

**The Batch reactor, so simple –  
so much Unpredictable**

**Part 2a: Visualising the Dangers**

**Editor**

SCHNYDER Safety in Chemistry Ltd.  
Gewerbehaus Oederlin  
Landstrasse 2 b  
CH-5415 Rieden/Nussbaumen  
Switzerland

Tel. +41-56-282 29 39

Fax +41-56-282 28 52

[Company Brochure](#)

[www.schnyderchemsafety.com](http://www.schnyderchemsafety.com)

[office@schnyderchemsafety.com](mailto:office@schnyderchemsafety.com)

**Author**

Alfred Schnyder  
Dipl. Chem. Ing. ETHZ  
(master of science)

## **Introduction**

Multi-Product Chemistry is probably the branch of industry that has the broadest spectrum of dangers. Liquid, solid and gaseous chemicals are processed partly under high pressure and at high temperatures. They might be toxic, combustible, decomposable and explosive. Multi-product chemistry manufactures, transports and stores chemicals with technical methods that might be faulty and susceptible to faults. The vast crux lies in the fact that chemical processes must be carried out in plants that cannot be tailored to the particular problems that arise for batch processes in question. And all that in plants that are not designed and built for a production in question, organised divisionally of labour and controlled by personnel that make mistakes occasionally.

The profile of requirement of a chemical production process as a rule does not suit the profile of performance of a Multi-product plant (MPP). Shortcomings will be removed by appropriate completion. Those shortcomings that cannot be removed economically by technical measures will be bridged by organisational measures.

For the system –process/MPP/organization– the risks are inherent. Hence, for each process that is performed in the MPP, it must be demonstrated that the system is able to control the risks of the process.

Desirable for the safety assessment of the MPP is a holistic approach that illustrates the risk for each chemical process carried out in such facilities, and makes it possible to compare different operating modes with each other and to facilitate dialogue between management, chemists, plant manager and engineers.

In this issue we show a proven methodology to visualise the dangers of chemical processes. Based on this method, it is possible to study chemical batch processes using fault tree analysis. The next issue shows the approach with a case study of the sulphonation of an aromatic nitro compound.

To be able to deal confidently with thermal risks, it is necessary to know what they are, estimate how likely they are to occur and how serious the consequences would be.

Traditionally, risk is defined as the mathematical product of severity and probability of occurrence.

$$\mathbf{risk = severity * probability}$$

The thermal risk linked to a chemical reaction is the risk of loss of control of the chemical reaction or of triggering a runaway reaction. But what is the meaning of severity and probability in the case of thermal risks linked to chemical reactions?

From the analysis of the risks of thermal explosions and the lessons learned from thermal incidents, it is clear that in order to operate chemical reactors safely it is not enough to consider data on the thermal

stability of the reagents and the reaction mixture. Hence it is necessary to understand how a chemical reaction can deviate from its usual behaviour and turn into a runaway reaction.

### **Assessing chemical processes**

We use the following systematic methodology to assess chemical processes. It is the result of long experience in this matter and has been proven on working together with small to big-sized companies <sup>[1][3]</sup>. The methodology helps the plant manager

- to be aware of the hazard potentials inherent in the chemical process
- to implement the proper technical and organizational measures and the proper personnel selections for a safe operation of his chemical plant which are deduced from the knowledge of the hazard potentials.

## Hazards are inherent properties of the interaction of chemical process, plant and organisation

Because, very different chemical processes are performed in the same Multi-product facility and because the control of the process is determined to a large extent by the particular characteristics of the appropriate chemical process, it is necessary to understand to what extent the process is controlled by the plant and to what extent by the operator. Consequently, the systematic approach consists in four tasks (figures 1 and 2):

- First, visualising the dangers of the chemical process.
- Second, visualising the capabilities of the plant to control the dangers of the chemical process.
- Third, visualising the need in organisation to handle the process in the plant.

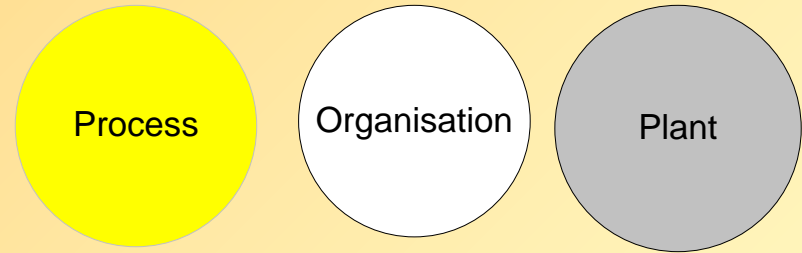


Figure 1

- Fourth, putting the elements together to visualise the potential risk.

