A thermodynamic Lyapunov Approach to the Stability Analysis of a Nonlinear Irreversible Process Having Multiplicity

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Following the second law of thermodynamics, the entropy is always created in irreversible processes such as reacting systems, etc. Under certain operating conditions, the reaction system can be operated with multiple steady states (also called the steady state multiplicity behavior). This behavior is considered for the illustration of the stability analysis of all possible steady states by Lyapunov methods using thermodynamics. More precisely, a novel symmetric storage function (or Lyapunov function candidate) is proposed on the basis of the so-called (non-symmetric) thermodynamic availability function. The acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol subject to steady state multiplicity is used for further technical developments. The results are discussed with the inclusions of the simulations.

Keywords: Dynamical systems, multiplicity, Lyapunov function, stability, control, thermodynamics

INTRODUCTION

"A theory is the more impressive the greater the simplicity of its premises, the more varied the kinds of things that it relates and the more extended the area of its applicability. Therefore classical thermodynamics have made a deep impression on me. It is the only physical theory of universal content which I am convinced, within the areas of the applicability of its concepts, that it will never been overthrown." (Albert Einstein, 1949)

In chemical engineering, the reaction kinetics plays a central role as the source generating the abnormal dynamical behavior of the reaction system (e.g. non-minimum phase behavior, limit cycle or multiple steady states, etc. (Bayer et al. 2011, Hoang et al. 2013a)). On the other hand, the reaction kinetics can be modeled within the framework of thermodynamics (Dammers and Tels 1974, Tarbell 1977, Ydstie and Alonso 1997). In that respect, the use of thermodynamics for the stability analysis and control design of chemical reaction networks is

This paper focuses on the stability analysis of all possible steady states of the acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol modeled with CSTR subject to the steady state multiplicity behavior is given in section 4. From this, the stability analysis of the system dynamics is developed. Section 5 ends the paper with conclusions.

Throughout the paper, the following notations are used:

- \( \mathbb{R} \) is the set of real numbers.
- \( m \) and \( n \) are the positive integers.
- \( R \) can be either the (ideal) gas constant or thermodynamic storage function.
- \( t \) can be either time or matrix transpose.

**THE LYAPUNOV STABILITY THEORY**

**LYAPUNOV’S SECOND METHOD FOR STABILITY OR LYAPUNOV’S DIRECT METHOD**

Let us consider a nonlinear dynamical system which is affine in the control input \( u \) and whose dynamics are given by the following set of ODE’s:

\[
\frac{dx(t)}{dt} = x(t) = f(x(t)) + g(x(t))u, \quad x(t=0) = x_0 \tag{1}
\]

where \( x = x(t) \in \mathbb{R}^n \) is the state vector, \( f(x(t)) \in \mathbb{R}^n \) represents the smooth nonlinear function with respect to \( x \), \( g(x(t)) \in \mathbb{R}^{m \times n} \) is the input-state map and \( u \in \mathbb{R}^m \) is the control input.

A positive continuous function \( V : \mathbb{R}^n \rightarrow \mathbb{R}^+ \) is called a Lyapunov function candidate for the stability analysis at a desired state \( x_0 = 0 \) (i.e, at the origin) if
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and only if the three following conditions are met (Khalil, 2002):

i) \( V(x(t)) = 0, \ x(t) = 0 \)

ii) \( V(x(t)) > 0, \ \forall x(t) \neq 0 \) \hspace{1cm} (2)

iii) \( \dot{V}(x(t)) \leq 0, \ \forall x(t) \)

Then, the state \( x_e = 0 \) is said to be (locally) stable. Moreover, if \( \dot{V}(x(t)) < 0, \ \forall x(t) \neq 0 \) then \( x_e = 0 \) is (globally) stable.

**Remark 1:** If \( V(x(t)) > 0, \ \forall x(t) \neq 0 \), then \( V \) is positive definite. If \( V(x(t)) \geq 0, \ \forall x(t) \neq 0 \), then \( V \) is positive semi-definite.

**Remark 2:** If \( \|x\| \to +\infty \Rightarrow V(x) \to +\infty \) then \( V \) is said to be radically unbounded. In this case, if \( \dot{V}(x(t)) < 0, \ \forall x(t) \neq 0 \) then \( x_e = 0 \) is asymptotically stable.

