**UNIVERZITY OF PARDUBICE**
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Energetic Materials

# INTEGRATION OF THERMAL EXPLOSION MODEL INTO RISK ANALYSIS

*Theses of the Doctoral Dissertation*

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## References

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## Abstract

The work's starting point is the Multilevel Risk Analysis Procedure (MLRAP), the difficulty of which sits comfortably between the easiest qualitative risk studies and the most complicated quantitative analysis. MLRAP was originally developed for use in explosive-handling plants in our Institute of Energetic Materials. During the application of MLRAP on plants which are not explosive-handling ones, a gap in the procedure was found. The approach was not easily applicable to functional nodes with possible exothermic reactions, which may runaway to a thermal explosion. This work describes the identification of a reasonable number of LOPA thermal explosion scenarios for such functional nodes. Two tools are utilized for this purpose: the Stoessel's concept of criticality classes and the use of adiabatic calorimetry results to classify functional nodes with the possibility of an exothermic reaction. The work modifies the original MLRAP so that for functional nodes, where an exothermic reaction is possible, it identifies initiating events and scenarios depending on the criticality class and the type of reactor. The application of the modified MLRAP for the identification of thermal runaway scenarios processes is illustrated by three examples.

### Abstrakt

Základem práce se stal víceúrovňový postup analýzy rizika (multi-level risk analysis procedure, MLRAP), jehož obtížnost je kompromisem mezi nejjednoduššími kvalitativními odhady a nejsložitějšími kvantitativními analýzami rizika. MLRAP byl původně vyvinut na půdě Ústavu energetických materiálů pro použití v provozech, kde se zachází s výbušinami. Pokusy aplikovat jej i na jiné provozy však odhalily jeho limity. Postup totiž nebyl zcela vhodný pro funkční uzly, kde probíhá exotermní reakce, jejíž ujetí může vést k tepelnému výbuchu. Tato práce popisuje postup vedoucí k identifikaci rozumně malého počtu scénářů tepelného výbuchu, které mohou být následně analyzovány metodou LOPA. Pro tento účel slouží hlavně dva nástroje: Stoesselovo dělení procesů do tříd kritičnosti a adiabatická kalorimetrie, která je použita pro klasifikaci procesů zahrnujících exotermní reakci. Tato práce se věnuje úpravě původního postupu MLRAP, aby byl použitelný i pro provozy zahrnující exotermní reakci, věnuje se identifikaci možných iniciačních událostí a scénářů v závislosti na třídě procesu a typu reaktoru, v němž probíhá reakce. Použití upraveného postupu MLRAP je demonstrováno na třech příkladech.

## Keywords

risk analysis, thermal explosion, multilevel risk analysis procedure, LOPA scenario

### Klíčová slova

analýza rizika, tepelný výbuch, víceúrovňový postup analýzy rizika, scénář LOPA

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# 1 INTRODUCTION

A risk analysis is capable of solving scenarios connected with releases of poisonous gases or flammable liguids. However, no approach for identification of scenarios arising from a thermal explosion has been developed yet. Small sets of scenarios created using the modified so-called Multi Level Risk Analysis Procedure (MLRAP) provide an image of the structure of the risk associated with nodes where exothermic reactions are possible. The diversity of results for individual scenarios allows well-targeted prevention. At the same time, it illustrates why we believe that identifying a small set of scenarios prevents much better against the tolerance of intolerable risk than the identification of scenarios with a single unspecified initiating event. This was basically the main aim of the work.

Experimental part deals with the application of the modified MLRAP and prerequisities must be fulfilled - Accelerating Rate Calorimetry (ARC) usage for detrmining thermal parameters, upon which a reaction can be sorted according to the existing classification framework developed by STOESSEL (2008). The next section describes the ideas on which the development of scenarios for LOPA from the classification results is based, the procedure for the development of incident scenarios, and how it is integrated into MLRAP.

Results contain the example of how it would be applied. Our technique is demonstrated using the so-called Hock process – the widely used procedure which produces two important products – phenol and acetone – from cumene hydroperoxide (CHP). This example was inspired by the accident which took place in a plant using this process - see SCHWAB (1982). Hock process example demonstrates that the technique is applicable in other environments than those where explosives are handled.

# 2 CURRENT STATE OF KNOWLEDGE

## 2.1 Comprehension of a thermal explosion

The term thermal explosion is thoroughly reviwed and explained at the very beginning of the work. Because there is a great difference between its precise physical interpretation and its rather more general meaning in a risk analysis.

A physics of explosion deals with a path leading towards a thermal explosion. It is based upon energy balances, which explains the theoretical background of a thermal explosion. However, any theoretical calculations cannot provide a solid foundation for a risk analysis. A risk analysis is an analysis of scenarios. Whilst a physics of explosion deals with theory of a thermal explosion, this work is focused on its results.

Figure 1 shows the differences of the two viewpoints on a thermal explosion. Physics of explosion reserves the term “thermal explosion” only for reactions with high adiabatic temperature rise $\Delta T_{ad}$ which may lead to a rapid temperature rise resulting in a thermal explosion. The rapid rise of temperature is followed by a pressure wave. On the other hand, STOESSEL (2008) explains that a path leading towards a thermal explosion is not so important for a risk analysis as well as resulting pressure wave. Risk analysis takes into account even scenarios, which would not fit into the definition of a physics of explosion. In contrast with high adiabatic temperature rise $\Delta T_{ad}$, reactions with lower adiabatic temperature rise $\Delta T_{ad}$ have also potential to cause an explosion scenario with adverse effects like a vessel failure followed by its flying fragments. For a risk analysis is not important, whether such scenario was caused by a rapid temperature rise or whether a scenario is caused by a slow temperature and consequent pressure rise. Only damages done to a people or a property are in the scope of a risk analysis.From a physics of explosion viewpoint only reactions with high adiabatic temperature rise $\Delta T_{ad}$ like 400 K on the picture are capable to cause a thermal explosion. In contrast with this, a risk analysis includes even reactions with lower adiabatic temperature rise $\Delta T_{ad}$ which are illustrated by the bottom line for $\Delta T_{ad}$ 50 K on the picture.

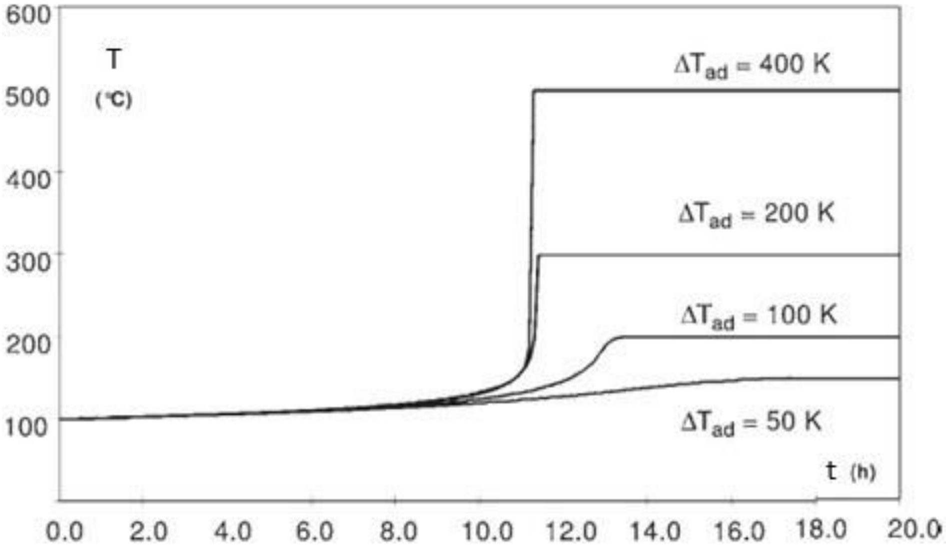


Figure 1 Dependence of temperature no time according to reaction´s $\Delta T_{ad}$, see STOESSEL (2008).

## 2.2 General scenario of thermal explosion

Preceding chapter defined the term “thermal explosion.” It is the starting point for the scenario development described herein.

There are numerous ways, with varying difficulty, to perform a risk analysis and obtain an accident scenario. In real risk analyses, we try not to do anything that is superfluous. That is why approaches with various difficulties are combined for use in real-life situations. Figure 5 depicts such combination of approaches called the multilevel risk analysis procedure (MLRAP).

