

Early warning monitoring of exothermic batch reactions: a kinetic-free approach.

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Abstract

In the multipurpose fine chemical industry, several performance goods are produced in the same plant at relatively low volumes: the reactor is therefore typically operated on a discontinuous campaign basis. Moreover, if the reaction is not excessively fast and exothermic, the process is often performed in the simple batch mode, according to which all the raw materials are initially loaded into the reactor and the reaction is then triggered. The monitoring of the safe operation of a batch reactor is therefore even more critical than that of a fed-batch one, because all the reactants are in contact since from the beginning.

In this work a kinetic-free approach is presented, through which the quasi-adiabatic unsafe operation of a batch reactor can be early detected before an excessive temperature peak, where an incidental scenario could occur: this allows for preventively adopting emergency actions aimed for example to quench the system or to bottom relieve the reaction mass. The proposed criterion has been validated through some industrial data of a potentially runaway reaction of the fine chemical industry, that is, the solvent-based batch polymerization of acrylic acid.

Keywords: Multipurpose Plant; Batch Reactor (BR); Thermal Explosion; Early Warning; Kinetic-Free; Moving Temperature Recording (MTR); Energy Criteria.

1. Introduction

Multipurpose processes of the fine chemical and pharmaceutical industries are normally performed on a discontinuous campaign basis, because of the relatively low volumes and high complexity of the involved products [1]. More in detail, the chemical reaction can be carried out either in the batch mode, according to which all the reactants are initially loaded in a stirred tank reactor and the reaction is then triggered, or in the semibatch mode, that is, gradually feeding one of the reactants onto a preloaded stoichiometric amount of the others: the choice between the two modes of operation is normally related to the intrinsic rate and exothermicity of the involved chemical reaction [2], which can be better controlled, if excessive, spreading the reaction heat over a sufficient time period, as occurs in a stirred tank semibatch reactor (SBR).

In general, the thermal control of both batch (BR) and semibatch (SBR) reactors in which exothermic reactions are performed can be kept if the reaction heat is removed at a much lower time scale than that at which it is evolved [3]: under such conditions, the reactor behavior is not sensitive and the temperature time-profile is pseudo-isothermal with relatively low and smooth peaks; if, however, the rate of heat release by the chemical reaction is excessive compared to the available heat removal efficiency, the reactor behavior becomes sensitive and the temperature time-profile is pseudo-adiabatic with relatively high and sharp peaks [4-5].

In the process safety literature of the last thirty years, a number of safety criteria have been developed in particular for SBRs [6-16], with the common goal of simplifying for the industrial end user the selection of safe operating conditions through the use of boundary regions or curves in a suitable dimensionless space. However, even if they do not require the solution of the mathematical model of the reactor, they still need the kinetic parameters of the system to be known, since the low-accumulation target conditions of the SBR are identified comparing the coreactant dosing time with the reaction characteristic time, which is directly linked to the reaction rate.

Since in the fine chemical industry the kinetic characterization of all the reaction processes is not feasible because of time and resources constraints, in the last years a novel approach has been developed according to which the set of safe operating conditions for a SBR can be identified through a kinetic-free approach [8,17-21], comparing the measured heat removal rate from the reactor with the expected one under target conditions. Such an approach allows for a preventive monitoring at the industrial scale of any deviation of the reactor from the normal operating regime, hence minimizing the frequency of occurrence of accidental scenarios [19].

However, there are also a number of fine chemical processes which under normal conditions can be performed in the simpler batch mode [2] which can runaway under abnormal conditions. The adoption of the batch mode of operation, whenever possible, leads sometimes to a preferred product quality than that achievable in an SBR, as occurs for a number of acrylic polymerization processes [22, 23]. When facing an incidental scenario, a BR is even more critical than an SBR, because all the reactants are in contact since the beginning.

In the process safety literature of the last twenty years, a family of criteria has been proposed [24-27], allowing for a kinetic-free early warning monitoring of both BRs and SBRs through space reconstruction techniques: however, the sensitivity of such criteria to the measurement noise of the involved process variables, leading to false alarms at the industrial scale [28], limited in some way their implementation.

Developing a simple and robust method for the early detection of pseudo-adiabatic BR conditions is therefore still of interest when dealing with potentially dangerous fine chemical reactions performed in the batch mode: such a tool would allow the process engineer for early adopting, only when needed, emergency procedures before the temperature peak is reached, where the reactor thermal control could be definitely lost [29]. These measures could be a simple cooling of the reactor if the installed heat transfer efficiency is sufficiently high or, in the most critical cases, a bottom relief of the reaction

mass towards a non-confined space, where the reaction can achieve its peak rate without causing dangerous overpressures of the containment vessel.

However, when dealing with multipurpose processes of the fine chemical industry, the lack of information about the reaction kinetics could be a limit for the development of such a criterion, in particular for BRs [17-21]: this because if the low-accumulation operating conditions of a SBR correspond to an operating regime in which the conversion rate is at the limit independent on the reaction rate itself, the operation of a BR is always determined by the rate of the chemical reaction.

In this work, on the basis of a moving temperature recording (MTR) approach, a general criterion is proposed which allows for a kinetic-free early detection of sensitive regimes of a BR after the reaction triggering. The criterion is based on two energy parameters which can be on going measured during each reaction batch through normally recorded temperatures and flowrates.

The proposed criterion has been validated against some industrial data of a batch fine chemical reaction, that is, the solvent-based polymerization of acrylic acid to produce rheology modifiers.

2. Early warning safety criterion

In order to develop a general criterion for monitoring the safe operation of an indirectly cooled BR in which an either homogeneous or heterogeneous reaction process of the type $\nu_A A + \nu_B B \rightarrow P$ is carried out, the mathematical model of the reactor must be preliminarily expressed in a suitable form.

Reactants A and B are initially loaded in fairly stoichiometric ratio, even if a slight excess of one of them (in the following referred to as reactant A) is normally adopted, in order to bring the reaction to completion in finite times.

The reactor is assumed to be equipped with measurement devices of the internal temperature, as well as of the flowrate and temperature increase of the coolant through the reactor jacket or coil: in particular a system of two or more internal thermocouples is suggested, in order to have a redundancy of a critical measurement in case of failure of one of them and to minimize the instantaneous temperature noise through averaging the signals of different devices.

The main physical properties of the reaction mass and of the coolant (that is, the average density and heat capacity) are finally supposed to be known, as well as the reaction heat.

The macroscopic energy balance for a batch reactor can be written under isoperibolic conditions in the following form:

$$(m\hat{C}_P) \frac{dT}{dt} = \dot{Q}_r - \dot{Q}_{cool} \quad (1)$$

where $\dot{Q}_r = r^{eff}V_r(-\Delta\tilde{H}_r)$ and $\dot{Q}_{cool} = UA(T - T_{cool})$.

Under thermal control operating conditions, the cooling system of the reactor counteracts at a much lower time scale the temperature increase due to the exothermic reaction, so that a pseudo-steady state behavior of the reaction temperature is reached:

$$\frac{dT}{dt} \cong 0 \Rightarrow \dot{Q}_r \cong \dot{Q}_{cool} \quad (2)$$

Therefore, after the reaction onset the reactor behavior will be pseudo-isothermal with relatively low and wide temperature peaks, as well as a low parametric sensitivity to the operating parameters [4-5]. Note that a pseudo-isothermal and non-sensitive reactor operation allows also for keeping more uniform reaction conditions with positive consequences on the product quality.

