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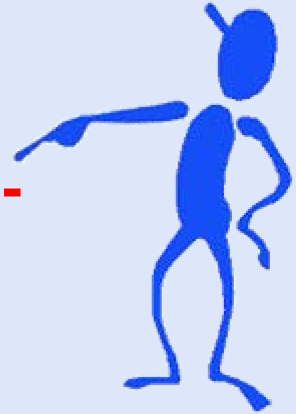
Kinetics-based simulation – how can this approach help when assessing reaction hazard?

A. Kossoy, ChemInform, St. Petersburg, Russia

Thermal Hazards: Introduction

What is Thermal Hazard?

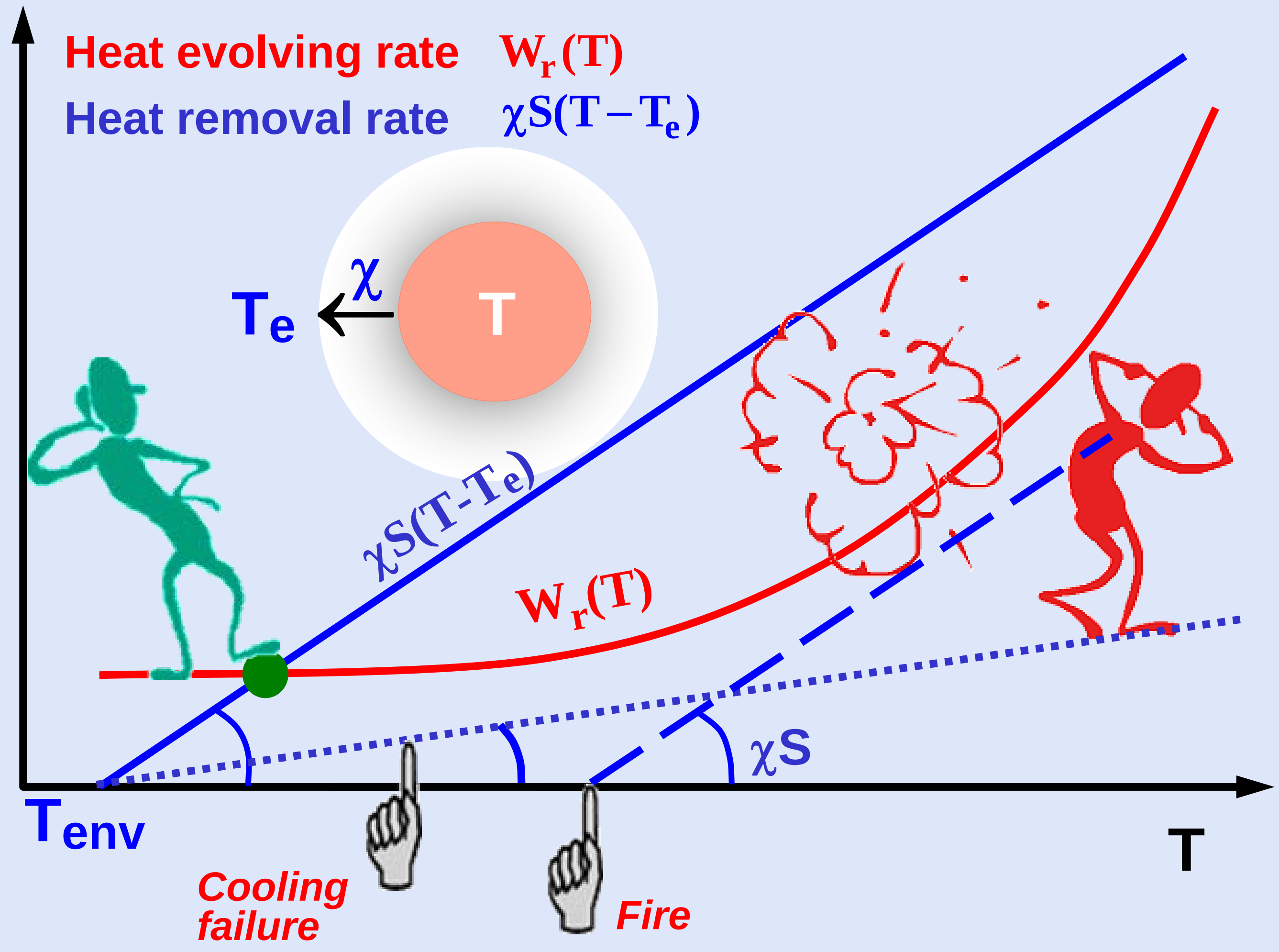


Potential thermal (or reactive) hazard - reactive properties and physical conditions of a single chemical or mixture that have the potential to generate heat, gas product,…, that have the potential to harm

Main Sources of Thermal Hazards:

- ✓ **Synthesis reaction**
- ✓ **Instability of reactants and products (side reactions);**
- ✓ **Heat accumulation in a reactor;**
- ✓ **Pressure rise.**

Thermal Hazard: Origins of Runaway



Assessing Hazards: General Scheme

Thermal Hazards of

Chemical Process

- ✓Energy Potential and Reactivity of Reactants, Intermediates;
- ✓Energy Potential and Kinetics of Synthesis and Secondary Reactions;
