

**The batch reactor, so simple –  
so much unpredictable**

**Part 1: Beginning and a Case Study**

**Editor**

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# Beginning

A considerable number of the products produced by the chemical industry are manufactured by the batch method. This enables a manufacturer to respond very quickly to changes in the market. Complicated, multistage processes can be handled in «Multi-product facilities» using relatively simple production equipment. Expensive, speciality chemicals are made in such plants. Often very different chemical processes are performed in the same Multi-product facility. Control of the process is then to a large extent determined by the particular characteristics of the chemical reaction in question. Further, with batch wise production the actual targets of optimum process control are more difficult to quantify than with continuous processes. As a rule, a batch process is examined less thoroughly because the operations are usually small scale. Not infrequently, chemical processes are transferred directly from laboratory to a Multi-product facility, scaled up by a factor of 10000. Reactor construction and the tactics of process management are based chiefly on past experience. The possibly dangerous thermal behaviour of reaction mass and their components constitutes a serious hazard in the chemical industry. A thermal explosion is therefore of particular concern in Multi-product facilities.

Our long-term experience in the safety analysis of chemical processes as well as the investigation of reactor incidents have shown that it is not sufficient for safe operation of Multi-product facilities to evaluate data on the thermal stability of the reactants and the reaction mixtures. The possibilities for triggering the potential of a substance release due to a «runaway reaction» are complex. These always consist of a combination of characteristics that come from different risk areas. Figure 1 shows the «and-shortcuts» of the preconditions for a runaway reaction.

## Causes of dangers from different areas of the system «process, Multi-product facility and Organization»

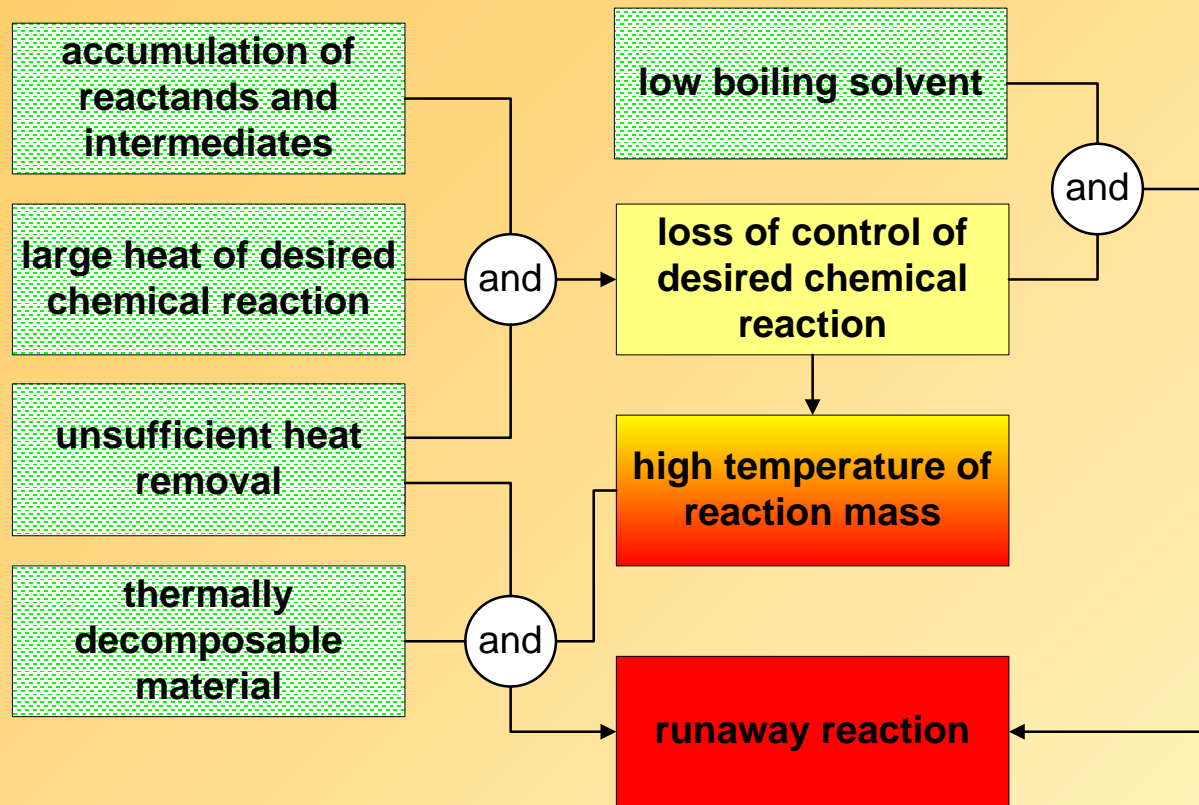


Figure 1

### Causes for accumulation of reactants or intermediate products:

- incorrect assumptions of the reaction kinetics
- excessive dosing
- too low process temperature
- insufficient mixing
- incorrect or lack initiation
- inhibiting impurities

### Causes of not enough heat removal:

- stirrer failure
- insufficient cooling capacity
- excessive heat insulation
- incorrect assumptions about the heat transport
- cooling failure

### Causes of too high a temperature:

- wrong temperature selection
- unintentional heating
- energy input by stirring
- intrusion of heat transfer fluid
- catalysing impurities

A statistical review of incidents of thermal explosions in the chemical industry due to chemical reactions of the type  $A + B \rightarrow \text{product}$  revealed the causes

- insufficient knowledge of the process chemistry and thermochemistry

For the failed chemical processes

- wrongly designed cooling systems
- wrongly designed monitoring and safety systems
- incorrect process management and
- poorly trained personnel.

