Boundary Diagrams Safety Criterion for Liquid Phase Homogeneous Semibatch Reactors

K. Roel Westerterp,[†] Michał Lewak, and Eugeniusz J. Molga*

Chemical and Process Engineering Department, Warsaw University of Technology, Waryńskiego 1, 00-645 Warszawa, Poland

ABSTRACT: In this work a summary of safety assessments based on a concept of boundary diagrams safety criterion (BDSC) is given and adapted for liquid phase homogeneous reactions carried out in batch and semibatch reactors. First, on the basis of theoretical considerations, the operating diagrams have been elaborated, which make possible a selection of safe or inherently safe operating conditions for any liquid homogeneous reaction, even with limited information on the reaction kinetics. To use the proposed method, a detailed reaction mechanism is not required; only fundamental kinetic information is necessary. Usually, the reaction kinetic constants at two chosen temperatures should be determined. Next the reaction enthalpy and a few well-known parameters used for characterization of the reacting system are utilized. The proposed approach is crucial for practical applications of this method, because in industrial practice—e.g., in the fine chemicals industry—usually there is no time and there are no funds for detailed investigations of the reaction kinetics. The proposed BDSC method has been verified with our own experimental data. Despite the fact that this method has been developed for a single second order reaction, it can be conservatively applied also for reactions of an order different from two as well as for parallel reactions.

1. INTRODUCTION

For the production of small quantities of chemicals, usually a batch reactor is used. In case the executed reaction exhibits too large a heat effect, the cooling of the reaction becomes a crucial problem and the reactor temperature may runaway to extremely high temperatures that cannot be accepted in view of the reactor materials or the thermal stability of the reaction mixture components. If this is the case, the usual solution is to run the reaction in the so-called semibatch mode, in which one of the reactants is added slowly in order to control the heat evolution.

But also in semibatch reactors (SBR) the temperature may runaway. In this work we will develop a method to run a SBR in such a way that runaways are always avoided. We first define a target temperature, which is the SBR temperature trajectory for the ideal case, in which all of the added reactant is reacted away instantaneously. In the following we consider the reactor operation safe if this target temperature during the reaction course never is surpassed. In practice, several different situations may develop during the semibatch run. At too-low starting temperatures the reaction may not even ignite or may react far too slowly. At higher starting temperatures the reaction does start but in the beginning is still too slow, so that dangerous accumulations of the dosed reactant occur, which later may lead to dangerous runaways. At even higher starting temperatures, these accumulations are avoided and the reactor operates safely over the whole dosing period.

We develop a boundary diagram for safe conditions, which enables the reader to select the correct operation conditions under all circumstances. After that we give recommendations for the practicing engineer to run safely a dangerous reaction in a SBR.

2. LITERATURE SURVEY

A comprehensive survey of studies on the safety of batch and semibatch reactors and runaway prevention is given in the review paper by Westerterp and Molga.[1] In this review, on the basis of developments in the past 25 years, the authors consider two from three lines of defense against thermal runaway in chemical reactors—i.e., namely, choice of the right operating conditions and early warning detection systems. Also the most efficient methods used for a correct choice of safe operating conditions in two cases—when the reaction kinetics is known and when it is not available, respectively—are discussed.

As is concluded in the review previously cited, in attempts to develop practical criteria for safe operation and runaway prevention, the following two most important mile stones could be distinguished: (1) the observation by Hugo and Steinbach[2,3] that an accumulation of the dosed component at too-low reactor temperatures is the cause of the runaway in homogeneous semibatch reactors and (2) the development by Steensma and Westerterp[4,5] of safety boundary diagrams (SBDs) for heterogeneous liquid–liquid semibatch reactions carried out in the dispersed phase as well as in the continuous one.

Since the year 2006, when the previously cited review was completed, in the field of the safety of batch and semibatch reactors, some of the newest contributions have to be taken into account. Among others the book by Stoessel[6] should be mentioned. In this book, in addition to the general aspects and fundamentals of thermal process safety, the entire part II is devoted to problems with mastering exothermal reactions and among others contains characterization of safety in batch and semibatch chemical reactors.

Also a contribution given in a series of papers by Maestri and Rota and their co-workers should be commented on. In the

papers by Maestri and Rota,[7,8] they discuss for homogeneous as well as heterogeneous SBR's the influence of the reaction order of the two reactants on the shape of the boundary diagrams (BD). The influence of the order is very small or negligible for the initially charged reactant. However, for the dosed reactant it is not negligible, and for orders smaller than one they find that the boundary for inherently safe reactors is extended to higher values of the Ry (reactivity number). The influence is the same for slow as well as for fast reactions. Further Maestri and Rota[9] demonstrate that for multiple reactions one cannot use one single BD but must experimentally derive a maximum allowable temperature (MAT) and calculate temperature profiles to make sure that the MAT is not surpassed. In the next two papers by Maestri and Rota,[10,11] the authors demonstrate that the value of Ry for inherently safe reactors increases with a factor of 2 in the case in which the order of the dosed reactant decreases from 1.0 to 0.5.

Maestri and Rota[12] discuss autocatalytic reactions, where the autocatalysis is caused by the dosed reactant, which must be present at the start of the reaction with a concentration equivalent to a conversion $\zeta_{B,0}$. Further the reactions are second order. For different conversions of B at the start they give a number of BDs and also temperature profiles. In their next contribution by Maestri et al.[13] the authors develop a design procedure, which is based on the use of a MAT, on known kinetics of the reaction involved and on estimated temperature increases as a function of the value of Ex (exothermicity number), while in the paper by Maestri et al.[14] they discuss experimental work to obtain the data required for their design procedure.

In the paper by Copelli et al.[15] they propose to calculate autocatalytic multiple reactions, where the kinetics are known. In this case there are too many variables to derive BDs. Next in the paper by Copelli et al.[16] they introduce the concept of the topological curve, which is a plot of $T_{max}/T_{coolant}$ versus the conversion in the point where the T_{max} has been reached. On such a curve the area for QFS (quick onset, fair conversion, and smooth temperature profile; always safe) reactions can be distinguished. They discuss three experiments to verify such with a topological curve. In the paper by Copelli et al.[17] they demonstrate that a topological curve can also be determined by plotting experimentally determined values of T_{max}/T_{cool} versus the dosing time for single reactions. Also polymerizations can be regarded as single reactions, provided there is only one reactant involved as monomer.

In their last paper Maestri and Rota[18] discuss an application of the boundary diagrams to increase the reactor productivity in the case where the reactor, in which multiple reactions are executed, is combined with a separation process, over which one of the reactants is circulated.

We should be aware of the fact that in most cases studied by Rota and his group the reaction kinetics is assumed to be known. The obtaining of that kinetics, of course, is the main time-consuming job in the case of fine chemicals production, especially for heterogeneous reactions. To solve such problems some new approaches are proposed—among others see the paper by Copelli et al.,[17] in which the topological criterion is extended. This criterion can be applied for the optimization procedure of complex highly exothermic reacting systems (e.g., polymerization reactions), even in a case in which the reaction scheme and all required kinetic data are not available.

Recently, a detailed comparison of various runaway criteria has been given by Casson et al.,[19] who have studied both geometry and sensitivity based approaches as they are formulated by Varma et al.[20] The geometry based criteria assume that detailed reaction kinetics is known, so temperature trajectories at different operating conditions can be estimated. However the model based criteria do not give any measure of the approaching runaway. The runaway and nonrunaway behavior can be distinguished with sensitivity based criteria, which indentify the parametrically sensitive region using online measured temperature trajectories. In the cited work the very well-known Hub and Jones[21] derivative criterion as well as the divergence criterion elaborated by Strozzi and Zaldivar[22] have been considered.

Safety aspects in modeling and operating of batch and semibatch stirred tank reactors are considered in the paper by Milewska and Molga,[23] where an integrated approach to process safety is presented and illustrated with experimental and simulation results. In this study a particular attention has been devoted to the formulation of robust CFD reactor models, which can be used to perform numerical simulations of a dynamic reactor behavior at any circumstances, among others after failures of the reactor cooling and/or stirring systems.

Also the paper by Srinivasan and Natarajan[24] should be mentioned, in which a review of the progress and developments in inherent safety analysis is reported. Although mainly statistical information is specified in this review, it contains a valuable summarization of 187 papers that have appeared during the considered period in the literature of the subject.

3. SAFETY BOUNDARY DIAGRAMS

In this work the safety boundary diagrams have been developed here for a semibatch stirred tank reactor equipped with the cooling jacket, where a single second order, strongly exothermic liquid phase homogeneous reaction is carried out. This reaction is described with the following stoichiometric equation:

$$\nu_A A + B \rightarrow \nu_C C + \nu_D D \tag{1}$$

where this equation is transformed in such a way that stoichiometric coefficient $\nu_B = 1$.

