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

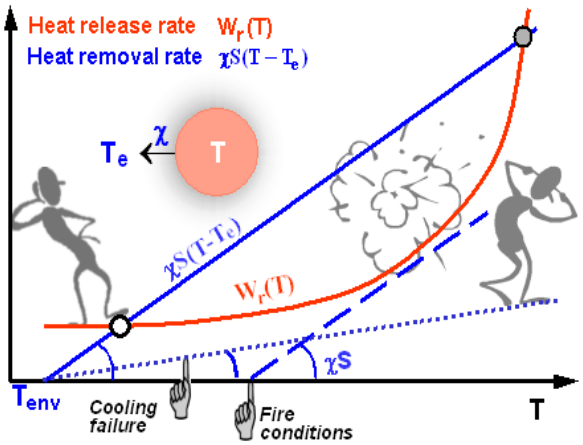
This is the first newsletter form the series aimed at better acquaintance of our readers with the features of the simulation-based approach to reaction hazard assessment and CISP Thermal Safety Software (TSS) series that brings it closer to the research practice.

Introduction

Reaction hazard of a chemical process, along with toxic and fire hazards, is one of the main aspects of the general problem of safety in chemical industry. The term "thermal (or reaction) hazard" covers variety of hazards dealing with heat evolving in a chemical process. Improper choice of operational conditions or accidental deviations from the normal course of an exothermic process may result in development of runaway (thermal explosion) and cause severe consequences. Unfortunately many of the known industrial accidents were bound up with those processes that could be easily identified as potentially hazardous but weren't investigated properly from the safety point of view. Therefore the problem of ensuring thermal safety of chemical processes remains of significant practical importance.

There are 3 main sources of reaction hazard:

- Instability of reactants and products;
- Heat accumulation in a reactor; it can result in temperature rise in a reactor due to lack of the control under exothermic reactions and, hence, may cause over-pressurization due to boiling of volatile components and trigger secondary, often highly exothermic reactions resulting in runaway with severe consequences;
- Pressure rise due to generation of gaseous reaction products.



The well-know Semenov diagram demonstrates vividly what the origins of thermal hazard are.

In case of properly chosen cooling capacity the balance between heat generated by an exothermic reaction and heat removal from a reactor is ensured and the thermal mode of a process is stable and safe.

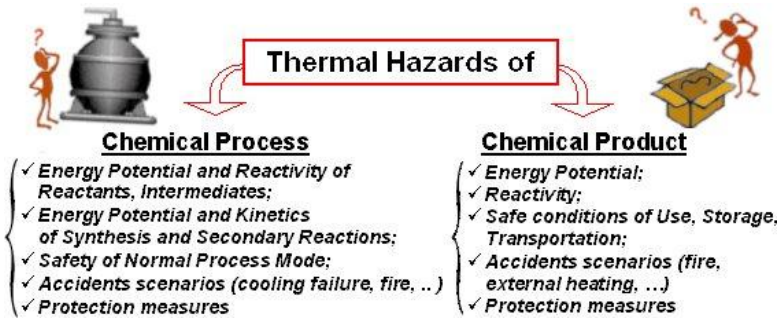
If the heat balance isn't provided by some reasons then heat will be accumulated in a reactor, which will result in runaway.

There are two main origins of loss of control:

- unsafe choice of normal operational conditions (inadequate cooling capacity, too high temperature of cooling agent)
- Accident (cooling failure, fire…)

Evidently assessment of thermal hazard should purpose two objects – evaluate safety of normal process conditions and analyze various accident scenarios.

In fact, assessment of thermal hazard should accompany the whole life cycle of a process from the very beginning of its development. Moreover, thermal hazards can be bound up not only with processes but also with products. The following scheme depicts what should be done in either case.



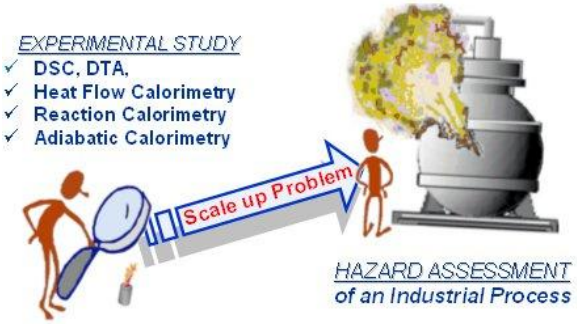
When assessing a process, one should answer numerous questions.

