**RISK ANALYSIS BASED ON THE CRITICALITY CLASSES AND THEIR DETERMINATION USING ACCELERATING RATE CALORIMETRY**

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## Abstract

The scope of this paper is to incorporate thermokinetic parameters determined by Accelerating rate calorimetry (ARC) into risk analysis framework. This approach provides a reliable way for identification and consequent prevention of the risks resulting from the thermal hazards of the assessed processes. ARC is used to determine adiabatic temperature rise ($\Delta T_{ad}$), self-accelerating decomposition temperature (SADT) and time to maximum rate (TMR). The other two temperatures are known from the process characteristics: process temperature ($T_p$) and maximal temperature for technical reasons (MTT). The relation among these temperatures determines the critical class of an assessed process. Event tree analysis (ETA) was used to construct the prefinished event tree for every particular class, which universally describes developments of thermal runaway scenarios. The critical scenarios are consequently analysed using Layer of protection analysis (LOPA) in order to obtain probability of a particular scenario. New method is demonstrated on phenol plant explosion, where the explosion of cumene hydroperoxide (CHP) occurred.

## Introduction

Some processes performed on the industrial scale use the chemical reactions associated with a thermal hazards. Major accidents like Seveso1 or T2 laboratories[2] served like motivation to fully comprehend the thermokinetic behavior of reactions with a runaway potential. Although the field of thermal hazard prevention registered great advancements in the past decades, we believe there is need for a practical hazard analysis method, which would incorporate the results of a thermal analysis into the existing hazard analysis framework. New proposed approach uses generalized event trees to identify critical scenarios which are consequently evaluated by layer of protection analysis (LOPA).

Event tree analysis (ETA) and LOPA deploy systematic approach which should be the key to avoid the omission of any credible accident scenario. However none of these methods takes implicitly into account the results of the calorimetric measurements of the reactions possessing a thermal hazard. Conversely the calorimetric measurements yield results, which are used to develop more or less complicated mathematical models of the examined reactions. These models are difficult to be applied in a practical risk analysis.

The aim of this work is to overcome the disadvantages of both traditional risk analysis methods and thermal hazard analysis. The solution of disadvantages connected with both approaches is to combine them. Or more precisely to use only basic parameters defining thermal hazard of the assessed reaction and use them in the risk analysis.

This paper describes how to use the results obtained from the ARC for dividing the examined processes into the criticality classes. Consequently ETA is used to derive the generalized event tree for the each criticality class. Once all the credible scenarios are identified, their likelihood is evaluated with LOPA.

## Accelerating rate calorimetry

In accelerating rate calorimeters a tested sample is measured in an enclosed bomb allowing monitoring the temperature and pressure changes. A bomb is placed in the environment, where temperature can be regulated precisely. Usually so called "heat-wait-search" mode is used for determination of thermokinetic behavior of a sample. In this mode a tested sample is kept at certain temperature for some time interval (e.g. 15 min). If the instrument does not detect any temperature change caused by samples decomposition, the temperature is elevated (e.g. by 5 °C) and this procedure is repeated untill a sample begins to decompose. Once decomposition starts, the calorimeter switches to the adiabatic mode, maintaining zero temperature gradient between the bomb and its surroundings. The decomposition characteristics are recorded in the terms of the temperature and pressure rise.

For the scope of this work three parameters were calculated from the ARC measurements using the calorimeter software: self-accelerating decomposition temperature (SADT), adiabatic temperature rise ($\Delta T_{ad}$) and time to maximum rate (TMR).

Since the adiabatic conditions in the calorimeter are not ideal, the obtained parameters must be corrected with so called Φ-factor, which is the measure of the adiabaticity. The Φ-factor is given by relation between thermal masses of the sample and its surroundings:

$$\Phi = 1 + \frac{m_B c_B}{m_S c_S}$$

Where *m* are masses, *c* are specific heats, indexes *S* are for the sample and indexes *B* are for the surroundings (bomb). In the case of ideal adiabaticity Φ-factor would be equal to 1, but the bomb serves as a cooler, absorbing a part of the released heat, increasing Φ-factor. That is why the measurements conducted with higher Φ-factor values have to be recalculated to achieve real adiabatic values.