- ✓Safety of Normal Process Mode;
- ✓Accidents scenarios (cooling failure, fire, …)
- ✓Protection measures

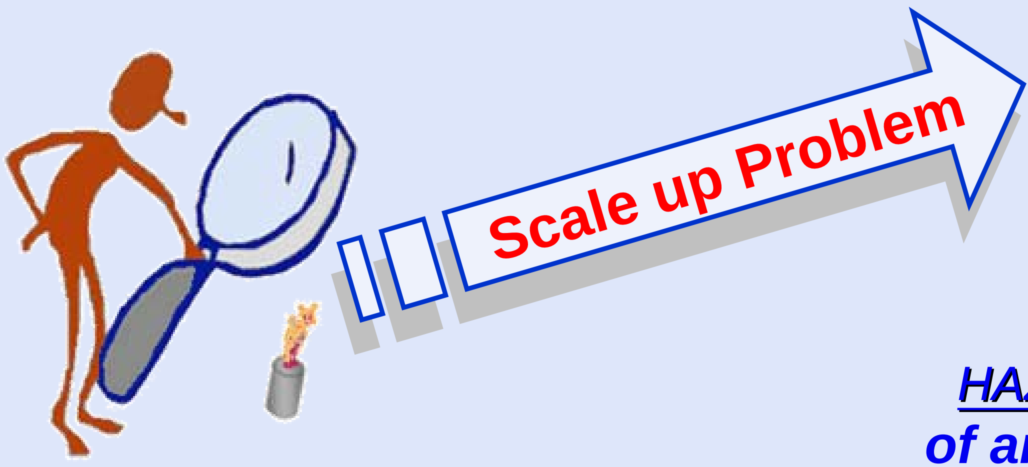
Chemical Product

- ✓Energy Potential;
- ✓Reactivity and Kinetics;
- ✓Safe conditions of Use, Storage, Transportation;
- ✓Accidents scenarios (fire, external heating, …)
- ✓Protection measures

Key Problem of Assessing Thermal Hazard

EXPERIMENTAL STUDY

- ✓ DSC, DTA,
- ✓ Heat Flow Calorimetry
- ✓ Reaction Calorimetry
- ✓ Adiabatic Calorimetry



HAZARD ASSESSMENT
of an Industrial Process

Key Problem of Assessing Thermal Hazard

The basic problem:

HOW TO PREDICT REACTION COURSE UNDER SOME CONDITIONS OF INTEREST?

Can be solved either

BY USING CUSTOMARY METHODS

- Methods are mostly based on simplest models
- Qualitative or semi-quantitative results
- Problems with scaling
- Incomplete use of experimental data

Key Problem of Assessing Thermal Hazard

The basic problem:

HOW TO PREDICT REACTION COURSE UNDER SOME CONDITIONS OF INTEREST?