This approach was originally developed for use in explosive handling plants. This work seeks way how to use the same approach for thermal explosion scenarios. The most important inspiration for us was STOESSEL (2008) which is focused on the planning safety measures in functional nodes where a runaway reaction is possible. It aims on determining the probability of loss of control during a runaway. However, it works with a single scenario whose initiating event is an unspecified cooling failure.The article uses the risk assessment of scenarios using the LOPA method. LOPA method is described in AICHE IEIPL (2015) and AICHE LOPA (2001).

We realized that many components of the approach to thermal explosion scenarios from STOESSEL (2008) is perfectly suitable for our MLRAP since the application of MLRAP to a functional node, in which an exothermic reaction may occur, inevitably leads to the estimation of risk using LOPA. The only thing we considered to be oversimplified was the use of single initiating event.

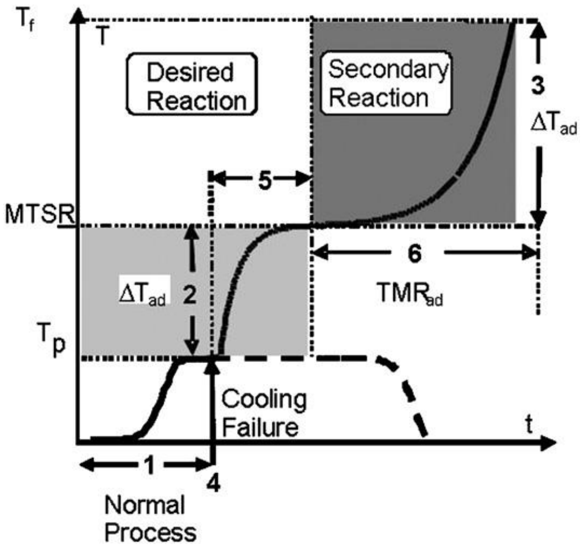


Figure 2 General cooling failure scenario, see GYGAX (1993). The left part of the scheme is devoted to the desired reaction and the temperature increase to the *MTSR* in case of a failure. In the right part, the temperature increase due to a secondary exothermalreaction is shown, with its characteristic time to maximum rate.

Figure 2 shows a general cooling failure scenario, which can cover too diverse range of incidents given the varied nature of functional nodes in which an exothermic reaction may occur. We believe that the identification of a single unspecified initiating event can too easily lead to the omission of possible unacceptable development and thus to the tolerance of intolerable risk.

We decided to make the determination of criticality classes based on the results from using calorimetric methods the starting point of our description of scenarios. The same approach is described by STOESSEL (2009). But this work distinguishes somewhat finer initiating events and incident scenarios than the article.

## 2.3 Criticality classes specifying thermal explosion scenario

STOESSEL (2008) divides processes with runaway potential into five criticality classes. See Figure 3. Stoessel´s approach uses the juxtaposition of four temperatures for the determination of the process class. The first temperature is the process temperature $T_p$, the temperature at which the reaction takes place in normal circumstances. The second temperature is the maximum temperature for technical reasons (*MTT*), a point where the process can cool itself via evaporation. This would be the boiling point for an open vessel/reactor. For closed systems this would be the point when the vessel´s pressure reaches its acceptable level.

These two temperatures are those temperatures inherent in the particular process concerned. The other two temperatures need to be measured by an adiabatic calorimetry method, for instance, by ARC, which is explained in the next chapter. The maximum temperature of synthesis reaction (*MTSR*), defines how far the temperature of the process can rise due to the heat of the reaction. The self accelerating decomposition temperature $T_D$, which marks the point at which the decomposition of any part

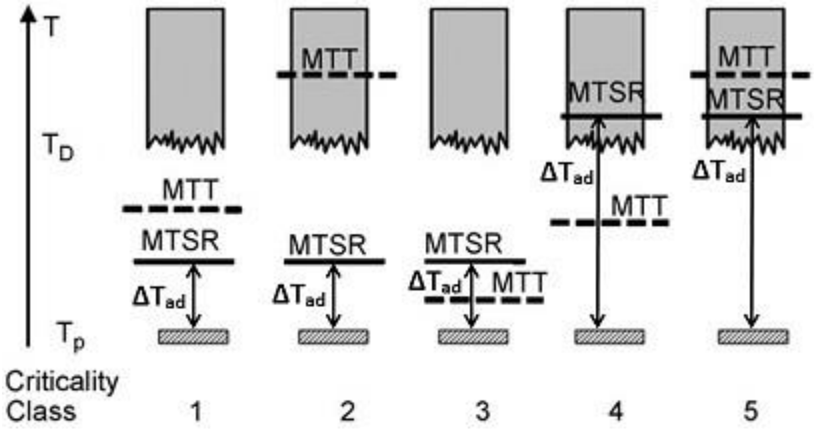


Figure 3 Criticality classes according to STOESSEL (2008).

of a reaction mixture begins. Figure 3 illustrates above mentioned temperatures and their possible relations.

The parameters serve as the foundation for the criticality class determination upon which the scenarios to be analyzed by LOPA will be chosen. Example: If for instance $T_p = 20°C$, $\Delta T_{ad} = 93°C$, $MTT = 80°C$, and $T_D = 100°C$, then criticality class = 4.

## 2.4 Accelerating rate calorimetry results determining the criticality class

The accelerating rate calorimetry (ARC) technique and its mathematical background are thoroughly explained by its inventors TOWNSEND & TOU (1980). Using ARC for the criticality class determination is described in the earlier paper by MASIN (2017) concerning the example of the explosion in the cumene hydroperoxide plant described by SCHWAB (1982). However, this earlier work was more focused on calorimetry, while the recent work deals with the scenario development. ARC serves only as a tool which allows us to measure the values needed to determine the criticality class. Hence, only the results from the ARC measurements are presented in Table 2 (page 19).

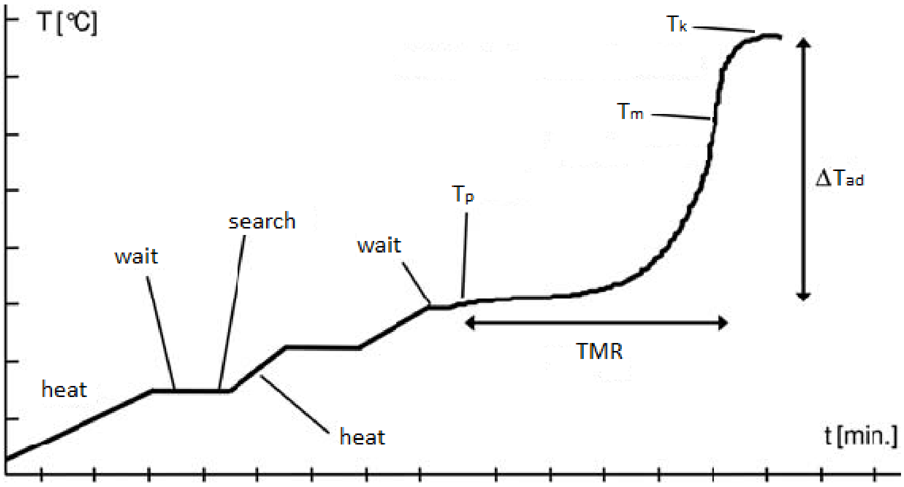


Figure 4 The typical record of an ARC measurement

Table 2 shows the results for seven specific concentrations of CHP. Onset temperature marked as $T_O$ in the table clearly shows that the temperature of the sample decomposition decreases with increasing concentration. The phi corrected values of the adiabatic temperature increase $\Delta T_{AB}$ conversely increase with increasing concentration. A similar rise can be seen with the enthalpy values $H$. On the other hand, values of the time to maximum rate (*TMR*) decrease with increasing concentration. Finally, the last column shows the increasing pressure $p_{max}$ with increasing concentration of the sample.

An experiment must be set to mimic practical conditions in a reactor. The calorimeters, where substances can be added during an experiment belong among the reaction calorimeters. In our adiabatic calorimeter initial substances must be present in the bomb from the start of an experiment. This reflects a setting of a batch reactor so there is no problem with an assessment of this reactor type. Another type of a reactor is semibatch. The whole amount of the substance, which is added gradually to a reactor, is present from the beginning. This fact may bias results. The bias is provided mainly by the reactivity of the chemicals involved. An even larger bias is encountered when testing a reaction carried out in a continuously stirred tank reactor (CSTR). In such a case results might be negatively influenced not only by the precursors but also by the products not removed. The influence cannot be described generally and needs to be appraised for each particular case.

