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Detection of thermal runaway in highly reactive systems

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The comprehensive study of highly reactive systems is essential to achieve a safe and productive operation of existing processes. Such study is also fundamental for inherently safe new designs. Hence, the thermal runaway phenomena must be studied to determine the safe operating range conditions from a material and a human point of view.
This work shows a comparison between steady state and dynamic thermal stability study. Indeed, the steady state analysis is necessary but not sufficient to ensure the thermal stability. Even if the reactor is stable according to the van Heerden criterion, small perturbations of inlet parameters of the system can lead to the conditions of thermal runaway or quench of the reactions. The differences between the stationary and dynamic stability curves are illustrated with a simple CSTR case. Finally a criterion valid under dynamic conditions is proposed to determine the regions of safe operability of the reactor.

1. Introduction

One of the security priorities involving highly reactive systems is the risk of thermal runaway. The temperature increase for the reactions that follow an Arrhenius law, induces the rise of the heat generation that further increases the reaction temperature; this situation may result in a thermal runaway. The consequences of a runaway can be: the early deactivation of the catalyst (coking), lost of selectivity, conversion or the operability of the unit, the onset of secondary reactions and in some cases even the reactor explosion.
The design of industrial reactors must rely on an accurate thermal stability study. Indeed, the design of the whole reactive system (reactor and the devices used for heat input/removal) should ensure *a priori* the thermally stable operation of the reactor. It is also important to determine the regions of operating conditions where the reactor has an unreliable behavior (runaway regions). In practice, most of the industrial designs of reactive systems are based only on the van Heerden (1953) criterion. This criterion imposes that the slope of heat generated by the reactions (dQ_{gen}/dT) must be lower than the slope of the heat extracted from the

system (dQ_{exc}/dT). Since this comparison is realized only under stationary conditions the dynamic behavior of the system is not taken into account and the thermal stability cannot be guaranteed. This work makes a comparison between steady state and dynamic thermal stability study for a simple CSTR case. It is shown that the stability conclusions may be completely different between both approaches. The importance to apply an appropriate stability criterion is clearly demonstrated. A dynamic runaway criterion for this ideal reactive system is proposed.

2. Case study

A one phase Continuous Stirred Tank Reactor was chosen as a study case (Froment & Bischoff, 1979). The following exothermic reaction is used with a first order kinetics.

$$A \rightarrow B \qquad r_{(mol/s)} = k_o.e^{-\frac{E}{RT}}.C_A \tag{1}$$

The dependency of the reaction rate with the temperature is taken into account with the Arrhenius law. A heat exchanger was considered to remove the heat generated by the reaction. Transient material and thermal balances are written as follows:

$$\frac{\partial C_A}{\partial t} = \frac{C_{A,i} - C_A}{\tau} - r \tag{2}$$

$$\frac{\partial T}{\partial t} = \frac{T_i - T}{\tau} + \frac{r \cdot (-\Delta H_r)}{\rho \cdot C_p} - \frac{U \cdot A \cdot (T - T_c)}{\rho \cdot C_p} \tag{3}$$

In stationary regime, the conversion and the temperature become:

$$\chi = \frac{C_{A,i} - C_A}{C_{A,i}} = \frac{k \cdot \tau}{1 + k \cdot \tau} \tag{4}$$

$$T_c = T - \frac{\rho \cdot C_p}{U \cdot A \cdot \tau} \cdot (T_i - T) - \frac{r \cdot (-\Delta H_r)}{U \cdot A} \tag{5}$$

3. Stationary analysis

The van Heerden criterion was tested for a given set of operating conditions. The reactor operating point was set to 90°C, and the effect of the variation of the heat exchange surface was evaluated. As shown in Fig. 1a) for a CSTR with 25 m^2/m^3 of heat exchange surface, the system is thermally stable according to the van Heerden criterion. A dynamic simulation of this case was realized (Eq. 2 and 3) and is illustrated in Fig. 1b). The reactor behavior was simulated with a reactor temperature controller (Harriot 1964). While the regulation is activated the reactor temperature is controlled at 90°C. The regulation was shut-down after

10000 seconds. The reactor is thermally stable since in the absence of regulation the reactor temperature remains stable at 90°C.

