ALFRED SCHNYDER
SCHNYDER Safety in Chemistry Ltd.
Gewerbehaus Oederlin, Landstrasse 2B, CH-5415 Rieden-Nussbaumen, Switzerland


Alfred Schnyder

PEER REVIEWED

Safe outsourcing of chemical processes
not an easy task

KEYWORDS: Multi-product plant, safe chemical process steps, holistic approach for process risk analysis, process modules, safety modules, risk modules, modular fault tree analysis.

Abstract The outsourcing of chemical productions with all its technologically sophisticated process steps is a big business today. This involves the manufacture of chemicals that have been produced for several years already, as well as new developed chemicals that never have been produced on large scale. Most of these are realized batch wise in Multi-product plants, expensive specialty chemicals as well as cheap chemicals. That is why; custom synthesis is of economic interest. However, with all their advantages, Multi-product plants have system-inherent drawbacks with respect to safety. For each process step one must prove with the systematic approach whether the existing plant and the existing organisation are capable to control the risks of the process. Thus, the challenge for Multi-product chemistry is not only to avoid disastrous accidents but also production losses.

MULTI-PRODUCT CHEMISTRY CONTROLS A BROAD 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 explosible. Production is realized in multi-product plants. Complicated, multi-steps processes are performed in such plants using relatively simple production facilities. In these facilities, the safety installations are not tailored for all the processed chemicals, because their flexibility and their particularity would be lost.
Control of the process is largely determined by the particular characteristics of the chemical reaction and by the capabilities of the existing facility. 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 production volume typically is small.
Multi-product chemistry is the field of organic chemists. Traditionally, their education is based on molecular chemistry, where the emphasis is on product development and not on process development. This, after all, is what earns a company money. Chemical engineers, who by education are more process oriented, tend to be employed in bigger companies where a large product line merits the building of plants, which are tailored for their task. Multi-product chemistry, on the other hand, seek product-oriented chemists, who mostly have not the specialised education of chemical engineers. In these companies, the process development usually belongs to the duties of newly trained chemist who are at the beginning of their careers. However, for many of them chemical plants are like enlarged laboratory flasks. The experimental skill that they usually use for developing chemical reaction steps for Multi-product plants reflects the accumulated experience of the synthetic chemists but not on that of chemical engineering. Not infrequently chemical processes are transferred directly from laboratory into the plant, scaled up by a factor of 10.000. The tactics of process management are based chiefly on experience.

FROM SAFETY POINT OF VIEW: A BIG DIFFERENCE BETWEEN MONO-PRODUCT PLANT AND MULTI-PRODUCT PLANT

For the planned manufacture of a chemical bulk product, it pays to build a "Mono-product plant". In such a plant, only one particular product will be produced. All dangers of the chemical and physical processes and the used chemicals as well as their interactions with construction materials and environment are investigated first. On the basis of the data a plant is designed with which the production can be operated economically and safely for humans, environment and machines. That is not so in the Multi-product plant! Here, the procedure is given and that must be transferred into an existing plant.

The multi-product plant

The multi-product plant is a system of equipment in which different products can be produced. The specific work steps — such as charging of chemicals, chemical reaction and separation steps as well as thermal and mechanical processes — are processed in given modules.
Multi-product chemistry uses different — on occasion historically grown — plant systems as well as plants that were built already for the use as multi-product plant. Up-to-date facilities are designed that a large number of the process parameter can be varied in a wide range.

The desired range of variation usually exceeds the allowable safety limits for a specific process. With cut-offs that can be adjusted from case to case; the system tries to limit the operating conditions for a particular procedure at a non-hazardous level of safety. However, the ability of customizing the limits also increases the risk of human and organisational faulty operation. No matter what kind of a Multi-product plant it is, a longstanding or an up-to-date facility. Having a modern installation does not necessarily mean that this is suitable for all types of chemical processes. Also the fact that in a plant a chemical production process has been carried out for years does not prove that the process is safe. The following facts are mostly misjudged but undeniable. The performance profile of the Multi-product plant fits usually not the requirements of the chemical production process. Deficiencies are remedied by additions. Those that not can be remedied economically by technical measures are bridged by organisational measures. The concomitant result is that the system in the course of time changes continuously. Thus, the dangers of chemical processes are inherent for the system —process, plant and organisation. It follows that for each process step that is performed in the system must be proven that this is able to control its dangers. Often one is not aware that for a Multi-product plant the necessary effort for the safety planning has to be done with every new chemical process, which is performed in it.

