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Runaway Boundaries for PI Controlled Tubular Reactors

Marco Barozzi, Martina Silvia Scotton, Sabrina Copelli *

University of Insubria, Department of Science and High Technology, Via Valleggio 9, 22100, Como, Italy
sabrina.copelli@uninsubria.it

In the last decades, tubular reactors have found an extensive application in chemical industry, spacing from conventional catalytic oxidations to the intensification of highly exothermic discontinuous processes. The main advantage offered by these reactors consists in a strong reduction of reaction volumes, which is possible due to the fast kinetics promoted by the segregated flow within the reactor. This feature is also well-known to be one of the causes for the complex temperature control along the tubular reactor when highly exothermic chemical reactions are carried out. For this reason, several studies concerning the safety of tubular reactor-based processes have been carried out. Many works have been focused on providing methods and dissertations with the ultimate goal of making processes based on tubular reactors ever more intrinsically safe and optimized. In this work, a mathematical model used to simulate a catalytic oxidation process in a tubular jacketed reactor is proposed. The effect of both unsteady state operating conditions and the Proportional-Integral controller on the location of the hot-spot and the definition of the runaway boundary are also analyzed. The final aim is the implementation of safety criteria capable of defining the parametric sensitivity boundaries of a controlled tubular reactor.

1. Introduction

Thermal runaway is among the most severe causes of industrial accidents when working with exothermic reactions. According to statistics, it is reasonable to assume that around 100 runaways per year occur in Europe only (Benuzzi and Zaldivar, 1991). Sometimes, such accidents may lead to catastrophic results (Stoessel, 2008). More specifically, a runaway is a phenomenon where, when operating with an exothermic reaction, the rate of heat production is higher than the heat removal rate, leading to a temperature loss of control. Many industrial processes are based on fast and strongly exothermic reactions so that a small variation in the system operating conditions can lead to a much larger output in the system thermal behaviour. This work digresses on the safety of tubular reactors, precisely Plug Flow Reactors (PFRs), which are commonly used for conducting exothermic reactions, such as catalytic oxidations.
One of the most appealing aspect is the presence of a segregated flow, which enhances the reaction kinetics by maximizing reactants concentration. This means that there is a very poor longitudinal mixing within the fluid which leads to high reaction rates and allow for considerable volume reductions with respect to Continuous Stirred Tank Reactors (CSTRs) (at equal conversion). For this reason, even if a lot of literature has been proposed to increase productivity by introducing more sophisticated continuous production strategies (Copelli et al., 2018), shifting to PFRs syntheses is an appealing solution for process intensification (Florit et al., 2020).
However, PFRs are also well known regarding thermal safety issues: that is, PFRs exhibit a temperature peak along the reactor length called hot spot. The magnitude and the position of the hot spot should be carefully studied as it may severely affect the stability of the reactor and trigger side reactions. For such reasons, Plug Flow Reactors process safety is a topic of great interest in the scientific literature. The first relevant studies have been carried out during the ‘70s (Welsenaere, and Froment, 1970) and in the ‘80s (Henning and Perez, 1986). Most of the developed parametric sensitivity models used the steady state assumptions, based on the hypothesis that the PFR transitory is very fast. But even more recent studies on parametric sensitivity (Morbidelli and Varma, 1999) have used limiting assumptions in the mathematical model, i.e. a constant temperature of the cooling fluid. Nowadays, the increase of performances of computers allows to solve more complex problems in relatively small computational times, and it is possible to address the safety of such

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systems by loosening the assumptions, such as the introduction of the unsteady state, which allows to account for reactor start-up (Copelli et al., 2016).
This work aims at studying the effect of a real jacket (that is, a cooling system with an axial temperature profile along with the reactor), axial diffusion and the presence of a Proportional-Integral temperature controller (Stephanopoulos, 1984) on the parametric sensitivity. A mathematical model was developed for describing such a system and applied to estimate the runaway boundaries using the parametric sensitivity criterion proposed by Morbidelli and Varma (1999). The model was then applied to the naphthalene catalytic oxidation to phthalic anhydride, which is a very exothermic reaction usually carried out in tubular reactors, and it has been already subject of theoretical studies concerning its safety (Morbidelli and Varma, 1999).
The reaction is represented in Eq.(1):

