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A thermodynamic approach to the stabilisation of tubular reactors

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Abstract

This paper deals with the stabilization of a non isothermal tubular reactor in which convection, diffusion and chemical reaction occur. The tubular reactor is modelled by a set of non-linear partial differential equations and the distributed jacket temperature is used as control input. Two stabilizing control laws are derived using the thermodynamic availability function as a Lyapunov function. It is shown how the closed loop performances, in terms of settling time and input control amplitude can be improved by modifying the availability function. Simulation results show the effectiveness of the proposed state feedback controls.

Keywords: Infinite-dimensional systems, Tubular reactors, Irreversible Thermodynamics, Lyapunov function, Distributed control

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1. Introduction

In this paper we study the stabilization of a tubular chemical reactor described by a set of non-linear Partial Differential Equations (PDEs). The proposed model is derived using mass and enthalpy balance equations in the context of irreversible Thermodynamics. Such system can be actuated at the upstream and the downstream of the tubular reactor and/or ideally along the reactor by using the heat exchanged with the jacket that delimits radially the reactor. In this paper, the stabilization problem is formulated for a desired (possibly unstable open loop) stationary profile with the use of the distributed jacket temperature as a control variable.

Stabilization of non-linear tubular reactors has drawn a particular attention over the last decade. In [29], the stability analysis of the open loop tubular reactor system is derived using a Lyapunov function issued from irreversible thermodynamic considerations. The thermodynamic function that is used is the so-called thermodynamic availability. Its positivity and convexity are by definition directly related to the properties of the entropy function issued from the second law of Thermodynamics [7]. A link with passivity is also proposed in [3, 30]. Nevertheless the study is proposed only for open loop stability analysis and by considering linear constitutive laws only valid close to the thermodynamic equilibrium. Recently, thermodynamics based approach motivated by the availability function for the boundary control of tubular reactors are proposed in [18, 31].

The proposed approach is a generalization of the work presented in [16] where the authors treated the stabilization of a continuous stirred tank reactor (finite dimensional system) around an unstable steady state by the use of the jacket temperature as control input.

The approach presented in the paper is also the extension to the previous work [34, 35]. In [34], a multi-variable approach for the control of tubular reactor is considered. The inlet temperature as well as the distributed jacket temperature were used as the control variables and no simulations were given. A stabilizing distributed control based on thermodynamic availability is proposed in [35] for stabilization around a stationary profile.

Here we consider the one dimensional model of a non isothermal tubular chemical reactor in which occur convection, dispersion, conduction and chemical reaction phenomena. The model is established in the framework of irreversible Thermodynamics by using the so called local equilibrium assumption [9]. Using the global availability function,i.e. the spatial integral of the local availability as a Lyapunov candidate function, we design a state feedback control which stabilizes the reactor at the desired stationary profile. Based on thermodynamic considerations, we then propose a modified availability function, called reduced availability, in order to improve the performances of the closed loop system (time response and control input amplitudes).

Depending on the operating conditions, the considered system can have more than one steady state. In [19, 20], this possibility is numerically and analytically shown. Recently, the existence of equilibrium profiles for non-isothermal tubular reactors has been mathematically investigated in [10, 14], one or three equilibria can be exhibited, depending on the parameters of the system, especially on the dispersion constant. Local exponential stability of equilibrium profiles is studied in [15], on the basis of stability properties of the linearised model and some relaxed Frechet differentiability conditions of the nonlinear semi-group generated by the dynamics. From this set of possible equilibria, the unstable steady state is usually of industrial interest as it corresponds to a high reaction efficiency with admissible temperature. Thus, many studies have been dedicated to the control of tubular reactors described by partial

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differential equations models around the unstable steady state profile [1, 6, 8, 13, 12, 22, 24, 28, 32].

The paper is organized as follows: in Section 2 we present the model of the tubular reactor issued from the mass and energy balances and give some simulation of the open loop system. In Section 3 we recall the main properties of irreversible Thermodynamics and define the availability function for finite and infinite dimensional systems. In Section 4, we propose a distributed stabilizing control law by the use of the availability function. In Section 5, the reduced availability function is defined and used in Section 6 as Lyapunov function to stabilize the system. We discuss the well-posedness for the non-linear feedback controls in Section 7. We give in section 8 some simulation results. The paper ends with some conclusions and perspectives.

2. The model of the reactor

We consider a tubular reactor in the longitudinal domain (1D) based on [5]. We note by $x \in [0, L]$ the spatial variable representing the position inside the reactor, where L is the total length of the reactor. We consider the following assumptions:

A1. We assume symmetries in the radial direction inside the reactor so only longitudinal axis is under consideration, which means uniform radial velocity,uniform radial temperature and concentration distribution.

A2. The total mass concentration ρ is constant.

A3. The dispersion flow of species i is given by $F^i_{dis} = -D\rho\frac{\partial \theta_i}{\partial x}$ where $\theta_i = \frac{\rho_i}{\rho}$ is the mass fraction of species i (for $i = A, B$), ρ_i the mass concentration of species i and D the dispersion constant.

A4. The conduction flow is chosen as $F_{cond} = -\lambda\frac{\partial T}{\partial x}$ where λ is the conduction coefficient considered constant, and T is the temperature inside the reactor at x.

A5. We consider the chemical reaction $\nu_A A \longrightarrow \nu_B B$ with ν_A, ν_B the stoichiometric coefficients considered as positive coefficient. The reaction rate r is first order with respect to the concentration of species A and the kinetic constant is given by the Arrhenius law : $r = k_0 exp(\frac{-E}{RT})\rho\frac{\theta_A}{\mathcal{M}_A}$[16] where k_0 is the reaction constant, E is the activation energy, R is the ideal gas constant and $\mathcal{M}_i$ is the molar mass of species i.

A6. The distributed heat exchange q with the jacket is considered proportional to the difference of temperature $q = C(T - T_j)$ according to Newton's law of cooling where T_j is the jacket temperature and C is the heat transfer coefficient of the jacket.

A7. The pressure P is constant.

A8. The reacting mixture is ideal and incompressible.

A9. The partial mass enthalpy of species is given by: $h_i = c_{p_i}(T - T_{ref}) + h_{iref}$ for $i = A, B$. The specific heat capacities c_{p_A} and c_{p_B} are constant. T_{ref} and h_{iref} are the references for the temperature and the enthalpy respectively.

A10. We suppose that for a desired steady state temperature profile $T_d(x)$ inside the reactor there exists a unique steady state concentration profile.

Remark 1. *This assumption does not mean that the reactor does not admit multiple steady states (stable or unstable) for a given set of input (see [10] for a discussion about multiple steady state). It is used in the finite dimensional case in [4].*

The model of the tubular reactor is given as follows [5]:

$$\frac{\partial z}{\partial t} = -\frac{\partial}{\partial x}(\overbrace{F_{conv} + F_d}^{F}) + R_e + gq \tag{1}$$

where $z^T = \begin{pmatrix} h & \rho_A & \rho_B \end{pmatrix}$ is the vector of state variable with h the enthalpy densities (per unit volume), ρ_A, ρ_B the density of species A and species B respectively. $F^T_{conv} = vz^T$is the vector of convective flows, with v the average fluid velocity. $F^T_d = \begin{pmatrix} F^h_{dis} + F_{cond} & F^A_{dis} & F^B_{dis} \end{pmatrix}$ is the vector of dispersion and conduction flows with $F^h_{dis} = h_A F^A_{dis} + h_B F^B_{dis}$, $R^T_e = \begin{pmatrix} 0 & -\nu_A r & \nu_B r \end{pmatrix}$ is the vector of reaction rates and $g^T = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix}$.

Based on the assumption that there is no dispersion outside the reactor and that we impose the input flow of reactant A, the boundary conditions are the following at the inlet of the reactor:

$$F^h_{conv}|_{in} = F^h|_0 = (F^h_{conv} + F^h_d)|_0 \tag{2}$$

$$F^A_{conv}|_{in} = F^A|_0 = (F^A_{conv} + F^A_{dis})|_0 \tag{3}$$

$$0 = F^B_{conv}|_{in} = F^B|_0 = (F^B_{conv} + F^B_{dis})|_0 \tag{4}$$

and at the outlet of the reactor(expressed using the mass fractions):

$$F^A_{dis}|_L = 0 \Longrightarrow \frac{\partial \theta_A}{\partial x}|_L = 0 \tag{5}$$

$$F^B_{dis}|_L = 0 \Longrightarrow \frac{\partial \theta_B}{\partial x}|_L = 0 \tag{6}$$

$$F_{cond}|_L = 0 \Longrightarrow \frac{\partial T}{\partial x}|_L = 0 \tag{7}$$

Finally we consider the following initial conditions:

$$\theta_A(0, x) = \theta_{A\,initial} \tag{8}$$

$$\theta_B(0, x) = 1 - \theta_{A\,initial} \tag{9}$$

$$h(0, x) = h_{initial} \tag{10}$$

2.1. Open loop simulations

This sub-section illustrates the open loop behaviour of the system through simulations with the use of a centred finite differences scheme for the discretization.Table 1 gives the numerical values of the parameters used for this simulation. We consider as initial conditions the steady state profile obtained for

$T_j = 350K$ with $T(t,0) = 330K$, $\theta_A(t,0) = 1$. We note this initial steady state $z^T_{initial} = \begin{pmatrix} h_{initial} & \rho\theta_{A\,initial} & \rho\theta_{B\,initial} \end{pmatrix}$ with $h_{initial}$ corresponding to an initial temperature profile $T_{initial}$. We simulate a uniform step change of the jacket temperature from $T_j = 350K$ to $T_j = 370K$ while keeping the same boundary conditions

Symb.	Numerical value	Symb.	Numerical value
c_{p_A}	$150.48\ J/(K \cdot g)$	c_{p_B}	$120\ J/(K \cdot g)$
C	$1.25 \cdot 10^5\ W/(m \cdot K)$	D	$4.5 \cdot 10^-5\ m^2/s$
E	$72.335\ KJ/mol$	h_{Aref}	$0\ J/g$
h_{Bref}	$-9150\ J/g$	k_0	$0.12\ 10^{10}\ 1/s$
L	$1\ m$	$\mathcal{M}_A$	$0.5\ g/mol$
$\mathcal{M}_B$	$0.5\ g/mol$	R	$8.314\ J/(K \cdot mol)$
s_{Aref}	$210.4\ J/(K \cdot g)$	s_{Bref}	$180.2\ J/(K \cdot g)$
T_{ref}	300 K	v	$0.0005\ m^3/mol$
λ	$1.25 \cdot 10^8\ J/(K \cdot m \cdot s)$	ρ	$1 \cdot 10^6\ g/m$

Table 1: Numerical values of parameters.

In Figure 1 is given the time response of the error between reactor temperature T and its initial profile $T_{initial}$ and in Figure 2 the error between mass fraction θ_B and its initial profile $\theta_{Binitial}$. The settling time for the open loop system is about $200s$.

