

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

Part 2b: Case study, methodology

Editor

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In the **foregoing issue**, we have shown a proven methodology for visualising the dangers of chemical processes. This issue explains the approach with the case study of the sulphonation of an aromatic nitro-compound. The cause for most accidents of chemical reactions is an insufficient process knowledge. This is still strongly underestimated by the Multi-product chemistry as well as by the authorities. The economic potential of a good process knowledge is underestimated as well.

Case Study A chemical company specialized in custom synthesis has the opportunity to perform several 10 tons of a two-step synthesis for a customer. The synthesis is as follows

- **First step** Sulphonation of 1-chloro-4-nitrobenzene
- **Second Step** Hydrogenation of the nitro compound.

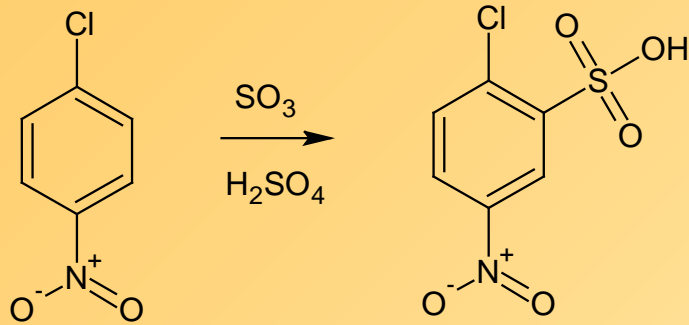
The company has planned to perform the sulphonation in an 8 m³ reactor of a Multi-product plant. The plant is not automated. On the base of a process risk analysis, the company has to decide whether the production of the process step in the existing facility is safe^[*]. The case study explains the methodology for the safety assessment of chemical reaction steps. It includes the following approach:

- Visualising the inherent dangers of the chemical reaction step ^[3].
- Classification of the dangers ^[1].
- Assessment of the step according to the planned process procedure. Definition of measures in order to prevent the reactor explosion.
- Definition of the criteria, which the system must meet, in order to initiate the preventing measures.
- Modular Fault Tree Analysis of the system «process, Multi-product plant and organisation» ^[2].

[] In the past, some serious accidents occurred at the production of 2-chloro-5-nitro-benzene sulphonic acid. We have tailored the described chemical process procedure for this case study as a demonstration example. The process safety analysis has been carried out in our laboratories.*

Description of sulphonation step

Chemistry



temperature: 65 °C, batch mode

The defined normal operation

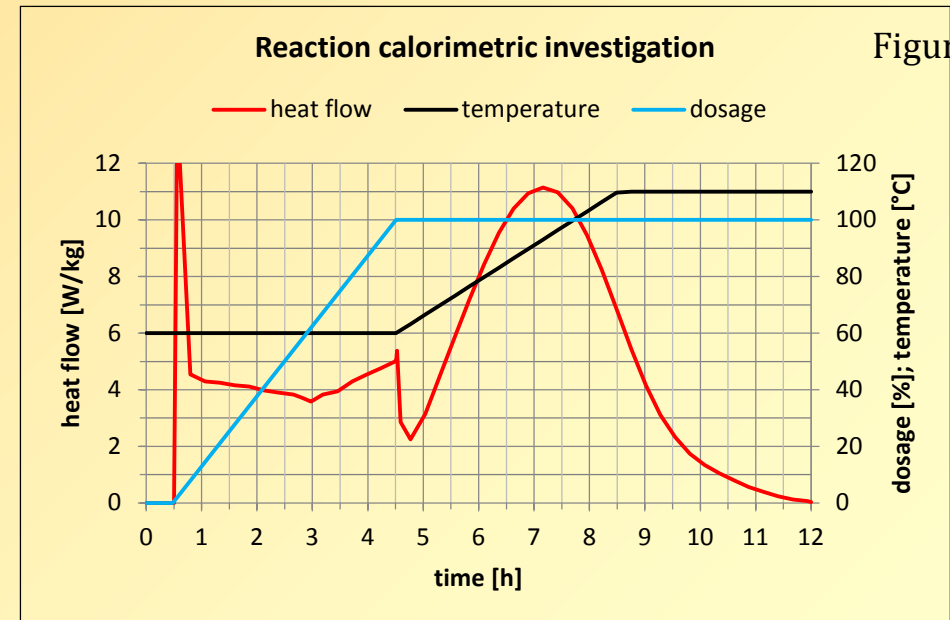
- Anhydrous sulphuric acid is loaded into the reactor. The temperature is stabilised at 25 °C.
- The Nitro halogen derivative is added under stirring.
- The resulting suspension is heated to the temperature of 60 °C. The suspension becomes a solution.
- Under stirring and cooling, the fuming sulphuric acid (oleum) is added within 4 hours.
- The reaction mixture is heated within 4 hours to 110 °C.
- The mass is allowed to react for several hours at 110 °C.

Safety Investigation of the reaction step

The sulphonation step is investigated, for inherent dangers to both for the defined normal operation and for deviations from normal operation.

Investigation of the desired reaction

Figure 1 shows the reaction calorimetric experiment of the planned procedure of the sulphonation step. The red curve shows the heat flow, the blue curve shows the dosage of oleum and the black curve shows the temperature.



During the dosing of oleum, mixing heat, heat of solution and heat of reaction are liberated. The exothermic peak at the beginning of the oleum dosing might be the heat of hydration of oleum with traces of water in the sulphuric acid.

During the heating phase (black curve), the heat flow increases slowly and reaches at the temperature of 90 °C its maximum. The measured heat of reaction is 136 kJ/kg and the heat capacity of the final reaction mass is 1.86 kJ/kg/K.

Figure 2 shows the course of the temperature that will be set at a cooling failure («worst-case temperature») and the course of the reaction temperature.

If in the sulphonation process a cooling failure or a stirring failure occurs, the temperature of the reaction mass can rise to 140 °C.

Investigation of the undesired reaction

The micro-thermal analysis study shows that the end reaction mass decomposes thermally with the potential of a high significance (figure 3).

