Thermodynamics based control for three-phase catalytic fed-batch reactor

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Abstract: This paper deals with the nonlinear Lyapunov based control of a fed-batch reactor. The aim of this paper is to describe control law synthesis that finds its basis in irreversible thermodynamics. For this the so called thermodynamic availability function is used as Lyapunov function in order to track some temperature trajectory for the fed-batch reactor. The case of a three-phase catalytic hydrogenation reaction is taken as a representative test example.

Keywords: Nonlinear control, Lyapunov functions, Irreversible thermodynamics, Fed-batch reactor.

1. INTRODUCTION

Thermodynamics-based control design is an approach for the control of physical systems. The first works were published in the seventies (Tarbell, 1977). A growing interest has risen in the recent years (Ydstie and Alonzo, 1997), (Antelo et al., 2007), (Haddad et al., 2010), (Favache and Dochain, 2009, 2010).

In this paper, it is proposed to synthesize the control of a three-phase catalytic fed-batch reactor with this thermodynamics-based approach. Several nonlinear techniques have been applied to batch/fed-batch reactors control (Chang et al., 1995), (Bouhenchir et al., 2006), (Aziz et al., 2000), (Mihoub et al., 2009). Such techniques are based on mathematical tools for control and do not take energy and thermodynamic considerations into account.

The goal of the paper is to synthesize nonlinear control laws based on irreversible thermodynamics concepts, the availability function, proposed by Ydstie and co-workers (Ydstie and Alonzo, 1997) (Ruszkowski et al., 2005). In our previous work (Bahroun et al., 2010), we focused on the use of the availability function to synthesize stabilizing control laws for the temperature control of three-phase catalytic continuous reactors. This function has also been used previously in the case of the stabilization of a non-isothermal CSTR operating at an unstable steady state in (Hoang et al., 2008, 2009).

This paper is organized as follows: in section 2, a Lyapunov function: the thermal availability is deduced from the availability function. In section 3, we present a simplified model of the three-phase catalytic fed-batch reactor. Section 4 is devoted to the design of a feedback control law for the temperature trajectory control of the jacketed batch/fed-batch reactor based on the use of the thermal availability as Lyapunov function. Finally, some simulation results are presented.

2. THE THERMAL AVAILABILITY AS LYAPUNOV FUNCTION

The availability is a function issued from the second law of thermodynamics that is positive for homogeneous systems (Ruszkowski et al., 2005). In the case of isobaric systems that we consider here, the availability is a definite positive function defined as follows:

$$A(Z) = S(\bar{Z}) + \overline{w} (Z - \bar{Z}) - S(Z) > 0$$

where the overbar stands for a given reference state. $Z = (H, N)^T$ is the vector of extensive variables and $w = \left(1 - \frac{\mu_k}{T}\right)$ is the vector of intensive variables (Callen, 1985).

Provided that some constraint is assumed for some extensive variables, the availability is a Lyapunov function candidate since in this case, it is a strictly convex function (Bahroun et al., 2009).

Property 1 (Bahroun et al., 2010): The availability function is an homogenous function of degree 1 with respect to $Z$.

Finally let us remark that in (Hoang et al., 2008), the use of availability as Lyapunov function led to oscillatory controls and fast dynamics. Under some assumptions related to the thermodynamic nature of the phase under consideration, a new Lyapunov function candidate is proposed that is derived from the original availability function in order to overcome this problem (Hoang et al., 2009). In order to present this new Lyapunov function candidate, let us give some preliminary results:
1.1 Preliminary

The chemical potential of the k species $\mu_k$ is defined as follows:

$$\mu_k = h_k - T s_k$$  \hspace{1cm} (2)

If we consider an ideal liquid mixture, the partial molar enthalpy and entropy of a k component $h$ and $s$ are respectively given by:

$$h_k = c_{pk} \left( T - T^0 \right) + h_k^0$$ \hspace{1cm} (3)  

$$s_k = c_{pk} \ln \left( \frac{T}{T^0} \right) + s_k^0 - R \ln \left( \frac{N_k}{N_{tot}} \right)$$ \hspace{1cm} (4)

provided that the heat capacities $c_{pk}$ are assumed to be constant. By using the eq. (3) and (4), eq. (2) becomes:

$$\mu_k = c_{pk} \left( T - T^0 \right) + h_k^0 - T \left( c_{pk} \ln \left( \frac{T}{T^0} \right) + s_k^0 - R \ln \left( \frac{N_k}{N_{tot}} \right) \right)$$ \hspace{1cm} (5)