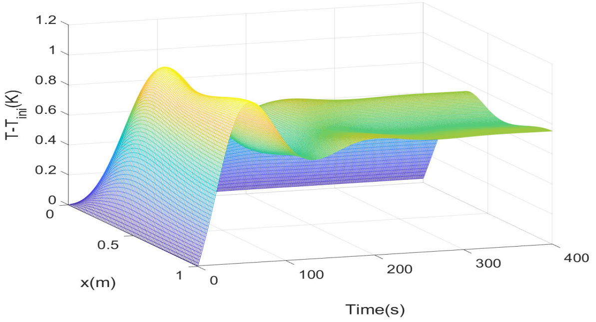

Figure 1: Time response of temperature deflection to a step change on T_j

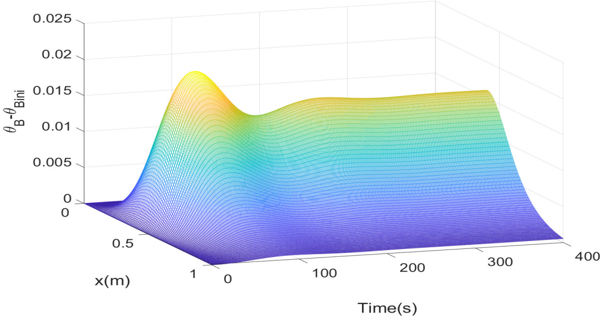

Figure 2: Time response of the composition deflection to s a step change on T_j

In Figure 3 we give the proposed steady state profile for the temperature and mass fraction θ_B which will be taken as the target profile for the stabilizing control law.

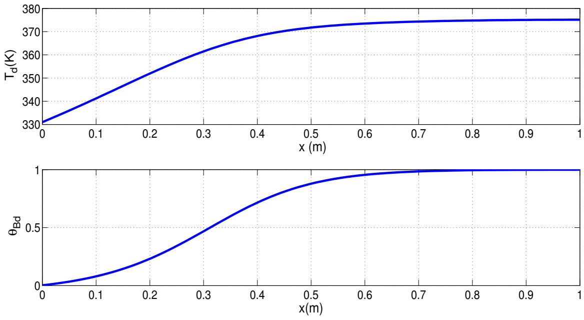

Figure 3: Temperature and B mass fraction (θ_B) Steady state profile (Open Loop)

3. Availability function for infinite dimensional thermodynamic systems

3.1. Gibbs Equation for infinite dimensional thermodynamic systems

In equilibrium Thermodynamics, the fundamental thermodynamic equation, the Gibbs equation states that the change in internal energy U of a system can always be written as the product of intensive variables $I^T = \begin{pmatrix} T & -P & \mu_i \end{pmatrix}$ with the differential of extensive variables $E^T = \begin{pmatrix} S & V & M_i \end{pmatrix}$ (see [7, 9]):

$$dU = I^T dE \tag{11}$$

where P is the pressure, T is the temperature and μ_i is the chemical potential of the species i, S is the entropy of the system, V the volume of the matter and M_i the mass of the species i. The internal energy U is also an extensive quantity which is an homogeneous function of degree one with respect to elements of E. From this property, we have also $U = I^T E$ and $I = \frac{\partial U}{\partial E}$. We can rewrite the Gibbs equation in entropic vision as follows(the precedent Gibbs equation (11) can be qualified as energetic version):

$$dS = W^T dZ \tag{12}$$

with $W^T = \begin{pmatrix} \frac{1}{T} & \frac{P}{T} & -\frac{\mu_i}{T} \end{pmatrix}$ and $Z^T = \begin{pmatrix} U & V & M_i \end{pmatrix}$. We can write the definition of intensive variables in the entropic vision as $W = \frac{\partial S}{\partial Z}$

In the case of infinite dimensional thermodynamic systems the Gibbs equation (11) can be restated by using quantities per unit of mass. Using the fact that the total mass concentration is constant we use quantities per unit of volume (concentrations) to write the Gibbs equation. With the assumption of constant pressure we can use the volume density of enthalpy $h(x,t)$ instead of the internal volume density of internal energy $u(x,t)$.

$$H = h(x,t)V = U + pV = (u + p)V \tag{13}$$

With $h(x,t) = u(x,t) + P$, the corresponding Gibbs equation is given by (see [7, 9]):

$$\begin{aligned} ds(x,t) &= \frac{1}{T}dh(x,t) - \sum_{1}^{n}\frac{\mu_i}{T}d\rho_i(x,t) \\ &= w^T(x,t)dz(x,t) \end{aligned} \tag{14}$$

where $s(x,t)$ is the volume density of entropy and $\rho_i(x,t)$ represents the volume density of species i, $z^T = (h\ ,\rho_i)$ and $w^T = (w_h,\ w_i) = (\frac{1}{T},\ -\frac{\mu_i}{T})$. From (14) and the relation $s = w^T z$ we derive the Gibbs-Duhem relation [29] :

$$dw^T z = 0 \tag{15}$$

We gives the entropy balance from (14) :

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x}(F^s_{conv} + F^s_{dis} + F^s_{cond}) - \frac{q}{T_j} + \sigma_s \tag{16}$$

where $F^s_{dis} = \sum_{i=A,B} F^i_{dis} s_i$ is the entropy diffusion flow induced by the diffusion of species, s_i is the partial entropy of species i and $F^s_{cond} = \frac{1}{T}F_{cond}$ is the entropy flow due to the heat conduction. The irreversible entropy production is deduced from (14) and (16). The detail of calculation is given in Appendix A :

$$\begin{aligned} \sigma_s &= \overbrace{q\Big(\frac{1}{T} - \frac{1}{T_j}\Big)}^{\sigma_{ext}} + \overbrace{\sum \mathcal{M}_i \nu_i r\Big(-\frac{\mu_i}{T}\Big)}^{\sigma_r} \\ &\quad + \overbrace{\sum F^i_{dis}\frac{\partial}{\partial x}\Big(-\frac{\mu_i}{T}\Big)}^{\sigma_d^{mat}} + \overbrace{F^h_d \frac{\partial}{\partial x}\Big(\frac{1}{T}\Big)}^{\sigma_d^{therm}} \end{aligned} \tag{17}$$

The irreversible entropy production (17) is assumed to be positive in the context of irreversible thermodynamics [7] with local equilibrium assumption.

The first term (σ_{ext}) in (17) (σ_{ext}) is due to the exchange with the jacket of the reactor. The positivity of this term can be easily verified by calculation $\sigma_{ext} = \frac{C(T-T_j)^2}{TT_j}$

The third and the fourth terms (σ_d^{mat} and σ_d^{therm}) are due to diffusion in the material domain and heat conduction in the thermal domain respectively. With Fourier law for heat conduction, σ_d^{therm} is shown to be quadratic and then positive [11]. Material dispersion σ_d^{mat} is quadratic and positive if the constitutive dispersion is expressed as $-D\frac{\partial \mu_i}{\partial x}$ (see also [11]). In this paper we choose mass fraction for representing the dispersion phenomena.

For the second term (σ_r) due to the chemical reaction, the reaction rate is non-linear with respect to the driving force. Since an academic example is treated, we choose thermodynamic parameters such that irreversible entropy production for reaction and dispersion remain positive in order to be consistent with thermodynamics.

The positivity of the fourth terms of irreversible entropy production is illustrated by simulation in Appendix A

3.2. Distributed Thermodynamic availability function

It has been shown in [29] that the thermodynamic availability function, in the case of finite dimensional system is defined as :

$$A(Z) = -\Big(W(Z) - W_d\Big)^T Z = (W_d)^T Z - S(Z) \tag{18}$$

with Z the vector of state variables, $W(Z)$ the intensive variables and $S(Z)$ the entropy of the system. This function is defined with respect to some reference state Z_d and the corresponding intensive variable $W_d = W(Z_d)$. This reference state may be a stationary point or a desired stationary point in the case of a closed loop control. The availability function $A(Z)$ is a positive and convex function [29] due to the second law of Thermodynamics. As consequence this function can be used as a Lyapunov function candidate for stability analysis of the open loop system [29] or for closed loop control synthesis [16, 17].

In the case of distributed parameter systems a particular care has to be taken to define adequately the local availability function and its link with the Lyapunov function candidate usable for control purpose. Indeed the Gibbs equation (14) and convexity properties can only be used in the case of local thermodynamic equilibrium assumption. The local availability function can be defined as follows:

$$a(z(x,t)) = -(w(z(x,t)) - w_d(x))^T z(x,t) \tag{19}$$

where $w_d(x) = w(z_d(x))$ refers to the desired time invariant intensive variables and $z_d(x)$ refers to the desired steady state. In the context of local thermodynamic equilibrium, the local availability $a(z(x,t))$ is a positive and convex function.

It is straightforward that $a(z) = 0$ if and only if $w(z) = w_d$ but this, in general, corresponds to a singular line in the state space defines by $z = \gamma z_d$ where γ is a positive homogeneity coefficient. In [21] the authors gives a theorem on the uniqueness of state variables z for a given intensive variables which is conditioned by fixing an inventory variable (in the case of homogeneous systems (one phase process)). In our case, the fixed inventory corresponds to the total mass inside the reactor induced by a constant total mass density ρ on a fixed total volume. Then we can write:

$$\begin{aligned} a(z(x,t)) = 0 \qquad &\Leftrightarrow w = w_d \\ &\Leftrightarrow z = z_d \end{aligned} \tag{20}$$

Under this assumption the local availability function becomes a strict convex and positive function:

$$\begin{cases} a(z(x,t) > 0\ \ ,\forall z \neq z_d \\ a(z(x,t) = 0\ \ ,z = z_d \end{cases} \tag{21}$$

Thanks to equation (14) and (15), the time derivative of $a(z)$ along the system trajectories is given by:

$$\frac{\partial a}{\partial t} = -(w - w_d)^T \frac{\partial z}{\partial t} \tag{22}$$

Let us define $\tilde{w} = w - w_d$ and consider the global availability function

$$A(z) = \int_0^L a dx = -\int_0^L \tilde{w}(x,t)^T z(x,t) dx \tag{23}$$

The global function $A(z)$ is a positive function[29]. From (22) and (1) the time derivative of A has the following expression:

$$\begin{aligned} \frac{dA(z)}{dt} &= \int_0^L \frac{\partial a}{\partial t} dx \\ &= \int_0^L -\tilde{w}^T \frac{\partial z}{\partial t} dx \\ &= \int_0^L \tilde{w}^T \left(\frac{\partial F}{\partial x} - R_e \right) dx - \int_0^L \tilde{w}^T g q dx \\ &= \int_0^L \tilde{w}^T \left(\frac{\partial F}{\partial x} - R_e \right) dx - \int_0^L \tilde{w}_h q dx \end{aligned} \tag{24}$$

where we used for the last computation $\tilde{w}^T g = \tilde{w}_h$.