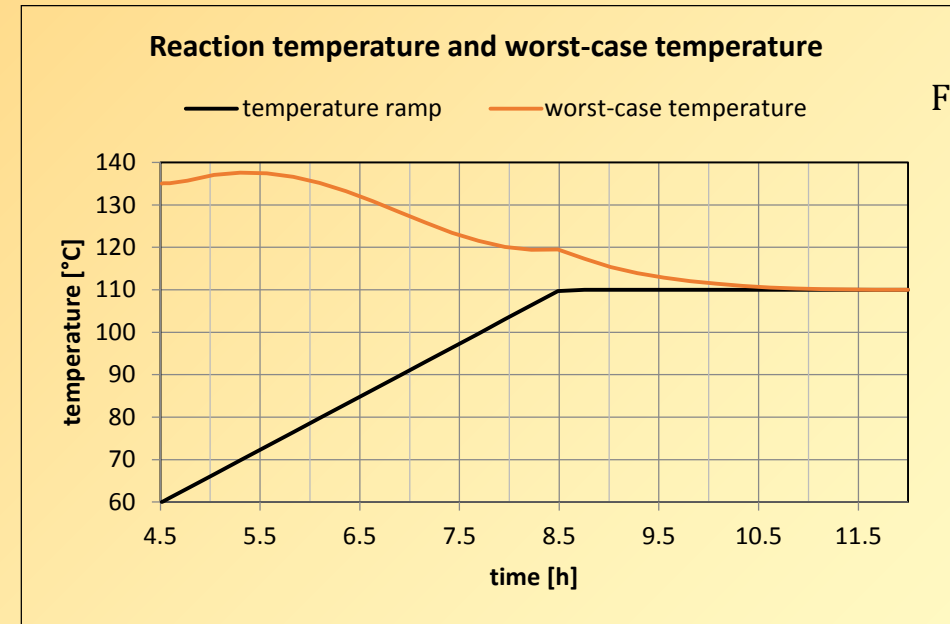


Figure 2

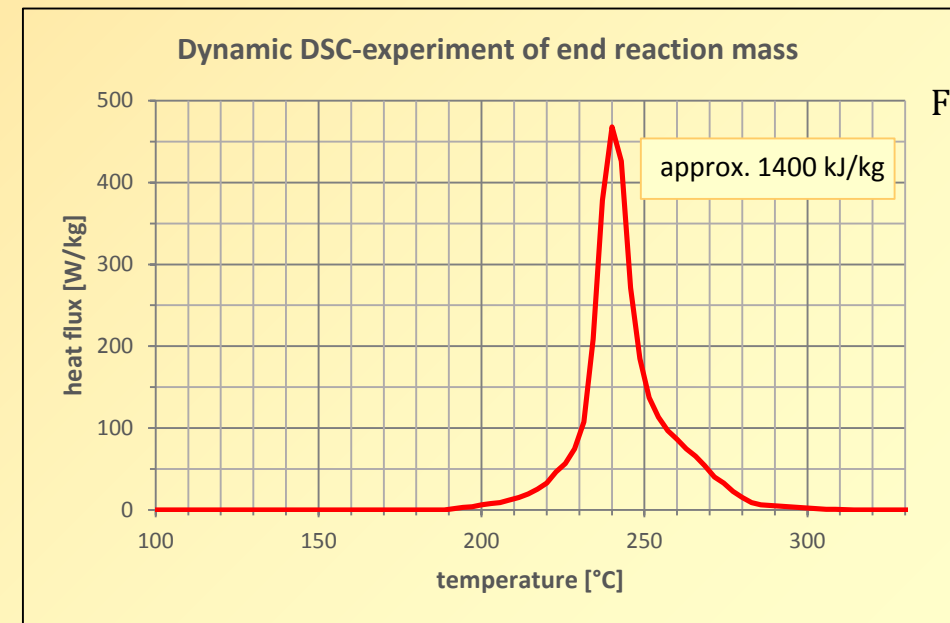


Figure 3

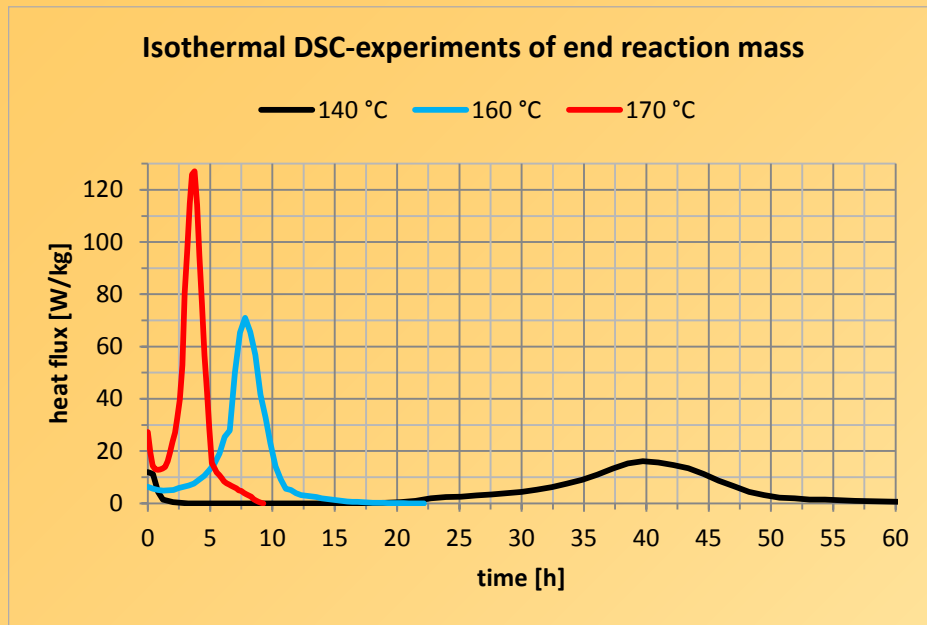


Figure 4

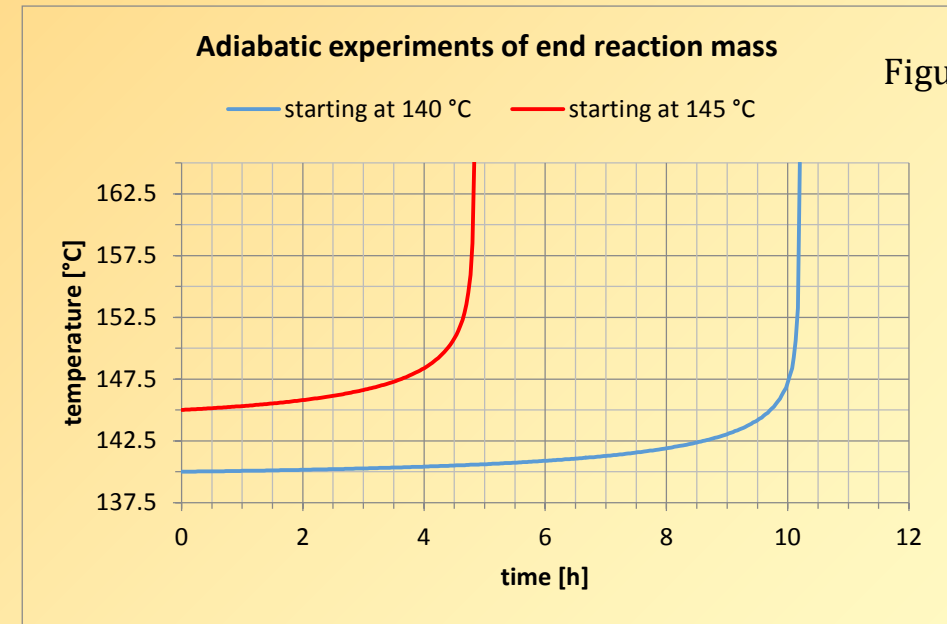


Figure 5

Isothermal DSC experiments show that the heat flux of the exothermic reaction passes its maximum after an «induction time», which is shorter at higher temperatures (figure 4). The decomposition of the reaction mass shows an autocatalytic behaviour. A statement about the stability of this reaction mass is in principle only possible by temperature and by time. From several isothermal experiments, thermo-kinetic parameters were derived and with this the adiabatic behaviour of the decomposition simulated. Figure 5 shows two adiabatic SEDEX-experiments starting at the temperatures 140 °C and 145 °C. Figure 6 shows the extrapolated TMRad values for the temperatures of 130 to 180 °C.

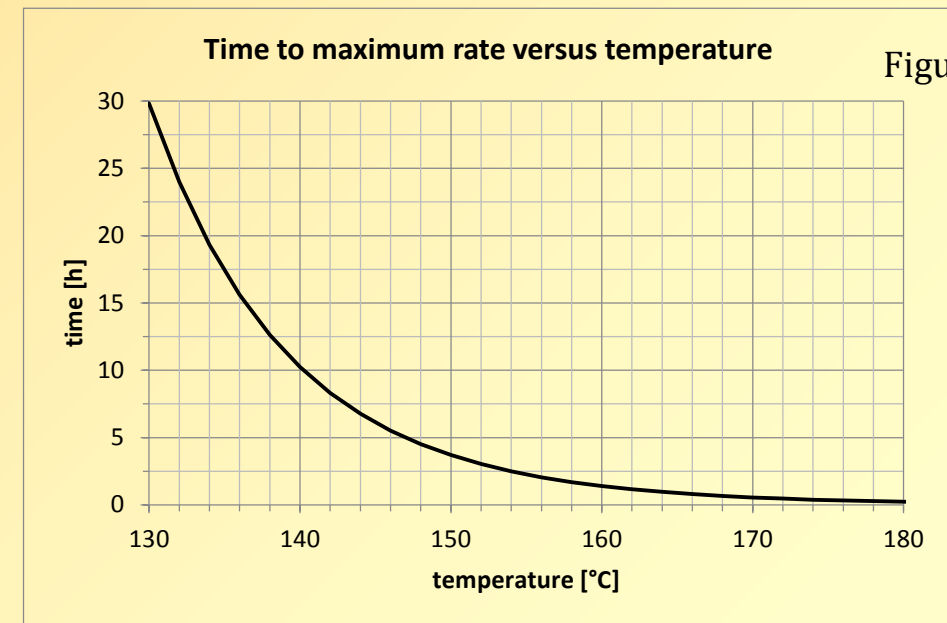


Figure 6

Assessing the sulphonation step

Figure 1 shows that the sulphonation takes place within the heating phase from 60 to 110 °C. That means that at end of dosing oleum almost all of the reaction heat is accumulated. Figure 2 shows that if the cooling or the stirring fails within the temperature ramp at 70 °C, that the temperature rises to about 140 °C. The adiabatic experiment starting from the temperature of 140 °C shows that in this case the TMR_{ad} takes 10 hours (figure 5). But when starting from 145 °C, the temperature which is reached when the temperature after the dosage of oleum is 65 °C, instead of the prescribed 60 °C, the TMR_{ad} will be so short, that it –in a Multi-product plant– hardly will be possible to initiate counter-measures (figure 6). The sulphonation step is thermally not safe. The severity and the probability are high that a thermal explosion occurs. At deviations from normal operation the reaction step can only be controlled with emergency measures. Figure 7 shows the procedure for the classification of the process step. The decisions that ultimately lead to criticality class 5 are shown in red.