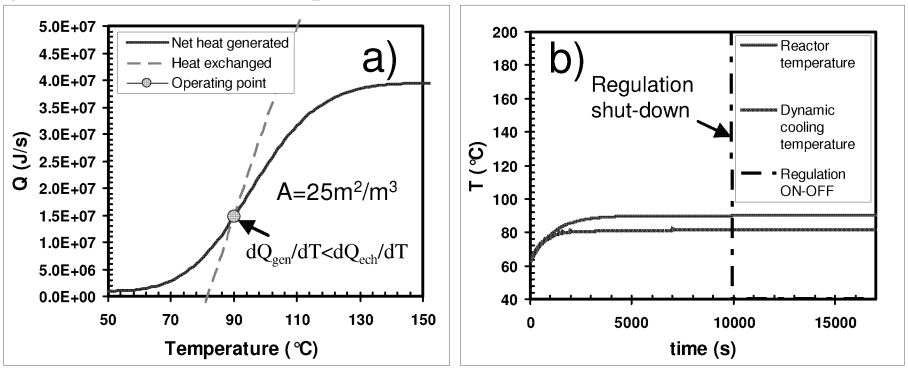

Fig. 1 – a) Diagram of heat production and consumption for a 25 m^2/m^3 heat exchange surface. b) Dynamic simulation of the CSTR

Another case was simulated where the heat exchange surface was reduced to 16 m^2/m^3. Since dQ_{gen}/dT is lower than dQ_{exc}/dT, the van Heerden criterion clearly indicates that the reactor is thermally stable (Fig. 2a). A dynamic simulation of this case was realized (Fig. 2b). The reactor temperature is maintained at 90°C while the regulation is activated, however, if the controller is shut-down (8000 s), the reactor temperature rises leading to a thermal runaway. Indeed, since the dynamic heat accumulation term is not taken into account, the heat exchange capacities are not sufficient to evacuate the heat production. This example clearly illustrates that the van Heerden criterion is necessary but it is not the ultimate condition to guarantee the thermal stability.

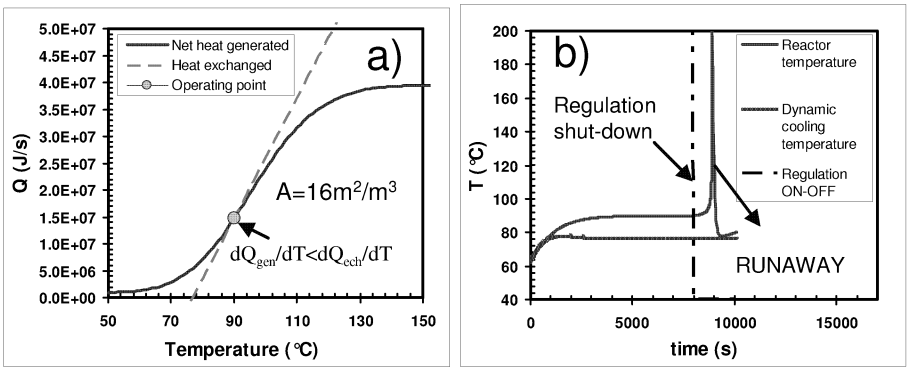

Fig. 2 – a) Diagram of heat production and consumption for a 16 m^2/m^3 heat exchange surface. b) Dynamic simulation of the CSTR

It is also possible to represent the reactor temperature (T) as a function of the variation of the cooling temperature (T_c) (Song et al. 2003). The simulations of a 6 m^2/m^3 heat exchange surface case are presented in Fig. 3. Equations (4) and (5) were used to calculate the stationary trajectory of

