Optimization of a procedure for emergency cooling and pressure relief for reactors with exothermal processes

Dissertation

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von: Dipl.-Ing. Dariusz Jabłoński
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Gutachter: Prof. Dr.-Ing. habil. Ulrich Hauptmanns
Prof. Dr. rer. nat. Axel Schönbucher

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To warn of an evil is justified only if, along
with the warning, there is a way of escape.

Cicero

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Magdeburg, Spring 2008 Dariusz Jabłoński

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Abstract

In many chemical and processing industries and chemical manufacture, particularly in the fine, pharmaceutical and speciality chemical industries, there is an increasing trend towards the production of very high value products, such as polymers, pharmaceuticals, and speciality chemicals, in batch reactors. As a result, there is an increasing dependence in the sector on the existence of smaller, more flexible enterprises, especially in Europe, capable of providing specialised skills and products in niche markets.

The reliability of a chemical batch reactor depends on the capability of the control/supervision system to monitor its state and, in time, to identify its operational functions or failure modes. It is estimated that around 20% of the process industries carry out exothermic reactions that require detailed investigations of the associated reactive hazards and the design and installation of safety systems.

The control systems are of great importance. They have to ensure that the desired operating conditions can be maintained as closely as possible during the course of a batch operation. However, achieving such optimal conditions and control of batch processes is still quite difficult and provides challenging and interesting problems. The most important of these are due to the inherent complexity of the batch reactors, characterized by many parameters, such as highly nonlinear behaviour resulting from the dependence of reaction rates on concentrations and temperature and so forth.

Specifically for chemical batch reactors carrying out exothermic reactions, the major problem is the loss of temperature control. In this situation, when the rate of heat generation of the chemical reaction exceeds the rate of heat removal by the cooling system, there is a positive feedback mechanism, since the temperature of the reaction mass will rise, thereby increasing in turn the rate of heat generation if the temperature dependence of the reaction can be described by Arrhenius' law. In this situation, if no countermeasures are taken, a runaway may occur.

The consequence of such a reaction is often a loss of process containment. Although the safety records of the process industries have improved in recent years, fires, explosions and other incidents due to runaway reactions still occur. In view of the likely reasons for these occurrences, such as overfilling, pipe blockage, excessive initial heating, loss of power, coolant or stirring, it is clear that there is a vital need for reliable safety systems.

Therefore, batch reactors used for exothermal reactions are, amongst other safety features, equipped with trip systems. These may be based on the fast injection of a reaction inhibitor, the quick addition of a compatible diluter or fast dumping of the reactor contents into a knock-out tank. The measures mentioned are active, namely they require a number of components (such as sensors, pumps, valves) to function in order to be successful. In order to reach a high availability, a redundant design is often used. Additional gains in availability by further increasing the degree of redundancy are, however, limited by the possible occurrence of common cause failures. Nevertheless, the availability of the trip function can be improved if a passive trip system is used instead.

In general, passive means reducing or eliminating hazards by processes and equipment features which work without active components and energy supply from outside. The working principle of the passive trip system is to utilize the natural driving force of the pressure built up during a runaway reaction, either by gas production, evaporation or both. The passive trip system prevents damage simply by being present. There is no need for any additional action from outside.

The goal of the present work is to show the system's feasibility, as well as to design and develop the passive trip system for batch chemical reactors and to optimize its key parameters. The system to stop runaway reactions was mounted on a reactor and theoretically modelled with the computer programs. The representative reactions were identified and carried out. In every case, there was no operational cooling and hence the reaction temperature increased. The ensuing runaway reaction was in each case successfully stopped by the passive trip system. An experimental and theoretical proof of the success criterion of the passive trip system was provided.

Zusammenfassung

In vielen Betrieben der Chemie und Verfahrenstechnik, besonders in der Feinchemie und Arzneimittelherstellung, gibt es eine zunehmende Tendenz zur Herstellung von Produkten mit einer hohen Wertschöpfung, wie Polymere, Arzneimittel und Spezialchemikalien in Batch-Reaktoren. Infolgedessen gibt es besonders in Europa auf diesem Sektor eine zunehmende Abhängigkeit von der Existenz kleiner, flexibler Unternehmen, die fähig sind, spezielles Wissen und Produkte in Nischenmärkten zur Verfügung zu stellen.

