a):

$$\left(\sum_i N_i c_{p,i}^*\right) \frac{dT}{dt} = \left(\sum_i F_i^{in} c_{p,i}^*\right) (T^{in} - T) + \dot{Q}_j + (-\Delta_r H) r_m M + \Delta Q \quad (15)$$

where $\Delta_r H = \sum_i \nu_i h_i$ is the reaction enthalpy and

ΔQ is an extra term accounting for possible mechanical dissipation and mixing effects. The reaction described by (8)(9) is considered as a pseudo first order reaction with $c_{H^+} = 3 \times 10^{-8} \text{ mol.kg}^{-1}$, $k_0 = 86 \times 10^9 \text{ kg.mol}^{-1}.\text{s}^{-1}$ and $T_a = 8822 \text{ K}$ (Vleeschhouwer *et al.*, 1988). Tables 1, 2 extracted from (Hoang *et al.*, 2013a) propose thermodynamic and operating parameters of the reaction system (10)(15).

Table 1: Thermodynamic properties and parameters

Symbol (unit)	C ₃ H ₆ O ₂ (1)	H ₂ O (2)	C ₃ H ₈ O ₃ (3)
ρ_i^* (kg.m ⁻³)	1117	1000	1261.3
$c_{p,i}^*$ (J.mol ⁻¹ .K ⁻¹)	128.464	75.327	221.9
$h_{i,ref}$ (J.mol ⁻¹)	-2.95050×10 ⁵	-2.8580×10 ⁵	-6.6884×10 ⁵
$s_{i,ref}$ (J.K ⁻¹ .mol ⁻¹)	316.6	69.96	247.1

Table 2: The CSTR operating conditions

Symbol (unit)	Numerical value
T^{in} (K)	298
T_j (K)	298
q (kg.s ⁻¹)	0.46 × 10 ⁻³
F_1^{in} (mol.s ⁻¹)	0.0013
F_2^{in} (mol.s ⁻¹)	0.0200
F_4^{in} (mol.s ⁻¹)	6.9 × 10 ⁻⁶
M (kg)	75 × 10 ⁻³
α (W.K ⁻¹)	0.4
ΔQ (W)	8.75

Let $(\bar{T}, \bar{N}_1, \bar{N}_2, \bar{N}_3)$ be the steady state of the system. We derive the following relations after some elementary calculations:

$$(-\Delta_r H) r_m M = -\left\{ \left(\sum_i F_i^{in} c_{p,i}^* \right) (T^{in} - \bar{T}) + \alpha (T_j - \bar{T}) + \Delta Q \right\} \quad (16)$$

The left term and right term of the equation (16) correspond strongly to the energy produced E_p

and the energy consumed E_c during the reaction course. The geometrical representation of these energies with respect to the stationary temperature \bar{T} shows the Van Heerden diagram of the reaction system (Van Heerden, 1953; Hoang and Dochain, 2013b). The intersection point of those two curves presents the stationary heat balance and therefore, this gives possible steady states. It is shown that a steady state is said to be (dynamically) stable if the

tangent of the heat production lies below the heat consumption, i.e.:

$$\frac{dE_p}{dT} < \frac{dE_c}{dT}$$

According to the operating conditions imposed, as shown in Figure 1, the system exhibits three stationary operating points denoted by P_1 , P_2 and P_3 .