## 2.5 Multilevel Risk Analysis Procedure (MLRAP)

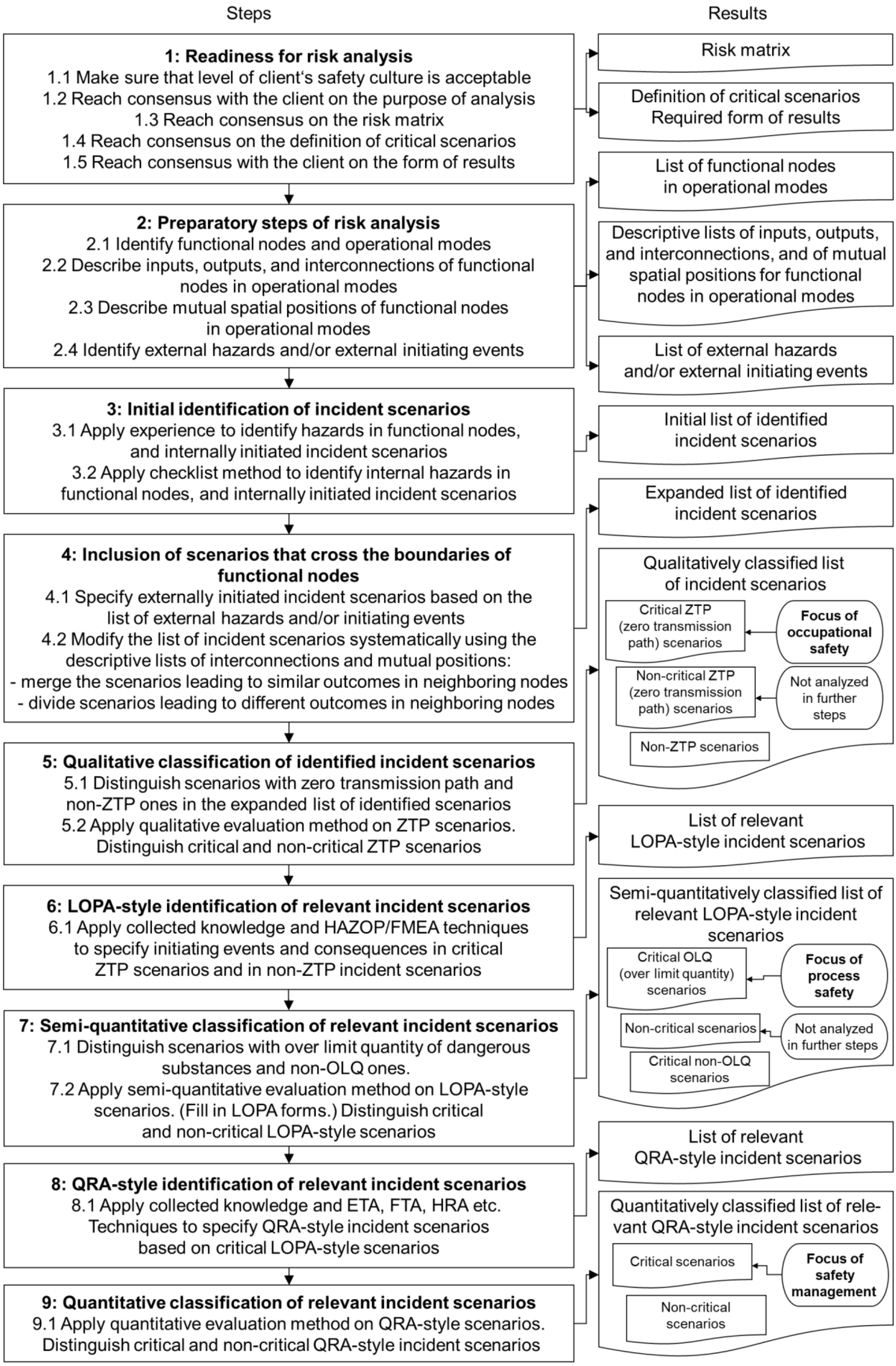
The preceding parts introduced the general scenario of a thermal explosion and described the tools for its identification and classification. This part describes the risk analysis framework, which will be modified by these tools in the experimental part.

During an application of MLRAP to explosive-handling factories, it was found that such a multilevel approach may be suitable for risk analysis concerning loss of control over volumes of dangerous substance or over accumulated energy, but it does not offer a very satisfactory solution for risk analysis connected with a thermal runaway. In case of dangerous substances, conventional instructions for selection of representative scenarios can be used. In case of accumulated energy, analogous approach is possible. But in case of a thermal runaway, no similar aid is available.

Functional nodes mostly contain hazards represented by a presence of hazardous substance or energy. The identification of incident scenarios in such cases is based on the identification of initiating events which open paths for contact of the substance/energy with a receptor. Such initiating events are in the nature releases of substance/energy. A hole size selection for releases is a long-standing problem, as shown e.g. by AICHE CPQRA (2000). To date, no single guideline exists, but we can use various options to obtain a small number of representative incident scenarios that are initiated by a release.

Difficulties start with functional nodes where an exothermic reaction is possible. Not only explosive industry can contain such functional nodes: Hock process serves as an example here. The identification of satisfactory sets of initiating events and incident scenarios for thermal explosions turned out not to be straightforward.

Figure 5 shows steps of a risk analysis according to MLRAP. The experimental part deals with its modification using criticality classes described in the preceding chapter.



**1: Readiness for risk analysis**
1.1 Make sure that level of client‘s safety culture is acceptable
1.2 Reach consensus with the client on the purpose of analysis
1.3 Reach consensus on the risk matrix
1.4 Reach consensus on the definition of critical scenarios
1.5 Reach consensus with the client on the form of results

**2: Preparatory steps of risk analysis**
2.1 Identify functional nodes and operational modes
2.2 Describe inputs, outputs, and interconnections of functional nodes in operational modes
2.3 Describe mutual spatial positions of functional nodes in operational modes
2.4 Identify external hazards and/or external initiating events

**3: Initial identification of incident scenarios**
3.1 Apply experience to identify hazards in functional nodes, and internally initiated incident scenarios
3.2 Apply checklist method to identify internal hazards in functional nodes, and internally initiated incident scenarios

**4: Inclusion of scenarios that cross the boundaries of functional nodes**
4.1 Specify externally initiated incident scenarios based on the list of external hazards and/or initiating events
4.2 Modify the list of incident scenarios systematically using the descriptive lists of interconnections and mutual positions:
- merge the scenarios leading to similar outcomes in neighboring nodes
- divide scenarios leading to different outcomes in neighboring nodes

**5: Qualitative classification of identified incident scenarios**
5.1 Distinguish scenarios with zero transmission path and non-ZTP ones in the expanded list of identified scenarios
5.2 Apply qualitative evaluation method on ZTP scenarios. Distinguish critical and non-critical ZTP scenarios

**6: LOPA-style identification of relevant incident scenarios**
6.1 Apply collected knowledge and HAZOP/FMEA techniques to specify initiating events and consequences in critical ZTP scenarios and in non-ZTP incident scenarios

**7: Semi-quantitative classification of relevant incident scenarios**
7.1 Distinguish scenarios with over limit quantity of dangerous substances and non-OLQ ones.
7.2 Apply semi-quantitative evaluation method on LOPA-style scenarios. (Fill in LOPA forms.) Distinguish critical and non-critical LOPA-style scenarios

**8: QRA-style identification of relevant incident scenarios**
8.1 Apply collected knowledge and ETA, FTA, HRA etc. Techniques to specify QRA-style incident scenarios based on critical LOPA-style scenarios

**9: Quantitative classification of relevant incident scenarios**
9.1 Apply quantitative evaluation method on QRA-style scenarios. Distinguish critical and non-critical QRA-style incident scenarios

Figure 5 Original MLRAP

# 3 EXPERIMENTAL PART

## 3.1 Objectives of the dissertation

- Revise the use of the term "thermal explosion".
- Acquire the thermoanalytical methods used to assess the susceptibility to thermal explosion available at IEM, especially the ARC method (accelerating rate calorimetry).
- Use knowledge about the susceptibility to thermal explosion when compiling accident scenarios and assessing their severity and frequency.
- Introduce a procedure to integrate thermal explosion accident scenarios into the risk analysis.
- Use the knowledge gained from the use of ARC to improve occupational safety in IEM laboratories; summarize recommendations for using ARC.