The reactant B is initially placed into the reactor vessel; then the reactant A is dosed with the chosen and constant addition rate. We only consider the process most often met in industrial practice when the stoichiometric amount of the dosed reactant A is added. In that case there is no need to separate the overdose of any reactant, so also additional separation costs are avoided. A perfect mixing of the reactor content is assumed, so no temperature and concentration gradients are detected inside the reacting mixture. Also the following assumptions and simplifications are additionally held: (1) no heat and volume change effects due to mixing of the reactants A and B are noticed; (2) unlimited mutual solubility of reactants A and B as well as the reaction products can be assumed; (3) physicochemical parameters of the reacting mixture do not depend on its temperature and composition; (4) the overall heat transfer coefficient in the system, the reactor content-cooling liquid, is constant; (5) heat capacity of the reacting mixture can be determined additively; and (6) during the reactor performance the temperature of the cooling liquid circulating in the reactor jacket is constant (which is the case often met in industrial practice).

A schematic diagram of the considered reactor is shown in Figure 1, for which general mass balance equations read as follows:
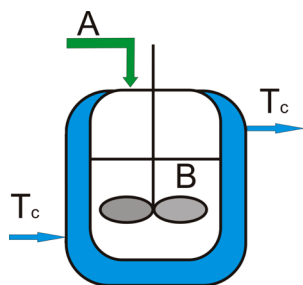
Figure 1. Schematic diagram of the semibatch stirred tank reactor.

for reactant A:

$$\frac{dn_A}{dt} = \Phi_{V,A} c_{A,dos} - |\nu_A| r V \tag{2}$$

for reactant B:

$$\frac{dn_B}{dt} = -rV \tag{3}$$

where, of course, after finishing of the dosing period—i.e., for $t > t_{dos}$, the addition rate of reactant A becomes equal to zero: $\Phi_{V,A} = 0$.

The instantaneous volume of the reacting mixture V, as it appears in eqs 2 and 3, can be estimated with the following relationships:

for the dosing period $(0 < t < t_{dos})$:

$$V = V_{B,o} + \Phi_{V,A} t \tag{4}$$

for $t > t_{dos}$:

$$V = V_{B,o} + \Phi_{V,A} t_{dos} \tag{5}$$

The mass balance equations (eqs 2 and 3) are accompanied by the energy balance, which for the considered case reads as follows:

$$(\rho V C_p)_{rm} \frac{dT}{dt} = (-\Delta H_R) r V - (\rho \Phi_{V,A} C_p)_{dos} (T - T_{dos})$$
$$- (UA)(T - T_c)$$
$$= \dot{Q}_{gen} - \dot{Q}_{rem} \tag{6}$$

where two terms can be distinguished: the heat generation rate due to the reaction course, expressed as $\dot{Q}_{gen} = (-\Delta H_R) r V$, and the heat removal rate due to reactor cooling as well as heating the stream of dosed reactant A from the temperature T_{dos} to T, which reads as $\dot{Q}_{rem} = (\rho \Phi_{V,A} C_p)_{dos} (T - T_{dos}) + (UA)(T - T_c)$. Also in eq 6, for $t > t_{dos}$ the addition rate of reactant A becomes equal to zero: $\Phi_{V,A} = 0$.

Notice that, during the addition period, the active heat exchange surface area, A, appearing in eq 6 is changed. In a general case, due to a dependence of the mixing conditions on the reacting mixture volume, V, also the overall heat transfer coefficient, U, is changed during the addition period. However, for the reactor equipped with a cooling jacket the following relationship can be used to estimate the instantaneous values of the product (UA):

$$(UA) = (UA)_o \frac{V}{V_{B,o}} = (UA)_o \left(1 + \frac{\Phi_{V,A} t}{V_{B,o}}\right) \tag{7}$$

in which we roughly assume that this product varies proportionally to the dosing time.

The expression of eq 7 is a simplified one, because it does not take into account an influence of changes in the physicochemical properties of the reacting mixture on U. In a general case these properties can change due to the reaction progress as well as the increase of the reactor temperature. However, for most homogeneous reacting systems such an influence of composition and temperature on the values of the product (UA) is much weaker in comparison to the influence of changes of the heat transfer surface area—A. For the systems in which during the reaction progress a viscosity of the reacting mixture changes significantly (e.g., for polymerization reactions), eq 7 cannot be utilized.

For $t > t_{dos}$ the product (UA) is constant and equal to

$$(UA) = (UA)_o \left(1 + \frac{\Phi_{V,A} t_{dos}}{V_{B,o}}\right) = (UA)_o (1 + \varepsilon) \tag{8}$$

where ε is the relative increase of the reacting mixture volume due to dosing.

For the considered second order homogeneous reaction, the reaction rate, r, can be determined from the following relationship:

$$r = k_o \exp\left(\frac{-E}{RT}\right) \frac{n_A}{V} \frac{n_B}{V} \tag{9}$$

The system of balance equations (eqs 2–9), as they are formulated above, can be solved numerically, giving information on a dynamic behavior of the reactor at any operating condition—i.e., supplying the appropriate temperature and concentrations time profiles. Characteristic influence of the cooling temperature, T_c, on the reactor temperature is shown in Figure 2, where evolutions of the reactor temperature, T, vs the
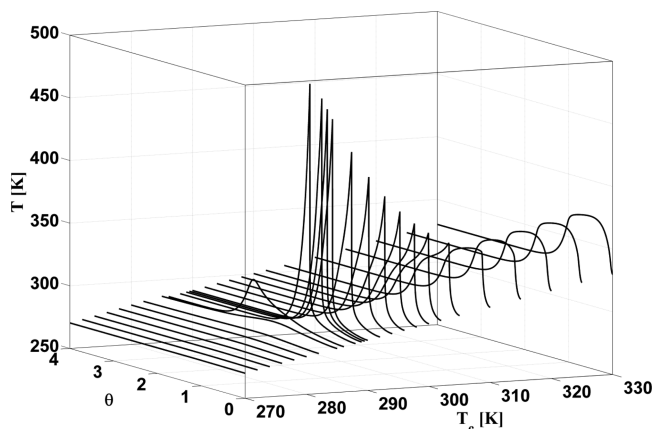

Figure 2. Typical reactor temperature trajectories, T, vs dimensionless time, θ, for various cooling liquid temperatures, T_c. Exothermic reaction carried out following semibatch operating mode: $Wt = 20$, $Da = 1$, $\varepsilon = 0.3$, $T_R = 300$ K, $\Delta\gamma_{ad,o} = 1$, $\gamma = 40$, $R_H = 1$.

dimensionless time, θ, are shown, each obtained at different T_c. Notice that an increase of the cooling temperature results first in a sharp increase of the reactor temperature, while farther increase of T_c gives more smooth profiles of the reactor temperature with lower values of the maximal one.

In the ideal situation in a SBR, when the reaction rate is equal to the addition rate, the dosed reactant reacts away immediately. In that case the reactor temperature follows a trajectory called

the target temperature, which can be estimated according to the following relationship (see also the Appendix, where this relationship is derived):

$$T_{ta} = T_c + \frac{1.05\Delta T_{ad,o}}{\varepsilon[Wt(1 + \varepsilon\theta) + R_H]} \tag{10}$$

It should be noticed that the recommended operation of the reactor along the target temperature line is safe only in a case when the reactor cooling system capacity is large enough to absorb the heat generated due to reaction progress at the chosen operating conditions. It should be always checked by comparing the maximal reactor cooling capacity and the heat generation rate and then adjusted by choosing the appropriate dosing time—see Appendix.

The target temperature defined as in eq 10 can be expressed in terms of the dimensionless numbers defined with use of the following process parameters: Wt, ε, R_H, $\Delta T_{ad,o}$—see Notation. After a dosing completion (for all $\theta > 1$) the target temperature, T_{ta}, can be determined with eq 10 as exactly at the end of dosing—i.e., at $\theta = 1$.

The concept of the target temperature has been proposed by Steinbach[40] and developed by Westerterp et al.[1,4,5,25] We call this temperature the target temperature because an operator should try to work near that temperature, as at such conditions the reaction rates are high and at the same time there is no accumulation of the nonconverted dosed reactant, so the reactor is operated safely. Thermal runaway now is defined as the situation where the T_{ta} line is surpassed.

The Westerterp number, Wt, appearing in eq 10 and called previously also the cooling number—see Pohorecki and Molga[26]—is defined as

$$Wt = \frac{(UA)_o t_{dos}}{\varepsilon(\rho C_p V)_o} = \frac{(UA)_o}{(\rho C_p)_o \Phi_{V,A}} \tag{11}$$

So, Wt characterizes the cooling ability, $(UA)_o$, related to the heat capacity of the reactor content, $(\rho C_p V)_o$, both taken at the process beginning. This parameter takes into account also the dosing time, so the rate of heat evolution due to the reaction progress.

Notice that during the dosing period the heat exchange surface area gradually increases so also gradually the value of T_{ta} decreases, while at the end of the dosing it remains constant—see Figures 3, 5, and 7.

