

**Simple monitoring of semibatch polymerization processes:
an integrated criterion**

Francesco Maestri, Renato Rota*

Politecnico di Milano
Dip. di Chimica, Materiali e Ingegneria Chimica “G. Natta”
Piazza Leonardo da Vinci, 32 – 20133 Milano – Italy
*renato.rota@polimi.it, fax: +39 0223993180

Abstract

A number of potential runaway reaction systems of the fine chemical industry (e.g. polymerization processes) undergo significant changes of their physical properties with the reaction extent, resulting in thickening phenomena of the reaction mass and in a consequent decay of the reactor heat transfer efficiency.

In this work, a set of key process indicators has been developed allowing for monitoring safe operating conditions of industrial semibatch polymerization reactors without requiring any kinetic characterization of the reaction system. The only required information are the heat of reaction and some fully available process variables that are normally recorded for any industrial reactor.

The proposed criterion has been successfully validated using some experimental data measured on an industrial polymerization reactor used for the production of polyacrylic reology modifiers.

Keywords:

Semibatch reactor (SBR); Polymerization; Viscosity; Heat transfer; Ψ number; X number; Key Process Indicator (KPI); Early warning.

1. Introduction

In the fine chemical industry several potential runaway reaction processes can be found that are characterized by significant viscosity changes with the reaction conversion¹.

Among these, a number of polymerization processes can be mentioned, undergoing a peak in the reaction mass viscosity at the higher polymer fractions^{2,3}.

Performing such reactions in indirectly cooled semibatch reactors (SBRs) operated under isoperibolic conditions, the reactor heat transfer efficiency can significantly drop in the late part of the supply period, even if the reaction ignition is kept all along the coreactant supply.

Provided that the resulting temperature increase can be accepted from both a safety and a product quality point of view, this SBR operating regime is still safe, since the coreactant accumulation is in any case minimized and no loss of control of the reaction can occur.

In the process safety literature of the last decades, a number of criteria have been developed allowing for selecting safe operating conditions of exothermic SBRs as well as for early detecting anomalous operating regimes of the reactor leading to the thermal loss of control of the reaction⁴⁻¹⁷.

These criteria do not require the mathematical model of the reactor to be solved by the end user, but still need a kinetic characterization of the reaction system, which is often not straightforward to be performed when dealing with multipurpose processes of the fine chemical industry and with the simultaneous occurrence of mass transfer phenomena in heterogeneous systems.

For this reason, recently Maestri and Rota^{18,19} developed a general safety criterion, referred to as the Ψ criterion, allowing for selecting safe operating conditions of the SBR as well as to monitor the reactor operation at the industrial scale, without a kinetic characterization of the system, but only on the basis of the heat of reaction and of fully available process variables that are normally recorded for any industrial SBR. In particular, the quick increase of the Ψ number up to values ranging from 80 to 100, that are then kept all along the supply period, characterizes an operating regime of the SBR in which the conversion rate is fully determined by the coreactant supply rate and the reaction heat is removed at a much lower time scale than that at which it is evolved.

However, when dealing with well ignited reaction systems that undergo significant variations of the reaction mass viscosity and hence of the reactor heat transfer efficiency, the Ψ criterion cannot be univocally adopted to monitor the reactor operation because a Ψ number sudden decrease during the coreactant supply could be related to both an undesired drop of the system reactivity or to a normal thickening of the reaction mass, such as that occurring in a number of polymerization systems^{2,3}.

In this work, on the basis of the integral form of the energy balance for the SBR, an on-going measure of the coreactant conversion degree, X , is proposed to face the aforementioned limitation of the Ψ number approach. This allows for promptly distinguishing between anomalous or even dangerous process scenarios and normal variations of the SBR heat transfer efficiency, resulting from an expected thickening of the reaction mass: as a result, only in the former cases an interruption of the coreactant feed could be promptly triggered.

The aforementioned process indicators Ψ and X are independent on the reaction kinetic parameters and can be easily measured all along the supply period through some suitable process variables.

The described criterion has been finally successfully validated monitoring the operation of an industrial SBR, in which the solvent based precipitation polymerization of acrylic acid is performed for the production of a class of reology modifiers.

2. Mathematical model

It is assumed that a single, irreversible, potential runaway reaction of general kinetic expression is performed in an isoperibolic SBR, either in a homogeneous or in a heterogeneous reaction system.

In order to develop a simple and general criterion for the on-going measurement of the reaction extent during the coreactant supply, an integral form of the SBR mathematical model is required, being the reaction conversion an integral property of the reaction system.

Dosing at a constant rate a stoichiometric amount of coreactant A, n_{A1} , onto a previously loaded amount of reactant B, n_{B0} , the mass balance equation for an SBR in terms of molar conversion of reactant B can be written as:

$$\frac{d\zeta_B}{dt} = \frac{v_B r^{eff} V_r}{n_{B0}} \quad (1)$$

where the effective reaction rate, r^{eff} , depends on the reaction microkinetic expression and, for heterogeneous systems, on the phase in which the reaction occurs as well as on the rate determining step between the chemical reaction and the mass transfer phenomena.

The energy balance equation for the SBR during the supply period is:

$$\left[(n\tilde{C}_P)_0 + (n\tilde{C}_P)_{fed} \right] \frac{dT}{dt} = (F\tilde{C}_P)_{dos} (T_{dos} - T) + V_r r^{eff} (-\Delta\tilde{H}_r) - UA(T - \bar{T}_{cool}) \quad (2)$$

according to which the reactor temperature behavior is determined by the reaction enthalpy contribution and the combined cooling effect of the external coolant and the dosing stream.

Combining equations (1) and (2) and integrating the resulting equation (see the Supporting Information section for the mathematical details), the following general expression of the molar conversion, ζ_B , can be derived:

$$\zeta_B = \frac{(n\tilde{C}_P)_0(T - T_0) + (n\tilde{C}_P)_{fed}(T - T_{dos}) + \int_0^t (\dot{m}\tilde{C}_P\Delta T)_{cool} dt}{(-\Delta\tilde{H}_r)n_{B0}/v_B} \quad (3)$$

where the heat removal rate by the external coolant has been expressed in terms of directly measurable process variables, that is the coolant flowrate and temperature increase across the reactor jacket, coil or external heat exchanger^{18,19}.

It must be noticed that equation (3) allows for on-going detecting the reaction extent on the basis of the SBR initial conditions and of process variables which trends are normally recorded on any industrial SBR, that is, the dosing stream and reactor temperatures, the amount of coreactant fed to the reactor and the coolant mass flowrate and temperature increase across the heat transfer surfaces. Moreover, no kinetic characterization of the system must be performed, since the only required information related the chemical reaction is the reaction enthalpy: such a feature is of particular

importance when dealing with multipurpose processes of the fine chemical industry, because of the huge variety of reactions involved.

It must be stressed that the reaction conversion (3) is only marginally influenced by any variation of the reactor heat transfer efficiency, due for the sake of example to thickening phenomena of the reaction mass: a potential thermal insulation of the reactor at constant feed rate leads in fact to an increase of the reaction temperature, so that in terms of overall energy balance the heat evolved by the chemical reaction is balanced by the initial and dosed reaction mass enthalpy contributions. In the limit case of infinite time, equation (3) provides:

$$(-\Delta\tilde{H}_r)n_{B0}/v_B \cong (n\tilde{C}_P)_{dos}(T_0 - T_{dos}) + \int_0^\infty UA(T - \bar{T}_{cool})dt \quad (4)$$

stating that the overall energy released by the chemical reaction equals the whole energy removed by the external coolant and the energy required for heating the dosed mass from T_{dos} to T_0 . In deriving equation (4) it has been taken into account that as $t \rightarrow \infty$ the conversion is quantitative, the reaction temperature comes back to T_0 (equal to the coolant temperature) and the amount of fed coreactant is equal to its overall dosed amount.

Operating the SBR under conditions in which the coreactant accumulation is at the limit negligible, the conversion rate is fully determined by the coreactant supply rate^{4,5,12} and therefore, at a constant feed rate, the instantaneous conversion equals the current fraction of the overall dosing period:

$$\zeta_{B,ta} = \frac{t}{t_{dos}} \quad (5)$$

where the subscript “ta” identifies the so called target operating conditions that, however, are here limited to the chemical reaction ignition, independently on the reactor heat transfer efficiency.

Calculating the percentage ratio, expressed in mass terms, of the current reaction conversion (3) to its target value (5), the conversion degree of the dosed coreactant, A, can be obtained:

$$X = \frac{(m\tilde{C}_P)_0(T-T_0) + (m\tilde{C}_P)_{fed}(T-T_{dos}) + \int_0^t (m\tilde{C}_P\Delta T)_{cool}dt}{(-\Delta\tilde{H}_r)m_{fed}\omega_A/v_A} \times 100 = \zeta_A \quad (6)$$

where ω_A is the mass fraction of component A.

The full ignition of the SBR can be now easily recognized from a X time profile quickly approaching values at the limit equal to 100 during the coreactant supply period.

The calculation of X according to equation (6) has to be performed after the coreactant dosing has been started, that is for $t > 0$, since expression (6) is indeterminate from a strictly mathematical point of view at $t = 0$. This is physically sound since at $t = 0$ any semibatch reaction system is not triggered: in fact, an even minimum coreactant accumulation has to be previously built up in the reactor to provide a consumption rate of the coreactant balancing its supply rate at a much lower time scale. From that time on the unreacted coreactant concentration in the system reaches a pseudo steady state behavior, to which X number values close to 100 correspond.

It must be observed that whereas Ψ is an instantaneous process variable useful to monitor the pseudo-steady-state regime of the SBR with respect to the combined effect of the chemical reaction ignition and heat removal efficiency^{18,19}, X is an integral process variable which provides the conversion degree of the fed coreactant under general non-isothermal conditions, independently on any variation of the heat removal efficiency.

In the reaction engineering literature¹, the conventional expressions for the measurement of the reaction extent define the calorimetric conversion as the ratio of the energy removed from the system under isothermal conditions to the whole energy evolved by the chemical reaction. From a physical point of view the X number (6) corresponds instead to the conversion degree of the dosed coreactant, that is, to the ratio of the reacted to the fed coreactant at the current time.

Therefore X numerically equals the reaction conversion referred to the previously loaded reactant B only at the end of the dosing period, whereas during the coreactant supply it is a meaningful process variable allowing for early detecting unexpected reaction inhibitions, that could lead to an uncontrolled coreactant accumulation in the system.

Moreover, through the measured value of X the Maximum Temperature of the Synthesis Reaction (MTSR) under adiabatic conditions can be easily estimated⁸:

$$MTSR_{ad} = T + (1 - \beta X/100)\Delta T_{ad} \quad (7)$$

where $\vartheta = t/t_{\text{dos}}$. Relationship (7) provides (for homogeneous as well as heterogeneous systems) the final reaction temperature that can be reached when, starting from the actual time, the coreactant supply is carried out under adiabatic conditions and the coreactant conversion is complete. MTSR_{ad} is therefore an index of the instantaneous hazard potential of the system accounting for both the coreactant to be dosed as well as for the coreactant accumulated.

As a key difference with other process variables (such as reaction temperature), it must be stressed that both Ψ and X reach a univocal target value (for instance, 100), that is independent on the reaction system as well as on the adopted operating conditions, so that any displacement from an original Quick Onset, Fair Conversion, Smooth Temperature Profile (QFS) reactor regime^{4,5,12} can be easily recognized on the basis of their instantaneous values.

In particular, through the resulting set of KPIs (that is Ψ , X and MTSR_{ad}) the prompt interruption of the coreactant feed can be limited to specific process scenarios, that is to undesired or even dangerous reactivity drops as well as to an early decay of the SBR heat transfer efficiency, hence excluding the effect of a normal thickening of the reaction mass occurring at sufficiently late fractions of the dosing period.

Such a feature is of particular importance when monitoring the safe and productive operation of semibatch polymerization processes, a huge number of which undergoes relevant viscosity increases with the polymer fraction¹⁻³.