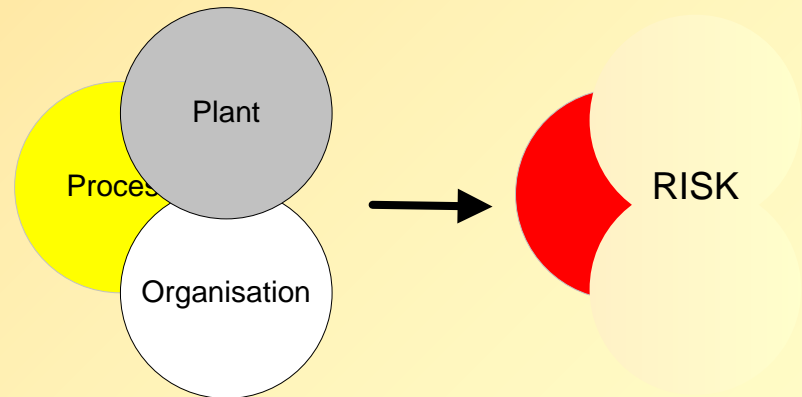


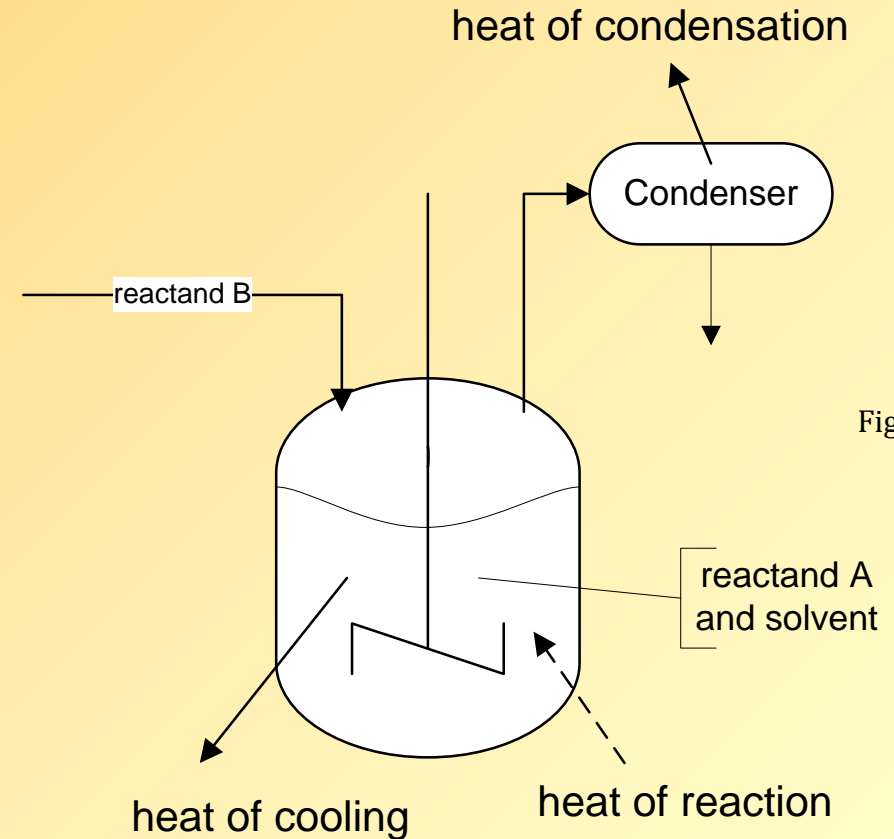
Figure 2

### Use of runaway scenario, a duty

The behaviour of a chemical system in the phase of the runaway can be explained by the example of an exothermic semi-batch reaction. A widely used production procedure is as follows (figure 3):

- one reactant and a solvent are charged into a reactor at room temperature
- the pre reaction mass is heated up to the reaction temperature
- the other reactant is dosed into the reactor during a certain time
- the temperature is maintained for a certain period
- the reactor is cooled down and emptied then.

Assume now that a cooling failure occurs while the reactor is at the reaction temperature. If at this incident unconverted reactants are still present in the reactor mass they will react and release heat. The temperature of the reaction mass increases due to the completion of the chemical reaction and the so called MTSR will be reached.



At this temperature a secondary decomposition reaction may be triggered, which causes a further increase in temperature (figure 4).