Referring the reactor temperature profiles to T_{ta}, three very characteristic types of reactor behavior can be distinguished: (1)
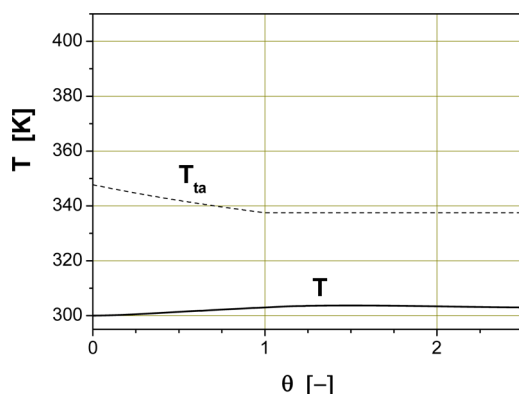

Figure 4. MI case: dimensionless numbers of moles, N_i, vs θ.
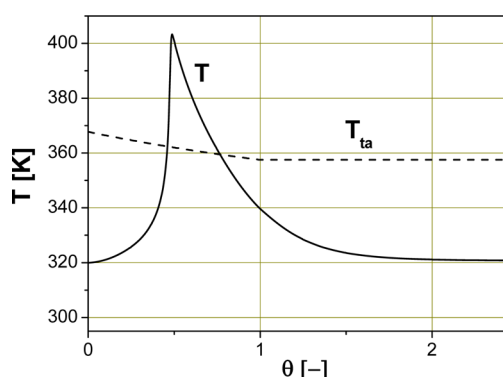
Figure 5. Thermal runaway case (TR): T and T_{ta} vs θ.
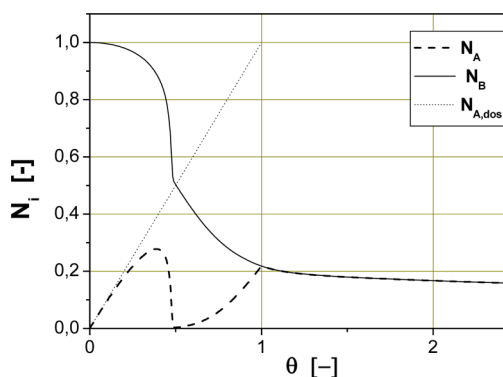
Figure 6. TR case: N_i vs θ.

Figure 7. QFS: T and T_{ta} vs θ.

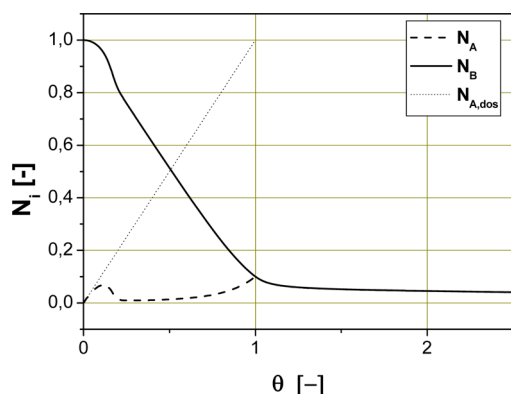**Figure 3.** Marginal ignition case (MI): T and T_{ta} vs θ.
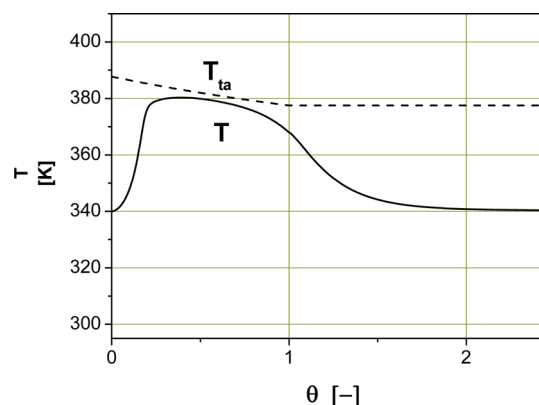
Figure 8. QFS: N_i vs θ.

the marginal ignition (MI), where the reactor temperature is always much lower than T_{ta} (see Figure 3), (2) the thermal runaway (TR), where the reactor temperature surpasses the target temperature line and approaches values much higher than T_{ta} (see Figure 5), and (3) the QFS case , where the reactor temperature trajectory is very close to the target temperature profile (see Figure 7).

Profiles of reactant concentrations, each corresponding to the case as was previously discussed, are displayed in Figures 4, 6, and 8, respectively. It is worth distinguishing that dynamic behaviors of the reactor presented in Figures 3–8 have been obtained for the same reacting system and at the same operating conditions, except of the cooling temperature which varies from $T_c = 300$ K (MI case) through $T_c = 320$ K (TR case) to $T_c = 340$ K (QFS case).

As it is visible in the presented diagrams, within the dosing period (for $0 < \theta < 1$) T_{ta} decreases due to an increase of the reactor cooling capacity.

The MI case seems to be thermally safe, but due to a relatively low reactor temperature during the reaction progress it is usually not acceptable economically. Additionally, due to a huge accumulation of the nonconverted reactants, see Figure 4, this process can be potentially dangerous because in a case of unexpected local temperature increase—e.g., caused by a failure of the stirring or/and cooling system—the reactor performance becomes similar to batch operating mode, so thermal runaway can be easily provoked.

In the QFS case, due to a relatively high reactor temperature at the process beginning, the reaction rate is also high, so reactant A is consumed practically immediately after its addition into the reactor.

For each considered case, i.e., for the chosen reacting system and reactor configuration, if all assumptions and simplifications previously listed are held, the reactor performance can be unambiguously defined with only two operating parameters: t_{dos} and T_c. So, an influence of those two parameters on a safe performance of the reactor should be determined.

The safety criterion based on boundary diagrams is related to the concept of the target temperature. As it is visible in Figure 7, the QFS case is a safe and simultaneously efficient way of process performance. For this case, during a main period of the process performance the reactor temperature trajectory follows the target temperature. Therefore, at any time moment, a difference between the actual reactor temperature $T(t)$ and the actual target temperature $T_{ta}(t)$ is a measure of the distance between the reactor state and the safe operating conditions. This distance can be quantified by defining a specific

mathematical function—F. To search border lines between the MI case and the TR case as well as between the thermal runaway case and the QFS one, it is enough to find the roots (values of the appropriate T_c) of the following equation:

$$F = \max\big[T(t) - T_{ta}(t)\big] = 0 \tag{12}$$

For any known reacting system and the defined reactor configuration, at the chosen operating conditions t_{dos} and T_c, the reactor temperature trajectory $T(t)$ can be found with a solution of the preceding reactor model (eqs 2–9), while the target temperature, with eq 10, respectively. So, further, the appropriate value of the function F can be easily determined.

Observing a dependence of the F values vs the T_c plotted in Figure 9, one can notice that this function has two roots:
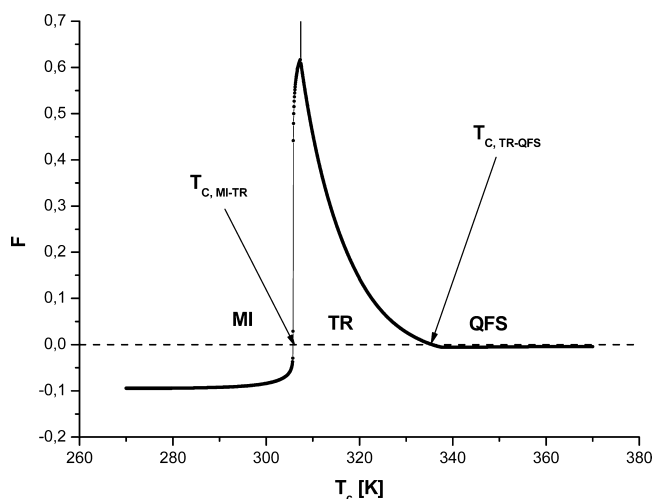

Figure 9. Construction of the boundary diagram: values of F (eq 12) vs T_c. Plot obtained for the following: $Da = 0.1$, $R_H = 1$, $T_R = 300$ K, $Wt = 100$, $\varepsilon = 0.1$, $\Delta\gamma_{ad,o} = 1$, $\gamma = 40$, and $T_{dos} = T_c$.

$T_{c,MI-TR}$ and $T_{c,TR-QFS}$, respectively—these two specific root values of the cooling liquid temperature determine the boundary between the MI–TR and TR–QFS regions, respectively. It should be noticed that the plot presented in Figure 9 has been obtained for the chosen value of the second operating parameter—t_{dos}, which is incorporated into Wt. Repeating the presented calculation procedure for the reactions of different exothermicity—i.e., for different values of the reaction enthalpy, ΔH_R (so also for the appropriate values of the dimensionless adiabatic temperature rise, $\Delta\gamma_{ad,o}$)—the specific boundary diagram can be obtained as it is shown in Figure 10. As can be seen in Figure 10, the root temperatures $T_{c,MI-TR}$ and $T_{c,TR-QFS}$, plotted as a function of the appropriate $\Delta\gamma_{ad,o}$, clearly distinguish the MI, TR, and QFS operating regions.

