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Selection and Monitoring of Safe and Productive Operating Conditions for Discontinuous Runaway Reactions: the Energy Release Monitoring System (ERMES) Method

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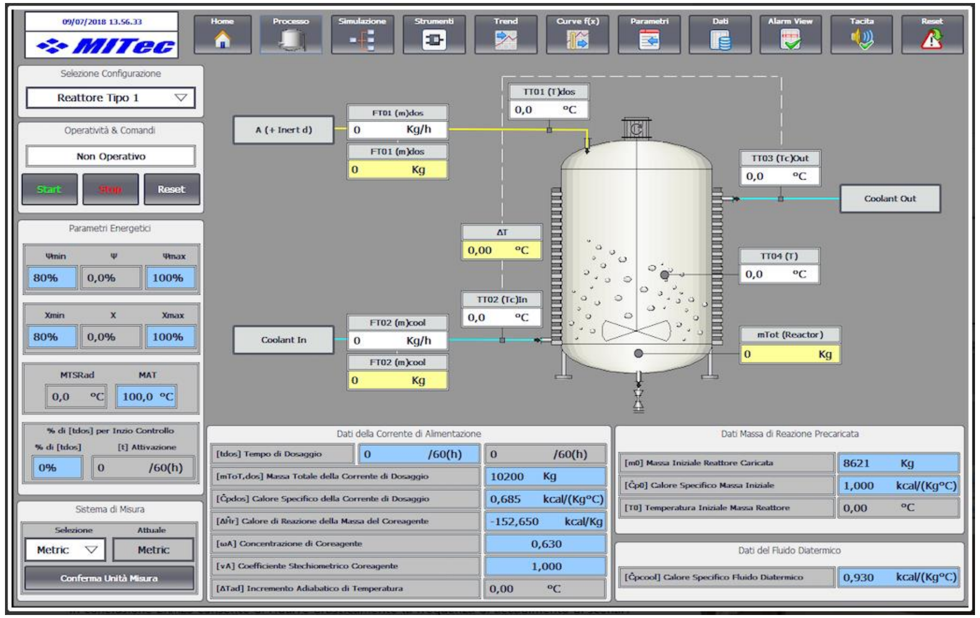


Runaway reactions: a long list of catastrophes

Phenolic resins, Italy 1997

Acrylic polymers, N.C. - USA 2006

Gasoline additives, FL - USA 2007

Introductory concepts

Fast and exothermic reactions: possible incidental scenarios

Thermal explosion: final consequence of the unbalance between heat generation by the chemical reaction and heat removal by the reactor cooling system.

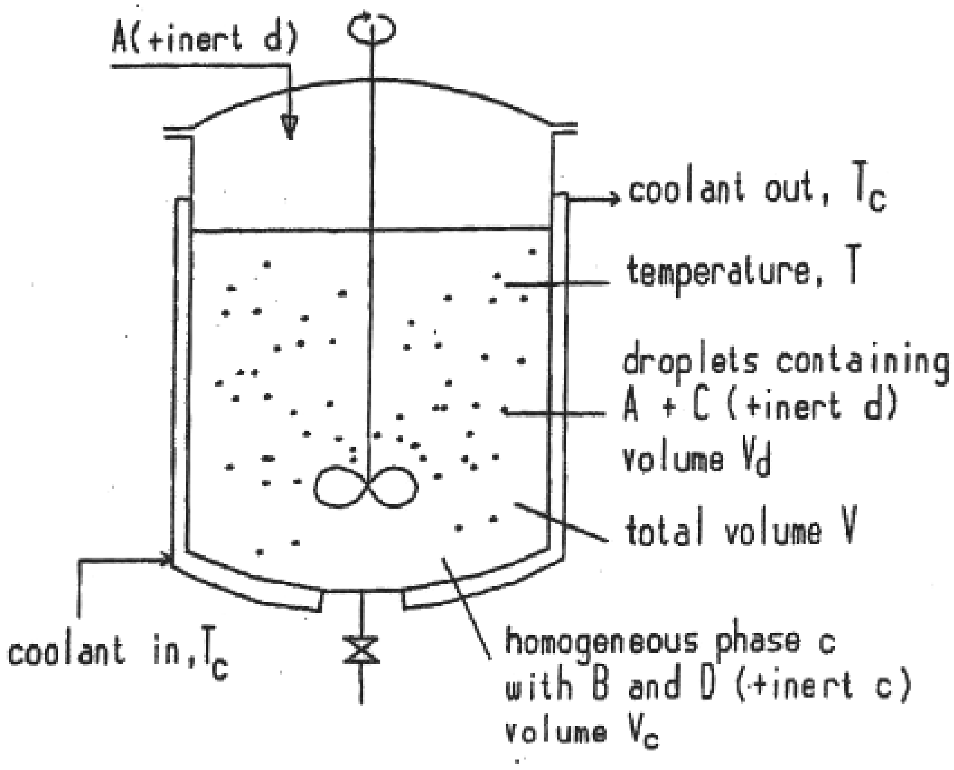
Thermal runaway: triggering of a consecutive decomposition of the reaction mass with sudden generation of permanent gases within a confined space (reaction vessel).