Or - IN GENERAL CASE UNDER ANY CONDITIONS

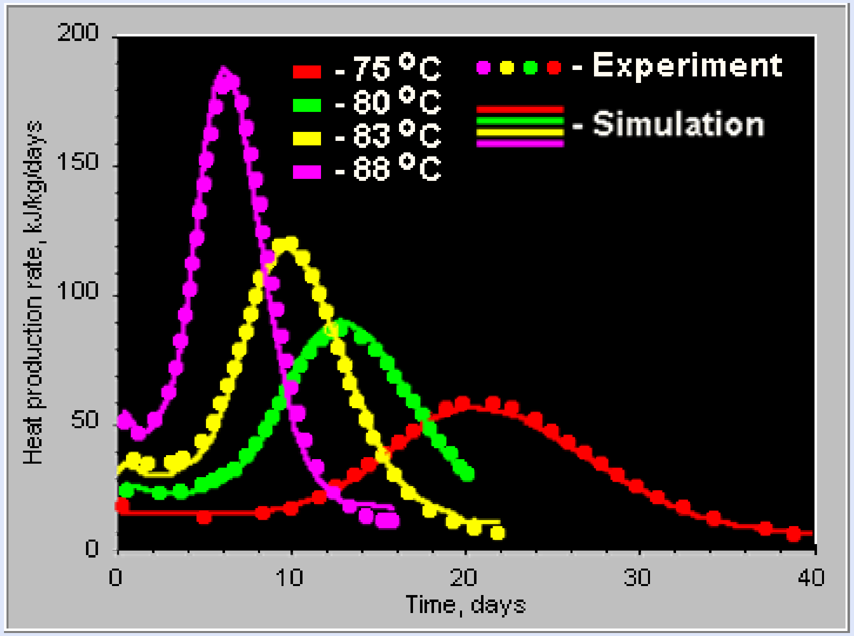
- **BY CREATING MATHEMATICAL MODEL OF A REACTION**
  AND THEN
- **BY SIMULATING PROCESS PROCEEDING**

Some Examples: 1. Analyzing Reactivity

Aim: Revealing influence of various factors

Reaction: Decomposition of Cumene Hydroperoxide (CHP) (80% solution in Cumene (C))