Let us consider the given reference state defined by the set of extensive variables $Z = \{H, N\}$ and the associated intensive variables $\bar{m} = \left( \frac{1}{T} - \frac{1}{T^0} \right)$. By using eq. (5), the reference chemical potential is as follows:

$$\bar{m}_k = c_{pk} \left( T - T^0 \right) + h_k^0 - T \left( c_{pk} \ln \left( \frac{T}{T^0} \right) + s_k^0 - R \ln \left( \frac{N_k}{N_{tot}} \right) \right)$$ \hspace{1cm} (6)

Let us now define $w_1$ and $w_2k$ as:

$$w_1 = \left( \frac{1}{T} - \frac{1}{T^0} \right)$$  \hspace{1cm} (7)

$$w_{2k} = \left( \frac{\mu_k}{T} - \bar{m}_k \right)$$ \hspace{1cm} (8)

By using eq. (5) and (6), we can express $w_{2k}$ as follows:

$$w_{2k} = w_1 \left( c_{pk} T^0 - h_k^0 \right) + c_{pk} \ln \left( \frac{T}{T^0} \right) + R \ln \left( \frac{N_k}{N_{tot}} \right)$$ \hspace{1cm} (9)

Let us now define the two following functions:

$$F_k(T) = w_1 \left( c_{pk} T^0 - h_k^0 \right) + c_{pk} \ln \left( \frac{T}{T^0} \right)$$ \hspace{1cm} (10)

$$G_k(N_k) = R \ln \left( \frac{N_k}{N_{tot}} \right) = R \ln \left( \frac{N_k}{N_{tot}} \right) = \sum_{k=1}^{c} \frac{N_k}{N_{tot}}$$ \hspace{1cm} (11)

By using equations (10) and (11), we can express eq. (9) as follows:

$$w_{2k} = F_k(T) + G_k(N_k)$$ \hspace{1cm} (12)

From this preliminary analysis, we will deduce a new Lyapunov function from the availability function: the thermal availability.

1.2 The thermal availability

By using eq. (12), we can express the equation (1) as follows:

$$A = \left( \frac{1}{T} - \frac{1}{T^0} \right) H + \sum_{k=1}^{c} F_k(T) N_k + \sum_{k=1}^{c} G_k(N_k) N_k$$ \hspace{1cm} (13)

Let us now define the two following functions such that $A = A_r + A_m$:

$$A_r = \left( \frac{1}{T} - \frac{1}{T^0} \right) H + \sum_{k=1}^{c} F_k(T) N_k$$ \hspace{1cm} (14)

$$A_m = \sum_{k=1}^{c} G_k(N_k) N_k$$ \hspace{1cm} (15)

$A_r$ represents the thermal contribution to the availability whereas $A_m$ represents the mixture one. Let us now consider $A_r$.

The enthalpy of the phase under consideration is given by the following equation:

$$H = \left( \sum_{k=1}^{c} \frac{h_k}{N_k} N_k \right) = \left( \sum_{k=1}^{c} \left( c_{pk} T^0 + h_k^0 \right) N_k \right)$$ \hspace{1cm} (16)

By using the equations (10) and (16) we can express eq. (14) as follows:

$$A_r = w_1 \sum_{k=1}^{c} \left( c_{pk} T^0 - h_k^0 \right) N_k + \sum_{k=1}^{c} \left( c_{pk} T^0 - h_k^0 \right) N_k + c_{pk} \ln \left( \frac{T}{T^0} \right) N_k$$ \hspace{1cm} (17)

$$= \left( \frac{T}{T^0} \right) - \ln \left( \frac{T}{T^0} \right) 1 - \left( \sum_{k=1}^{c} c_{pk} N_k \right)$$ \hspace{1cm} (18)

Let us now analyze the $A_r$ function.