Both the phenomena can generate a dangerous reactor overpressure:

- as a consequence of the ***reaction mass vapor pressure*** → **vapor pressure systems**;
- as a consequence of the ***reaction mass decomposition*** → **gassy systems**.

Reactor selection

- A number of reaction processes of this type can be found in the *fine chemical and pharmaceutical industries* and are therefore performed in *non-continuous multipurpose reactors (batch, BR, or semibatch, SBR)*;
- When a thermal loss of control of the reaction can occur, the choice of a *semibatch reactor (SBR)* is strongly recommended (that is, one reactant initially loaded and one reactant dosed in a suitable time period).
- This allows for **controlling the conversion rate and the reaction heat evolution.**



Chemical reaction:

$$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$$

Mathematical model

Macroscopic mass and energy balances:

$$\frac{dn_i}{dt} = F_{i,dos} + \nu_i r^{eff} V_r$$

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

Reaction macrokinetics

Reaction Enthalpy contribution

Combined cooling contribution

However, at the industrial scale:

- The **system modeling** is **not always feasible** for time and resources constraints (often when dealing with multipurpose processes);
- The **reaction macrokinetics** is **often unknown**.

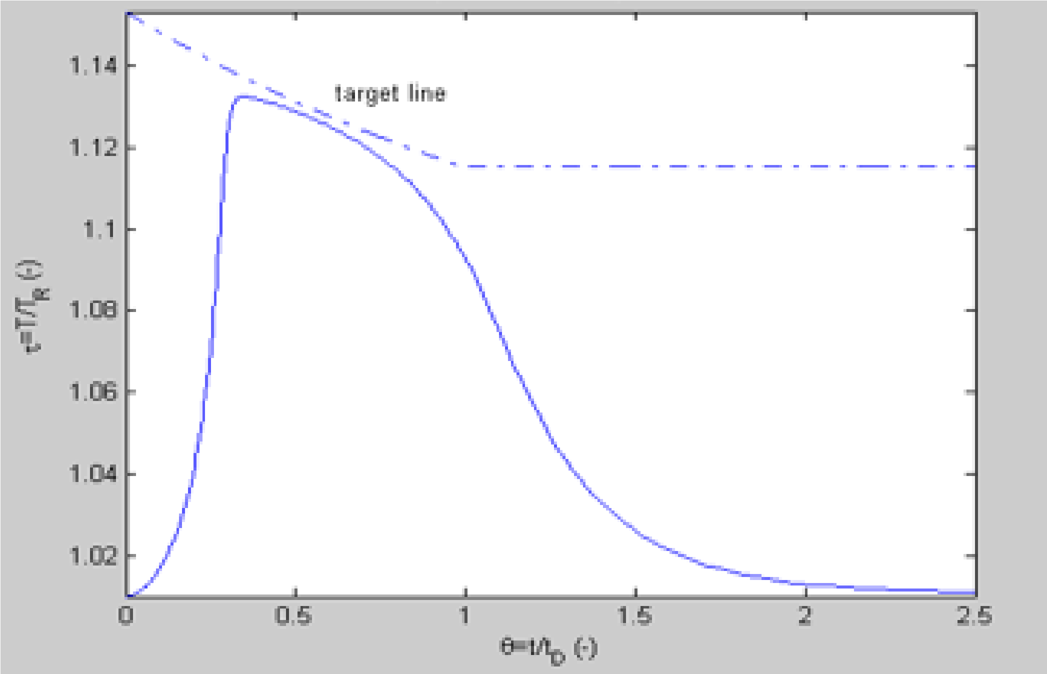
Target operating conditions

Definition and monitoring of a *set of safe and productive operating conditions of the SBR* through:

- *Effective limitation of the dosed reactant accumulation in the SBR* → conversion rate ≅ dosing rate **[(kinetic-free conditions)]**;
- *Effective removal of the reaction heat* → nearly isothermal SBR operation.

Such a regime is achieved adopting a suitable **dosing time** of the fed reactant, which has to be:

- *Enough high* to allow for a *safe SBR operation*;
- *Enough low* to allow for a *satisfactory SBR productivity*.