Experiment: Heat flux calorimetry, simultaneous use of 4 isothermal data sets



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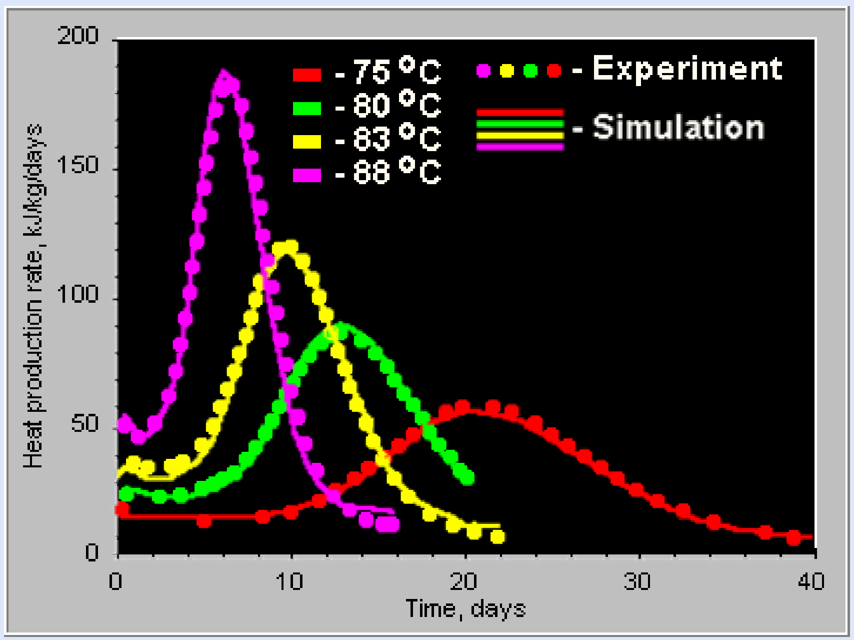
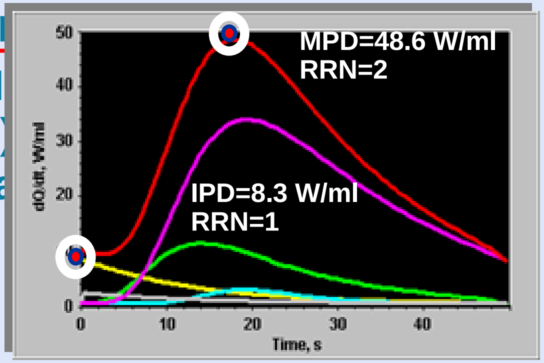
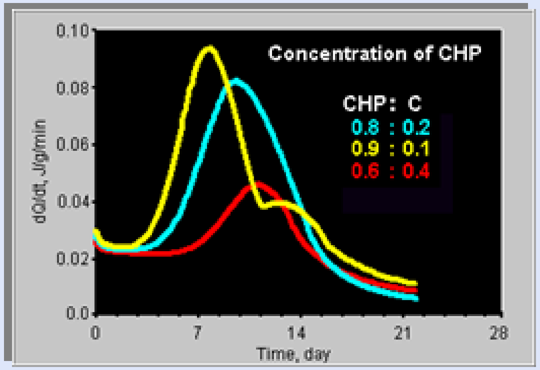
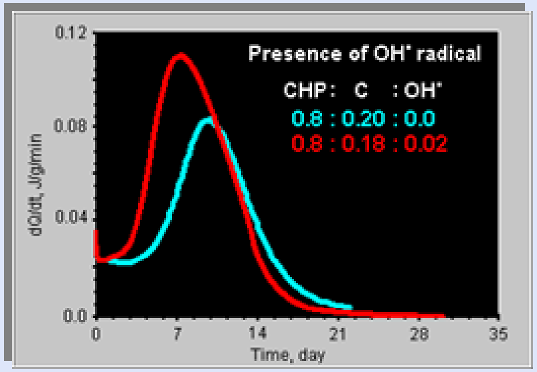








Some Examples: 2. Runaway & Vent Sizing

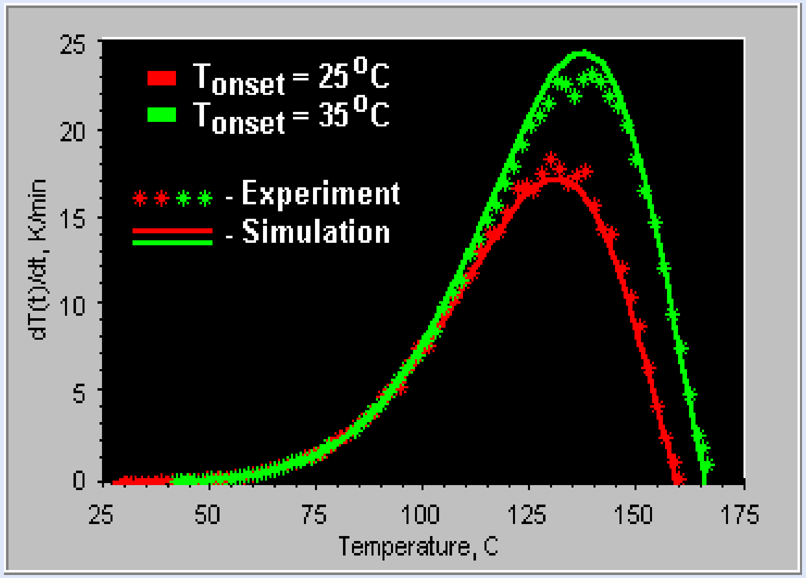
Aim: Verification of the software for ERS design,
(HSE Round-Robin test)