4. Non linear control using A as Lyapunov function candidate

The objective of the control law is to stabilize the system around a desired stationary profile. We consider the jacket temperature $T_j(t,x)$ as distributed control input. For the control design we use the availability function $A(z(t,x))$ defined by (23) as Lyapunov function candidate. We do not prove existence of solution nor pre-compactness of trajectories. At first we look for the expression of the jacket heat flow $q(t,x)$ to shape the derivative of the availability function (24) such that it fulfils the Lyapunov stability conditions for the closed loop system. With the use of the constitutive expression of the heat flow $q(t,x)$ we deduce the expression of the jacket temperature $T_j(t,x)$. Hereafter, we propose two control laws for the stabilization of the reactor.

Proposition 2. *The dynamic system (1) closed with the distributed non-linear state feedback:*

$$T_{j_1}(z) = -\frac{\left(\tilde{w}^T \frac{\partial F}{\partial x} - \tilde{w}^T R_e + \tilde{z}^T K(z) \tilde{z} \right)}{C \tilde{w}_h} + T \tag{25}$$

with $K(z)$ a positive definite matrix and $\tilde{w}_h = \left(\frac{1}{T} - \frac{1}{T_d} \right)$ is globally asymptotically stable at z_d.

Proof. Using the expression of the state feedback (25) in the constitutive equation of the heat flow we obtain:

$$q := C(T - T_{j_1}) = \frac{\left(\tilde{w}^T \frac{\partial F}{\partial x} - \tilde{w}^T R_e + \tilde{z}^T K(z) \tilde{z} \right)}{\tilde{w}_h} \tag{26}$$

Using this expression of q in (24) leads to:

$$\frac{dA(z)}{dt} = -\int_0^L \tilde{z}^T K \tilde{z} dx \Rightarrow \begin{cases} \frac{dA(z)}{dt} < 0 & , \forall z \neq z_d \\ \frac{dA(z)}{dt} = 0 & , z = z_d \end{cases} \tag{27}$$

Thus $A(z)$ is a Lyapunov function candidate for the closed loop system. Using the uniqueness property (20) and the positivity of $A(z)$ we can write:

$$\begin{aligned} \lim_{t\to\infty} A(z) = 0 \quad &\Leftrightarrow \lim_{t\to\infty} a(z) = 0 \ \ \forall x \in [0, L] \\ &\Leftrightarrow \lim_{t\to\infty} z = z_d \ \ \forall x \in [0, L] \end{aligned} \tag{28}$$

We conclude that the closed loop system using the non linear state feedback (25) is globally asymptotically stable. □

We give hereafter another non linear state feedback control that shapes the derivative of $A(z)$ along the closed loop system trajectories in a different way.

Proposition 3. *The dynamic system (1) in closed loop with the non-linear state feedback:*

$$T_{j_2} = -\frac{\left(\tilde{w}^T \frac{\partial F}{\partial x} - \tilde{w}^T R_e + K(z) a \right)}{C \tilde{w}_h} + T \tag{29}$$

with $K(z)$ a positive definite real valued function is globally asymptotically stable at z_d.

Proof. Using the expression of the state feedback (29) in the constitutive equation of the heat flow we obtain:

$$q := C(T - T_{j_2}) = \frac{\left(\tilde{w}^T \frac{\partial F}{\partial x} - \tilde{w}^T R_e + K(z) a \right)}{\tilde{w}_h} \tag{30}$$

Using this expression of q in (24) we obtain:

$$\frac{dA(z)}{dt} = -\int_0^L K(z) a(z) dx \tag{31}$$

By the positivity of K and the property (21) of the local availability $a(z)$ we can write:

$$\frac{dA(z)}{dt} = -\int_0^L K(z) a(z) dx \Rightarrow \begin{cases} \frac{dA(z)}{dt} < 0 & , \forall z \neq z_d \\ \frac{dA(z)}{dt} = 0 & , z = z_d \end{cases} \tag{32}$$

Thus $A(z)$ is a Lyapunov function candidate for the closed loop system. Using the uniqueness property (20) and the positivity of $A(z)$ we can write:

$$\begin{aligned} \lim_{t\to\infty} A(z) = 0 \quad &\Leftrightarrow \lim_{t\to\infty} a(z) = 0 \ \ \forall x \in [0, L] \\ &\Leftrightarrow \lim_{t\to\infty} z = z_d \ \ \forall x \in [0, L] \end{aligned} \tag{33}$$

We conclude that the closed loop system obtained by using the non linear state feedback (29) is globally asymptotically stable. □

5. Reduced availability function A_r

In [16] in which lumped systems are considered, the authors propose to separate the availability function into two parts, denoted A_r and A_M. A_r corresponds to the thermal part of the original availability function A and A_M corresponds to its material counter part. They are mainly derived from the partition of the chemical potentials μ_i in ideal mixtures. This partition is as follows:

$$\begin{aligned} w_i &= \frac{\mu_i}{T} \\ &= \underbrace{\frac{1}{T}\left(c_{p_i}(T - T_{ref}) - c_{p_i} T \ln(\frac{T}{T_{ref}}) + h_{iref}\right) + s_{iref}}_{w_{ir}} \\ &\qquad + \underbrace{R \ln\left(\frac{\rho_i}{\rho}\right)}_{w_{iM}} \qquad , i = A, B \end{aligned} \tag{34}$$

The thermal and material parts of the local availability function $a(z(x,t))$ can be written as follows:

$$\left\{ \begin{array}{lcl} a_r &=& \tilde{w}_r z = -\tilde{w}_h h - \sum_i \tilde{w}_{ir}\rho_i \\ a_M &=& - \sum_i \tilde{w}_{iM}\rho_i \end{array} \right. \tag{35}$$

Where

$$\tilde{w}_r = \begin{pmatrix} \tilde{w}_h \\ \tilde{w}_{Ar} \\ \tilde{w}_{Br} \end{pmatrix} = \begin{pmatrix} \frac{1}{T} - \frac{1}{T_d} \\ (\frac{1}{T} - \frac{1}{T_d})(c_{p_A} T_{ref} - h_{Aref}) + c_{p_A} \ln(\frac{T}{T_d}) \\ (\frac{1}{T} - \frac{1}{T_d})(c_{p_B} T_{ref} - h_{Bref}) + c_{p_B} \ln(\frac{T}{T_d}) \end{pmatrix} \tag{36}$$

and

$$\tilde{w}_{iM} = R \ln\left(\frac{\rho_i}{\rho_{id}}\right) \tag{37}$$

As a consequence $a = a_r + a_M$. In the sequel we refer to a_r as the reduced local availability function. The global reduced and material availability functions, A_r and A_M respectively, can be defined as follows :

$$\left\{ \begin{array}{lcl} A_r &=& \int_0^L a_r dx = - \int_0^L \left(\tilde{w}_h h + \sum_i \tilde{w}_{ir}\rho_i\right) dx \\ A_M &=& \int_0^L a_M dx = - \int_0^L \left(\sum_i \tilde{w}_{iM}\rho_i\right) dx \end{array} \right. \tag{38}$$

Using Equation (36) and the fact that $h = \sum_i h_i \rho_i$ where $h_i = c_{p_A}(T - T_{ref}) + h_{iref}$ we can write a_r in the following form:

$$a_r = -\left(1 - \frac{T}{T_d} + ln\left(\frac{T}{T_d}\right)\right) C_p \tag{39}$$

With $C_p = c_{p_A}\rho_A + c_{p_B}\rho_B$ the total heat capacity.

Proposition 4. *From Assumptions A2 and A10, the reduced availability function is a positive and strictly convex function.*

Proof. Except for the trivial and excluded case where $\rho_A = \rho_B = 0$, from thermodynamic considerations, heat capacities are strictly positive so total heat capacity C_p is positive[7]. It is shown in [16] that :

$$\left(1 - \frac{T}{T_d} + ln\left(\frac{T}{T_d}\right)\right) < 0 \qquad \forall T, T_d > 0 \tag{40}$$

As a consequence, function $a_r(z)$ is also a positive function. By a formal computation of the eigenvalues for the hessian of $a_r(z)$ we obtain two zero eigenvalues and only one positive one given by:

$$\lambda = \frac{C_p^2 + (hc_{p_A} + \rho_B\gamma)^2 + (hc_{p_B} + \rho_A\gamma)^2}{C_p(\rho_A\beta_A + \rho_B\beta_B - h)^2} > 0 \tag{41}$$

where $\beta_A = (h_{A_{ref}} - c_{p_A}T_{ref}), \beta_B = (h_{B_{ref}} - c_{p_B}T_{ref})$ and $\gamma = \beta_A c_{p_B} - \beta_B c_{p_A}$. Hence a_r is convex but not strictly convex. This lack of strict convexity can be shown otherwise by the existence of a set in the state space where the temperature is constant and equal to T_d . Using the expression of the enthalpy h:

$$\begin{aligned} h &= \rho_A h_A + \rho_B h_B \qquad (42) \\ &= \rho_A(c_{p_A}(T - T_{ref}) + h_{iref}) + \rho_B(c_{p_B}(T - T_{ref}) + h_{iref}) \\ &= T(c_{p_A}\rho_A + c_{p_B}\rho_B) + (\rho_A(h_{A_{ref}} - c_{p_A}T_{ref}) \\ &\quad -\rho_B(h_{B_{ref}} - c_{p_B}T_{ref})) \end{aligned}$$

we can rewrite the temperature T as a function of the state variables :

$$T = \frac{h - \rho_A(h_{A_{ref}} - c_{p_A}T_{ref}) - \rho_B(h_{B_{ref}} - c_{p_B}T_{ref})}{c_{p_A}\rho_A + c_{p_B}\rho_B} \tag{43}$$

One can deduce from the expression (39) of the reduced availability function that $a_r = 0$ if and only if $T = T_d$. Using the expression (43) we derive the set of the state space where $a_r = 0$:

$$\begin{aligned} a_r(z) = 0 \quad &\Leftrightarrow \quad T = T_d \\ &\Leftrightarrow \quad h + \alpha_1\rho_A + \alpha_2\rho_B = 0 \end{aligned} \tag{44}$$

where $\alpha_1 = c_{p_A}(T_{ref} - T_d) - h_{A_{ref}} = -h_A(T_d)$ and $\alpha_2 = c_{p_B}(T_{ref} - T_d) - h_{B_{ref}} = -h_B(T_d)$. By Assumption A10 this set reduced to the desired steady state z_d and at the same time the reduced availability function $a(z(x,t))$ becomes strictly convex. Thus the global reduced availability function (38) is also a positive function of z that vanishes when $T = T_d$ which is equivalent (by Assumption A10) to $z = z_d$. □

The time derivative of the reduced global availability function A_r along the system trajectory (1) is given by:

$$\begin{aligned} \frac{dA_r(z)}{dt} &= \int_0^L \frac{\partial a_r}{\partial t} dx \\ &= \int_0^L \tilde{w}_r{}^T \left(\frac{\partial F}{\partial x} - R_e\right) dx - \int_0^L \tilde{w}_h q dx \end{aligned} \tag{45}$$

6. Non linear control using A_r as Lyapunov function candidate

We decline hereafter the nonlinear control feedbacks given in Proposition 2 and 3 with the use of A_r instead of A as a new Lyapunov function candidate.