## 3.2 Relation of a criticality class to LOPA scenario

The parameters determine the class of a process, which can be further separated into two categories. The first category includes classes one, two, and three. These three classes cannot give rise to a thermal explosion without an external heating source. Conversely the remaining two classes describe processes which include a reaction sufficient to heat a system to $T_D$. Thus, the first category is *de facto* associated with higher inherent safety than the second one. The first class defines those processes with a runaway potential where cooling by evaporation can prevent the system reaching $T_D$. The difference between classes one and two is that cooling by evaporation does not apply in class two since *MTT* lies above $T_D$. The third class represents processes possessing sufficient energy to heat up to $T_D$ but which can be hindered/prevented by evaporation. The fourth class, belonging to the second category, defines the processes able to reach $T_D$ despite a lower *MTT*. The fifth class represents the worst possible temperature configuration because *MTT* is higher than $T_D$ rendering cooling by evaporation impossible. Mathematically the sixth class is possible, where *MTSR* is above the *MTT* and both are above the $T_D$, but this class has no relevance from a safety engineering point of view.

## 3.3 Relation of a reactor type to an initiating event

The identification of incident scenarios for functional nodes where an exothermic reaction may occur will follow the classification of the nodes into criticality classes. Initially we imagined that, for each class, we would develop an event tree with a cooling failure as the initiating event (IE) and with developing events that correspond to the gradual exceeding of up to three temperatures defining the class. We called these trees ‘generalized event trees. We have chosen a thermal explosion as the consequence qualifying the scenario for the use in the LOPA method.

We soon realized that the analysis could not be limited to the cooling failure IE understood as a failure of dissipation of released heat. For example, in classes 1 to 3, a mere cooling failure IE cannot cause a thermal explosion. But it is clear that even in these classes it is possible to reach a thermal explosion. Other failures must interact.

We assume that the functional nodes where an exothermic reaction is possible is depicted in Figure 6. It is permissible for some of the parts shown in Figure 6 to be missing in the real system. So, the scheme in Figure 6 covers batch and semibatch reactor and CSTR. The scheme highlights the five points, where a failure could initiate a runaway. Thus, five IEs are generally possible. In addition to the cooling failure (in narrow sense, i.e. failure of cooling system or agitator), the following four:

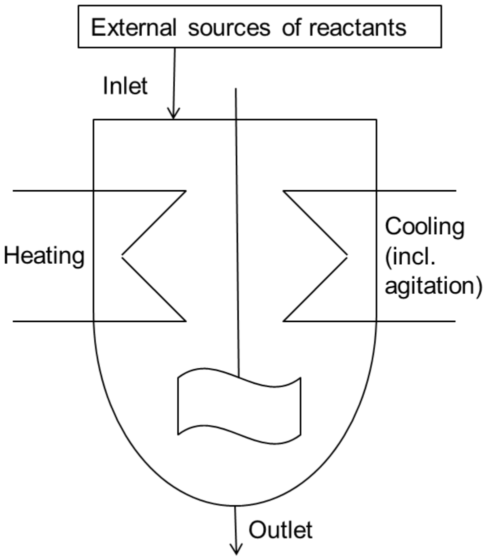


Figure 6. Scheme of a functional node where an exothermic reaction may occur.

a) External influence. An event outside the functional node with a possible exothermic reaction that causes the introduction of incorrect substances or incorrect quantities of substances into the functional node. External influences can be identified based on the data resulting from step 2 of the MLRAP.

b) Non-stop heating. An event that causes heating in the functional node for reasons other than the exothermic reaction, i.e. the heat source is external to the functional node.

c) Inlet malfunction is possible only in a semibatch reactor or CSTR. An event that causes a failure in controlling the supply of substances into the functional node.

d) Outlet malfunction is possible only in a CSTR. An event that causes a failure in controlling the removal of substances from the functional node.

Hazard identification methods such as HAZOP or FMEA can be used to determine whether these events can occur in the specific functional node. The relation of IEs and reactor types served as a foundation for the scenario matrix development in the next chapter.

## 3.4 Identification of the sets of initiating events for step 6 of MLRAP

Functional nodes with possible exothermic reactions, where a thermal explosion could be possible are expected to be identified in step 3 of MLRAP. After the identification of nodes, we need to identify the consequences and possible types of initiating events in these functional nodes that should define the LOPA scenarios. This will lead to results similar to results of step 6 of MLRAP. The consequences are in all cases thermal explosions. The set of five initiation events from the previous section is the most general list of possible types of initiating events in a node. For a particular functional node, the set of IE types to be considered may be only a subset of the five, depending on the criticality class of the functional node and the corresponding reactor type. Based on the knowledge from section 2, we were able to complete Table 1, below.

The table contains sets of possible initiating events for LOPA scenarios representing functional nodes with a possible exothermic reaction. All these initiating events may or may not be relevant to a particular functional node under specific local conditions. Their inclusion depends on the results of appropriate analysis. In some sets, it follows from the nature of the criticality class that a certain protection layer applies, specifically the barrier associated with the MTT temperature. This is indicated in the table by a note (+ MTT).

Table 1. Sets of possible initiating events for LOPA scenarios.

| **Criticality class** | **Batch reactor** | **Semibatch reactor** | **CSTR** |
|---|---|---|---|
| **1** | External influence<br>Non-stop heating<br>(+ MTT) | External influence<br>Non-stop heating<br>Inlet malfunction<br>(+ MTT) | External influence<br>Non-stop heating<br>Inlet malfunction<br>Outlet malfunction<br>(+ MTT) |
| **2** | External influence<br>Non-stop heating | External influence<br>Non-stop heating<br>Inlet malfunction | External influence<br>Non-stop heating<br>Inlet malfunction<br>Outlet malfunction |
| **3** | External influence<br>Non-stop heating<br>(+ MTT) | External influence<br>Non-stop heating<br>Inlet malfunction<br>(+ MTT) | External influence<br>Non-stop heating<br>Inlet malfunction<br>Outlet malfunction<br>(+ MTT) |
| **4** | Cooling failure<br>External influence<br>Non-stop heating<br>(+ MTT) | Cooling failure<br>External influence<br>Non-stop heating<br>Inlet malfunction<br>(+ MTT) | Cooling failure<br>External influence<br>Non-stop heating<br>Inlet malfunction<br>Outlet malfunction<br>(+ MTT) |
| **5** | Cooling failure<br>External influence<br>Non-stop heating | Cooling failure<br>External influence<br>Non-stop heating<br>Inlet malfunction | Cooling failure<br>External influence<br>Non-stop heating<br>Inlet malfunction<br>Outlet malfunction |

## 3.5 Modification of MLRAP

For functional nodes where thermal explosion is possible, it is necessary to create a special path in MLRAP. It consists of three steps similar to steps 4 through 6 in the original MLRAP, as shown in Figure 7. This figure depicts the incorporation of thermal explosion scenarios into the MLRAP, the special path is highlightend by the grey colour.

A detailed description of how to arrive at the LOPA-style identification of relevant thermal explosion scenarios is based on Table 1. To find the result, we created a flow chart in Figure 8, where the user's task is to analyze whether each type of initiation event can be applied to a particular functional node. Only IEs that can lead to a thermal explosion are identified. The flow chart starts at step 4 of MLRAP, which is the reason why the numbering of steps in the flow chart starts with number 4.