## Dividing processes with runaway potential into criticality classes

According to Stoessel[3] all the processes with a thermal risk can be divided into five criticality classes. The advantage of this approach is that it uses four temperatures and their relation to characterize the assessed process, so every particular process can be incorporated into one of the classes. The first temperature is the temperature of the process ($T_p$), the temperature at which process normally operates. The second temperature is the maximum temperature for technical reasons (MTT), for opened systems it is the boiling point, for enclosed systems it is the point when pressure reaches the highest acceptable pressure. These two temperatures are given by the process technology, while remaining two temperatures can be obtained by ARC measurement. The third temperature is the maximum temperature of synthesis reaction (MTSR). This temperature is equal to sum of $T_p$ and adiabatic temperature rise ($\Delta T_{ad}$), which determines how much the reaction mass can heat itself when cooling fails. The last self-accelerating decomposition temperature ($T_D$) represents the thermal stability limit of reaction mass, at which runaway commences. Relation among the temperatures upon which particular classes are based is depicted in Fig. 1.

The first two classes represent low risk, because their $\Delta T_{ad}$ cannot heat the system to the $T_D$ without an external source of heat. The third class represents the case where evaporative cooling can prevent reaching $T_D$ level in an opened system. Last two classes are the most critical, since they possess enough energy to heat up to decomposition levels, despite evaporative cooling in the fourth class case.

As the temperatures reflect the dynamic character of an analyzed process, time to maximum rate (TMR) simply describes its kinetics. This temperature-dependent parameter is used as the measure of the examined reaction controllability. It can be calculated from $T_D$, the calculation is based on measured data and thus provide quite reliable information of time, at which the reaction can be controlled before it reaches its peak. However Stoessel[3] uses $T_{D24}$; this is the temperature at which TMR is 24 hours. For the calculation of this temperature TMR must be extrapolated. The extrapolated values do not represent exact TMR values. Besides $T_{D24}$ can be overly conservative for some processes.

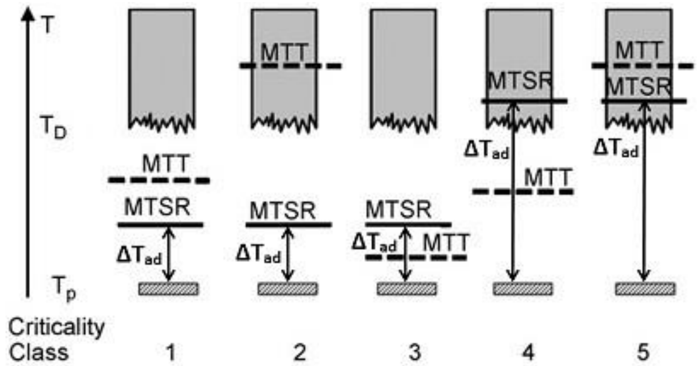


Figure 1. Dividing scenarios into classes according to relation among $T_p$, MTSR, MTT and $T_D$.[3]

## ETA

This scenario-based qualitative method of risk analysis is used to identify how an initiating event can develop into an accident. The possible development of a scenario is expressed in the form of the graphical tree describing successes/failures of the protective measures. The technique is good for analyzing the complex cases, where more layers of protection plays role in the scenario development. This is also the reason why ETA was chosen as a tool for constructing prefinished event trees (ET), which describe possible runaway development for each criticality class.[4]

## LOPA

LOPA is the semi-quantitative risk assessment method used in the process industries. Once a scenario of interest is identified (in our case using prefinished ETs), it is analyzed like the initiating event – consequence pair. The analysis is focused on identification of so called independent protection layers (IPLs) which should lower a risk to tolerable level and whether they are sufficient. The technique assigns order-of-magnitude values to both initiating event to quantify its occurrence and to each IPL to quantify its reliability. This allows an analyst to decide whether the frequency of the risk is acceptable.[5]