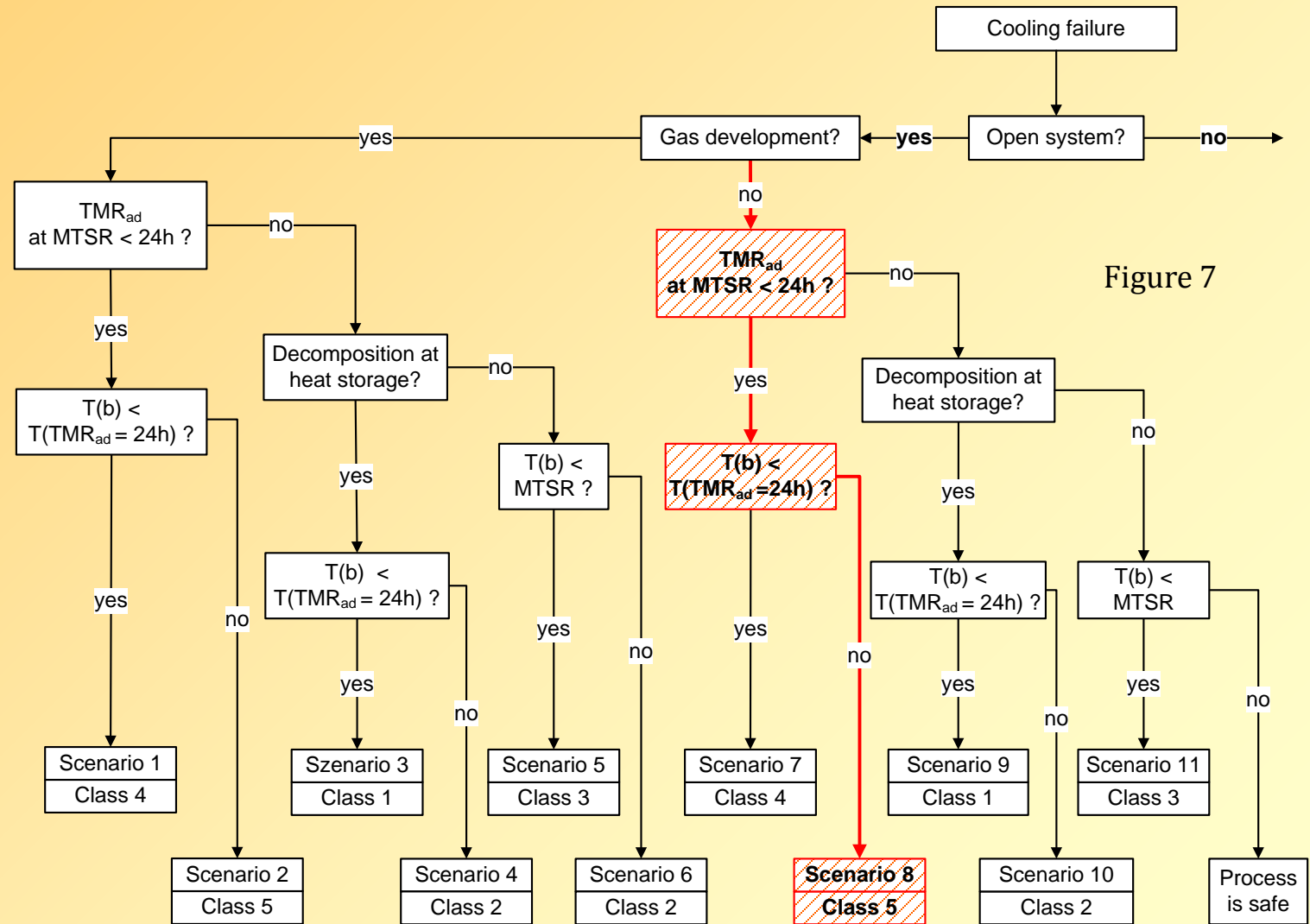


Figure 7

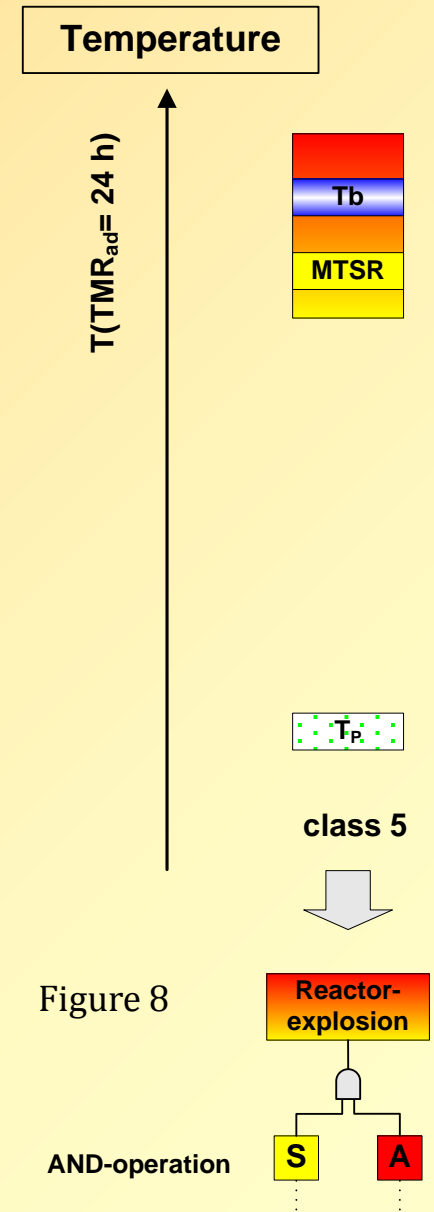
The MTSR and the boiling temperature are in the temperature region where the TMRad for the thermal explosion is lower than 24 hours (figure 8). This process step must not be run in the manually controlled installation. Process deviations from normal operation due to a cooling failure or a stirring failure results in an event of considerable severity, and that this event occurs with high probability, if the heat storage lasts for several hours. If errors are made in the temperature ramp, the risk is too big that the MTSR is higher than 140 °C. But a higher MTSR leads to a shorter TMRad.

Considering the fact that the process is dangerous, the management has to decide, whether

- it refuses the chance to produce the chemical.
- it would be better to develop a new process, with which the chemical can be produced less risky.

In the case that management decides to produce, a chemical plant must be available, in which a defined emergency measure automatically is initiated. A production facility for which with a risk analysis can be proven, that the defined emergency measure with high reliability starts. So that the probability of a failure is extremely low.

Fortunately, the experience shows that in most cases chemical processes can be designed such, that high severities of possible incidents are reduced. Or else the procedures can be designed in a way that the probability of occurrence of an incident with high severity is as low as possible. See the example in the publication [«Chemical process safety begins with chemical process development»](#).



Following it is not the aim to extol quantitative risk analysis systems. The aim is to show, how much the knowledge of failure data of the system modules influences the result of fault tree analysis.