Proposition 5. *The dynamic system (1) in closed loop with the following nonlinear state feedback:*

$$T_{j3} = -\frac{\left[\tilde{w_r}^T \frac{\partial F}{\partial x} - \tilde{w_r}^T R_e + \tilde{z}^T K(z)\tilde{z}\right]}{C\tilde{w}_h} + T(x) \tag{46}$$

where $K(z)$ a positive definite matrix valued function and $\tilde{w}_h = (\frac{1}{T} - \frac{1}{T_d})$ is globally asymptotically stable and converges to the desired state z_d.

Proof. As for Proposition 2 the time derivative of A_r along the closed loop system trajectories using the non-linear state feedback (46) is given by :

$$\frac{dA_r(z)}{dt} = -\int_0^L \tilde{z}^T K(z)\tilde{z}dx \tag{47}$$

Then we can write:

$$\begin{aligned} \left\{\begin{array}{l} \frac{dA_r(z)}{dt} < 0 \text{ for } z \neq z_d \\ \frac{dA_r(z)}{dt} = 0 \text{ for } z = z_d \end{array}\right. & \Rightarrow \lim_{t\to+\infty} A_r(z) = 0 \\ & \Leftrightarrow \lim_{t\to+\infty} a_r(z) = 0 \ \forall x \in [0, L] \\ & \Leftrightarrow \lim_{t\to+\infty} z = z_d \qquad (48) \end{aligned}$$

Where we used the last Assumption A10 for $T = T_d$. We conclude that A_r is a Lyapunov function candidate for the closed loop system and that the closed loop system is globally asymptotically stable in z_d. ☐

Proposition 6. *The dynamic system (1) in closed loop with the following non-linear state feedback:*

$$T_{j4} = -\frac{\left[\tilde{w_r}^T \frac{\partial F}{\partial x} - \tilde{w_r}^T R_e + K(z)a_r\right]}{C\tilde{w}_h} + T(x) \tag{49}$$

With $K(z)$ a positive function of z, is globally asymptotically stable in z_d.

Proof. The proof follows the same steps as the one of Proposition 5.

☐

7. Well-posedness for non-linear feedback controls

The four non linear feedbacks that have been proposed contain a division by $\tilde{w}_h = (\frac{1}{T} - \frac{1}{T_d})$. In order to validate the control law we have to check if this term does not blow up when T converges to T_d. So we have to make sure that the non-linear expression of the jacket temperature (input control) is bounded.

Proposition 7. *The control law T_{j_1} defined by Proposition 2 which renders the system globally asymptotically stable in z_d is bounded.*

Proof. We recall the asymptotic expression of the jacket temperature T_{j_1}

$$\begin{aligned} T_{j_1}(z) &= -\frac{\left[\tilde{w}^T \frac{\partial F}{\partial x} - \tilde{w}^T R_e + \tilde{z}^T K(z)\tilde{z}\right]}{C\tilde{w}_h} + T \\ &= T + \overbrace{\frac{\tilde{z}^T K\tilde{z}}{C\tilde{w}_h}}^{\phi_1(z)} + \overbrace{\frac{\tilde{w}_r^T(\partial_x F - R_e)}{C\tilde{w}_h}}^{\phi_2(z)} + \overbrace{\frac{\tilde{w}_M^T(\partial_x F - R_e)}{C\tilde{w}_h}}^{\phi_3(z)} \end{aligned}$$

where $\phi_2(z)$ and $\phi_3(z)$ are issued from the thermal and material split of the intensive variables, respectively.

By using a Taylor series development of the term $\ln \frac{T}{T_d}$ around $T = T_d$ (36), we obtain the asymptotic equation for the thermal part of intensive variables when $T \to T_d$:

$$\tilde{w}_r = \tilde{w}_h \begin{pmatrix} 1 \\ -h_A \\ -h_B \end{pmatrix} \tag{50}$$

where h_A and h_B are linear functions of T given in Assumption A9. The asymptotic expression of the jacket temperature T_{j_1} becomes:

$$T_{j_1} = \begin{pmatrix} -1 & h_A & h_B \end{pmatrix}(\partial_x F - R_e) + T + \phi_1(z) + \phi_3(z) \tag{51}$$

Firstly, we study the boundedness of the state variables z, reaction rate R_e, and transport vector $\partial_x F$ near the equilibrium profile.

Near the equilibrium profile, $(h_i(T))_{T\to T_d} = h_i(T_d)$. By definition the mass fraction of species i $\theta_i \in [0, 1]$ and $\rho_i = \rho\theta_i$ is bounded, so $(h)_{T\to T_d} = (\rho \sum \theta_i h_i)_{T\to T_d}$ is bounded. Thus the state variable $z = \begin{pmatrix} h & \rho_A & \rho_B \end{pmatrix}^T$ is bounded.

By the boundedness of θ_A, the reaction rate $r = k_0 exp(\frac{-E}{\bar{R}T})\rho\frac{\theta_A}{\mathcal{M}_A}$ is also bounded near the equilibrium profile so that the reaction matrix R_e is bounded.

$F_{conv} = vz$ is bounded by the boundedness of z. It is clear that $F_{cond} = -\lambda\frac{\partial T}{\partial x}$ is bounded near the equilibrium profile. $F^i_{dis} = -D\rho\frac{\partial\theta_i}{\partial x}$ is bounded near the equilibrium profile by the boundedness of θ_i, and then $F^h_{dis} = \sum h_i F^i_{dis}$ is bounded. As the result, the vector of total flow $F = F_{conv} + F_d$ is bounded and it's evident that its derivative of space $\partial_x F$ is bounded.

From equation (51) and the boundedness of the state variables z, reaction R_e and the transport vector $\partial_x F$ we can conclude that the thermal part of control law $\begin{pmatrix} -1 \\ h_A \\ h_B \end{pmatrix}^T (\partial_x F - R_e) + T$ is bounded when $T \to T_d$.

Let's study the boundedness of the material part $\phi_3(z)$ and control part $\phi_1(z)$ of control equation (51). The idea is to eliminate the division term in denominator by expressing the vector of state variables z and vector of the materiel part of intensive variables ω_M by the same variable ρ_A near the equilibrium profile.

As mentioned in section 5, a_r is null on the subspace of the state space defined by:

$$T = T_d \Leftrightarrow h + \alpha_1\rho_A + \alpha_2\rho_B = 0 \qquad (52)$$

With the condition (52) around $T = T_d$ and $\rho = \rho_A + \rho_B$, we can write near the equilibrium profile that :

$$\rho_A = \frac{h + \alpha_2\rho}{\alpha_2 - \alpha_1} \quad => \quad \tilde{\rho_A} = \frac{\tilde{h}}{\alpha_2 - \alpha_1} \qquad (53)$$

We can check that $\alpha_2 = \alpha_1$ if and only if $T_d = T_{ref} + \frac{h_{A_{ref}} - h_{B_{ref}}}{c_{p_A} - c_{p_B}}$. Hence, this particular steady state T_d is excluded in order to avoid a singular value for ρ_A.

Using Taylor series development of the term $ln\frac{\rho_i}{\rho_{id}}$ around equilibrium profile, the materiel part becomes :

$$\tilde{w}_M = \begin{pmatrix} 0 \\ ln\frac{\rho_A}{\rho_{Ad}} \\ ln\frac{\rho_B}{\rho_{Bd}} \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{\rho_A - \rho_{Ad}}{\rho_{Ad}} \\ \frac{\rho_B - \rho_{Bd}}{\rho_{Bd}} \end{pmatrix} = \begin{pmatrix} 0 \\ \frac{\tilde{\rho_A}}{\rho_{Ad}} \\ -\frac{\tilde{\rho_A}}{\rho_{Bd}} \end{pmatrix} = \frac{\tilde{h}}{\alpha_2 - \alpha_1} \begin{pmatrix} 0 \\ \frac{1}{\rho_{Ad}} \\ -\frac{1}{\rho_{Bd}} \end{pmatrix} \qquad (54)$$

The vector of extensive variables around the equilibrium is equal to

$$\tilde{z} = \begin{pmatrix} \tilde{h} \\ \tilde{\rho_A} \\ \tilde{\rho_B} \end{pmatrix} = \begin{pmatrix} \tilde{h} \\ \tilde{\rho_A} \\ -\tilde{\rho_A} \end{pmatrix} = \tilde{h} \begin{pmatrix} 1 \\ \frac{1}{\alpha_2 - \alpha_1} \\ -\frac{1}{\alpha_2 - \alpha_1} \end{pmatrix} \qquad (55)$$

According to (54) and (55), $\phi_3(z)$ and $\phi_1(z)$ can be written as :

$$\begin{aligned} \phi_3(z) &= -\frac{\tilde{h}}{\tilde{w_h}} \frac{1}{C(\alpha_2 - \alpha_1)} \begin{pmatrix} 0 \\ \frac{1}{\rho_{Ad}} \\ -\frac{1}{\rho_{Bd}} \end{pmatrix}^T (\partial_x F - R_e) \\ \phi_1(z) &= \frac{\tilde{h}}{\tilde{w_h}} \begin{pmatrix} 1 \\ \frac{1}{\alpha_2 - \alpha_1} \\ -\frac{1}{\alpha_2 - \alpha_1} \end{pmatrix}^T \frac{K\tilde{z}}{C} \end{aligned}$$

Let us study the term $\frac{\tilde{h}}{\tilde{w_h}}$ in order to eliminate the division part in the denominator.

The enthalpy h can be linearised near the desired profile with respect to the intensive variables $\frac{1}{T}$,$-\frac{\mu_A}{T}$ and $-\frac{\mu_B}{T}$, see the details in [33] or in Appendix B :

$$\tilde{h} = \theta_1 \left(\frac{\tilde{1}}{T}\right) + \theta_2 \left(-\frac{\tilde{\mu}_A}{T}\right) + \theta_3 \left(-\frac{\tilde{\mu}_B}{T}\right) \qquad (56)$$

with $\theta_1 = -(\rho C_{p_d} T_d^2 + \frac{h_{A_d}^2 \rho_{A_d}}{R} + \frac{h_{B_d}^2 \rho_{B_d}}{R})$ $\theta_2 = -\frac{h_{A_d}\rho_{A_d}}{R}$ $\theta_3 = -\frac{h_{B_d}\rho_{B_d}}{R}$ and $C_{p_d} = C_{p_d}\frac{\rho_{A_d}}{\rho} + C_{p_B}\frac{\rho_{B_d}}{\rho}$, R is the ideal gas constant.

$$\frac{\tilde{h}}{\tilde{w_h}} = \frac{\theta_1 \frac{\tilde{1}}{T} + \theta_2(-\frac{\tilde{\mu}_A}{T}) + \theta_3(-\frac{\tilde{\mu}_B}{T})}{\frac{\tilde{1}}{T}} \qquad (57)$$