The multi-product plant has a modular structure

Both the chemical reaction as well as the processing of chemicals are performed in existing modules. Likewise, the safety installation is built in modules. Figure 1 shows simplified the operation modules as well as the monitoring and protection modules of a chemical reactor.

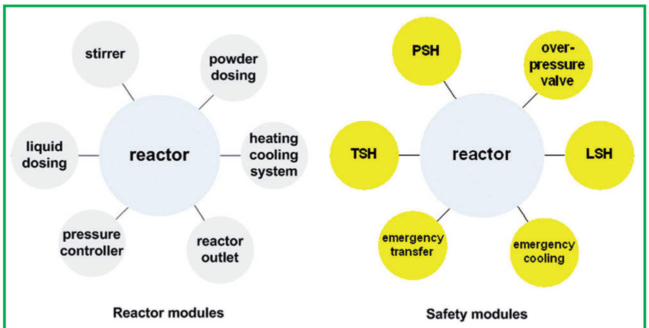

Figure 1. Modular structure of a chemical batch reactor.

Figure 2 shows some operation modules and safety modules for the powder processing. For each module one must know whether this is able, to handle its task. It is essential to know the reliability and the failure frequency of the appropriate modules. The modules must be categorised. Consequently, the safety assessment of chemical processes in the multi-product facility needs a holistic approach and must be modular, because the process steps run as Process-modules in plant-modules. For each process step one must prove with the systematic approach — search for hazards, minimisation of hazards and risk analysis — whether the existing plant and the existing organisation are capable to control the risks of the process. The systematic procedure consists of several stages.

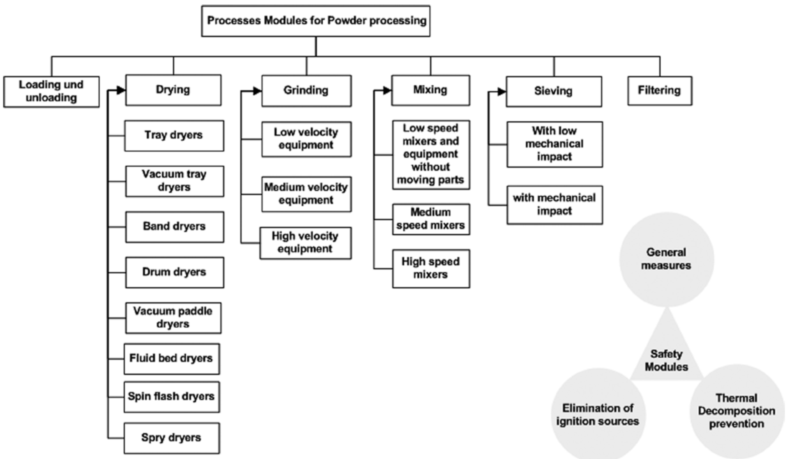

Figure 2. Process modules and safety modules

<u>First:</u> With safety studies, the inherent hazards of the chemical system in every process step are shown. Thereby, the hazards of the process steps will be visible and risk modules are definable.
<u>Second:</u> With this knowledge, the requirement profiles for the process modules, which are necessary to control the inherent dangers of the modules of the multi-product facility, become definable. In addition, the requirements for the Safety modules — that control the process modules — become visible.
<u>Third:</u> By superimposing of the modules will be checked whether they fulfil the requirements (Figure 3). The remaining risk becomes visible. Thus, the question can be answered: Is the risk acceptable?

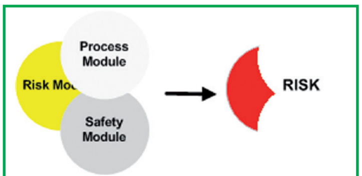

Figure 3. Superimposing of the modules.

Only the knowledge of the risk allows to decide whether the plant is able to control the process or whether it is necessary to define technical or organisational measures, in order to perform the process safely. If the risk is too high, the process must not be run in the existing facility. In this case the procedure of the chemical process has to be adapted to the capabilities of the Multi-product facility.

VISUALISING THE DANGERS OF CHEMICAL REACTION STEPS

Wat are the dangers with chemical reaction steps? The cause of a dangerous substance loss from its safe containment of a chemical reactor is complex and always consists of a combination of characteristics that come from different risk areas. Figure 4 shows the "and-shortcuts" of the preconditions for a runaway reaction.