In this publication series we show with case studies and process simulations how the complex interactions of the hazard areas —outlined in figure 1— influences the safety of chemical processes. It is our target to show that even for discontinuous chemical productions in Multi-product plants general applicable criteria can be derived, with which chemical processes can be adapted to given facilities.

As a case study we have chosen an incident which happened in a classical Multi-product facility and that has triggered a runaway-reaction. The case study is deliberately broadly discussed because it shows some historically grown deficits of Multi-product chemistry. The affected Multi-product plant was built many years ago in order to perform a specific type of chemical reaction within a homologous series. This chemical reaction type is used for more than 50 years in order to produce several —chemically closely related— economically interesting products.

These products are only competitive because they can be produced in an already amortized Multi-product facility. The method is technically not complicated, the system is quite simple and undemanding. It was always believed that the dangers posed by the facility are small. To the authorities, the risk could be explained as manageable and easy to understand. The approval of the plant was never a concern, even not after the accident.

## Case study 1

**The incident:** On the day of incident above a chemical plant a huge pungent gas cloud arose, which was slowly blown by the wind over the neighbouring city (figure 2).

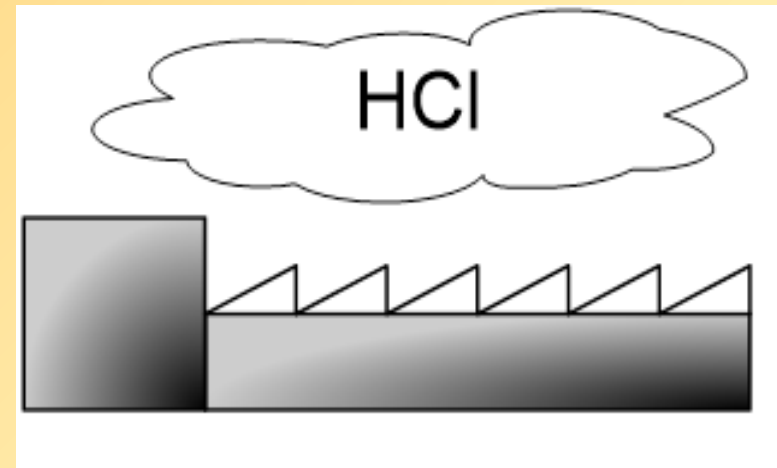


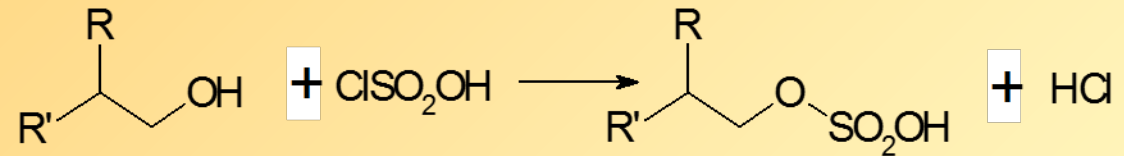
Figure 2

Shortly after the gas cloud was visible, the police was on the spot. It was immediately clear that a chemical process led in a runaway reaction. The chemical plant-owners could not explain what had happened. He gave the information that the product has been produced for more than 30 years, every year for a few weeks, without that ever an event have occurred. The question whether the accident was caused by a technical or human error could not be answered directly.

### Description of the failed process:

In a first reaction step, a fatty alcohol is sulphated with chlorosulfonic acid. The chemical reaction is carried out without solvent. In a second reaction step, the resulting mass is transferred to another reactor in order to neutralize it in diluted sodium hydroxide. Figure 3 shows the pathway.

#### Sulphation step



#### Neutralisation step

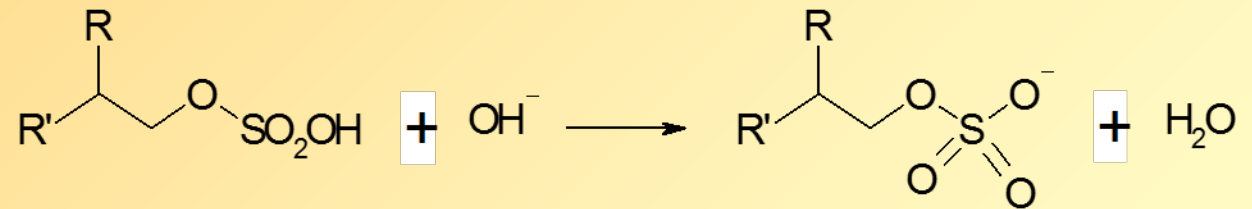


Figure 3

### Description of normal operating conditions, which has been applied:

The corresponding fatty alcohol is loaded from silos or drums into the reactor. Chlorosulfonic acid is added manually, so that at the maximum possible jacket-cooling the temperature does not exceed a certain value. After completion of chlorosulfonic acid addition, the reaction mass is stirred for a prescribed period of time. The cooling is switched off. The end reaction mass is transferred to the second reactor, neutralized and adjusted by dilution to a defined concentration.