According to the extension of Gibbs–Helmholtz equation (see detail in Appendix C), when the system is near the equilibrium,

$$\begin{aligned} \lim_{T \to T_d} \begin{pmatrix} \frac{-\frac{\tilde{\mu}_A}{T}}{\frac{\tilde{1}}{T}} \end{pmatrix} &= \begin{pmatrix} \frac{\partial(-\frac{\mu_A}{T})}{\partial(\frac{1}{T})} \end{pmatrix}_{T \to T_d} &= h_A(T_d) \\ \lim_{T \to T_d} \begin{pmatrix} \frac{-\frac{\tilde{\mu}_B}{T}}{\frac{\tilde{1}}{T}} \end{pmatrix} &= \begin{pmatrix} \frac{\partial(-\frac{\mu_B}{T})}{\partial(\frac{1}{T})} \end{pmatrix}_{T \to T_d} &= h_B(T_d) \end{aligned} \qquad (58)$$

then

$$\left(\frac{\tilde{h}}{\tilde{w_h}}\right)_{T \to T_d} = \theta_1 + \theta_2 h_A(T_d) + \theta_3 h_B(T_d) = \beta \qquad (59)$$

The denominator $\tilde{w_h}$ is eliminated by calculation and then the term $\frac{\tilde{h}}{\tilde{w_h}}$ converges to the constant β.

$$\begin{aligned} \lim_{T \to T_d} T_{j_1} &= \begin{pmatrix} -1 \\ h_A \\ h_B \end{pmatrix}^T (\partial_x F - R_e)|_{T=T_d, z=z_d} + T_d \\ &- \frac{\beta}{(\alpha_2 - \alpha_1)C} \begin{pmatrix} 0 \\ \frac{1}{\rho_{Ad}} \\ -\frac{1}{\rho_{Bd}} \end{pmatrix}^T (\partial_x F - R_e)|_{T=T_d, z=z_d} \\ &+ \begin{pmatrix} 1 \\ \frac{1}{\alpha_2 - \alpha_1} \\ -\frac{1}{\alpha_2 - \alpha_1} \end{pmatrix}^T \frac{\beta K \tilde{z}}{C} < +\infty \end{aligned}$$

According to the boundedness of K, z, reaction R and transport vector $\partial_x F$, we can conclude that T_{j_1} is bounded when $T \to T_d$.

□

Proposition 8. *The control variable T_{j_2} defined by proposition3 which renders the system globally asymptotically stable in z_d is bounded.*

Proof. By Taylor series development of the term $\ln\frac{T}{T_d}$ around $T = T_d$ in the expression (36) of the reduced intensive variables, we obtain the asymptotic equation for the intensive variables when $T \to T_d$:

$$\tilde{w_r} = \tilde{w_h} \begin{pmatrix} 1 \\ -h_A \\ -h_B \end{pmatrix} \qquad (60)$$

where h_A and h_B are linear functions of T given in assumption A9. Thus the asymptotic expression of the jacket temperature is given by:

$$\begin{aligned} T_{j_2} &= \begin{pmatrix} -1 \\ h_A \\ h_B \end{pmatrix}^T (\partial_x F - R_e - Kz) + T \\ &+ \frac{\tilde{w}_M^T(\partial_x F - R)}{C\tilde{w}_h} \end{aligned} \qquad (61)$$

by boundedness of the state variables z, reaction R and transport vector $\partial_x F$ we can conclude that $\begin{pmatrix} -1 \\ h_A \\ h_B \end{pmatrix}^T (\partial_x F - R_e - Kz) + T$ is bounded when $T \rightarrow T_d$.

As demonstrated in proposition7, $\frac{\tilde{w}_M^T(\partial_x F - R_e)}{C\tilde{w}_h}$ is bounded when $T \rightarrow T_d$. As a result, we can conclude that T_{j2} is bounded when $T \rightarrow T_d$.

□

Proposition 9. *The control variable T_{j3} defined by proposition5 which renders the system globally asymptotically stable at z_d is bounded.*

Proposition 10. *The control variable T_{j4} defined by proposition6 which renders the system globally asymptotically stable at z_d is bounded.*

For the demonstration for the two control laws proposed in Proposition 9 and 10 using A_r as Lyapunov function candidate, the expressions contain only the thermal part, which has been proven to be bounded and well defined in proposition 7 and 8

8. Simulation results

In this section, we illustrate through simulations for the performances of the closed loop system with the designed nonlinear state feedback controls.

The control objective here is to stabilize the system at a specific steady state corresponding to the following operative conditions:

$$\begin{cases} T_j & = & 370K \\ T_{in} & = & 330K \\ \theta_{A_{in}} & = & 1 \end{cases} \tag{62}$$

This desired steady state is the one presented in Figure 3. The initial state of the system corresponds to $T_j = 350K$ and the same boundary conditions as the ones given in (62) are used.

The feedback gain K for proposition 1 and 3 is chosen as follows:

$$K = \begin{pmatrix} \delta & 0 & 0 \\ 0 & \frac{\delta}{100} & 0 \\ 0 & 0 & \frac{\delta}{100} \end{pmatrix} \tag{63}$$

With δ a positive constant. For each designed state feedback control T_{j_1} to T_{j4}, we illustrate the performance using the closed loop response of the temperature T and mass fraction θ_B (equivalently θ_A) in term of stabilization error. We plot the time evolution for the jacket temperature T_j (control input) as well as for T_{j_1} and T_{j3}, the time evolution of the local and the global (reduced) availability functions . Finally we compare the global availability function with the reduced availability function for the case of T_{j3}.

8.1. Case 1: simulation results with T_{j1}

First we present the simulations results using the command T_{j_1} given in Proposition 2 with $\delta = 6000$. The temporal and spatial evolutions of the error between the closed loop temperature T of the reactor and its equilibrium profile T_d as well as the closed loop mass fraction θ_B are presented in Figure 4 and 5. We observe that these errors converge globally and asymptotically to zero, which involves the global and asymptotic convergence of state variables z to the desired equilibrium profile z_d .

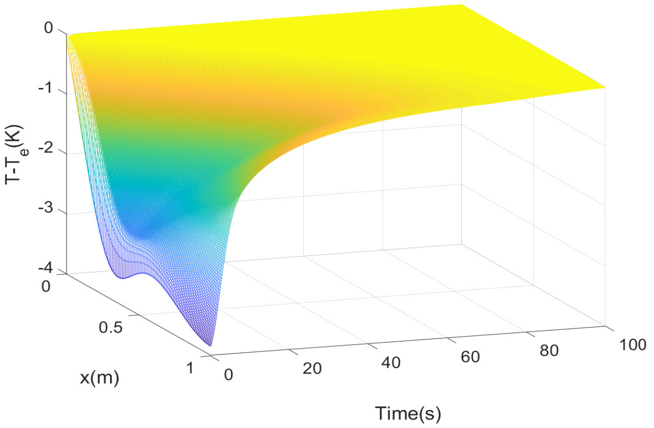

Figure 4: case 1-Time response of temperature error for the closed loop system

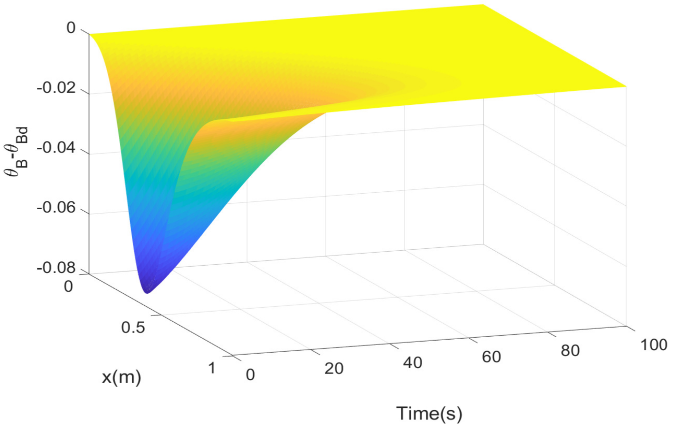

Figure 5: case 1-Time response of mass fraction error for the closed loop system

We can notice that the closed loop system converges faster than the open loop system to the desired equilibrium profile z_d (approximatively 2 hours faster). The amplitude of the temperature of the jacket is excessively high during the transient regime. Figure 7 shows the time and spatial evolution of the local availability function. It converges globally and asymptotically to zero along the tubular reactor. Figure 8 shows that the global availability function converges asymptotically to zero.

8.2. Case 2: simulation results with T_{j2}

We present now the simulation results of the closed loop system with the feed-back T_{j2} given in proposition 3. We use the same expression for K_1 than the one in proposition 2 with $\delta = 0.02$.

The temporal and spatial evolution of the error between the closed loop temperature T of the reactor and its equilibrium profile T_d as well as the closed loop mass fraction θ_B are presented in Figure 9 and 10. These errors converge also globally and asymptotically to zero, which involves the global and asymptotic convergence of state variables z to the desired equilibrium profile z_d.

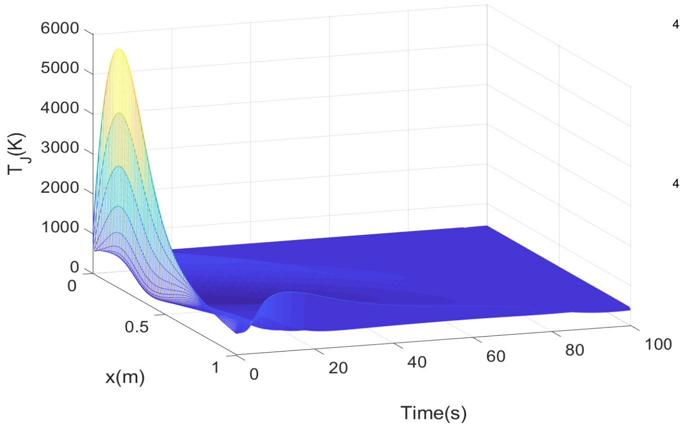

Figure 6: case 1-Time evolution of the jacket temperature at different x

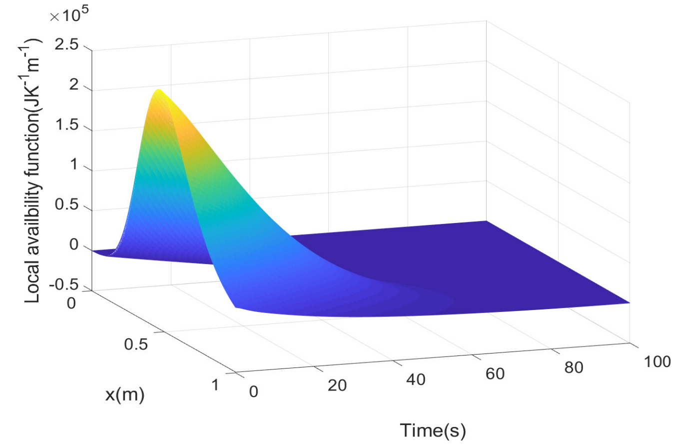

Figure 7: case 1-Time evolution of the local availability function at different x