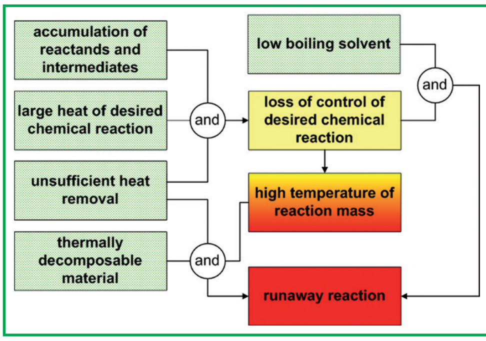

Figure 4. Preconditions for a runaway reaction.

Reasons for accumulation of reactants or intermediates

- Wrong assumptions on reaction kinetics
- Feed rate too high
- Temperature too low
- Inadequate mixing
- Initiation wrong or omitted
- Inhibiting impurities

Reasons for insufficient heat removal

- Inadequate cooling capacity
- Excessive thermal insulation
- Wrong assumptions on heat transfer
- Cooling system failure
- Stirrer failure

Reasons for elevated temperature

- Wrong choice of temperature
- Unintentional heating
- Energy introduced by stirring
- Coolant flow failure
- Catalysing impurities

How to visualise the risk module of the chemical reaction step?

The unknown thermal behaviour of reaction mixtures and their components constitutes a serious hazard in the Multi-product chemistry. Runaway reactions are therefore of particular concern in multi-product facilities. From analysis of the risks of thermal explosions and the lessons learned from thermal incidents, one can see 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. Designing a safe chemical process calls for quantitative data both on the desired and on the undesired reactions caused by process deviations.

Regarding the **desired reaction**, certainly the following questions must be answered:

- How large is the potential adiabatic temperature rise?
- What is the heat accumulation profile under the chosen process conditions?
- How does the heat accumulation behave in the event of process deviations?
- What cooling capacity is required?

Concerning the **undesired reactions**, answers are needed to the following questions:

- In what temperature range do undesired reactions occur?
- What scale of energy is involved in the undesired reactions?
- What are the consequences of a runaway of the undesired reactions?
- Are there catalytic effects, which accelerate the undesired reactions?

In order to process thermal hazards safely, it is necessary to know what they are, estimate how likely they occur and how serious their consequences would be. That means, both the severity of an event as well as its probability of occurrence have to be known. A measure for the severity of a runaway-reaction is the reachable temperature if the desired and the undesired reaction proceed under adiabatic conditions. A measure for the probability of occurrence is the time to maximum rate of a runaway-reaction (figure 5). A large value indicates that more time for countermeasures remains as if the value is small.

With the knowledge of the risk and the process characteristics of the chemical process step, criticality classes should be defined according to Francis Stössel (1).

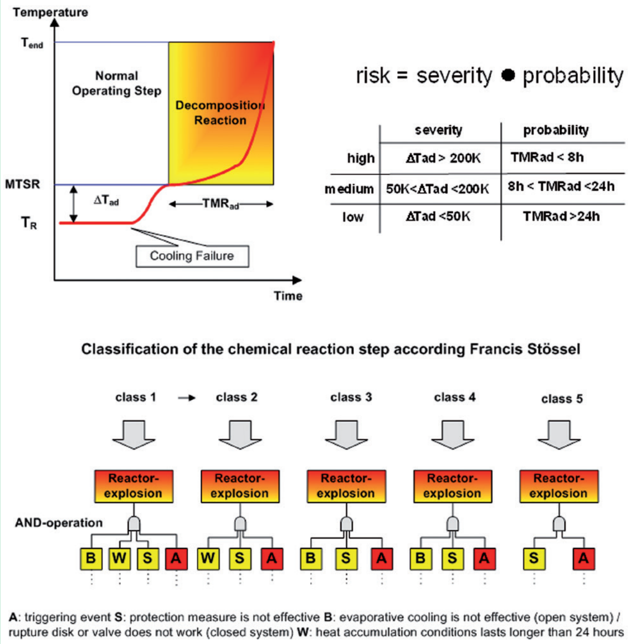

Figure 5. Defining severity, probably and risk of a runaway of a chemical reaction step.

Case study: A Grignard-reagent formation should be performed in a given batch reactor.