Property 2: $A_r$ is a continuous positive definite function.

Proof. The quantity $\sum_{k=1}^{c} c_{pk} N_k = C_p$ is positive as the heat capacity of a stable phase with respect to heat transfer (Sandler, 1999). We have only to consider the $\xi(x)$ function given by the following equation:

$$\xi(x) = x - \ln(x) - 1, \forall x = \frac{T}{T^0} \in R.$$ \hspace{1cm} (18)
From the concavity property of the logarithm function, we immediately deduce that \( x - \ln(x) - 1 \geq 0, \forall \left( x = \frac{T}{T} \right) > 0. \)

The previous analysis enables to consider \( A_{\mu} \) as a Lyapunov candidate function. We now give the expression of its time derivative. To this end, we have to consider the properties of the \( A_{\mu} \) function.

**Property 3:** \( A_{\mu}(N_k) \) is a homogeneous function of degree one with respect to mole numbers \( N_k \).

**Proof.** The partial derivative of \( A_{\mu} \) with respect to \( N_k \) is given by the following equation:

\[
 \frac{\partial A_{\mu}}{\partial N_k} = \ln\left( \sum_{j=1}^{N_k} \frac{\sum_{j=1}^{N_j} N_j}{N_k} \right) + R\left( \sum_{j=1}^{N_j} \frac{N_j}{\sum_{j=1}^{N_k} N_k} \right) + R\left( \sum_{j=1}^{N_j} \frac{N_j}{\sum_{j=1}^{N_k} N_k} \right)
\]

Thus, we can express \( A_{\mu} \) as given by eq. (15) as follows:

\[
 A_{\mu} = \sum_{k=1}^{c} \frac{\partial A_{\mu}}{\partial N_k} N_k
\]

Let us now focus on the calculation of the time derivative of the thermal availability. By using the decomposition of the availability function given by the eq. (14) and (15), we have:

\[
 \frac{dA_{\mu}}{dt} = \frac{dA}{dt} - \frac{dA_{\mu}}{dt}
\]

According to Property 1, the availability function is a homogeneous function of degree 1 with respect to extensive variables \((H, N)\), thus its time derivative is given by:

\[
 \frac{dA}{dt} = \left( 1 - \frac{1}{T} \right) \frac{dH}{dt} + \sum_{k=1}^{c} \frac{F_k(T) dN_k}{dt} + \sum_{k=1}^{c} G_k(N_k) \frac{dN_k}{dt}
\]

According to Property 3, \( A_{\mu} \) is a homogeneous function of degree one with respect to the mole number \( N_k \). Its time derivative is given by the following equation:

\[
 \frac{dA_{\mu}}{dt} = \sum_{k=1}^{c} \frac{\partial A_{\mu}}{\partial N_k} \frac{dN_k}{dt} = G(N_k) \frac{dN_k}{dt}
\]

By using eq. (22) and (23), we obtain:

\[
 \frac{dA_{\mu}}{dt} = w_1 \frac{dH}{dt} + \sum_{k=1}^{c} \frac{dN_k}{dt}
\]

Before presenting the nonlinear control law, let us present the model of the three-phase catalytic jacketed fed-batch reactor under some simplifying assumptions.

3. DYNAMIC MODEL OF A FED-BATCH REACTOR

The system under consideration is made of three phases: the liquid phase containing the suspended catalyst pellets (the solid phase) onto the reaction takes place between the reactants A and B, and the gas phase containing the reactant A that dissolves into the liquid phase. The reactor is fed with a gas flow containing the reactant A. The reaction

\[
 3A_i + B_i \rightarrow C_i
\]

occurs in presence of a solvent. The number of mole of solvent \( N_{slv} \) is constant since it does not participate to the reaction. In order to use the thermal availability as a Lyapunov function, some simplifying assumptions have to be made.

