Thermal Explosions in Alkenes Epoxidation Processes

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1 Introduction

A significant number of petrochemical accidents can be ascribed to the thermal explosion [1,2]. This phenomenon, often referred as runaway reaction, is defined as a self accelerating, exothermic reaction producing heat with a faster rate with respect to the heat removal. In this case, a positive feedback on the reactive system occurs because of the Arrhenius theory; the bulk temperature of reactants increases, possibly leading to the over-pressurization of the process equipment due to gas phase, or for the evaporation of liquid, or for the occurrence of secondary decomposition reactions. The pressurisation is followed by the activation of process safety barriers (e.g. pressure safety relief valves), or by the emergency shut-down of the process plants, or, in the worst case, by the structural damage of the process equipment. Although the robust, dynamic process control systems adopted in modern chemical processes, thermal explosions are still far to be avoided and fully understood, as confirmed by the recent report on the French industry, which indicates this phenomenon as the origin of the 25% of the total industrial accidents [3]. Several approaches and criteria have been then developed to individuate safe region conditions [4,5]. Most of them are based on the pioneering studies of Semenov and Frank-Kamenetskii devoted to the physical and chemical characterization of thermal runaway [6]. More recent principles on the kinetic characterization and reactors design have been developed and reported in several textbooks [7,8]. Among chemical processes, the catalytic epoxidation of alkenes is particularly prone to thermal explosion [9]. As a matter of fact, the operative conditions of these processes are addressed by safety consideration [10]. Besides, there is as strong need for quick, safe and fair process (QFS) for the direct epoxidation of ethylene oxide (EO) and propylene oxide (PO), two processes which have been largely incentivized in the recent years by the significant increase of the worldwide demand and products applications [11,12]. Here, it should be noted that computer-aided methods for the evaluation of chemical systems have led to the development of detailed kinetic mechanisms suitable for a wide range of conditions and compositions, allowing further insight on the subject. These models take into account hundreds of reactants, including radicals, and thousands of reactions; they are often obtained by unifying separate reactions schemes by hierarchical approach [13]. Hence, catalytic reactions may be added to homogeneous models. In the following, either simplified or detailed kinetic models were adopted and compared to evaluate the occurrence of thermal explosions in EO and PO production.

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2 Methodology

Kinetic and thermal aspects are commonly coupled to evaluate process safety and reactor design, as reported in the comprehensive studies of Morbidelli and Varma for a wide range of processes [14,15]. The most common approach utilizes simplified chemical paths, e.g. reactions in parallel or series. The catalytic reaction mechanism ruling the EO production from ethylene has been largely investigated. Most of the authors agree that the simplified mechanism proposed by Wersterterp and Ptasinski (1984) [16] consisting in two parallels reactions, i.e. complete and partial oxidation of ethylene, fairly represents the chemical phenomena occurring under the operative conditions of this process. For what concern direct oxidation of propylene to PO, suitable catalysts have been only recently developed [17]. Hence, studies focused on the optimization of catalyst composition and development of accurate kinetic mechanisms are still ongoing [18]. A simplified scheme for the PO synthesis has been proposed for gold-based catalyst [19]. The cited model can be further simplified by individuating the rate determining steps and considering negligible - by the kinetic point of view - the other reactions, thus resulting in two parallel reactions as for the EO case. For the aims of this work a detailed kinetic mechanism referred as KIBO, which has been already validated for the alkenes and methane (often mixed to the reactants) [20,21] oxidation has been adopted. However, the cited version consists in a list of homogeneous reactions, only. Hence, the cited catalytic reactions were added to the previous list. Under these assumptions, steady-state, one-dimensional plug-flow reactor mass and energy balances were adopted. For the sake of simplicity, heat and mass balances were expressed in the dimensionless form and including the catalytic reactions, exclusively. However, the reported structure can be adopted for detailed kinetic mechanism, as well.

$$\frac{dx_a}{dz} = -Da \cdot \left(R_1 + R_2 \cdot \frac{k_{2,0}}{k_{1,0}} \right) \tag{1}$$

$$\frac{dx_b}{dz} = Da \cdot R_1 \tag{2}$$

$$\frac{d\theta}{dz} = Da \cdot \left[B \cdot \left(R_1 + \Delta H_r \cdot \frac{k_{2,0}}{k_{1,0}} \cdot R_2 \right) - \frac{St}{Da} \cdot (\theta - \theta_{Co}) \right] \tag{3}$$

where x, z, ΔH, R, θ stand for the dimensionless mole fraction, axial position, heat of reaction, reaction rate (see Eqs 4, 5) and dimensionless temperature (see Eq 6). The subscripts a, b, 1, 2, r and Co represent the limiting reactant (i.e. oxygen), desired product (i.e. epoxidized alkene), combustion, partial oxidation reactions, ratio of 2 to 1 and coolant, respectively.