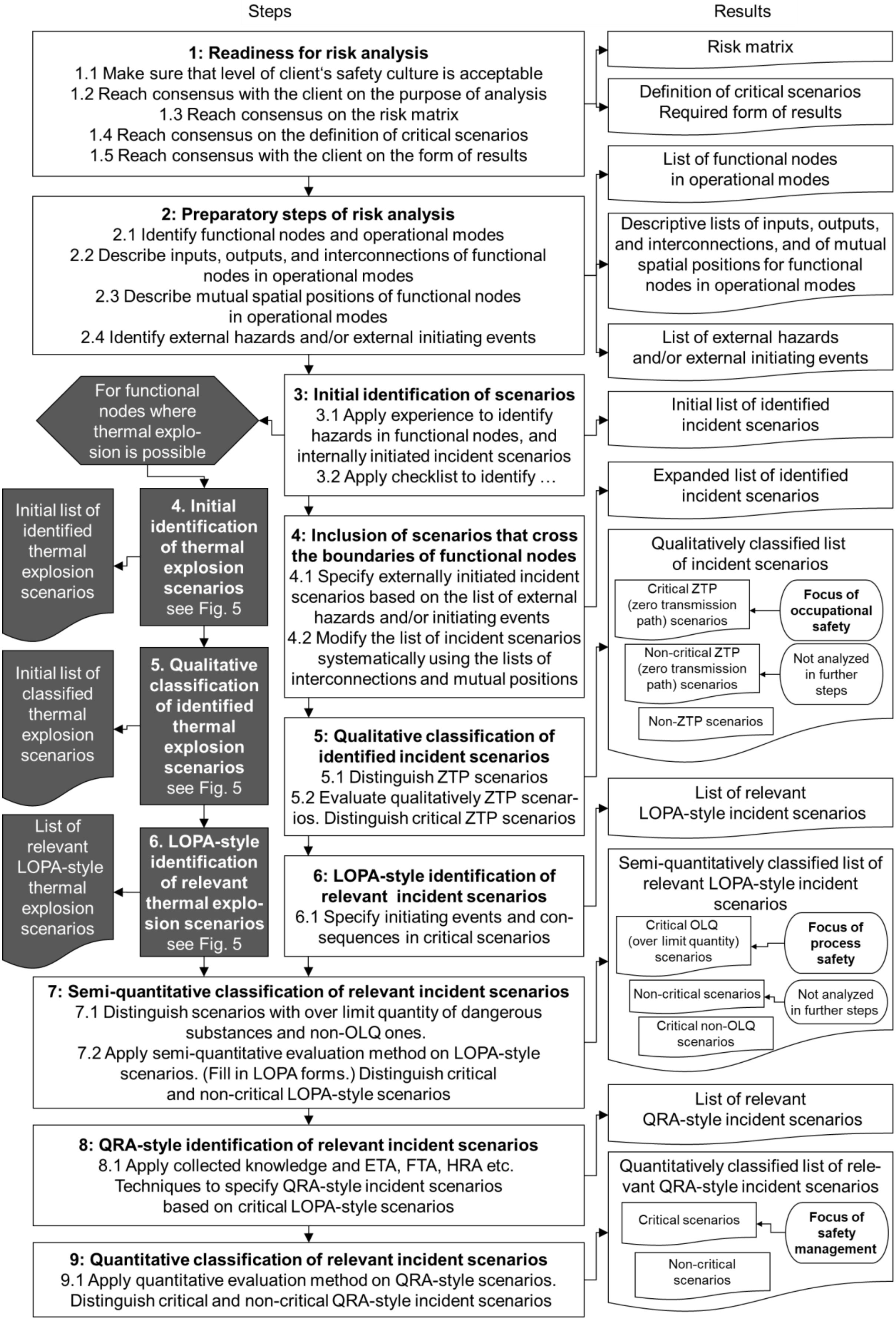
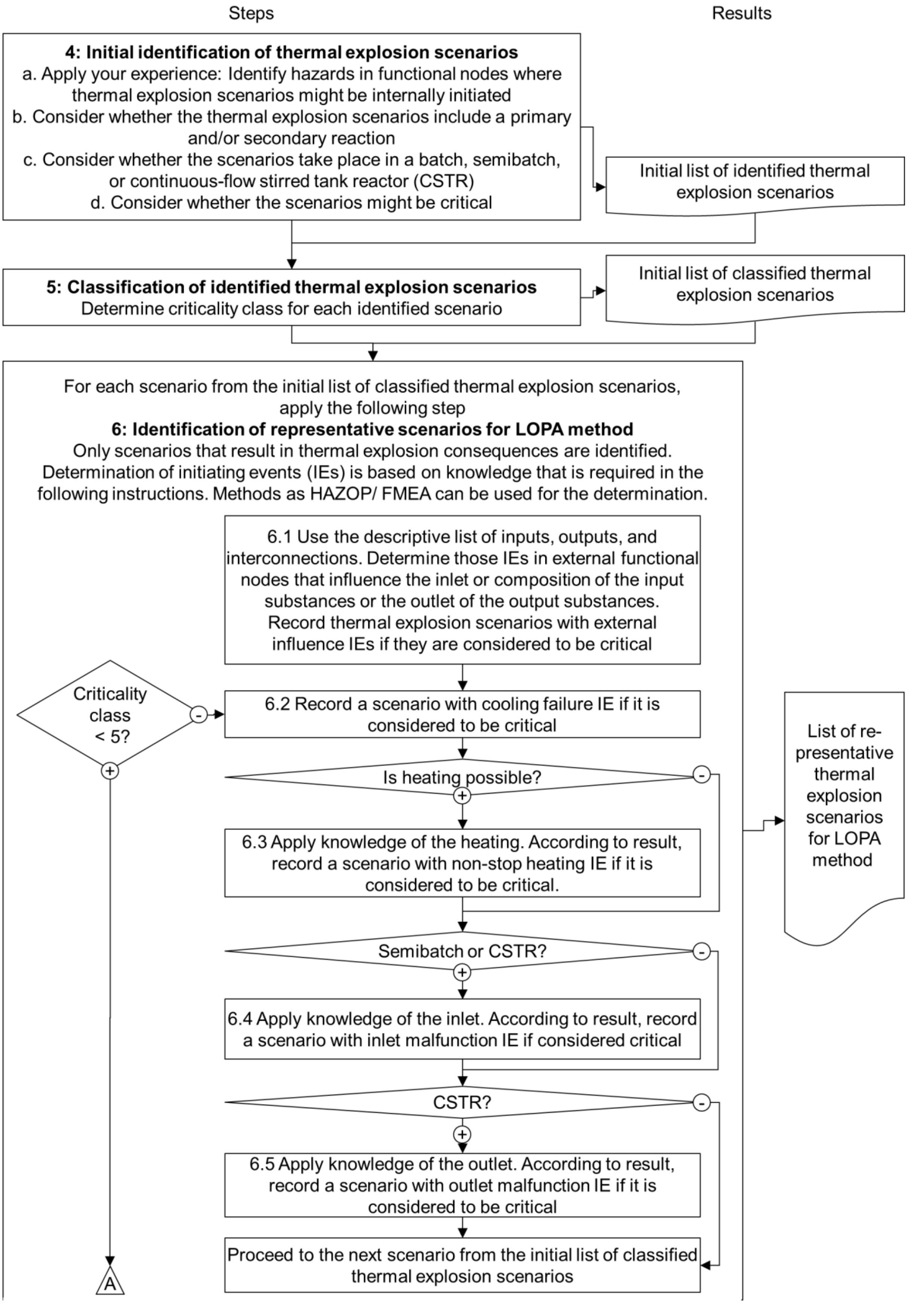


Figure 7 Modified MLRAP



**4: Initial identification of thermal explosion scenarios**

a. Apply your experience: Identify hazards in functional nodes where thermal explosion scenarios might be internally initiated

b. Consider whether the thermal explosion scenarios include a primary and/or secondary reaction

c. Consider whether the scenarios take place in a batch, semibatch, or continuous-flow stirred tank reactor (CSTR)

d. Consider whether the scenarios might be critical

Initial list of identified thermal explosion scenarios

**5: Classification of identified thermal explosion scenarios**

Determine criticality class for each identified scenario

Initial list of classified thermal explosion scenarios

For each scenario from the initial list of classified thermal explosion scenarios, apply the following step

**6: Identification of representative scenarios for LOPA method**

Only scenarios that result in thermal explosion consequences are identified. Determination of initiating events (IEs) is based on knowledge that is required in the following instructions. Methods as HAZOP/ FMEA can be used for the determination.