the reactor temperature. In this case, the reactor is not stable as stated by the van Heerden criterion. In the T_c range from about 33°C to 64°C, a multiplicity of steady states is observed. For example for the reactor temperature of 90°C (point②) a cooling temperature of 55°C is required, however, a hot point ① and a quench point ③ also correspond to this T_c. The region A corresponds to stationary unstable operating points. Without an efficient control system, these points can never be reached. Starting from T_c=40°C and by increasing cooling temperature, the operating point will directly pass from the lower part of the curve to the upper part that leads to runaway. Then, starting from T_c=75°C and by decreasing the cooling temperature, the operating point will follow the upper part of the curve until T_c=36°C. At this T_c, the reactor temperature T falls to the zone of the quench of the reaction. This hysteresis phenomenon is well known. The dynamic trajectory was also determined. As illustrated, the stationary and dynamic trajectories are different. Indeed, when the cooling temperature is diminished and the reactor temperature is in the hot region (T > 140°C), the dynamic behavior indicates that at about T=145°C the reactor starts a temperature oscillation and T suddenly falls to the quench zone. According to the stationary hysteresis, this temperature drop should had been taken place at about T=116°C. As shown in Fig. 3, the unstable region obtained under stationary conditions (Zone A) does not fit with the dynamic unstable region (Zones A+B). We can conclude that even for an unstable reactor, the thermal stability regions must be determined under dynamic conditions.

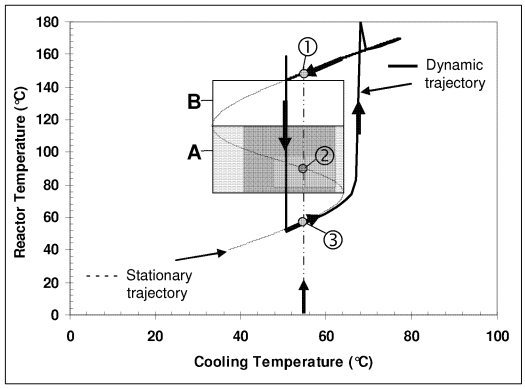

Fig. 3 – Cooling temperature vs. reactor temperature. Stationary and dynamic trajectories.

4. Dynamic analysis

According to the previous CSTR analyses, it was pointed out that an unstable dynamic region exists which is not predicted by the van Heerden criterion. Therefore, a dynamic analysis must be systematically carried out to determine if a runaway may occur. Indeed, the boundaries of these unstable dynamic regions must be taken into account for the reactor design and operation (Perlmutter 1972). The methodology of the dynamic analysis consists in three steps:

a- Perturbation of the dynamic reactor model around a stationary operating point.
b- Linearization of the perturbation model.
c- Resolution of the perturbation model and analysis of the solution (perturbations should tend to zero when time tends to infinity).

4.1 Perturbation of the dynamic reactor model

The reactor model can be written into a generalized formalism as follows

$$\frac{\partial y_i}{\partial t} = f_i(y_1, y_2, ..., y_i, ..., y_n) \tag{6}$$

where y_i=T, C_1, C_2,… are the model variables. The perturbation variables x_i around a stationary operating point are defined as the difference between the variable y_i at time t and its value at stationary conditions $y_{i,s}$.

$$x_i = y_i - y_{i,s} \qquad \Rightarrow \qquad y_i = y_{i,s} + x_i \tag{7}$$

Substituting Eq. (7) into Eq. (6), the reactor model becomes:

$$\frac{\partial(y_{i,s} + x_i)}{\partial t} = f_i(y_{1,s} + x_1, y_{2,s} + x_2, ..., y_{i,s} + x_i, ..., y_{n,s} + x_n) \tag{8}$$

4.2 Linearization of perturbation model

If the perturbation variables are very small, the first order Taylor expansion can be applied to linearize the reactor model around the stationary operating point.

$$\frac{\partial(y_{i,s} + x_i)}{\partial t} = f_i(y_{1,s}, y_{2,s}, ..., y_{i,s}, ..., y_{n,s}) + \left(\frac{\partial f_i}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_i}{\partial y_2}\right)_s \cdot x_2 + ... + \left(\frac{\partial f_i}{\partial y_i}\right)_s \cdot x_i + ... + \left(\frac{\partial f_i}{\partial y_n}\right)_s \cdot x_n \tag{9}$$

Under stationary conditions Eq. (9) becomes:

$$\frac{\partial x_i}{\partial t} = \left(\frac{\partial f_i}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_i}{\partial y_2}\right)_s \cdot x_2 + ... + \left(\frac{\partial f_i}{\partial y_i}\right)_s \cdot x_i + ... + \left(\frac{\partial f_i}{\partial y_n}\right)_s \cdot x_n \tag{10}$$

Using a matrix formalism, the dynamic model for all perturbations is given by Eq. 11:

$$\dot{X} = J \cdot X \tag{11}$$

with $X = (x_1 \quad x_2 \quad ... \quad x_n)^T$, $\dot{X} = \left(\partial x_1 / \partial t \quad \partial x_2 / \partial t \quad ... \quad \partial x_n / \partial t\right)^T$ and J the Jacobian matrix.