**THERMODYNAMICS AND THERMODYNAMIC STORAGE FUNCTION**

**The Overview of Thermodynamics**

Let us consider a reaction mixture composed of \( n \) (active) chemical species. In thermodynamics, the system variables are divided into extensive variables (such as the internal energy \( U \), the entropy \( S \), the volume \( V \), and the molar number \( N_i \)) and intensive variables (such as the temperature \( T \), the pressure \( p \), and the chemical potential \( \mu_i \)). 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):

\[
dH = TdS + \sum_{i=1}^{n} \mu_i dN_i
\]

(3)

From (3), since the absolute temperature \( T > 0 \) we have:

\[
dS = \frac{1}{T} dH + \sum_{i=1}^{n} \frac{-\mu_i}{T} dN_i
\]

(4)

As the entropy \( S \) is also an extensive variable, it is a homogenous function of degree 1 of \((H, N_i)\), we get by using the Euler’s theorem (Callen 1985, Hoang et al. 2009):

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

(5)

Equivalently, one can write the variation of the entropy as:

\[
S(Z) = w'Z \Rightarrow w = w(Z) = \frac{\partial S(Z)}{\partial Z}
\]

(6)

where:

\[
w = \left( \frac{1}{T}, -\frac{\mu_1}{T}, -\frac{\mu_2}{T}, \ldots, -\frac{\mu_n}{T} \right)^T, \text{ and}
\]

\[
Z = (H, N_1, N_2, \ldots, N_n)^T
\]

(7)

**Thermodynamic Availability**

Based on the second law of thermodynamics, in case of homogenous thermodynamic systems, the entropy function \( S(Z) \) is concave with respect to its arguments \( Z \) (Ruszkowski et al. 2005, Hoang et al. 2011). The strict concavity of the entropy function \( S \) with respect to the extensive variable \( Z \) induces that the
intersection between the tangent plane and the entropy surface $S(Z)$ reduces to a point. Such a situation is depicted in Figure 1 (Alonso and Ydstie 2001).

It can be shown that the non-negative function (Ydstie and Alonso 1997),

$$A(Z,Z^*) = \left[ S(Z) + w^*(Z - Z^*) \right] - S(Z) \geq 0$$

(8)

where $Z^*$ is a fixed reference state (for example, the desired set point for the control design), is the so-called thermodynamic availability (Keenan 1951). From a mathematical point of view, the thermodynamic availability $A(Z,Z^*)$ is the distance between the entropy $S(Z)$ and the tangent plane passing through $Z^*$. As a consequence, one concludes:

$$A(Z,Z^*) > 0, \forall Z \neq Z^*; \text{ and } A(Z^*,Z^*) = 0$$

(9)

Similarly, it is shown that $A(Z, Z^*)$ is the distance between the entropy $S(Z)$ and the tangent plane passing through $Z$. In other words, we have:

$$A(Z^*,Z) = [S(Z) + w^*(Z^* - Z)] - S(Z^*) \geq 0$$

(10)

$$A(Z^*,Z) > 0, \forall Z^* \neq Z; \text{ and } A(Z,Z) = 0$$

(11)

Also, it is worth noting that the availability function $A(Z, Z^*)$ is not symmetric, i.e. $A(Z, Z^*) \neq A(Z^*,Z)$.

**Thermodynamic Storage Function**

Let us define the following non-negative potential function:

$$R(Z,Z^*) = A(Z,Z^*) + A(Z^*,Z)$$

(12)

It is shown that when $Z \to Z^*$ then $R(Z,Z^*) \to 0$ since $A(Z, Z^*) \to 0$ (from Eq. (9)) and $A(Z^*,Z) \to 0$ (from Eq. (11)).

From Eq. (6), Eq. (8) and Eq. (10), Eq. (12) becomes:

$$R(Z,Z^*) = -(w - w^*)' (Z - Z^*)$$

(13)

Where:

$$w - w^* = \frac{1}{T} - \frac{1}{T^*}, -\frac{\mu_1}{T} + \frac{\mu_1^*}{T^*}, -\frac{\mu_2}{T} + \frac{\mu_2^*}{T^*}, ..., -\frac{\mu_n}{T} + \frac{\mu_n^*}{T^*}$$

$$Z - Z^* = (H - H^*, N_1 - N_1^*, N_2 - N_2^*, ..., N_n - N_n^*)$$

**Fig. 1: Entropy with respect to Z**
Let us state the following proposition.

**Proposition 1.** The storage function \( R(Z, Z^*) \) has the following properties:

- The non-negative definiteness \( R(Z, Z^*) \geq A(Z, Z^*) \geq 0 \) and \( R(Z^*, Z^*) = 0 \).
- The symmetry \( R(Z, Z^*) = R(Z^*, Z) \).