The reaction that is considered here to illustrate our approach is the catalytic hydrogenation of o-cresol. The reaction rate of this reaction is given by using the Langmuir-Hinshelwood model (Hichri et al., 1990):

\[
 \dot{R}(C_{Al}, C_{Bl}, T) = \frac{K_AL(T)K_BT(C_ALC.BL)}{(1 + K_AL(T)C_AL)(1 + K_BT(T)C_BL)}
\]

where \( A \) stands for hydrogen, \( B \) for o-cresol, \( C \) for 2-methylcyclohexanol. \( C_{Al} = \frac{N_{Al}}{V_i} \), \( C_{Bl} = \frac{N_{Bl}}{V_j} \) and \( V_i \) are the hydrogen and o-cresol concentrations within the catalyst pellets and the volume of the pellets respectively. The rate constant \( k \) is given by an Arrhenius law while those of the adsorption constants \( K_A \) and \( K_B \) are derived from the mass action law (Hichri et al., 1990). The following assumptions are considered to derive the model (Li et al., 2010):

**Assumption A1**

- the temperatures of the liquid and gaseous phases are considered to be equal;
- a global mass transfer coefficient is used to represent hydrogen transfer from the liquid surface to the bulk. Equilibrium conditions at the gas–liquid interface are assumed;
- the gaseous phase is assumed to be ideal;
- the chemical reaction occurs in a perfectly mixed pseudo fluid phase containing the liquid phase and the suspended catalyst pellets;
- a perfect pressure regulation in the gas phase is assumed;
- the thermal availability of the gaseous phase is neglected since its mass is very low with respect to that of the liquid phase.

The model consists of mass and energy balances for the pseudo-fluid bulk phase as follows:

\[
 \frac{dN_{Al}}{dt} = F_{Ae} - 3 \tilde{R}(N_{Al}, N_{Bl}, T)
\]

\[
 \frac{dN_{Bl}}{dt} = -\tilde{R}(N_{Al}, N_{Bl}, T)
\]
\[
\frac{dN_{Cl}}{dt} = \bar{R} \left( N_{Al} \cdot N_{Bl}, T \right) 
\]
\[
\frac{dN_{slv}}{dt} = 0 
\]
\[
\frac{dT}{dt} = \frac{hS}{\psi} (T_j - T) + \frac{F_{Ac} \rho_A k_A}{\psi} (T_{Ac} - T) - \frac{\Delta H}{\psi} \bar{R}(N_{Al}, N_{Bl}, T) 
\]

Where:

\[ F_{Ac} : \text{inlet molar flow of component } A \text{ (mol/s)} \]

\[ F_{Ac} = k_{in} \left( N_{Al}^* - N_{Al} \right) = k_{in} \left( V_i \frac{p}{h_0 \exp \left( \frac{-\Delta h_{abs}}{RT} \right)} - N_{Al} \right) \]

\[ \psi = V_i \rho_B C_{pBl} + V_i \rho_{sh} C_{pslv} + V_k \rho_A C_{pAe} + V_i \rho_{AI} C_{pAI} + V_i \rho_{CI} C_{pCI} + V_i \rho_s C_{ps} \]

Let us note that the mole number of \( A \), \( N_{Al} \) is bounded by its solubility \( N_{Al}^* \). Thus the inlet molar flow \( F_{Ac} = k_{in} \left( N_{Al}^* - N_{Al} \right) \) remains positive (\( F_{Ac} \in R^+ \)).

As a consequence of the assumption \( A1 \), we have:

(P1) The mole number of the reactant \( A \), \( N_{Al} \), is a continuous differentiable definite positive bounded function.

\[ 0 \leq N_{Al}(t) \leq N_{Al}^*(T) \]

(P2) The mole number of the reactant \( B \), \( N_{Bl} \), is a continuous differentiable definite positive bounded function.

\[ 0 \leq N_{Bl}(t) \leq N_{Bl}^* \]

(P3) The mole number of the product \( C \), \( N_{Cl} \), is a continuous differentiable definite positive bounded function.

\[ 0 \leq N_{Cl}(t) \leq N_{Bl}^* \]

This model is based on the assumption that the bulk is homogeneous so that its thermal availability function can be calculated. In the next section we will design a control scheme for the temperature control of the reactor under consideration based on the use of the thermal availability as Lyapunov function, the jacket fluid temperature being used as the manipulated variable.