3. SBR monitoring

The safe and productive operation of an isoperibolic SBR in which a potential runaway reaction is performed is characterized by a quick ignition of the chemical reaction once the coreactant supply is started and by a nearly isothermal reactor behavior due to a relatively high heat removal efficiency^{4,5,12}. Such operating conditions, corresponding to a pseudo-steady-state regime of the SBR,

can be easily identified at the laboratory or pilot scale through the Ψ criterion and finally scaled up to the industrial plant, even without a kinetic characterization of the reaction system^{18,19}.

On this basis, for a given process productivity, a required heat transfer surface at the industrial scale can be calculated.

However, a number of potential runaway non-continuous processes can be mentioned undergoing a significant viscosity rise at the higher conversions, to which a decay of the reaction heat removal efficiency corresponds¹.

In these cases, yet developing the synthesis recipe at the laboratory scale, a suitable reaction mass concentration has to be adopted, so that the aforementioned thickening phenomena occur at relatively high reaction extents, that is, when the energy potential of the system in terms of coreactant to be dosed as well as of accumulated coreactant is sufficiently low to prevent the overcoming of a Maximum Allowable Temperature (MAT), even under adiabatic conditions⁸.

Once the selected operating conditions have been scaled up to the industrial plant, each reaction batch must be monitored in order to promptly trigger the coreactant feed interruption^{18,20-23}, when detecting any incidental drop of the system reactivity as well as any early decay of the heat removal efficiency. In the former scenario, even if the reaction system can be reignited (e.g. through an additional catalyst shot), the coreactant feed must be restarted after the system reactivation.

Such a way to proceed is mandatory if the reactivity drop occurs at early fractions of the dosing period, since the sudden reaction of the coreactant residual amount would lead, if fully accumulated, to the thermal loss of control of the chemical reaction and to the triggering of the further incidental scenarios related to it.

However, even if the reactivity drop occurs at sufficiently late fractions of the supply period to make the MAT overcoming impossible, the coreactant feed must be stopped as well. In fact, in particular when dealing with polymerization processes, if the reaction system can be reignited the further sudden reaction of the residual coreactant amount could lead, among the others, to uncontrolled viscosity rises and to the final blockage of the stirrer, due to the formation of a sticky mass.

Instead, if the reaction cannot be reactivated, the further accumulation of unreacted coreactant in the system is not economical, since it implies additional costs either for separating the reaction mass from the unreacted coreactant or for wasting a higher amount of chemicals, one of which (that is, the coreactant) could be recovered as a raw material.

Moreover, when dealing with polymerization processes, it cannot be neglected that the further separation (typically through distillation) of the residual monomer amount from the reaction mass could be even dangerous, since the distillation of the monomer would be performed under uninhibited conditions and could therefore lead to uncontrolled polymerizations occurring in ancillary equipment, that are not designed for safely performing the polymerization reaction.

Dealing with a number of polymerization processes, a huge oversizing of the initially estimated heat transfer surface should be adopted in order to keep nearly isothermal conditions, because of thickening phenomena of the reaction mass occurring at the higher polymer fractions¹⁻³. According to Steinbach¹, such overestimations can be even of a factor ranging from 6 to 10, which would require the installation of relatively large heat transfer equipment.

In these cases, if the reaction temperature increase due to the partial reactor insulation can be accepted, higher conversions can be reached in lower time periods, as a consequence of the higher reaction rates: dealing with polymerization reaction processes, this could be even useful for effectively minimizing the residual monomer amount.

As mentioned above, once the SBR operating conditions have been identified, the reactor operation during each batch of a productive campaign must be monitored, in order to promptly detect unexpected reaction inhibitions or early drops of the SBR heat transfer efficiency that could lead to undesired or even dangerous process scenarios.

Such scenarios can be represented by an uncontrolled coreactant buildup in the system or by an excessive temperature rise even under fully ignited operating conditions.

Instead, late drops of the SBR heat transfer efficiency can be accepted, provided that the resulting temperature rise does not allow for overcoming a threshold temperature, arising either from safety or from product quality constraints.

If the reactor undergoes a significant drop of the heat removal efficiency due to thickening phenomena of the reaction mass, the Ψ criterion cannot be univocally adopted for monitoring the ignition of the reaction system during the coreactant supply. Ψ is in fact a combined process variable, taking into account for both the reaction ignition and the heat transfer efficiency^{18,19}. This means that Ψ numbers ranging from 80 to 100 during the coreactant supply correspond to an SBR operating regime in which the coreactant accumulation is effectively limited and the reaction heat is removed at a relatively low time scale.

However, if during the coreactant supply a partial thermal insulation of the reaction system occurs, due to a viscosity increase, Ψ typically undergoes a sudden and significant drop even if the chemical reaction is fully ignited. The same qualitative behavior of Ψ would be instantaneously detected if an unexpected reaction inhibition occurred, even with an optimal heat transfer efficiency of the reactor. Typical QFS trends (obtained through integration of equations (1) and (2)) of reactor temperature, Ψ , X and $MTSR_{ad}$ of an exothermic SBR (see Figures 1A, 1B, 1C and 1D) are compared with the same profiles for two scenarios, corresponding to a sudden reactivity drop (Figures 2A, 2B, 2C and 2D) and to a heat transfer efficiency sudden decay to $\frac{1}{4}$ of its original value (Figures 3A, 3B, 3C and 3D), both occurring at the 70% of the coreactant supply. In plotting the aforementioned profiles, the initial reaction temperature has been taken as the reference temperature, so that at $t=0$ the dimensionless reaction temperature is equal to 1. Ψ and X move instead from 0 at $t \rightarrow 0$, since at the very beginning of the supply period the system ignition has not yet occurred and therefore the consumption rate of the dosed coreactant is initially equal to 0 as well. Finally, at $t=0$ all the coreactant to be dosed is available to react, so that the maximum temperature of the synthesis reaction under adiabatic

conditions, $MTSR_{ad}$, at $t=0$ is equal to the initial system temperature plus the adiabatic temperature rise.

It can be noticed that whereas the Ψ number time profile undergoes a sudden decay in both the aforementioned incidental scenarios, the X number quickly decreases only when the reaction heat evolution drops as a consequence of a reaction inhibition. Moreover, according to the X time profiles represented in Figure 4, even ignited reaction systems from which the reaction heat is effectively removed undergo a partial accumulation of the dosed coreactant in the final part of the dosing period, where the reactant B consumption goes to completion and the reaction characteristic time consequently increases. However, as the SBR heat transfer efficiency decreases, the resulting increase of the reaction temperature and hence of the reaction rates in the final part of the dosing period overrules the aforementioned effect related to the reactant B consumption, so that the conversion degree of the fed coreactant increases as well, up to values close to 100%.

On the contrary, if the SBR undergoes an even partial thermal insulation, the Ψ number suddenly drops to values well below the recommended 80-100 range, with a trend that cannot in principle be distinguished from that characterizing a reactivity drop scenario. Subsequently, as can be observed from the time profile represented in Figure 3B, a partial Ψ number recovery occurs in the final part of the dosing period, because of the reaction temperature rise (see Figure 3A), to which an increase of the cooling contribution of the dosing stream corresponds. Therefore, the Ψ number alone is not useful for distinguishing between a reaction inhibition and a reactor thermal insulation scenario.

In fact, according to the monitoring logic discussed elsewhere in the literature^{18,19}, if a Ψ drop below the 80-100 range is detected during the coreactant supply, a prompt feed interruption is triggered, in order to prevent an uncontrolled buildup of unreacted coreactant in the system.

However, if the aforementioned Ψ drop is due to a normal heat transfer efficiency decay, a false alarm and a consequent undue feed interruption would be triggered, with detrimental consequences on the process productivity and even on the final product quality. It must in fact be considered that for a

number of semibatch polymerization processes a regular monomer feed rate has a significant influence on the characteristics of the final polymer and that a feed interruption can be itself the cause of a further reaction inhibition once the monomer feed is restarted.

As can be noticed from the trends of Figures 3A to 3D, if a reactor partial insulation occurs in an ignited reaction system, the Ψ number drop is coupled with a simultaneous reaction temperature rise, which does not occur in an inhibited reaction system. Such a combined behavior could in principle be useful for distinguishing between a reaction inhibition and a reactor thermal insulation scenario.

However, in order to keep a simple and therefore robust monitoring logic at the industrial scale, it is useful to identify a process variable other than temperature which displacement from a well-defined and univocal target value allows for selectively identifying reaction inhibition scenarios independently on the heat removal efficiency of the reactor.

Such a goal can be reached through the X parameter (6) that, in strict analogy with Ψ , can be on-going detected during the coreactant supply on the basis of fully available process variables, that is the initial reactor load and temperature, the currently dosed mass and dosing temperature, the reaction temperature and the coolant mass flowrate and temperature increase across the heat transfer surfaces^{18,19}.

In particular, a full and selective monitoring of the SBR operation can be performed through the integrated set of KPIs given by the Ψ number, the X number and the resulting maximum temperature of the synthesis reaction under adiabatic conditions, $MTSR_{ad}$. Such parameters can be on-going detected through simple elaboration of the aforementioned process variables, according to the expression of Ψ provided in the mentioned literature¹⁸ and to Equations (6) and (7) for X and $MTSR_{ad}$, respectively.

More in detail, starting at a not too early time to let the system trigger and on the basis of the current values of Ψ , X and $MTSR_{ad}$, the monitoring logic represented in the flow chart of Figure 5 could be implemented, acting on switching off the coreactant feed as a final action.

According to such a logic, a current Ψ value ranging from 80 to 100 is assumed to be a sufficient condition for going ahead with the coreactant supply, since it corresponds to SBR operating conditions in which the chemical reaction is fully ignited and the reaction heat is effectively removed from the system.

If at any time a Ψ value below 80 is detected, the instantaneous value of the measured $MTSR_{ad}$ is compared with the MAT: if $MTSR_{ad}$ is higher than the MAT the coreactant feed is suddenly stopped without any further check. In fact, even if the Ψ drop were related to an early decay of the SBR heat transfer efficiency without any inhibition of the chemical reaction, the coreactant feed must be stopped as well, since the energy evolved by the conversion of the residual coreactant would be sufficient to gradually heat up the system above the MAT. In this way, even if a temperature switch high logic acting to stop the coreactant feed is normally installed on any industrial equipment, the prompt detection of an early reactor insulation due e.g. to unexpected thickening phenomena is useful to adopt the necessary preventive actions, such as the dilution of the reaction mass with additional solvent, in order to recover the system fluidity.

If instead the Ψ drop is due to a reactivity loss, the sudden reaction of the further accumulated coreactant would potentially lead to an increase of the reaction temperature above the MAT, without any control chance by the plant operator.

If at the time at which the Ψ drop is detected the $MTSR_{ad}$ is lower than the MAT, the check on the X number is finally performed, with respect to a minimum expected value (for instance, 90) for a satisfactory conversion degree of the dosed coreactant: even in this case a sudden feed interruption is triggered if a low X number is detected, in order to prevent the coreactant buildup in the system with the mentioned process consequences related to it.

Therefore, monitoring the safe SBR operation through the set of KPIs given by Ψ , X and $MTSR_{ad}$ allows for selectively stopping the coreactant feed only when facing a reactivity drop or an early decay of the SBR heat transfer efficiency. On the contrary, when dealing with reaction systems

undergoing normal thickening of the reaction mass occurring when most of the coreactant has been fed, a selective SBR monitoring can be performed, without the need of adopting excessive dilutions of the reaction mass for smoothing or even suppressing such phenomena, with detrimental consequences on the process productivity.

4. Case study: solvent based precipitation polymerization of acrylic acid

The X number criterion for on-going detecting the coreactant conversion degree in exothermic SBRs has been tested analyzing a polymerization process of relevant importance in the fine chemical industry, that is the solvent based polymerization of acrylic acid for the synthesis of polyacrylic reology modifiers^{2,3}. The reaction, commonly performed in solvents such as aliphatic, cycloaliphatic and aromatic hydrocarbons as well as in esters, is strongly exothermic and is characterized by thickening phenomena of the reaction mass as the polymer volume fraction increases.

In order to better control the heat evolution, the reaction can be performed by dosing the monomer over a suitable time period, that is in an indirectly cooled SBR.