The resolution of this linear first order differential equation system allows to know if the perturbation of one of the whole set of variables diverge with time. In this case the dynamic runaway conditions are achieved.

4.3 Resolution of the perturbation model and analysis of the solution

Since all the equations are independent, the Jacobian can be diagonalized. The solution of the perturbation around the stationary point

is given by Eq. 12 where U_i is the i^{th} eigenvector of the Jacobian and λ_i is the corresponding eigenvalue. Eigenvalues can be real or complex.

$$\begin{aligned} x_1 &= U_{1,1}.a_1.e^{\lambda_1.t} + U_{1,2}.a_2.e^{\lambda_2.t} + ... + U_{1,n}.a_n.e^{\lambda_n.t} \\ &\vdots \\ x_n &= U_{n,1}.a_1.e^{\lambda_1.t} + U_{n,2}.a_2.e^{\lambda_2.t} + ... + U_{n,n}.a_n.e^{\lambda_n.t} \end{aligned} \quad (12)$$

It clearly appears that $x_i \rightarrow \infty$ with time only when one of the n eigenvalues has a positive real part. Hence, the condition for stability is:

$$\forall \; i \quad \lim_{t \to \infty} x_i = 0 \quad (13)$$

$$if \quad \lambda_i \in \mathbb{R} \Rightarrow \lambda_i < 0 \quad , \quad if \quad \lambda_i \in \mathbb{C} \Rightarrow Re(\lambda_i) < 0 \quad (14\text{ a,b})$$

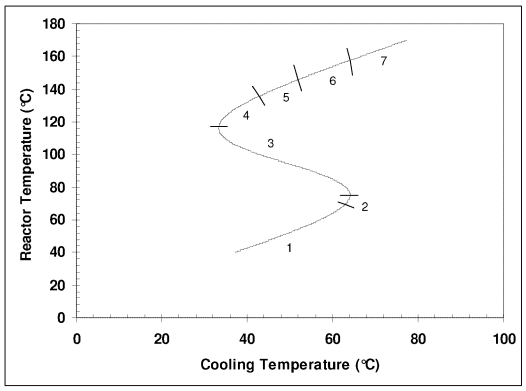

Fig. 4 - Dynamic propagation zones

The perturbation method was applied for each stationary point of the S curve (c.f. Fig. 3). The analysis of the eigenvalues allows determining different zones of this curve which correspond to different propagation modes of the perturbations. Fig. 4 shows these zones for the CSTR model using only two variables (T and C_A). For this reactor model, only two eigenvalues have to be analyzed. Table 1 shows the analysis of the eigenvalues corresponding to the temperature and the concentration. The eigenvalues can be real or complex. In the case of real eigenvalues, when both are negative, perturbations are exponentially attenuated (Fig. 4, Zones 1 and 7). If the eigenvalues are real but at least one is positive, runaway conditions are achieved and perturbations are exponentially amplified (Zones 3 and 4).

However, for complex eigenvalues, oscillatory behavior of the perturbation is observed. Then, two situations are possible:

- Both real parts of the eigenvalues are negative. In this case the perturbation is attenuated with an oscillatory behavior (Zones 2 and 6).
- One ore both real parts of the eigenvalues are positive. In this case, exponential amplification of the perturbation is observed with an oscillatory behavior (Zone 5).

These behaviors can be illustrated with phase plane diagrams. The phase plane diagram is a representation of variable trajectories (Strozzi and Zaldívar, 1994). It consists to draw one variable as a function of the

others in dynamic conditions. For the CSTR case study, the phase plane diagram is the representation of the reactor temperature as a function of concentration. Simulations were carried out in each zone using a temperature controller (Harriot 1964) to stabilize a stationary point which could be unstable. Then, the control system of the reactor is stopped and the dynamic behavior is observed. Figure 5 shows the dynamic behavior in different zones. Zones 2 and 6 correspond to stable operating points. The perturbations are attenuated with an oscillatory behavior. On the contrary, in Zone 5 the operating points are unstable; in this case the perturbations are amplified with an oscillatory behavior. The Zone 3 corresponds to unstable operating points that lead to runaway.

