Runaway Problems in Unsteady State Tubular Reactors

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In the specific literature of the last seventy years, the problem of identifying the operating conditions (temperatures, pressures, concentrations, residence times, etc..) in correspondence of which, for different types of reactor and operating modes (e.g., isothermal and isoperibolic), the thermal control of a reacting system can be lost, has been widely analyzed. For some industries, the conversion of chemical reactants is carried out using Plug Flow Reactors (PFRs), because continuous production is required or strongly advised. Throughout the scientific literature, the thermal behavior of these reactors have been always characterized referring to steady state operating conditions neglecting axial diffusivities (some models took into account radial diffusivities). The reason has been found in the extremely rapid dynamics that characterizes these systems and, consequently, leads them to rapidly approach steady state conditions. But in some cases, i.e., a change in operating conditions, originated by unexpected failures or just by wrong operations, can shift the process course from steady to unsteady state. Another case could be the start-up procedure: according to many industrial accidents reports that involved fast and highly exothermic reactions, this is one of most susceptible moments. For all these cases, from the safety point of view, the system dynamical behavior could be very important and cannot be neglected.

The aim of this work has been to compare runaway boundaries obtained for steady state conventional operations of PFRs with that obtained under unsteady state operating conditions considering axial diffusivities. Obtained results have shown that the unsteady state aspect is very important to be considered in a safety analysis: this is because, even setting operating parameters ranges that a conventional steady state model predicts to be safe, during a start-up (or simply unsteady) operations temperatures capable of causing a runaway phenomenon can be reached.

1. Introduction

In chemical industry, one of the major causes of accident during the run of a desired reaction is thermal runaway (that is, an unwanted exothermic phenomenon consisting in the reactor thermal loss of control due to an unbalance between the rate of heat release and the rate of heat removal). Many industrial processes are based on fast and strongly exothermic reactions. In these system, a small variation in the system operating conditions can lead to a much larger change in the system thermal behavior. As the sake of example, if the efficiency of a reactor cooling system drops (this can happen for many different reasons in a chemical plant), the reactor temperature will rise very quickly. This sharp temperature rise, which characterizes thermal runaway conditions, can lead to serious consequences, from the opening of a relief system to the physical explosion of the reactor.

For these reasons, fast and strongly exothermic (that is, potentially runaway) reactions have been the object of a huge number of studies, aimed at identifying both safe and unsafe operating conditions. Being such reactions typical of pharmaceutical and fine chemical industries, mainly batch (B) reactors have been taken into account (Semenov, 1928, Frank-Kamenentskii, 1939, Thomas, 1961, Adler and Enig, 1964). Only later (say, from the late 50s), both ad hoc techniques and methods developed for BRs have been applied to continuous reactors, i.e. Plug Flow Reactor (PFR) (Bilous and Amundson, 1956, van Welsenaere and Froment, 1970, Soria Lopez et al, 1981, Varma et al., 1999, Zaldívar at al., 2003) and Continuous Stirred Tank Reactor (CSTR). Focusing on PFR, it is possible to underline that they are typically used for large-scale

productions, in either gas or liquid phase systems. Common industrial applications are in gasoline production, oil cracking, ammonia synthesis and other processes of oil industry and basic chemical industry. Of course these processes are mainly endothermic but there are interesting synthesis, such as catalytic oxidations, that involve fast and exothermic reactions. The most used mathematical model employed for the characterization of a PFR is the so-called "conventional steady-state" model, which neglect both the transient behavior in the start-up operation and material and thermal transport by diffusion.

According to this model, PFR material and energy balance equations (Eq(1) and Eq(2)) can be written, for a single reaction system with constant external cooling, as:

$$v_0 \cdot \frac{\partial c_i}{\partial z} = v_i \cdot r \tag{1}$$

$$v_0 \cdot \frac{\partial T}{\partial z} = \frac{-\Delta H}{\rho \cdot c_p} \cdot r - \frac{4U}{d_t \cdot \rho \cdot c_p} \cdot (T - T_w) \tag{2}$$

with the initial conditions reported in Eq(3):

$$I.C. \qquad c_i(z=0) = c_{i,IN} \qquad T(z=0) = T_{IN} \tag{3}$$

where: v_0 is the axial velocity (m s^{-1}), c_i is the molar concentration of the i-th species (kmol m^{-3}), z is the axial coordinate (m), v_i is the stoichiometric coefficient of the i-th species (-), r is the reaction rate (kmol m^{-3} s^{-1}), T is the temperature (K), ΔH is the reaction enthalpy (J kmol^{-1}), ρ is the mean reacting mixture density (kg m^{-3}), c_p is the specific heat capacity (J kmol^{-1} K^{-1}), d_t is the tube diameter (m) and T_w is the wall temperature (K, considered equal to that one of the external coolant).