Definition of measures in order to prevent the reactor explosion

The safety investigation has shown that the deviation from normal operation due to a cooling failure or a stirring failure results in an event of considerable severity, and that this event occurs with high probability, if the heat storage lasts for several hours.

To run this process safely, a system is needed with which the heat storage can be excluded by preventing measures. A possible preventing measure is an **emergency transfer** of the reaction mass in a stirred tank with plenty of ice and water.

Figure 9 shows the scheme of a system in which such an emergency transfer can be carried out. The system consists of the reactors R0, R1 and R2 and a rubberised tank R3, which is used as **emergency vessel**. R0 is equipped with a hot water circuit. R1 and R2 are connected to heat transfer systems.

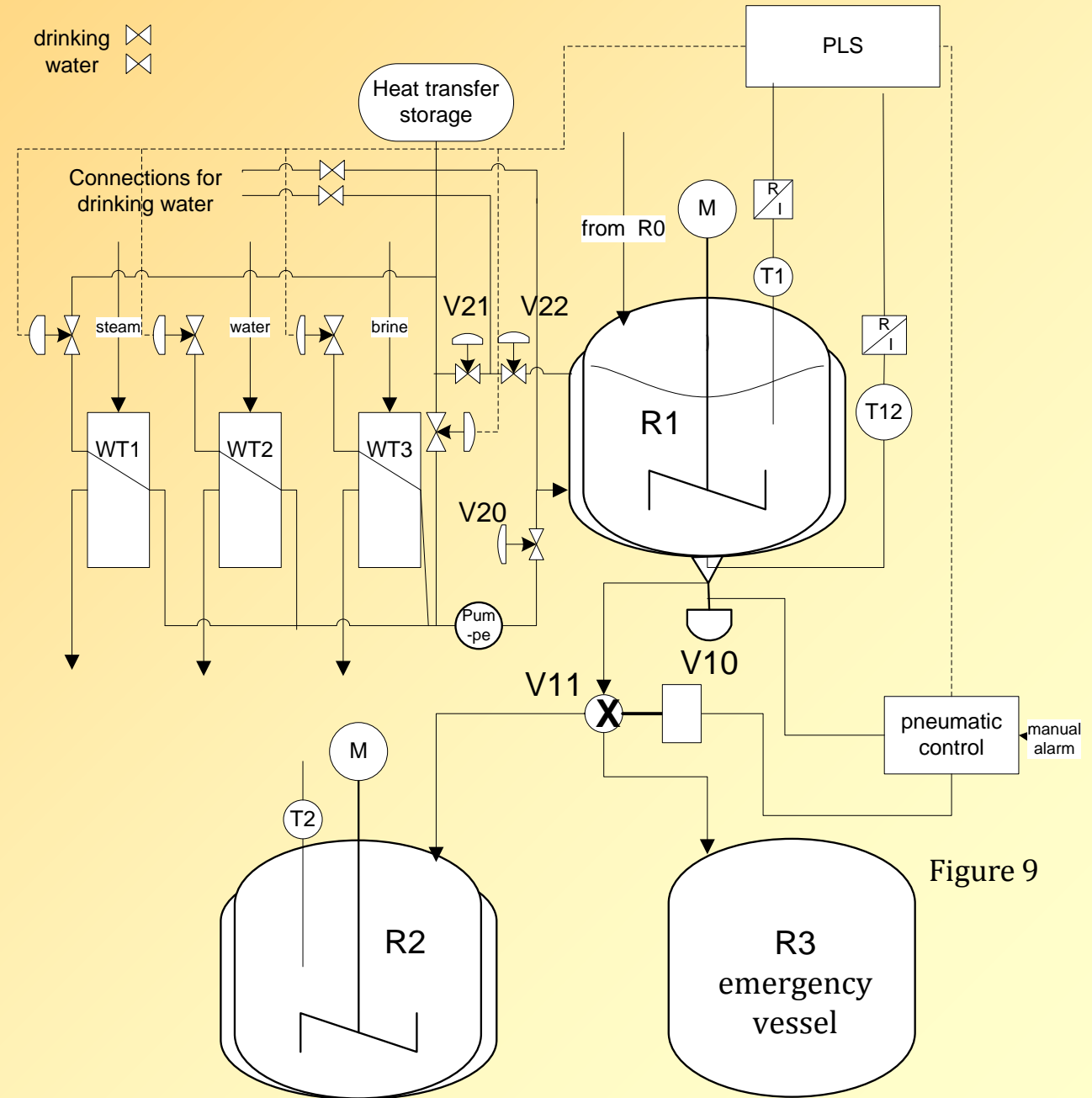


Figure 9

Planned processing of the sulphonation step

- In R0 the halogen derivative is dissolved in sulphuric acid at 60 °C. The resulting solution is moved to R1.
- In R1, the dosage of oleum is done first and the temperature-ramp is carried out then. Thereafter, the reaction mass is transferred to R2.
- In R2 the post reaction phase is carried out.

Search for dangers, assessment and action planning

Based on the defined production plant and the defined procedure, a systematic search for dangers is carried out. Dangers that arise at deviations from normal operation are classified as hazardous. Now –against each hazard– measures must be defined, for which it is believed, that they reduce risk to an acceptable level. Figure 10 shows an excerpt of a list in order to illustrate scenarios with high severity.

Risk analysis of the sulphonation step

The scenarios that lead to events with high severities are analysed with the Modular Fault Tree Analysis^[2]. Because it is an excellent tool to combine the method of assessment of chemical processes with the proven method of risk analysis

RISK ANALYSIS		Level IV and V Risks catalogue / risk assessment / measures		
PROJECT: Case study sulphonation				
Work step	Hazard	Risk		Measures
		P	S	
	Stirrer failure: Without stirring, no heat can be dissipated. Without heat dissipation, the temperature rises in the decomposition range. Without stirring the emergency cooling is ineffective.	M	H	<ul style="list-style-type: none"> • Stirrer monitoring • During failure temperature monitoring of the reaction mass • Emergency transfer •
	Cooling failure: Without heat dissipation, the temperature rises in the decomposition range.	H	H	<ul style="list-style-type: none"> • Activate emergency cooling (organizational measure) • During standstill monitoring temperature of the reaction mass • Emergency transfer

Figure 10

of technical systems. The scenarios include the technical failures and the technical failures that are relevant in combination with human wrongdoing. With the detailed modeling of dependent failures, caused by shared support facilities as well as failures caused by component failure, are also considered

Considered events

The top event of modular fault trees is the reactor explosion due to thermal decomposition of the sulphonation step. The sulphonation step was classified by the safety analysis into the criticality class 5 (see figure 8).