**Proof.** From Eq. (9), Eq. (11) and Eq. (12), we have: \( A(Z^*, Z) \geq 0 \). Consequently, we derive:

\[
A(Z^*, Z) = R(Z, Z^*) - A(Z, Z^*) \geq 0
\]

Or we have \( R(Z, Z^*) \geq A(Z, Z^*) \geq 0 \). In other words, from (12) and (13), it follows that \( R(Z, Z^*) = R(Z^*, Z) \) since:

\[
R(Z^*, Z) = -(w^* - w)'(Z - Z) = R(Z, Z^*)
\]

and

\[
-(w^* - w)'(Z - Z) = -(w - w')'(Z - Z^*) = R(Z, Z^*)
\]

Finally,

\[
R(Z^*, Z^*) = -(w^* - w)'(Z^* - Z^*) = 0
\]

The latter completes the proof.

Let us consider the following example for the sake of illustration of the thermodynamic concepts.

**Example 1.** We consider a jacketed homogeneous CSTR involving one exothermic irreversible chemical reaction \( v_A A \rightarrow v_B B^2 \). Assume that the reaction solution is ideal and under isobaric and isochoric conditions. The mixing entropy \( S^m \) of the reaction mixture can be expressed as follows (Hoang et al. 2012):

\[
S^m(Z) = -RN_A \ln \left( \frac{N_A}{N_A + N_B} \right) - RN_B \ln \left( \frac{N_B}{N_A + N_B} \right)
\]  

(14)

where \( R \) is the (ideal) gas constant and the extensive variable vector \( Z = (N_A, N_B)' \). We can check easily that the intensive variable vector

\[
w = \left( -R \ln \left( \frac{N_A}{N_A + N_B} \right), -R \ln \left( \frac{N_B}{N_A + N_B} \right) \right)'
\]

and,

\[
S^m(Z) = w'Z
\]

Let \( Z^* = (N_A^*, N_B^*)' \) be the reference state. In this case, the availability is derived using Eq. (8) as follows:

\[
A(Z, Z^*) = RN_A \ln \left( \frac{N_A}{N_A + N_B} \right) + RN_B \ln \left( \frac{N_B}{N_A + N_B} \right)
\]

(15)

Consequently, the storage function \( R(Z, Z^*) \) is given by considering Eq. (13):

\[
R(Z, Z^*) = R(N_A - N_A^*) \ln \left( \frac{N_A}{N_A + N_B} \right) + R(N_B - N_B^*) \ln \left( \frac{N_B}{N_A + N_B} \right)
\]

(16)

The geometric representation of \( R(Z, Z^*) \) (15) is given in **Figure 2**.

As a consequence of Proposition 1, \( R(Z, Z^*) \) is a natural Lyapunov candidate. For the dynamical stability analysis, it remains to check the sign condition of \( \frac{dR(Z, Z^*)}{dt} \) (see Section 2 for the Lyapunov stability theory), i.e.:

\[
\frac{dR(Z, Z^*)}{dt} < 0
\]

(17)
Hence, the function $R(Z, Z^*)$ is strongly related to the availability function $A(Z, Z^*)$ (see Eq. (12)). In some instances, this function is strictly convex and usable as a Lyapunov function for open loop stability analysis or closed loop control design.

THE LIQUID PHASE ACID – CATALYZED HYDRATION OF 2 – 3 – EPOXY – 1 – PROpanOL TO GLYcerOL

Let us consider an irreversible reaction, namely the liquid phase acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol taking place in a CSTR (continuous stirred tank reactor). For this reaction system, oscillations or unstable states have been experimentally shown (Heemskerk et al. 1980, Rehmus et al. 1983, Vleeschhouwer et al. 1988, Vleeschhouwer and Fortuin 1990). The stoichiometry equation is written as follows:

$$C_3H_6O_2 + H_2O \rightarrow C_3H_8O_3$$

(18)

where the subscripts 1, 2 and 3 stand for the three active chemical species involved in Eq. (18). The reaction rate per mass unit (i.e., mol.kg$^{-1}$.s$^{-1}$) of the reaction is given by (Vleeschhouwer et al. 1988, Hoang et al. 2013a):

$$r_m = \left(k_0 c_{H^+}\right)^{\frac{T_a}{T}} c_i$$

(19)

where $c_{H^+}$, $c_i$, $k_0$ 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 the inlet total mass flow rate $q_{in}$ containing a mixture of 2-3-epoxy-1-propanol, water and sulfuric acid where the mass fraction of the sulfuric acid is much smaller and negligible compared to
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The reaction system is operated with the mass maintained to be constant (i.e., the inlet total mass flow rate equals the outlet total mass flow rate, $q^{in} = q$).

For the modeling purposes, the following hypotheses are made.