A reaction inhibition during the dosing period and/or an early decay of the heat removal efficiency are root causes of dangerous scenarios

The ERMES approach

Based on a set of **KPIs**

Key <u>PROCESS</u> indicators

Key <u>PERFORMANCE</u> indicators

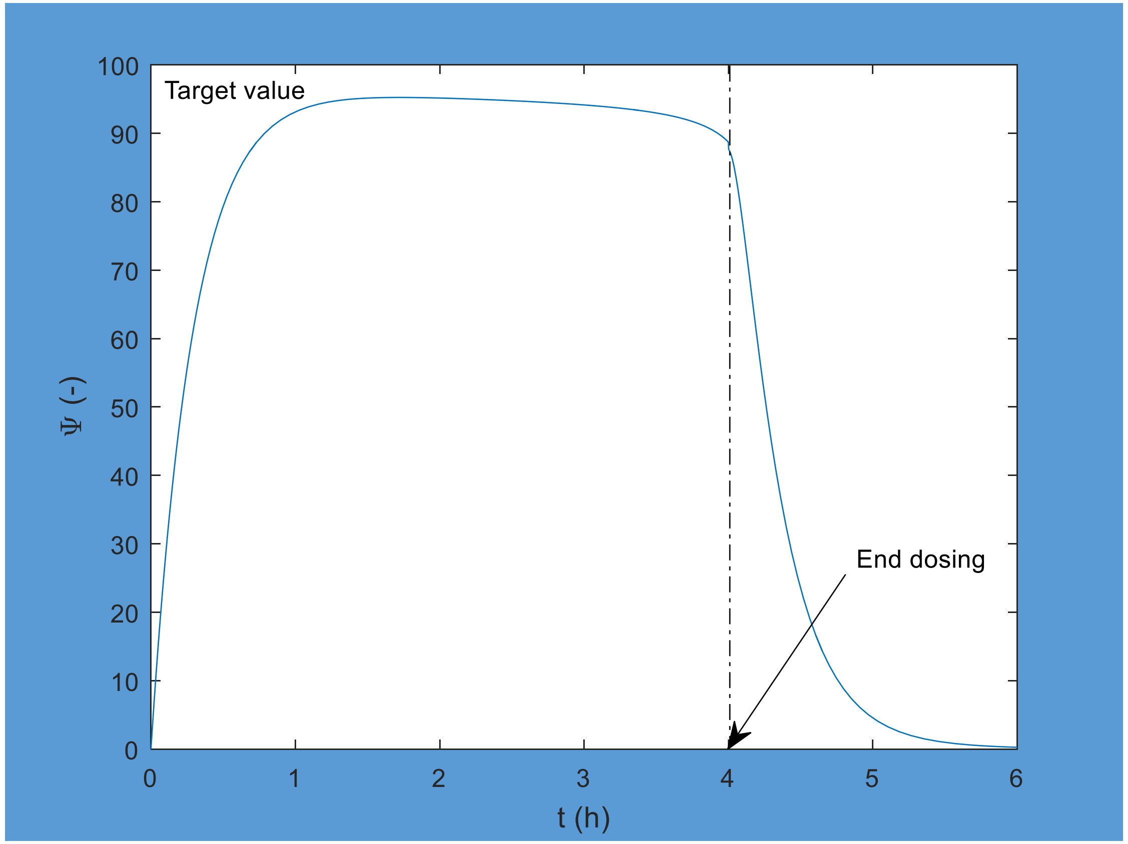
The measurement of the energy KPIs can be on-going performed during each reaction batch:

- Through *available process variables (to be measured through dedicated SIL II instruments)*:
  - dosing stream flowrate and temperature;
  - reactor temperature;
  - external coolant flowrate and temperature increase across the jacket, coil or external heat exchangers.
- Through *simple mathematical relationships*;
- *Knowing just the reaction enthalpy and the average specific heats* of the reaction mass and the dosing stream (no kinetic characterization necessary).