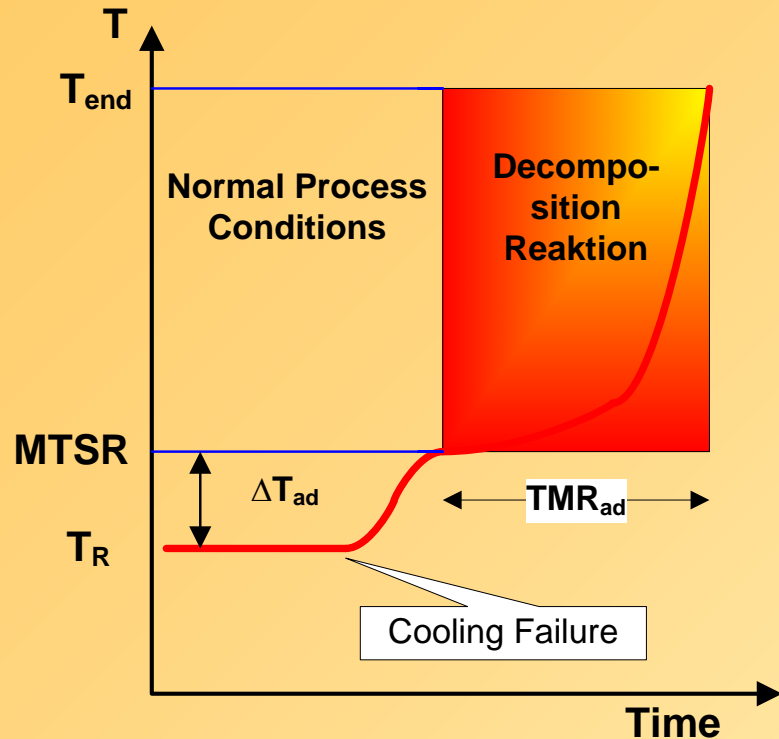


Figure 4

The following questions help to understand the runaway scenario and to provide data for the risk assessment. The experimental methods are also indicated.

1. Can the process temperature be controlled by the cooling system? (Reaction Calorimetry)

2. Are there any accumulation of reaction partners within the dosing step? (Reaction Calorimetry)
3. What temperature can the runaway of the desired reaction reach? (Reaction Calorimetry. For that purpose we use the concept of **Maximal Temperature of the Synthesis Reaction MTSR.**)
4. What temperature can the runaway of the decomposition reaction reach? (DSC, RADEX, SEDEX and SIKAREX)
5. At what moment does the cooling failure has the gravest consequences? (Reaction Calorimetry)
6. Of what speed is the runaway of the desired reaction? (Reaction Calorimetry)
7. Of what speed is the runaway of the decomposition reaction starting at the MTSR? (DSC, RADEX, SEDEX and SIKAREX)

## What is the meaning of severity and probability in the case of thermal risks?

Most reactions in the Multi-product chemistry are exothermic. The energy of chemical reaction or of decomposition is a direct measure of the severity of a runaway. The severity of the runaway can thus be evaluated using the levels of temperature attained if the desired reaction (question 2) and the decomposition reaction (question 3) proceed under adiabatic conditions.

There is still no quantitative measure of the probability of the occurrence of a thermal runaway reaction.

But when we consider the runaway curves presented in the above sketch, it is obvious that in case 2 there is more time left to take measures to regain control of the process than it is in case 1 where the runaway reaction takes a very fast course and less time is left to take measures. Hence it is more likely that in case 1 a process reveals its severity after loss of control than it is in case 2. Although it is not possible to quantify the probability that a reactor incident happens, it is possible to compare them on a semi-quantitative scale.

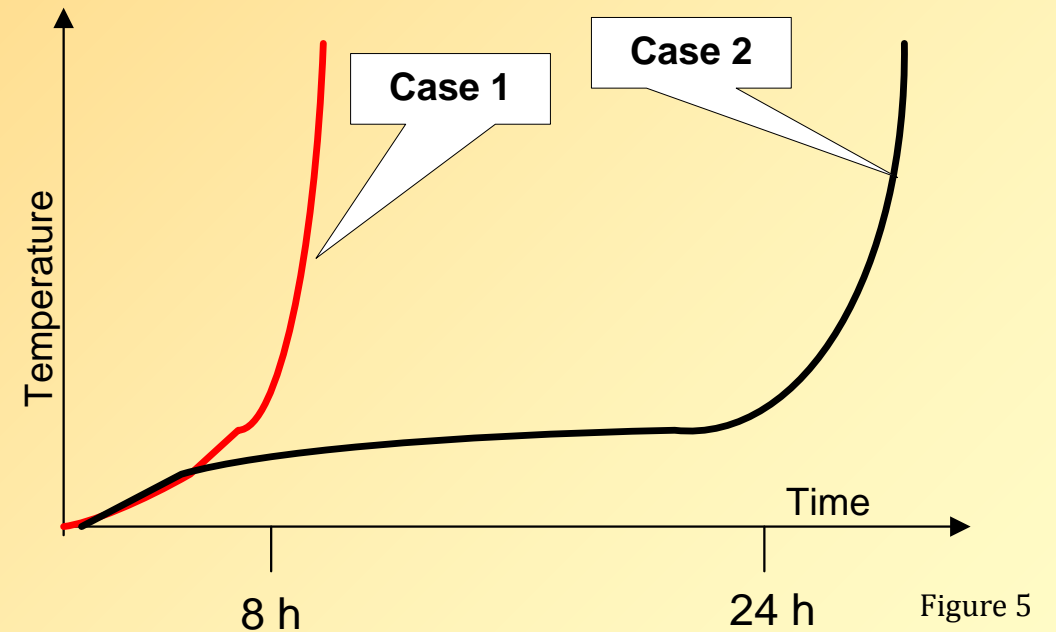


Figure 5



The probability can be evaluated using the time span that is needed to speed up a runaway reaction in an adiabatic system to its maximum rate, the so called TMRad. If there is enough time left (questions 5 and 6) after the cooling failure (question 4) to take emergency measures before the runaway becomes uncontrollable, the probability of the runaway will remain low. Three levels of probability are sufficient for the risk assessment low, medium and high. For assessing chemical reaction steps, we can consider a probability to be low if the TMRad is larger than one day. The probability becomes high if the TMRad becomes lower than eight hours.