Concerning the determination of the so-called runaway boundaries (that is, the critical operating conditions corresponding to the triggering of a thermal loss of control), it has been observed by the authors of this work that and previously by Koning and Westerrterp (1999) and Henda et al. (2008), in some cases, such a model provides non-conservative values that, for an industrial application, can not been accepted. Therefore, there is the need to introduce both the reactor transient behavior and material and thermal diffusivities (axial) to obtain a more realistic simulation of the process. In this work, the generalized parametric sensitivity criterion, developed by Varma et al. (1999), has been used to determine the runaway boundary since it is one of the most general and effective criteria actually available.

Particularly, the purpose of this work has been to determine whether the conventional steady state approach for a PFR can be considered conservative or not with respect to the calculation of the runaway boundary. As it will be shown in the following, such an approach has been found to be unsafe since, during start up operation, higher temperature values with respect to those ones registered during the conventional steady state can be easily reached. Moreover, the use of the generalized parametric sensitivity criterion clearly shows how the runaway boundaries can be substantially different from steady to unsteady state operations.

2. Mathematical Model

A Plug Flow Reactor (PFR) consists basically of a tube (with constant cross-sectional area) through which the reacting mixture flows, in a continuous reaction process. The plug flow is a simple model of the velocity profile of a fluid through a pipe, where the velocity is assumed to be constant across any cross-section of the pipe perpendicular to the axis of the pipe. As a consequence of this hypothesis, it is assumed that there is no mixing in the direction of the flow and complete mixing in the direction perpendicular to the flow. As long as the axial dimension of the reactor is larger than the radial one, which is the case for tubular reactors, all radial variations in the reactor variables can be neglected.

PFRs are normally handled in steady state continuous operation: that is, the inlet mass flow rate is equal to the outlet one, and temperatures and concentrations in correspondence of all axial coordinates do not change with time. In the case of exothermic reactions, a cooling system is necessary to remove the heat generated by the reactions. There are many ways to design a heat removal system. In this case, the simplest one is considered: co-current external cooling at constant temperature. For the sake of simplicity, a single exothermic reaction is considered. The physical properties of the species involved (i.e., reactant density and specific heat) are considered constant. According to such hypothesis, the constitutive equations for a generic species i and energy can be written as reported in Eqs(1) to (3).

Unsteady state operation must be considered under some circumstances such as during start-up and shut-down operations, or after a change in one or more of the process variables, due to unexpected failures or

setting changes. In the present work, the proposed model takes into account not only the accumulation term, (that is, the variations of temperatures and concentrations with time) in order to be able to model also unsteady state operations, especially start-up operations where a safety concern may arise, but also thermal and material diffusivity, in order to evaluate the effect of these phenomena on the thermal behavior of the reactor. All other assumptions are maintained. Using such hypothesis the transport equations for a generic species i and for energy can be written as follows:

$$\frac{\partial c_i}{\partial t} = \wp \cdot \frac{\partial^2 c_i}{\partial z^2} - v_0 \cdot \frac{\partial c_i}{\partial z} + \upsilon_i \cdot r \tag{4}$$

$$\frac{\partial T}{\partial t} = \alpha \cdot \frac{\partial^2 T}{\partial z^2} - v_0 \cdot \frac{\partial T}{\partial z} + \frac{-\Delta H}{\rho \cdot c_p} \cdot r - \frac{4U}{d_t \cdot \rho \cdot c_p} \cdot (T - T_w) \tag{5}$$

with the initial and boundary conditions reported in Eqs(6):

$$I.C. \qquad c_i(t=0,z) = c_{i,IN} \qquad T(t=0,z) = T_{IN} \tag{6a}$$

$$B.C. \qquad c_i(t,z=0) = c_{i,IN} \qquad T(t,z=0) = T_{IN} \tag{6b}$$

$$B.C. \qquad \partial c_i/\partial z(t,z=L) = 0 \qquad \partial T/\partial z(t,z=L) = 0 \tag{6c}$$

3. Case Study

In order to show that taking into account, in the mathematical model describing a PFR, both unsteady state operating conditions and axial thermal and material diffusivities terms can strongly affect both the location of the runaway boundary and the magnitude of the explosion phenomenon (for a given fast and exothermic process), the relevant case study of the naphthalene catalyzed oxidation has been considered. Such a reacting system has been already analyzed by van Welsenaere and Froment (1970) and it has been reconsidered by Varma et al. (1999) in order to show the results of their generalized parametric sensitivity criterion for the determination of the runaway boundary in a catalytic PFR.