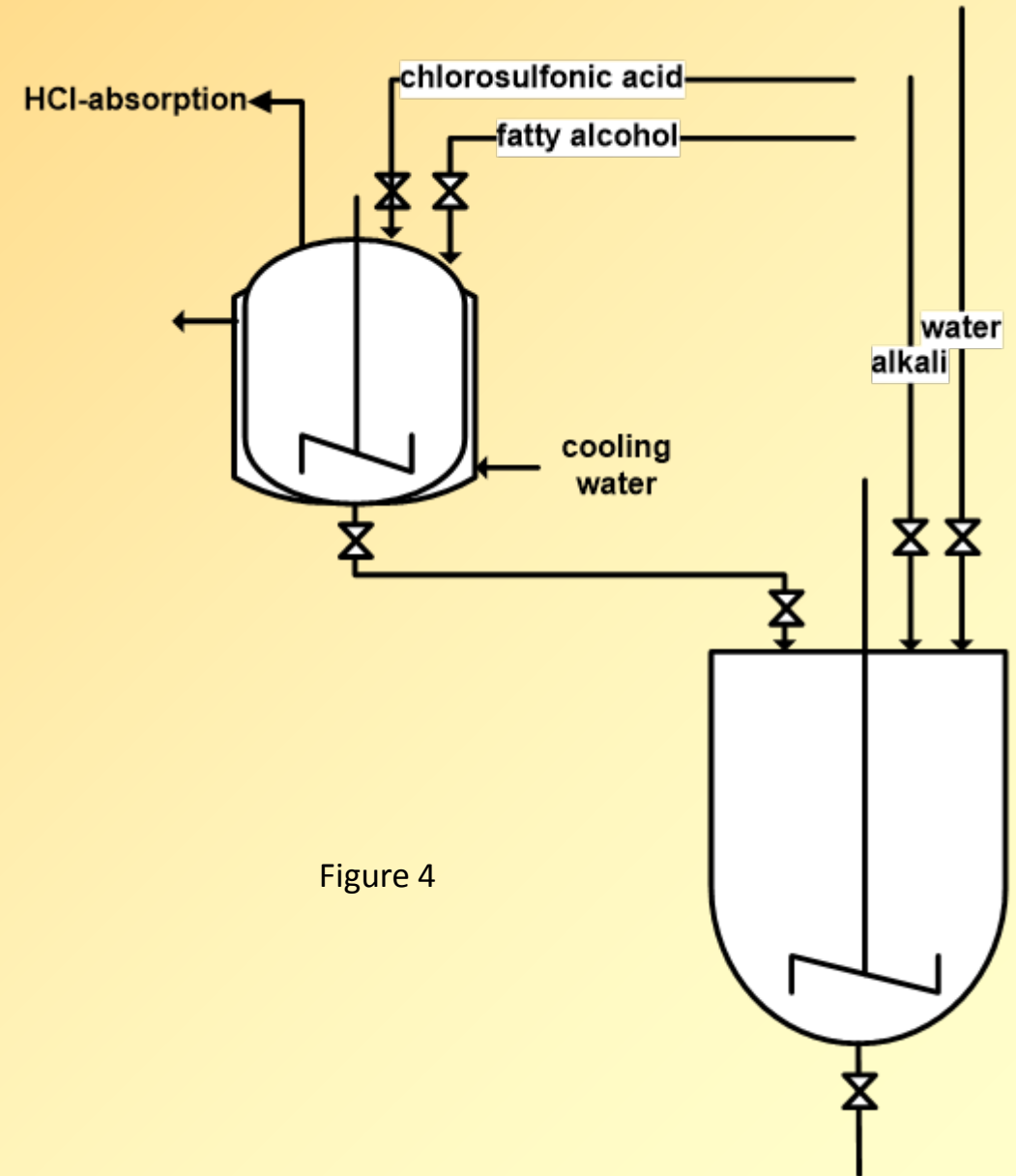
## Description of the plant:

The plant is built quite simple (figure 4). The dosage of chlorosulfonic acid and the temperature control are not carried out by automated measurement and control technology. The reactor is cooled with cooling water. The cooling water is recycled with a cooling-water recovery system. The resulting cooling water temperature is random.

## Reconstruction of the course of events

The questioning of the operator revealed the following:

- The dosage of chlorosulfonic acid proceeded not exceptional. The temperature of the reaction mass did never exceed the limit.
- At the start of the transfer of the end reaction mass into the neutralisation reactor, the operator had heard a strange «popping».





