

# Batchsize and Topological Criteria: a Combined Approach to Safely Optimize Hazardous Polymerization Processes

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Small and medium chemical enterprises are widely diffused in Italy. Particularly, they operate batch and semi-batch processes working on job orders and making a massive use of multipurpose reactors having an Emergency Relief System (ERS) already installed. A batchsize approach is a method focused on finding the reactor fill level that can lead to a single phase vapor flow whether an external fire occurs, so that the installed ERS can protect the reactor from overpressures. In this work, such an approach has been revised, by choosing a runaway reaction as design incidental scenario, and integrated with a suitable optimization procedure based on topological criteria. The new batchsize approach allows for computing a reactor fill level which is much more reasonable for industrial applications with respect to that one predicted by the older method, while the topological approach permits to identify the minimum dosing time capable of guaranteeing both reactor safety and high productivity.

Theoretical results have been experimentally validated using data obtained by reaction calorimetry experiments, carried out in an isoperibolic RC1 equipment (1 L, Mettler Toledo), implementing the relevant case study of the solution homopolymerization of butyl acrylate.

## 1. Introduction

One of the most frequent causes of accidents in chemical industries can be ascribed to fast and highly exothermic reactions (Barton and Rogers, 2004). Such undesired events can lead to a reactor temperature loss of control, referred to as "thermal runaway" (occurring whenever the rate of heat evolution is much higher than the rate of heat removal provided by a dedicated cooling system), that can arise by a number of different root causes: 1) decompositions of the whole reacting mixture; 2) triggering of side reactions catalyzed by impurities or 3) process thermo-chemistry lack of knowledge.

As a consequence of these undesired phenomena, a number of studies concerning the detection of both marginal ignition (Morbidelli and Varma, 1988; Strozzi et al., 1999) and safe productive operating conditions (Steensma and Westerterp, 1988; Alós et al., 1998; Maestri and Rota, 2005) have been conducted.

In Italy there are almost 3,000 chemical plants with more than 3,400,000 employees and a production value of over  $53 \cdot 10^9$  EUR (Federchimica, 2012). Particularly, during the last thirty years, small and medium enterprises widely diffused. Such industries operate batch and semibatch processes working on job orders and making a massive use of multipurpose reactors having an emergency relief system (ERS) already installed. Such safety devices are normally sized when the reactor is designed assuming a single phase vapor flow generated by an external fire (worst incidental scenario). This assumption can lead to a big underestimation of the vent area if, precisely because of the triggering of an incidental phenomenon, the actual flow is two-phase (such as that one generated after the occurrence of a runaway reaction in a viscous polymerization system). Moreover, ERS sizing is particularly complex for small enterprises since they usually have narrow financial and personal resources. In many cases a complete safety study or the replacement of the ERS is not possible because of unsustainable costs.

A batchsize approach is a method focused on finding the reactor fill level that can lead to a single phase vapor flow whether an external fire occurs, so that the installed ERS can protect the reactor from explosions due to overpressures.

In this work, such an original approach has been revised, by choosing a runaway reaction as worst design incidental scenario instead of an external fire, and integrated with a suitable optimization procedure based on topological criteria. This new batchsize approach allows for computing a reactor fill level which is much more reasonable for industrial applications with respect to that one predicted by the older method, while the topological approach permits to identify the minimum dosing time capable of guaranteeing both reactor safety and high productivity (the so called QFS conditions).

Theoretical results have been experimentally validated using data obtained by reaction calorimetry experiments, carried out in an isoperibolic RC1 equipment (1 L, Mettler Toledo), implementing the relevant case study of the solution homopolymerization of Butyl Acrylate (BA) thermally initiated by Azobisisobutyronitrile (AIBN).

## 2. Batchsize Approach

Whenever a multipurpose reactor is used to carry out a new process, an actual value of the reacting mass to be loaded into the reactor (batchsize) should be calculated in order to guarantee, in case of runaway reaction triggering, a single phase vapor efflux through the reactor ERS. If such a condition is verified, it is possible to use the already installed ERS with the new synthesis.

In order to calculate the batchsize only one closed cell adiabatic calorimetric test is needed, so that time and economical saving can be achieved.

### 2.1 Runaway Scenario

In order to size whatever overpressure vent device it is necessary to define the way in which the pressure is generated into the system. Particularly, systems can be divided into three types (Fauske, 2006):

- Vapor: generated pressure is entirely due to the reacting mixture vapor pressure;
- Gassy: generated pressure is due to non-condensable gases formation;
- Hybrid: generated pressure is due to both non-condensable gases formation and vapor pressure.