Steensma and Westerterp[4] have proposed two dimensionless numbers to characterize the system properties and to generalize a concept of the safety boundary diagrams. These numbers have been defined as follows:

exothermicity number, Ex:

$$Ex = \frac{\Delta T_{ad,o}(E/R)}{T_c^2\varepsilon(R_H + Wt)} = \frac{\Delta\gamma_{ad,o}\gamma}{\beta_c^2\varepsilon(R_H + Wt)} \tag{13}$$
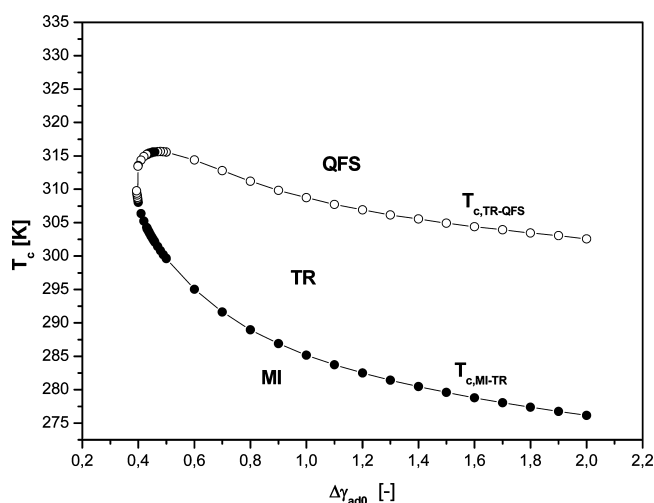
Figure 10. Construction of the boundary diagram: values of $T_{c,MI-TR}$ and $T_{c,TR-QFS}$ as a function of $\Delta\gamma_{ad,o}$. Plot obtained for the following: $Da = 2$, $R_H = 1$, $T_R = 300$ K, $Wt = 10$, $\varepsilon = 0.4$, $\Delta\gamma_{ad,o} = 1$, $\gamma = 40$, and $T_{dos} = T_c$.

reactivity number, Ry:

$$Ry = \frac{k(T_c)c_{B,o}t_{dos}}{\varepsilon(R_H + Wt)}$$

$$= \frac{k(T_R)c_{B,o}t_{dos}\exp\left(\gamma\left(1 - \frac{1}{\beta_c}\right)\right)}{\varepsilon(R_H + Wt)}$$

$$= \frac{Da(T_R)\exp\left(\gamma\left(1 - \frac{1}{\beta_c}\right)\right)}{\varepsilon(R_H + Wt)} \tag{14}$$

The exothermicity number gives the ratio of the maximal power generated due to the reaction progress to the reactor cooling abilities, while the reactivity number refers to the ratio of the reaction rate to the cooling rate. Both are very useful to generalize safety assessments based on the boundary diagrams approach—for account of which, see Westerterp et al.[1,4,25]

With these numbers, each boundary plot as it is shown in Figure 10 can be transformed into the system of coordinates: Ry vs Ex, giving the generalized safety diagram (see Figure 11). The boundary lines, obtained at the fixed values of Wt and R_H parameters, separates safe and unsafe regions and so determines the inherently safe operating conditions for which thermal runaway cannot occur.

A location of the boundary line on the diagram depends on the system properties—i.e., mainly on values of Wt and R_H, respectively. Influence of these parameters on the position of boundary lines, so also on the inherently safe operating conditions, is shown in Figures 12 and 13, respectively. Notice that for each boundary line (i.e., for each pair of values Wt and R_H) the specific limiting values of the exothermicity and reactivity numbers determine unambiguously the inherently safe operating region (see Figure 11), where these specific values of Ex_{max} and Ry_{min} are determined and the inherently safe region can be easily found for values of $Ex < Ex_{max}$ and/or for $Ry > Ry_{min}$, respectively. So with a plot of the dependence of these limiting values of Ex_{max} and Ry_{min} as a function of the characteristic parameters Wt and R_H, the very useful operation
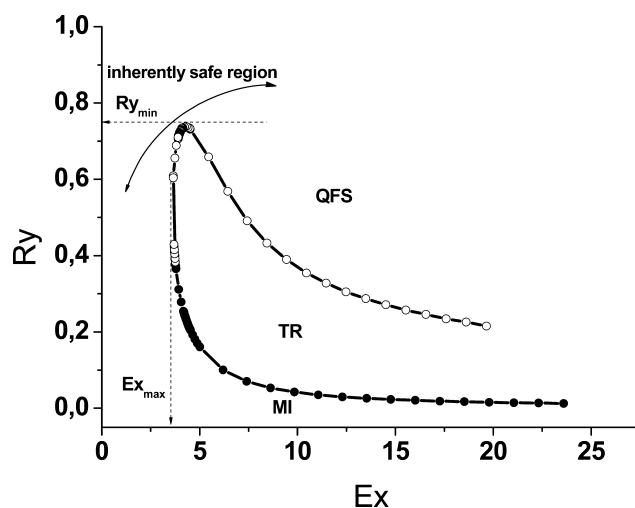

Figure 11. Safety boundary diagram: determination of the inherently safe region. Boundary line determined for $Wt = 10$ and $R_H = 1$.
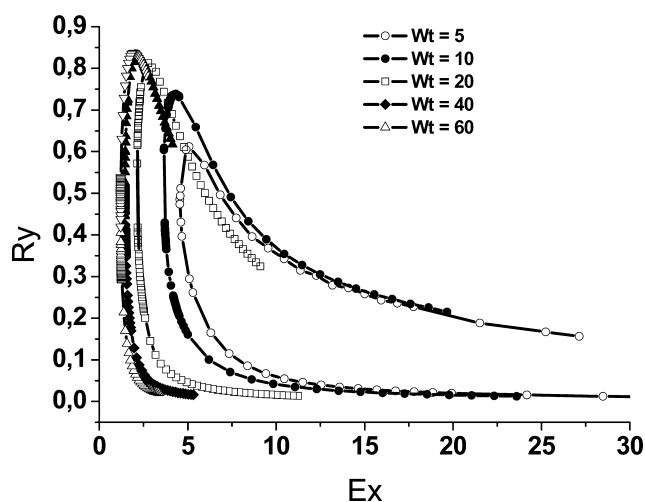

Figure 12. Safety boundary diagrams for different values of the Wt and at fixed value of $R_H = 1$.
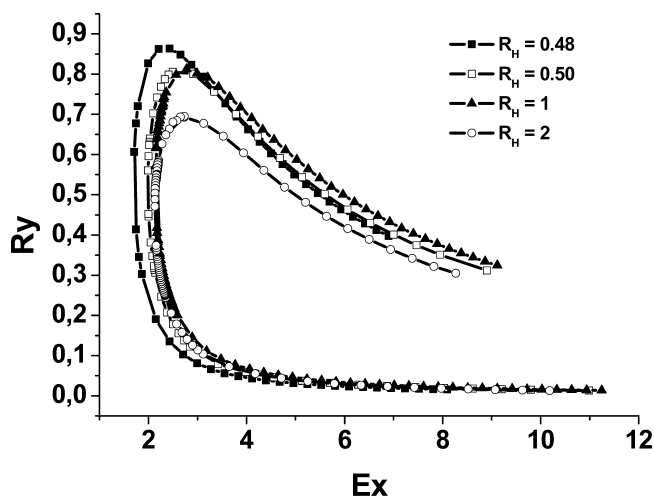

Figure 13. Safety boundary diagrams for different values of R_H and at fixed value of $Wt = 20$.

diagrams can be obtained to determine the inherently safe operation conditions (see Figures 14 and 15).
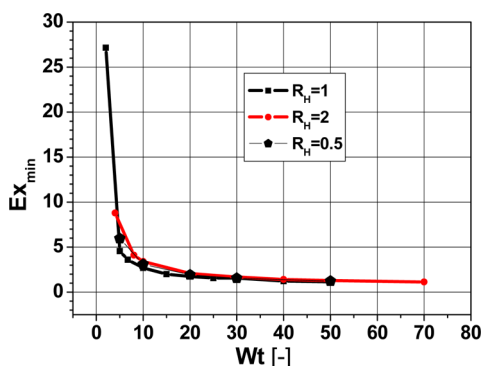
Figure 14. Limiting values of the Ex_{max} determined for different values of Wt and R_H.
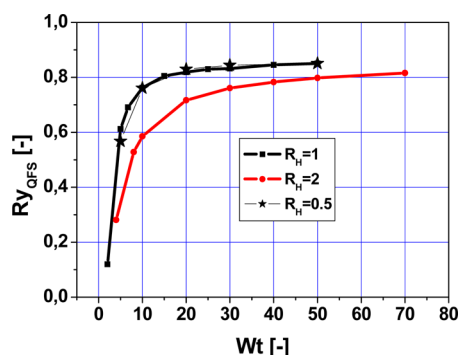

Figure 15. Limiting values of the Ry_{min} determined for different values of Wt and R_H.