To a defined reaction volume with magnesium a halide should be dosed within a certain time. The question now is whether the distillation system (reactor-module) can control the boiling process. Calculations based on the reaction calorimetric investigation of the reaction step give the result that a diameter of the vapour pipe of 0.24 m would be needed in order to control the back flow of solvent. Hence, the risk-module for running the dosing step at normal operating conditions is known. Therefore, the following restrictive conditions must be considered: In order to perform the dosing step of the halide safely, the reactor must be equipped with a vapour tube that has the cross section of at least 0.24 m. The process-module gives you the answer of what size the cross section of the vapour tube is. If not, the reaction step must be redesigned (2).

For more details about the approach see our publication: The batch reactor, so simple - so much unpredictable (3).

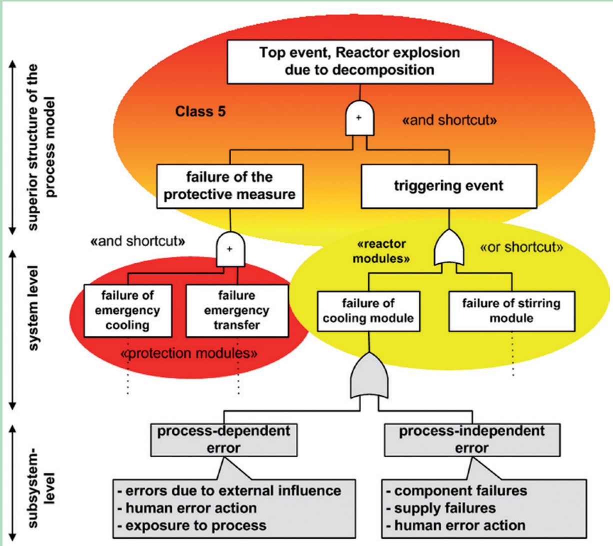

Figure 6. Modular Fault Tree Analysis of a class 5 reaction process.

Based on the classification and the knowledge of the probabilities of default of the modules a modular fault tree analysis of the process is feasible. Figure 6 shows an example of analysing a class five process. The figure shows the great benefit of the modular structure of risk analysis.

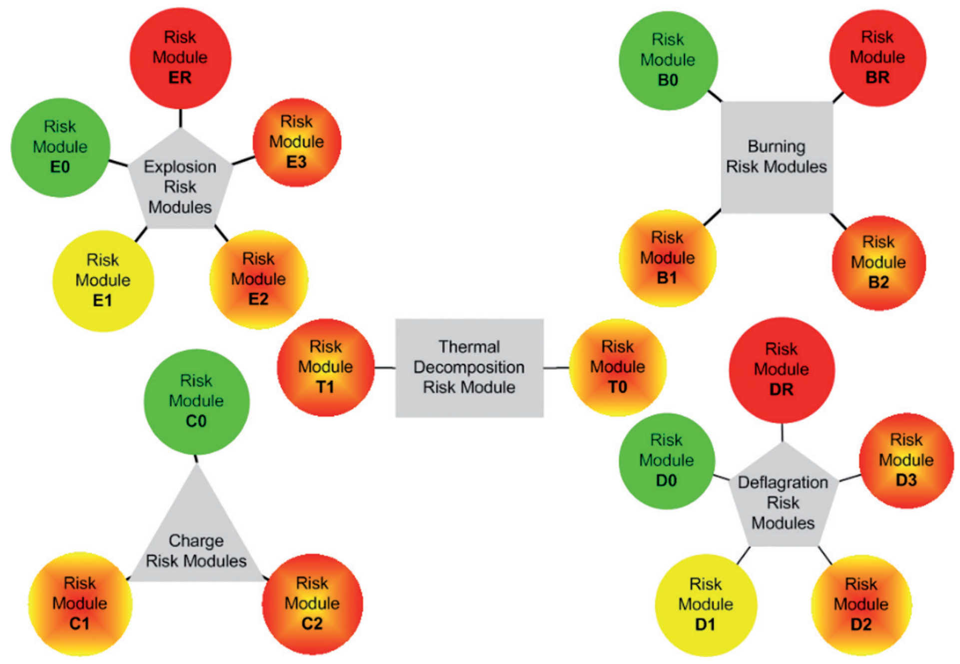

Figure 7. Powder Risk Modules.

VISUALISING OF INHERENT HAZARDS OF PROCESSING STEPS, SUCH AS POWDER HANDLING

Knowledge of the inherent hazard of a chemical includes the understanding of its tendency to react dangerously, as well as the violence of this reaction. The processing of a chemical involves the risk to trigger off a hazardous reaction. However, a chemical is not risky for itself. Its risk depends on how it is processed. As an example, let us look at cellulose – the raw material of paper. Cellulose is flammable and explosible. The process of reading a newspaper, we consider as non-hazardous – we do it every day, quite relaxed. However, the processing of the same weight of fine cellulose powder can be very dangerous. If it is swirled up – and ignited – it will explode and the pressure will increases within a very short time.
The processing of chemicals can be very dangerous. If this is not done properly, it can end in a catastrophe.