$$2C_{10}H_8 + 9O_2 \rightarrow 2C_8H_4O_3 + 4CO_2 + 4H_2O \quad (1)$$

Naphthalene oxidation generates a hot spot along the reactor length, and it was responsible for a severe accident happened on February 4th,1987 in Kawasaki, Kanagawa, Japan (Association for the Study of Failure, 2021). Here, a confined explosion (dead space of a reactor) in a naphthalene oxidation plant occurred. The explosion was caused by the accumulation of non-volatile components of raw materials, that formed an ignitable concentration at low temperatures. The mixture of naphthalene and air blew up causing the breaking of three rupture disks and the dispersion of other unit debris.
In this work two models are proposed: a first one, involving an uncontrolled PFR with a non-constant temperature jacket (co-current flow), and a model with a PI controller. The final equations system results in a system of Partial Differential Equations (PDEs). The problem is numerically solved using the Method of Lines, precisely the MatMol approach developed by Wouver, Saucez and Vilas (2014).

2. Mathematical Model

The aim of this work is the estimation of runaway boundaries for the considered system using the parametric sensitivity criterion defined by Morbidelli and Varma (1999). Particularly, it is possible to define the sensitivity coefficient of a given function y with respect a parameter Φ, as:

$$s_{\Phi}^{y} = \frac{\delta y}{\delta \Phi} \quad (2)$$

which is often used in the following normalized form:

$$S_{\Phi}^{y} = \frac{\Phi}{y} \cdot \frac{\delta y}{\delta \Phi} = \frac{\delta \ln(y)}{\delta \ln(\Phi)} = \frac{\Phi}{y} \cdot s_{\Phi}^{y} \quad (3)$$

where ϕ is the input parameter for the sensitivity evaluation, y is the investigated variable or function. The advantage of normalized sensitivity is that it normalizes the magnitude of both the input parameter ϕ and the function y. Such coefficients are theoretically obtained by solving a predictive model for the investigated variable/function, given a set of input parameters. For simple models, sometimes the sensitivity coefficient may appear in an analytical form. More often, numerical simulation is required. For this work, the objective function is defined as the maximum temperature along the reactor (y) and the investigated parameters with respect to calculate the parametric sensitivity (ϕ) is the inlet partial pressure of naphthalene (other model parameters were considered but not reported within this work). Two models were proposed, as already highlighted. For both cases, the following assumptions were considered:

1. Constant inlet velocity, which is equal to the axial velocity
2. Radial perfect mixing
3. Constant reaction mixture density and specific heat
4. No side-reactions or decomposition reactions
5. Jacket made of Heat Transfer Salts (40% NaN_2, 7% $NaNO_3$, 53% KNO_3) (Bohlmann, 1972)

Table 1 reports all the values of the main parameters involved. The resulting system of equations, reported in the following paragraphs, is a set of partial differential equations (PDEs). Method of Line was proposed to solve the problem. In short, the method consists in a discretization of the spatial derivative, transforming the PDEs system in a Differential Algebraic Equations (DAEs) system (where time is the only independent variable). The final DAE is solved using a fourth order Runge-Kutta method (function implemented in a Matlab code). Finally, the sensitivity of the maximum temperature with respect to a given parameter is obtained by the numerical solution of the system.

Table 1: Main parameters involved (van Welsenaere and Froment, 1970), (Bohlmann, 1972)

Parameter	Meaning	Value	Unit
A_i	Pre-exponential factor	11.16	kmol/(kg s kPa2)
E_{att}	Activation energy	$1.134 \cdot 10^8$	J/kmol
ρ	Mix density	1.293	kg/m^3
U	Global heat exchange coefficient	9.61	W/m^2/K
D	Diffusion coefficient (N_2 in O_2)	$2.05 \cdot 10^{-5}$	m^2/s
k	Thermal diffusivity	11.5	m²/s
ρ_{cat}	Catalyst density	1,820	kg/m^3
P	Totale pressure	101,325	Pa
P_0	Oxygen pressure	21,000	Pa
ΔH	Heat of reaction	$1.289 \cdot 10^9$	J/kmol
T_{in}	Inlet temperature	625	K
T_w	Jacket temperature	625	K
c_p	Mix specific heat	1,044	J/kg/K
$c_{p,cool}$	HTS specific heat	1,561	J/kg/K
MW	Molecular weight	29.48	kg/kmol
v_0	Inlet velocity	0.2	m/s
$v_{0,cool}$	Coolant inlet velocity	0.2-1	m/s