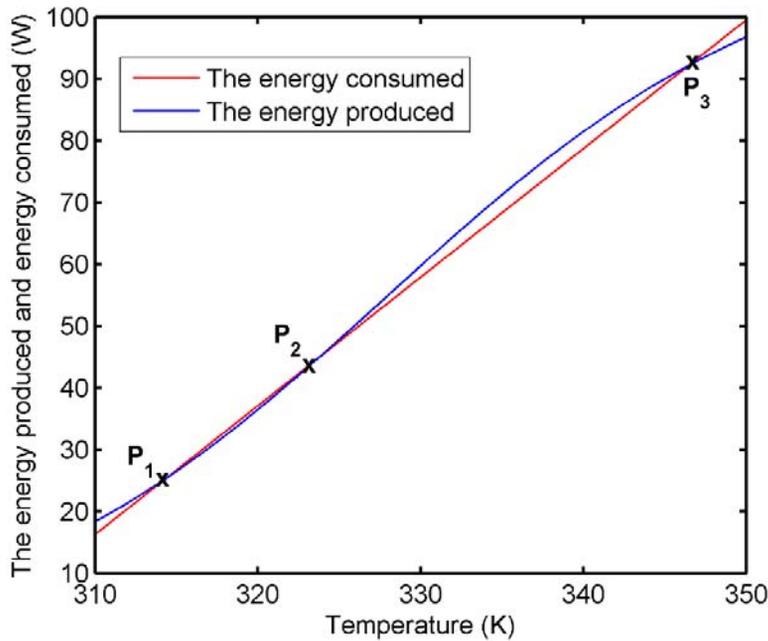


Fig. 1: The Van Heerden diagram of the CSTR

Table 3 gives the numerical values of these three stationary operating points, which calculated using MATLAB. It is worth noting from (17) that P_1 and P_3 are (dynamically) stable and P_2 is (dynamical-ly) unstable. From a physical point of view, it follows that as a small rise in temperature happens, (17) requires that the heat production E_p increases more rapidly than the heat consumption E_c and the temperature will continue to rise until a stable equilibrium at P_3 reached. In the opposite case of

a low temperature drop at P_2 the temperature will continue to fall until it reaches the value \bar{T}_1 at P_1 .

Table 3: The reaction system with three steady states (multiplicity behavior)

Symbol (unit)	\bar{T} (K)	\bar{N}_1 (mol)	\bar{N}_2 (mol)	\bar{N}_3 (mol)
Point P_1	314.35	0.1723	3.2181	0.0470
Point P_2	323.60	0.1364	3.1822	0.0829
Point P_3	346.47	0.0469	3.0927	0.1724

(De Groot and Mazur, 1962; Favache and Dochain, 2009; Hoang *et al.*, 2011):

$$\frac{dS}{dt} = \Phi_s + \sigma_s, \quad \sigma_s \geq 0$$

Where:

3.2 The dissipation and irreversibility of the system: A generalized energetic approach

Let us complete the system dynamics (10)(15) by considering the entropy balance on the basis of the Gibbs' relation in entropy representation (see also

$$\Phi_S = \sum_i (F_{il} s_{il} - F_i s_i) + \frac{\dot{Q}_J}{T_J}$$

$$\sigma_S = \sigma_S^{mix.} + \sigma_S^{heat conv.} + \sigma_S^{heat ex.} + \sigma_S^{reac.} \geq 0$$

with Φ_S and σ_S being the entropy exchange flow rate with surrounding environment (due to convection and thermal exchange) and the irreversible entropy production, respectively. The irreversible entropy production σ_S is expressed as the sum of four thermodynamically separate contributions as follows (Favache and Dochain, 2009; Hoang *et al.*, 2014):

$$\sigma_S^{mix.} = R \sum_i F_{il} \left(\ln \left(\frac{N_{il}}{N_I} \right) - \ln \left(\frac{N_i}{N} \right) \right) \geq 0 \quad (21)$$

$$\sigma_S^{heat conv.} = \sum_i c_{p,i}^* F_{il} \left(\frac{T_I}{T} - 1 - \ln \left(\frac{T_I}{T} \right) \right) \geq 0 \quad (22)$$

$$\sigma_S^{heat ex.} = \frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \geq 0 \quad (23)$$

$$\sigma_S^{reac.} = \left(\frac{\mu_1}{T} + \frac{\mu_2}{T} - \frac{\mu_3}{T} \right) r_m M \geq 0 \quad (24)$$

where $\sigma_S^{mix.}$, $\sigma_S^{heat conv.}$, $\sigma_S^{heat ex.}$ and $\sigma_S^{reac.}$ are the irreversible entropy productions due to mixing, heat convection, heat exchange and chemical reaction, respectively. Furthermore, these physical effects are intrinsically independent from each other, each constituent entropy production is therefore non-negative thanks to the second law of thermodynamics (De Groot and Mazur, 1962).