- Because he had never heard such a popping, he interrupted the transfer of the reaction mass and informed his superiors immediately.
- After a certain time, even before further action could be set, there was a very rapid temperature rise in the reactor. The reactor assemblies were broken and a large amount of HCl gas was blown-out. At the same time the staff fled into a sheltered place.

## Evaluation of accident cause

To get an overview of the «normal reaction» behaviour, experiments were run in a METTLER reaction calorimeter (RC1).

The dosage of chlorosulfonic acid was carried out as described in the operating instructions. The experiments showed a first surprising result (figure 5):

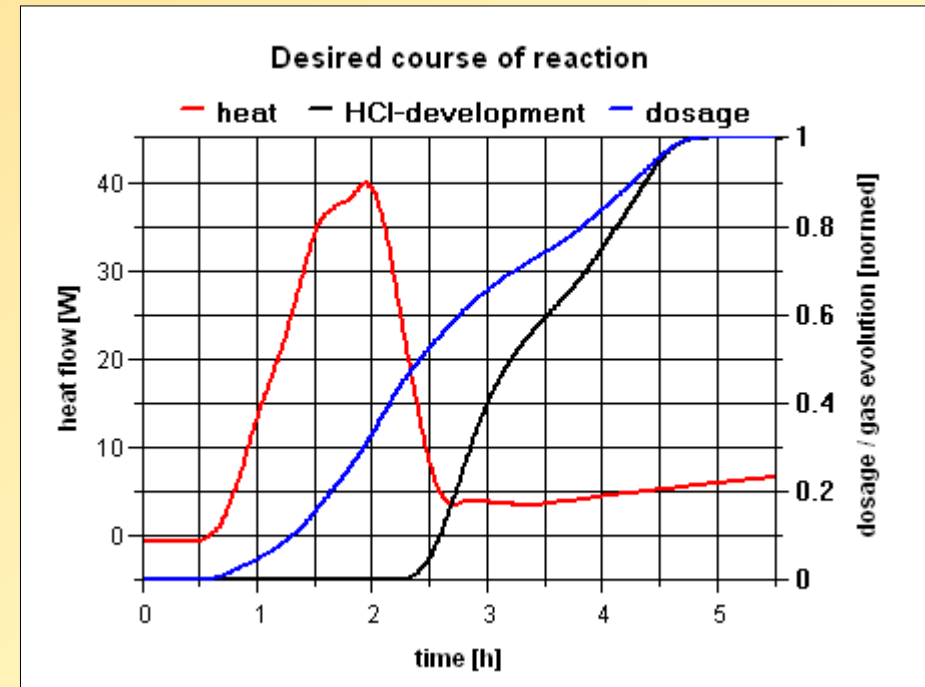


Figure 5

- The majority of the heat generation (red curve) takes place within the first half of chlorosulfonic acid dosage (blue curve).
- The evolution of HCl (black curve) begins only after the decay of the heat, but it is completed at the end of dosing.

To find out whether the delayed release of HCl gas is of physical or chemical nature, a number of reaction calorimetric experiments combined with online FTIR measurements were carried out. Figure 6 shows a plot of the changes in the online FTIR spectra in the wavenumber range 2000-600  $\text{cm}^{-1}$  in the course of dosing chlorosulfonic acid.

The IR-bands were assigned by measurements of the reactive starting materials, of the postulated intermediate and of the final product.