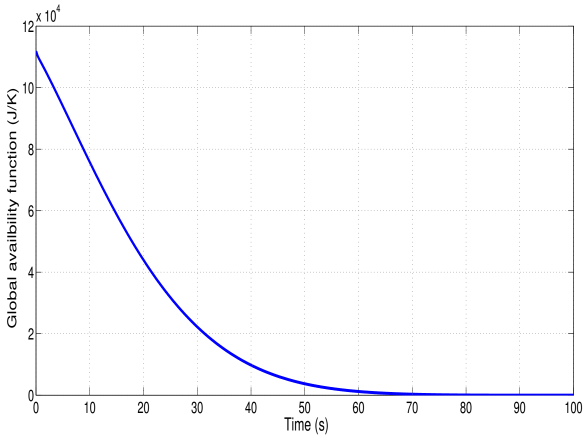

Figure 8: case 1-Time evolution of the global availability function

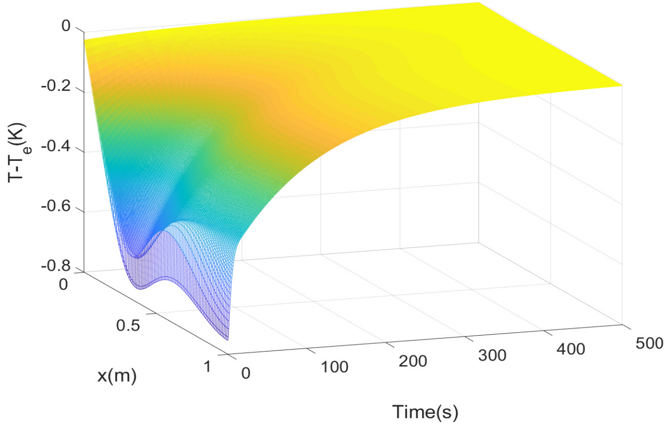

Figure 9: case 2-Time response of temperature error for the closed loop system

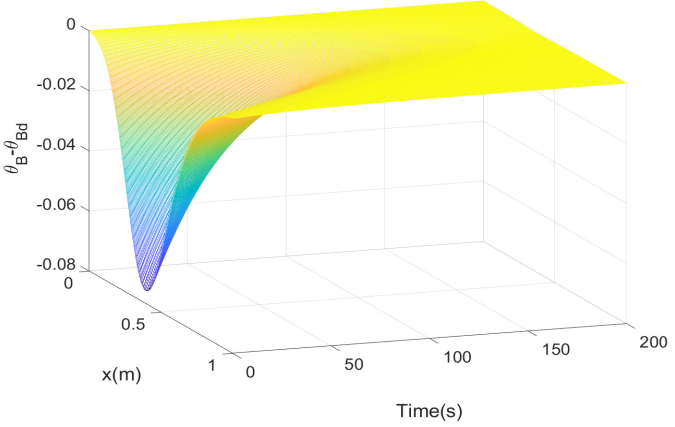

Figure 10: case 2-Time response of mass fraction error for the closed loop system

8.3. *Case 3: simulation results with T_{j_3}*

Here we present the simulations results using the command T_{j_3} given in proposition 5 with $\delta = 200$. The temporal and spatial evolutions of the error between the closed loop temperature T of the reactor and its equilibrium profile T_d as well as the closed loop mass fraction θ_B are presented in Figure 12 and 13.

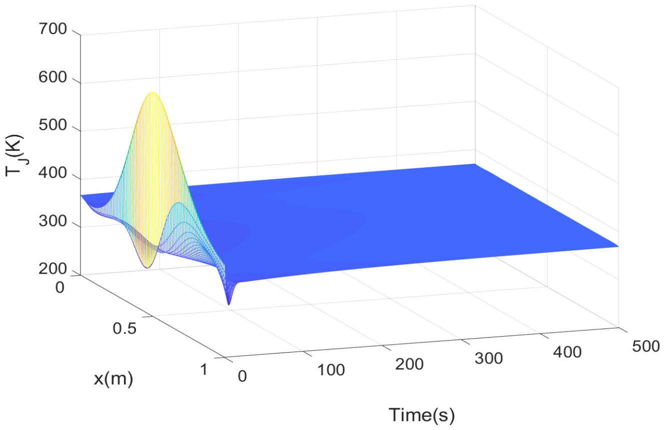

Figure 11: case 2-Time evolution of the jacket temperature at different x

We observe that these errors converge globally and asymptotically to zero, which involves the global and asymptotic convergence of state variables z to the desired equilibrium profile z_d .

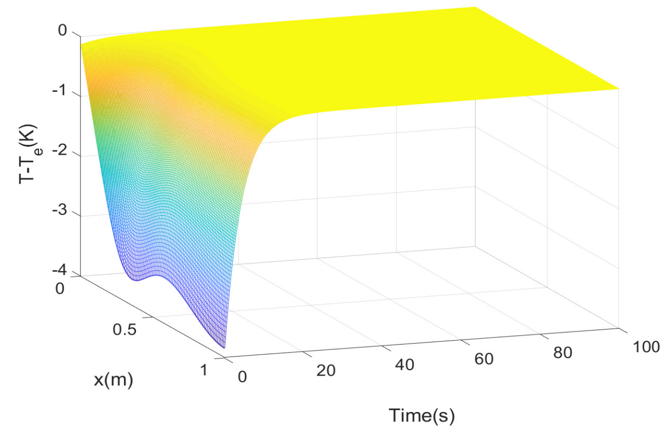

Figure 12: case 3-Time response of temperature error for the closed loop system

The system converges globally and asymptotically to the equilibrium profile in $60s$ compared to $100s$ with T_{j_1}. Figure 14 shows the temporal and spatial evolutions of the jacket temperature. We notice a decrease in amplitude and variations of T_j.

Figure 15 shows the time and spatial evolutions of the reduced local availability function. It converges globally and asymptotically to zero along the tubular reactor. We notice that it converges globally and asymptotically toward zero along the tubular reactor with a strong decrease of the amplitudes in amplitudes compared to a.

Figure 16 shows the time evolutions of the global availability function A and the global reduced availability function A_r with the same control laws T_{j_3}. We notice that A_r converges faster than A with also a smaller amplitude.

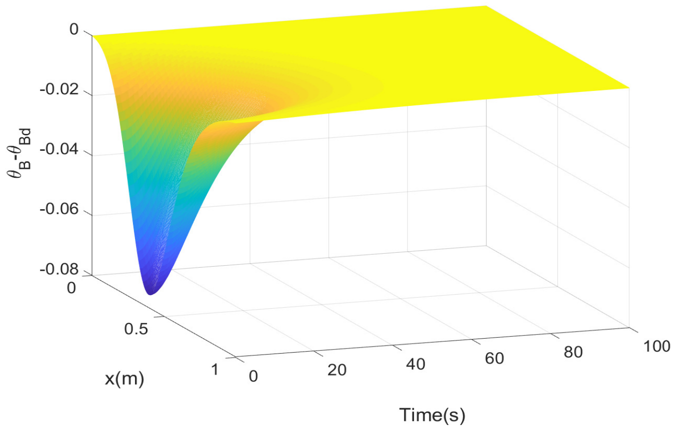

Figure 13: case 3-Time response of mass fraction error for the closed loop system

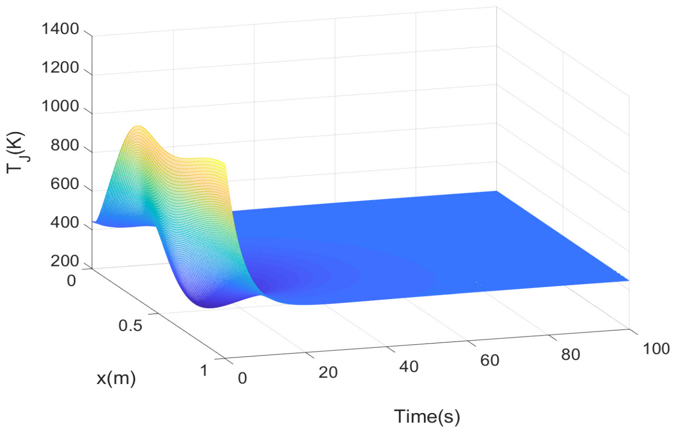

Figure 14: case 3-Time evolution of the jacket temperature at different x

8.4. *Case 4: simulation results with T_{j4}*

We present the simulation results using the command T_{j_4} given in proposition 6 with $\delta = 0.15$. The temporal and spatial evolution of the error between the closed loop temperature T of the reactor and its equilibrium profile T_d as well as the closed loop mass fraction θ_B are presented in Figure 17 and 18. We observe that these errors converge globally and asymptotically to zero, which involves the global and asymptotic convergence of state variables z to the desired equilibrium profile z_d .

From Figure 17 and 18, we observe that the response time is approximatively $80s$ instead of $200s$ with respect to case 2 for proposition 3. Figure 19 shows the temporal and spatial evolution of the jacket temperature. We notice that the amplitude is similar to T_{j_2} but with less abrupt variations.

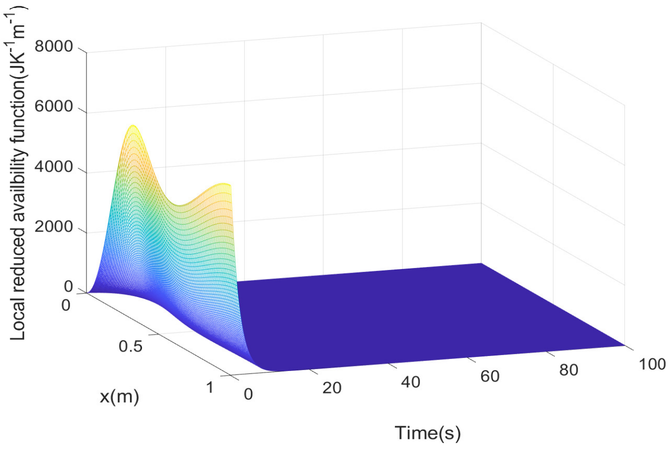

Figure 15: case 3-Time evolution of the reduced local availability function at different x

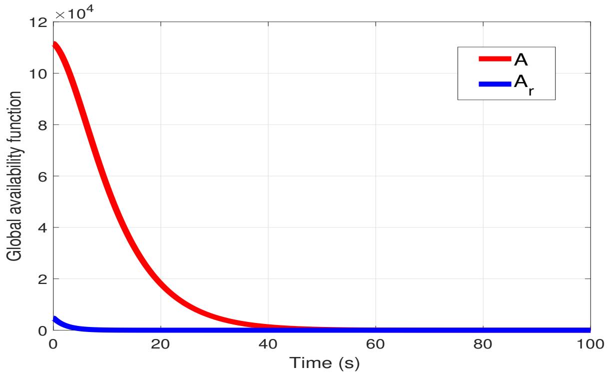

Figure 16: global availability function A and global reduced availability function A_r with T_{j3}