1. ***What is energy potential and reactivity of reactants and intermediates?*** These data allow selection of the reactants that minimize hazard of the future process
2. ***What is energy potential and kinetics of main (synthesis) and secondary (side) reactions?*** Results obtained on this step are the basis for solving next two problems:

3. ***How to choose properly conditions that would ensure safe normal operational mode?*** And
4. ***What are the possible scenarios of accidents?*** The results of this analysis in their turn are necessary for choosing the protection measures that would be able to prevent or at least mitigate consequences of an accident.

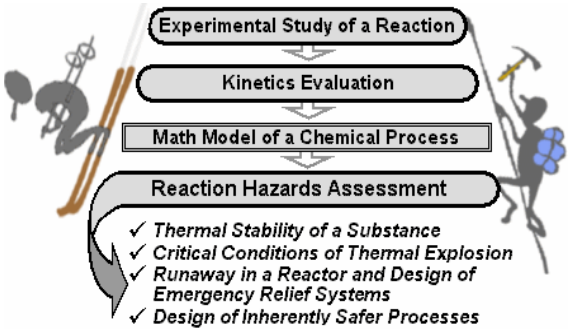
As far as **thermal hazard of a chemical product** is concerned the questionnaire is very similar with one important exception: the main aim of hazard assessment is the choice of safe conditions of storage, transportation and use of a product. As usual, there is no other way to get data necessary for assessing thermal hazard rather than by experimental study.

Typical technique, which is used in this area, is calorimetry of various kinds. Of course almost all experiments, especially when hazardous materials are investigated, are carried out in the laboratory small scale. At the same time the final result of investigation is prediction of behavior of full-scale industrial process. Therefore the key problem that has to be solved is the scale-up problem.



Kinetics-based simulation – principal solution of the scale-up problem

Among various methods (actually not numerous) that are used for scaling there is only one almost universal method that allows prediction of reaction course in general case under any conditions of interest. This is kinetics-based simulation. It involves 3 main steps.



In the first step necessary series of calorimetric experiments is carried out.

In the second step the mathematical model of a reaction is created.

Finally the created model is incorporated into the model of a process and the practical target is achieved by using mathematical (numerical) simulation.

Is this approach simple? No. We have to admit that this method is quite complex. In practice the presented procedure turns out to be iterative rather than the plain one.

From time to time we have to go back to experiment from the kinetics evaluation step to get more data necessary for validation of the model created or for discrimination of more relevant model from the set of competing ones. In the same way, the necessity may appear to perform some additional experiments and create more comprehensive kinetic model when a specific final problem is being solved.

Let us mention some other peculiarities that complicate application of the approach.

1. This is a knowledge-consuming way that requires applying methods from various fields - chemical kinetics, thermal physics, mathematics, numerical mathematics, etc.
2. Correctness of the results obtained on a certain step of investigation significantly affects the reliability and correctness of results of all the subsequent steps. Therefore every step should be provided with appropriate elaborate methods. It equally concerns experimental methods used for study of a reaction - they are familiar to everybody and therefore may seem to be well developed. Nevertheless many of such methods should be reviewed attentively to ensure obtaining real quantitative data suitable for kinetics creation.
3. As every step of the scheme is complex enough, involves many branches of knowledge and cannot be completely formalized, high demands have to be made to the professional skill of a researcher.

At the same time the approach has numerous merits that ensure its practical effectiveness. We mentioned one principal feature - the potential to solve scale-up problem. Some other advantages are:The possibility to apply more adequate complex mathematical models of processes;

- The possibility to simulate and analyze various scenarios of process proceeding;
- The possibility to determine critical conditions of thermal explosion in complex cases that cannot be considered by using popular simplified analytical methods.

What measures should be undertaken in order to simplify introduction of simulation-based methods into research practice? Apparently this can be resolved by creating the problem–oriented tools that would be convenient for researchers and would include relevant methods and corresponding software. This has been one of the main aims of CISP activity during last years.