Figure 11 shows the top structure of the fault tree for the scenario reactor explosion resulting from a decomposition reaction. This fault tree is used for analysing the triggering events and protective measures (see table).

Scenarios to be modelled		
no.	triggering event	protective measure
1	cooling failure	emergency transfer and emergency cooling
2	stirrer failure	
3	cooling- and stirrer failure	

Description of the technical subsystems

Based on the plant scheme in figure 9, the technical modules are modelled. The fault trees to the technical modules are not discussed in this paper.

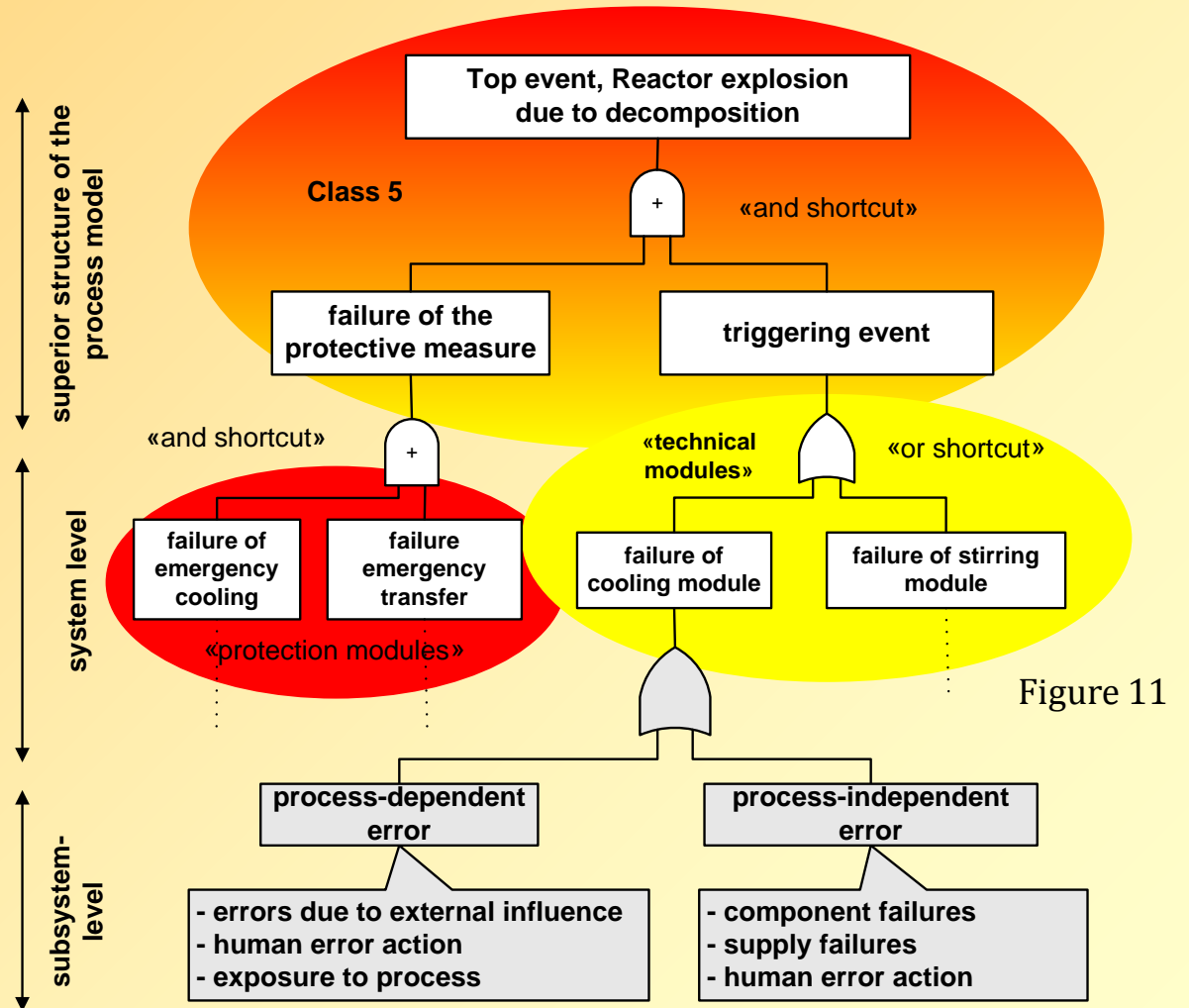


Figure 11

The **heating and cooling module** is designed for the temperature range -30 to 170 °C.

- Above 45 °C, the heat exchanger with water WT2 is used.
- Below 35 °C, the heat exchanger with brine WT1 is used.
- Between 35 °C and 45 °C, there is a smooth shift from cooling with brine to cooling with water.

The **temperature** is controlled by two sensors:

- Sensor T1 in baffles
- Sensor T2 in the bottom drain valve

The **stirrer module** allows adjusting the stirrer speed continuously by frequency inverter. Both the frequency inverter and the sealing liquid pump are monitored. A failure effects the status without energy. All valves are closed and the motor is turned off.

At a critical temperature increase, the emergency transfer is automatically initiated. The reactor content is emptied into the emergency tank, in which the necessary amount of ice and water was loaded. The pneumatic valves is actuated either via the process control system, the local computer or by hand over a sealed emergency valve. If the pneumatic control fails, an emergency tank with compressed air serves as a pressure pad.