For instance, the polymerization process taken into exam consists of two reaction steps: a pre-polymerization under batch conditions of the 25% of the whole monomer amount and a further semibatch polymerization in which the 75% of the monomer is dosed over the reaction mass in a suitable period of time, depending on the heat transfer characteristics of the reactor.

In precipitation polymerization processes, the reaction initiation occurs in the solvent continuous phase, whereas the propagation and termination reactions mainly take place in the dispersed polymer phase, after the precipitation of a critical polymer amount, on the surface of which the growing radical chains are fastened and the termination reactions are consequently slowed down^{2,3}. For this reason, the reaction is previously triggered under batch conditions, hence generating an active volume of dispersed polymer phase, where the subsequently dosed coreactant can be consumed from the beginning of the supply period at a much lower time scale than that at which it is fed. In this way, the great part of the reaction heat can be uniformly spread over the dosing period, at the end of which the

monomer conversion is relatively high. A final reaction completion under batch conditions allows then for lowering the residual monomer amount below a desired value.

The polymerization process in question has been developed at the laboratory scale in a 2L glass reactor. Under the selected operating conditions, roughly 30' after the catalyst loading, the initial reaction solution (containing the 25% of the whole monomer amount) becomes cloudy as a consequence of a proper triggering of the polymerization reaction. The 75% of the monomer is then dosed over a 2 hours period.

At the higher polymer volume fractions, the reaction mass is likely to undergo sudden viscosity peaks, which are expected to occur at the 70-80% of the monomer feed. Under these conditions, the SBR heat transfer efficiency drops and the reaction temperature begins to rise. Such a behavior has no influence neither on the process safety, nor on the final product quality, provided that the reaction temperature does not rise above the boiling point of the solvent used. In particular, a slight temperature increase in the final part of the coreactant supply is even useful for early minimizing the unreacted monomer amount, hence allowing for a shorter completion period after the monomer feed. In Table 1 the geometric and heat transfer characteristics of the laboratory and industrial reactors are summarized, on the basis of which a Westerterp number at the laboratory scale:

$$Wt = \frac{(UA)_0 t_{dos}}{\varepsilon(\rho C_P V_r)_0} \cong 15 \quad (8)$$

can be calculated.

According to the desired plant productivity, the monomer dosing period at the industrial scale cannot exceed 6 hours.

The scale-up of the selected operating conditions to the industrial plant can then be performed keeping the same Westerterp number (8) at the two scales¹². With an industrial monomer dosing period equal to 6 hours, the available heat transfer surface is sufficient.

With the aforementioned process and plant data and under full ignition SBR operating conditions, the reaction temperature behavior in the first fraction of the supply period (that is, before the reaction

mass viscosity rises above critical values) can be satisfactorily approximated through the following expression:

$$T \approx T_{dos} + \frac{\dot{m}_{A,dos}(-\Delta\hat{H}_r) - UA(T_{dos} - T_{cool})}{(\dot{M}\hat{C}_P)_{dos} + UA} \quad (9)$$

which in fact provides temperatures values in good agreement with the recorded plant data.

However, in the late fractions of the dosing period (depending on the selected reaction concentrations), thickening phenomena of the reaction mass have been observed, lowering the overall heat transfer coefficient down to about ¼ of its original value. Under such conditions, the reaction temperature rises, as can be noticed from the temperature time profile measured in the industrial scale reactor (see Figures 6A).

Coherently, Figure 7A shows the Ψ number trend measured in the industrial scale reactor that undergoes a sudden drop as the reaction mass thickening occurs, with a behavior that cannot be distinguished from the one characterizing a reaction inhibition scenario. It should be noted that when dealing with acrylic polymerizations, the reaction inhibition is likely to occur because of even minimum air leakages into the reaction system, as shown by the experimental data summarized in Figures 6B and 7B, which have been also measured in the industrial scale reactor.

In order to keep at the industrial scale a simple and reliable monitoring logic for the SBR safe operation, the measurement of the Ψ number trend must be coupled with those of the X number and the $MTSR_{ad}$. The experimental data measured in the industrial scale reactor for the two reaction batches involving mass thickening and reaction inhibition are summarized in Figures 8 and 9 (part A and B, respectively). As a relevant difference with respect to the Ψ number behavior shown in Figure 7, even when facing a normal decay of the reactor heat removal efficiency due to thickening phenomena the X number does not undergo any unexpected drop with respect to the typical range for ignited reaction systems, as shown in Figure 8A since the conversion degree of the coreactant is even favored by higher reaction temperatures. However, when facing a reactivity drop the X number undergoes a sudden decay (see Figure 8B), hence allowing for a prompt corrective action.

Therefore, through the set of KPIs given by Ψ , X and $MTSR_{ad}$, the polymerization process in question can be successfully monitored without undue monomer feed interruptions triggered by a normal decay of the SBR heat transfer efficiency, as the polymer volume fraction increases.

5. Conclusions

When dealing with fast and exothermic semibatch reaction systems which physical properties undergo significant changes, the safe reactor operation cannot be univocally monitored through the general Ψ criterion. A Ψ number drop during the coreactant supply could in fact be related to either a dangerous reaction inhibition or a normal decay of the reactor heat transfer efficiency.

In this work a general criterion has been developed that, through additional easy to measure process variables, allows for discriminating among safe and unsafe situations.

The resulting set of KPIs has been proven to be useful to monitor the operation of semibatch polymerization processes (a huge number of which undergoes significant viscosity changes with the polymer fraction), using some experimental data measured on an industrial SBR in which the solvent based precipitation polymerization of acrylic acid was performed.

Nomenclature

A	heat transfer surface, m ²
\tilde{C}_p	molar heat capacity at constant pressure, kJ/(kmol·K)
\hat{C}_p	mass heat capacity at constant pressure, kJ/(kg·K)
F	molar flowrate, kmol/s
m	mass, kg
MAT	maximum allowable temperature, °C or K
MTSR	maximum temperature of the synthesis reaction, °C or K
\dot{m}	mass flowrate, kg/s
n	number of moles, kmol
r	reaction rate, kmol/(m ³ ·s)
t	time, s
T	temperature, °C or K
\bar{T}	average temperature, °C or K
U	overall heat transfer coefficient, kW/(m ² K)
V	reaction volume, m ³
Wt	$= \frac{(UA)_0 t_{dos}}{\varepsilon(\tilde{\rho} \tilde{C}_p V_r)_0}$, Westerterp number, -

Subscripts and superscripts

ad	adiabatic
AA	acrylic acid
A and B	components A and B
cool	coolant
dos	dosing stream or dosing time
eff	effective
fed	fed
r	reaction
ta	target
0	start of the semibatch period
1	end of the semibatch period

Greek symbols

$\Delta\tilde{H}$	reaction enthalpy, kJ/kmol
$\Delta\hat{H}$	reaction enthalpy referred to the mass of reacted coreactant, kJ/kg
ΔT	temperature difference, °C or K
ε	$=V_{dos}/V_{r0}$, relative volume increase, -
ζ	molar conversion (normalized to unity), -
ϑ	$=t/t_{dos}$, dimensionless time, -
ν	stoichiometric coefficient, -
$\tilde{\rho}$	molar density, kmol/m ³

X X number, -
Ψ Ψ number, -
ω mass fraction, -

Supporting Information

Derivation of Equation (3)

This information is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Steinbach, J. *Safety Assessment for Chemical Processes*; Wiley-VCH: Weinheim, 1999.
- (2) Avela, A.; Poersch, H.G.; Reichert, K.H. Modelling the Kinetics of the Precipitation Polymerization of Acrylic Acid. *Die Angewandte Makromolekulare Chemie* **1990**, *175*, 107.
- (3) Poersch, H.G.; Avela, A.; Reichert, K.H. Precipitation Polymerization of Acrylic Acid: Kinetics, Viscosity and Heat Transfer. *Die Angewandte Makromolekulare Chemie* **1993**, *206*, 157.
- (4) Steensma, M.; Westerterp, K. R. Thermally safe operation of a cooled semi-batch reactor. Slow liquid-liquid reactions. *Chem. Eng. Sci.* **1988**, *43*, 2125.
- (5) Steensma, M.; Westerterp, K. R. Thermally safe operation of a semibatch reactor for liquid-liquid reactions. Slow reactions. *Ind. Eng. Chem. Res.* **1990**, *29*, 1259.
- (6) van Woezik, B.A.A.; Westerterp K.R. Runaway behavior and thermally safe operation of multiple liquid-liquid reactions in the semibatch reactor. The nitric acid oxidation of 2-octanol. *Chem. Eng. Process.* **2001**, *41*, 59.
- (7) Westerterp, K.R.; Molga, E.J. No more runaways in fine chemical reactors. *Ind. Eng. Chem. Res.* **2004**, *43*, 4585.
- (8) Maestri, F.; Rota, R. Temperature diagrams for preventing decomposition or side reactions in liquid-liquid semibatch reactors. *Chem. Eng. Sci.* **2006**, *61*, 3068.
- (9) Westerterp, K.R.; Molga, E.J. Runaway prevention in liquid-liquid semibatch reactors. *Inzynieria Chemiczna i Procesowa* **2004**, *25*, 2041.
- (10) Molga, E.J.; Lewak, M; Westerterp, K.R. Runaway prevention in liquid-phase homogeneous semibatch reactors. *Chem. Eng. Sci.* **2007**, *62*, 5074.
- (11) Maestri, F.; Rota, R. Safe and productive operation of homogeneous semibatch reactors involving autocatalytic reactions with arbitrary reaction order. *Ind. Eng. Chem. Res.* **2007**, *46*, 5333.
- (12) Maestri, F.; Copelli, S.; Rota, R.; Lunghi, A.; Gigante, L.; Cardillo, P. Simple procedure for optimal scale-up of fine chemical processes. I: practical tools. *Ind. Eng. Chem. Res.* **2009**, *48*, 1307.
- (13) Maestri, F.; Copelli, S.; Rota, R.; Lunghi, A.; Gigante, L.; Cardillo, P. Simple procedure for

optimal scale-up of fine chemical processes. II: nitration of 4-Chlorobenzotrifluoride. *Ind. Eng. Chem. Res.* **2009**, *48*, 1316.

(14) Copelli, S.; Derudi, M.; Rota, R. Topological criterion to safely optimize hazardous chemical processes involving arbitrary kinetic schemes. *Ind. Eng. Chem. Res.* **2011**, *50*, 1588.

(15) Copelli S.; Torretta V.; Maestri F.; Sala Cattaneo C.; Nano G.; Rota R. Batchsize and topological criteria: A combined approach to safely optimize hazardous polymerization processes, *Chemical Engineering Transactions* **2013**, *33*, 613.

(16) Westerterp, K.R.; Lewak, M.; Molga, E.J. Boundary Diagrams Safety Criterion for Liquid Phase Homogeneous Semibatch Reactors. *Ind. Eng. Chem. Res.* **2014**, *53*, 5778.

(17) Bai, W.S.; Hao, L.; Guo, Z.C.; Liu, Y.Y.; Wang, R.; Wei, H.Y. A New Criterion to Identify Safe Operating Conditions for Isoperibolic Homogeneous Semi-Batch Reactions. *Chem. Eng. J.* **2017**, *308*, 8.

(18) Maestri, F.; Rota, R. Kinetic-free safe operation of fine chemical runaway reactions: a general criterion. *Ind. Eng. Chem. Res.* **2016**, *55*, 925.

(19) Maestri, F.; Rota, R. Kinetic-Free Safe Optimization of a Semibatch Runaway Reaction: Nitration of 4-Chloro Benzotrifluoride. *Ind. Eng. Chem. Res.* **2016**, *55*, 12786.

(20) Copelli, S.; Torretta, V.; Pasturenzi, C.; Derudi, M.; Cattaneo, C. S.; Rota, R. On the Divergence Criterion for Runaway Detection: Application to Complex Controlled Systems. *J. Loss Prevent. Proc. Ind.* **2014**, *28*, 92.