All the systems listed above can be further classified as tempered or non-tempered when pressure is a function only of temperature or not, respectively. Vapor systems are always temperate whereas gassy systems are always non-temperate (Etchells and Wilday, 1998).

Finally, reacting systems can be classified as foamy or non-foamy (Fauske, 2006). Concerning the flow regime into the reactor, three categories can be encountered (Etchells and Wilday, 1998): homogeneous (no disengagement between gas and liquid phase, leading to a great liquid swell), churn-turbulent (complete vapor - liquid disengagement and almost no reacting liquid mass swelling) and bubbly (in between the previous two). Moreover, the flow through the vent can be single-phase vapor flow, single-phase liquid flow, or two-phase flow.

During a runaway reaction solvent vapors or non-condensable gases can be generated (Dellavedova et al., 2010). Since the bubble volume is larger than the liquid one, the reaction mass level increases (swelling): when the foam level is higher than the available void reactor space, a two-phase flow through the vent occurs. For a given runaway scenario, the flow type can be foreseen through the operating procedure described by Fisher et al. (1992): 1) evaluate gas/vapor superficial velocity,  $j_g$ ; 2) estimate bubble rise velocity,  $U_\infty$ ; 3) calculate reaction mass volume swell,  $\alpha$ ; 4) compare  $\alpha$  to the available void fraction in the reactor  $\alpha_0$ ; when  $\alpha_0 > \alpha$ , a single-phase vapor flow occurs.

$j_g$  can be computed from the volumetric flow rate generated by the runaway reaction,  $W_{vol}$ , which is the sum of non-condensable ( $Q_g$ ) and vapor volumetric flow rate ( $Q_v$ ):

$$W_{vol} = j_g \cdot A_R = Q_g + Q_v \quad (1)$$

where  $A_R$  ( $m^2$ ) is the reactor section through which gas and vapor flow before reaching the vent. When the self-heating is due to runaway phenomena,  $Q_g$  and  $Q_v$  ( $m^3/s$ ) can be calculated as (Etchells and Wilday, 1998):

$$Q_g = \left[ \frac{V_e}{P_R} \cdot \left( \frac{dP}{dt} \right)_R - \frac{V_e}{T_R} \cdot \left( \frac{dT}{dt} \right)_R \right] \cdot \frac{m}{m_e} \quad (2)$$

$$Q_v = \frac{q \cdot m}{\Delta h_{ev} \cdot \rho_G} \quad (3)$$

where  $m$  is the reacting mass (kg),  $q$  is the specific heat flow generated by the runaway reaction (kW/kg),  $P$  is pressure (kPa),  $T$  is temperature (K),  $t$  is the time (s),  $V$  is volume (m<sup>3</sup>),  $\Delta h_{ev}$  is the evaporation heat (kJ/kg),  $\rho_G$  is the vapor density (kg/m<sup>3</sup>). Subscript  $e$  stands for the laboratory test device (closed cell) and  $R$  for the real size reactor relief conditions.

Bubble rise velocity,  $U_\infty$ , is linked to the physical properties of the reactive mass and can be calculated, for cylindrical reactors, as:

$$U_\infty = k \cdot (\sigma \cdot g \cdot (\rho_L - \rho_G))^{0.25} \cdot \rho_L^{-0.5} \quad (4)$$

where  $k = 2.5$  for churn-turbulent flow regime and  $k = 1.18$  for bubbly/homogeneous flow regime,  $\sigma$  is gas-liquid surface tension (N/m) and  $\rho_L$  is the liquid density (kg/m<sup>3</sup>).

Void fraction can be calculated from the following equations (Fisher et al., 1992):

$$\Psi = \frac{2 \cdot \alpha}{(1 - C_0 \cdot \alpha)} \quad \text{churn-turbulent} \quad (5a)$$

$$\Psi = \frac{\alpha \cdot (1 - \alpha)^2}{(1 - \alpha^3)(1 - C_0 \cdot \alpha)} \quad \text{bubbly} \quad (5b)$$

where  $\Psi = j_g / U_\infty$  and  $C_0$  is a correlation parameter related to the investigated system.