Table 1 - Eigenvalues analysis

Zone	$Re(\lambda_1)$	$Re(\lambda_2)$	$Im(\lambda_1)$	$Im(\lambda_2)$	Observations
1	<0	<0	0	0	No runaway: exponential attenuation of the perturbation
2	<0	<0	<0	>0	No runaway: oscillatory attenuation of the perturbation
3	>0	<0	0	0	Runaway
4	>0	>0	0	0	Runaway
5	>0	>0	>0	<0	Runaway: oscillatory amplification of the perturbation
6	<0	<0	>0	<0	No runaway: oscillatory attenuation of the perturbation
7	<0	<0	0	0	No runaway: exponential attenuation of the perturbation

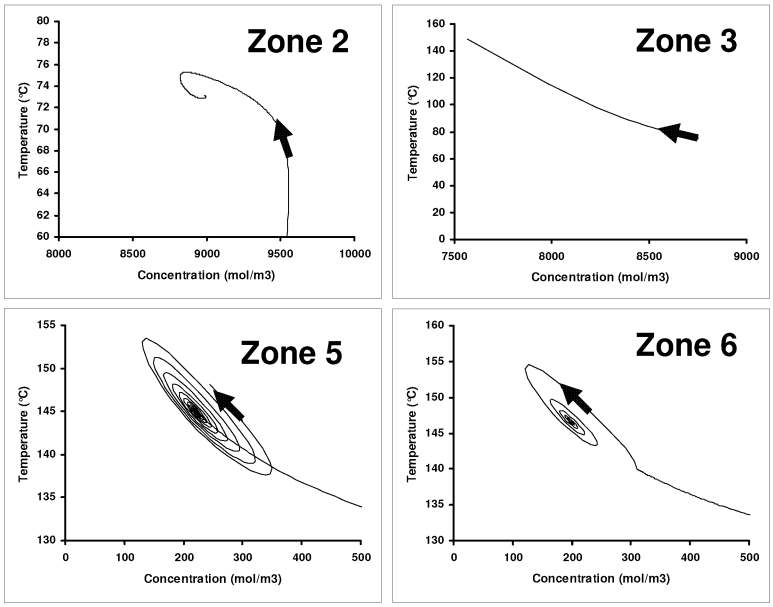

Fig. 5 – Phase plane diagrams of the CSTR system**.**

5. Conclusions

The reliable determination of the thermal stability regions in chemical systems is essential to ensure the safe and productive operation of industrial processes. In practice, the design of industrial reactors is commonly realized based only on the stationary regime. This work shows that the dynamic study of the chemical system is essential to guarantee that the reactor operates in a thermally stable region. A runaway criterion was presented for a CSTR simple case. It accurately predicts *a priori* the unstable dynamic zones. Further work will focus on the study of an industrial refining process taking into account a multiphase complex reactive system. For this case the space-time dimensions will be introduced in the stability analysis.

Nomenclature

A: volumetric heat exchange area (m^2/m^3)
C_A: concentration of A (mol/m^3)
$C_{A,i}$: concentration of A at reactor inlet (mol/m^3)
C_p: heat capacity (J/kg/K)
E: activation energy (J/mol)
f: model function
J: Jacobian
r: kinetic rate (mol/s)
R: gas constant 8.314 J/mol/K
t: time (s)
T: reactor temperature (K)
T_c: cooling temperature (K)
T_i: reactor inlet temperature (K)
U: heat transfer coefficient ($W/m^2/K$)
X: vector of perturbation
$\dot{X}$: vector of perturbation derivatives
x_i: perturbation of the variable y_i
y_i: model variable
$y_{i,s}$: variable at stationary condition

Greek letters:

χ: conversion of reactant A
ΔH_r: reaction heat (J/mol)
ρ: liquid density (kg/m^3)
τ: residence time of reactant A (s)
λ_i: eigenvalue

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