HOW TO VISUALISE THE INHERENT HAZARDS OF THE PROCESSED POWDER?

Mostly it is impossible to estimate the hazard of a powder by examining case histories or by carrying out computations. As well, it is no easy task to judge whether the operation will be safe when the powder is processed in a given facility. Experimental work is necessary to visualise the hazard that is associated with the handling of a powder in a process step.

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The most reliable method of estimating the hazard potential of a powder regarding to ignition, fire, explosion and thermal decomposition is to carry out a combination of standardized tests.

The knowledge of the risk of processing a powder involves the understanding of its tendency to trigger a dangerous reaction, as well as the violence of this reaction.
The tendency to react hazardously varies with the external stimuli.

It must be estimated regarding the way in which the powder is processed. The actual possible damage of a plant indicates the violence of decomposition. Characteristics for determining the violence of decomposition reactions are the rate of decomposition or explosion, the temperature and the pressure that is reached, the amount of gas produced and the heat of reaction.

Powder Testing — an absolute necessity!
For risk analysis, standardized tests must be carried out for the subjects dust fire, exothermic decomposition, dust explosion, mechanical sensitivity and electrostatic behaviour regarding their tendency and violence. Read more about this subject in our publication, powder as a risk factor in multi-product facilities (4).

CLASSIFICATION OF THE PROCESSED POWDER INTO RISK MODULES

The inherent hazards of a powder can be visualised on the base of the testing results by Risk Modules. In order to show the specific hazards of the powder, the risk modules are subdivided into risk module-sections (Figure 7).

Every risk module-section allows on the one hand analysing the powder process module and on the other hand, to decide whether the Safety Modules are designed properly. With the classified risk modules and the categorised process modules, the risk analysis can be done now.
It can be shown, whether the powder processing is safe in the appropriate process module. For more information see powder as a risk factor in Multi-product Facility.
The needed protection concepts then depend on the risk-modules and the equipment type — the Process-modules.

CONCLUSION

Fortunately, serious chemical accidents happen rare in multi-product chemistry. However, production losses and damage of the production plants are more frequent. In many cases, production delays and profit losses were caused, since too late identified risks had to be minimized first, close to the time when the product should be supplied already.

Often one is not aware that for multi-product plants the necessary safety planning effort has to be carried out with every new chemical process that will be performed in the plant. The real cause for most accidents of chemical processes is the insufficient process knowledge. This is still strongly underestimated by the multi-product chemistry as well as by the authorities.

Likewise underestimated is that a good process knowledge has an enormous economic potential. It is crucial to have this knowledge at the very beginning of the contract discussions. Because…

- it helps to accelerate the process of implementing a custom synthesis into a Multi-product plant;
- it is very expensive to make changes on the plant or extra development work, which not have been considered in the contract.

Case study: drying powders with risk module E3
For the process-modules — tray dryers, band dryers, fluid bed dryers, spray dryers without and with wall sensors — the following requirements for the safety modules are necessary.

- Areas inside the equipment, where an explosive atmosphere may be formed must be inert in order to avoid a gas or dust explosion.
- If inerting of the system is not possible, adequate protective measures have to be taken against the effects of a possible explosion.
- Ignition sources are eliminated according to Safety Module.

For the Process-modules — Vacuum tray dryers, Drum dryers (Twin Cone Dryers) and Vacuum paddle dryers — the following requirements for the safety modules are necessary.

- During loading the dryer measures are taken to avoid the formation of explosive vapour-air mixtures or hybrid mixtures, for example by ventilation or inert gas blanketing.
- During the process, the explosion risk is reduced by applying vacuum. Heating may only be started after the pressure is reduced to <100 mbar or to the vapour pressure of the solvent to be removed. Non-return valves should prevent back flow of air into the dryer in case of a failure of the vacuum pump. In case of failure of the vacuum the formation of an explosive vapour atmosphere should be avoided, for example by automatic inerting or adequate ventilation. The dryer is equipped with a pressure relief device for the case of plugging of the vapour filter (for example release of lid after evacuation, special port where the lid is held by vacuum only).
- Ignition sources are eliminated according to Safety Module 2.

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