## Results and discussion

## Example: Phenol plant explosion

In order to test how ARC results can be incorporated into the existing risk analysis framework, synthesis of phenol and acetone using Hock process was chosen as the testing example. Although the examined accident occurred almost thirty years ago, ongoing research concerning determination of safety parameters for cumene oxidation from the past decade proves the topic is still actual - typically thermal activity monitor III is used to determine CHP decomposition parameters.[6] Or DSC combined with other calorimetric methods such as vent sizing package 2.[7]

Hock process is based on oxidation of cumene to cumene hydroperoxide. The resulting organic peroxide is cleaved with catalytic quantity of mineral acid to yield phenol and acetone. Despite the simplicity of the involved chemical reactions, the peroxidic bond cleavage is highly exothermic, which is the source of serious thermal hazard.

On March 9, 1982 there was a great explosion in the phenol plant, during which 100 cubic meters of 50 % w/w cumene hydroperoxide exploded and consequently started fire in the plant. The explosion preceded problems with fueling the boilers, so the process was switched to standby mode. When the fueling problems were solved, another problem with vacuum for the distillation column emerged. While operators tried to reestablish vacuum, columns content was pumped into the remote tank. The steam regulation valve for the column was leaking steam, heating the columns content, but operators did not noticed the temperature rise. High temperature alarm was disconnected, so it did not warn operators either. These circumstances allowed temperature in the tank to rise from normal 70 - 80˚C to 149˚C. The solution in the tank started to boil and relief valves opened, leaking the vapors. Operators switched off the boiler, but it was too late. Vapors ignited first and the explosion of the tank followed.[8]

## ARC measurements

The thermal decomposition of CHP was studied with accelerating rate calorimetry. For this ARC-es, manufactured by Thermal Hazard Technology, UK, was used. The experiments were performed in heat-wait-search mode with starting temperature 50 ˚C, wait time 15 minutes and temperature step 5 ˚C. Temperature rate 0.02 ˚C/min was set as the detection limit for the decomposition of the sample.

The experiments were carried out in the Ti-LCQ titanium bomb with following parameters: (8 g, 0.54 J/g°C) with the diameter 25.4 mm and the volume 9.8 ml. 200 mg of 50 % w/w CHP solution in cumene was measured; $\Phi$ = 17,74.

## Assigning the criticality class to the examined process

According to description of the phenol plant explosion,[8] $T_p$ was given by interval 70 - 80˚C. $\Delta T_{ad}$ was measured to be 344 ˚C, which means, that MTSR as the sum of $\Delta T_{ad}$ and $T_p$ equals 524 ˚C. Boiling point of the solution is 152˚C at normal pressure, concerning that runaway occurred in the enclosed system, MTT is significantly higher than $T_D$, which was estimated to be 121 ˚C. The relation among the given and calculated temperature values indicates the evaluated process belongs to the fifth criticality class. TMR at $T_D$ equals 8.5 min; such low value only confirms that once decomposition starts control of the reaction is impossible. ARC results are illustrated in Figure 2.