6.1 Use the descriptive list of inputs, outputs, and interconnections. Determine those IEs in external functional nodes that influence the inlet or composition of the input substances or the outlet of the output substances. Record thermal explosion scenarios with external influence IEs if they are considered to be critical

6.2 Record a scenario with cooling failure IE if it is considered to be critical

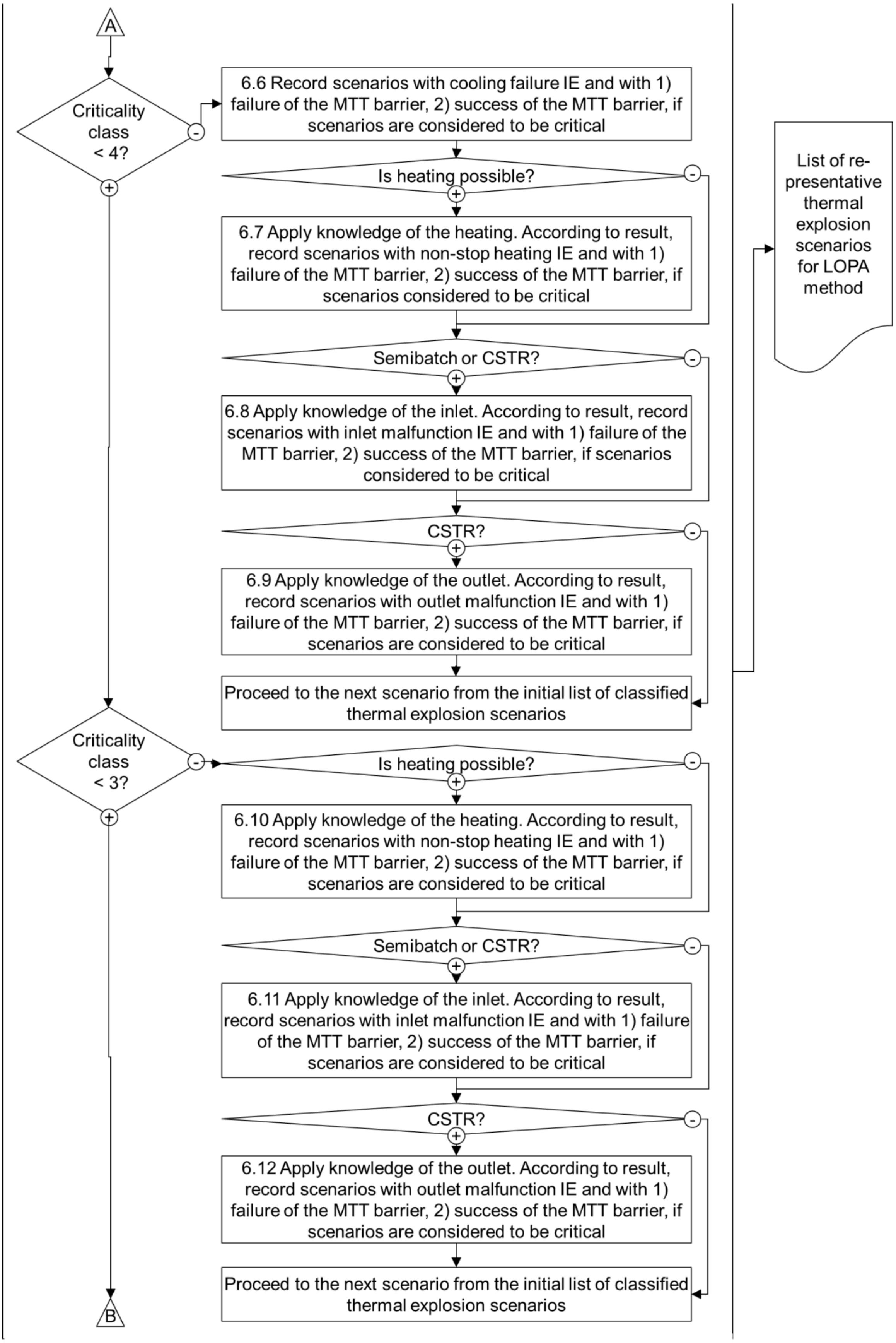
6.3 Apply knowledge of the heating. According to result, record a scenario with non-stop heating IE if it is considered to be critical.

6.4 Apply knowledge of the inlet. According to result, record a scenario with inlet malfunction IE if considered critical

6.5 Apply knowledge of the outlet. According to result, record a scenario with outlet malfunction IE if it is considered to be critical

Proceed to the next scenario from the initial list of classified thermal explosion scenarios

List of representative thermal explosion scenarios for LOPA method


A
Criticality class < 4?
-
+
6.6 Record scenarios with cooling failure IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios are considered to be critical
Is heating possible?
6.7 Apply knowledge of the heating. According to result, record scenarios with non-stop heating IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios considered to be critical
Semibatch or CSTR?
6.8 Apply knowledge of the inlet. According to result, record scenarios with inlet malfunction IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios considered to be critical
CSTR?
6.9 Apply knowledge of the outlet. According to result, record scenarios with outlet malfunction IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios are considered to be critical
Proceed to the next scenario from the initial list of classified thermal explosion scenarios
List of re-presentative thermal explosion scenarios for LOPA method
Criticality class < 3?
Is heating possible?
6.10 Apply knowledge of the heating. According to result, record scenarios with non-stop heating IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios are considered to be critical
Semibatch or CSTR?
6.11 Apply knowledge of the inlet. According to result, record scenarios with inlet malfunction IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios are considered to be critical
CSTR?
6.12 Apply knowledge of the outlet. According to result, record scenarios with outlet malfunction IE and with 1) failure of the MTT barrier, 2) success of the MTT barrier, if scenarios are considered to be critical
Proceed to the next scenario from the initial list of classified thermal explosion scenarios
B

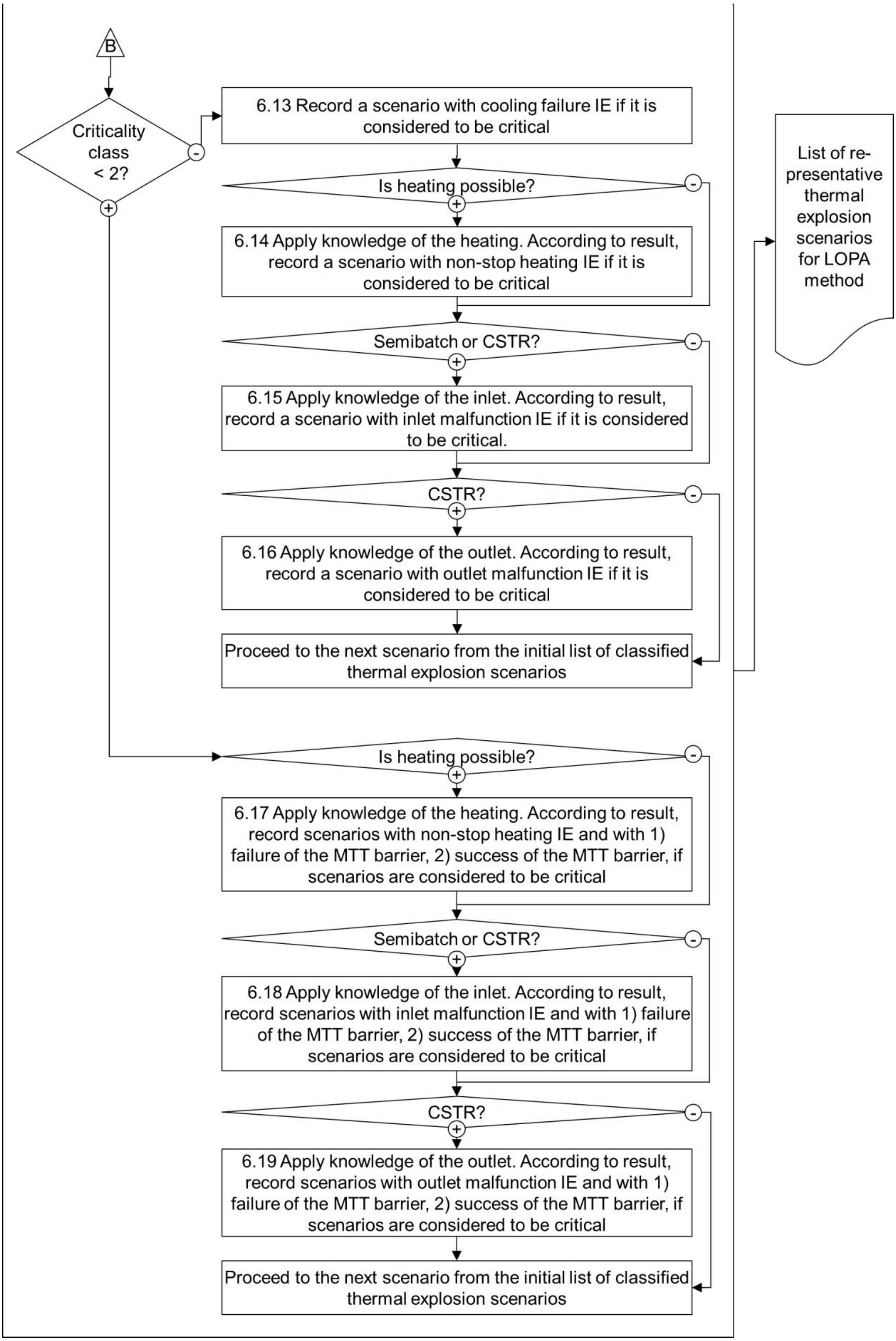


Figure 8 Detailed description of a risk analysis of functional nodes with a thermal explosion risk

# 4 RESULTS AND DISCUSSION

The work demonstrates newely developed method on the three examples – the production of methylnitrate, the production of methylcyclopentadienyl manganese tricarbonyl and the production of phenol using Hock process. Herein only Hock process was chosen as a representative example.