The KPIs

Ψ number

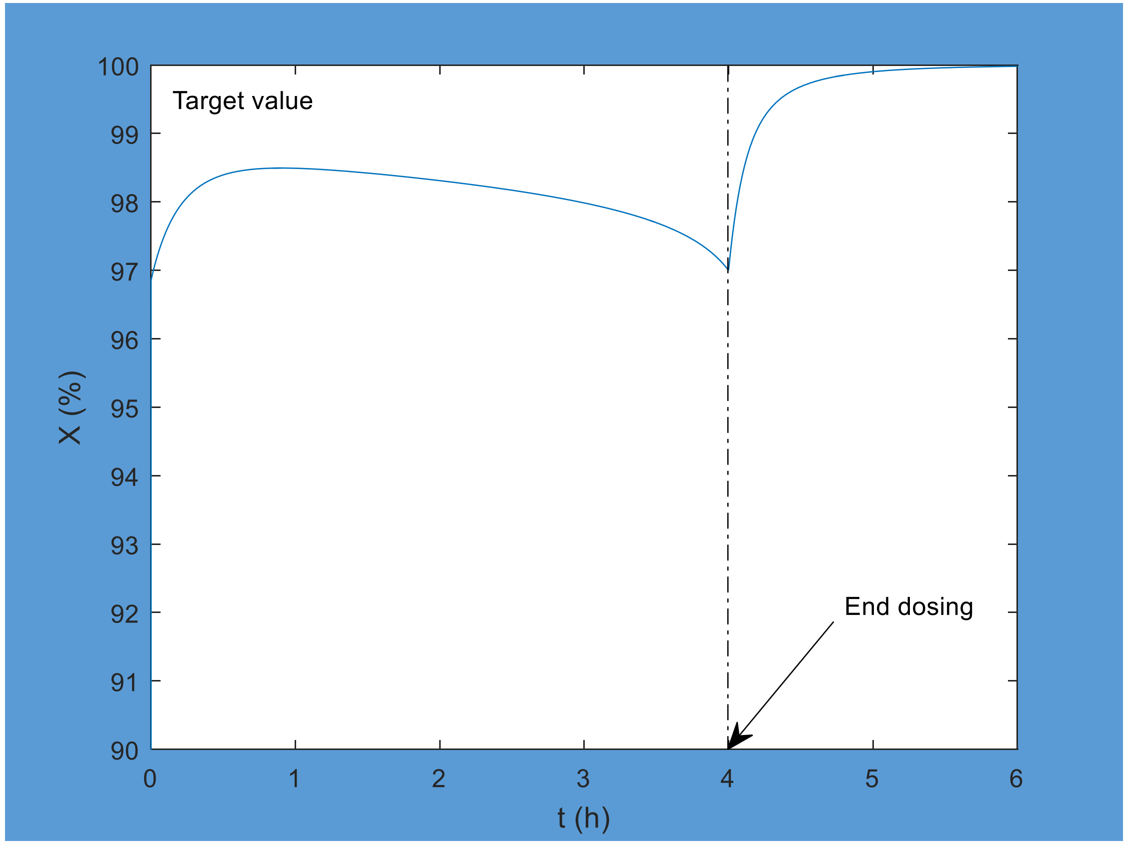
- it is the *ratio between actual and target heat removal rates*, through both the external coolant and the dosing stream;
- it is a *direct measure of the approach of the SBR operating regime to low accumulation – nearly isothermal conditions (target conditions)*;
- *under target conditions it univocally reaches values close to 100* (independently of the reaction system).



The KPIs

<u>X number</u>

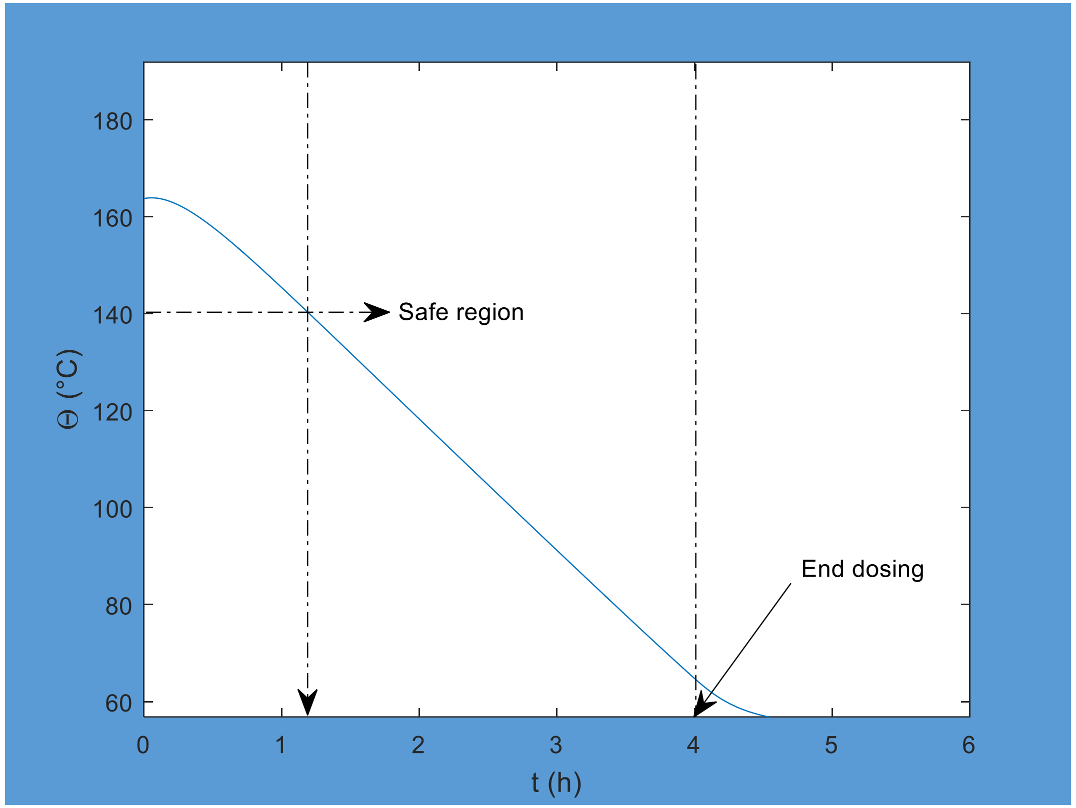
- it is the *ratio between energy sources (the reaction enthalpy) and uses (the heating enthalpy of the reaction mass and of the coolant) within the system*;
- it is a *direct measure of the conversion degree of the fed reactant (and hence of its accumulation)*;
- *if at a given time all the fed reactant has been converted, X univocally reaches values close to 100* (independently of the reaction system).