Die Zuverlässigkeit eines chemischen Batch-Reaktors hängt von der Fähigkeit des Kontroll- oder Überwachungssystems ab, dessen Zustand zu überwachen und rechtzeitig Fehlerzustände zu identifizieren. Schätzungsweise 20% der von der verarbeitenden Industrie durchgeführten exothermen Reaktionen erfordern ausführliche Untersuchungen zu den aus der Reaktion resultierenden Gefahren und zur Auslegung und Installation von Sicherheitssystemen erfordern.

Die Regelsysteme sind von besonderer Bedeutung. Sie müssen sicherstellen, dass die gewünschten Betriebsbedingungen während des Batch-Prozesses so gut wie möglich eingehalten werden. Jedoch ist das Erzielen solcher optimalen Bedingungen und die Kontrolle von Batch-Prozessen schwierig und bietet herausfordernde und interessante Problemstellungen. Die Wichtigsten beruhen auf der inhärenten Komplexität der Batch-Reaktoren, die charakterisiert sind durch ausgeprägtes nichtlineares Verhalten, das unter anderem von der Abhängigkeit der Reaktionsraten von den Konzentrationen und der Temperatur herrührt.

Das Hauptproblem chemischer Batch-Reaktoren, in denen die exotherme Reaktionen ablaufen, ist der Ausfall der Temperaturregelung. In dieser Situation, in der die Wärmeproduktion größer wird als die Wärmeabfuhr durch das Kühlsystem, kommt es zu einer positiven Rückkopplung, wenn die Temperaturabhängigkeit der Reaktionsgeschwindigkeit durch das Arrhenius-Gesetz beschrieben werden kann. Dabei steigt die Temperatur des Reaktorinhalts, was wiederum zu einem Ansteigen der Wärmeproduktionsrate führt und schließlich zum Durchgehen der Reaktion führt, wenn keine Gegenmaßnahmen getroffen werden.

Die Folge solch einer durchgehenden Reaktion ist häufig ein Verlust der Prozessumschließung. Obwohl sich die Sicherheitsmaßnahmen der Prozess-Industrien in den

letzten Jahren verbessert haben, kommen Brände, Explosionen und andere Ereignisse aufgrund durchgehender Reaktionen immer noch vor. Im Hinblick auf die Gründe für diese Vorfälle, wie Überfüllung, Rohrleitungs-Blockade, Ausfall der Versorgungsenergie, des Rührers oder Verlust des Kühlmittels, ist es klar, dass es ein dringendes Bedürfnis nach zuverlässigen Sicherheitssystemen gibt.

Deshalb sind Batch-Reaktoren, die für exotherme Reaktionen verwendete werden, neben anderen Sicherheitsmaßnahmen, mit Abschaltsystemen ausgestattet. Diese können auf der schnellen Einspritzung eines Reaktionshemmers, dem schnellen Einbringen eines geeigneten Verdünnungsmittels oder dem schnellen Ablassen des Reaktorinhalts in einen Notablasstank beruhen. Die erwähnten Maßnahmen sind alle aktiv, denn sie erfordern, um erfolgreich zu sein, dass mehrere Komponenten (wie Sensoren, Pumpen, Ventile) funktionieren. Ein zusätzlicher Gewinn an Verfügbarkeit durch einen höheren Redundanzgrad wird durch das Wirken von Fehlern aus gemeinsamer Ursache eingeschränkt. Trotzdem lässt sich die Verfügbarkeit von Abschaltsystemen durch den Einsatz von passiven Systemen verbessern.

Im Allgemeinen bedeutet passiv, Reduktion oder Beseitigung von Gefahren durch Eigenschaften von Prozessen und Apparaturen, die ohne aktive Bestandteile und Energieversorgung von Außen arbeiten. Das Arbeitsprinzip des passiven Abschaltsystems beruht auf der natürlichen Triebkraft des Drucks, der während des Durchgehens der Reaktion durch Gasproduktion, Verdampfung oder beides entsteht. Passive Abschaltsysteme verhindern Schäden durch ihr bloßes Vorhandensein. Es ist kein Eingreifen von Außen notwendig.