In order to relieve a single-phase vapor flow from the ERS once a runaway phenomenon arises, the following condition must be satisfied:

$$\alpha \leq 1 - \frac{m / \rho_L}{V} = 1 - \frac{m}{B} \quad (6)$$

where  $B = V \cdot \rho_L$  is the maximum reactor load. The solution of this equation represents the empty part of the reactor which is available for mass swelling. Once such a value has been computed for a given runaway scenario, it is possible to evaluate the maximum reagent mixture mass that can be loaded into the reactor in order to have a single-phase vapor flow through the relief device. Equation (6) can be used, together with proper equations representing the  $\alpha$  value for a given system, to obtain a constraint on the reactor load allowing for a single-phase vapor flow through the ERS. A summary of some resulting formula are reported in Table 1 (Dellavedova et al., 2010).

Table 1: Maximum reactor load,  $m_{\max}$ , for vapor reactive systems and different flow regimes.

$$A = 2U_\infty \Delta h_{ev} \rho_G A_R / q \quad \text{and} \quad C_0 = 1$$

Flow Regime	$\Psi(j_g / U_\infty)$	$\alpha(\Psi)$	$m_{\max}$ from $\alpha(\Psi) = \alpha_0$
Churn-Turbulent	$2m/A$	$(2m/A)/(2 + (2m/A))$	$m_{\max}^2 + A \cdot m_{\max} - AB = 0$
Bubbly	$2m/A$	$\alpha(1 - \alpha)/(1 - \alpha^3) = 2m/A$	$2B(1 - m_{\max}/B)^3 - m_{\max}(A/B) - 2B + A = 0$

### 3. Optimization

After a safe sizing of the initial reacting mass, it is necessary to search for a suitable optimization procedure aimed to maximize reactor productivity avoiding runaway conditions. Particularly, for isoperibolic semibatch reactors, such an optimization can be performed with respect to either the dosing time,  $t_{dos}$ , or the coolant temperature,  $T_{cool}$ . In this work dosing time has been chosen as optimization parameter for practical reasons.

The topological criterion theory states (Copelli et al., 2012) that, for a semibatch process carried out under isoperibolic temperature control mode, the boundary between runaway and QFS conditions with respect to

a desired product X is identified by an inversion of the topological curve showing a concavity towards right. Particularly, this curve shows all the possible thermal behavior regions of an isoperibolic SBR obtainable by varying one system constitutive parameter (e.g. dosing time) or initial condition (e.g. coolant temperature) in a suitable range. The topological curve can be drawn by solving the equations describing the analyzed system for each investigated value of the generating parameter and, then, reporting onto a bidimensional diagram the obtained reactor temperature maxima divided by the coolant temperature,  $\psi_{MAX} = T_{MAX} / T_{cool}$ , and the conversion with respect to the desired product in correspondence of such maxima,  $\zeta(\psi_{MAX})$ .

The optimization procedure based on the analysis of the topological curve uses the QFS inversion as a boundary beyond which the optimum operating conditions (that is, dosing time and coolant temperature) can be searched for accounting reacting mixture thermal stability ( $\Psi_{MAX,n} \cdot T_{cool} < MAT$ ) and desired productivity ( $\zeta_{dos,n} \geq \zeta_{dos,MIN}$ ) constraints. This optimization procedure is particularly useful for small and medium businesses, in which the number of experimental tests that can be carried out to completely characterize a new process is quite small.

## 4. Results

### 4.1 Reacting System

Since this reacting system has been extensively analyzed elsewhere (Copelli et al., 2011), here it will be only briefly summarized. The case study consists in the free radical solution homopolymerization of butyl acrylate (BA,  $\geq 99\%$ , Sigma-Aldrich) in ethyl acetate (EtOAc,  $\geq 99\%$ , Sigma-Aldrich). This polymerization is thermally initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN,  $\geq 98\%$ , Fluka) and it is performed, at laboratory scale, in an isoperibolic semibatch reactor (RC1<sup>e</sup>, 1 L, Mettler Toledo) refrigerated by an external jacket where a silicon oil is circulated. From experimental evidences (small and discrete bubbles rising into the reacting mass), the flow regime into the reactor has been classified as bubbly since viscosity (about 40-50 cP) are  $< 100$  cP (Etchells and Wilday, 1998).