Naphthalene oxidation is a highly exothermic reaction, carried out commercially on a V_2O_5 catalyst in multi-tubular reactors with external cooling. The reaction rate can be assumed of a pseudo first-order and given by:

$$r = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot P_{O_2} \cdot P_i \cdot \rho_{cat} \tag{7}$$

where A is the pre-exponential factor, E is the activation energy, P_{O_2} is the partial pressure of oxygen (Pa), which remains constant in the reactor since this reactant is in excess, ρ_{cat} is density of the catalyst (kg m^{-3}) and P_i is the partial pressure of naphthalene (Pa), which can be expressed in function of the naphthalene concentration, c_i, as:

$$P_i = \frac{MW \cdot P}{\rho} \cdot c_i \tag{8}$$

where MW is the reacting mixture molecular weight (kg kmol^{-1}), P is total pressure (Pa) and ρ is the average reacting mixture density (kg m^{-3}), which is considered constant.

Table 1 reports the constitutive parameters for the naphthalene oxidation reaction: note that material and thermal diffusivities have been added because they will be used later.

Table 1: Constitutive parameters for the naphthalene oxidation

Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
$A =$	11.16	[kmol / (kg s kPa^2)]	$\rho_{cat} =$	1300	[kg / m^3]	$\Delta H =$	1.289E9	[J / kmol]
$E =$	1.134E8	[J / kmol]	$P =$	101325	[Pa]	$c_p =$	1044	[J / (kg K)]
$\rho =$	1.293	[kg / m^3]	$P_O =$	21070	[Pa]	$MW_i =$	29.48	[kg / kmol]
$U =$	9.61	[W / (m^2 K)]	$\alpha=$	2.5E-5	[m^2 / s]	$T_w =$	625	[K]
$D =$	2.0E-5 (O_2 in N_2)	[m^2 / s]	$T_{in} =$	625	[K]	$v_0 =$	2.0 / 0.1	[m / s]

4. Results

As it has been said before, the main aim of this work is to demonstrate that the use of a conventional steady state PFR model in order to calculate runaway boundaries can lead to the establishment of unsafe operating conditions, expecially during the start-up phase. Such a criticality arises because, classically, in a PFR model both the transient behavior and material and thermal axial diffusivities are normally neglected. This is, of course, the case of a great number of industrial processes carried out in this reactors typology but, in some cases, these parameters can not be neglected because they play a relevant role for what concern both the thermal behavior of the reactor itself and the productivity.

For these reasons, it has been decided to perform a preliminary work in which the influence of the reacting mixture axial velocity on the determination of the runaway boundary, intended as critical inlet partial pressure of naphthalene, has been investigated during a critical reactor operating phase: the start-up. Such results have been then compared with those obtained for conventional steady state operations. At present, it has been decided to not investigate the influence of the values of both material and thermal diffusivities since, for gas catalytic systems, such values cannot change physically in a sufficient wide range. Anyway, some preliminary calculations have shown that the change in the diffusivities value affects mainly the magnitude of the runaway phenomenon (the runaway boundary is mainly influenced by the transient).

For what concern the technique employed to determine the runaway boundary, the generalized parametric sensitivity criterion (Morbidelli and Varma, 1999) has been chosen because, even if it is implicit, it is actually the most general criterion that can be applied to detect runaway boundaries and, in this particular case where partial differential equations must be solved, the only one applicable.

4.1 Runaway Boundary in Catalytic PFRs with High Axial Velocities

First of all, it has been studied the influence of the inlet partial pressure of reactant (that is, in this case, naphthalene) on the temperature maximum occurring along the reactor axis (that is, the so-called hot spot) (see Figure 1); then, the normalized parametric sensitivity of such temperature maximum with respect to the inlet partial pressure has been computed (see Figure 2) in order to determine the runaway boundary, that is, the critical value of the inlet partial pressure in correspondence of which the sensitivity coefficient exhibits a sharp maximum or a vertical asymptote.