The bottom drain valve V10 is closed in airless state and the three-way valve V11 is in direction to the reactor R2. The criteria for activating the emergency transfer are defined as follows:

- If the temperature exceeds 115 °C, is either via the process control system or by the local computer an alarm activated.
- If the temperature exceeds 118 °C, the emergency transfer started automatically. If the automatic system fails, a manual button can start the emergency transfer.

The sensors T1 and T2 are associated with both the heating module and the cooling module. T1 and T2 are also used for starting the emergency transfer. This does not affect the calculations. The triggering events, that in a fault tree several times occur, are reduced to one event. The following assumptions are used:

- The temperature measuring groups of the heating and cooling system and emergency transfer systems are independent.
- The temperature measuring groups of the heating and cooling system and emergency transfer systems are

independent of each other. They belong to subsystems which are controlled by another maintenance program. The dependent failures of redundant facilities (e.g., temperature sensors) were included in the analysis.

Furthermore, the following assumptions are taken:

- The valve V10 is operated once per process cycle.
- The three-way valve V11 is operated only once per month (for the simulation of an emergency transfer).

The **module of the emergency cooling system** is shown in figure 9. To initiate it, the drinking water has to be connected by hand due to organisational measures. But, that by the emergency cooling sufficient heat can be removed, the stirrer module must work. A failure of the stirrer module thus causes the failure of the emergency cooling.

Modular Fault Tree Analysis

The following notes show the method of «Modular Fault-tree Analysis». They are not complete. The discussion of the fault trees for the cooling- and the stirrer module is beyond the scope of this paper. The «minimal cut sets» are shown so that the weak points of the subsystems are visible.

Minimal cut sets: List of minimal, necessary and sufficient conditions for the occurrence of the top event.

Only the stirrer failure (scenario 2) is discussed. Figure 12 shows the structure of the scenario reactor explosion by stirrer module failure. This module was linked to the fault trees failure of the stirrer module, the emergency cooling module and the emergency transfer module. The top event «reactor explosion by decomposition» was calculated based on the minimum cut set determination.

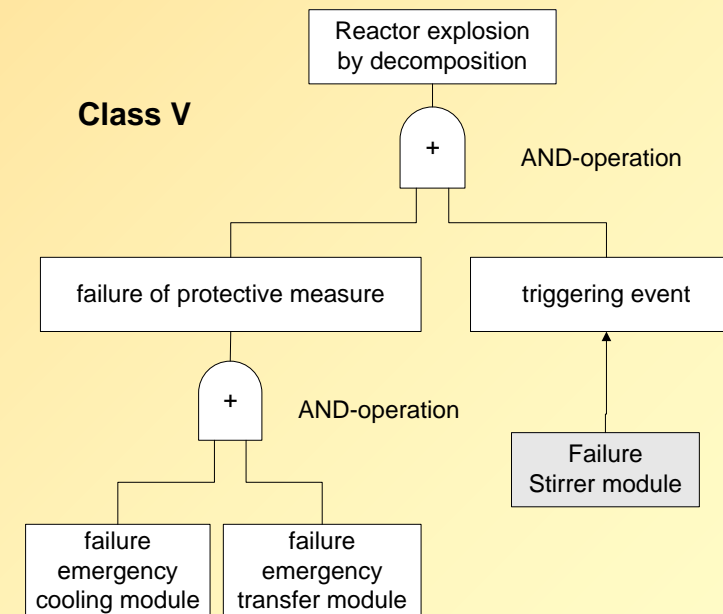
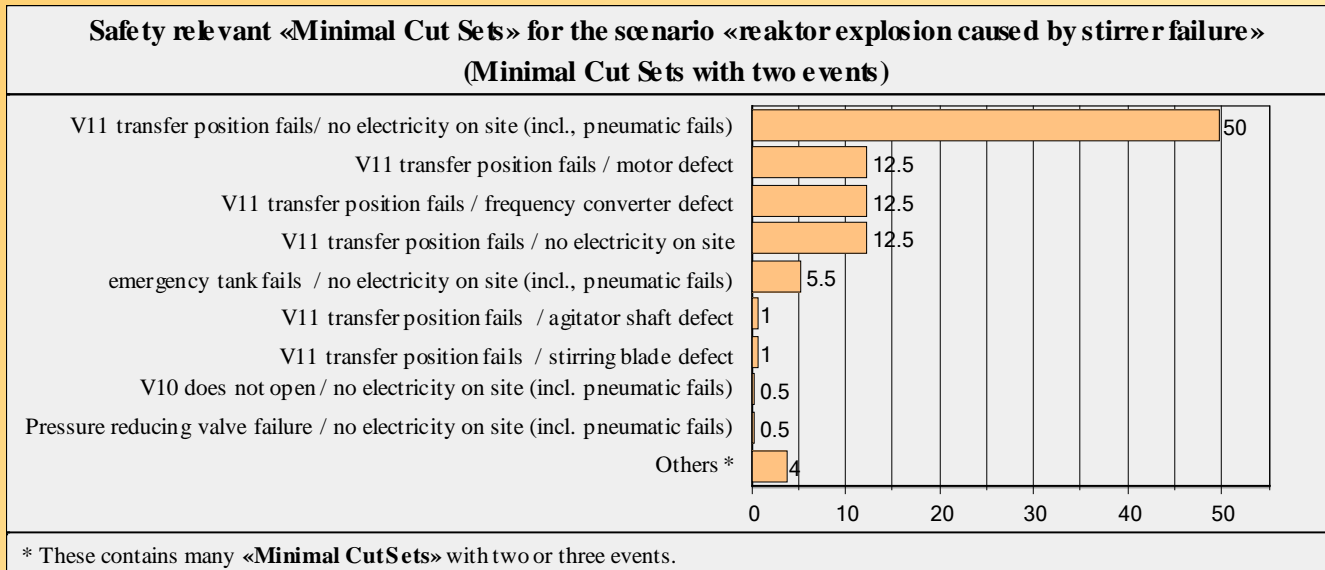


Figure 12

Figure 13 shows the triggering events whose «minimal cut sets» contribute 96% to the incident «reactor explosion by decomposition». The analysis of the «minimal cut sets»

shows that mainly the valve V11 contributes to this failure probability. This is at about 90% of the failure combinations that lead to the reactor explosion involved (figure 13). For this scenario, there are even more «minimal cut sets» with two or more events, but only contribute little to the top event. Related to the reactor occupancy, the quantitative risk analysis yielded the following values for the expected default frequency. For the scenario reactor explosion by a cooling module failure is it in the order of $4 \cdot 10^{-6}$. And for that of a stirrer module failure is it in the order of $5 \cdot 10^{-6}$.