	severity	probability
<b>high</b>	$\Delta T_{ad} > 200 \text{ K}$	$\text{TMR}_{ad} < 8 \text{ h}$
<b>medium</b>	$50 \text{ K} < \Delta T_{ad} < 200 \text{ K}$	$8 \text{ h} < \text{TMR}_{ad} < 24 \text{ h}$
<b>low</b>	$\Delta T_{ad} < 50 \text{ K}^*$	$\text{TMR}_{ad} > 24 \text{ h}$

\* caution with closed systems and chemical-loss

## Visualising the hazard potential

For reactions presenting a thermal potential we can consider the relative position of four temperature levels:

- the process temperature ( $T_p$ )
- the MTSR
- the temperature at which TMRad is 24 hours  $\{T(\text{TMRad} = 24\text{h})\}$
- the boiling point  $T_b$ . If the process runs in a closed reactor,  $T_b$  is replaced by the temperature at that the maximum tolerable pressure is reached, for example, the set pressure of the safety valve or of the rupture disk.

This allows to classify the scenarios according to F. Stössel<sup>[2]</sup> in five different classes going from the least critical (class 1) to the most critical (class 5).

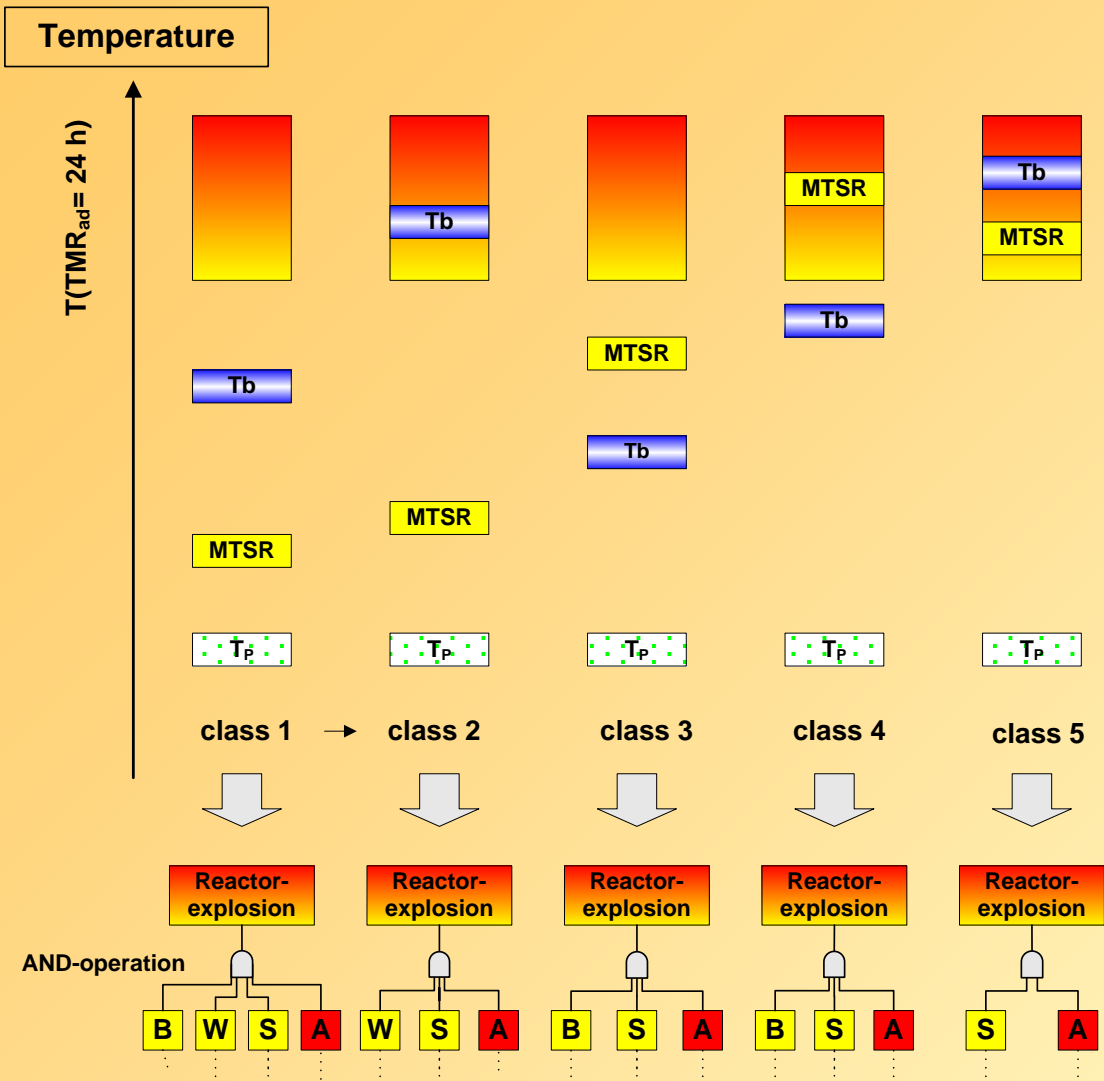


Figure 6 shows the classification of the chemical reaction step in criticality classes due to the four temperatures (see text). It also shows the fault trees as the top structures of the general fault trees [3].

**Meanings** A: triggering event S: protection measure is not effective B: evaporative cooling is not effective (open system) / rupture disk or valve does not work (closed system) W: heat accumulation conditions lasts longer than 24 hours.

### Description of the criticality class

**Class 1** After loss of control of the synthesis reaction, neither the boiling point can be reached nor the decomposition reaction can be triggered. Only if the reaction mass is maintained for a longer time under heat accumulation conditions, the boiling point could be reached. In such a case the evaporative cooling serves as a safety barrier. The process is thermally safe.

Figure 6

**Class 2** After loss of control of the synthesis reaction, neither the boiling point can be reached nor the decomposition reaction can be triggered. The situation is similar to the class 1, but if the reactor mass is maintained for a longer time under adiabatic conditions, the decomposition reaction could be triggered and reaches the boiling point. In this case, reaching the boiling point could be a hazard if the boiling rate is too high. For normal process time, the process is thermally safe.

**Class 3** After loss of control of the synthesis reaction, the boiling point will be reached, but the decomposition reaction cannot be triggered. The safety of the process depends on the heat release rate of the synthesis reaction at the boiling temperature.

**Class 4** After loss of control of the synthesis reaction, the boiling point will be reached and the decomposition reaction theoretically could be

triggered. In this situation, the safety of the process depends on the heat release rate of both – the synthesis reaction and the decomposition reaction at the boiling point. The evaporative cooling may serve as a safety barrier in open systems.

**Class 5** After loss of control of the synthesis reaction, the decomposition reaction will be triggered and the boiling point will be reached during the runaway of the decomposition reaction. It is very unlikely that the evaporative cooling can serve as a safety barrier in this case. The heat release rate of the decomposition at the boiling point determines the thermal safety of the process. That is the most critical of all scenarios.

Figure 7 shows the necessary systematic experimental approach for the assessment of the thermal safety of chemical processes.