As it can be seen from both Figure 1 (observing the sharp increase in the temperature maxima as a function of the inlet partial pressure) and Figure 2 (observing both the value and the sharp increase in the normalized sensitivity function), the runaway boundary can be identified in correspondence of a critical inlet partial pressure equal to 1.85 kPa. Such a value is in perfect agreement with that calculated by Varma et al. (1999).

Observing in more detail Figure 1, the temperature maxima predicted by the conventional PFR model are substantially the same of the unsteady state diffusivity model until values of the inlet partial pressure very close to the detected runaway boundary: at the critical value they differ significantly; particularly the conventional model seems to underestimate the real value of the temperature maximum of about 300 K.

Observing Figure 2, it is possible to note that sensitivity function generated using both the conventional steady and the unsteady state diffusivity model predict the same critical inlet pressure of 1.85 kPa: anyway, there is a significant difference in the sensitivity magnitude (greater for the unsteady state case). As a preliminary conclusion, it is possible to state that, with high axial velocities (that is, short contact times), the two models used to calculate the parametric sensitivity predict the same runaway boundary even if the magnitude of the phenomenon seems to be underestimated by the conventional steady state model.

Unfortunately, if we have a look at the values of the outlet conversion, it is possible to notice that, for all inlet partial pressures before the critical value of 1.85 kPa, they are very low: that is, lower than 0.5. This means that the process can not be performed industrially because the operating conditions employed lead to a

productivity which is too low. Therefore, there is the need for decreasing the axial velocity in order to increase the contact time and, consequently, the overall conversion at the reactor outlet.
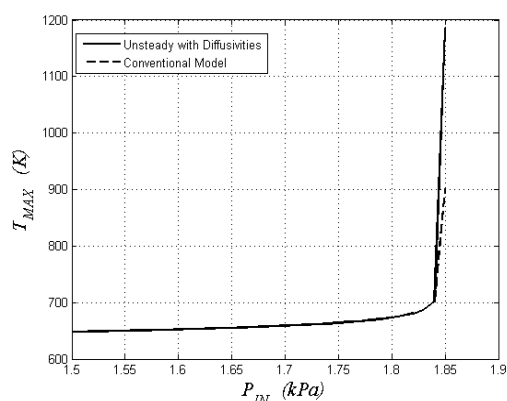

Figure 1: Temperature maxima as function of inlet partial pressure. High axial velocities.
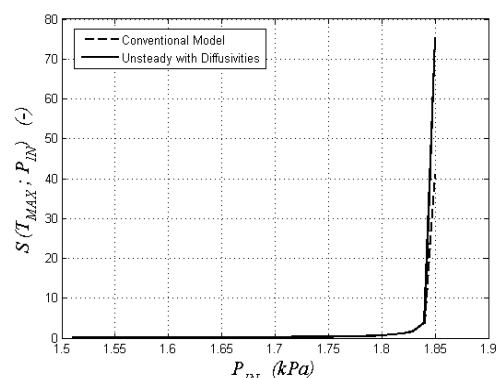

Figure 2: Normalized sensitivity of the temperature maximum with respect to the inlet partial pressure. High axial velocities.

4.2 Runaway Boundary in Catalytic PFRs with Low Axial Velocities

As stated in the previous paragraph, in order to make more competitive such industrial processes, they must be carried out both maximizing reactor productivity and maintaining the overall safety of the process itself.

The first aim can be achieved by decreasing the inlet axial velocity of the reacting mixture (that is, increasing the contact time in between the reactants). Unfortunately, when the fluid dynamical setup of a reactor is changed, thermal stability concerns may arise.

In this case, an axial velocity equal to 0.1 m/s has been considered because of two main reasons: 1) it is low enough to ensure a complete reactants conversion at the reactor outlet; 2) it is industrially sustainable (the value is not too low to lead to too low productivities).