Without stirring, no heat is removed. In this case, the temperature of the sulphonation mass increases into the decomposition range. Both the stirrer module failure and the cooling module failure triggers the reactor explosion. The fault tree in figure 11 makes this «or-shortcut» visible. In the «or-shortcut» suffices each triggering event to trigger the considered event. That means, probability is the sum of the probabilities of occurrence. With the assumption, that the process is carried out 300 days a year with three shifts per day, the accident rate for the scenario is calculated to $3 \cdot 300 \cdot (4 + 5) \cdot 10^{-6} = 8.1 \cdot 10^{-3}$ per year.



Assessment of the sulphonation step

The question now whether the sulphonation step shall be run in the considered system, is assessed on a semi-quantitative approach. Figure 14 shows an example of a half-quantitative assessment of the accident severity, and figure 15 shows that for the probability. This classification is for risk analysis teams – with members of different specializations– easy to imagine.

Figure 13 (based on [2])

The sulphonation step is thermally not safe. If the reaction mass decomposes, the severity is high. It is classified into the **severity class I**. By the fault tree analysis was calculated that the frequency about one hundredth per year is, that due to stirrer module or cooling module failure the thermal explosion is triggered. The **probability** is classified in **class E**. The risk matrix shows that the risk analysis depends on the credibility of the failure data. If they are less trusty, then the risk is more in the yellow or in the grey field of figure 16. Due to this uncertainty, the sulphonation step should not be run in the given system. The process step should be re-designed.

Severity class		Description
I	Man Environment Property values	fatality, people outside of site evacuated outside of the site long-term damage > 10 million CHF, > 1 year failure of system
II	Man Environment Property values	injured, outside of site irritation reversible damage in neighbourhood < 10 million CHF, < 1 year failure of system
III	Man Environment Property values	injured only on site, irritating people on site site, possibly affected wastewater plant < 2 million CHF, failure of system for weeks
IV	Man Environment Property values	minor injures only on sites only facility and site affected < 2 million CHF, failure of plant for days

Figure 14

probability	description	
A	frequent	more than once per year
B	often	once per year
C	occasionally	once per 5 years
D	rare	once per 30 years
E	unlikely	once per 100 years
F	very unlikely	once per 1000 years

Figure 15

possibility	A				
	B				
	C				
	D				
	E				
	F				
		IV	III	II	I
		severity			
		Above red line: Risk is not accepted			
		Below red line: Risk is accepted			
		estimated risk of the sulphonation step			

Figure 16

Closing Remarks

Risk assessments for chemical Multi-product plants are complex. The question, by what measures and methods the public demand for safety –in chemical production, storage and transportation– is met, is answered differently^[4]. For Multi-product plant owners some principles apply^[5].

Principle 1 Risk analysis that aims to get quantitative values of risks, are not able to increase the safety standard of Multi-product chemistry. This is because

- the uncertainty of the risk values are too large,
- very many influencing variables cannot be objectified,
- it is difficult to quantify the maximum extent of damage.

Principle 2 It is not necessary to improve the methods of quantitative risk analysis, because the problem is not the method, but the objectives pursued. However if fault tree analysis is used to evaluate different alternative systems, it is a good tool.

Principle 3 The most effective safety concept for the Multi-product chemistry is that which minimizes the risk potential itself and not its probability of occurrence. The inherent safety, which is achieved for the Multi-product plant by process development, is better than a later assessed risk value. Because

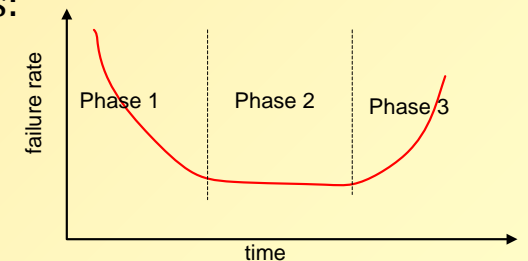
- the inherent safety of a chemical process minimizes any risk to humans and the environment,
- the inherent safety of the system cannot be affected by uncertainty,
- risk calculations are open for mathematical manipulations. In contrary, the inherent safety of a system is not.

The risk for thermal explosion –as discussed previously – is only effectively reduced with a re-designed process. The reaction step must be tailored, so that by the accumulated energy the temperature not rise so high, that the thermal decomposition is triggered. The safety of the reaction step is not increased by installing a valve with a lower failure frequency –designed by sophisticated engineering technique.

Further, it should be noted that **Multi-product chemistry** produces mainly small campaigns. However, the experience has taught us that risk is a function of time. It behaves like a bathtub curve with three phases:

- decreasing failure rate
- constant failure rate
- increasing failure rate

Small campaigns fall in phase 1.



Literature:

1. What is your thermal risk?, F. Stössel, Chem. 2 Eng. Progress 89, (1993), 10, pp 68-75
2. Madjar, M.; Methoden zur Risikoanalyse in der Fein- und Spezialitätenchemie, (ETH Eidgenössisch Technische Hochschule Zürich), Dissertation Nr. 11317
3. [Chemische Prozesse in Mehrproduktanlagen sicher fahren, Topic 1, Alfred Schnyder, Erstausgabe 2002 \(discussed example in more detail / more literature to this topic\)](#)
4. More to this topic see «Chemiepolitik: Gespräch über eine neue Kontroverse» Herausgegeben von Martin Held, VCH Verlag GmbH, Weinheim, 1988.
5. Based on an article by Hans-Nicolaus Rindfleisch «Perspektiven und Grenzen von Risikoabschätzungen für Unfälle in der chemischen Industrie» (citation [4]).

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, to show the methodology for visualising the dangers of chemical processes

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.



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- 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