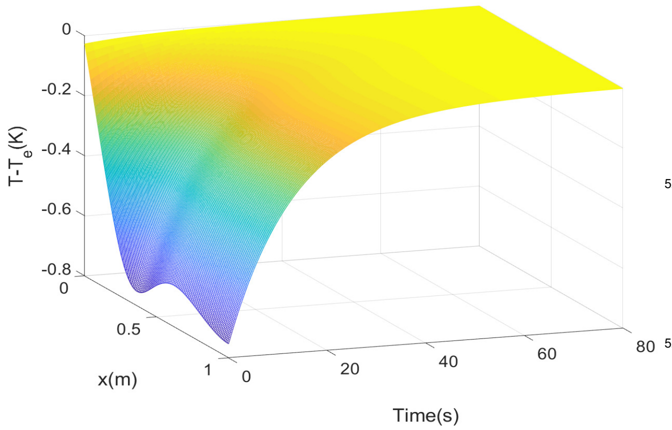

Figure 17: case 4-Time response of temperature error for the closed loop system

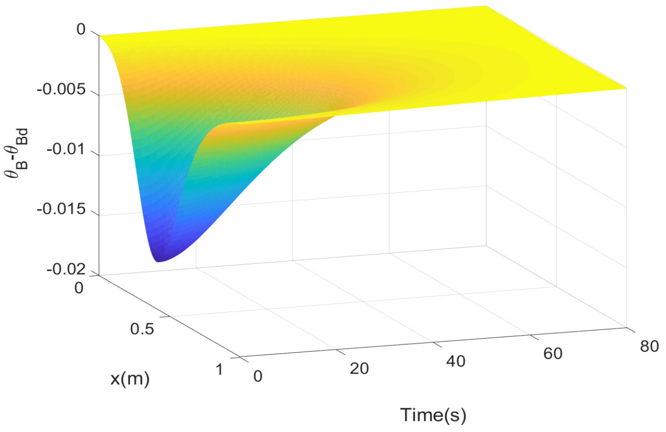

Figure 18: case 4-Time response of mass fraction error for the closed loop system

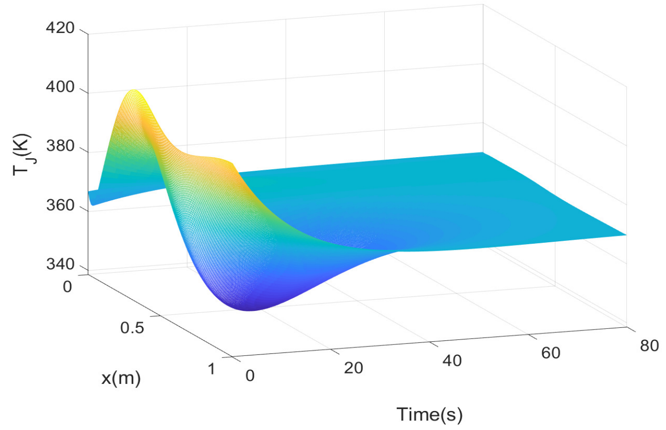

Figure 19: case 4-Time evolution of the jacket temperature at different x

From the comparison of the robust performance of the availability based (proposition 2 and 3) and reduced availability based (proposition 5 and 6) controllers, it can be concluded that the proposed reduced availability based controller have the better behaviour. The response times of proposition 5 and 6 using reduced availability are reduced compared to those of 2 and 3. Furthermore, the amplitudes of the jacket temperature using reduced availability are much lower so that the consumed energy to heat the jacket is economised.

8.5. *Robustness towards perturbations : numerical results:*

We consider in this subsection the perturbation rejection problem for the closed loop system using Proposition 3. We consider the simulation case of proposition 3 and apply a constant perturbation on the inlet species temperature $T_{in} = (330 - 5)K$ from $100s$. For this we compare the stationary profile of the open loop response (with $T_j = T_{jd} = 370K$) and the closed loop one starting from the same initial steady state used in the above simulation results. Figure 20 and Figure 21 illustrate the temperature and mass fraction error with respect to the desired steady state profile in closed loop at $t = 1500s$ in presence of the cited perturbation. From this comparison we conclude about the perfect rejection of the perturbation along the reactor when we use the non linear state feedback. However it is difficult to reject the perturbation on the inlet of reactor even if the control jacket temperature is inadmissibly high. In this condition we limited the control temperature to $1000K$. The ideal method to reject this perturbation should be a boundary control.

We observe from figure 22 that the local reduced availability function converges asymptotically to zero along the reactor, and state variables z converge to the desired equilibrium profile z_d .

From industrial considerations, only the temperature and mass fraction at the outlet of reactor is of interest, so we can conclude that from an industrial point of view the results in terms of perturbation rejection are satisfactory. It can be also concluded that the control law proposed is robust to perturbations.

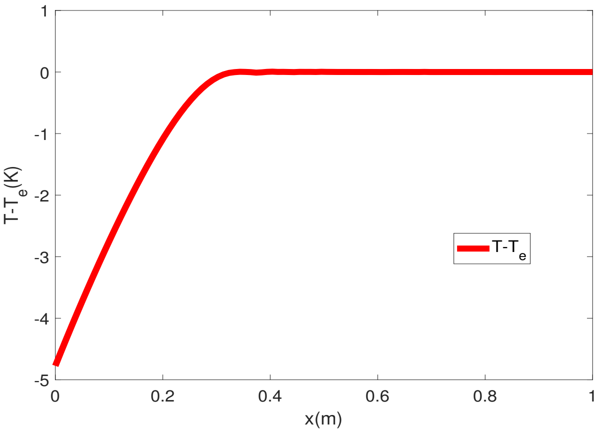

Figure 20: Temperature error with respect to the desired steady state profile at $t = 1500s$

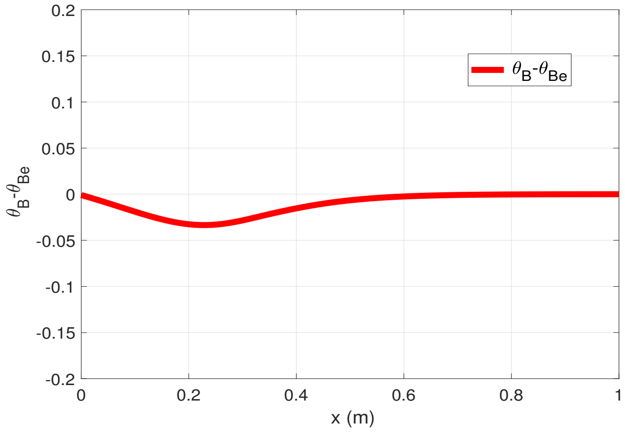

Figure 21: Mass fraction error with respect to the desired steady state profile at $t = 1500s$

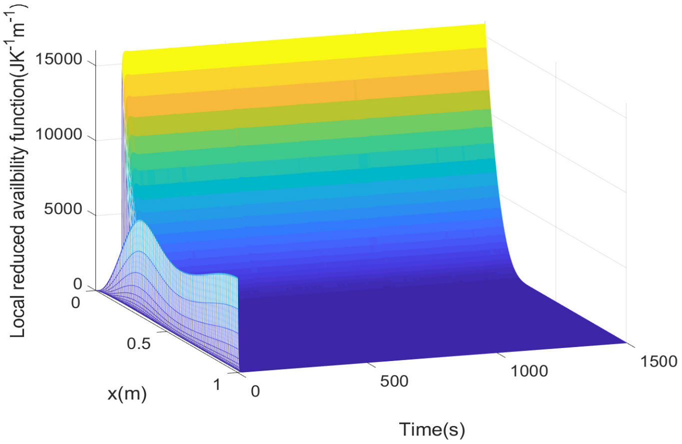

Figure 22: Local reduced availability function with at $t = 1500s$ closed Loop case

9. Conclusions and perspectives

In this paper we design non-linear state feedback control laws for the stabilization of a tubular chemical reactor where occur convection, dispersion, conduction and chemical reaction phenomena. From thermodynamic considerations, we use the availability function and reduced availability as Lyapunov candidate functions for the closed loop system. Two availability-based control strategies are designed for the jacket temperature which is considered as a distributed control input. By the use of the reduced availability function we design two other state feedback controls which allow to improve the performance of the closed loop system. The given simulations illustrate the effectiveness of the different state feedback controls. We give a proof of the boundedness of the proposed control laws around the equilibrium.

As a perspective for this work, we shall complete the study of existence of solutions for the designed controls. We shall also consider a boundary control problem for the tubular chemical reactor using inlet species flow and/or temperature as an input control. We also consider to apply the control law for a more complex reaction systems.

Appendix A. Irreversible entropy production

The irreversible entropy production is calculated from the entropy balance (16)

$$\sigma_s = \frac{\partial s}{\partial t} + \frac{\partial}{\partial x}(F^s_{conv} + F^s_{dis} + F^s_{cond}) + \frac{q}{T_j} \qquad (A.1)$$

In presence of transport phenomena, it is necessary to follow the materiel in its direction so that the material derivative is used to express the Gibbs equation [5] :

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{Dh}{Dt} - \sum_{1}^{n}\frac{\mu_i}{T}\frac{D\rho}{Dt} \tag{A.2}$$

where D is the materiel derivative with $D = \frac{\partial s}{\partial t} + (v \cdot \nabla)$. In 1D case, the differential of the Gibbs equation is defined by the convection speed and $D = \frac{\partial}{\partial t} + (v \cdot \frac{\partial}{\partial x})$. Thus equation (A.1) become :

$$\begin{aligned} \sigma_s &= \underbrace{\frac{\partial s}{\partial t} + \frac{\partial}{\partial x}F^s_{conv}}_{\frac{Ds}{Dt}} + \frac{\partial}{\partial x}(F^s_{dis} + F^s_{cond}) + \frac{q}{T_j} \\ &= \frac{1}{T}\frac{Dh}{Dt} - \sum_{1}^{n}\frac{\mu_i}{T}\frac{D\rho}{Dt} + \frac{\partial}{\partial x}(F^s_{dis} + F^s_{cond}) + \frac{q}{T_j} \end{aligned}$$

We recall the energy balance and materiel balance with materiel derivative $\frac{Dh}{Dt} = -\frac{\partial}{\partial x}(F^h_{dis} + F_{cond}) + q$, $\frac{D\rho_i}{Dt} = -\frac{\partial}{\partial x}(F^i_{dis} + M_i\nu_i r)$ and take into account $F^s_{cond} = \frac{1}{T}F_{cond}$, then we obtain the equation as below :

$$\begin{aligned} \sigma_s &= \frac{1}{T}(-\frac{\partial}{\partial x}(F^h_{dis} + F_{cond})) + \frac{\partial}{\partial x}(F^s_{dis} + F^s_{cond}) \\ &\quad - \sum_{1}^{n}\frac{\mu_i}{T}(-\frac{\partial}{\partial x}(F^i_{dis} + M_i\nu_i r)) - \frac{q}{T} + \frac{q}{T_j} \\ &= \overbrace{q\Big(\frac{1}{T_j} - \frac{1}{T}\Big)}^{\sigma_{ext}} + \overbrace{\sum M_i\nu_i r\Big(-\frac{\mu_i}{T}\Big)}^{\sigma_r} - \sum_{1}^{n}\frac{h_i}{T}\frac{\partial F^i_{dis}}{\partial x} \\ &\quad - \sum_{1}^{n}\frac{F^i_{dis}}{T}\frac{\partial h_i}{\partial x} + \sum_{1}^{n}\frac{\mu_i}{T}\frac{\partial F^i_{dis}}{\partial x} + \sum_{1}^{n}s_i\frac{\partial F^i_{dis}}{\partial x} \\ &\quad + \sum_{1}^{n}F^i_{dis}\frac{\partial s_i}{\partial x} - \frac{1}{T}\frac{\partial}{\partial x}F_{cond} + \frac{\partial}{\partial x}(\frac{1}{T}F_{cond}) \end{aligned}$$