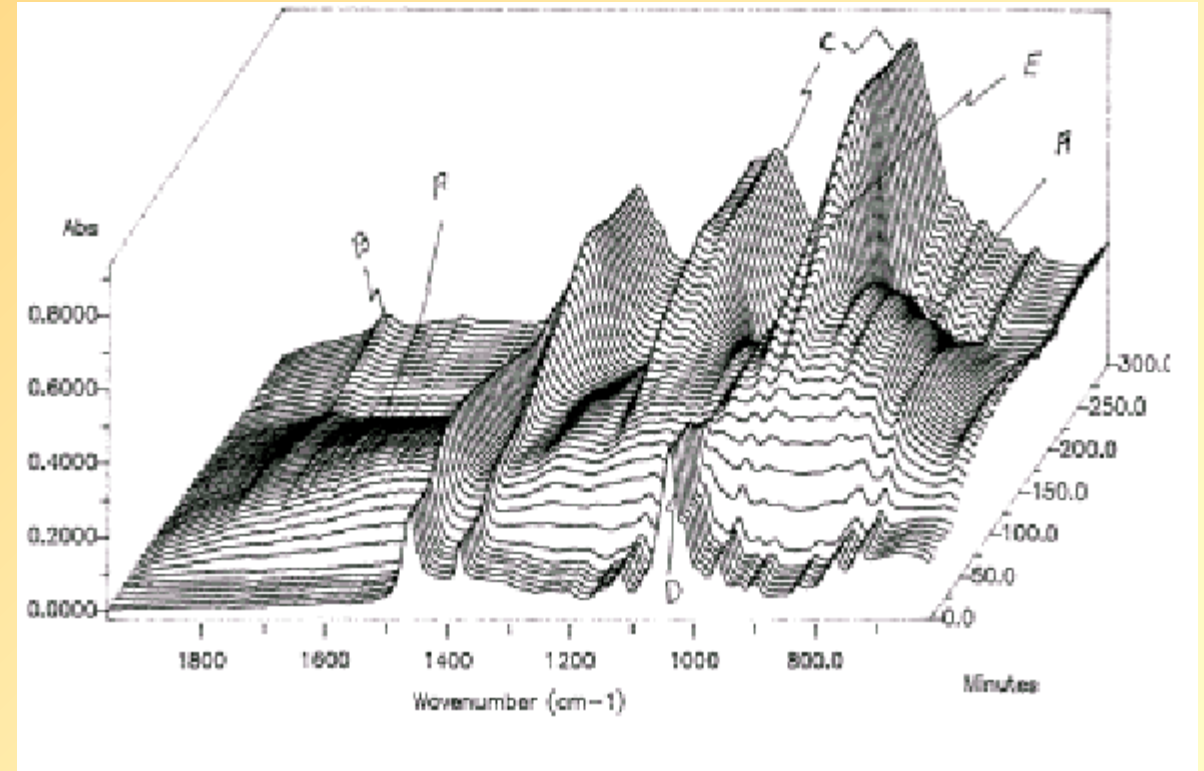


Figure 6

region	belong to
A	hydronium ion of fatty alcohol (oxonium)
B	sulphuric acid
C	product
D	fatty alcohol
E	Chlorosulfonic acid

Figure 7 shows the heat flow curve, the dosing curve of chlorosulfonic acid and the FTIR curves of the alcohol, the hydronium ion and the product.

The result –it is again surprisingly– shows the following:

The fatty alcohol disappears very quickly in the reaction mass (green curve in figure). When approximately one third of the stoichiometric amount of chlorosulfonic acid is dosed, only very little of the fatty alcohol is visible in the reaction mixture.

Immediately with the start of dosing of chlorosulfonic acid to the fatty alcohol an intermediate product becomes visible, which could be characterized as the hydronium ion of the alcohol (blue curve in figure).

This hydronium ion concentration reaches its maximum when approximately one third of the stoichiometric amount of chlorosulfonic acid are dosed and when the heat-flow curve has fallen to the minimum (red curve in figure). With the reduction of the concentration of hydronium ion the IR-bonds of the product (pink curve in the figure) starts to increase.

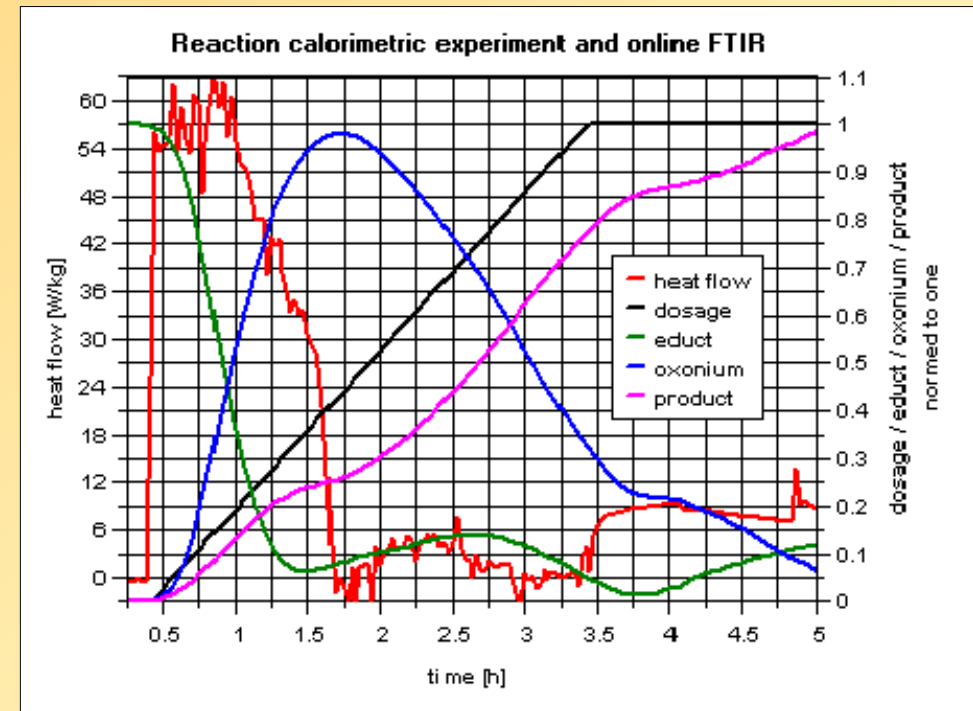


Figure 7

From the results, the following hypothesis could be derived for this phenomenon:

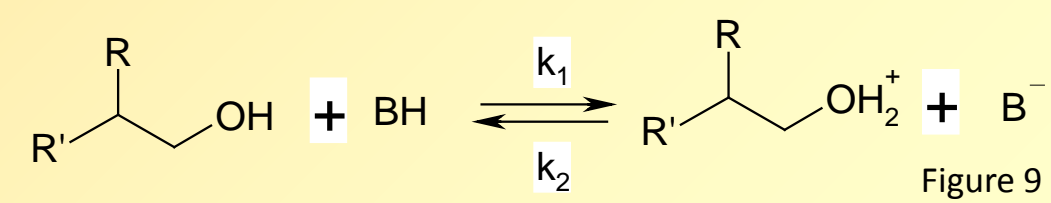
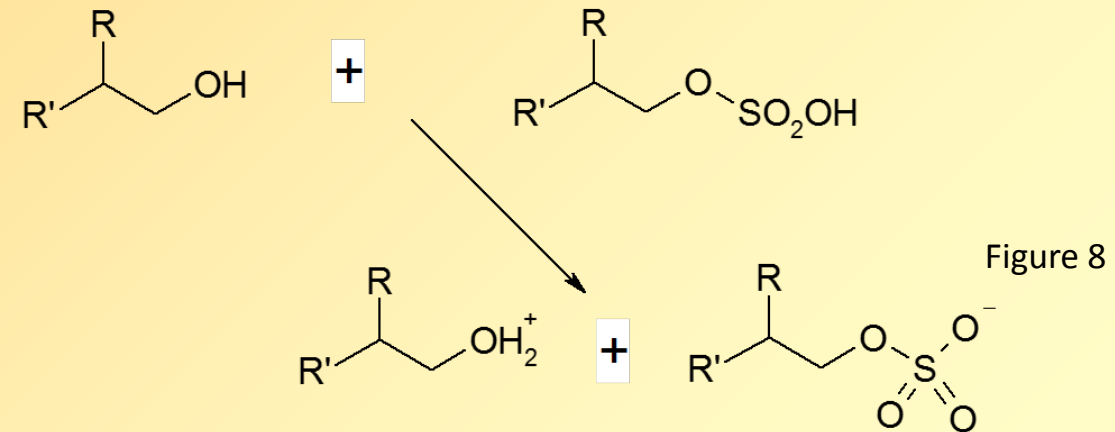
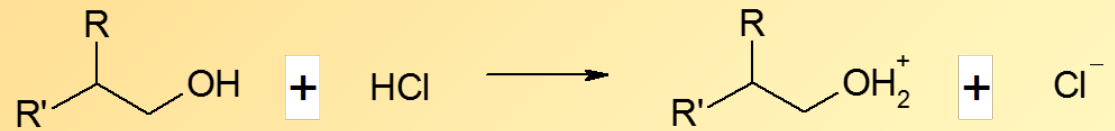
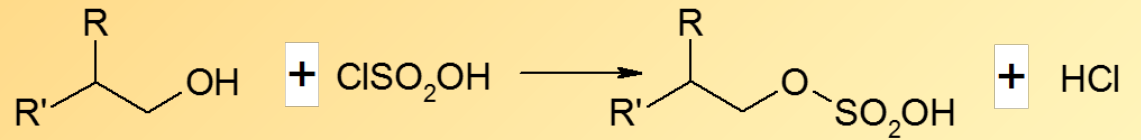
Fatty alcohol reacts first with chlorosulfonic acid to give hydrogen chloride and the corresponding fatty alcohol sulphate.

Both the hydrogen chloride as well as the sulphated alcohol are strong proton donors.

Hence, in presence of fatty alcohol (a proton acceptor), the chemical reactions run, which are sketched in figure 8.

A simple calculation shows now, when one-third mole of the alcohol reacts with chlorosulfonic acid, that one-third mole of HCl and one third mole of sulphate will be formed, which forms two-third mole of hydronium ion with the alcohol.

The speed at which the hydronium ion reacts in direction to alcohol sulphate, depends on the magnitude of the rate constants  $k_1$  and  $k_2$  (figure 9).



## **A working hypothesis for explanation of the accident cause**

The investigation of the incident gave the following possible accident cause as an explanation. By a side reaction to the sulphation of fatty alcohol with chlorosulfonic acid, the fatty alcohol is protonated by the products of sulphation (fatty alcohol sulphate, and hydrochloric acid). A hydronium ion is formed. The equilibrium position of the reaction –hydronium ion  $\rightleftharpoons$  fatty alcohol + H<sup>+</sup>– is strongly temperature dependent. At low temperatures, this equilibrium is shifted in favour of the extent of the hydronium ion, so that chlorosulfonic acid in the reaction mixture can accumulate. This working hypothesis was corroborated by experiments. The following causal chain could be derived.

## **The chain of events can be reconstructed as follows**

On the day of the incident, it was bitterly cold. So, the water recovery unit had generated cooling water having an abnormally low temperature. After about one-third of the chlorosulfonic acid amount had been added to the reaction mass, the heat generation had decreased due to the growing amount of hydronium ion.

Due to the exceptionally cold cooling water, the temperature of the reaction mass decreased to a value, at which the equilibrium was shifted to the favour of the hydronium ion. As a result, only a small amount of fatty alcohol could to react with chlorosulfonic acid. The further addition of chlorosulfonic acid into the reactor led to a dangerous accumulation.