If instead the heat of reaction is evolved at an excessive rate compared with that at which the reactor cooling system can remove it, the reactor behavior will be pseudo-adiabatic with huge and sharp temperature peaks leading to the further potential triggering of dangerous events; moreover, the reactor behavior will be typically sensitive with respect to small changes of the process variables [4-5].

Along the same line discussed elsewhere for SBRs [17-21], it can be introduced also for BRs the energy parameter:

$$\Psi = \frac{\dot{Q}_{cool}}{\dot{Q}_r} \times 100 = \frac{UA(T - T_{cool})}{r^{eff}V_r(-\Delta\tilde{H}_r)} \times 100 \quad (3)$$

which ranges, during the heating phase of the reaction mass in the reactor (that is, before the temperature maximum value), from 0 to 100 and provides a direct measure of the system approach to pseudo-isothermal and non-sensitive operating conditions.

However, if for a SBR operated at low accumulation levels the reaction enthalpy contribution in equation (3) is simply proportional to the coreactant feed rate (since it determines the conversion rate), for a BR the same contribution is in any case proportional to the rate of the chemical reaction, which cannot be directly measured and which dependence on conversion and temperature is often unknown when dealing with multipurpose processes of the fine chemical industry.

When monitoring a potentially dangerous batch reaction, the lack of information about the system macrokinetics can be overcome through the measuring, at a suitable sampling frequency, of the historical temperature-time profile.

Dividing the process time in a proper number, N , of discrete intervals $[t_{j-1} \ t_j]$ (with $j=1, \dots, N$), the energy balance equation (1) of the reactor can be rewritten in the following form, where the time derivative term has been replaced with the corresponding incremental ratio:

$$(m\hat{C}_p) \frac{T_j - T_{j-1}}{t_j - t_{j-1}} \cong r_j^{\text{eff}} V_r (-\Delta\tilde{H}_r) - UA(T_j - T_{\text{cool}}) = r_j^{\text{eff}} V_r (-\Delta\tilde{H}_r) - (\dot{M}\hat{C}_p\Delta T)_{\text{cool},j} \quad (4)$$

where $T_j = T(t_j)$ and $T_{j-1} = T(t_{j-1})$, whereas $(\dot{M}\hat{C}_p\Delta T)_{\text{cool},j} = \dot{M}(t_j)\hat{C}_p (T_{\text{cool}}^{\text{OUT}}(t_j) - T_{\text{cool}}^{\text{IN}}(t_j))$ equals the heat removal rate from the system for normally negligible residence times of the coolant in the reactor jacket or coil [17].

It should be stressed that, in order to avoid numerical problems related to the random fluctuations of the temperature measurements, either the choice of the time interval or the use of a suitable smoothing procedure of the measured data is crucial.

In particular, the time interval must be wide enough to make the ratio between the maximum temperature fluctuation (due to the measurement noise) and such a time interval small enough. Possibly, when the sampling frequency is too high, therefore making the time interval too small when

compared to the temperature fluctuation values, a suitable technique for smoothing the random fluctuations (such as a moving average over a suitable number of measurements) can be used to compute the temperature values to be used in equation (4).

On the basis of a set of easy to measure process variables (that is the reactor temperature, the inlet and outlet coolant temperatures and the coolant flowrate), equation (4) allows for estimating the enthalpy contribution of the chemical reaction in the Ψ number expression (3) without a kinetic characterization of the system:

$$\Psi_j = \Psi(t_j) = \left[1 + \frac{(m\hat{C}_p)^{T_j - T_{j-1}}}{(\dot{M}\hat{C}_p\Delta T)_{cool,j}} \right]^{-1} \times 100 \quad (5)$$

As can be noticed from equations (1), (3), and (5), in any temperature increasing time interval before each temperature peak, Ψ directly provides the extent at which the reaction enthalpy contribution splits between the heating of the reaction mass and the heat removal through the coolant. In particular, if almost all the reaction heat goes into heating of the reaction mass, the reactor behavior tends to be pseudo-adiabatic and sensitive: in this case Ψ is at the limit equal to zero, since the $(\dot{M}\hat{C}_p\Delta T)_{cool,j}$ term in equation (5) tends to zero as well. If instead the reaction heat is at the limit entirely removed at a much lower time scale through the cooling system, the reactor behavior tends to be pseudo-isothermal with a relatively low sensitivity with respect to the process and plant parameters: in this case Ψ is close to 100, since the $(m\hat{C}_p)^{T_j - T_{j-1}}$ term in equation (5) becomes negligible. At the temperature peak Ψ reaches the value of 100.

The on-going monitoring of the Ψ trend before a temperature peak is therefore a tool for early recognizing the evolution of the reactor towards a potentially dangerous temperature-sensitive regime, so that suitable emergency actions can be triggered, such as a sudden reactor cooling, a quenching of the reaction through an inhibitor shot, or a bottom relief of the reaction mass.

As shown in the following section, for moderately fast reactions (which are suitable to be carried out in the batch mode), the time interval between the reaction onset and the temperature peak is normally quite wide under both normal and upset operating conditions thanks to the initially limited self-heating rates of the system. In this case, the monitoring of the reactor through Ψ is effective and the needed emergency actions can be triggered in a suitable time period, hence minimizing the frequency of intervention of the pressure relief system protecting the reaction vessel. However, if for a given accidental scenario the time interval between the reaction onset and the temperature peak becomes too narrow, the present criterion cannot be considered a suitable basis of safety [29] in order to early detect the anomalous operating regime of the reactor.

In the temperature decreasing intervals after a temperature peak, Ψ would be higher than 100: however, the monitoring of Ψ in such intervals is not relevant from the safety point of view, since the heat removal contribution through the coolant is here higher than the heat release due to the chemical reaction.

In order to separate the low- Ψ region (where the reactor behavior is pseudo-adiabatic) from the high- Ψ region (where the reactor behavior is pseudo-isothermal), a Ψ value of 50 can be proposed. According with expression (5), at such a Ψ value the reaction heat contribution equally splits between the heating of the reaction mass and the heat removal from the system through the coolant.

Such a threshold value is consistent with the requirement that a safe BR behavior is characterized, during the heating period, by the condition [4,5]:

$$\frac{d^2T}{dt^2} \leq 0 \quad (6)$$

By deriving once more the time derivative of the temperature as given by the right-hand side of equation (1), together with the relations $\dot{Q}_r = r^{\text{eff}}V_r(-\Delta\tilde{H}_r)$ and $\dot{Q}_{\text{cool}} = UA(T - T_{\text{cool}})$, we can obtain the following relation:

$$\frac{d^2T}{dt^2} = \left(\frac{E}{RT^2} \frac{n_{B0}/v_B(-\Delta\tilde{H}_r)}{m\hat{C}_p} \frac{v_B r^{\text{eff}}}{C_{B0}} t_R - \frac{UA}{m\hat{C}_p} t_R \right) \frac{1}{t_R} \frac{dT}{dt} = \left(\frac{BDa}{St} - 1 \right) \frac{St}{t_R} \frac{dT}{dt} \quad (7)$$

In equation (7) $B = \Delta T_{ad} E / RT^2$ is the thermal reaction number, describing the thermal hazard potential of the reaction: in particular, through the B parameter the influences of the thermodynamic (ΔT_{ad}) and kinetic (E/R) parameters on the temperature dependence of the reaction rate are lumped; $Da = t_R v_B r^{eff} / C_{B0}$ is instead the Damköler number, relating the process characteristic time, t_R , to the kinetic time constant of the reaction (note that for batch reaction processes t_R is arbitrarily defined as the time period going from the initial loading of the reactants to the instant at which a given conversion value is reached [2]); finally, $St = t_R UA / m \hat{C}_p$ is the modified Stanton number, relating the process characteristic time (directly linked to the reaction heat evolution) to the characteristic time of the reactor cooling system.