# Systematic approach for the assessment of the thermal safety of chemical processes

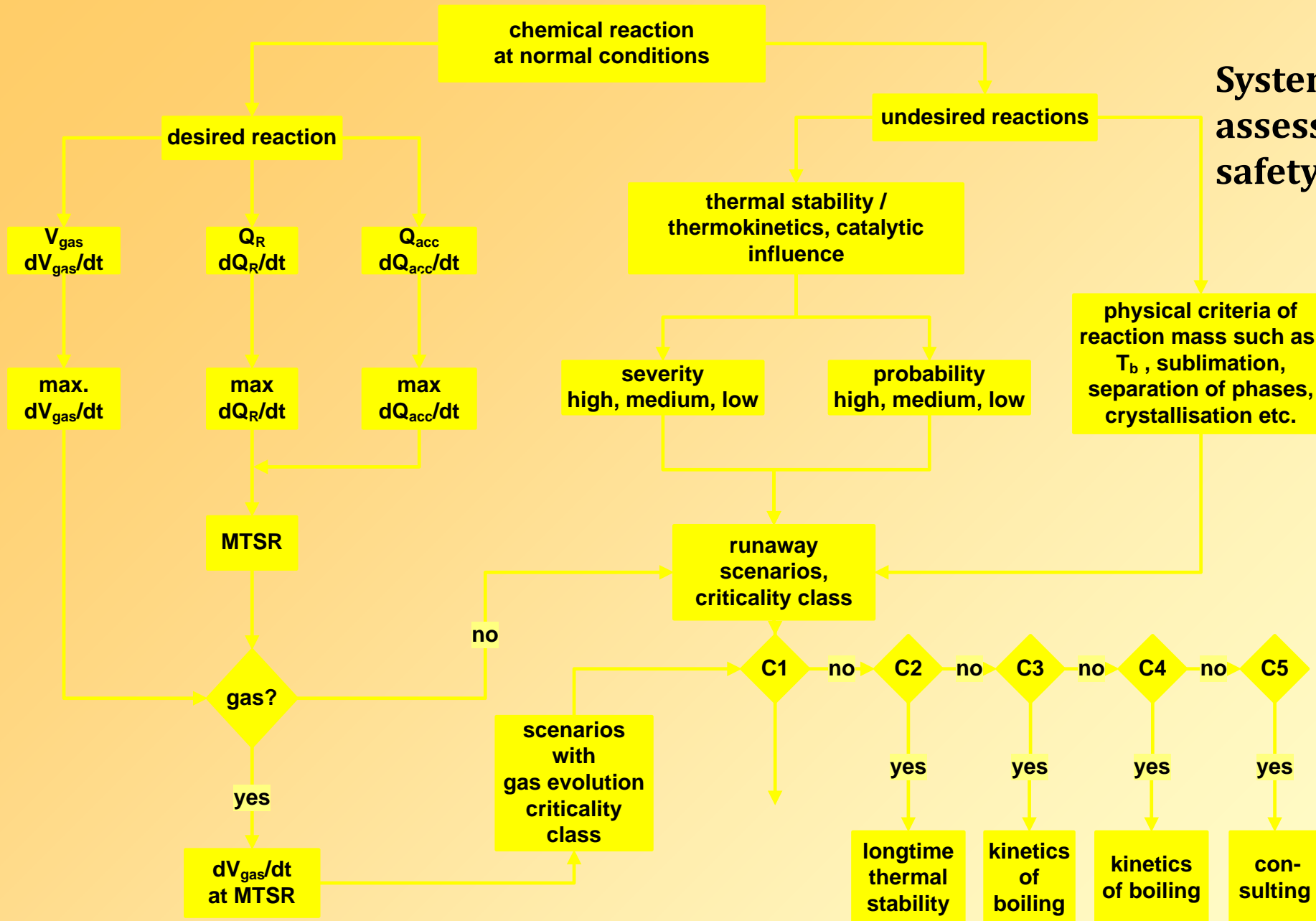


Figure 7

## **How can the presented methodology be embedded into the fault tree analysis?**

With a fault tree analysis explicitly systems are modelled that have time-invariant characteristics. They are particularly suitable for the analysis of continuous processes and for the analysis of time-invariant parts in discontinuous sub-processes, such as Protective devices.

Chemical batch processes are time-dependent. The process parameters (temperature, pressure, concentration, etc.) are dependent of the particular process step and within the process step by the time. If the system «process–Multi-product plant–organisation» is divided in the subsystems «technical system» and «process», then for this partial fault trees can be modelled. These are mutually independent and time-independent.

The partial fault trees can be linked to «modular fault trees». The result is an instrument with which the system «process–Multi-product plant–organisation»

release scenarios can be analysed. The fault trees for the subsystem «process» follow from the criticality classes that will derive from the safety analysis. They describe the overall structure of the complete fault trees, and can be modelled independent of standardised subsystems. The fault trees for the subsystem «technical system» follow from standardised modules of the Multi-product plant (figure 8). They are process-independent and are coupled with the top structure. The process-independent fault trees of the technical modules are coupled with the process-independent fault trees (component failures, power failures and human error) and process-dependent fault trees that are possible due to the operation of a particular process.

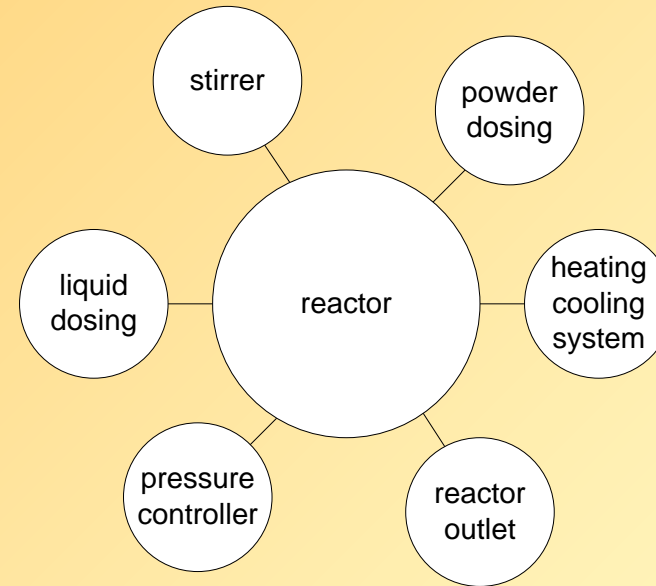
### **Risk assessment with modular fault trees**

Based on the classification of chemical process steps on the one hand and the modular understanding of MPP on the other hand, it is possible to perform a fault tree analysis.