2.1 Uncontrolled reactor model (constant jacket inlet temperature)

All transport equations are reported in their dimensionless form. The definition of each parameter is reported in the following.
Material balance on naphthalene:

$$\frac{\delta\chi}{\delta t} = \alpha \cdot \frac{\delta^2\chi}{\delta z^2} - \frac{\delta\chi}{\delta z} + Da \cdot \exp\left(\frac{\theta}{1+\frac{\theta}{\gamma}}\right) \cdot (1-\chi) \tag{4}$$

Reactor energy balance:

$$\frac{\delta\theta}{\delta t} = \lambda \cdot \frac{\delta^2\theta}{\delta z^2} - \frac{\delta\theta}{\delta z} + B \cdot Da \cdot \exp\left(\frac{\theta}{1+\frac{\theta}{\gamma}}\right) \cdot (1-\chi) - St \cdot (\theta - \theta_w) \tag{5}$$

Jacket energy balance:

$$\frac{\delta\theta_w}{\delta t} = -v_{o,cool} \cdot \frac{\delta\theta_w}{\delta z} - St_{cool} \cdot (\theta_w - \theta) \tag{6}$$

Equations from (4) to (6) are a PDE system with both first-order derivatives, representing convective phenomena, and second-order derivatives, representing diffusive phenomena. Initial conditions are:

$$\chi(t=0,z) = 0 \tag{7.1}$$
$$\theta(t=0,z) = 0 \tag{7.2}$$
$$\theta_w(t=0,z) = 0 \tag{7.3}$$

while boundary conditions are (corresponding to: constant inlet and no flux at the end of the reactor):

$$\chi(z=0,t) = 0 \tag{8.1}$$
$$\theta(z=0,t) = 0 \tag{8.2}$$
$$\theta_w(z=0,t) = 0 \tag{8.3}$$
$$\left.\frac{\delta\chi}{\delta z}\right|_{z=1,t} = 0 \tag{8.4}$$
$$\left.\frac{\delta\theta}{\delta z}\right|_{z=1,t} = 0 \tag{8.5}$$

Some dimensionless terms are well-known: *St* is the Stanton number, *Da* is the Damkohler number, χ is the chemical conversion of naphthalene.

2.2 PI controlled reactor

In the case of a PI controller, Equations from (4) to (8.5) hold. The addition of a PI controller requires the positioning of thermocouples around the reactor. From the read values, the controller can manipulate the inlet jacket temperature. This means that the controller works as a boundary condition for the jacket energy

balance equation (6). Hence, Eq.(8.3) becomes the following (considering a single thermocouple positioned at z_T, 0< z_T <z):

$$\theta_w(z=0,t) = -K_P \cdot \left(\left.\frac{\delta\theta}{\delta t}\right|_{z=z_T} - \frac{L^2}{v_o^2} \cdot \frac{1}{K_T}(\theta_{sp} - \theta(z=z_T)) \right) \tag{8.6}$$

where K_P is the static gain and K_T is the integral time. This means that, when applying the MOL, this condition enters inside the final DAEs system.
All dimensionless parameters involved are reported in Table 2.