Since in equation (7) both $St > 0$ and $t_R > 0$, and during the heating period also $dT/dt > 0$, the constraint (6) for safe conditions leads to:

$$\frac{BDa}{St} = \frac{100}{\Psi} \frac{(T - T_{cool}) E}{RT^2} \leq 1 \quad (8)$$

that is:

$$\Psi \geq 100 \frac{(T - T_{cool}) E}{T^2 R} \quad (9)$$

Since, as a reasonable order of magnitude for organic syntheses [2,10] it can be assumed: $T \cong 300K \Rightarrow T^2 \cong 10^5 [K^2]$, $E/R \cong 10^4 [K]$, and $T - T_{cool} \cong 5 [K]$, the requirement for safe BR conditions becomes $\Psi \geq 50$.

It must be noticed that the selection of 50 as a separation Ψ value between pseudo-adiabatic and pseudo-isothermal conditions is in any case arbitrary, even if it is supported by the order of magnitude analysis above in which the parameters used are valid for most of the organic reactions performed in the batch mode [2,10]. This holds true for any safety criterion in which the actual regime of a discontinuous reactor is compared with a target one: for the sake of example the 5% overestimation in the target temperature definition for SBRs can be mentioned [10], as well as the lower limit value of Ψ equal to 80 in the kinetic-free early warning criteria for SBRs [17-19].

In any case, the most suitable lower limit of Ψ can be better finetuned in this case from a statistically meaningful set of pseudo-isothermal batches with the corresponding Ψ trends.

It is finally worth stressing that the kinetic information mentioned in the order of magnitude analysis above are not at all related to the use of the presented criterion, which is kinetic-free: such information must be just intended as typical E/R values for typical organic reactions performed in stirred batch reactors [2,10], in order to estimate a general separation Ψ value between pseudo-isothermal and pseudo-adiabatic conditions.

As will be evident from the industrial data presented in the following section, considering that at the temperature peak Ψ reaches in any case 100, the pseudo-adiabatic trend of Ψ is typically characterized by a sharp decreasing behavior down to a relatively low minimum value, followed by a steep increase to 100 in a very short time period just before the peak. Such a step change in the slope of the Ψ trend is instead not present in the pseudo-isothermal cases.

When a pseudo-adiabatic behavior of the BR is detected, one can also decide to discriminate a really dangerous situation from a simpler loss of temperature control without any meaningful consequences from a safety point of view. This can be done by comparing the maximum temperature of the synthesis reaction under adiabatic conditions (M_{TSR_{ad}}, that is, the final temperature the system would reach if from that time on the residual conversion took place without any heat removal) to the Maximum Allowable Temperature (MAT).

Along the same line presented elsewhere in the literature for a SBR [19], the integral form of equation (1) provides the reaction extent, X, as a function of the same process data and information used for calculating Ψ :

$$X = \frac{(m\hat{C}_P)(T-T_0) + \int_0^t (\dot{M}\hat{C}_P\Delta T)_{cool} dt}{\frac{n_{B0}}{v_B}(-\Delta\hat{H}_r)} \times 100 \quad (10)$$

Equation (10) states that the energy corresponding to the conversion reached at any time splits between the heating contribution of the reaction mass from T_0 to T and the overall heat removed through the coolant.

The maximum temperature the reactor would reach if the residual conversion occurred under adiabatic conditions can be estimated as:

$$\text{MTR}_{\text{ad}}(t_j) = T_j + \Delta T_{\text{ad}}(1 - X_j/100) \quad (11)$$

Such a value can be compared with the MAT value, which is typically related to safety or product quality constraints.

If after the reaction onset the Ψ values are at any time in the range 50÷100, with a trend smoothly increasing towards 100, the reactor behavior is expected to be pseudo-isothermal, with a limited excursion above the initial temperature, therefore leading to more stable reaction conditions and a more uniform quality of the final product.

If after the reaction triggering a decreasing trend of Ψ is detected down to values below 50, the operating regime of the BR is expected to be pseudo-adiabatic and sensitive with respect to the plant and process variables. In such a regime, closer to an adiabatic than to an isothermal reactor behavior, the maximum temperature reached by the system can be conservatively estimated through the MTR_{ad} value computed at any time through equation (11) using the same process variables and information used for calculating Ψ . If at the time at which a Ψ value below 50 is detected the corresponding MTR_{ad} is higher than the MAT, the reaction temperature evolution is potentially dangerous and proper emergency actions must be early triggered.

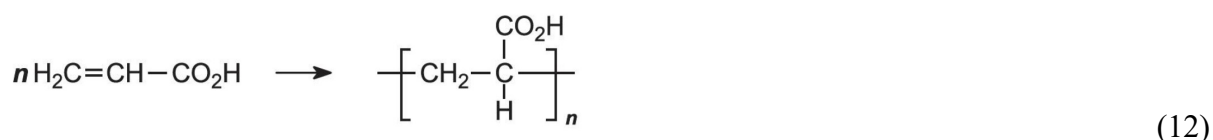
The described procedure provides therefore a criterion for early identifying potentially dangerous scenarios during a batch reaction process, also limiting false alarms which would affect the plant productivity.

Moreover, through the moving recording approach of the reactor temperature, the proposed criterion does not require a previous characterization of the system kinetics, even if the operation of a BR is

intrinsically determined by the reaction rate. Such a result is of particular importance when dealing with multipurpose processes of the fine-chemical industry, for which a full kinetic characterization is often unavailable because of time and resources constraints [17-21].

3. Case study: acrylic batch polymerization

The criterion presented in the previous section has been validated through a set of industrial data collected during the scale-up activity of a potentially dangerous batch reaction of the fine chemical industry, that is, the solvent-based polymerization of acrylic acid to produce a widely used class of rheology modifiers for cosmetic and pharmaceutical applications [30,31]:



In equation (12) the role of minor amounts of polyallylic crosslinkers has not been represented even if they can influence the final polymer performance, their contribution to the energy behavior of the polymerization process can be neglected.

The reaction, evolving a polymerization heat of 1075 kJ per kg of acrylic acid [30], can be performed in aromatic, cycloaliphatic or in ester type solvents, depending on the rheology characteristics of the final product and on the compatibility of the residual solvent in the final application of the product itself [23].

The process can be carried out either under fully batch conditions or in the fed-batch mode, according to which almost all the monomer is gradually fed to an initial reaction volume. The two modes of operation lead however to different characteristics of the final product, so that in many cases the selection of the batch mode of operation is driven by product quality constraints [22,23].

When performing acrylic polymerizations, the reactor must be carefully deoxygenated, not only to prevent the formation of explosive vapor mixtures, but also because even traces of oxygen activate

the inhibitor contained in the monomer (typically, hydroquinone monomethyl ether), hence preventing the radical polymerization of acrylic acid from starting.