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

(A2) The heat flow rate coming from the jacket is modelled by the following expression:

$$\dot{Q}_j = \alpha(T_j - T) \quad (20)$$

where $\alpha$ is the heat exchange coefficient and $T_j$ is the jacket temperature.

(A3) The specific heat capacities $c^*_{p,i}$ are assumed to be constant.

Mathematical Model of the System and Steady States Analysis

Using the material and energy balances, the reaction system dynamics is given as follows (Vleeschhouwer et al. 1988, Hoang et al. 2013a):

$$\begin{align*}
\frac{dN_1}{dt} &= q^n c_1^n - q c_1 - r_n M = F_1^n - F_1 - r_n M \\
\frac{dN_2}{dt} &= q^n c_2^n - q c_2 - r_n M = F_2^n - F_2 - r_n M \\
\frac{dN_3}{dt} &= - q c_3 + r_n M = - F_3 + r_n M \\
\frac{dH}{dt} &= \sum_{i=1}^{n} F_i h_i^n - \sum_{i=1}^{n} F_i h_i + \dot{Q}_j + \Delta Q
\end{align*} \quad (21)$$

where:

- $F_i^n$, $F_i$, $h_i^n$ and $h_i$ are the inlet molar flow rate, the outlet molar flow rate, the inlet molar enthalpy and the molar enthalpy, respectively;
- $c^*_{p,i}$ and $c_i$ are the concentrations per mass unit of species $i$ in the inlet and the reaction system, respectively;
- $M$ is the total mass;
- $\Delta Q$ is an extra term accounting for possible mechanical dissipation and mixing effects.

Note also that in an ideal mixture, the enthalpy of species $i$ can be expressed as follows (Sandler 1999):

$$\begin{cases}
h_i(T) = c^*_{p,i} (T - T_{ref}) + h_{i,ref} \\
s_i(T) = c^*_{p,i} \ln \left( \frac{T}{T_{ref}} \right) + s_{i,ref} - R \ln \left( \frac{N_i}{\sum_{j=1}^{n} N_j} \right)
\end{cases} \quad (22)$$

where $T_{ref}$, $h_{i,ref}$ and $s_{i,ref}$ are the reference values calculated at standard conditions. Hence the energy balance given in (18) can be rewritten in terms of the temperature $T$ by considering the hypothesis of local equilibrium (De Groot and Mazur 1962) and the expression of the total enthalpy and entropy as follows (Sandler 1999):

$$H = \sum_{i=1}^{n} N_i h_i \quad (23)$$

$$S = \sum_{i=1}^{n} N_i s_i \quad (24)$$
We therefore obtain (Luyben 1990):

\[
\left( \sum_{i} N_i c_{p,i}^* \right) \frac{dT}{dt} = \left( \sum_{i} F_{i,\text{in}} c_{p,i}^* \right) (T_{\text{in}} - T) + (-\Delta_r H) r_m M + \Delta Q
\]  

(25)

where \( \Delta_r H = (-h_1(T) - h_2(T) + h_3(T)) < 0 \) is the enthalpy of (exothermic) reaction.

Tables 1, 2 and 3 are extracted from (Vleeschhouwer et al. 1988, Hoang et al. 2013a) give thermodynamic, kinetic and operating parameters of the reaction mixture.

**Table 1.** Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Symbol (unit)</th>
<th>( C_4H_8O_2 ) (1)</th>
<th>( H_2O ) (2)</th>
<th>( C_3H_6O_3 ) (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_{p,i}^* ) ((J.mol^{-1}.K^{-1}))</td>
<td>128.464</td>
<td>75.327</td>
<td>221.9</td>
</tr>
<tr>
<td>( h_{i,\text{ref}} ) ((J.mol^{-1}))</td>
<td>-2.95050 x 10^5</td>
<td>-2.8580 x 10^5</td>
<td>-6.6884 x 10^5</td>
</tr>
<tr>
<td>( s_{i,\text{ref}} ) ((J.K^{-1}.mol^{-1}))</td>
<td>316.6</td>
<td>69.96</td>
<td>247.1</td>
</tr>
</tbody>
</table>

**Table 2.** Kinetic Parameters

<table>
<thead>
<tr>
<th>Symbol (unit)</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_H ) ((kg.mol^{-1}))</td>
<td>3 x 10^{-8}</td>
</tr>
<tr>
<td>( k_0 ) ((kg.mol^{-1}.s^{-1}))</td>
<td>86 x 10^9</td>
</tr>
<tr>
<td>( T_a ) ((K))</td>
<td>8822</td>
</tr>
</tbody>
</table>