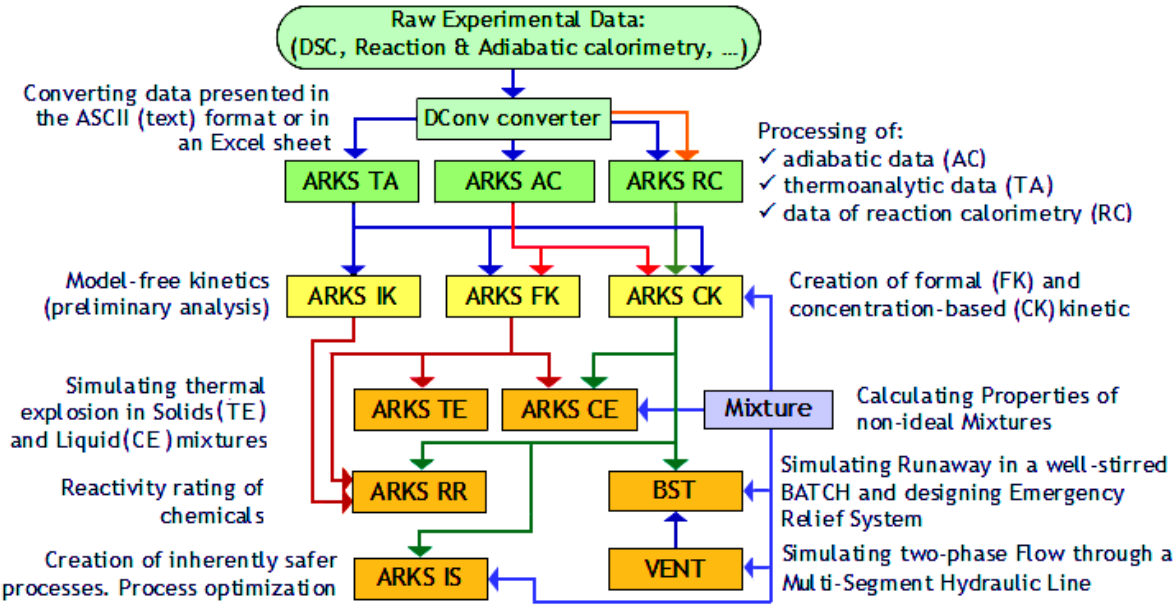
Today a problem-oriented system of this kind exists and corresponding commercially available software has been designed.

As far as methodology is concerned it is based on the up-to-date theoretical background and covers the whole spectrum of problems that arise when thermal hazard assessment, such as:

- 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.

Very important feature of the proposed methodology is that all the stages are coordinated with each other. This ensures the most correct and reliable final results. It is evident the use of this methodology would be impossible without appropriate software.

The Thermal Safety Series - Advanced Reaction Kinetic Simulation (TSS-ARKS) Software includes three groups of programs that correspond to the three-stage approach.



The programs of **the 1st group** support all the necessary procedures for proper preparing of adiabatic and thermoanalytical data for kinetics evaluation.

The 2nd group includes programs for creation of kinetic models. They differ from each other by classes of supported models.

ARKS IK is for creation of the so-called model-free (isoconversional) kinetics

ARKS FK allows creation of complex formal models based on conversions as state variables.

ARKS CK provides use of more conventional concentration-based models. In both cases a mathematical model of any complexity is synthesized easily without any programming.

Use of up-to-date methods of nonlinear optimization ensures efficient kinetics evaluation.

ARKS IK,FK and **CK** allow also solving many kinds of final problems by simulation.

The 3rd group unites applications intended for solving final practical tasks.

Solid (**ARKS TE)** and Liquid (**ARKS CE)** thermal Explosion program packages provide numerical simulation of thermal explosion development and allow determination of critical conditions. These data are necessary for proper choice of safe conditions of application, storage and transportation of a chemical product. **ARKS TE** is based on the assumption that internal heat transfer is effected by thermal conductivity whereas **CE** takes into account heat transfer due to thermal conductivity and natural convection. Both programs provide easy automatic determination such important practical parameters as critical temperature of thermal explosion and self accelerating decomposition temperature (SADT).

ARKS RR is the software for rating reactivity, it supports automatic determination of such hazard indicators as the Reactivity Rating Number (in accordance with the NFPA requirements), adiabatic Time to Maximum Rate, thermal stability and thermal aging of a chemical, and SADT for liquids.

ARKS IS provides design of inherently safer processes and can be used as well for optimizing them.

BST package which includes also the **VENT** and **Mixture** programs serves for simulation of runaway in well-stirred batch reactor equipped with the emergency relief system and provides choice of protective measures for industrial reactors.

The auxiliary **Mixture** program is the database of physical properties of chemicals and calculates properties of non-ideal multi component mixtures to supply all the programs that require these data.

In the following CISP newsletters we will give more details about programs of the TSS-ARKS series and main ideas they are based on. Now we will mention only some general features of the software:

- Incorporation of the most relevant up-to-date mathematical methods with knowledge and intuition of a researcher into unified strategy;
- Possibility to process simultaneously results of different multi-response experiments;
- Full interconnections and co-ordination between separate programs;
- Unified elements of project-oriented User's interface, flexible graphics
- Commercial availability
- Professional quality manuals.

Conclusion

To conclude this introduction we want to emphasize that by no means the approach described pretends to the complete replacement of more traditional, simpler ones. 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.