In order to limit the increase of viscosity during the process and hence to keep a satisfactory heat removal efficiency from the reaction mass, acrylic acid concentrations ranging from 9 to 12% w/w are normally adopted [22].

The polymerization temperature depends instead on the free radicals production rate of the organic peroxide selected as a catalyst: in this case 2,2'-azobis (2,4-dimethyl valeronitrile) of Wako, referred to as ADVN, has been used, to which polymerization temperatures ranging from 40 to 50°C correspond.

This does not allow in most cases for performing the reaction under reflux conditions, since the boiling points of a number of solvents used are higher than 40°C and operating the reactor under reduced pressure is not suitable because of the inhibition effects of the possible air intake.

Once the reactants have been loaded into the reactor previously purged with nitrogen and the system has been brought to the initial polymerization temperature, the catalyst is normally added in one shot. The polymerization of acrylic acid starts in the monomer-rich solvent phase and, after roughly 1% conversion has been reached [31], the polymer precipitates from the solvent as a dispersed phase where the polymerization of the monomer then occurs. The reduced mobility of the living chains in the polymer phase leads to a progressive decrease of the rate of the termination reactions, to which the typical self-accelerating kinetic behavior of such systems corresponds. The increase of the polymer volume fraction is finally characterized by a significant rise of the reaction mass viscosity, which typically reaches a peak close to 90% conversion values [31], with a corresponding huge decrease of the heat transfer efficiency.

In this case, the reaction was performed using a toluene-based recipe in a 20m³ batch reactor, equipped with a wide anchor-type stirrer (see Figure 1): the selection of such a solvent system allowed to perform all the scale-up trials under intrinsically safe conditions, according to which the maximum

attainable temperature even under adiabatic conditions could never reach the reaction mass boiling point (close to 110°C at atmospheric conditions). Therefore, even under pseudo-adiabatic conditions, the reaction had never to be inhibited. However, since the reaction in question is often performed using lower boiling point solvent systems (such as cyclohexane/ethyl acetate mixtures boiling slightly below 80°C), the early detection of a pseudo-adiabatic reactor behavior is in these cases of great importance to prevent potentially severe industrial accidents such as those described in the process safety literature for this reaction process [32].

In the trials considered in this work, the reactor was filled with 17m³ of a solution of acrylic acid in toluene, to which a final polymer concentration of about 10% w/w corresponds; a catalyst concentration of about 1.8 mmol/L has been used with a seven hours process time. The polymerization heat has been removed through cooling water, which temperature has been set just after the polymerization onset at 40°C, and to 30°C after 15' to control the heat of reaction.

As represented in Figure 1, the reactor was equipped with two Pt-100 thermocouples, which signals have been averaged in order to reach a temperature measurement accuracy of about 0.05°C. Moreover, the coolant flowrate, as well as its inlet and outlet temperatures, have been also measured. In Figure 1, the simple algorithm for calculating the instantaneous Ψ value from the aforementioned temperatures and flowrates has been also represented using the conventional P&Id symbols.

In Figure 2A the measured reaction temperature values under normal conditions is plotted, showing a peak close to 50°C occurring 1.7 hours after the reaction ignition, while Figure 2B shows the trend of the instantaneous heat removal rate, $\dot{Q}_{cool} = (\dot{M}\hat{C}_p\Delta T)_{cool}$. Moreover, through equation (10) the monomer conversion can be also calculated, generating the trend plotted in Figure 2C.

From the measured values of both the reaction temperature and the heat removal rate, the trend of Ψ has been computed through equation (5) and it is reported in Figure 2D.

It can be noticed from Figure 2D that, under normal conditions, after the reaction triggering Ψ starts from relatively high values, smoothly reaching 100 at the temperature peak. This confirms that the

reactor operating regime can be classified as pseudo-isothermal with a relatively low sensitivity to the plant and process parameters: such a conclusion is also consistent with the relatively low and wide temperature peak represented in Figure 2A.

Note that only the Ψ values after the reaction ignition have been reported, as previously discussed: in particular, the monitoring of Ψ was started in this case once an increasing temperature was detected after the coolant temperature step-change from the initial 40°C to the intermediate 30°C in order to counteract the peak of the reaction heat evolution. The increasing temperature behavior was for instance detected by the electronic device used comparing the $T_j - T_{j-1}$ difference with a lower limit input value, which was set up to 0.2°C according with a declared accuracy of the installed thermocouples equal to 0.1°C. This is the reason why in Figure 2D the monitoring of Ψ starts at $t=0.7$ h, that is the time at which the temperature time trend represented in Figure 2A starts increasing after the cooling temperature step-change from 40°C to 30°C, occurring 10' after the catalyst addition. Starting from these process conditions, the values of the catalyst concentration, of the monomer to solvent ratio and of the coolant temperature has been changed to investigate the sensitivity of the system with respect to their accidental variations.

In particular, an overloading of the catalyst of a factor up to three would bring the catalyst concentration to the values adopted in the laboratory scale recipe, that is 5.5 mmol/L. Such a scenario could occur because of a mistake in the preparation of the catalyst solution in toluene, taking also into account its relatively small amounts (of the order of 5 g per kg of monomer [30]). Moreover, the reactivity of the system can vary even with the same catalyst concentration because of the inhibition level of the monomer used and of the effectiveness of the initial deoxygenation process of the reactor depending, among the others, on the purity of the purging nitrogen itself. Performing trial batches at different catalyst concentrations below that adopted in the laboratory recipe, allowed also for optimizing such a parameter at the industrial scale, where the system reactivity must be normally limited because of the lower heat transfer efficiency of the full-scale reactor.

The second accidental scenario tested at the plant scale was the monomer overloading. Before each batch, the monomer is in fact previously loaded in a 2m³ tank discharging by gravity into the reactor (see Figure 1). The monomer amount per batch is controlled through the weight of the tank, installed on loading cells, which, however, have a not negligible maloperation frequency. In any case the tank is equipped with an overfull system preventing the loading of the tank itself with acrylic acid volumes higher than 1750 L, that is 25% higher than the amount normally used in each reaction batch: this is the reason why a monomer overloading up to 25% has been considered as a credible scenario. Under such conditions the final monomer concentration would reach 12.5% w/w.

The third considered accidental scenario was instead the maloperation of the temperature control system of the coolant, according to which the programmed decrease of its temperature from 40°C to 30°C after the reaction onset fails to occur and the initial system temperature of 40°C is therefore kept all along the process.

In Figures 3 to 5 the trends of the reaction temperature and the corresponding Ψ number for the three accidental scenarios are represented.

It can be noticed that in all the accidental cases a much higher and sharp temperature peak is reached in a shorter time period, that is 0.5 h in the worst case (see Figure 3A) vs. the 1.7 h for the normal operating conditions (see Figure 2A). In particular, the peak temperature is in any case close or higher than 80°C, which is the MAT value for this process because of product quality constraints. As can be noticed from Figures 3B to 5B, the Ψ trend undergoes after the reaction onset a decrease down to values lower than 50, to increase then suddenly up to 100 near to the temperature peak. Moreover, as soon as the decreasing Ψ trend below 50 is detected, the local $MTSR_{ad}$ values in Figures 3B to 5B are higher than the MAT value, which makes the reactor regime potentially dangerous.