4. BOUNDARY DIAGRAM SAFETY CRITERION (BDSC)

4.1. Practical Application of BDSC. For any reacting system the inherently safe operating conditions can be determined with Figures 14 and 15. The preceding method, based on the safety boundary diagrams, can be employed even in a case where no systematic kinetic information is available—see Molga et al.[27] The required kinetic investigations can be restricted to isothermal measurements of the reaction rate at only two temperatures, including the chosen reference temperature, T_R. Further, the activation energy, E, should be estimated. It should be pointed out that the range of temperatures, where these kinetic measurements are carried out, should at least cover the usual reactor running temperatures. Such measurements can be easily carried out in a laboratory reaction calorimeter, and no systematic studies of the reaction mechanism are required. For some reacting systems also a differential scanning calorimeter (DSC) can be utilized for this purpose.

Except for the reaction rate constant at the reference temperature, $k(T_R)$, and E, the following values characterizing the reactor as well as the reacting system should be also known: $(UA)_o$, ε, $(\rho C_P)_o$, $\Delta T_{ad,o}$, R_H, V_o, and $c_{B,o}$. Notice that the products $(UA)_o$ and $(\rho C_P)_o$ can be easily estimated from a cooling curve for an originally loaded batch, while $\Delta T_{ad,o}$ is determined with the measured or calculated reaction enthalpy. A practical procedure to determine inherently safe operating conditions is summarized in Figures 16 and 17, where two characteristic calculation paths are presented.

Following path I, first the Ex_{max} criterion should be checked (see Figure.16). So, for the appropriate values characterizing the system (see Figure 16) and for the chosen t_{dos}, T_c is assumed, then Wt calculated, and further the actual value of Ex evaluated.
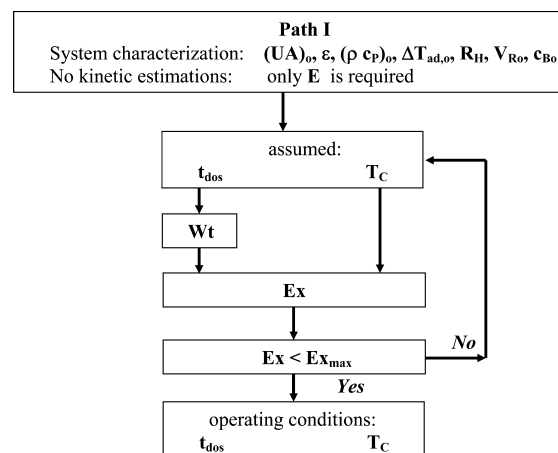

Figure 16. Determination of the inherently safe operating conditions: path I, based on Ex criterion.
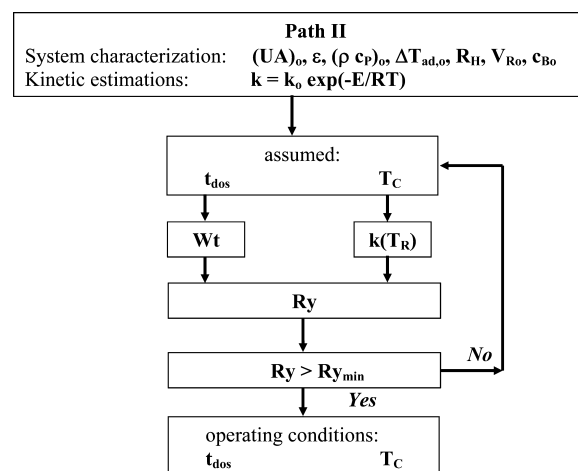

Figure 17. Determination of the inherently safe operating conditions: path II, based on Ry criterion.

This value of Ex is compared to the value of Ex_{max}, which is estimated from Figure 14 for the just calculated value of the Westerterp number. Such searching is repeated until the appropriate set of operating conditions (t_{dos} and T_c) is found, which fulfills this criterion. At these conditions a productivity of the reactor should be always checked.

If due to a high exothermicity of the reaction, the criterion of Ex_{max} cannot be fulfilled or when the reactor productivity is not satisfied, the Ry_{min} criterion should be checked (path II; see Figure.17). In this case, $k(T_R)$ should be additionally estimated. Then the calculated value of Ry is compared to the limiting value of Ry_{min}. Also in this case a searching is repeated until the operating conditions satisfying this criterion are found.

Each time after determination of the inherently safe operating conditions (T_c and t_{dos}) the appropriate target temperature at the process beginning $T_{ta,max}$ should be estimated: this can be done with eq 10, just taking $\theta = 0$. Because at the chosen inherently safe operating conditions the maximal reactor temperature is always below $T_{ta,max}$, it is quite easy to check if the reactor temperature is never higher than the admissible temperature, T_{adm}, so the following relationship is fulfilled

$$T_{ta,max} < T_{adm} \tag{15}$$

This T_{adm} temperature can be the boiling temperature of the reaction mixture or the temperature at which thermal decomposition of the reacting species and/or side reactions can be initiated. In a case of boiling, an installation of condenser with full reflux solves the problem. Because the boiling is a strongly endothermic process, it significantly influences the heat balance over the reactor and makes the process safe. In a case when T_{adm} describes a triggering thermal decomposition or side reactions, a new set of the safe operating conditions should be determined for which $T_{ta,max}$ is smaller than before. Usually it is a searching for a new set of inherently safe operating parameters with a larger value of Wt—i.e., longer t_{dos}.

4.2. Comparison to Other Safety Criteria. Comparison of the elaborated BDSC to the other safety criteria is shown in Figure 18. Two criteria, the Morbidelli−Varma criterion
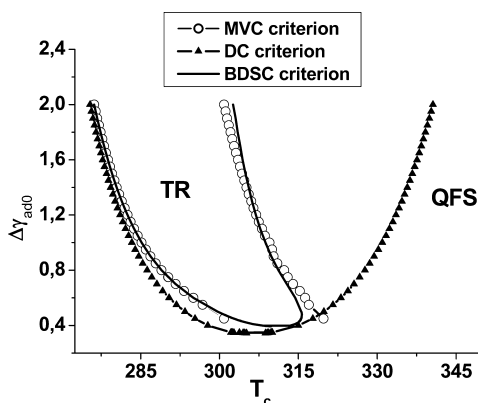

Figure 18. Comparison of the BDSC criterion to the MVC and DC ones (see section 4.2).

(MVC) (see Morbidelli and Varma[28] and Varma et al.[20]) and the divergence criterion (DC) (see Strozzi et al.,[22] Zaldival et al.,[29] and Bosch et al.[30]), have been used for this purpose. As can be observed in Figure 18, the results predicted with the MVC criterion and with the BDSC one are very similar; however, we have to take into account that a tremendous amount of work has to be done to execute numerical simulations required for the MVC criterion. From this point of view an application of the MVC is very limited, and for sure this criterion cannot be used in everyday industrial practice.

Comparison of the DC criterion and the BDSC shows that the DC one indicates a higher T_c to operate within the inherently safe region QFS. The DC method is based on the searching for conditions for which the divergence is equal to zero. Therefore this method demands more drastic values of the cooling temperature, which usually is far away from the real situations.

Taking the preceding discussion into account, one can conclude that the elaborated BDSC is an efficient and robust tool for prediction of safe operating conditions without reactor modeling and with limited information on the reaction kinetics.

4.3. Specific Properties of BDSC. Notice, that due to possible physicochemical properties of reactants A and B, the range $R_H = 0.5$−2.0 covers practically all possible cases, while the values of Wt, which depend on the dosing time as well as some reactant properties and also on equipment character-ization—i.e., the reactor cooling capacity, can be varied in a quite wide range. E.g. see estimations given in the paper by Westerterp and Molga,[25] where Wt values for the industrial jacketed and well-agitated reactor vessels with $H = 2D$ and

addition time equal to 1 h have been roughly estimated. In such a case, depending on the reactor volume, these Wt values are in the range 1.5−6 for the aqueous phase present in the reactor at the process beginning and the range 3.5−10.8 for the organic one, both limiting values calculated for the reactor volume equal to 100 and 1 m^3, respectively. Van Woezik and Westeretrp[31] show some estimations for a small industrial reactor of nominal volume equal to 3 m^3 employed to the nitric acid oxidation of 2-octanol, which reaction is characterized with high exothermicity. In such a case a rather low dosing rate should be applied, which results in the Westerterp numbers within a range of 10−40. For the laboratory reactors, for which the ratio of the heat exchange surface area to the reactor volume is much higher, the values of Wt number can be as high as 100 or even more.