## Defining the system levels

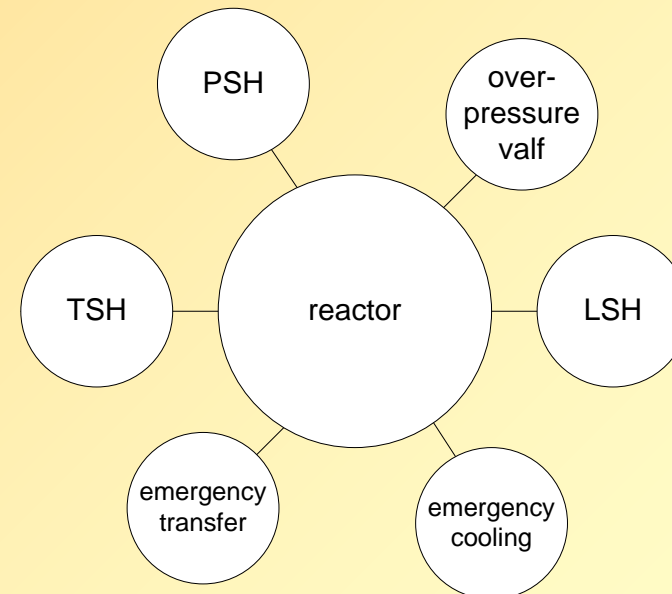
The criticality class of the chemical process forms the level of «superior structure», **the process module.**

**The fault trees for the technical modules** are separate from the chemical process. They form the system level of the modular fault tree analysis. The technical modules describe the subsystem which are used for monitoring and protecting the facility. There are two groups of modules. These are independent of each other. The **operation-modules** represent a triggering event if they fail. These modules are only temporarily active at Multi-product plants. After a process deviation the **monitoring and protection modules** bring the plant back in the safe state. In contrast to the operation-modules this devices are permanently active in the background. Figures 8 and 9 show the modules that can be divided. This modules have process-independent functions.



## Operation Modules

Figure 8



## Monitoring and Protection Modules

**PSH** (Pressure Level Switch High)  
**TSH** (Temperature Level Switch High)  
**LSH** (Level Switch High)

Figure 9

These functions in addition with piping and instrumentation flow diagrams are process-independent fault trees.

### The subsystem level

In this level, the fault trees of the technical modules are coupled with the process-independent fault trees (component and supply failures and human error) and the process-dependent fault trees. Process-dependent errors are possible due to carry out a particular process. Through the influence of the chemical process reliability characteristic values can be changed, for example, can the probability of failure of a valve, which is a protection module, increase as a result of corrosive media. When carrying out chemical processes, new triggering events can occur. For example, the probability of failure of the cooling module may increase because a substance is crystallised from the reaction mass, which reduces the thermal conductivity.