As mentioned before, the presented criterion can be considered a basis of safety to prevent a dangerous scenario if even under incidental conditions the time going from the reaction onset to the peak conditions is sufficient to trigger the required emergency actions. For the reaction system in

question, such a time interval never fell below 10', allowing for example to trigger the reactor emergency cooling or the quench of the system through the inhibitor bomb, or to transfer the reaction mass to an emergency bigger vessel through a 100m³/h centrifugal pump.

4. Conclusion

A number of reaction processes of the fine chemical and pharmaceutical industry are performed in the batch mode of operation, being under normal conditions sufficiently slow to be controlled through the installed heat transfer efficiency.

However, even for such systems accidental scenarios can occur leading to a self-accelerating behavior of the reaction temperature and potentially dangerous events, such as a reaction vessel overpressurization or the triggering of side or decomposition reactions.

Therefore, the monitoring of a pseudo-adiabatic reactor regime is of interest for batch reactors, where all the reactants are in contact since from the beginning and a limited number of emergency actions can be adopted to quench the system.

Moreover, when dealing with multipurpose processes of the fine chemical industry the kinetic characterization of the reaction system is often unavailable: such a limitation is even more critical when dealing with batch reactors, which behavior is always influenced by the reaction rate.

In this work, on the basis of a time recording of the reaction and cooling temperature together with the coolant flowrate, a kinetic-free criterion has been presented allowing for detecting dangerous operating regimes of a batch reactor.

The criterion has been tested against some industrial data of a batch reactor, where the solvent-based polymerization of acrylic acid was performed.

Nomenclature

A	heat transfer surface, m ²
A	reactant A
B	= $\Delta T_{ad}E/RT^2$, thermal reaction number, -
B	reactant B (limiting reactant)
C	molar concentration, kmol/m ³
\tilde{C}_p	molar heat capacity at constant pressure, kJ/(kmol·K)
\hat{C}_p	mass heat capacity at constant pressure, kJ/(kg·K)
Da	= t_R/t_r , Damköhler number, -
E	activation energy, kJ/kmol
F	molar flowrate, kmol/s
m	mass, kg
\dot{M}	mass flowrate, kg/s
MAT	maximum allowable temperature, °C
MTR	moving temperature recording
MTSR	maximum temperature of the synthesis reaction, °C
n	number of moles, kmol
P	reaction product
\dot{Q}	heat duty, kW
r	reaction rate, kmol/(m ³ ·s)
R	gas constant, =8.314 kJ/(kmol K)
St	= $UA t_R/m\hat{C}_p$, Stanton number, -
t	time, s (or other units, where specified)
T	temperature, °C
ΔT_{ad}	= $\frac{n_{B,0}/v_B(-\Delta\tilde{H}_r)}{m\hat{C}_p}$, adiabatic temperature rise, °C
ΔT_{cool}	= $T_{cool}^{OUT} - T_{cool}^{IN}$, coolant temperature rise, °C
U	overall heat transfer coefficient, kW/(m ² K)
V	volume, m ³

Subscripts and superscripts

ad	adiabatic
A	reactant A
B	reactant B (limiting reactant)
cool	coolant
dos	dosing
eff	effective
I	initiator (catalyst)
IN	inlet
j	j-th time
M	monomer
OUT	outlet
r	reaction
R	reference
0	initial

Greek symbols

$\Delta\tilde{H}$	reaction enthalpy, kJ/kmol
ΔT	temperature rise or difference, °C
ν	stoichiometric coefficient, -
X	X number, -
Ψ	Ψ number, -

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Captions to the figures

Fig. 1

Industrial batch polymerization of acrylic acid: reactor monitoring system and operating algorithm.

Fig. 2

Industrial batch polymerization of acrylic acid under normal operating conditions ($C_{M0}=1.2 \text{ kmol/m}^3$, $C_{I0}=1.8 \text{ mmol/L}$, $T_{\text{cool}}=30^\circ\text{C}$ from $t=15'$ to $t=2.5 \text{ h}$ and 40°C elsewhere): (A) reactor temperature vs. time; (B) heat removal rate vs. time; (C) calorimetric conversion vs. time; (D) Ψ number vs. time.

Fig. 3

Industrial batch polymerization of acrylic acid under upset operating conditions due to a catalyst overloading ($C_{M0}=1.2 \text{ kmol/m}^3$, $C_{I0}=5.4 \text{ mmol/L}$, $T_{\text{cool}}=30^\circ\text{C}$ from $t=15'$ to $t=2.5 \text{ h}$ and 40°C elsewhere): (A) reaction temperature vs. time; (B) Ψ number vs. time.

Fig. 4

Industrial batch polymerization of acrylic acid under upset operating conditions due to a monomer overloading ($C_{M0}=1.5 \text{ kmol/m}^3$, $C_{I0}=1.8 \text{ mmol/L}$, $T_{\text{cool}}=30^\circ\text{C}$ from $t=15'$ to $t=2.5 \text{ h}$ and 40°C elsewhere): (A) reaction temperature vs. time; (B) Ψ number vs. time.

Fig. 5

Industrial batch polymerization of acrylic acid under upset operating conditions due to a cooling system failure ($C_{M0}=1.2 \text{ kmol/m}^3$, $C_{I0}=1.8 \text{ mmol/L}$, $T_{\text{cool}}=40^\circ\text{C}$ at any time): (A) reaction temperature vs. time; (B) Ψ number vs. time.