In definitions of the Ex and Ry numbers the sum of R_H +Wt always appears. To investigate specific properties of the BDSC criterion, additional series of calculations have been carried out, in which, for values of the sum $Wt + R_H$ = constant, an influence of the mutual distribution of Wt and R_H values on the location of boundary lines has been investigated. Typical results obtained are summarized in Figures 19 and 20, respectively. It has been
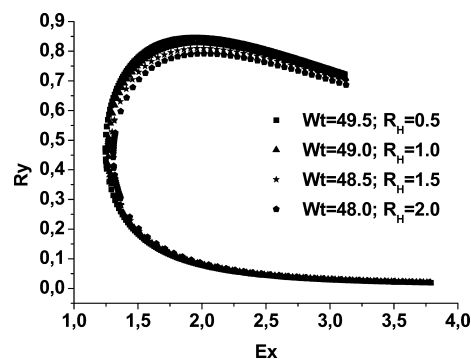
Figure 19. Influence of a mutual distribution of the R_H and Wt values on a localization of boundary lines: $Wt + R_H = 50$.
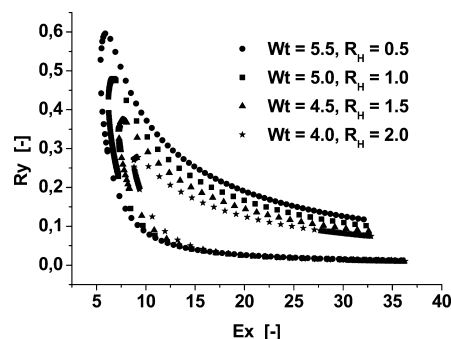
Figure 20. Influence of a mutual distribution of the R_H and Wt values on a localization of boundary lines: $Wt + R_H = 6$.

found that for values of the sum $Wt + R_H$ that are relatively large in comparison to the actual R_H value, an influence of the distribution of mutual values of Wt and R_H on a location of boundary lines can be practically negligible (see Figure 19), while, with a decrease in the value of the sum $Wt + R_H$, an influence of this distribution becomes more pronounced (see Figure 20), where significant differences between upper boundary lines are visible. This is probably caused by the fact that although the sum of $(Wt + R_H)$ is expressed directly in the numerators of the definition equations for the Ex and Ry

numbers (eqs 13 and 14), in a definition of T_{ta} (eq 10) a more complex expression being a kind of weighted sum of Wt and R_H values is used.

For relatively small values of Wt, the considered BDSC criterion should be used with a special caution. This is particularly the case for industrial reactors, which—as has been mention previously—are characterized with rather small Wt numbers. Notice that for each considered reacting system a decrease of the Westerterp number causes a strong increase of the target temperature (see eq 10), where for $Wt \rightarrow 0$ the reactor performance tends to the adiabatic operating mode. Boundary diagrams for small Wt numbers are plotted in Figure 21, where a strong influence of the Wt values on a location of
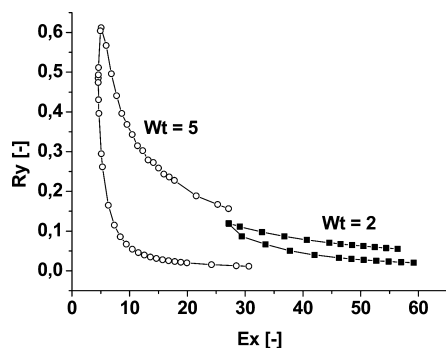

Figure 21. Boundary diagrams for small values of Wt. Plots obtained for $R_H = 1$.

the boundary line is visible. In consequence, in the range of $Wt < 20$, a strong increase of the Ex_{max} and also an expressive decrease of the Ry_{min} values are noticed, when Wt decreases (see also Figures 14 and 15). However, values of the Westerterp number can be easily increased just by increasing t_{dos}.

The presented BDSC criterion can be directly used to predict safe operation conditions also in batch industrial reactors just by taking a very short t_{dos}. It has been also proved—see Westerterp and Molga[1,25]—that the proposed BDSC method can be conservatively applied for reactions of an order different from two. The presented boundary diagrams have been developed for single second order reactions; however, the elaborated criterion is conservative for parallel reactions, while for the consecutive ones a specific analysis is always required (Westerterp and Molga[25]).

5. EXPERIMENTAL VERIFICATION OF THE BDSC

A series of experimental investigations has been carried out to check the accuracy and robustness of the previously proposed

BDSC. The hydrolysis reaction of acetic anhydride (AAh) has been used for this purpose. All experiments have been performed in a RC1Mettler-Toledo reaction calorimeter of a nominal volume of 2 dm³.

Operating conditions for experiments carried out with the testing hydrolysis reaction are shown in Table 1. All listed experiments have been carried out following a semibatch operating mode at isoperibolic conditions—i.e., at a constant temperature of the cooling liquid circulating in a reactor jacket, T_c. For each run, the acetic anhydride with the appropriate addition of the acetic acid has been initially placed in the reactor vessel, while the second reactant (water) was added into the reactor with a constant dosing rate. The acetic acid has been added to increase the solubility of the anhydride in the aqueous phase and keep the reacting mixture always homogeneous. T_c, t_{dos}, and the stirrer speed, R (so also the overall heat transfer coefficient), have been changed from run to run.

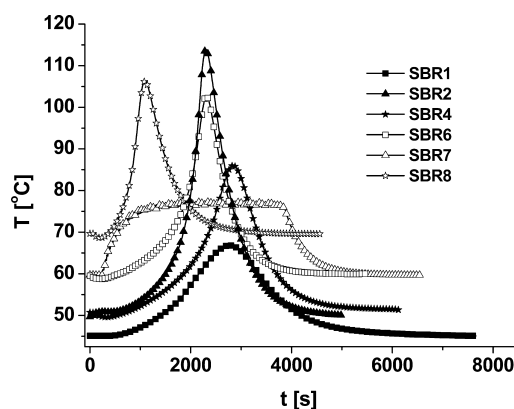The obtained results of experimental runs are shown in Figure 22.

Figure 22. Results of experimental runs carried out in the RC1 reaction calorimeter. Reactor temperature vs time plots obtained for experiments listed in Table 1.

Applying the elaborated safety criterion (BDSC) to all performed experiments and comparing the obtained safety predictions to the results of experiments, we can conclude that this criterion is able to distinguish clearly between safe and not-safe reactor performance and predicts very well the inherently safe operating conditions.

Results of calculations required to use the BDSC criterion are collected in Table 2. Values of the Westerterp number have been calculated with eq 11, taking values of the product $(UA)_o$ estimated directly from the calibration procedure provided for

Table 1. Hydrolysis of Acetic Anhydride: Experiments Carried Out in a RC1Mettler Toledo Reaction Calorimeter To Verify the BDSC Criterion[a]

run	T_c, °C	$n_{AAh,o}$, mol	$n_{AAc,o}$, mol	n_W, mol	t_{dos}, s	R, rpm	$(UA)_o$, W/K	ε	R_H	$\Delta T_{ad,o}$, K
SBR1	44	10.24	4.33	10.22	3486	600	8.69	0.149	1.99	155.6
SBR2	50	10.75	4.86	11.02	1918	300	7.34	0.150	1.97	207.9
SBR3	50	7.80	3.60	7.98	3670	300	5.74	0.149	1.97	175.0
SBR4	51	6.91	3.08	7.09	2456	300	5.71	0.151	1.97	180.8
SBR5	51	7.21	3.25	7.10	6484	300	5.73	0.144	1.97	161.8
SBR6	60	7.80	1.74	5.05	3510 (2270[b])	400	5.78	0.163	1.95	235.1
SBR7	60	7.05	2.34	7.03	3818	400	5.72	0.153	1.95	233.4
SBR8	70	9.99	4.93	4.36	2083 (910[b])	300	7.47	0.062	1.91	204.3

[a]AAh, acetic anhydride; AAc, acetic acid; W, water. [b]Time after which the experiment has been stopped.

Table 2. Hydrolysis of Acetic Anhydride: Values of *Wt, Ex,* and *Ry* Numbers Estimated for the Experiments Carried Out in a RC1 Reaction Calorimeter

run	T_o, °C	t_{dos}, s	Wt	$Da(T_R)$	Ex	γ	Ry
SBR1	44	3486	78.6	0.1144	1.44	37.627	0.073
SBR2	50	1918	33.5	0.0081	4.98	44.451	0.037
SBR3	50	3670	69.2	0.0615	2.03	43.075	0.127
SBR4	51	2456	51.8	0.0269	2.77	43.506	0.085
SBR5	51	6484	137.4	0.1401	0.99	42.826	0.170
SBR6	60	2270	104.4	0.0380	1.58	43.184	0.161
SBR7	60	3818	80.5	1.9592	1.73	34.706	4.889
SBR8	70	910	90.2	0.0239	1.70	42.588	0.388

the RC1Mettler Toledo reaction calorimeter.[32] The reaction kinetic data (E and k_o), required to estimate Ex and Ry, are collected in Table 3a,b and discussed as follows.