Observing Figure 3 and Figure 4, it is possible to state that the conventional steady state model does not predict a shift of the runaway boundary with respect to the previously analyzed case of high axial velocities: even the same maximum temperature rise (equal to about 900 K) is always reached. Analyzing the conversion vs. the axial coordinate (or the temperature vs. the axial coordinate) profiles, it is possible to compute that, decreasing the axial velocity of the reactants, the location of the hot spot along the reactor shifts from about 0.76 times the full length of the reactor to about 0.038: no other relevant effects of can be detected.
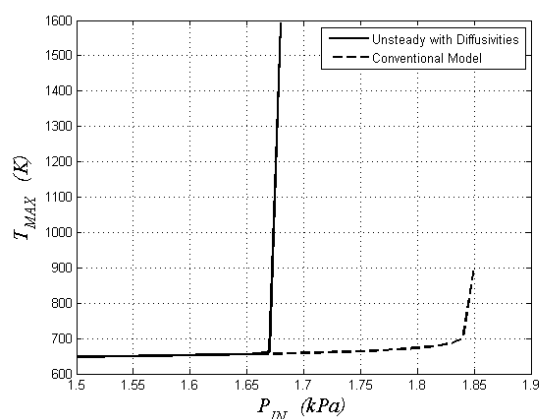

Figure 3: Temperature maxima as function of inlet partial pressure. Low axial velocities.
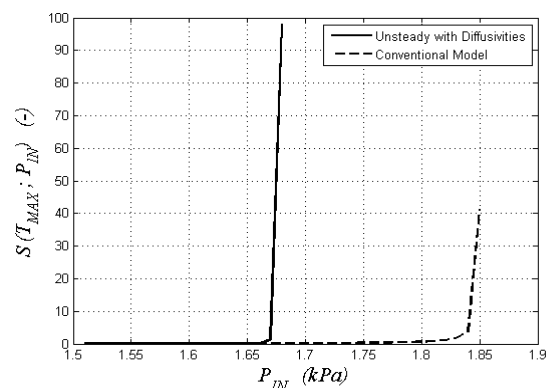

Figure 4: Normalized sensitivity of the temperature maximum with respect to the inlet partial pressure. Low axial velocities.

This behavior is in perfect agreement with what it has been already observed in the scientific literature (Soria Lopez et al., 1981): a decrease in the axial velocity imply a shift of the reactor thermal behavior towards progressively more dangerous states (the so-called MARFP, acronym of "Maximum occurred at a Finite Axial Reactor Position"); while, an increase of the values of this parameter lead to progressively safer reactor operations (the so-called PAO, acronym of "Pseudo-Adiabatic Operation"; that is, theoretically, when the reactor approaches a temperature maximum at $z \rightarrow \infty$ - of course such a maximum can correspond to runaway conditions).

On the contrary, the unsteady state model considering axial diffusivities predicts a clear shift in the runaway boundary: the critical inlet partial pressure changes from 1.85 kPa to 1.68 kPa. Such a difference, even if it seems quite small, it is definitely significant since a small uncertainty in the determination of the inlet reactant concentration can lead to the triggering of strong runaway phenomena.

In fact, theoretically, basing only on the results of the conventional model (the only one used till now) that detects the runaway boundary at 1.85 kPa, we can operate the reactor using an inlet partial pressure equal to 1.80 kPa. Unfortunately, such conditions fall inside the runaway region of the reactor; therefore, even if they are able to guarantee a high productivity, can not be practically employed. In fact, the inlet partial pressure must be necessarily lower than 1.68 kPa (that is, the value of the runaway boundary calculated using a more complete and realistic mathematical model for the dynamical simulation of a tubular reactor) in order to avoid that, during start-up operations, the thermal control is lost.

Even if this work is only preliminary because a complete experimental validation has not been carried out (van Welsenaere and Froment analyzed only the case of high axial velocities), the conclusions arising are important because they suggest that a more deep study concerning runaway in PFRs should be performed.

5. Conclusions

In this work it has been demonstrated that the calculation of the runaway boundary for a tubular reactor considering both the transient behavior and the axial diffusivities is a critical operation independently of the criterion adopted for its calculation. This is because unjustified assumptions that assume conventional steady state operating conditions (that is, considering neither the transient nor the diffusivities) can lead to the determination of unsafe runaway boundaries. Particularly, considering the relevant case study of the naphthalene catalytic oxidation in a PFR, it has been found that the critical inlet partial pressure is underestimated whenever the inlet axial velocity of the reactants becomes too low. Even if further studies of other relevant constitutive model parameters must be carried out, these preliminary results suggest that these systems deserve some more attention.

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