4. CONTROLLER SYNTHESIS

The target in this section is to design a control scheme for the temperature control of the reactor by using the thermal availability \( A_T \) as Lyapunov function. For this, we will focus on the system given the time evolution of the temperature \( T \) (31) and we will consider that \( N_{Al}, N_{Bl}, N_{Cl} \) and \( N_{slv} \) given by the equation (27)-(30) are inputs time varying functions of the previous system.

For this we will prove first that \( A_T \) is a definite positive bounded function with respect to the temperature \( T \). Then we have to bound the derivative of \( A_T \) along the trajectories of \( T \).

\( \text{Khalil,2002) } \)

\textbf{Proposition 1:} \( A_T \) is a positive bounded definite function with respect to the temperature \( T \).

\textbf{Proof}. Let \( A_T(t,T) : \{0, \infty \} \times R_+ \rightarrow R_+ \) be a continuously differentiable function. From the equation (17), the thermal availability of the system under consideration is:

\[
A_T(t,T) = \left[ c_{pAl} N_{Al}(t) + c_{pBl} N_{Bl}(t) + c_{pCl} N_{Cl}(t) + c_{pAl} N_{slv}(t) \right] \times \left( \frac{T}{T} - \ln \left( \frac{T}{T} \right) - 1 \right) 
\]

(P4) - From property 2, \( A_T \) is positive.

(P5) - \( A_T \) is bounded by \( \gamma_{min}(T) \) and \( \gamma_{max}(T) \), which are two continuous positive definite functions on \( R^*_+ \):

\[
\gamma_{min}(T) = \left( \frac{T}{T} - \ln \left( \frac{T}{T} \right) - 1 \right) \min_k \left( c_{pk} \right) N_{tot-min} \]

\[
\gamma_{max}(T) = \left( \frac{T}{T} - \ln \left( \frac{T}{T} \right) - 1 \right) \max_k \left( c_{pk} \right) N_{tot-max} \]

Where \( N_{tot-min} \) represents the minimum of the total number of moles and \( N_{tot-max} \) represents the maximum’s one.

Finally, by using (P4) and (P5), we have:

\[
\forall t \geq 0 \text{ and } T \in R^*_+, \gamma_{min}(T) \leq A_T(t,T) \leq \gamma_{max}(T) \]

By using the proposition 1, \( A_T(t,T) \) becomes a Lyapunov candidate function for (31).

Let us now calculate the derivative of \( A_T(t,T) \) along the trajectories of (31). The time derivative of the \( A_T(t,T) \) is given by the equation (24). Thus, let us first calculate the time derivative of the enthalpy \( H \):

\[
\frac{dH}{dt} = \bar{A}(T_j - T) + \frac{F_{Ac}}{\psi} \left( T_{Ac} - T^0 \right) + h_A^0 
\]

By using the equations (27)-(30); (35) and the equation (10) for the component \( A, B \) and \( C \), the time derivative of \( A_T(t,T) \) is given by:

\[
\frac{dA_T(t,T)}{dt} = w_1 \bar{A}(T_j - T) + \left[ c_{pAl} F_{Ac} T_{Ac} + c_{pBl} F_{Ac} \ln \left( \frac{T}{T} \right) \right] - w_1 \left[ c_{pAl} + c_{pBl} - c_{pCI} \right] R \]

\[
\Delta_T H(T) = -3h_A^0(T) - h_B^0(T) + h_C^0(T) 
\]
**Proposition 2:** The system described by eq. (31) is uniformly asymptotically stable with the following feedback control law:

$$
T_n = T + \frac{1}{A} \left[ -K_w + \{3c_{pt} + c_{pt} - c_{pc}\} \ln \left( \frac{T}{T} \right) \right]'
$$

$$
T_n = T + \frac{1}{A} \left[ +\Delta H - c_{pt}
K_w T' \right]'
$$

$$
\frac{1}{w} \left[ c_{pt} F_a h (\frac{T}{T})' - (3c_{pt} + c_{pt} - c_{pc}) \ln \left( \frac{T}{T} \right) \right]'
$$

(37)

Where $K_w$ is some positive constant control parameter.