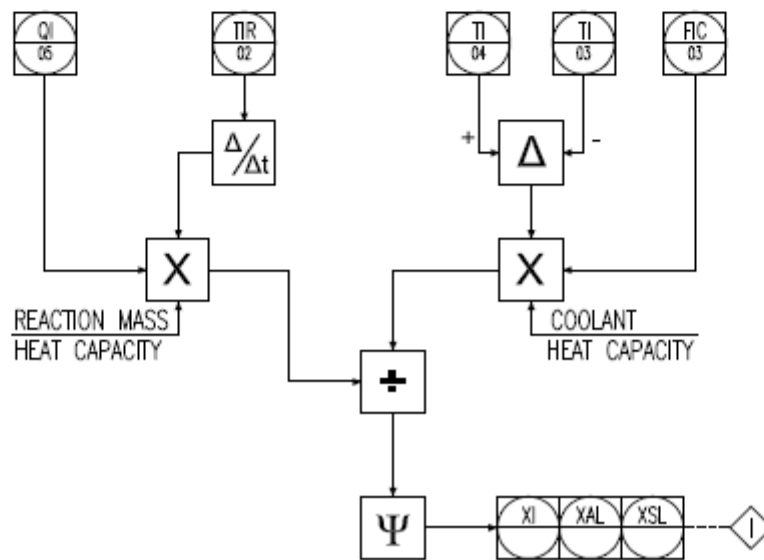
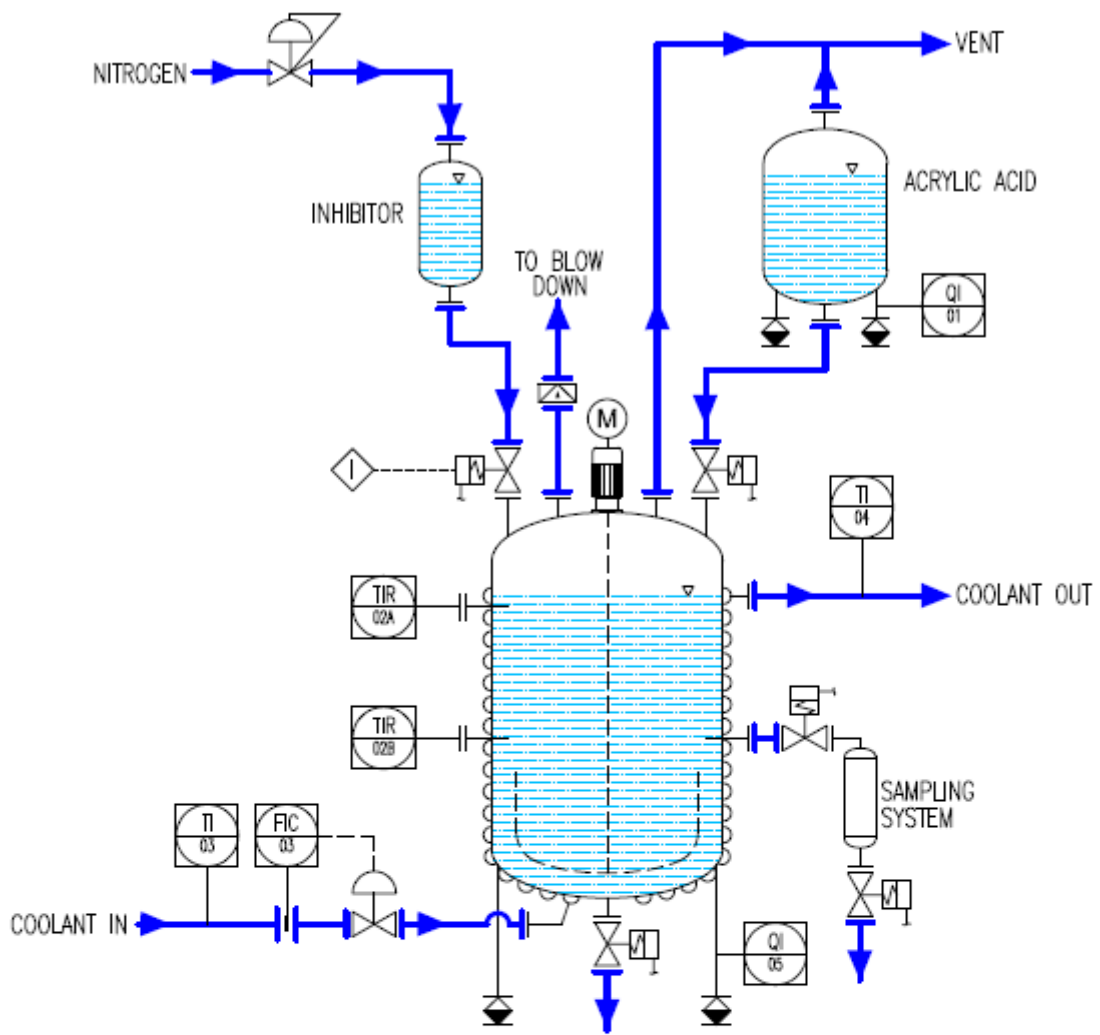