$$R_1 = \exp\left[\frac{\left(\theta \cdot \frac{E_{a,1}}{R_g \cdot T_0} \right)}{\left(\theta + \frac{E_{a,1}}{R_g \cdot T_0} \right)} \right] \cdot x_a^{n_1} \tag{4}$$

$$R_2 = \exp\left[\frac{\left(\theta \cdot \frac{E_{a,2}}{R \cdot T_0} \right)}{\left(\theta + \frac{E_{a,1}}{R_g \cdot T_0} \right)} \right] \cdot x_a^{n_2} \tag{5}$$

$$\theta = (T - T_0) \cdot \left(\frac{E_{a,1}}{R_g \cdot T_0} \right) \tag{6}$$

where T, E_a, R_g and n represent temperature, activation energy, ideal gas constant and reaction order, respectively. The terms k, L, d_t, v, U, $c_{a,0}$, ρ and c_p are respectively the kinetic pre-exponential parameter, reactor length and diameter, gaseous velocity, the overall heat transfer coefficient, initial concentration of limiting reactant, density and heat capacity. Finally, the Damkholer number (Da), Stanton number (St) and the heat to reaction parameter (B) are defined as:

$$Da = \frac{\left(k_0 \cdot c_{a,0}^{n_1 - 1} \cdot L\right)}{v} \tag{7}$$

$$St = \frac{4 \cdot U \cdot L}{d_t \cdot v \cdot \rho \cdot c_p} \tag{8}$$

$$B = \frac{\left(\Delta H \cdot c_{a,0} \cdot \frac{E_{a,1}}{R \cdot T_0}\right)}{\rho \cdot c_p \cdot T_0} \tag{9}$$

It is worth noting that the ratio St/Da (i.e. the Semenov number) was conveniently adopted in the reported dimensionless form of the heat balance (Eq. 3) to avoid the dependence on the reactor length, thus allowing the calculation of a constant value for each analysed process and investigated conditions. For the sake of this work, in Table 1, the representative initial conditions as reported by Rebsdat and Mayer (2012) [22] for EO and Kahlich et al. (2005) [23] for PO and threshold temperature to avoid sintering [4, 19] are indicated.

Table 1: Representative conditions of ethylene oxide and propylene oxide processes.

	EO	**PO**
Temperature [K]	450 – 500	320 – 400
Pressure [bar]	10 - 22	1.0 – 1.5
Alkene (molar fraction)	0.15 – 0.40	0.1
O_2 (molar fraction)	0.05 – 0.90	0.1
H_2 (molar fraction)	-	0.1
Threshold Temperature [K]	560	460
Dimensionless threshold temperature θ_{tr}	1.90	3.57

The reported governing equations and boundary conditions were adopted for the evaluation of safe operative conditions in the Da-B plane. Indeed, under these boundary conditions, a plug flow reactor was modelled to monitor axial temperature and products profile. Starting from these results, different criteria were defined and compared for the sake of either process safety or effectiveness, i.e. the optimal Da value for each condition was identified as that giving maximum temperature (θ_{max}), maximum rise in temperature $(d\theta/dt)_{max}$, maximum content of desired specie $u_{b,max}$ or temperature equal to the threshold value (θ_{tr}).

3 Results and Discussion

The overall reactivity and exothermicity of EO and PO production processes have been evaluated in terms of Da and B, respectively and represented in Figure 1, which includes the optimal conditions identified by simplified, catalytic mechanisms or by the complete, homogeneous detailed kinetic model (KIBO). For the sake of clarity, curve based on the $(d\theta/dt)_{max}$ criterion obtained by using the KIBO model have been reported, exclusively. Following the approach proposed by Varma et al. (1999) [15], we can say that regardless the adopted criteria, the critical conditions can be identified as the Da-B peak for the curve $u_{b,max}$ (B_c) The obtained values for B are respectively 36.9 for EO (which is similar to that reported in the literature) and 16.9 for PO. Furthermore, three different regions can be represented on the Da-B plane: hotspots (HS), runaway (RUN) and pseudo-adiabatic operation (PAO). The HS can be represented by the area above the curve of $u_{b,max}$, for $B < B_c$. Indeed, this limit corresponds to favourable conditions for the complete oxidation of reactants, hence the maximum adiabatic temperature. The RUN area corresponds to the same region as HS but $B > B_c$, where the process meets a non-return requirement. In this condition, the complete oxidation occurs but the heat removal system is insufficient to control the reactor temperature. Finally, the PAO region corresponds to the area below the $u_{b,max}$ curve, where safe process conditions are respected. The runaway region can be also identified by applying the Strozzi and Zaldivar criterion (SZ) [24], often referred as the divergence criterion. This methodology defines the runaway conditions for the positive ordinary differential equation system describing the thermal behaviour of the reactor on a section of the reaction path, i.e. where the sum of the first derivate term of the dimensionless reactant and coolant temperatures and the conversion is non-negative. The derivate of the coolant temperature with respect to the axial position is tautological null for the analysed processes, because large flowrate are typically fed to guarantee constant coolant temperature [17]. Consequently, this condition is satisfied when the curves representing $u_{b,max}$ and θ_{max} criteria are overlapped so that, in other words, both approaches give the same B_c, as expected and negligible differences can be observed in case of $B > B_c$.