**Proof.** By using eq. (37), we can express eq. (36) as follows:

$$
\frac{dA_T(t,T)}{dt} = -K_c \left( \frac{1}{T} - \frac{1}{T} \right) \leq \kappa(T)
$$

(38)

Lets us now define $\kappa(T)$ a continuous positive definite function on $R^*_+$:

$$
\kappa(T): R^*_+ \rightarrow R^*_+
$$

$$
\kappa(T) = K_c \left( \frac{1}{T} - \frac{\alpha}{T} \right)^2 , \forall T \in R^*_+ \text{ and } \forall \alpha > 1
$$

(39)

From eq.(39) we can rewrite eq.(38) as follows:

$$
\frac{dA_T(t,T)}{dt} = -K_c \left( \frac{1}{T} - \frac{1}{T} \right) \leq \kappa(T)
$$

$\forall t \geq 0$ and $\forall T \in R^*_+$, since $K_c$ is strictly positive, the system described by (31) is uniformly asymptotically stable.

**Remarks:**

* The control law as given by the equation (37) is well defined for $T = \bar{T}$ since

$$
\lim_{T \rightarrow \bar{T}} \left[ \frac{1}{w} \left( c_{pt} F_a h (\frac{T}{T}) - (3c_{pt} + c_{pt} - c_{pc}) \ln \left( \frac{T}{T} \right) \right)' \right] =
$$

$$
-\bar{T} F_a c_{pt} F_a - (3c_{pt} + c_{pt} - c_{pc}) \bar{T}
$$

* The solvent number of moles and the volume of the bulk phase are constant. Thus, the entropy function of the system is strictly concave (Bahroun et al., 2010) and the convergence of $T$ to $\bar{T}$ is insured.

4.1 Simulation results

The control objective is to maintain the reactor temperature $T$ in a neighbourhood of a given desired temperature trajectory $\bar{T}(t)$, by manipulating the jacket temperature $T_j$. For this we use the control law given by the equation (37).

For each sample period $(ST)$, we can see that $A_T$ decreases during a sample period $n$ and rises sharply to a new initial value at the beginning of the next interval $[t_n, t_{n+1}]$.

Fig.1 presents the input/output behaviour of the reactor, i.e. the jacket temperature $T_j$ and the reactor temperature $T$. The desired temperature trajectory is also presented. From Fig.1 we can observe that the reactor temperature follows the desired temperature $\bar{T}(t)$ with some practically achievable dynamics of $T_j$. Note also that the system admits a small temperature error in the phase 1 and the phase 3.
sample period $n+1$. As is can be seen in this figure, the thermal availability function converges to zero when the system reaches the desired set point. Except at the instants $t_n$, the time derivative of $A_t$ remains strictly negative and the thermal availability function plays the role of a Lyapunov function.

6. CONCLUSION

In this paper the temperature nonlinear control of fed-batch reactor using Lyapunov methods is proposed. We deduced from the availability function a Lyapunov function candidate for homogeneous systems: the thermal availability. We used this function in order to design a stabilizing control law for a three-phase catalytic fed-batch reactor by manipulating the jacket fluid temperature. The simulations results confirm the good performances of the control scheme that we propose. Furthermore, the dynamic behaviour of the manipulated variable $T_j$ is realistic and could be implemented. Nonetheless, further investigations will be undertaken in order to estimate the reaction rate since the proposed control law depends on the values of reaction rate. For this we plan to use the high gain observer proposed by (Farza et al., 1999) in order to estimate the reaction rate.

NOMENCLATURE

- $h^0$, $h$: Reference molar enthalpy, molar enthalpy (J/mol)
- $H$: Enthalpy (J)
- $N$: Mole number (mol)
- $N_{\text{tot}}$: Total number of moles (mol)
- $N_{\text{sol}}$: Mole number of the solvent (mol)
- $\dot{R}$: Reaction rate (mol/s)
- $s^0$, $s$: Reference molar entropy, molar entropy (J/K/mol)
- $S$: Entropy (J/K)
- $T$, $T_j$: Temperature, double jacket temperature (K)
- $V$: Volume (m$^3$)
- $\lambda$: Heat transfer coefficient (W/K)
- $\mu$: Chemical potential (J/mol)
- $g$, $l$, $s$: Gas, liquid, solid

REFERENCES