After the interruption of the transfer from the sulphation reactor to the neutralisation reactor a certain amount of unreacted reaction material –which was in the open transfer line to the sulphation reactor– was exposed to room temperature. Hence, the mass in the transfer line was heated up slowly.

This led to the displacement of the equilibrium position of hydronium ion  $\rightleftharpoons$  fatty alcohol + H<sup>+</sup>. Fatty alcohol and hydrochloric acid gas –which could flow into the reactor– were set free. The liberated fatty alcohol had reacted with chlorosulfonic acid. Heat and hydrochloric acid gas were released, which streamed to the sulphation reactor. In the reactor, the described process had continued, accelerated itself and coursed a runaway reaction.

**Learning lesson:** The triggering event in the case study was a too low reaction temperature. However, the reason for the event was not the extraordinary cold day of the accident. Also not the fact that it has caused such a low coolant temperature. No, the real cause was insufficient knowledge of the process chemistry and thermochemistry. If the consequences of a too cold reaction temperature had been known, the company would have taken appropriate measures to ensure that the reaction temperature cannot reach such a low level.

### **Historically grown deficits of Multi-product chemistry, mostly misjudged but undeniable**

Based on statistics we state the following:

- A growing proportion of chemicals can only be produced economically in flexible Multi-product plants.
- About 75% of the events that occur in the chemical industry due to Runaway reactions drop to the Multi-product chemistry.
- More than 90% of those incidents can be classified into seven «triggering causes» : (1) incorrect loading of reactors, (2) lack of knowledge of the process chemistry and thermochemistry, (3) insufficient cooling, (4) exothermic reactions due to impurities (5) false stirring, (6) excessive heating and (7) incorrect reactor control. Graphically represented as classes lack of process knowledge und human errors (figures 10 and 11).

### Lack of process knowledge

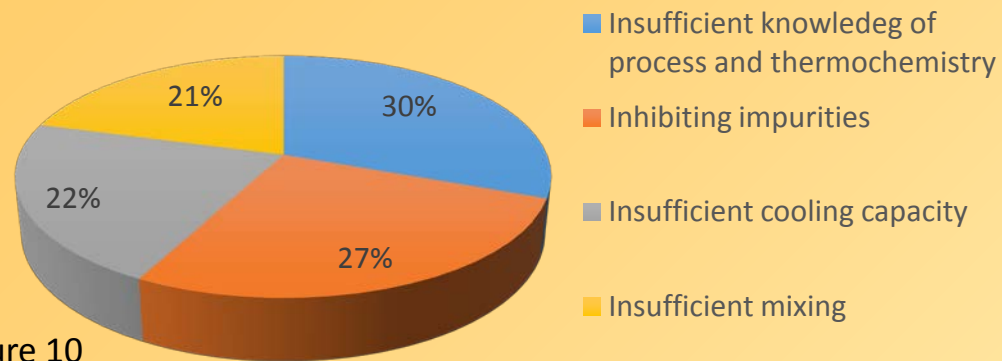


Figure 10

### Human errors

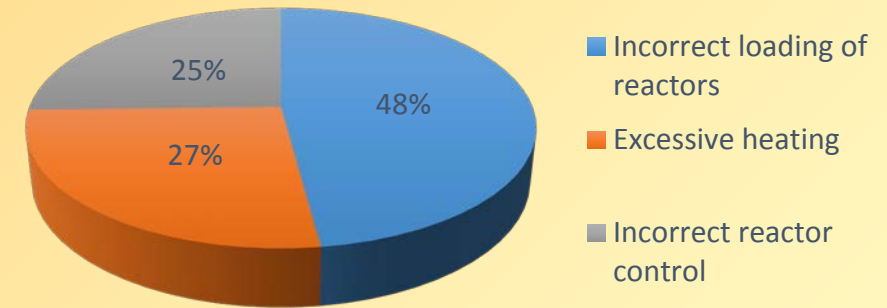


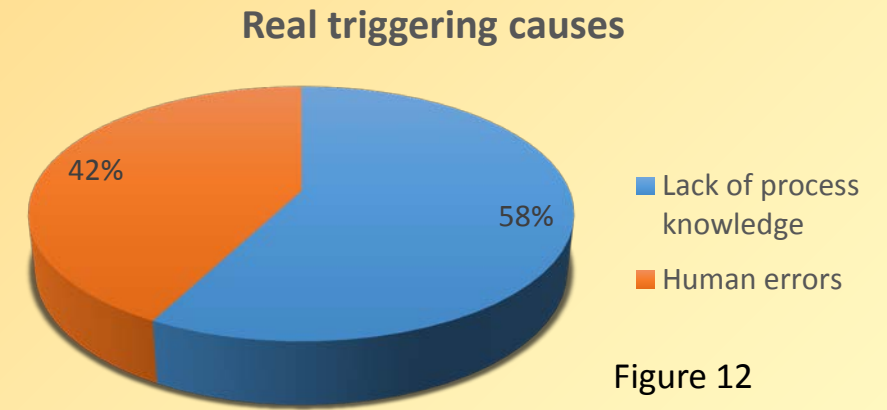
Figure 11

It is impossible to protect the Multi-product plant effectively with technical measures against this triggering causes. This is because, when a Multi-product plant is built, it is not yet known, what chemical process steps are to be run in it –nota bene process steps, of which only insufficient understanding of the process chemistry and thermochemistry is usually available.