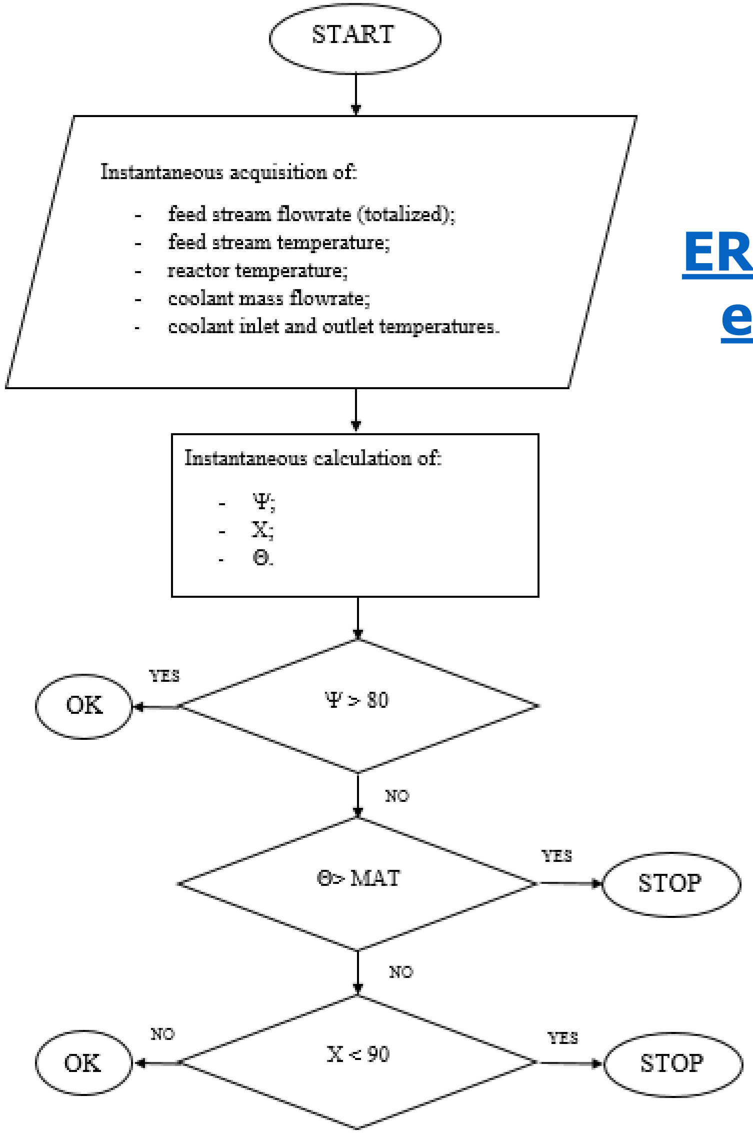
The KPIs

Θ parameter

- it is the *energy potential of the system in terms of maximum attainable temperature under adiabatic conditions because of the conversion of all the reactant to be fed and of its accumulated amount;*
- *it must be compared with the maximum allowable temperature for the system (arising from safety or quality constraints).*