## 4.1 Hock process

Hock process normally uses cumene hydroperoxide as the intermediate from which acetone and phenol are produced. The unit, in which the accident according to SCHWAB (1982) happened, used wet technology described by US patent PUROLA & MANNERLA (2015). However, in this example we suppose that the dry technology described in US patent FULMER ET AL (2002) was used instead. In such a way we avoid the complication connected with the fact that, in the wet technology, water is incorporated in the reaction mixture in the form of an emulsion. This fact would complicate the calculation of the MTT.

For our example we selected the functional node that is shown by the dotted line in Figure 9. This tank is not intended to perform a chemical reaction. However, if the flow through the tank is stopped, the tank is considered to be a functional node where, under certain conditions, an exothermic reaction may occur unintentionally. The steam line passing near the tank can contribute to the occurrence of undesirable conditions. The node represents a batch reactor according to Figure 9 where “heating” possibly exists but “cooling” is not present.

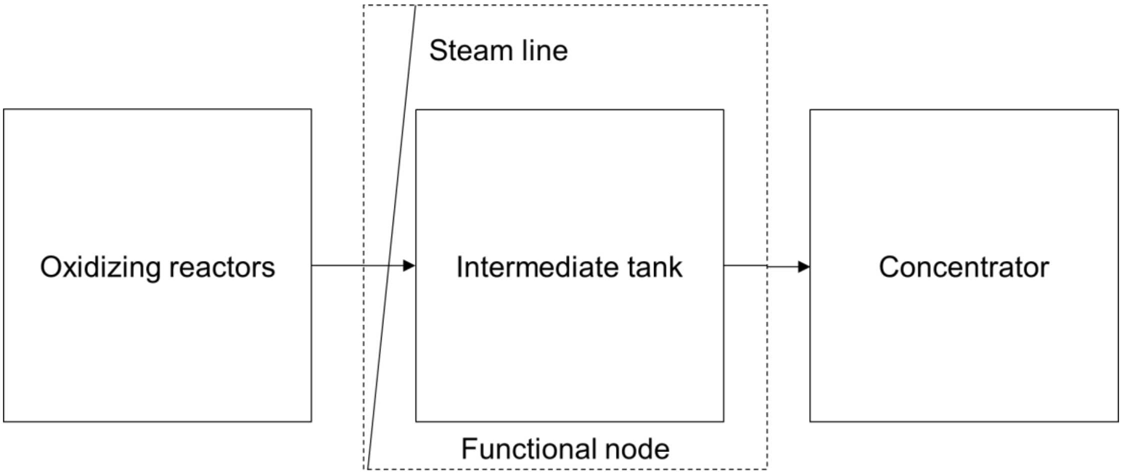


Figure 9 Intermediate tank situation

## 4.2 Results from Accelerating Rate Calorimetry

Table 2 shows how parameters determined with the help of ARC change with concentration of CHP. This explains how the increasing concentration of CHP can shift criticality classes. CHP of the first class has the lowest concentration, where the system does not have a sufficient energy to heat itself to temperature $T_D$ plus the system contains water, which can cool the entire system by an evaporation. Thus, the system requires an external source of heat to create a runaway situation. Conversely, the second class does not have the evaporation cooling barrier, because the MTT lies above $T_D$. However, the water in the system of the third class can prevent a runaway reaction occurring. In this case the evaporation cooling energy is the only barrier preventing a runaway, because the CHP is in sufficient concentration to heat the system to $T_D$. Consequently, CHP of the fourth class is present in such a concentration that it provides enough energy to both evaporate the water and to heat itself to $T_D$.

However, our example Hock process operates with 50% concentration and belongs to the fifth criticality class. It might appear that water is present and that cooling by evaporation is possible, but water is emulsified in CHP thus preventing any possible cooling by evaporation.

Table 2. ARC results with various concentrations of CHP.

| % hm. | $T_p$ [°C] | $\Delta T_{AD}$ [°C] | *TMR* [min] | $T_{D24}$ [°C] | $p_{max}$[bar] |
|---|---|---|---|---|---|
| 20 | 140,6 | 33,8 | 11,4 | - | 1,792 |
| 30 | 130,8 | 103,5 | 9,8 | - | 1,814 |
| 40 | 125,9 | 139,3 | 8,5 | - | 1,982 |
| 50 | 120,8 | 344,1 | 7,5 | 84 | 2,857 |
| 60 | 120,6 | 407,1 | 6,5 | 83 | 4,122 |
| 70 | 116,7 | 567,6 | 6,1 | 82 | 4,569 |
| 80 | 116,0 | 704,4 | 4,5 | 78 | 4,601 |

## 4.3 Cumene hydroperoxide scenarios

In step 4 of MLRAP, the intermediate tank from Figure 9 is identified as a functional node where a thermal explosion scenario might be initiated. It takes place in a batch reactor and might be critical. The initial list of identified thermal explosion scenarios contains Initial CHP Scenario.

In step 5, Initial CHP Scenario is classified. CHP in our example is in 50% concentration so, according to Table 2 - fourth row. Initial CHP Scenario belongs to the fifth criticality class. Table 3 indicates there are up to three initiating events to be analyzed: a cooling failure, an external influence and a non-stop heating.

In step 6.1, the external failure IE might be the impurities resulting from cumene oxidation. Such runaway only stops the process without any damage to personnel. One representative thermal explosion scenario for LOPA method with external influence IE is identified.

In step 6.2, we omit a cooling failure, because the technology does not include a cooling.

In step 6.3, a steam pipe failure may cause a non-stop heating. Such a scenario corresponds with the situation described by SCHWAB (1982). The steam leakage IE only causes the thermal explosion when the piping corrosion takes place in the wrong place. The fact is represented by the coincidence of two enabling events. The second representative thermal explosion scenario for LOPA method is identified, in this case with non-stop heating IE.

Steps 6.4 and 6.5 do not relate to the functional node that is a batch reactor.

Table 3. LOPA scenarios summary.

| Scenario title | CHP external influence | CHP non-stop heating |
|---|---|---|
| **Initiating event (/ year)** | 0.1 | 0.5 |
| **Enabling event or condition** | 0.1 | 0.1x0.1 |
| **Conditional modifiers** | N/A | N/A |
| **Total PFD for all IPLs** | 0.1 | N/A |
| **Frequency of mitigated consequence** | 0.001 | 0.005 |
| **Risk tolerance criteria** | 0.001 | 0.0001 |
| **Risk tolerance criteria met** | Yes | No |

CHP external influence scenario is tolerable. Again, it is mainly because the scenario causes only material damage. But CHP non-stop heating scenario does not meet the tolerance criteria. The criteria are set low, because consequences of this scenario include high material damages and fatalities.

# CONCLUSIONS

The work begins with the the revision of the term “thermal explosion”. The beginning of the work provides the thorough comparison of the physical understanding of the thermal explosion and the broader understanding from a risk analysis viewpoint. Generally, the physics of explosion deals more with a way leading to a thermal explosion, which must be followed by a shock wave to fulfill the definition of a thermal explosion. The broader definition provided by a risk analysis was found. This definition is focused only on undesired results of a thermal explosion. That is why it is more suitable for a scenario development. The scenarios are developed according to the processe´s criticality class, which is determined by its thermal parameters.