(21) Zaldívar, J.M.; Cano, J.; Alós, M.A.; Sempere, J.M.; Nomen, R.; Lister, D.; Maschio, G.; Obertopp, T.; Gilles, E.D.; Bosch, J.; Strozzi, F. A general criterion to define runaway limits in chemical reactors. *J. Loss Prevent. Proc. Ind.* **2003**, *16*, 187.

(22) Maria, G.; Stefan, D.N. Evaluation of critical operating conditions for a semi-batch reactor by complementary use of sensitivity and divergence criteria. *Chem. Biochem. Eng.* **2011**, *Q. 25*, 9.

(23) Bosch, J.; Strozzi, F.; Lister, D.G.; Maschio, G.; Zaldívar, J.M. Sensitivity analysis in polymerization reactions using the divergence criterion. *Process Saf. Environ.* **2004**, *81*, 18.

Tables

	V (m³)	V₀ (m³)	V_{dos} (m³)	A₀ (m²)	U (W/m²K)
Laboratory reactor	2×10^{-3}	3.1×10^{-4}	9.4×10^{-4}	2.1×10^{-2}	145
Industrial reactor	20	3.71	11.4	53.0	230

Table 1. Solvent based polymerization of acrylic acid: laboratory and industrial reactor characteristics.

Captions to the figures

Figure 1. Exothermic SBR reactor operated under QFS conditions. Typical trends for: reaction temperature vs. time (A); Ψ number vs. time (B); X number vs. time (C); $MTSR_{ad}$ vs. time (D).

Figure 2. Exothermic SBR reactor with reactivity drop occurring at the 70% of the supply period. Typical trends for: reaction temperature vs. time (A); Ψ number vs. time (B); X number vs. time (C); $MTSR_{ad}$ vs. time (D).

Figure 3. Exothermic SBR reactor with heat transfer efficiency drop occurring at the 70% of the supply period. Typical trends for: reaction temperature vs. time (A); Ψ number vs. time (B); X number vs. time (C); $MTSR_{ad}$ vs. time (D).

Figure 4. Exothermic SBR reactor. Typical trends of the X number vs. time at decreasing UA values.

Figure 5. Monitoring logic for the SBR monitoring through the set of KPIs given by Ψ , X and $MTSR_{ad}$.

Figure 6. Semibatch solvent based polymerization of acrylic acid. Experimental reaction temperature trends at the industrial scale during the monomer supply period when thickening of the reaction mass occurs at the 70% of the monomer supply (A); and when reaction inhibition occurs at the 40% of the monomer supply (B).

Figure 7. Semibatch solvent based polymerization of acrylic acid. Experimental Ψ number trends at the industrial scale during the monomer supply period when thickening of the reaction mass occurs at the 70% of the monomer supply (A); and when reaction inhibition occurs at the 40% of the monomer supply (B).

Figure 8. Semibatch solvent based polymerization of acrylic acid. Experimental X number trends at the industrial scale during the monomer supply period when thickening of the reaction mass occurs at the 70% of the monomer supply (A); and reaction inhibition occurs at the 40% of the monomer supply (B).

Figure 9. Semibatch solvent based polymerization of acrylic acid. Experimental $MTSR_{ad}$ trends at the industrial scale during the monomer supply period when thickening of the reaction mass occurs at the 70% of the monomer supply (A); and reaction inhibition occurs at the 40% of the monomer supply (B).