Table 2: Dimensionless variables

Parameter	Meaning	Definition
χ	Naphthalene conversion	$\frac{C_{in,napht} - C_{napht}}{C_{in,napht}}$
θ	Dimensionless reactor temperature	$\frac{T - T_{in}}{T} \cdot \gamma$
θ_w	Dimensionless wall temperature	$\frac{T_w - T_{in}}{T_w} \cdot \gamma$
z	Dimensionless axial coordinate	$\frac{l}{L}$
t	Dimensionless time	$\tau \frac{v_o}{L}$
γ	Arrhenius number	$\frac{E_{att}}{R \cdot T_{in}}$
Da	Damkohler number	$\frac{L \cdot A \cdot \exp(-\gamma) \cdot \rho_{cat} \cdot P_{ox,0} \cdot P_{napht,0} \cdot MW}{\rho \cdot v_o}$
St	Stanton number	$\frac{4 \cdot U \cdot L}{\rho \cdot c_p \cdot d_R \cdot v_0}$
St_{cool}	Jacket Stanton number	$\frac{4 \cdot U \cdot L}{\rho_{cool} \cdot c_{p,cool} \cdot d_w \cdot v_{0,cool}}$
B	Adiabatic temperature rise	$\frac{(-\Delta H) \cdot C_{in,napht}}{\rho \cdot c_p \cdot T_{in}} \cdot \gamma$
α	Material diffusion parameter	$\frac{D}{l \cdot v_0}$
λ	Thermal diffusion parameter	$\frac{k}{l \cdot v_0}$

3. Results

The two models presented were applied to calculate the sensitivity of the maximum temperature inside the reactor (that is, the hot spot) as a function of the inlet partial pressure of naphthalene, which represents a variation of the inlet composition which can occur while performing a chemical synthesis. At first, the model was used to simulate well-known literature results.

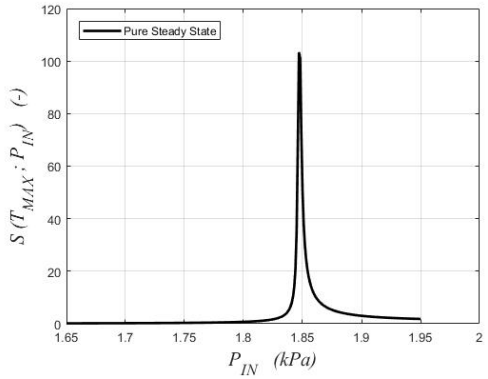

Figure 2a: Sensitivity graph for steady state with constant jacket temperature

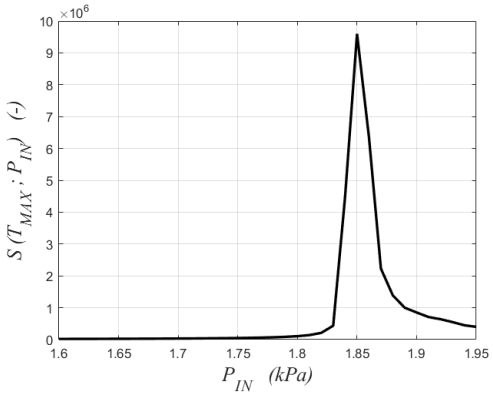

Figure 2b: Sensitivity graph including the transient and constant jacket temperature

In Figure 2b the unsteady-state condition was imposed, and it is possible to notice that the sensitivity peak is almost the same of the pure steady state model (1.82 [kPa]). This indicates that, for this type of reactors, the reactor start-up (that is considering the unsteady state) has low impact on process safety. It is well known that PFRs reach the steady state very fast, and it is confirmed by this result (Residence Time is around 1 [s]).

3.1 Effects due to the presence of a jacket

After that, the detailed model which included the jacket temperature profile (co-current flow) was considered. Several simulations were carried out by investigating a range of $v_{0,cool}$ from 0.1 to 1 [m/s]. Inlet temperature is kept at 625 [K]. A summary of the results is reported in Figure 3: according to the behavior of the sensitivity graph, decreasing the coolant flowrate led to a less safe process, having the maximum sensitivity lowering from 1.82 [kPa] (with $v_{0,cool}$ equal to 1 [m/s]) to 1.75 [kPa] (with $v_{0,cool}$ equal to 0.1 [m/s]). This is a remarkable result: a slower fluid experiences a less efficient heat exchange, as it locally heats up due to the presence of the hot spot, lowering the temperature difference with the reactor. For very high fluid velocities (> 1 [m/s]), the coolant refreshes itself so fast that the jacket behaves similarly to a wall at a constant temperature. Indeed, under such conditions, the sensitivity peak is close to the constant jacket temperature case (1.85 vs 1.82 [kPa]).