A method which would enable a measurement of chemical reaction´s thermal parameters was needed. The accelerating rate calorimetry (ARC) is commonly used for such measurements. The chapter in the work describes ARC only on a level necessary for its use for a thermal risk analysis, it does not have any ambitions to fully explain the method itself.

The theoretical part ends with Multi Level Risk Analysis Procedure (MLRAP). This approach is modified and brings the demonstration of its use. A modified procedure by which thermal explosion accident scenarios can be incorporated into the MLRAP risk analysis is presented in Figure 7 and the flowchart in Figure 8.

The experimental part starts at the relating the class of a process and its possible scenario leading to a thermal explosion. The Layer of Protection Analysis (LOPA) framework is used for this purpose. The next chapter puts a type of a reactor into a consideration. That leads to the identification of initiation events which may trigger a thermal explosion scenario. These sets of initiating events are then integrated into the original MLRAP.

The application of the modified MLRAP is demonstrated on so-called Hock process in result part. Measurement results of cumene hydroperoxide are presented. Upon these results the criticality class is determined. In the dissertation, two additional examples of the MLRAP use are included.

# REFERENCES

AICHE CPQRA (2000)

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS – CENTER FOR CHEMICAL PROCESS SAFETY, *Guidelines for Chemical Process Quantitative Risk Analysis, Second Edition*; American Institute of Chemical Engineers - Center for Chemical Process Safety, 2000. 784 s. ISBN: 978-0-816-90720-5.

AICHE IEIPL (2015)

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS – CENTER FOR CHEMICAL PROCESS SAFETY, *Guidelines for Initiating Events and Independent Protection Layers in Layer of Protection Analysis,* Wiley, Hoboken, 2015. 384 s. ISBN: 978-0-470-34385-2.

AICHE LOPA (2001)

CENTER FOR CHEMICAL PROCESS SAFETY/AICHE, *Layer of Protection Analysis, Simplified Process Risk Assesment*, American Institute of Chemical Engineers - Center for Chemical Process Safety, 2001. 292 s. ISBN: 978-0-816-90811-0.

DOSTÁL (2013)

DOSTÁL L, 2013. *Integrace přenosů detonací do analýzy rizika v provozech, kde se zachází s výbušinami,* Pardubice, Disertační práce, Univerzita Pardubice, Fakulta chemicko technologická, Ústav energetických materiálů. Vedoucí práce Miloš FERJENČÍK.

FULMER ET AL (2002)

FULMER J. W., SCOTT, E., KIGHT, W. D., Method and System for Manufacturing Cumene Hydroperoxide, USA, 2002. Patent No. US 6 465 695 B1.

GYGAX (1980)

GYGAX R., *Differential scanning calorimetry-Scope and limitations of its use as tool for estimating the reaction dynamics of potential hazardous chemical reactions*, 6th International Conference on Thermal Analysis and Calorimetry, Birkhauser Verlag, Basel, 1980.

GYGAX (1993)

GYGAX R., *Thermal Process Safety*, Data Assessment, Criteria Measures, ESCIS Lucerne, Vol. 8, 56 s., 1993.

MASIN & FERJENCIK (2020)

MASIN J., FERJENCIK M., Incorporation of thermal explosion scenarios into the multilevel risk analysis procedure, *Process Safety Progress*, 2020; e12191. Published online 04 September 2020.

MASIN (2017)

MASIN J., FERJENCIK M., SELESOVSKY J., Risk Analysis Based on the Criticality Classes and Their Determination Using Accelerating Rate Calorimetry, *Proceedings of the 5th International Conference on Chemical Technology,* Praha, Česká společnost průmyslové chemie, 2017, s. "BR2-1"-"BR2-6". ISBN 978-80-86238-65-4.

PUROLA & MANNERLA (2015)

PUROLA V., MANNERLA A., Cumene Oxidation, Austria, 2015. Patent No. US 8 975 444 B2.

SCHWAB (1982)

SCHWAB R. F., *Explosion & Fire at a Phenol Plant*, 1. Chemical Engineering Symposium Series NO. 110, IChemE: The Institution of Chemical Engineers, London, 1988, pp. 683-685.

STOESSEL (2008)

STOESSEL F., *Thermal Safety of Chemical Processes*, Risk Assessment and Process Design, WILEY-VCH Verlag GmbH & Co. KGaA Weinheim, 2008. 374 s., ISBN: 9783527317127.

STOESSEL (2009)

STOESSEL F., Planning protection measures against runaway reactions using criticality classes, *Process Safety and Environmental Protection*, 2009, Vol. 87, No. 2 pp. 105-112.

TOWNSEND & TOU (1980)

TOWNSEND D. I., TOU J. C., Thermal Hazard Evaluation by an Accelerating Rate Calorimeter, *Thermochimica Acta*, 1980, Vol. 37, No. 1, pp. 1-30.

# LIST OF AUTHOR'S PUBLICATIONS

## Articles in impacted journals

PLUESS D., MEYER T., MASIN J., MIKULASEK P., FERJENCIK M., Joint applicability test of software for laboratory assessment and risk analysis, *Journal of Loss Prevention in the Process Industries*, 2016, Vol. 40, 2016, pp. 234-240.

MASIN J., FERJENCIK M., Incorporation of thermal explosion scenarios into the multilevel risk analysis procedure. *Process Safety Progress*, accepted 2020.

FERJENCIK M., CARDOSO ANASTÁCIO A., MASIN J., The Great Commandment of Process Safety, *Process Safety Progress*, 2016, Vol. 35, No. 3, pp. 300-300.

## International conference papers

SELESOVSKY J., PACHMAN J., MASIN J., Accelerating rate calorimetry - decomposition of nitroesters. In 18th Seminar „New Trends in Research of Energetic Materials“: proceedings. Pardubice: Univerzita Pardubice, 2015, pp. 789-793. ISBN 978-80-7395-891-6.

PLUESS D., MEYER T., MASIN J., MIKULASEK P., FERJENCIK M., Joint applicability test of software for laboratory assessment and risk analysis. In Safety and Reliability: Methodology and Applications. London: CRC Press, 2014, pp. 1393-1399. ISBN 978-1-138-02681-0.

JALOVY Z., JANCIK M., MASIN J., HUSSEIN AKM., LISKA F., SELESOVSKY J., DUDEK K., Synthesis of 2,2-dinitroethene-1,1-diamine from 2-methylpyrimidine-4,6-diol and treatment of the dinitromethane produced. In Proceedings of the 21st Seminar on New Trends in Research of Energetic Materials. Pardubice: Univerzita Pardubice, 2018, pp. 703-712, ISBN 978-80-7560-136-0.

FERJENCIK M., MASIN J., Law on Prevention of Major Accidents Versus Real Prevention of Major Accidents. In Proceedings of the 4th International Conference on Chemical Technology. Praha: Česká společnost průmyslové chemie, 2016, pp. 539-544. ISBN 978-80-86238-94-4. ISSN 2336-811X.

MASIN J., FERJENCIK M., SELESOVSKY J., Risk Analysis Based on the Criticality Classes and Their Determination Using Accelerating Rate Calorimetry. In Proceedings of the 5th International Conference on Chemical Technology. Praha: Česká společnost průmyslové chemie, 2017, pp. "BR2-1"-"BR2-6". ISBN 978-80-86238-65-4.

MASIN J., FERJENCIK M., SELESOVSKY J., Using the Accelerating Rate Calorimetry for Determination of Energetic Materials Thermal Hazards. In Proceedings of the 4th International Conference on Chemical Technology. Praha: Česká společnost průmyslové chemie, 2016, pp. 557-563. ISBN 978-80-86238-94-4. ISSN 2336-811X.

FERJENCIK M., SELESOVSKY J., MASIN J., Nač by měla být zaměřena výuka bezpečnosti na chemických VŠ?. In Proceedings of the 1st International Conference on Chemical Technology. Praha: Česká společnost chemická, 2013, pp. 0109-0109. ISBN 978-80-86238-55-5.

FERJENCIK M., MASIN J., Unwelcome results of safety analyses. In Proceedings of the 3rd International Conference on Chemical Technology. Praha: Česká společnost průmyslové chemie, 2015, pp. 494-499. ISBN 978-80-86238-82-1. ISSN 2336-811X.