Fig. 1

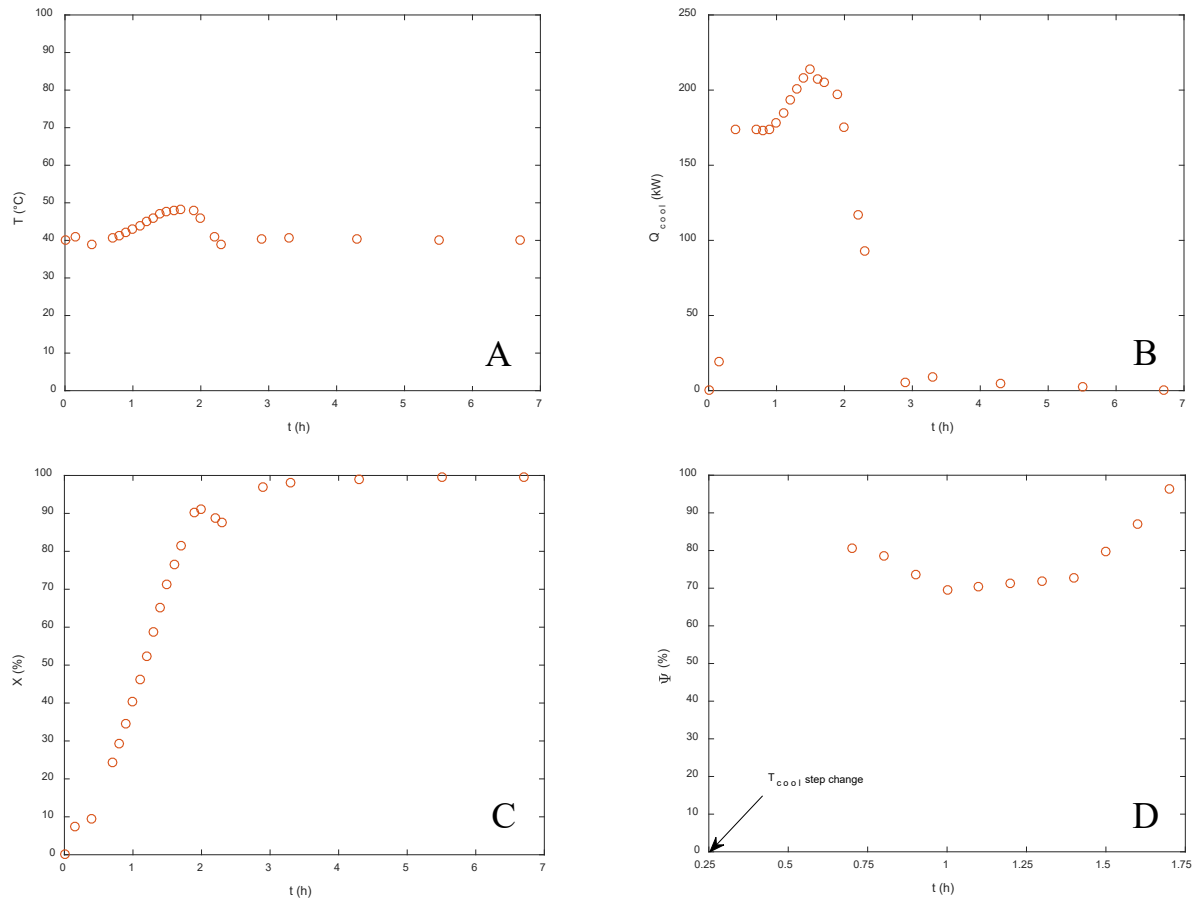


Fig. 2

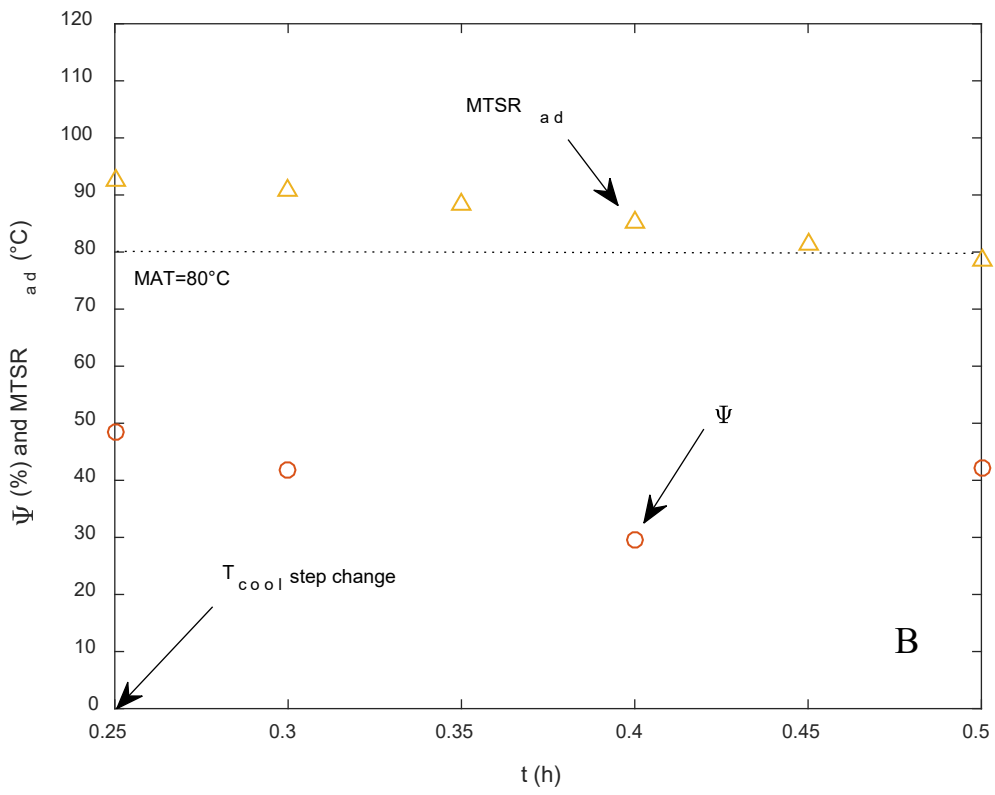
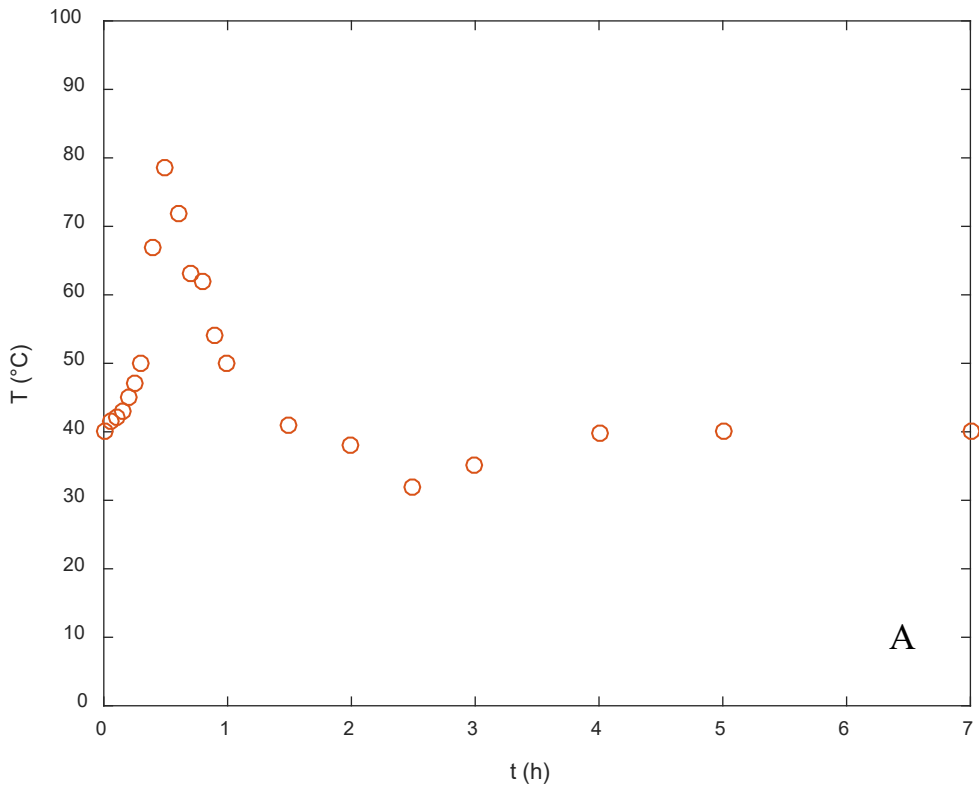


Fig. 3

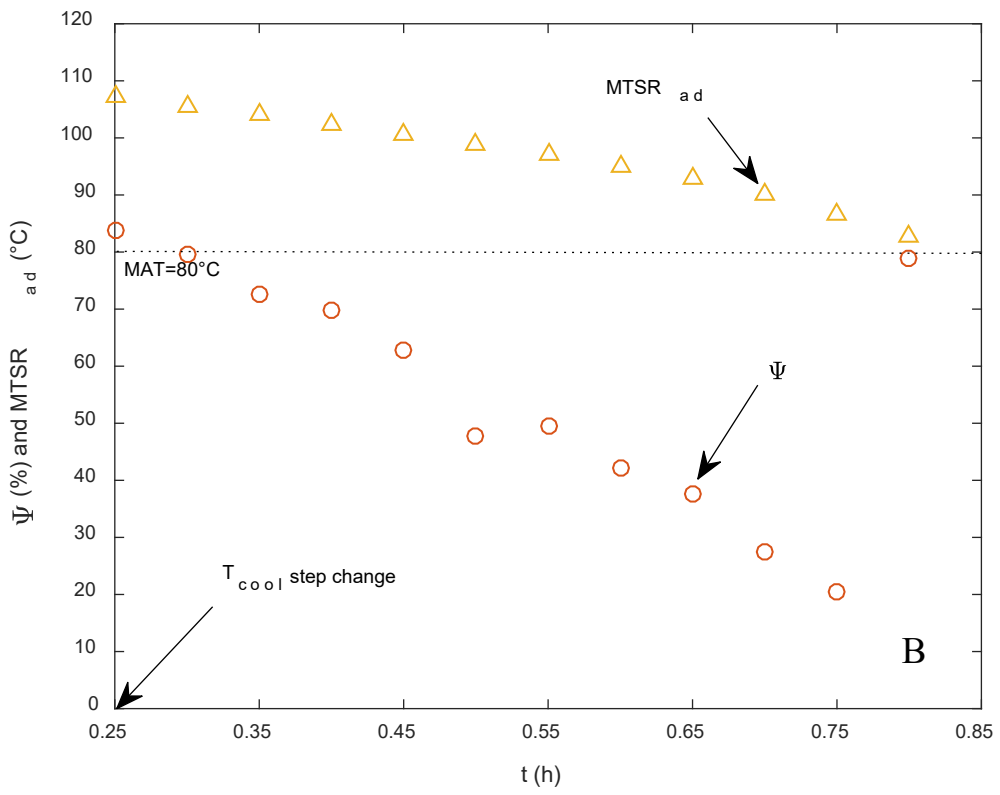
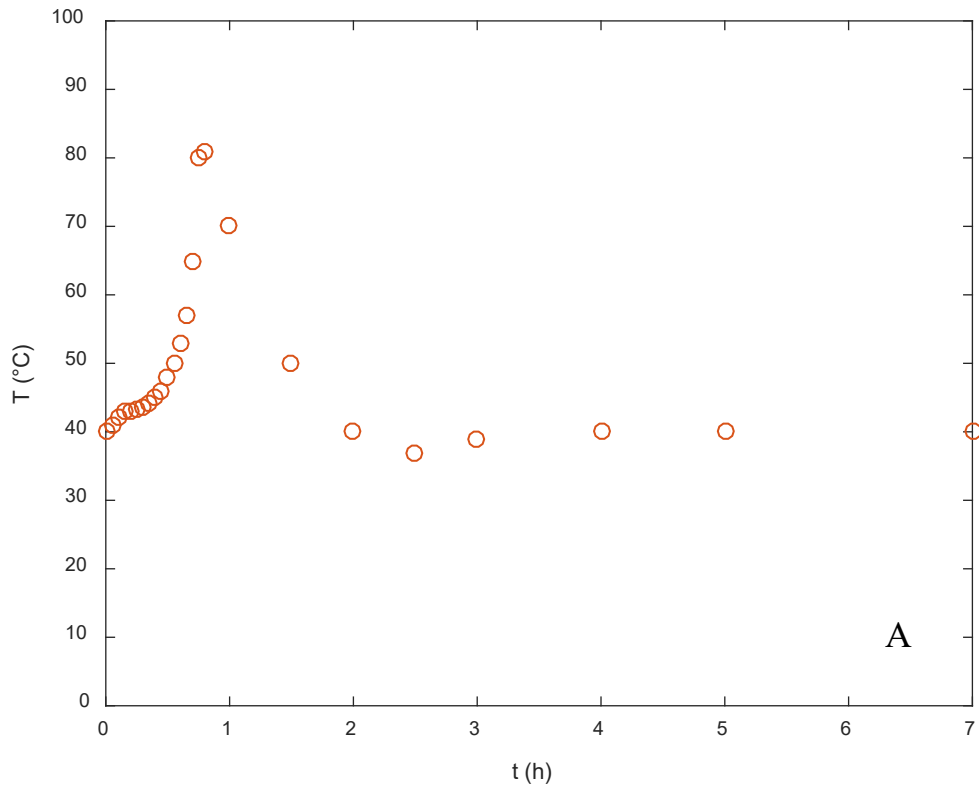