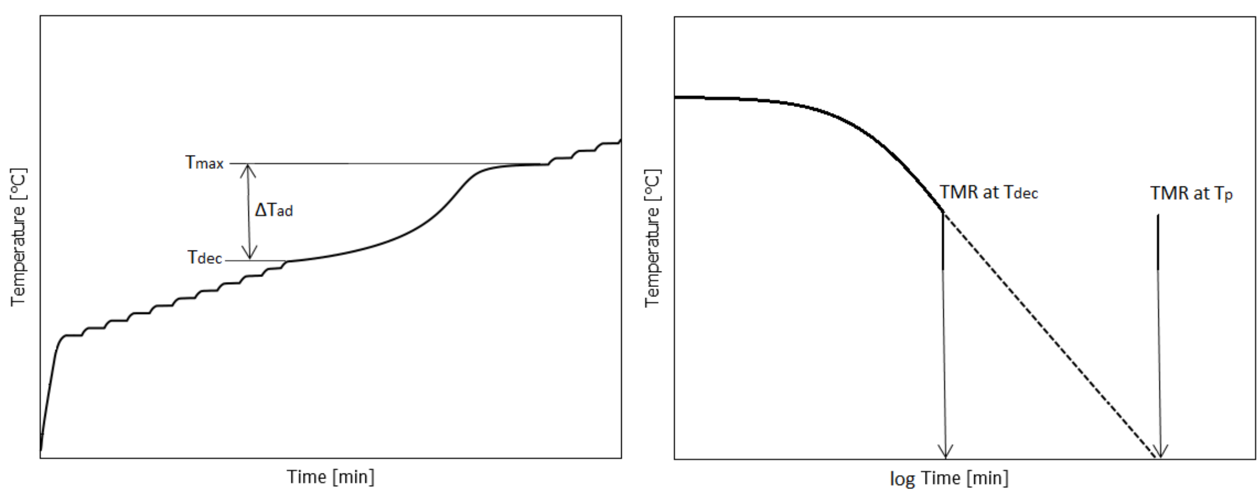


Figure 2. The first graph depicts temperature vs time dependency obtained by ARC measurement. The second graph represents TMR dependency on temperature. Full line is based on measured data, dashed line represents values extrapolated to $T_p$.

## Generalized event trees

ETA was used in order to obtain the prefinished event trees which would serve as a tool systematically describing possible development of thermal runaway scenarios, taking into account results of ARC measurements. The analysis was focused on the criticality classes instead on particular systems. Resulting event trees serve as a list of all the credible scenarios caused by any undesired temperature rise in an analyzed system.

Applying the event trees allows an analyst to address the critical scenarios and the factors influencing their development. This qualitative analysis serves like a basis for LOPA, which deals with particular scenarios and facilitates quantitative estimation of their likelihood. For the fifth class decomposition and thermal explosion scenarios are imminent, since both MTSR and MTT are above $T_D$.

## Application of generalized event trees to the phenol plant explosion example

As described above, the assessed example of the phenol plant explosion belongs to the fifth criticality class. Prefinished ET for this class includes overall six possible scenarios; four of them are critical. At the beginning of the ET it has to be decided whether an external heating of the system is possible, although in the fifth class the reaction mass possess enough energy to heat to $T_{dec}$ by itself, but external heating increases probability of the critical scenarios to develop. It means although the runaway in the solved example was caused by the unintended external heating, the critical scenarios without external heating remain credible, even though less probable.

In the next step we decide whether the system reaches $T_D$, which depends mainly on the amount of the unreacted reaction mass. From the accident description it is known, that the runaway involved almost 100 $m^3$ of 50 % w/w of cumene hydroperoxide solution. Because $T_p$ is 80 ˚C, $\Delta T_{ad}$ is 344˚C and SADT is 121 ˚C, we can exclude any non-critical scenario, in which a temperature rise would terminate by itself.

At the end of ETA there are two possibilities of the scenario severity: either decomposition or thermal explosion. Like in the preceding decision, it depends mainly on the amount of the unreacted reaction mass and the system parameters which scenario applies. If we take into account the amount of unreacted CHP and its decomposition properties, it is highly probable, that any decomposition would develop into thermal explosion as highlighted in Fig. 3.