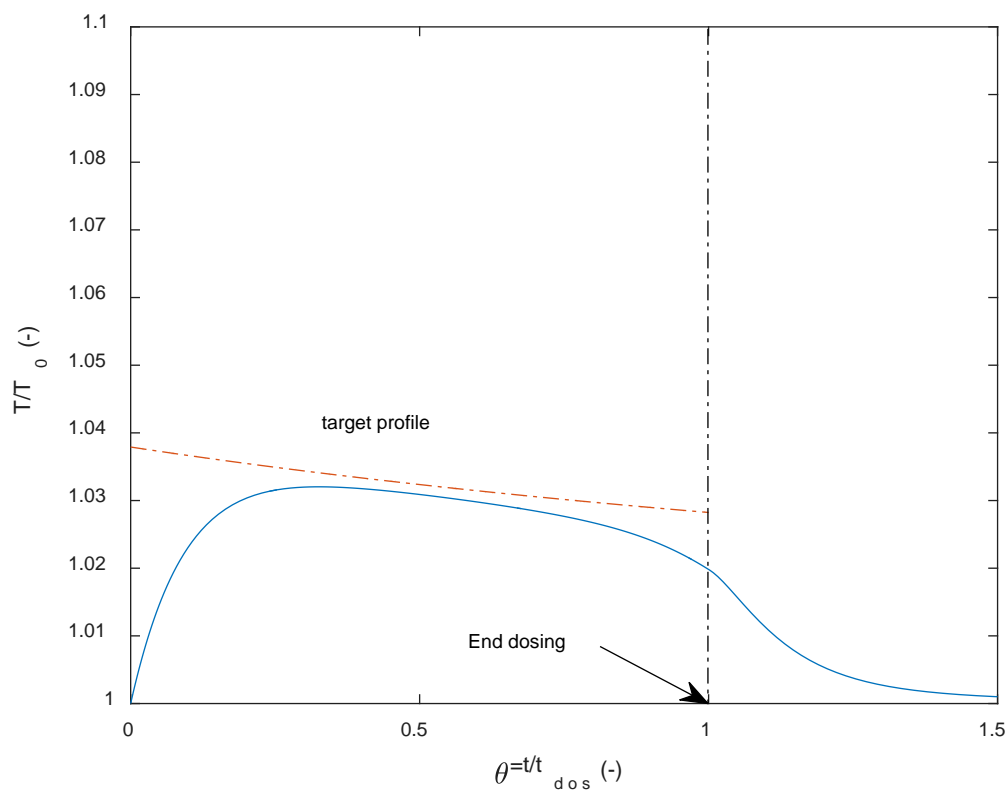


Fig. 1A

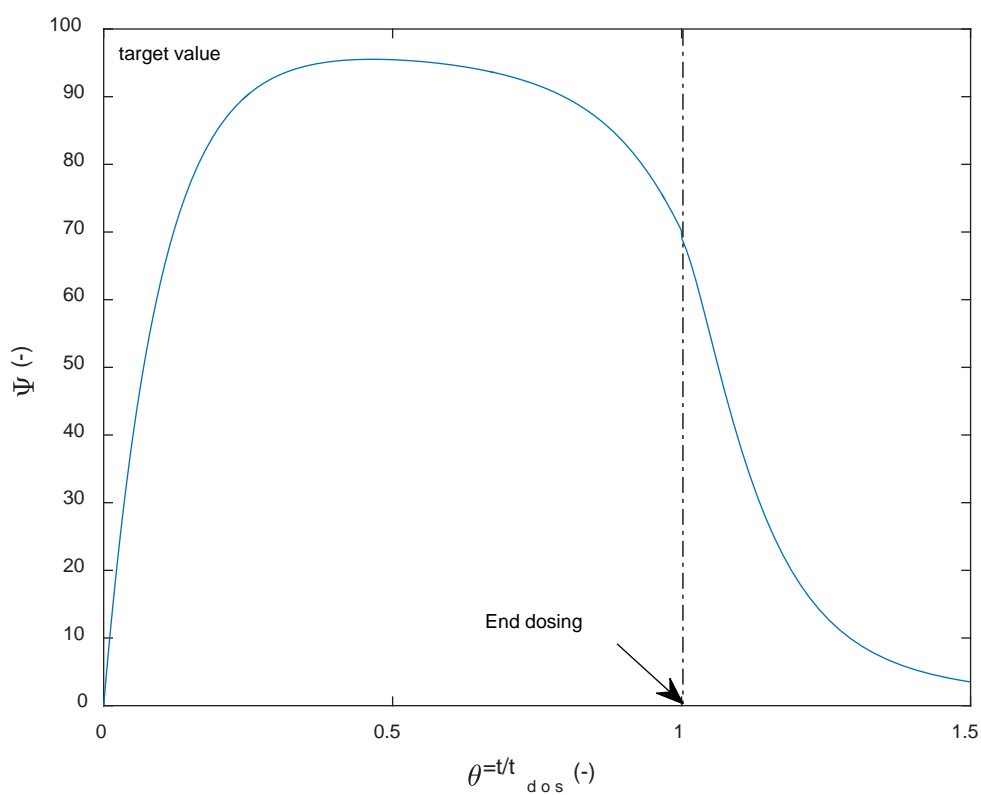


Fig. 1B

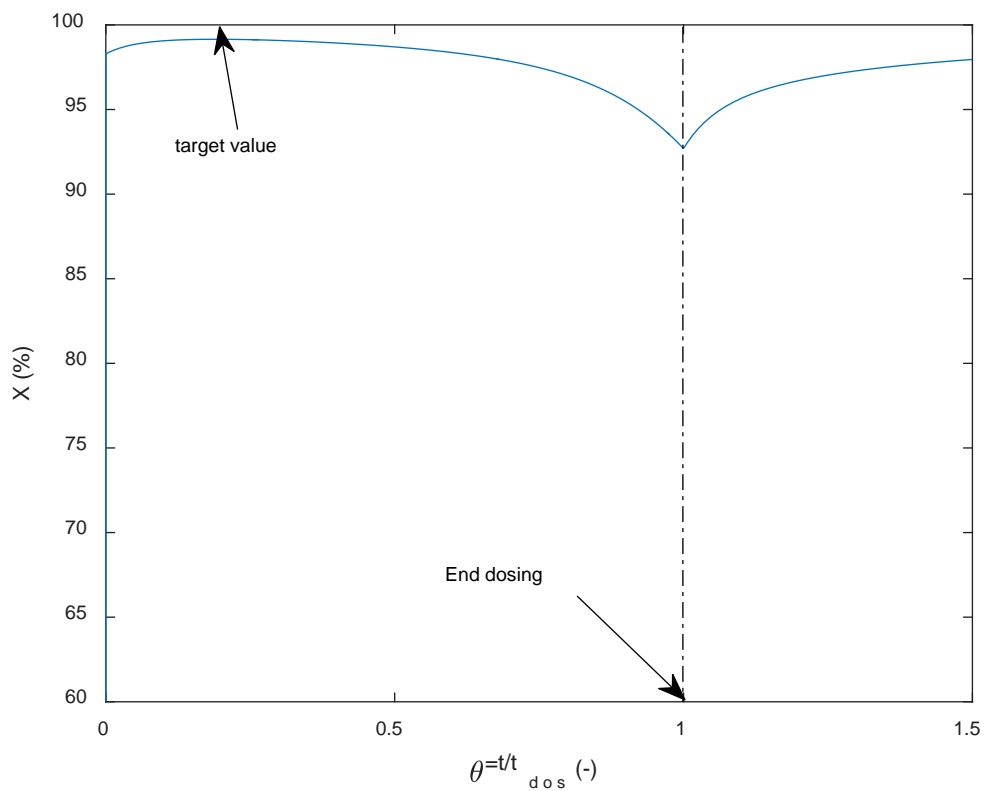


Fig. 1C

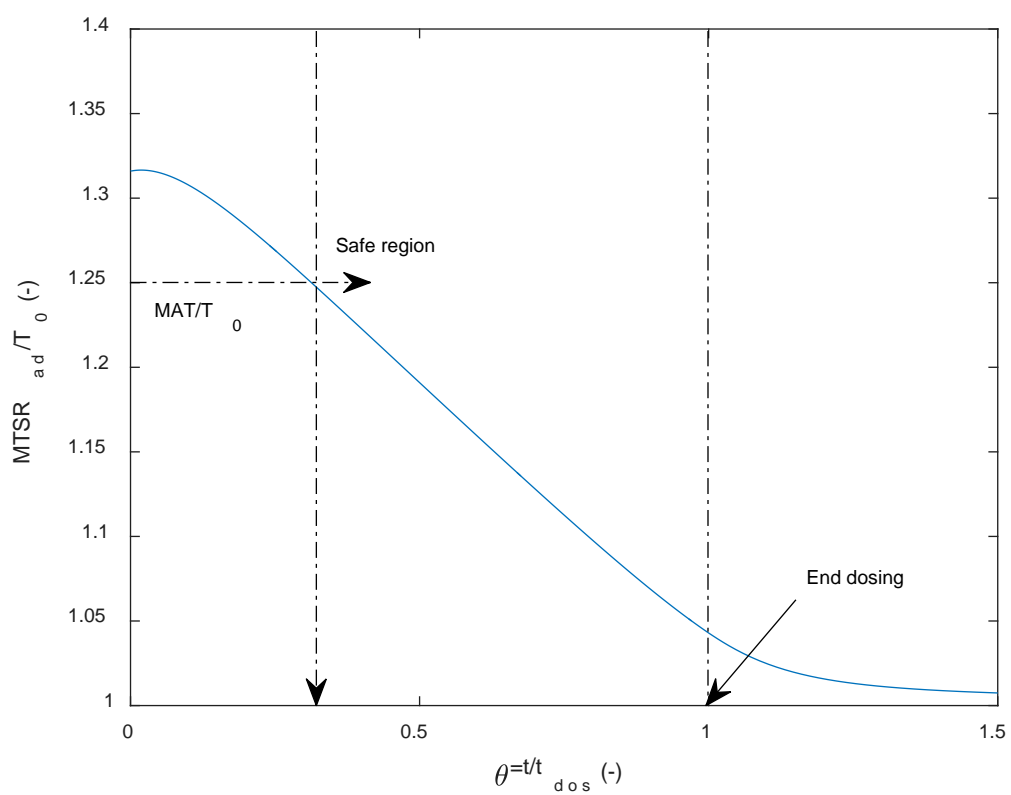


Fig. 1D

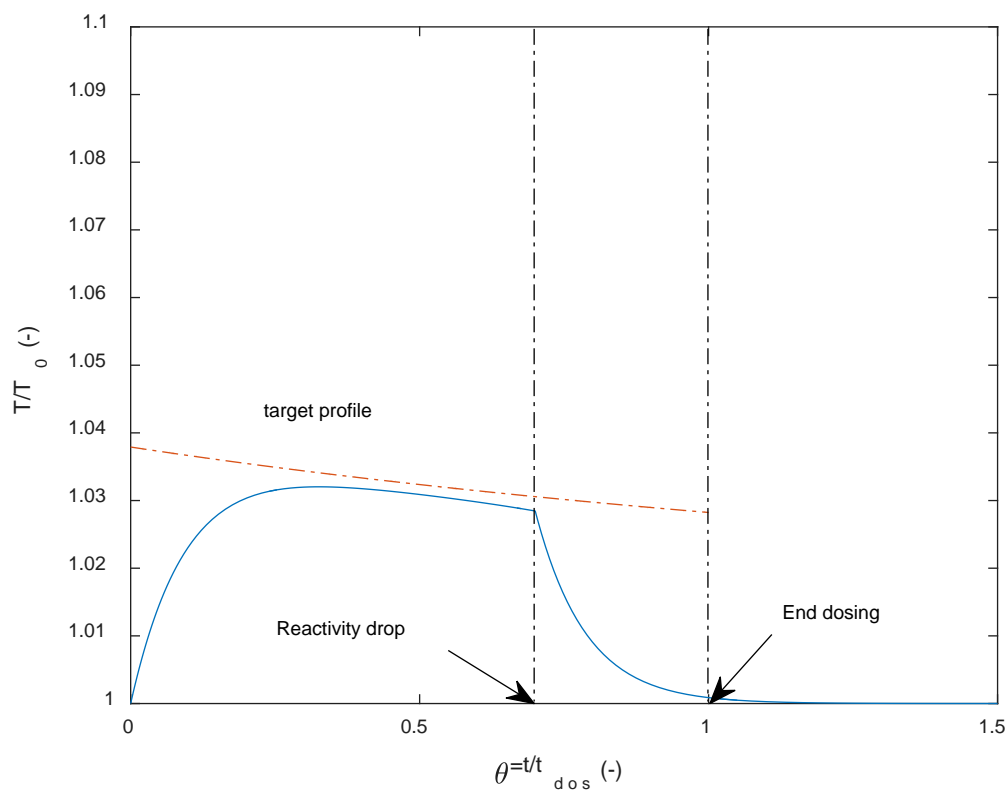


Fig. 2A

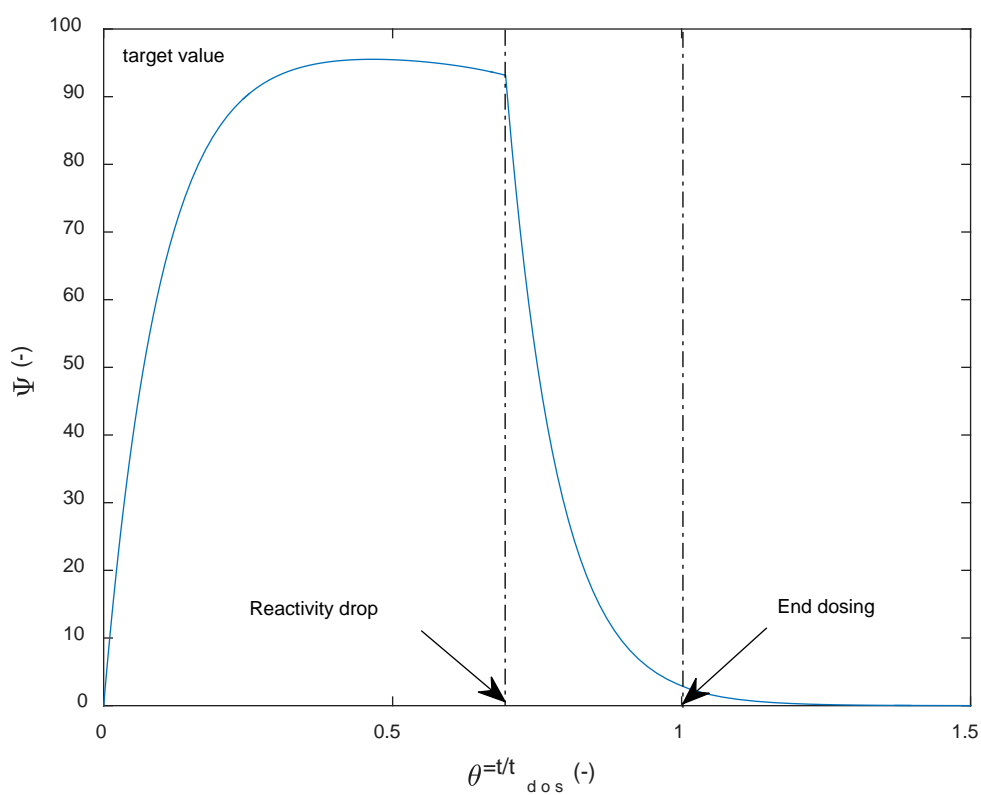


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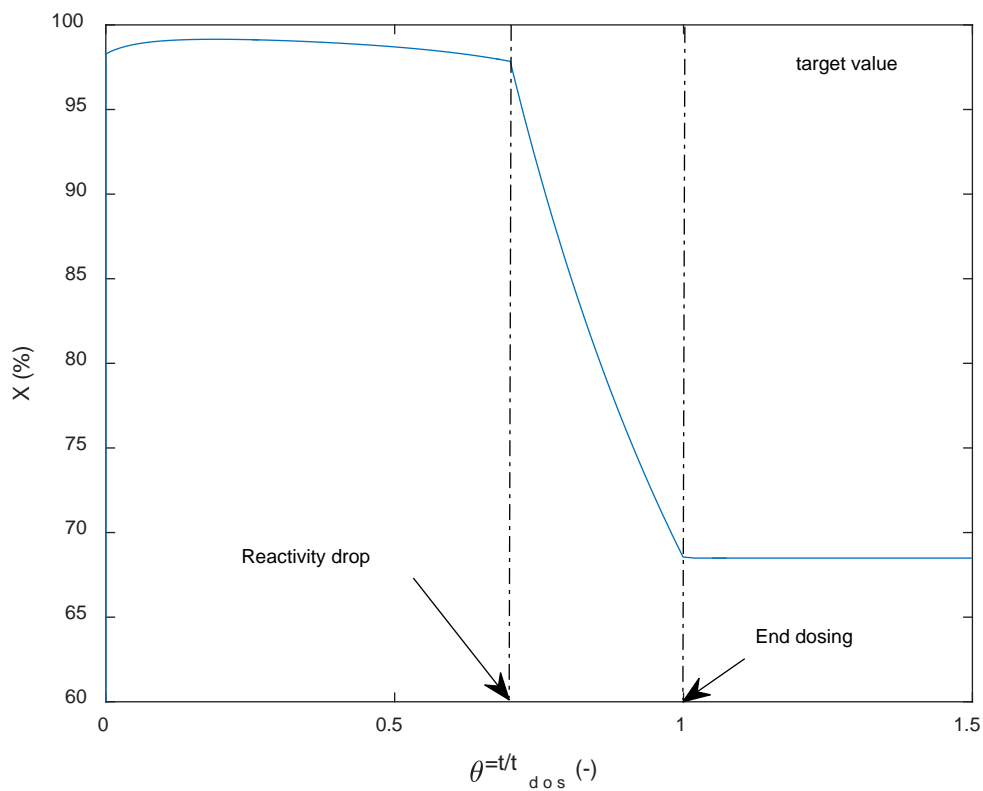