For Multi-product operation, the following applies: Because the Multi-product plant is given, to two of the defined triggering causes –namely insufficient cooling capacity and insufficient stirring– can only be influenced so far, that the suitability or the unsuitability of the system is determined. To make this statement, the relevance of these triggering causes must be recognized as a protective effect. However, this is possible only based on sufficient process knowledge.

In figure 12, the seven «triggering causes» are summarized in two groups of causes «insufficient process knowledge» and «human errors».

On this way is visible that nearly 60% of reactor accidents are caused by insufficient process knowledge. A closer look shows that the proportion is even greater, since many of these human errors are only done, because the effect of the errors to the process chemistry are not understood and the system therefore technically is not hedged. [Learn more about this statistical study.](#)



**Take another example:** A worker had forgotten to switch-on the reactor stirrer. The consequence was a reactor explosion that led to disaster. If the consequences of an unstirred reactor had been known, the company would have taken appropriate measures, either to ensure that the stirrer is switched on, or to put the necessary infrastructure in place to prevent an explosion. There are very many such examples.

Our long-term experience in the safety analysis of chemical processes have taught us:

- In the multi-product chemistry one is not always aware that the necessary effort for the safety planning has to be done with every new chemical process, which is performed in a given facility.
- For the chemical process steps, which are performed in the Multi-product plant exist mostly an insufficient knowledge of the process chemistry and the thermochemistry.
- Seldom is proven with a systematic approach –search for hazards, minimisation of hazards and risk analysis– whether an existing Multi-product facility is able to control the risks of a chemical process step.
- With the transfer of chemical processes in the Multi-product facility often lack an effective dialogue between process chemists on the one hand and engineers and safety officers on the other hand.



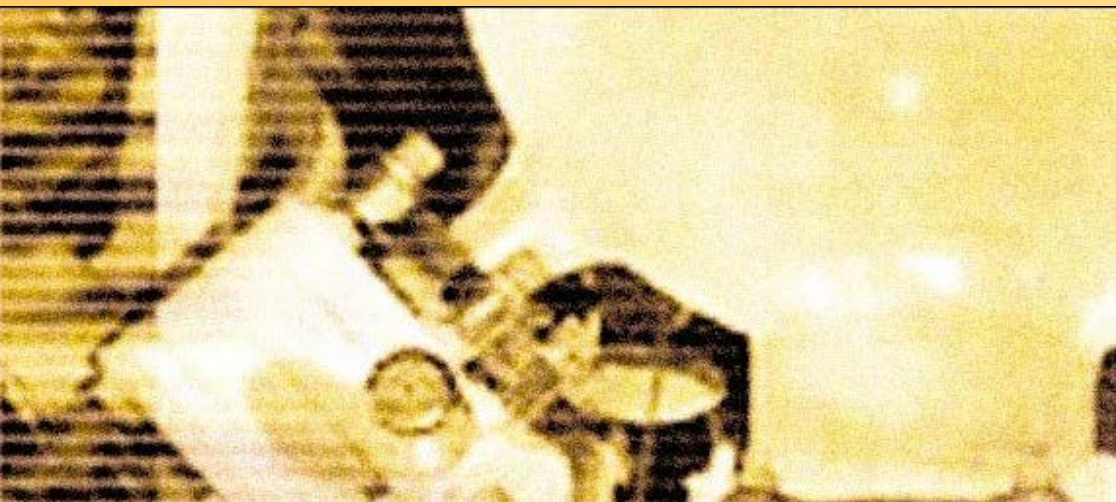
With this publication series, we want show how complex the interactions of Multi-product plant, process step and organization are. This understanding is essential to decide whether a chemical process can be operated safely in the Multi-product plant. The articles are written deliberately broad. They shall show that for plant safety of Multi-product plants it is essential to assess the chemical process steps holistically. Our goal is to show that it is possible economically to assess whether a chemical process can be operated safely in a given installation. Furthermore, that even for discontinuous chemical productions in Multi-product plants general applicable criteria can be derived, with which chemical processes can be adapted to given production facilities.

The following two parts deal with the subject

- Methodology for visualising the dangers in batch and semi-batch processes  
[BatchReaktorSoSimple part 2a](#) and [BatchReaktorSoSimple part 2b](#)

In preparation are the subsequent parts, which deal with the problem areas of

- heat generation and heat removal
- accumulated heat and the avoidances of it
- decomposable reaction masses and distillation masses.



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**Our service includes**

- visualisation of the hazards of all process steps of chemical processes such as safety analysis and assessment
- 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 optimization of safe chemical processes

**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