Table 3. Kinetic Data for the Acetic Anhydride Hydrolysis Reaction

(a) Pseudo-First-Order Reaction: Significant Excess of Water (Anhydride Dosed into the Water)			
ref	range of T, °C	E, kJ/mol	$\ln(k_o)$ (with k_o, 1/s)
Gold[34]	5−25	45.784	12.54
Zogg et al.[35]	25−55	55.77	16.61
Haji and Erkey[36]	15−35	54.42	15.86
Kralj[37]	20−26	50.15	14.22
Lewak[33]	20−80	38.5	9.26

(b) Second-Order Reaction: Significant Excess of the Anhydride (Water Dosed into the Anhydride)			
ref	range of T, °C	E, kJ/mol	$\ln(k_o)$ (with k_o, dm³/(mol s))
Hiriota et al.[38]	25−85	66.30	15.15
Bell et al.[39]	73−112	102.61	28.0
Lewak[33]	30−118	93−110	25.2−30.0

Despite the fact that the stoichiometric equation of this testing reaction is rather simple, its kinetic mechanism is quite complex and uncertain.[33] So, also a significant discrepancy of the measured kinetic data can be noticed in the literature on the subject (see Table 3). The kinetic expressions for this reaction depend on the way of the process performance.

(1) For a significant excess of water (for the semibatch process it corresponds to the situation in which the anhydride is dosed into the water), the reaction kinetics can be described with the expression for the pseudo-first-order reaction:

$$r = k_1 c_{AAh} \tag{16}$$

(2) For a significant excess of the anhydride (when water is added into the anhydride), reaction kinetics is given as that for a second order reaction:

$$r = k_2 c_{AAh} c_W \tag{17}$$

where both reaction rate constants k_1 and k_2 can be expressed with the Arrhenius equation as

$$k_i = k_{o,i} \exp\left(\frac{-E_i}{RT}\right)$$

For the process carried out as in our experimental investigations—i.e., when, at the process beginning the reactor contains the acetic anhydride with the appropriate addition of the acetic acid, next an equivalent molar amount of water is

slowly added into the reactor—the values of the activation energy should be taken as that for the second order reaction—e.g., E = 95.56 kJ/mol and $\ln(k_o)$ = 25.2 (data taken from our own experiments (see the last row in Table 3b)).

Using these kinetic data, values of Ex and Ry numbers have been calculated according to eqs 13 and 14 and collected in Table 2. Then for each experimental run the appropriate values of Ex and Ry, both vs Wt, have been plotted in Figures 23 and
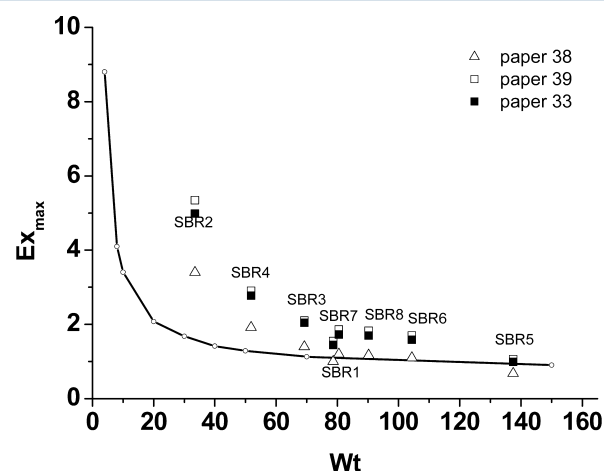
Figure 23. Safety predictions obtained with the BDSC criterion for different literature values of E (see Table 3b). Values of Ex estimated for each experimental run as compared to the BDSC boundary line: Ex_{max} vs Wt.
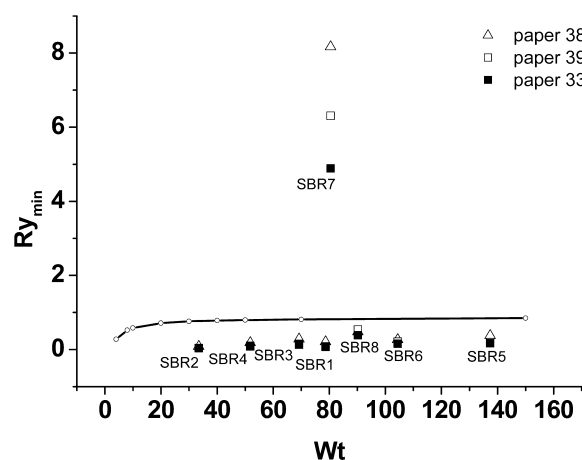
Figure 24. Safety predictions obtained with the BDSC criterion for different literature kinetic data (see Table 3b). Values of Ry estimated for each experimental run as compared to the BDSC boundary line: Ry_{min} vs Wt.

24, respectively. The obtained characteristic experimental points are related to the boundary lines taken for the considered process (for R_H = 2) from Figures 14 and 15, respectively. A location of each experimental point in relation to those boundary lines predicts that all experiments (except of run SBR7) have been carried out at runaway conditions—because in Figure 23 all experimental points are above the operating line and simultaneously in Figure 24 all experimental points (except of run SBR7) are below the appropriate operating line. For run SBR7 the considered BDSC predicts an inherently safe

operation within a QFS region. These safety predictions are in very good agreement with experimental observation (see in Figures 25 and 26). In Figure 25 a difference ($T_{max} - T_{ta,max}$)
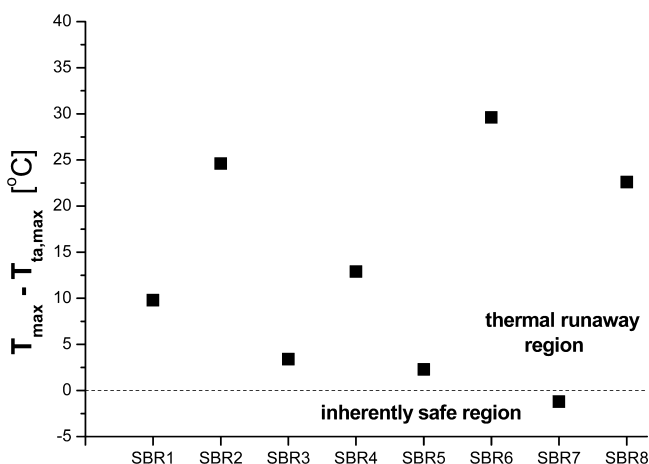

Figure 25. Difference between the maximal temperature measured during each experimental run and the appropriate maximal value of the target temperature (calculated from eq 10 for $\theta = 0$).
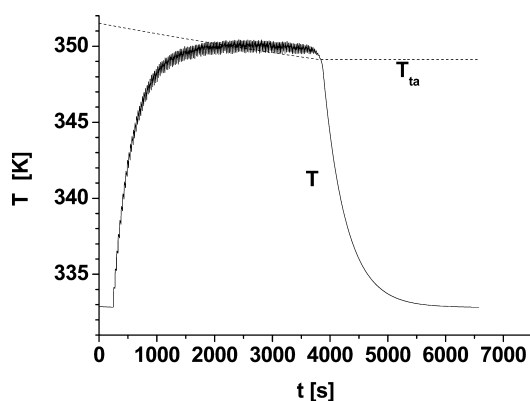

Figure 26. Run SBR7 carried out at inherently safe operating conditions. Comparison of the experimentally measured T to the estimated T_{ta} (eq 10).

between the maximal temperature measured during each experimental run and the appropriate maximal value of the target temperature (as it is calculated from eq 10 for $\theta = 0$) is plotted. Only for run SBR7 is this difference negative, which indicates that the process is inherently safe. In Figure 26 the experimental reactor temperature profile obtained for run SBR7 is compared to the target temperature profile—it confirms that a dynamic behavior of the reactor is typical for the QFS region. For the rest of the experiments the measured reactor temperature trajectory always surpassed the target temperature line (similarly as it is shown in Figure 5)—i.e., an observed dynamic behavior of the reactor is typical for a thermal runaway event.

Accuracy of safety predictions carried out with use of the BDSC criterion depends directly on the estimation accuracy of parameters appearing in the definition equations (see eqs 11, 13, and 14). At this point an accuracy of determination of the activation energy is crucial, as Ry depends exponentially on E. Therefore, for operating points laying on plots of Figures 14 and 15 very close to the boundary lines, safety predictions should be carried out particularly carefully. For the proposed

safety assessment procedure, a sensitivity of the proposed BDSC to the inaccuracy of the experimental kinetic data can be observed on Figures 23 and 24, where the location of points calculated with different values of the kinetic data collected in Table 3b are compared. As can be seen on these safety diagrams (Figures 23 and 24), the observed differences in the locations of the points are particularly distinctive for large values of Ry. Special attention should be also paid always when the operating points are located close to the appropriate borderline.