### 4.2 Experimental method

In order to calculate the batchsize only one closed cell adiabatic test is needed. Such a test has been performed in an Accelerating Rate Calorimeter (ARC) using a standard Heat – Wait – Search (HWS) method. An ARC apparatus is an adiabatic calorimeter particularly suitable to study reacting systems subject to decomposition. It is composed of: a spherical sample holder, built of Hastelloy C and placed in an insulated vessel; a radiant heater, which raises sample temperature up to a determined value; a thermocouple connected to the sample holder wall; an insulated covering (jacket) with three thermocouples and eight heaters and a capillary tube that links the sample holder to a pressure transducer. A dynamic standard HWS test can be performed according to the following procedure: the sample is warmed up (Heat) by the radiant heater at a desired temperature, then the instrument waits (Wait) until all temperatures are stabilized, and, finally, it starts to search for exothermic effects (Search), namely, a self-heating rate of reaction mass into the sample larger than  $0.02$  °C/min. This research terminates when either a predetermined time is passed (15 min) or a sample self-heating rate that exceeds  $0.02$  °C/min is detected. If an exothermic reaction is revealed, the instrument automatically collects temperature and pressure data as functions of time, shifting to adiabatic mode until the reaction ends (self-heating rate lower than the fixed limit). If an exothermic reaction is not revealed, a new sequence of HWS is started at a higher temperature.

Table 2 reports all the experimental data that can be collected from the ARC test.

Table 2: Results Obtained by the Standard HWS ARC Test on the Analyzed Reacting Mixture

$(dT/dt)_{MAX}$ (°C/s)	0.0781	$\Phi$ factor, (-)	2.15	$(dT/dt)_{MAX}$ corrected by $\Phi$ , (°C/s)	0.8401
Reaction enthalpy, (J/g)	-187	Exothermic effect initial temperature, (°C)	65	Final pressure = Initial pressure, (bar)	3.4

Moreover, Figure 1 reports temperature and pressure vs. time (a) and logarithmic pressure vs.  $-1000/T$  (b) profiles. From Figure 1a it can be noted that, in correspondence of  $65$  °C, an exothermic effect followed by a pressure increase (that, starting from about  $77$  °C, cannot be ascribed to the temperature increase

only) can be recognized. This phenomenon extinguishes at 112 °C and it has been ascribed to the thermally initiated polymerization of BA combined with the reacting mixture boiling (the occurrence of this phenomenon is proved by the lower reaction enthalpy detected from this test, that is - 194 J/g vs. 504 J/g). Moreover, it can be observed that, after this exothermic effect no decomposition event takes place until 300 °C, where the experiment has been terminated (Copelli et al., 2011). From Figure 1b, also referred to as the Clapeyron plot, it can be observed a monotonic quasi linear increase during all the exothermic effect. Such a behavior, together with the experimental information about the residual pressure (which is equal to the starting one, see Table 1), confirms that the system can be classified as vapor.

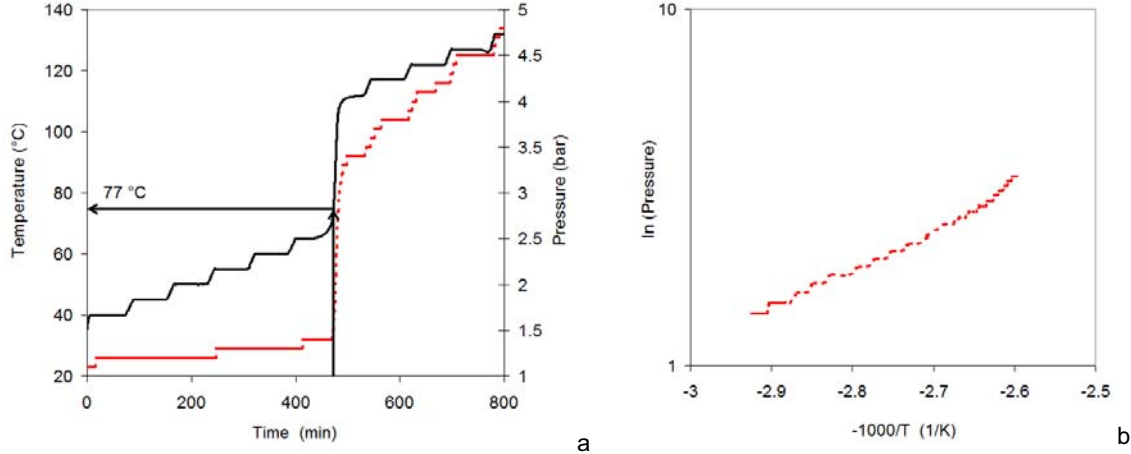


Figure 1: a) Sample temperature (continuous) and pressure (dotted) vs. time profile for the whole ARC HWS test and b) logarithmic pressure vs.  $-1000/T$  profile during the exothermic effect.