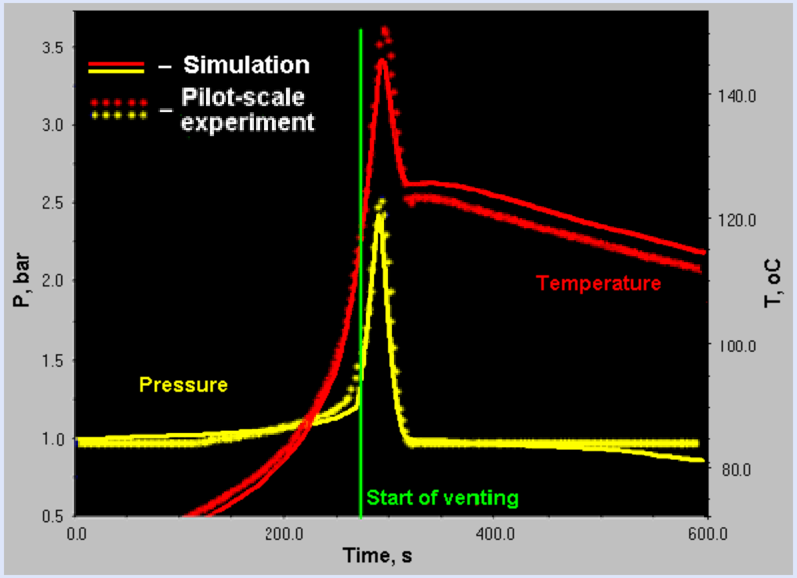
Reaction: I + PA → IP + PAc

Experiment: Adiabatic Calorimetry; simultaneous use of 2 data sets: To 25 ºC & 35 ºC

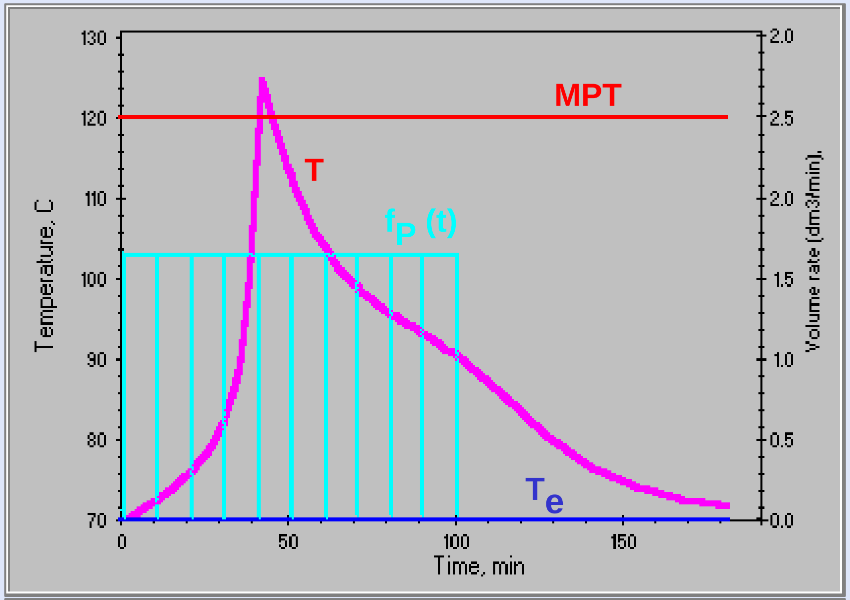
Reactor: Vertical tank, V = 312 liters; U = 270 W/m2/K, S = 1.53 m2