We recall the relation $\mu_i = h_i - Ts_i$ [3], the equation can be simplified :

$$\begin{aligned} \sigma_s &= \sum_{1}^{n}\underbrace{(\frac{\mu_i}{T} - \frac{h_i}{T} + s_i)}_{=0}\frac{\partial}{\partial x}F^i_{dis} - \sum_{1}^{n}(\frac{1}{T}\frac{\partial h_i}{\partial x} - \frac{\partial s_i}{\partial x})F^i_{dis} \\ &\quad + \frac{\partial}{\partial x}(\frac{1}{T})F_{cond} + \sigma_r + \sigma_{ext} \\ &= -\sum_{1}^{n}(\frac{1}{T}\frac{\partial h_i}{\partial x} - \frac{\partial}{\partial x}(\frac{h_i - \mu_i}{T}))F^i_{dis} \\ &\quad + \frac{\partial}{\partial x}(\frac{1}{T})F_{cond} + \sigma_r + \sigma_{ext} \\ &= \sigma_r + \sigma_{ext} + \frac{\partial}{\partial x}(\frac{1}{T})F_{cond} \\ &\quad + F^h_{dis}\frac{\partial}{\partial x}(\frac{1}{T}) + \overbrace{\sum_{1}^{n}\frac{\partial}{\partial x}(-\frac{\mu_A}{T})F^i_{dis}}^{\sigma^{mat}_d} \\ &= \sigma_r + \sigma_{ext} + \sigma^{mat}_d + \overbrace{F^h_d\frac{\partial}{\partial x}(\frac{1}{T})}^{\sigma^{therm}_d} \end{aligned} \tag{A.3}$$

In Figure A.23 we illustrate the closed loop time response of the four terms of irreversible entropy production using the command T_{j_4} given in proposition 6 . We observe that each term remains positive.

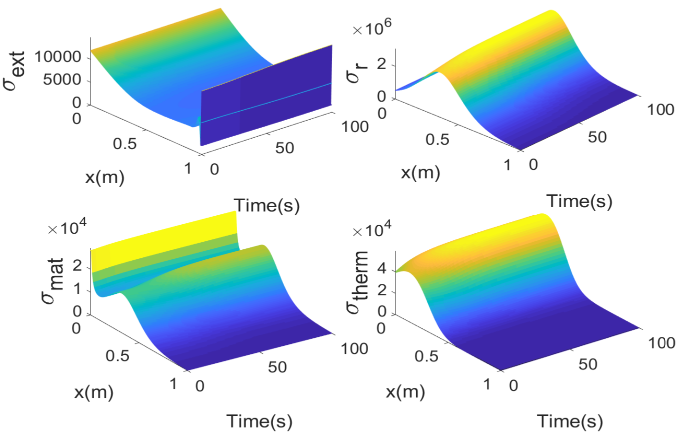

Figure A.23: case 4-Time response of each term of irreversible entropy production

Appendix B. linearisation of enthalpy equation

The linearised non-isothermal system used in section 7 is based on the entropy vision of tubular reactor model. We linearised the system around a equilibrium profile $\begin{pmatrix} T_d & \theta_{A_d} & \theta_{B_d} \end{pmatrix}$ considering $\begin{pmatrix} \frac{1}{T} & -\frac{\mu_A}{T} & -\frac{\mu_B}{T} \end{pmatrix}$ as state variables. In this appendix, we show only the linearisation of enthalpy equation $h = \rho_A h_A + \rho_B h_B$. We note that $\frac{1}{T} = \omega_1$, $-\frac{\mu_A}{T} = \omega_2$, $-\frac{\mu_B}{T} = \omega_3$

We start by linearise the terms $h_i = c_{p_i}(T - T_{ref}) + h_{iref} = c_{p_i}(\frac{1}{\omega_1} - T_{ref}) + h_{iref}$:

$$\begin{aligned} \lim_{\epsilon\to 0}\left(\frac{\partial h_i}{\partial\epsilon}\right) &= \lim_{\epsilon\to 0}\frac{\partial}{\partial\epsilon}(c_{p_i}(\frac{1}{\omega_{1_d} + \epsilon\bar{\omega}_1} - T_{ref}) + h_{iref}) \\ &= c_{p_i}\lim_{\epsilon\to 0}\frac{\bar{\omega}_1}{(\omega_1 + \epsilon\bar{\omega}_1)^2} \\ \bar{h}_i &= c_{p_i}\frac{\bar{\omega}_1}{(\omega_{1_d})^2} = c_{p_i}T_d^2\bar{\omega}_1 \end{aligned} \tag{B.1}$$

As for $\rho_i = \rho\theta_i$, we can linearise it from chemical potential expression $\mu_i = c_{p_i}(T - T_{ref}) + h_{iref} - T(c_{p_i}ln(\frac{T}{T_{ref}}) + s_{iref}) + RTln\theta_i$, then we have the expression of $\theta_A(\omega_1, \omega_2)$. With the same step we can obtain the linearised mass fraction

$$\bar{\theta}_A = \lim_{\epsilon\to 0}\frac{\partial\theta_A}{\partial\epsilon} = -\frac{\theta_{A_d}}{R}(\bar{\omega}_2 + h_{A_d}\bar{\omega}_1) \tag{B.2}$$

and

$$\bar{\theta}_B = \lim_{\epsilon\to 0}\frac{\partial\theta_B}{\partial\epsilon} = -\frac{\theta_{B_d}}{R}(\bar{\omega}_3 + h_{B_d}\bar{\omega}_1) \tag{B.3}$$

The enthalpy equation $h = \rho_A h_A + \rho_B h_B$.

$$\begin{aligned} \bar{h} &= \lim_{\epsilon\to 0}\frac{\partial\rho_A h_A + \rho_B h_B}{\partial\epsilon} \\ &= \rho(\theta_{A_d}\bar{h}_A + h_{A_d}\bar{\theta}_A + \theta_{B_d}\bar{h}_B + h_{B_d}\bar{\theta}_B) \end{aligned} \tag{B.4}$$

Let's replace the linearised terms, then we have :

$$\tilde{h} = \theta_1(\frac{\tilde{1}}{T}) + \theta_2(-\frac{\tilde{\mu}_A}{T}) + \theta_3(-\frac{\tilde{\mu}_B}{T}) \tag{B.5}$$

with $\theta_1 = -(\rho C_{p_d} T_d^2 + \frac{h_{A_d}^2 \rho_{A_d}}{R} + \frac{h_{B_d}^2 \rho_{B_d}}{R})$ $\theta_2 = -\frac{h_{A_d}\rho_{A_d}}{R}$ $\theta_3 = -\frac{h_{B_d}\rho_{B_d}}{R}$ and $C_{p_d} = C_{p_d}\frac{\rho_{A_d}}{\rho} + C_{p_B}\frac{\rho_{B_d}}{\rho}$, R is the ideal gas constant.

Appendix C. Gibbs Helmholtz equation

The Gibbs–Helmholtz equation is a thermodynamic relation used for calculating changes in the Gibbs free energy of a system as a function of temperature [25].

$$\left(\frac{\partial(\frac{G}{T})}{\partial T}\right)_P = -\frac{H}{T^2} \tag{C.1}$$

where H is the enthalpy, T the absolute temperature and G the Gibbs free energy of the system, all at constant pressure p. The equation states that the change in the $\frac{G}{T}$ ratio at constant pressure as a result of an infinitesimally small change in temperature is a factor $\frac{H}{T^2}$.

It can be written in a equivalent form :

$$\begin{aligned} H &= -T^2\left(\frac{\partial(\frac{G}{T})}{\partial T}\right)_P = (-T^2\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}\frac{\partial(\frac{1}{T})}{\partial T})_P \\ &= \left(-T^2\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}(-\frac{1}{T^2})\right)_P \\ &= \left(\frac{\partial(\frac{G}{T})}{\partial\frac{1}{T}}\right)_P \end{aligned} \tag{C.2}$$

We study this equivalent form in infinite dimensional thermodynamic so that :

$$\frac{\partial(\frac{g}{T})}{\partial\frac{1}{T}} = h \tag{C.3}$$

where g is volume density of Gibbs free energy and h is volume density of enthalpy.

We recall the local Gibbs equation $h = Ts - \sum\rho_i\mu_i$ and $g = h - Ts$. From the 2 equation we can obtain that $g = -\sum\rho_i\mu_i$. Let's replace g in equation (C.3) and we consider the $A => B$ reaction case :

$$\begin{aligned} \frac{\partial(\frac{g}{T})}{\partial\frac{1}{T}} &= \frac{\partial(\frac{-\sum\rho_i\mu_i}{T})}{\partial\frac{1}{T}} \\ &= \rho_A\frac{\partial(-\frac{\mu_A}{T})}{\partial(\frac{1}{T})} + \rho_B\frac{\partial(-\frac{\mu_B}{T})}{\partial(\frac{1}{T})} - \frac{\mu_A}{T}\frac{\partial\rho_A}{(\partial(\frac{1}{T})} - \frac{\mu_B}{T}\frac{\partial\rho_B}{\partial(\frac{1}{T})} \end{aligned} \tag{C.4}$$

Hence the Gibbs free energy is a function of T, P and ρ_i we have $(\frac{\partial(\rho_A)}{(\partial\frac{1}{T})} = 0$ $\frac{\partial(\rho_B)}{(\partial\frac{1}{T})} = 0)$. As a result, we can obtain the volume density of enthalpy :

$$h = \rho_A\frac{\partial(-\frac{\mu_A}{T})}{\partial(\frac{1}{T})} + \rho_B\frac{\partial(-\frac{\mu_B}{T})}{\partial(\frac{1}{T})} \tag{C.5}$$

As $h = \rho_A h_A + \rho_B h_B$, we can identify that $\frac{\partial(-\frac{\mu_A}{T})}{\partial(\frac{1}{T})} = h_A, \frac{\partial(-\frac{\mu_B}{T})}{\partial(\frac{1}{T})} = h_B$, then we conclude that around the desired profile with small variation :

$$\begin{aligned} \lim_{T\to T_d}\left(\frac{(-\frac{\tilde{\mu}_A}{T})}{(\frac{\tilde{1}}{T})}\right) = \left(\frac{\partial(-\frac{\mu_A}{T})}{\partial(\frac{1}{T})}\right)_{T\to T_d} &= h_A(T_d) \\ \lim_{T\to T_d}\left(\frac{(-\frac{\tilde{\mu}_B}{T})}{(\frac{\tilde{1}}{T})}\right) = \left(\frac{\partial(-\frac{\mu_B}{T})}{\partial(\frac{1}{T})}\right)_{T\to T_d} &= h_B(T_d) \end{aligned} \tag{C.6}$$

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