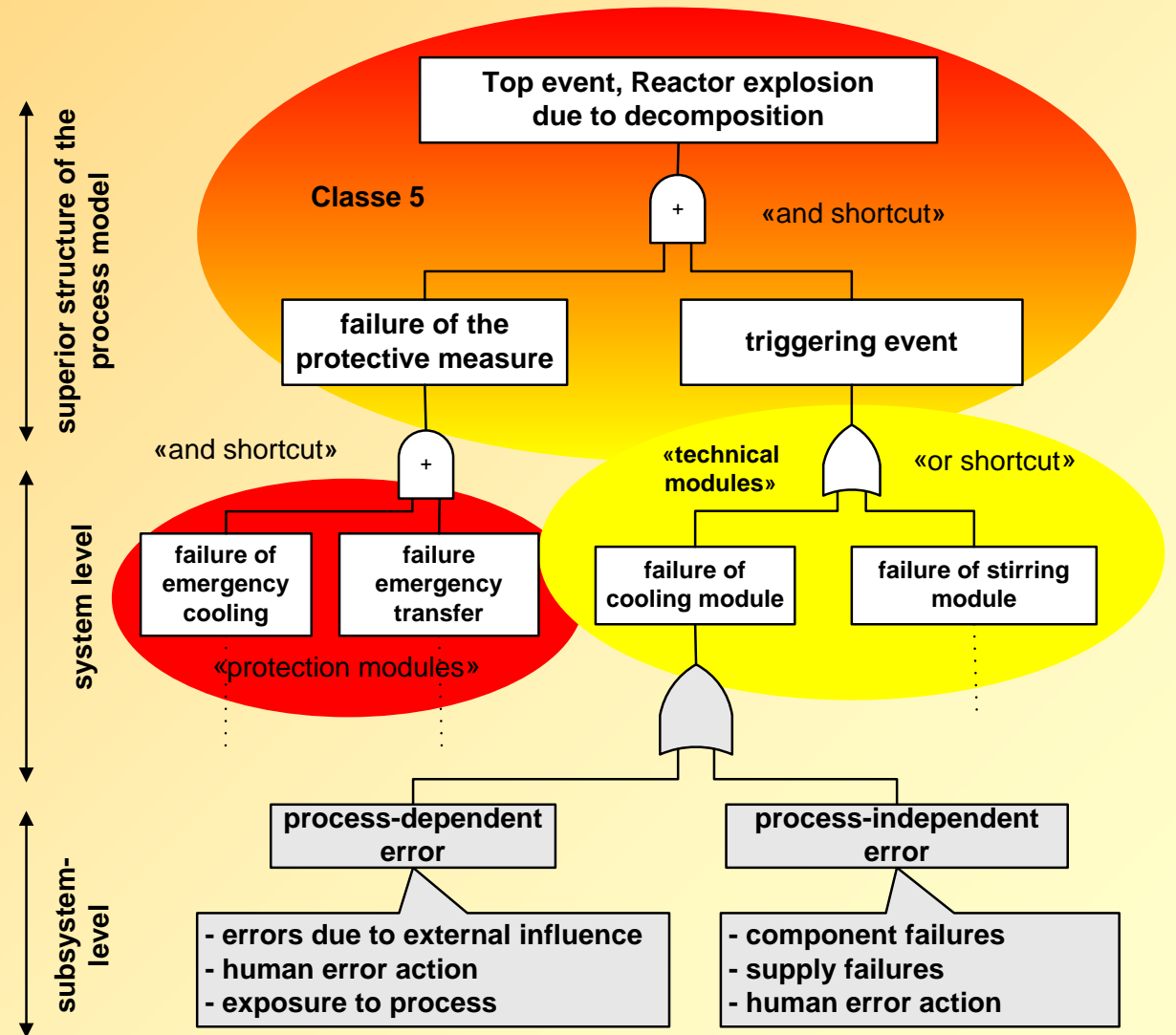


Figure 10

## System modeling

With the partial fault trees, the fault tree now can be constructed (figure 10).

First, based on the criticality classes the level of «superior structure», the process module is formed. To the system level, the independently created fault trees of technical failures is coupled to the «superior structure». To the subsystem level, the interaction of process and system, that may lead to «triggering events», is coupled to the system level.

In this way, the interaction of process, structure and organisation are visible and weaknesses in the system «process–Multi-product plant–organisation» are recognised.

## System Assessment

From the release scenarios, the probabilities of the individual events are determined. The search for relevant failures consists of three steps:

- Define the minimal combinations of failures that are sufficient to change a system of the state of function in the state of fault, the «Minimal Cut Sets».
- Search of the critical paths, resulting from those «Minimal Cut Sets» with few incidents and high probabilities.
- Checking of the used data for the critical paths on its plausibility.

Now, the process step is assessed. Because, the «Minimal Cut Sets» show those chains of events with the largest share in total failure. So that action can be targeted where they most affect the system reliability.

**Part 2b** shows the approach with a case study of the sulphonation of an aromatic nitro compound. The benefits and difficulties will be worked out.

### Literature:

- [1] Erkennen und Beherrschen chemischer exothermer Reaktionen, TRAS 410 (09.10.2012)
- [2] What is your thermal risk?, F. Stössel, Chem. 2 Eng. Progress 89, (1993), 10, pp 68-75
- [3] [Chemische Prozesse in Mehrproduktanlagen sicher fahren, Topic 1, Alfred Schnyder, Erstaugabe 2002 / Includes literature for Modular Fault Tree Analysis](#)