#### 4.3 Batchsize

In order to calculate the maximum reacting mass to be loaded into the reactor, Equation (6) has been used in combination with Equation (5b). Particularly,  $\Psi$  has been computed using Equation (1) and Equation (4). The resulting expression (see also Table 1) is reported in the following:

$$2B(1 - m_{\max}/B)^3 - m_{\max}(A/B) - 2B + A = 0 \quad (7)$$

From Eq. (7), it is possible to calculate the maximum reacting mixture mass to be loaded into the reactor. Such a value, for the investigated system, is equal to 0.4362 (kg). Introducing an arbitrary safety factor of about 0.75, the operative amount of reacting mixture has been taken equal to 0.3272 (kg). This value has been used to scale up the recipe to the RC1 scale for the optimization process.

#### 4.4 Optimization

Concerning this case study, an experimental optimization based on the topological criterion has been already presented in the literature (Copelli et al., 2011). In this work, a theoretical version of the optimization procedure, arising from the development of a detailed mathematical model aimed to simulate the process in all the experimentally investigated RC1 operating conditions, has been implemented. Particularly, during normal operating conditions the process can be modeled through a system of ordinary differential equations (ODE) expressing: isoperibolic proportional-integral temperature control, energy balances on both jacket and reactor, material balances on both the initiator (AIBN) and the monomer (BA), global material balance, mixing rules and dosing policy (in this case, linear). Such a set of ODEs, together with all kinetics parameters taken from the literature, has been used to simulate a series of RC1 synthesis at varying dosing times (from 15 min to 65 min) with the aim of generating the topological curve necessary for the optimization procedure implementation. Figure 2 reports the comparison among some experimental results (Copelli et al., 2011) and their related theoretical predictions for what concern temperature vs. time profiles. As it can be noted, a good agreement has been reached. Therefore, extracting from the theoretical simulations at different dosing times (index  $n$ ) all the values of  $\psi_{MAX,n}$  and  $\zeta(\psi_{MAX,n})$  it is possible to generate the topological curve and detecting both the QFS inversion and the optimum dosing time,  $t_{dos,OPT}$ , fulfilling all the previously cited constraints (see Section 3). The resulting  $t_{dos,OPT} = 65$  min has been found to be in perfect agreement with those one already presented in the literature (Copelli et al., 2011).

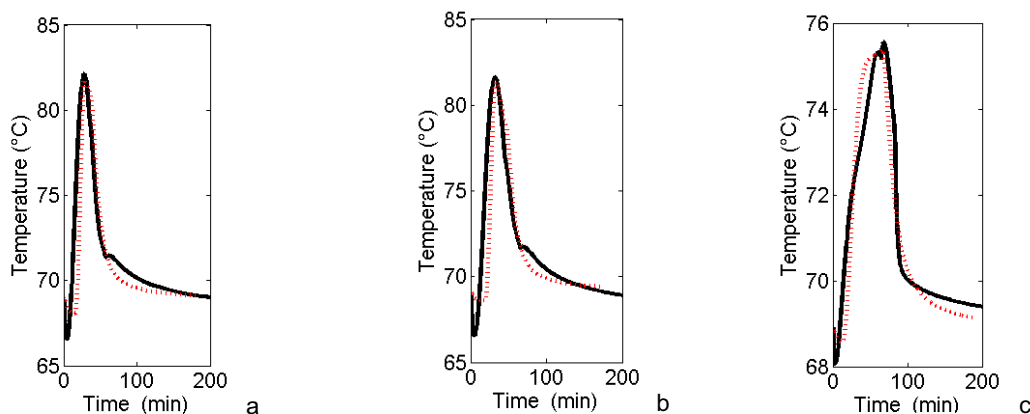


Figure 2: Comparison between some theoretical (continuous) and experimental (dotted) temperature vs. time profiles for different dosing times: a)  $t_{dos} = 35$  (min), b)  $t_{dos} = 45$  (min) and c)  $t_{dos} = 65$  (min)

## 5. Conclusion

In this work, two procedures concerning the semibatch reactors safety optimization have been coupled. The first one is based on DIERS methods for safe relief sizing and it concerns the calculation of the maximum amount of reacting mixture (batchsize) to be loaded into a reactor to ensure a single phase vapor relief in runaway condition. The second one is based on the topological criterion for QFS detection and it concerns a safe process optimization accounting for reactor thermal stability and productivity constraints. This procedure can be applied both experimentally, carrying out a sufficient number of calorimetric tests and theoretically, writing an ODE system that describes the reactor thermal behavior. The combination of such procedures has been used for a safe process optimization of the Butyl Acrylate homopolymerization. All obtained results are in agreement with what has been already found in literature, confirming the reliability of both procedures.

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