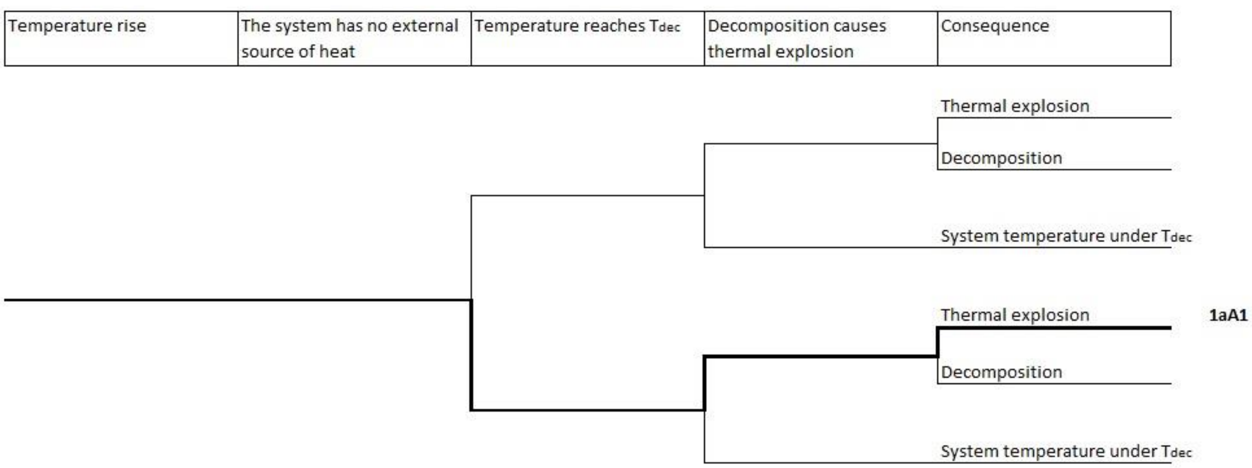


Figure 2. Generalized event tree of the fifth class highlighting the thermal explosion scenario.

## LOPA

Thermal explosion scenario was identified as logical result of any temperature rise, use of LOPA is demonstrated and summarized in the Tab. I. Order of magnitude estimations of the probabilities are usually used for the analysis and our example is not an exception. At the beginning the risk tolerance is set; for accidents with catastrophic consequences value $10^{-4}$ is usually used. Frequency of initiating event (steam leakage in our case) was estimated to be 0.1. The analysis does not take into account any enabling events or conditional modifiers, because more information about the plant operation conditions would be necessary to estimate these parameters. It was assumed that frequency of unmitigated consequence has the same value as the initiating event, because it is probable that every steam leakage in the assessed point leads to decomposition and consequent thermal explosion.

In next phase the particular IPLs are evaluated. Probability of failure on demand (PFD) for the basic control process system (BCPS) alarm and human action was assumed to be 0.01. The pressure relief device is completely ineffective in the thermal explosion scenario, its PFD is 1. Taking into account these values, frequency of mitigated scenario 1aA1 is still ten times higher than tolerance criteria. Conversely scenario 1aA2 demonstrates, that tolerance criteria could be met e.g. by introducing a safety instrumented function (SIF) with PFD 0.1.

Table I
Simplified LOPA sheet

| Scenario title | 1aA1 | | 1aA2 | |
|---|---|---|---|---|
| | PFD | Frequency [/yr] | PFD | Frequency [/yr] |
| Risk tolerance criteria | | 0.0001 | | 0.0001 |
| Initiating event frequency (/yr) | | 0.1 | | 0.1 |
| Frequency of unmitigated consequence | | 0.1 | | 0.1 |
| BCPS alarm and human action | 0.01 | | 0.01 | |
| Pressure relief device | 1 | | 1 | |
| Safety instrumented function | N/A | | 0.1 | |
| Total IPLs | 0.01 | | 0.01 | |
| Total PFD for all IPLs | 0.01 | | 0.01 | |
| Frequency of mitigated consequence | | 0.001 | | 0.0001 |

## Conclusion

A new approach for evaluation of thermal hazard was proposed. This approach was applied on the risk analysis of the phenol plant explosion example. Accelerating rate calorimetry was used to analyze thermokinetic behavior of CHP decomposition. Results of the ARC measurements were incorporated into existing risk analysis methods. Risk analysis results proved its applicability for the practical thermal hazard evaluation.

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