The E-lecture on this topic will be continued. The following parts deal with the subjects

- [Beginning and a Case Study](#)
- Methodology for visualising the dangers in batch and semi-batch processes
- Case Study, showing the methodology for visualising the dangers

and the problem areas

- heat generation
- heat removal
- accumulated heat
- heat generation and heat removal
- decomposable reaction masses and distillation masses.

After completing the series, we summarise the articles and create an E-book. This is provided to interested readers free of charge.



**SCHNYDER Safety in Chemistry Ltd.** [Company Brochure](#)

Gewerbehaus Oederlin  
Landstrasse 2B  
5415 Rieden-Nussbaumen  
Switzerland

Tel. +41 (0) 56 282 29 39  
Fax +41 (0) 56 282 28 52

[office@schnyderchemsafety.com](mailto:office@schnyderchemsafety.com)  
[www.schnyderchemsafety.com](http://www.schnyderchemsafety.com)

### **Our service includes**

- visualisation of the hazards of all process steps of chemical processes such as safety analysis and assessment of chemical processes
- defining safe process conditions
- investigation of the thermal stability of substances and mixtures
- investigation of the explosion hazards of gases and dusts
- flammability of liquids and bulk material
- electrostatic hazards
- transport classification of Dangerous Goods
- process development and process optimization are our strengths

### **In addition, we provide technical support for ...**

- outsourcing of chemical processes on MPA in other organisations
- project teams as process owners responsible for planning and construction of plant facilities
- plant engineering contractors by providing chemical and physical process descriptions and simulation of chemical processes

### **... and scientific support for reactor accidents**

- for investigation of the cause after a reactor accident
- explanation of the course of chemical accident
- creating expertise
- development of a new, safe and efficient process