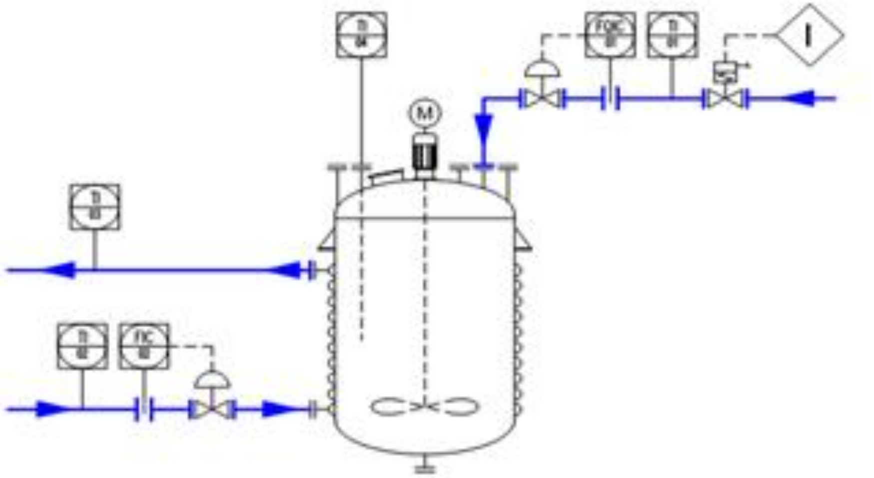


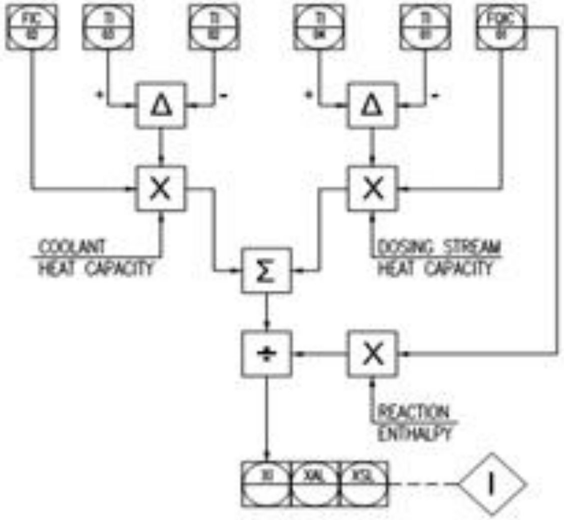
ERMES operating logic



ERMES allows for "seeing" the energy behavior of the SBR

Feed interruption without false alarms!!



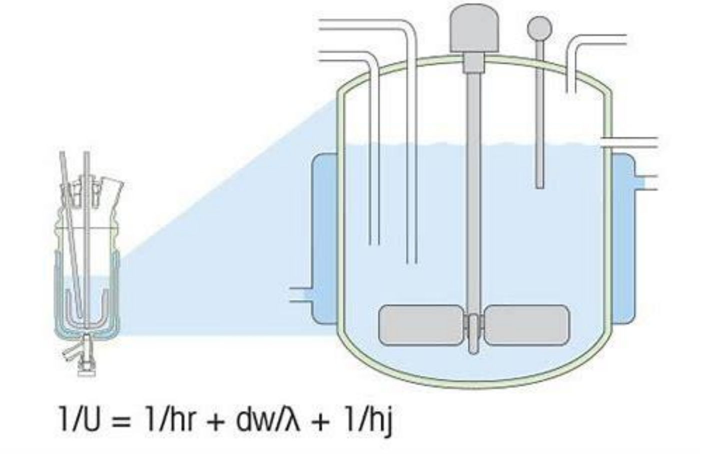


ERMES applications

At the lab/pilot scale

kinetic-free setup of the safe operating conditions of the SBR

SAFE SCALE-UP



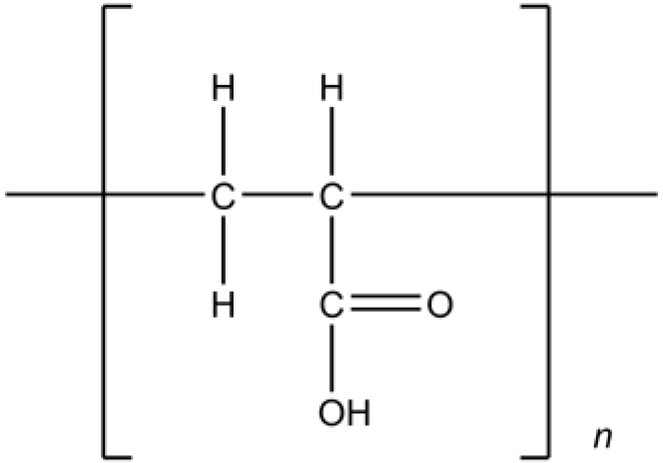
At the industrial scale

ERMES acts as an early messenger against unsafe scenarios (preventive NOT protective approach)