Fig. 4

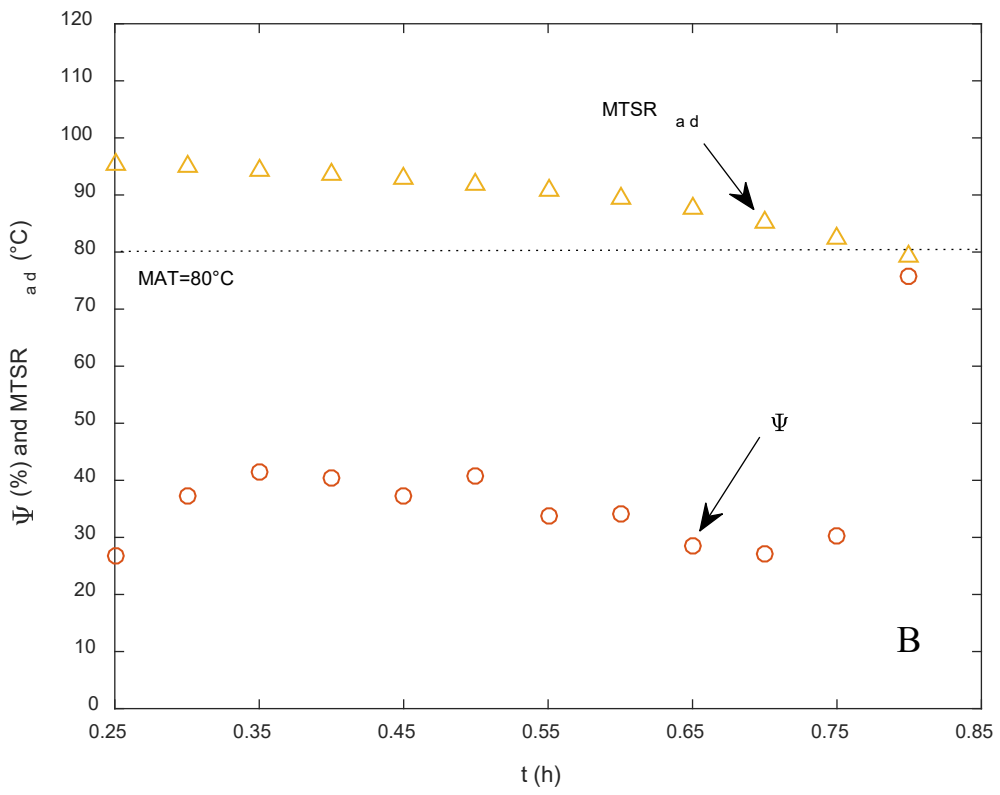
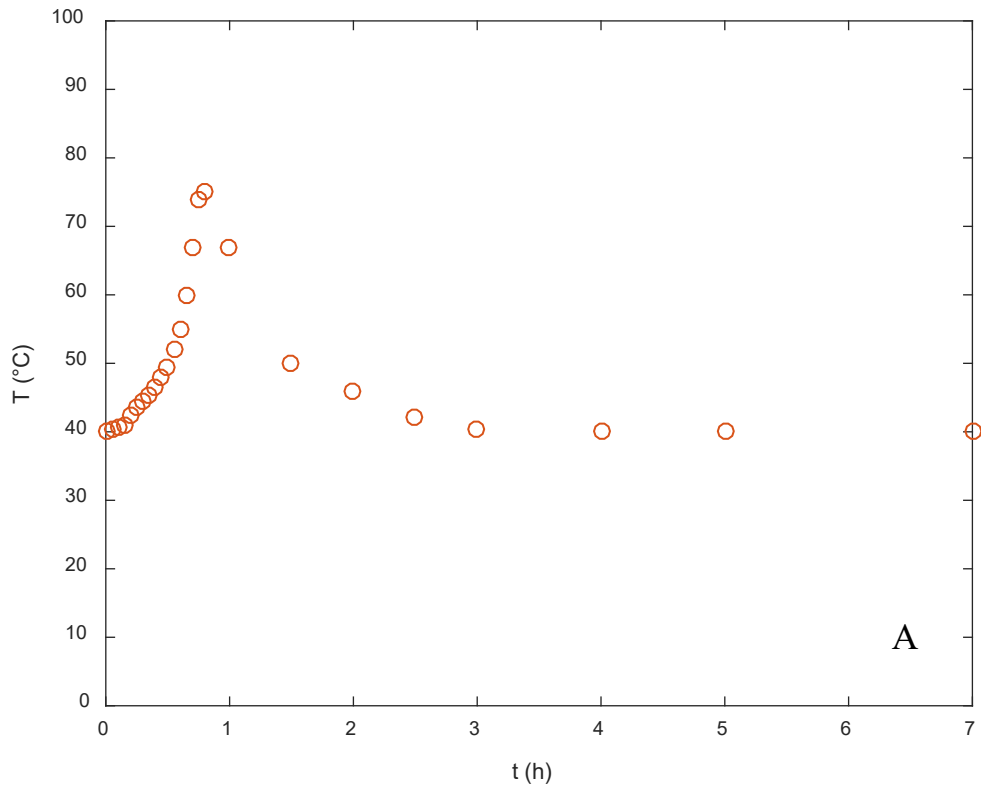


Fig. 5