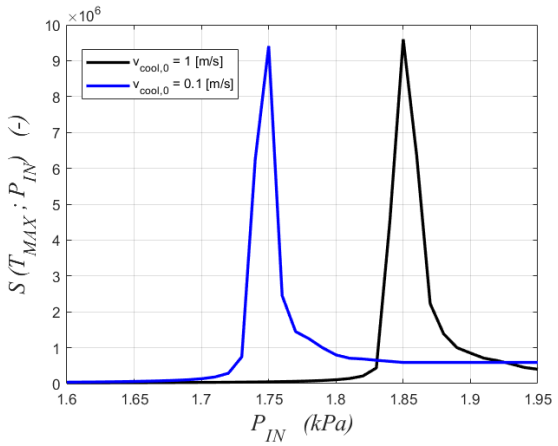

Figure 3: Effect of the jacket fluid velocity on system sensitivity

Hence, the correct design of the cooling system is an important issue when addressing plug-flow reactors safety. Hypothesizing a constant wall temperature is legit only when the jacket exchanges heat fast enough.

3.2 Effects of controller

The second model included the presence of a PI controller. In this case, it also important to define the logic of the control system. It is well known that the temperature in a PFR highly depends on the axial coordinate, exhibiting a maximum value at the so-called hot spot, in a similar way batch reactors reach a peak temperature over reaction time. For this reason, the location of the thermocouple, whose measure could be used by the controller, is crucial for a proper system characterization. Usually, a PFR is equipped with multiple thermocouples, and, depending on the available measures, a control strategy can be chosen.

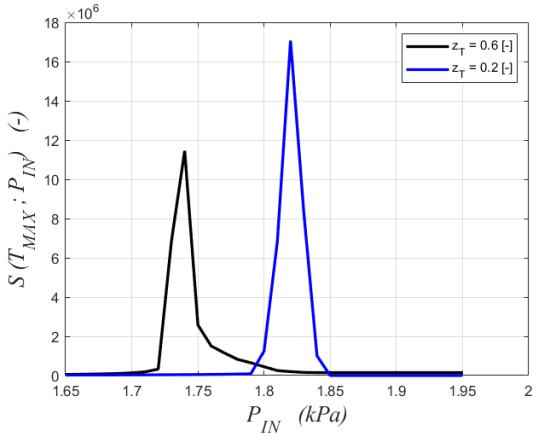

Figure 4: Effect of a PI controller with a single thermocouple placed at L on system sensitivity

In this work, different simulations were carried out considering a single thermocouple installed at different locations. Figure 4 describes the main results. First, with the introduction of a control logic, safer sensitivity graphs were not achieved. At the very least, with a thermocouple positioned at z_T equal to 0.2 (20% of reactor length), the peak is reached at 1.82 [kPa], similarly to the unsteady state with a jacket at constant temperature. In this case, the thermocouple is positioned very close to the hotspot, and the controller action is maximized. If the thermocouple is moved at more distant points, the system exhibit sensitivity at lower values (1.73 [kPa] for z_T equal to 0.6). This result is interesting and shows that the introduction of a temperature controller, which theoretically should help in keeping the temperature under control, may worsen system safety if designed incorrectly.

4. Conclusions

In this work, the parametric sensitivity criterion was applied to the naphthalene oxidation to phthalic anhydride process. The criterion was applied by including models more complex compared to historical literature works. Axial diffusion, unsteady state, a more realistic cooling system and the presence of a PI controller were considered together with their impact on process safety.

It was found that, considering an unsteady state, parametric sensitivity leads to results similar to traditional literature: this fact is confirmed by the fact the transient state of a PFR is very fast. Axial diffusion is negligible, and this is consistent with low Peclet numbers involved for a gaseous state reaction. However, considering a more realistic reactor jacket and a temperature controller led to interesting results: if the coolant flowrate is too low, the reaction temperature control is compromised, leading to unsafe conditions (sensitivity shifts from 1.85 [kPa] to 1.75 [kPa]). Including a temperature controller also does not give a safer process: depending on the position of the controlling thermocouple(s), sensitivity may occur at lower values (from 1.85 [kPa] to 1.72 [kPa] in the worst case).

Nomenclature

C: Concentration, mol/m³
T: Temperature, K
P: Pressure, Pa
L: Reactor axial coordinate, m
L: Reactor length, m
d_R: Reactor diameter, m

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