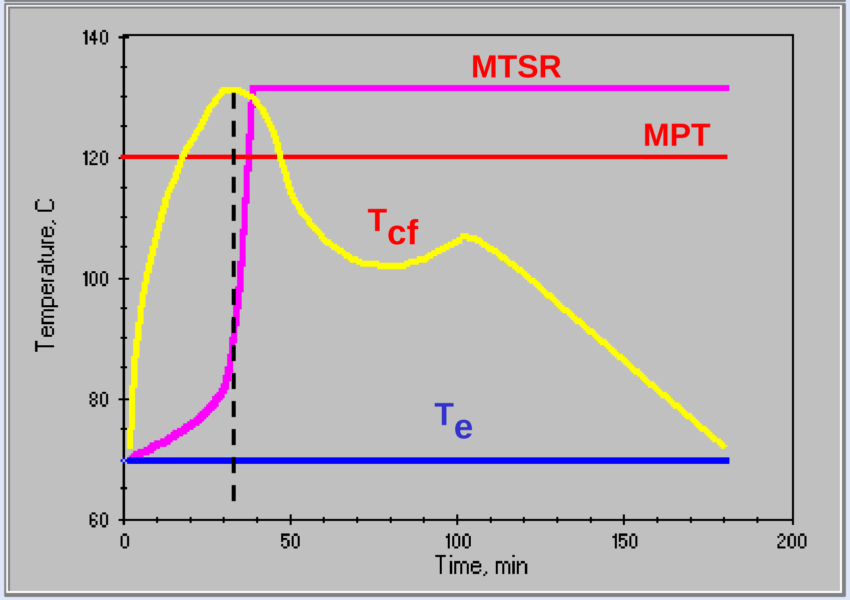
Vent system: Type: **Valve**; Position: **Top**; Length: **4.82 m**; Diameter: **7 cm**
Actuation Conditions: **Pressure 1.5 bar, Overpressure 5%;**





Example 3: Optimizing Semi-BATCH





1. Optimization criterion - Inherent Safety

$$\max(MPT - MTSR);\ MPT = 120\ C$$

2. Expediency and Engineering constraints: same as in Example 1

3. Controls to be optimized:

$f_P(t)$ defined as Sequence of Pulses:

10 identical pulses:

distance (i) = 0 min   fixed

$f_P(t)$ = 1.65 dm^3/min   var

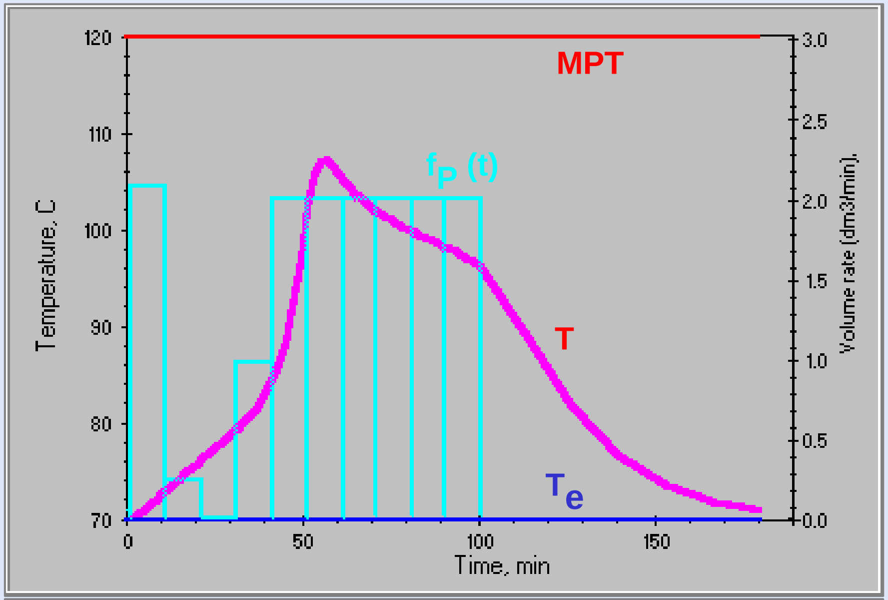
duration (i) = 10 min   fixed

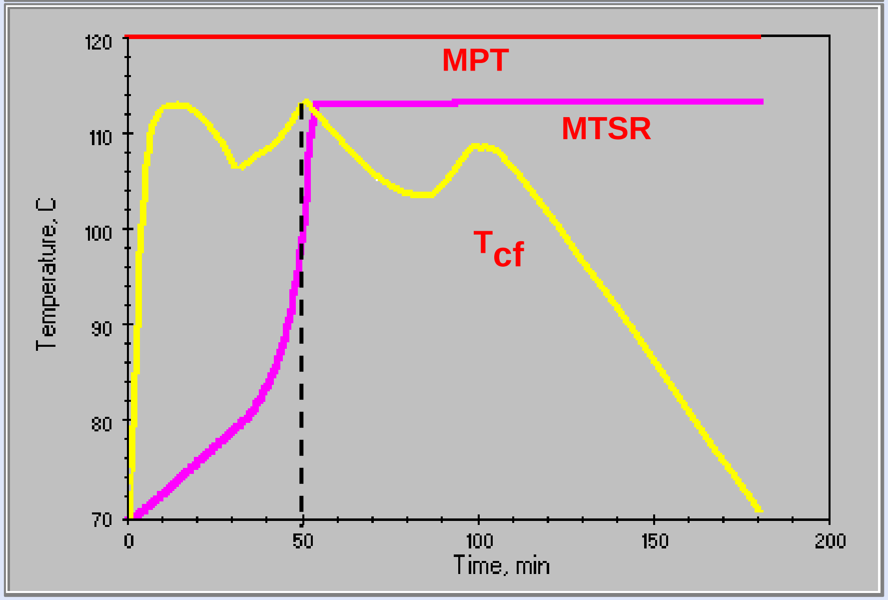
Initial Mode (before optimization)

T_e = 65 C, initial filling - 100 l of P; feed of I until reaching equimolar composition

Normal mode:	Accident:
$T_{max} \approx 124$ C	MTSR ≈ 132 C
$t_{max} \approx 42$ min	$t_{cf\ max} \approx 30$ min

Example 3: Optimizing Semi-BATCH





Optimized Normal Mode:

$f_P = f_P$ (t)

$T_{max} \approx 107.5$ C ; $t_{max} \approx 57$ min

$t_f \approx 170$ min

$C_I (t_f) = 0.02$

$C_P (t_f) = 0.0003$

Accident:

MTSR ≈ 113.3 C ; $t_{cf\ max} \approx 50$ min

Inherent Safety is provided

General Approach to Assessing Hazard

Experimental study

↓

Kinetics Evaluation

↓

Math Model of a Chemical Process

↓

Hazard assessment

- ✓Reactivity of a Material / Mixture
- ✓Critical Conditions of Thermal Explosion
- ✓Runaway in a Reactor and Design of Emergency Relief Systems
- ✓Design of Inherently Safer Processes

Difficulties of introducing the Approach

- **A knowledge- consuming way: requires applying methods from various fields - mathematics, numerical methods, chemical kinetics, thermal physics, etc.;**
- **Every step should be provided with the appropriate elaborate methods;**
- **High demands have to be made to the professional skill of a researcher.**

Main merits of the approach

- **Allows applying more adequate complex mathematical models of processes;**
- **Allows investigating various scenarios of process proceeding;**
- **Gives the principal solution of the scale-up problem.**

How to simplify its use in practice ?

By creating the problem - oriented tools that are convenient for Researchers and include relevant METHODS and the corresponding SOFTWARE.