Fig. 2C

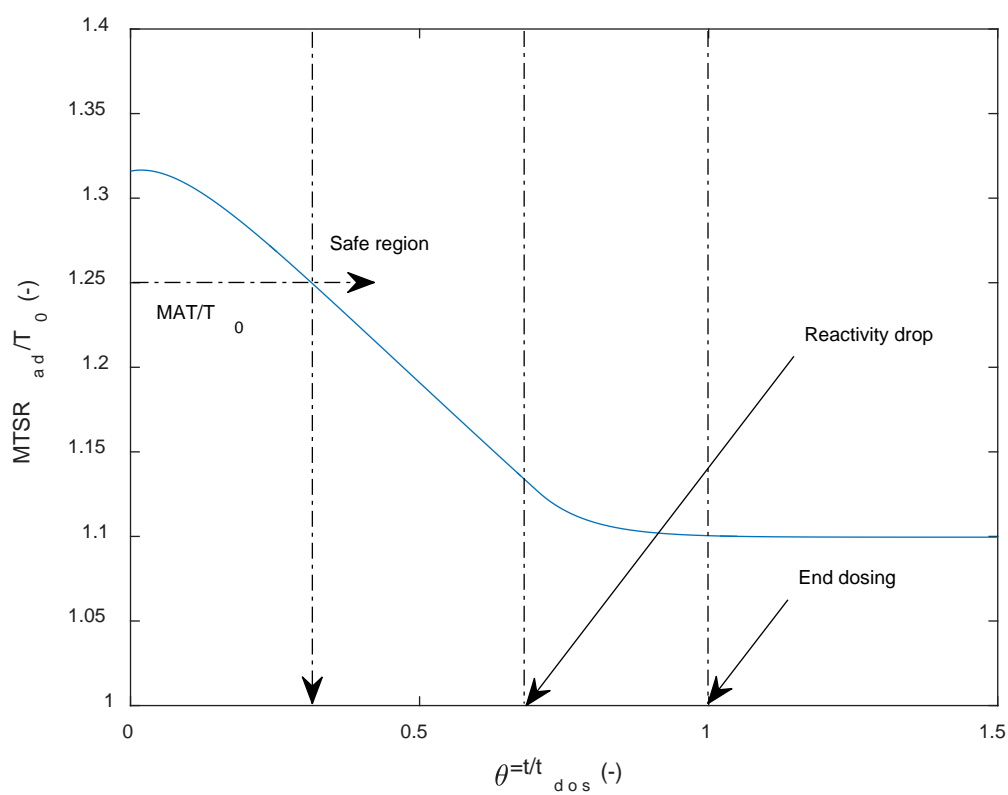


Fig. 2D

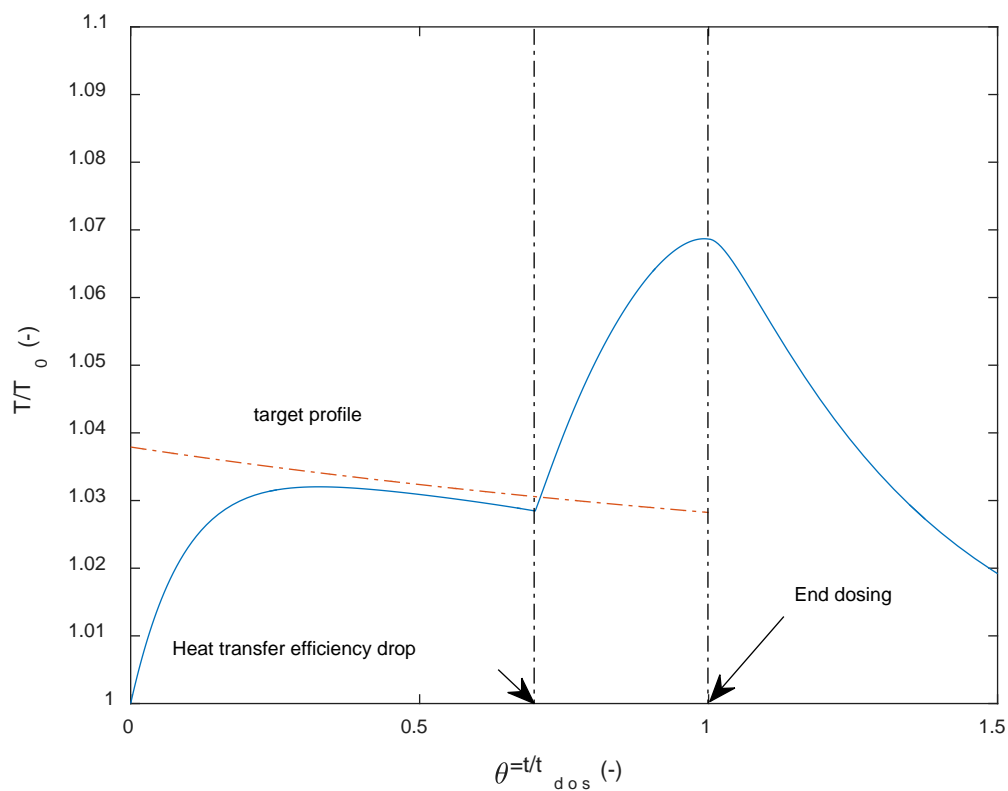


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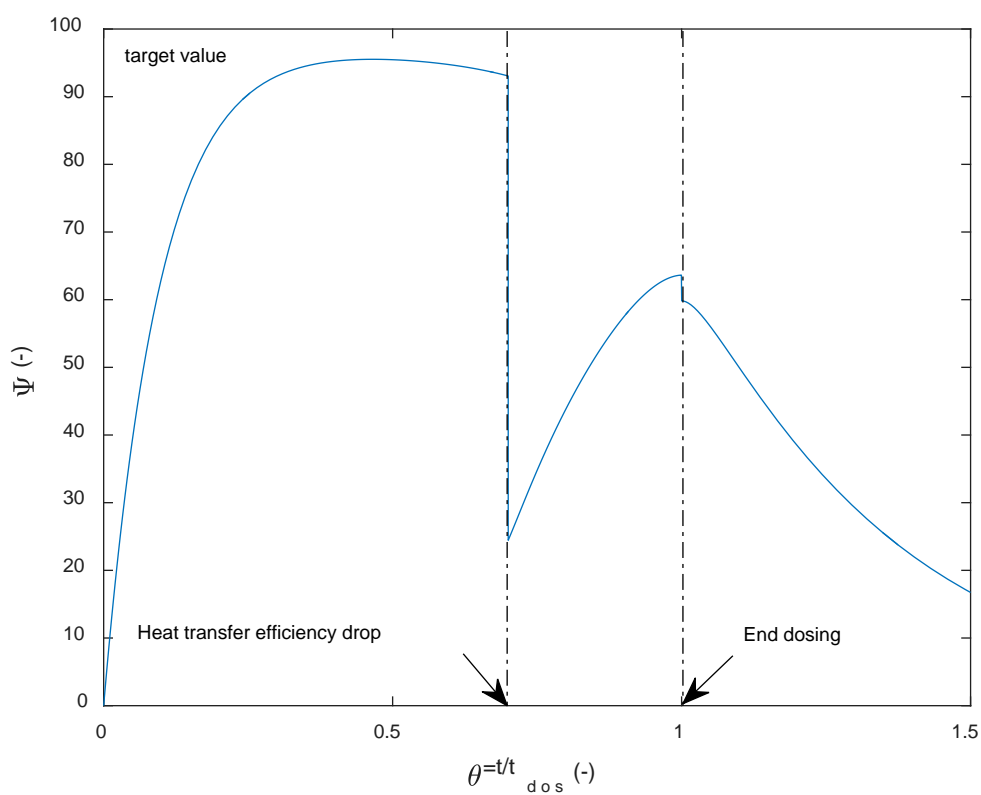