**Table 3.** The CSTR Operating Conditions

<table>
<thead>
<tr>
<th>Symbol (unit)</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{in}} ) ((K))</td>
<td>298</td>
</tr>
<tr>
<td>( T_f ) ((K))</td>
<td>298</td>
</tr>
<tr>
<td>( q_{\text{in}} ) ((kg.s^{-1}))</td>
<td>0.46 x 10^3</td>
</tr>
<tr>
<td>( F_{1,\text{in}} ) ((mol.s^{-1}))</td>
<td>0.0013</td>
</tr>
<tr>
<td>( F_{2,\text{in}} ) ((mol.s^{-1}))</td>
<td>0.0200</td>
</tr>
<tr>
<td>( M ) ((kg))</td>
<td>75 x 10^{-3}</td>
</tr>
<tr>
<td>( \alpha ) ((W.K^{-1}))</td>
<td>0.4</td>
</tr>
<tr>
<td>( \Delta Q ) ((W))</td>
<td>8.75</td>
</tr>
<tr>
<td>( T_{\text{ref}} ) ((K))</td>
<td>298</td>
</tr>
</tbody>
</table>

Under the operating conditions imposed, as shown in Figure 3 (Hoang et al. 2013a, Nguyen et al. 2016a, 2016b), the system exhibits three stationary operating
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Table 4. The Numerical Values of the Three Steady States (Hoang et al. 2013a)

<table>
<thead>
<tr>
<th>Symbol (unit)</th>
<th>( T ) (K)</th>
<th>( \bar{N}_1 ) (mol)</th>
<th>( \bar{N}_2 ) (mol)</th>
<th>( \bar{N}_3 ) (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point ( P_1 )</td>
<td>314.35</td>
<td>0.1723</td>
<td>3.2181</td>
<td>0.0470</td>
</tr>
<tr>
<td>Point ( P_2 )</td>
<td>323.60</td>
<td>0.1364</td>
<td>3.1822</td>
<td>0.0829</td>
</tr>
<tr>
<td>Point ( P_3 )</td>
<td>346.47</td>
<td>0.0469</td>
<td>3.0927</td>
<td>0.1724</td>
</tr>
</tbody>
</table>

Fig. 4: The time evolution of the storage function \( R(Z,Z^*) \) with \( Z^* = P_1 \)

points denoted by \( P_1, P_2 \) and \( P_3 \). Table 4 gives the numerical values of these three stationary operating points, which are calculated using MATLAB.

In the next part, the dynamical stability analysis of these three steady states is given on the basis of the availability function by considering the sign condition (17). This condition is indeed checked through the numerical simulations. All these are the main contributions of the paper.

Simulation Results

For the sake of illustration, three different initial conditions are considered. Their values given in Table 5 are chosen close enough to the steady states.

Table 5. Initial Conditions for Simulations

<table>
<thead>
<tr>
<th>( T(t=0) ) (K)</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_1(t=0) ) (mol)</td>
<td>0.05</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>( N_2(t=0) ) (mol)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( N_3(t=0) ) (mol)</td>
<td>0.1880</td>
<td>0.0835</td>
<td>0.0817</td>
</tr>
</tbody>
</table>

Figures 3 and 4 show the time evolution of the storage function \( R(Z,Z^*) \) for the different initial conditions. It is shown that the dynamical stability analysis consists in deriving \( \frac{dR(Z,Z^*)}{dt} < 0 \). The simulations results of Figures 4 (with the initial condition \( C_1 \)) and 5 (with the initial condition \( C_2 \)) show that \( P_1 \) and \( P_3 \) are stable. Otherwise, the
point $P_2$ is unstable since $R(Z,Z^*)$ does not asymptotically tend to zero in Figure 6 (with the initial condition $C_1$). Figure 7 presents the open loop phase plane. The results presented here are satisfactory from both a qualitative and a quantitative point of view.

**CONCLUSION**

In this paper, the stability analysis of the acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol subject to the steady state multiplicity behavior is proposed through the support of Lyapunov methods together with thermodynamic properties related strongly to the so-called thermodynamic availability. It is shown that the (non-symmetric) thermodynamic availability is derived directly from the second principle. Consequently, this function is convex for single-phase reaction mixture. From this, a
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novel (non-negative and symmetric) storage function is shown on the basis of the availability for further studies. In other words, thermodynamics naturally proposes a Lyapunov function candidate usable for the dynamical stability analysis of open reaction systems. It remains now to stabilize the reaction system at the unstable middle steady state that possible drives the closed loop dynamics to an optimal process performance (Bruns and Bailey 1975).

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