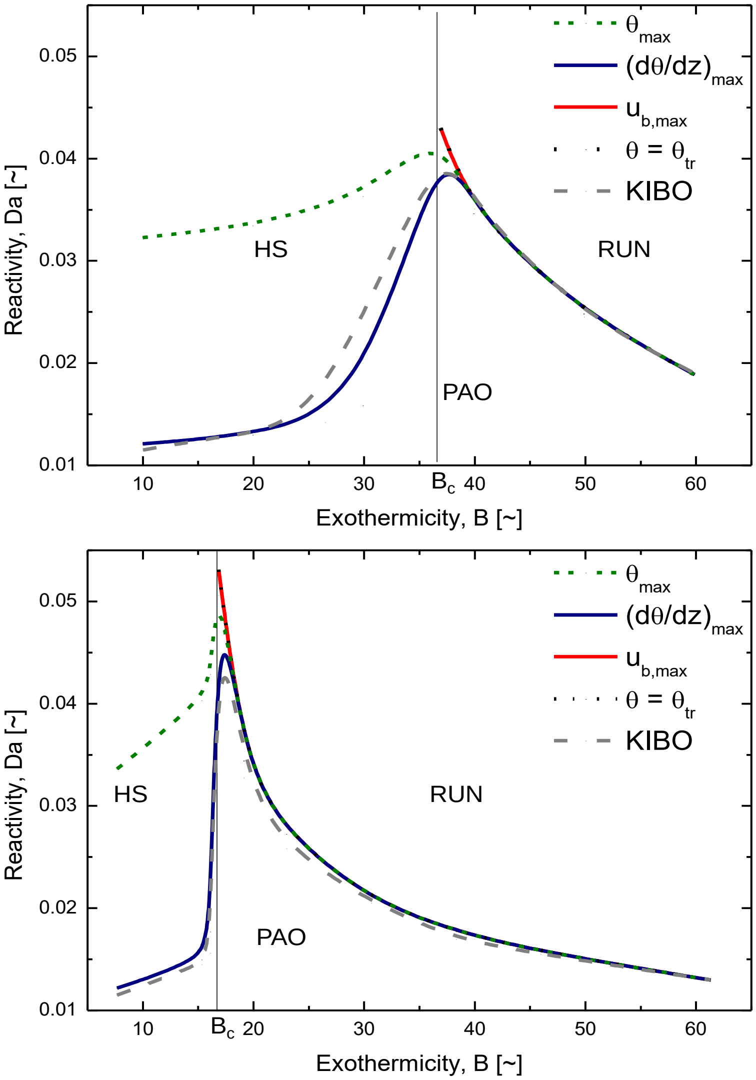

Figure 1. Left: Da-B plane for ethylene; top and propylene (bottom). θ_{tr} curve is over-imposed to $u_{b,max}$ curve.

Hence, it can be concluded that the epoxidation of propylene is inherently safer than ethylene process. This occurrence can be attributed to the elevated selectivity of the gold-based catalysts utilized in the PO process, which is higher than 99% [21], and to the lower initial temperature and pressure, which result in the reduced rate of side-reactions. Hence, well designed mixing features should be sufficient to guarantee the absence of runaways in the case of PO. Noteworthy, θ_{tr} and $u_{b,max}$ curves assume asymptotic behaviour for the right limit of B_c, whereas they are not reported for $B < B_c$ i.e. $B < B_c$ corresponds to concentration of reactants so low that they are unable to generate sufficient heat to self-sustain the reaction kinetics for the given reactor layout. Quite clearly, the adoption of $(d\theta/dt)_{max}$ and θ_{max} criteria as stand-alone parameters may lead to significant over-conservative or unsafe choices, because absolute temperature values were not considered. Indeed, low temperatures are achieved as indicated by the absence of θ_{tr} curve, thus the risks of offset conditions due to side reactions are negligible. On the contrary, at elevated concentration, the corresponding curves are almost overlapped, thus indicating the existence of reactor conditions potentially leading to unwanted kinetics. These observations suggest that the safety of reactor can be characterized by coupling the information obtained by means of $(d\theta/dt)_{max}$ and θ_{max} criteria, whereas the $u_{b,max}$ and θ_{tr} criteria can be considered as stand-alone parameters and benchmark in the investigated conditions, since they account either for safety or for the selectivity aspects. The criteria referred as KIBO gives curve slightly shifted to lower B with respect to the simplified chemistry, especially for EO, whereas negligible differences are noted for PO. This indication suggests that non-catalytic reactions may play a significant role in case of dilution, at least for the EO process. At elevated concentration of reactants ($B > B_c$) the curves of KIBO and the abovementioned criteria are almost perfectly overlapped, thus KIBO is in agreement with SZ criterion. Hence, the homogeneous reactions can be neglected and the negligible role of EO oxidation in reactor relevant conditions confirmed. These observations can be extended to PO, as well.

4 Conclusions

Detailed kinetic models as KIBO have the potential to evaluate the generic reactivity of homogeneous mixtures in details and may include the heterogeneous/catalytic phenomena. The utilization of accurate kinetic models suitable for process conditions can lead to increased selectivity and reactor design optimization because of the simultaneous evaluation of safety aspects and products distributions.

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