Fig. 3B

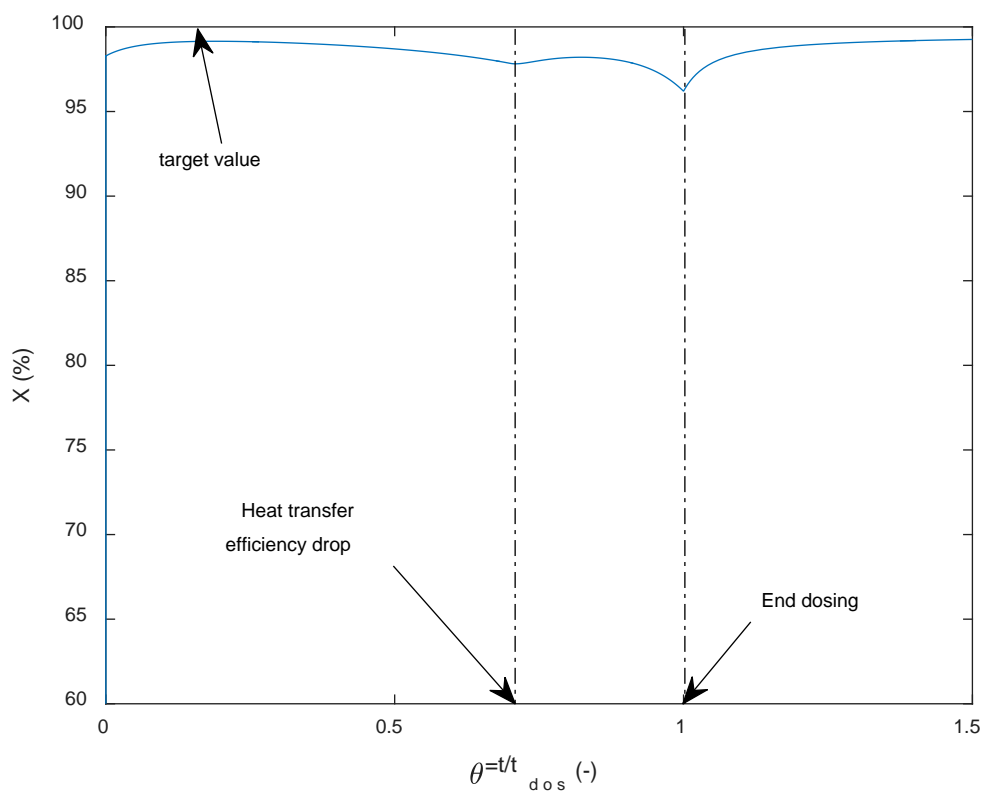


Fig. 3C

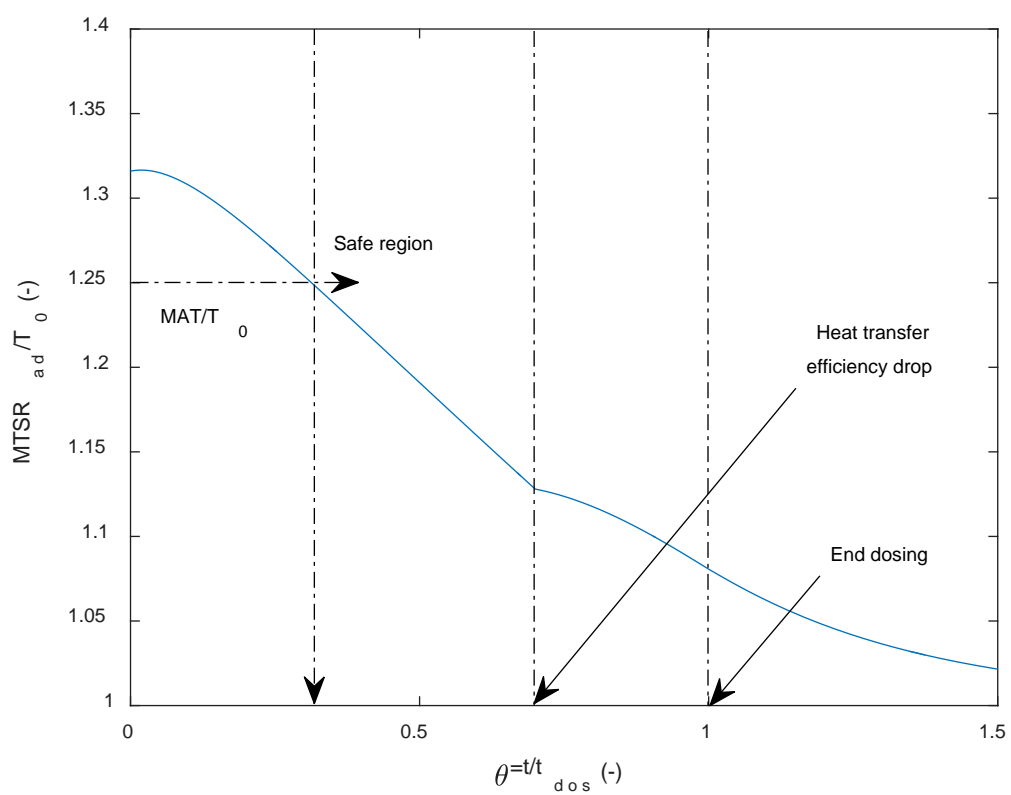


Fig. 3D

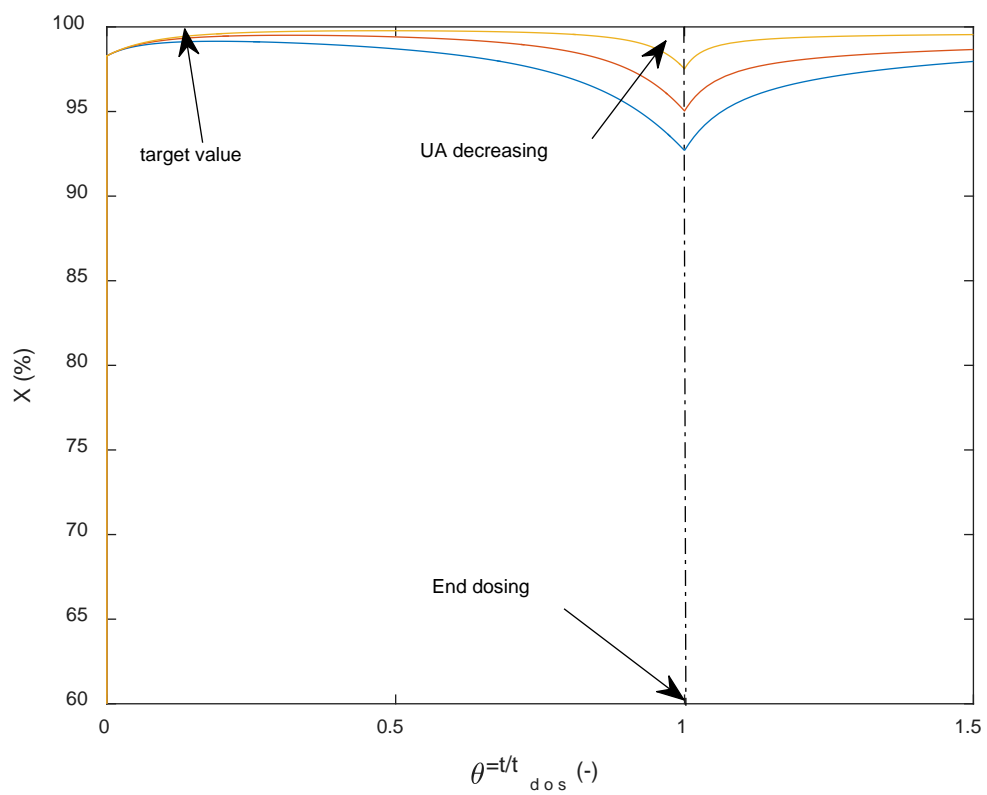


Fig. 4

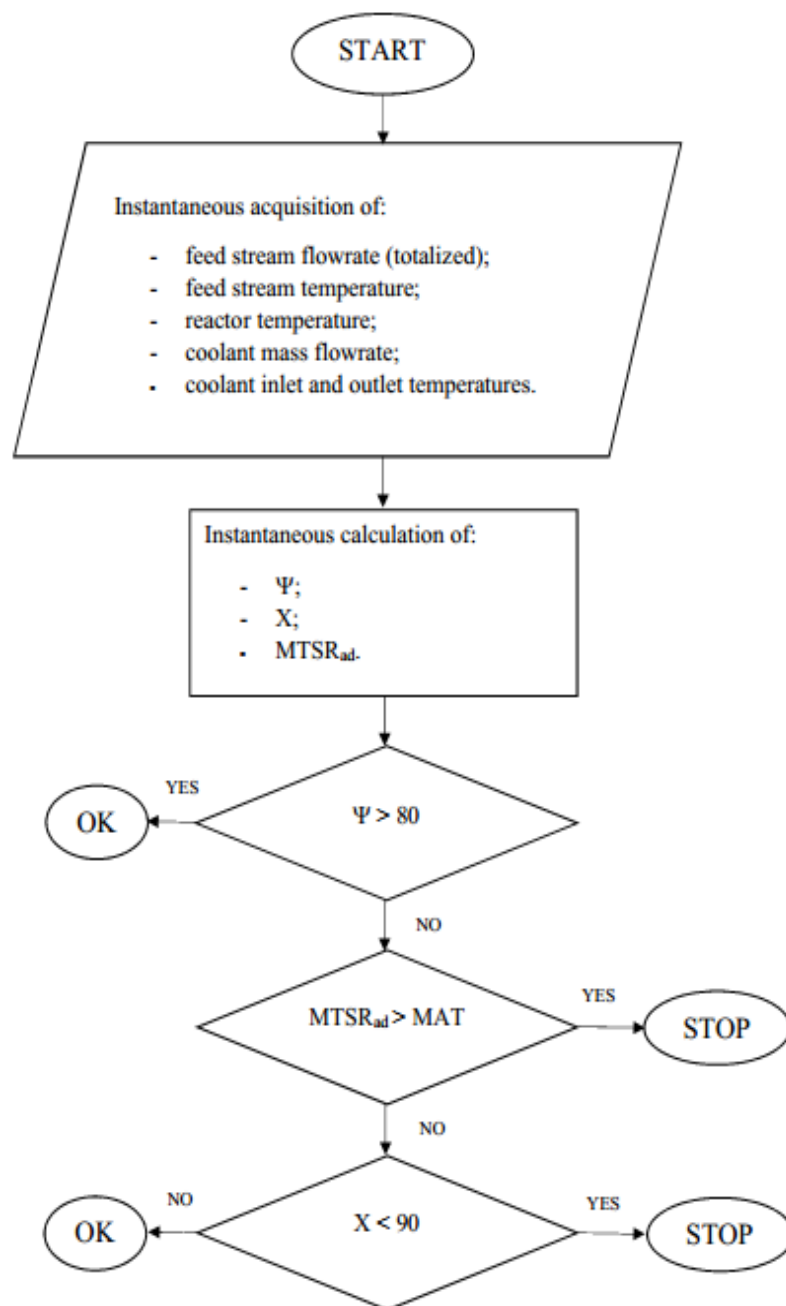


Fig. 5

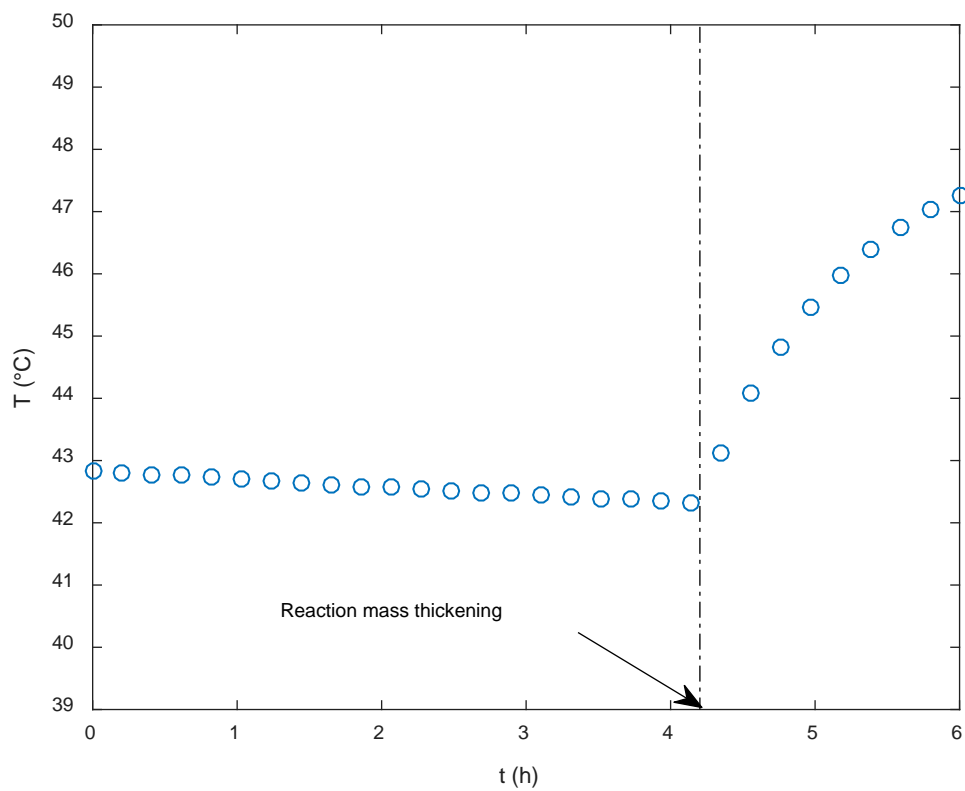


Fig. 6A

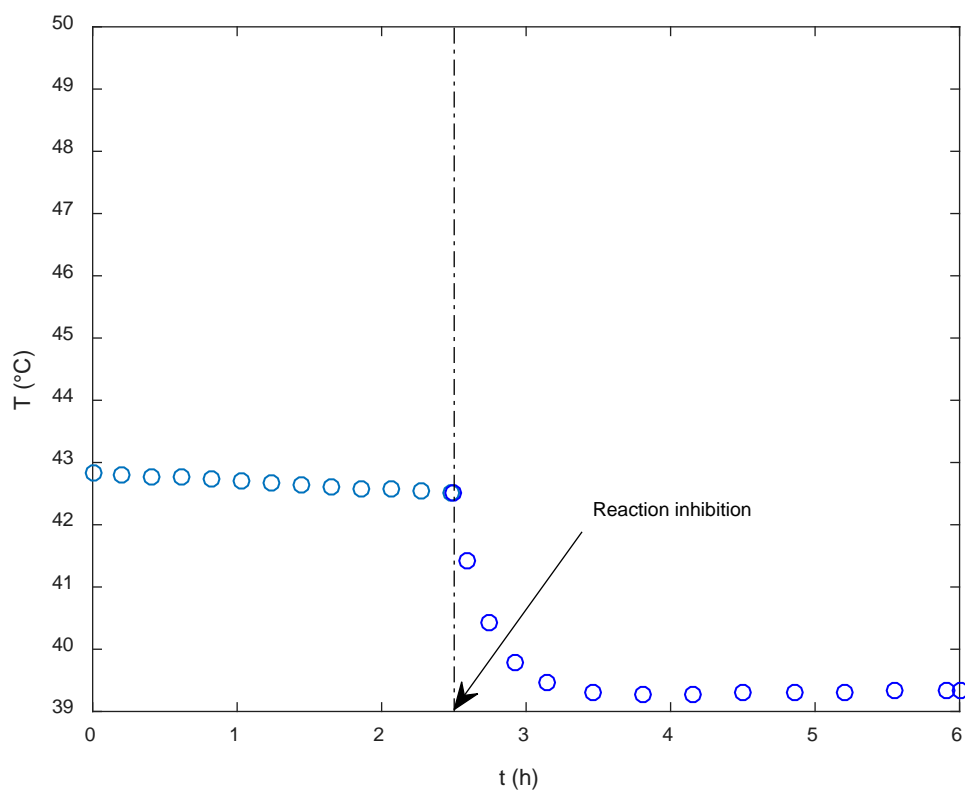


Fig. 6B

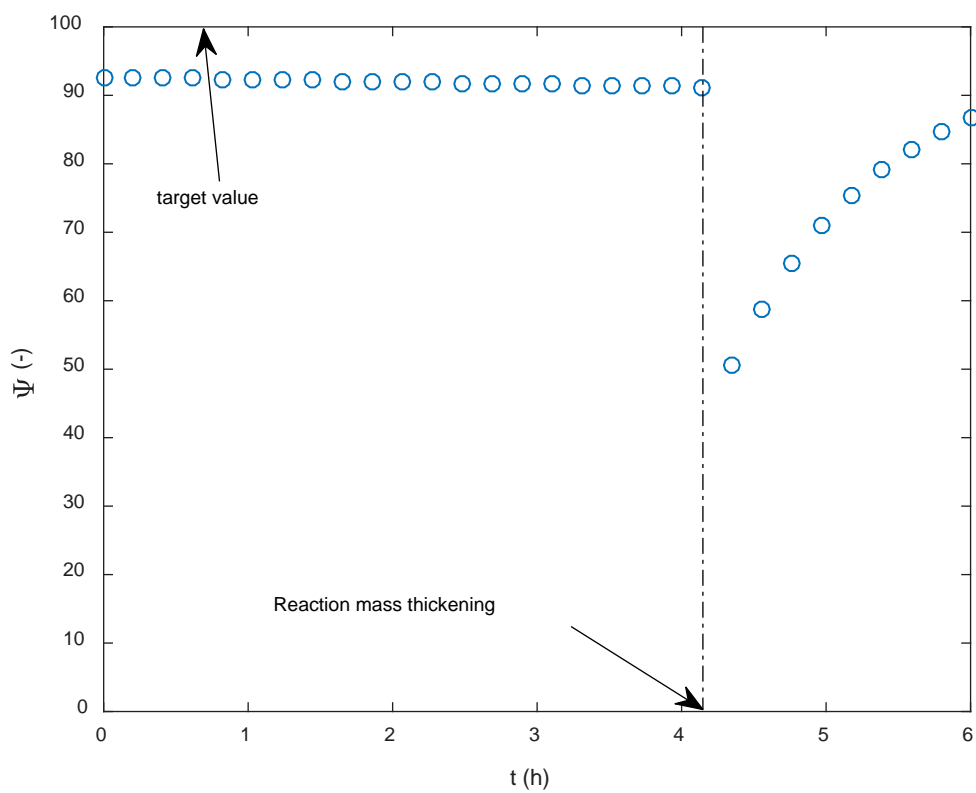