The considered hydrolysis reaction supplies a very useful example to illustrate how carefully should be used the reaction kinetic data taken from the literature to predict the inherently safe operating conditions with the BDSC criterion.

Let us explain this problem in details for experiment SBR2 (see Table 1). Because water was the reactant dosed into the reactor vessel, second order reaction kinetics is expected, so values $E = 95.56$ kJ/mol and $\ln(k_o) = 25.2$ have been taken for safety predictions (see Table 3b). With these kinetic data the values of $Ry = 0.037$ and $Ex = 4.98$ have been estimated (see Table 2, row SBR2). To check if the operating conditions chosen for the run SBR2 are inherently safe, the location of the operating points (Ex vs Wt) and (Ry vs Wt) on the diagrams of Figures 23 and 24, respectively, should be determined. As it is visible in these figures, for coordinates describing experiment SBR2—i.e., for ($Ex = 4.98$, $Wt = 33.5$) and ($Ry = 0.037$, $Wt = 33.5$)—the applied BDSC procedure indicates that experiment SBR2 will be carried out within thermal runaway region.

In a case in which for safety assessments carried out with BDSC somebody by mistake or oversight takes kinetic data determined for the pseudo-first-order reaction—i.e., the values of the activation energy $E = 38.5$ kJ/mol and $\ln(k_o) = 9.26$ (see last row in Table 3a)—the predictions indicate wrongly a safe QFS operating conditions. Therefore taking wrong kinetic data or changing wrongly the way of the process performance—i.e., switching by mistake from addition of anhydride into the water to a dosing of water into the anhydride—one can provoke thermal runaway.

6. SUMMARY

For the considered liquid phase homogeneous SBRs, the safety criterion based on a boundary diagram (BDSC) has been developed and discussed. This enables one to select safe or inherently safe operating conditions for any liquid homogeneous reaction even with limited information on the kinetics.

On the basis of the operating diagrams elaborated in this work (Figures 14 and 15), two practical paths to determine the inherently safe operating conditions have been proposed (see Figures 16 and 17). So for any reacting system, knowing parameters used for system characterization [$(UA)_o$, ε, $(\rho C_p)_o$, $\Delta T_{ad,o}$, R_H, $V_{R,o}$, and $c_{B,o}$] as well as fundamental kinetic information [E and k_o], the safe operating conditions—i.e., t_{dos} and T_c—can be easily determined. Notice that no systematic kinetic studies are required, since with use of path I only E and by following path II the simple kinetic estimation [$k = k_o \exp(-E/RT)$] are needed.

For practical use of the proposed method, first the reaction enthalpy, ΔH_R, should be determined. This can be easily done with use of the reaction calorimeter or the DSC. Each of these mentioned previously measuring devices can be also used to determine the reaction kinetic constants at two chosen temperatures to estimate E and $k(T_R)$. This is crucial for practical application of the proposed method, as in industrial

practice usually there is no time and there are no funds for detailed investigations of the reaction kinetics.

The presented method can be applied for single second order reactions; however it has been proved that it can be conservatively applied also for reactions of an order different from two. This method can be also conservatively applied for parallel reactions.

■ APPENDIX

We assume that at the process beginning the temperature of the original batch with a volume of $V_{B,o}$ is equal to the cooling temperature T_c. Additionally, the dosing stream (reactant A) temperature during the addition is also equal to T_c.

In the ideal situation in a SBR, to avoid accumulation of the nonreacted dosed reactant, the reaction rate should be equal to the dosing rate; this means that the dosed reactant reacts away immediately. Under such conditions the conversion rate during the dosing period is constant and equal to $n_{A,o}/t_{dos}$. If we neglect for a moment the derivative of T in eq 6, we can express the difference between the temperature of the reaction mixture—T—and the coolant temperature—T_c—at the start of the reaction as

$$T - T_c = \frac{\Delta T_{ad,o}}{\varepsilon(Wt + R_H)} \tag{A1}$$

while at the end of addition as

$$T - T_c = \frac{\Delta T_{ad,o}}{\varepsilon(Wt(1 + \varepsilon) + R_H)} \tag{A2}$$

See Notation for definitions of dimensionless parameters used in eq A1.

Notice that due to the gradual filling of the reactor with the dosed reactant, the total reacting volume will gradually increase and as a consequence the useful cooling area too. Taking this into account, a general expression for the difference $(T - T_c)$ as a function of the dimensionless time—θ—can be derived. Additionally, to compensate for neglecting the value of dT/dt in eq 6, we increase this $(T - T_c)$ value by 5%, so finally we obtain:

$$T_{ta} - T_c = \frac{1.05\Delta T_{ad,o}}{\varepsilon[Wt(1 + \varepsilon\theta) + R_H]} \tag{A3}$$

where the reactor temperature obtained at the assumed ideal conditions is called the target temperature, T_{ta}. The reactor operator should try to follow this temperature trajectory because it is safe and simultaneously efficient from a reactor productivity point of view.

The recommended operation of the reactor along the target temperature line is safe only in a case when the reactor cooling system capacity at these operating conditions is large enough to absorb the heat generated due to reaction progress.

Knowing the maximal cooling capacity of the reactor cooling system—i.e., the value of the heat flow $\dot{Q}_{max,cool}[W]$—it can be immediately checked to see if the chosen operating conditions are safe. The heat generation rate in the case when the reactor is operated along T_{ta} can be accurately estimated, as the conversion rate in this case is equal to the dosing rate. So, this heat generation rate can be calculated as follows:

$$\dot{Q}_{gen,ta} = (-\Delta H_R)rV = \frac{(-\Delta H_R)n_{A,o}}{t_{dos}}[W] \tag{A4}$$

Always when

$$\dot{Q}_{gen,ta} > \dot{Q}_{max,cool} \tag{A5}$$

the chosen operating conditions should be changed just by increasing the dosing time—see eq A4.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: e.molga@ichip.pw.edu.pl.

Notes
The authors declare no competing financial interest.
†During preparation of this work Professor K. Roel Westerterp (K.R.W.) passed away, on August 24, 2013. M.L. and E.J.M. express their deepest sorrow as well as state that they have been very honored because of the exceptional opportunity to colaborate with Professor K.R.W.

■ NOTATION

A_o	initial heat exchange surface area, m^2
$c_{A,dos}$	concentration of the reactant A in the dosing stream, $mol\ m^{-3}$
$c_{B,o}$	initial concentration of the reactant B in the reactor, $mol\ m^{-3}$
C_p	specific heat capacity, $J\ kg^{-1}\ K^{-1}$
$Da(T_R) = k(T_R)c_{B,o}t_{dos}$	Damköhler number at the reference temperature, T_R
E	activation energy, $J\ mol^{-1}$
Ex	exothermicity number (eq 13)
F	safety measure function (eq 12), K
k_o	frequency factor in the reaction rate equation
$k(T_R)$	kinetic rate constant at the reference temperature, T_R, $m^3\ mol^{-1}s^{-1}$
n_i	number of moles of the ith species, mol
$N_i = n_i/n_{i,o}$	dimensionless number of moles
$N_{A,dos} = \Phi_{V,A}t\rho_{M,A}/n_{A,o}$	dimensionless number of moles of the reactant A added into the reactor during an addition period, -
r	reaction rate, $mol\ m^{-3}\ s^{-1}$
U_o	overall heat transfer coefficient at the process beginning, $m^{-2}\ K^{-1}$
$R_H = (\rho C_p)_A/(\rho C_p)_B$	ratio of the heat capacities of the reactant A (added into the reactor) and the reactant B (initially present in the reactor)

Ry	reactivity number (eq 14)
t	time, s
T	temperature of the reaction mixture, K
T_c	cooling temperature, K
T_R	reference temperature, K
T_{ta}	target temperature, K
V	actual volume of the reactor content
$V_{R,o} = V_{Bo}$	volume of the reactor content at the process beginning, m^3
Wt	Westerterp number (eq 11)
$\beta_c = (T_c/T_R)$	dimensionless temperature
ΔH_R	enthalpy of the reaction, J mol^{-1}
$\Delta T_{ad,o} = (-\Delta H_R n_{B,o})/((\rho C_p)_o V_{R,o})$	adiabatic temperature rise at the initial conditions, K
$\varepsilon = (\Phi_A t_{dos})/V_{R,o}$	relative volume increase due to addition of the reactant A
$\gamma = E/RT_R$	dimensionless parameter from the Arrhenius equation
$\Delta\gamma_{ad,o} = \Delta T_{ad,o}/T_R$	dimensionless adiabatic temperature rise
$\theta = t/t_{dos}$	dimensionless time
ν_i	stoichiometric coefficient in the reaction equation
$\Phi_{V,A}$	volumetric dosing rate of the reactant A, m^3 s^{-1}

Subscriptsand Superscripts

A, B   reactants A and B
c   cooling
dos   dosing
rm   reacting mixture

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