From a mathematical point of view, it is straightforward to show the non-negative definiteness properties of $\sigma_S^{mix.}$ (21), $\sigma_S^{heat conv.}$ (22), $\sigma_S^{heat ex.}$ (23). Contrary to the entropy productions $\sigma_S^{mix.}$,

$\sigma_S^{heat conv.}$, $\sigma_S^{heat ex.}$, the entropy production resulting from the reaction $\sigma_S^{reac.}$ (24) depends only on the internal state variables (i.e., the intensive variables) and the reaction rate $r_m M$ (9). Consequently, the non-negative property of $\sigma_S^{reac.}$ (24) has been largely accepted as an *a priori* postulate of irreversible thermodynamics (Favache and Dochain, 2009; Hoang *et al.*, 2014).

In what follows, we shall show that the non-negative property of $\sigma_S^{reac.}$ (24) holds via the numerical simulations using SIMULINK through the case study considered. In Table 4, four different initial conditions are used. The SIMULINK interconnection schema for the simulations is given in Appendix A.

Table 4: Initial conditions for simulations

Symbol (unit)	Point C ₁	Point C ₂	Point C ₃	Point C ₄
$T(0)$ (K)	330	320	310	315
$N_1(0)$ (mol)	0.05	0.18	0.14	0.135
$N_2(0)$ (mol)	3	3	3	3
$N_3(0)$ (mol)	0.1880	0.0835	0.1157	0.1197

The simulations in Figure 2 show entropy production due to chemical reaction are always positive regardless of the initial conditions. This inherent property characterizes the amount of energy lost due to irreversible transformations and is strongly related to the energy dissipation as shown in (Ydstie, 2007). Nevertheless, the time variation and amplitude of the entropy production depend strongly on the changes of system variables (see also Eq. (24)). As shown in Figure 1, the system variables converge to the steady states P_1 or P_3 and these states are absolutely different.

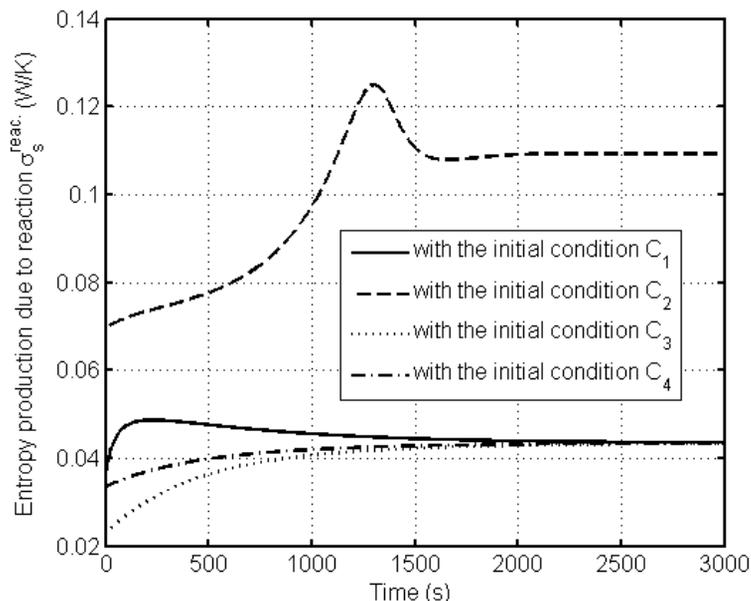


Fig. 2: Entropy production due to reaction

4 CONCLUSIONS

In this work, we have combined thermodynamic properties with numerical simulations to calculate steady states via heat balance based on Van Heerden diagram; and to verify the thermodynamic stability condition of reaction process systems. It is shown that the practical operation of the reaction system at some stationary equilibrium from any initial operating condition releases certain generalized energy which characterized by the non-negative property of entropy production rate (i.e., the irreversibility of the reaction system). It remains now to stabilize the chemical reaction system at a desired steady state (for example, the unstable middle point P_2) via energy-based approaches or thermodynamics.

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Appendix A. The SIMULINK interconnection schema