Case study: solvent based acrylic acid polymerization

Process description

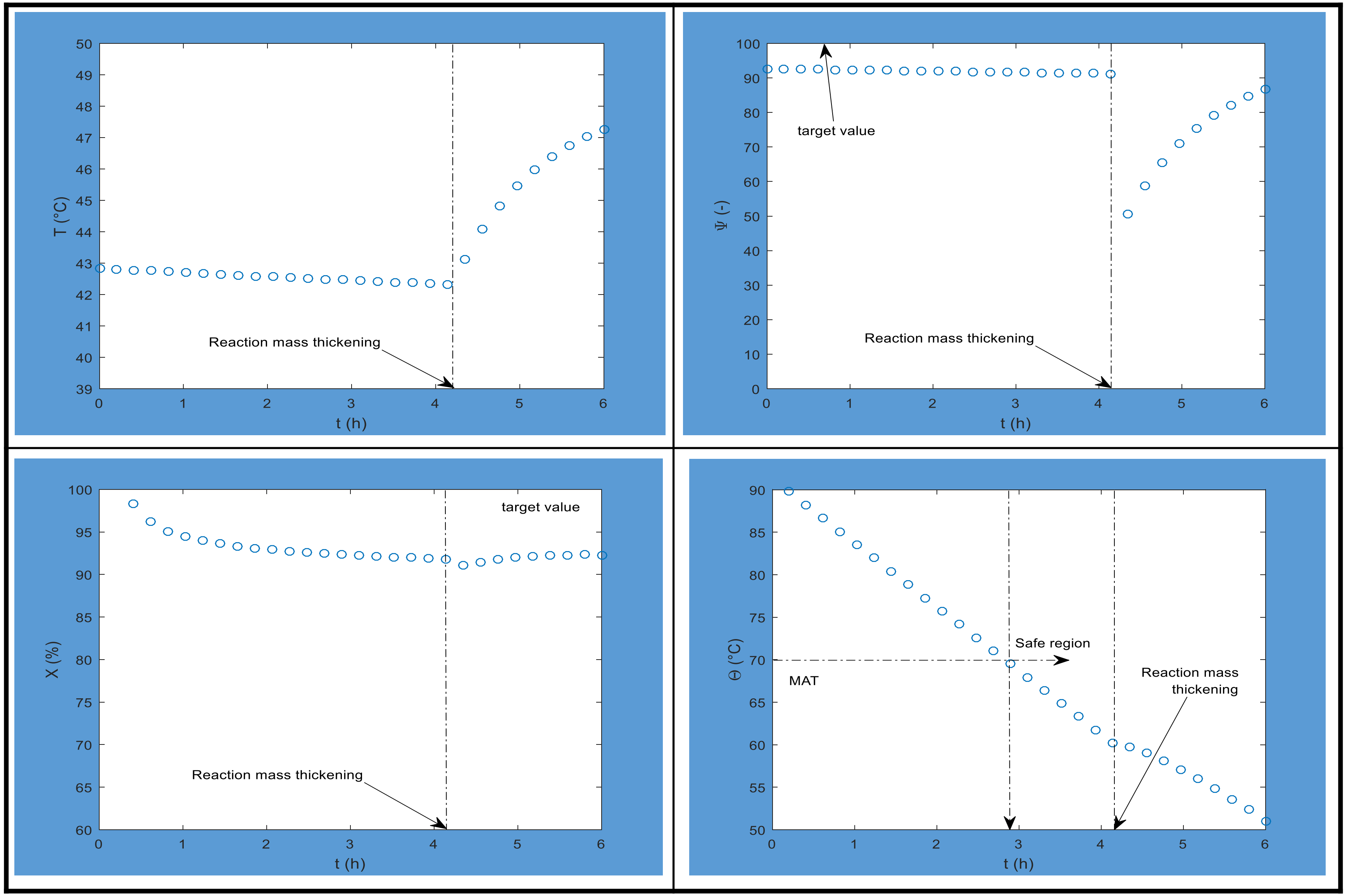
Solvent based precipitation polymerization of acrylic acid to produce crosslinked polyacrylic acids (INCI name: Carbomer®) of general formula, widely used as thickening agents for the cosmetic industry;



Acrylic acid monomer unit in carbomer polymers.