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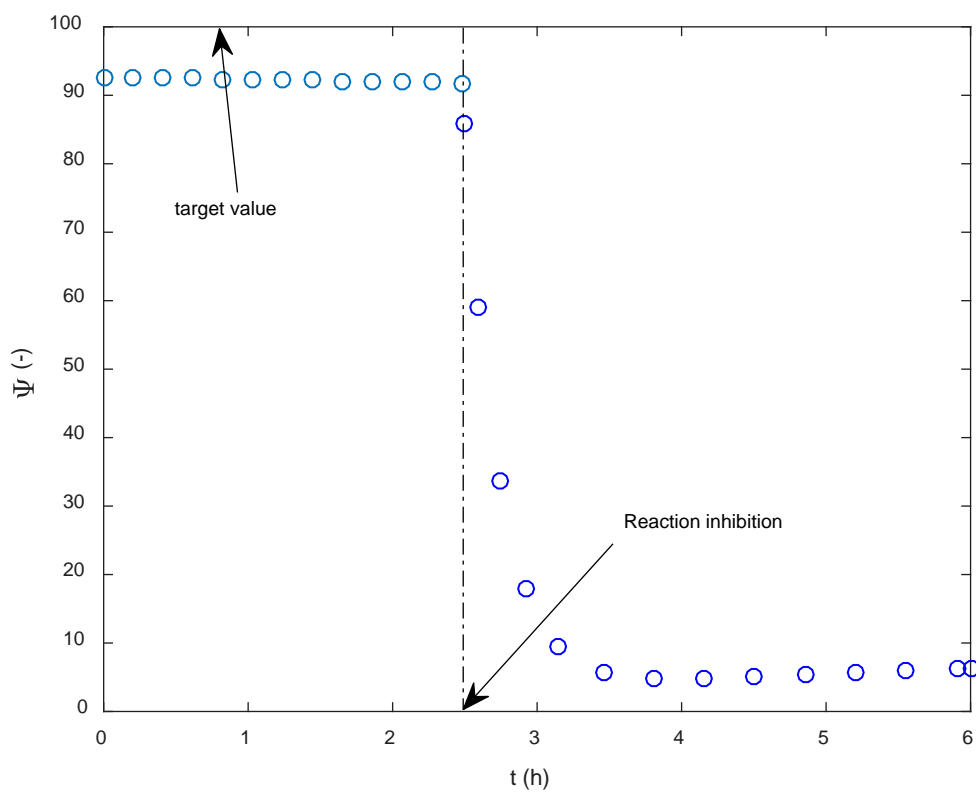


Fig. 7B

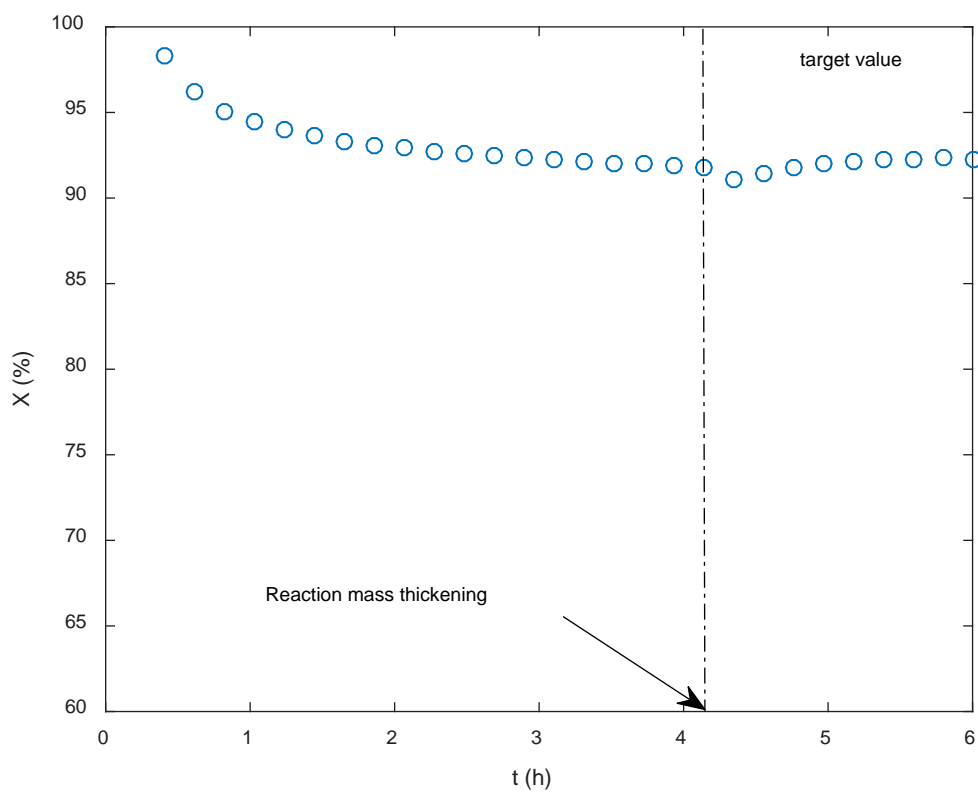


Fig. 8A

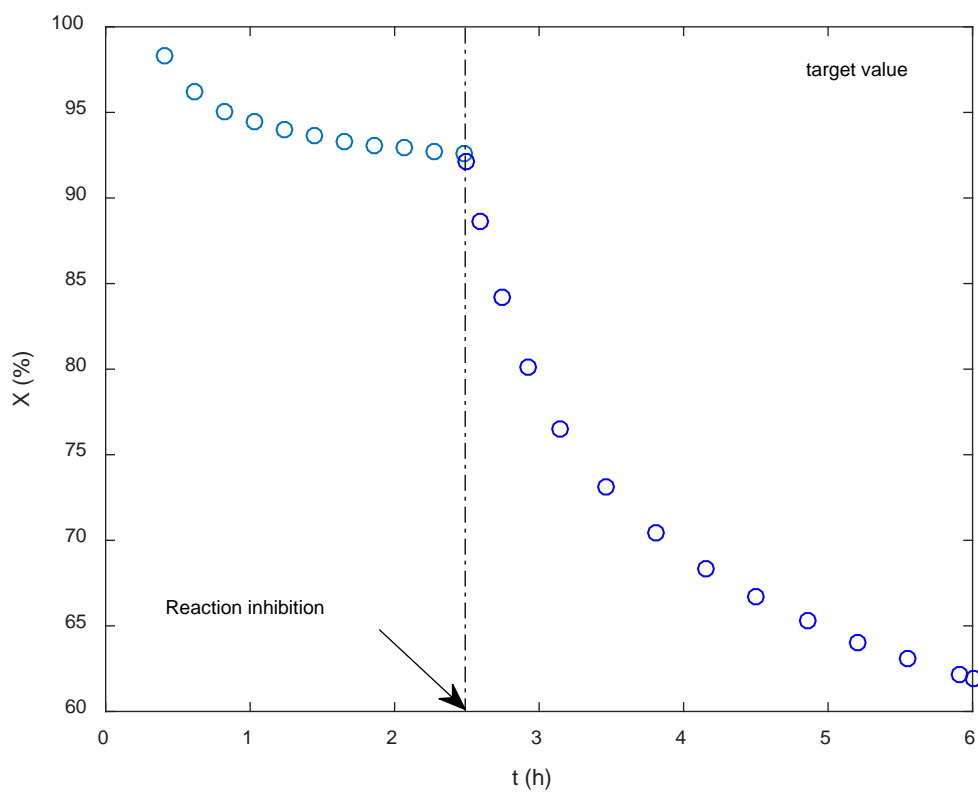


Fig. 8B

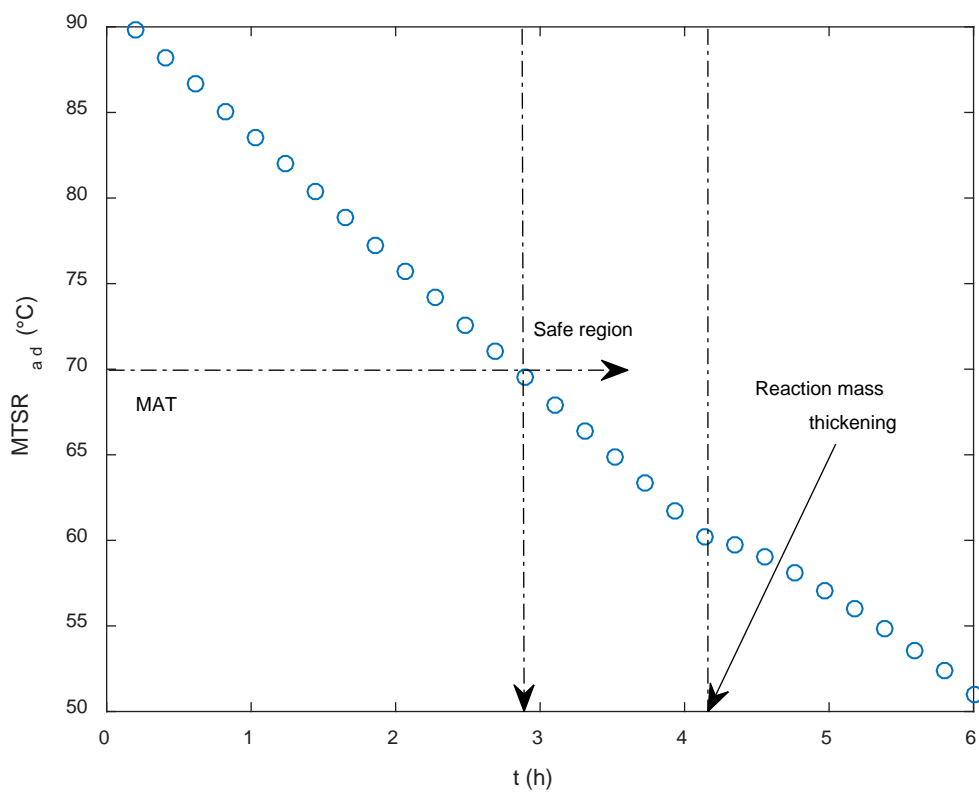


Fig. 9A

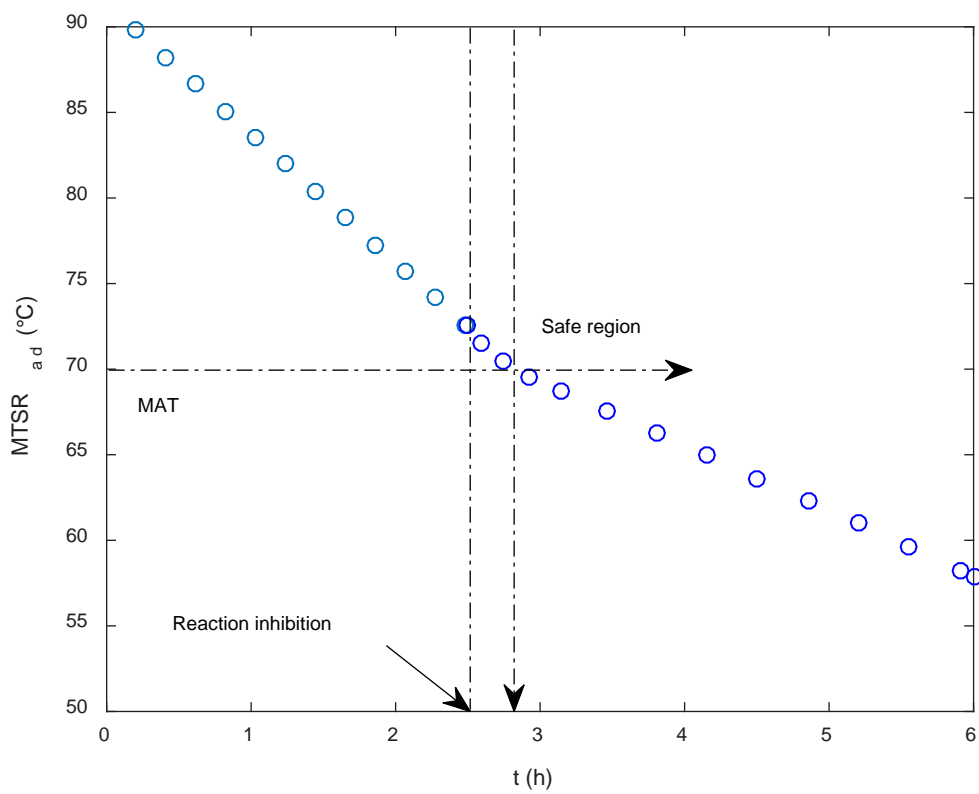


Fig. 9B

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