Thermal Safety System : Methodology

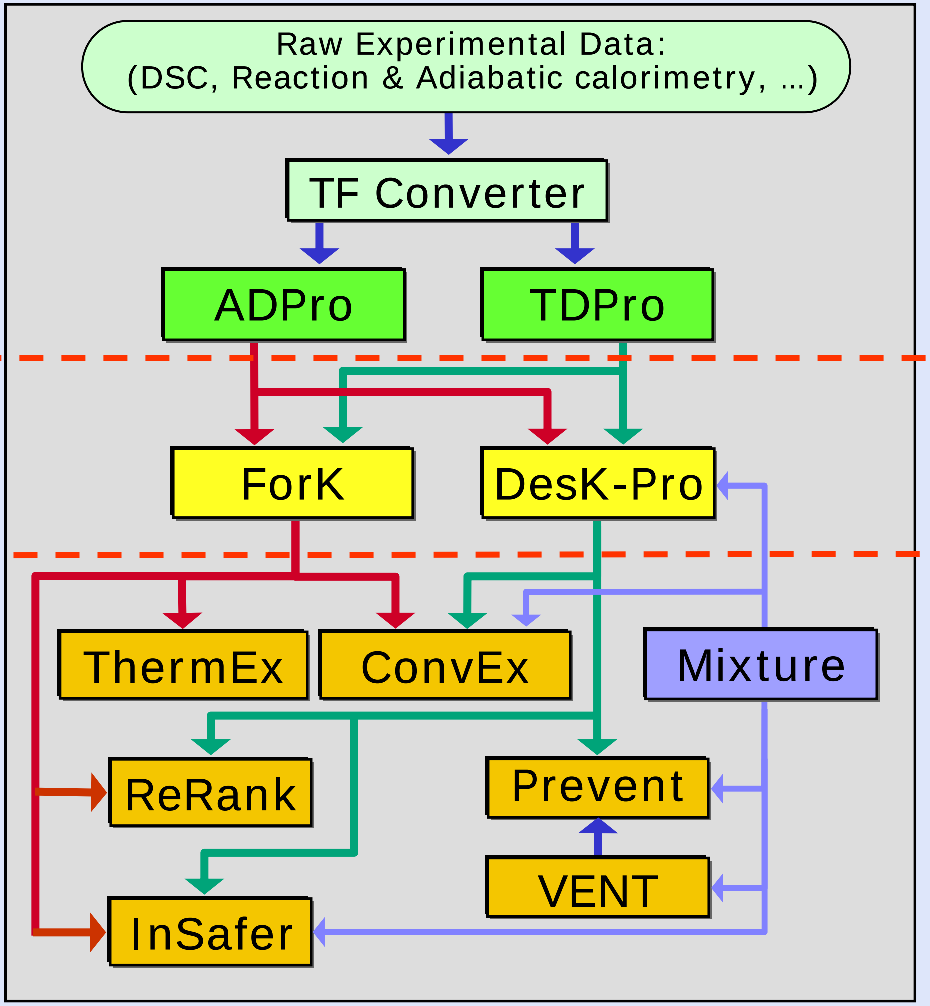
- *Up-to-date theoretical basis for:*
  - ✓ **Thorough processing of various calorimetric data;**
  - ✓ **Creation of mathematical models of chemical reactions;**
  - ✓ **Simulation of thermal explosion in solid and liquid substances;**
  - ✓ **Simulation of runaway in industrial reactors and Design of Emergency Relief Systems for protecting them**
- *Coordination of all the stages.*

TSS– Tool for Hazard Assessment

Thorough processing of experimental data

Creation of math models of chemical reactions

Assessment or reaction hazards;
inherent safety, runaway simulation



TSS – major features

- Elaborate problem-oriented methodology as the basis;
- Incorporation of mathematical methods with knowledge and intuition of a researcher into unified strategy;
- The most relevant up-to-date mathematical methods for solving problems;
- Possibility to process simultaneously results of different multi-response experiments;
- Full interconnections and co-ordination between separate programs;
- Unified elements of User’s interface, flexible graphics

TSS: To Whom it is addressed

- R&D Centers of Chemical and Pharmaceutical Companies;
- R&D Centers of Manufacturers and Users of Explosives;
- Consulting Firms dealing with Chemical Processes and Hazard Assessment;
- Thermal-analytical Laboratories;
- Chemical Engineering Departments of Universities

Conclusions

- The kinetics-based simulation is a very efficient method for solving such complex challenge as assessment of reaction hazards. Being free of essential simplifications this approach can be applied to a wide variety of practical problems
- This approach is not for complete replacement of the traditional methods. Quite the contrary they mutually complement each other and simulation will be most helpful when the potential danger of a reaction or process has been revealed by using simplified empirical methods