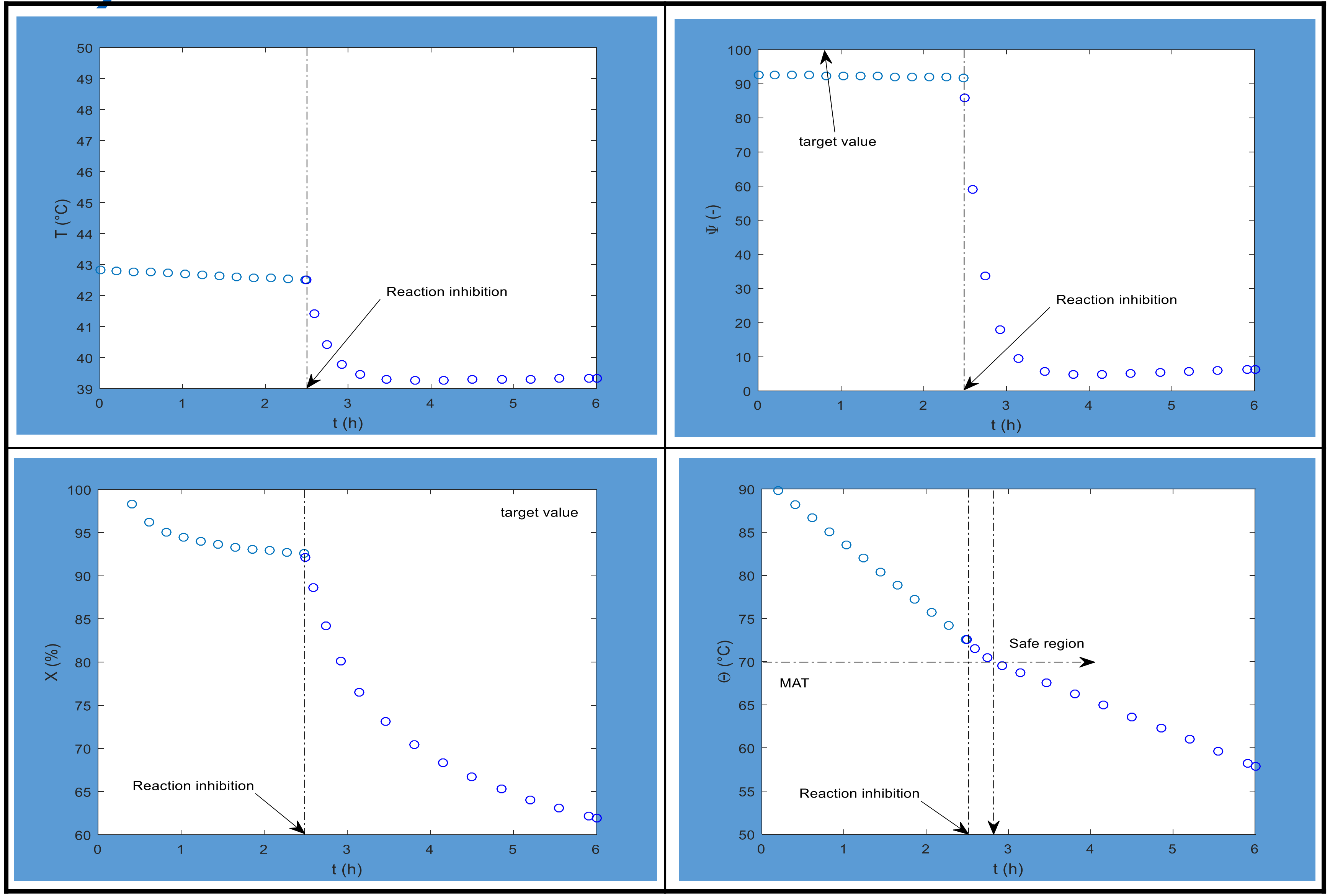
Scenario 1): normal reaction mass thickening

In this case only Ψ drops as a late and normal reaction thickening occurs. Therefore, the monomer feed is not interrupted.



Scenario 2): incidental reaction inhibition

In this case both Ψ and X drop as an incidental reaction inhibition occurs. Therefore, the monomer feed is interrupted.



Final remarks

- ERMES is a useful device for significantly lowering the frequency of occurrence of incidental phenomena in SBRs, with a main focus on process safety but with a relevant saving of time and money even when facing non-catastrophic events.
- ERMES is generally useful to monitor the expected energy behavior of an exothermic semibatch reaction system, even with reference to product quality constraints.
- The installation of **ERMES cannot in any case replace a properly sized pressure relief system** (PSV or RD) on the SBR to face the worst case process scenario.
- A PCT patent application (PCT/EP2018/061657) has been filed in May 2018 about the ERMES method and related devices.