Ziele der vorliegenden Arbeit sind, die Machbarkeit des Systems nachzuweisen, sowie ein passives Abschaltsystem für chemische Batch-Reaktoren zu entwerfen, zu entwickeln und Schlüsselparameter zu optimieren. Das Abschaltsystem zum Aufhalten durchgehender Reaktionen wurde an einem Laborreaktor montiert und theoretisch mit Computerprogrammen modelliert. Repräsentative Reaktionen wurden identifiziert und durchgeführt. Es gab grundsätzlich keine betriebliche Kühlung, und folglich nahm die Reaktionstemperatur zu. Das daraufhin einsetzende Durchgehen der Reaktion wurde in allen Fällen durch das passive Abschaltsystem gestoppt. Ein experimenteller und theoretischer Nachweis der Wirksamkeit des passiven Abschaltsystems wird erbracht.

Schriftliche Erklärung

Ich erkläre hiermit, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht.

Insbesondere habe ich nicht die Hilfe einer kommerziellen Promotionsberatung in Anspruch genommen. Dritte haben von mir weder unmittelbar noch mittelbar geldwerte Leistungen für Arbeiten erhalten, die im Zusammenhang mit dem Inhalt der vorgelegten Dissertation stehen.

Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form als Dissertation eingereicht und ist als Ganzes auch noch nicht veröffentlicht.

Magdeburg, 22.04.2008
Jabłoński Dariusz

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1

Introduction

1.1 Background

The chemical industry in Europe is increasingly expanding into the pharmaceuticals and speciality chemicals sectors **[1, 2]**. These types of production are characterized by the use of batch reactors and, in many cases, exothermal reactions. The design of safe and reliable batch reactor safety systems is a big challenge, especially due to the inherent complexity of some of the reactions and the possibility of a runaway reaction.

How do we prevent undesirable events like thermal runaway? How do we prevent such incidents like Seveso and Bhopal? How do we make safety systems more efficient and reliable? These are only some of the questions which safety engineers have to answer when considering batch reactor safety. The fact is that the major causes of accidents in the chemical industry are exothermic runaway reactions (35% according to the U.S.C.S.B. report **[3]** and 26% according to Balasubramanian **[4]**). The control of these reactions is an important issue for chemical process safety. The consequence of such a reaction is often a loss of the process containment. This can lead to hazardous situations: fires, explosions, missiles or toxic hazards and can cause the death of both employees and the population at large, in addition to harm to the environment and loss of property (c.f. **[5, 6, 7], Appendix A**).

In view of the likely reasons for these reactions, such as loss of cooling capacity or too high temperature of the coolant, loss of stirring, reactants accumulation or external heating, there is a need for a reliable safety system. Conventional systems for dealing with a possible runaway are, for example, the injection of an inhibitor, the fast dumping of the reactor contents into a knock-out tank or the reduction of the concentration by introducing an inert gas. The measures mentioned are active in that they require a number of components (such as sensors, pumps, valves and the corresponding energy supplies) to function for being successful. In order to reach a high availability a redundant design is often used. Additional gains in availability by further increasing the degree of redundancy are, however, limited by the possible occurrence of common cause failures **[8]**. Furthermore, the resulting increase in complexity makes it more difficult to discover possible design flaws and maintenance errors. However, the availability of the trip function may be improved if a passive trip system i.e. a system which works without energy supply from outside is used instead (c.f. **Chapter 3, Chapter 4**). Therefore, the design, conditions of operation and availabilities of such passive trip system are investigated in this work.

1.2 Runaway reactions in hindsight

Many chemical reactions within the chemical process industries are exothermic. The heat which is released during such reactions is usually controlled by equipping the reactor with cooling jackets or cooling coils. In some cases, the rate of heat generation can exceed the rate of heat removal and an uncontrolled runaway reaction may occur. Runaway reactions continue to be a major problem in the process industry. A recent study showed that 26.5% of the major chemical plants accidents are due to runaway reactions **[4]**. Unfortunately, this fact is not apparent when reviewing the major accidents reported on an annual basis. The Chemical Safety Board CSB **[3, 5]** emphasizes the relevance and importance of consulting more than one database. Safety authorities in one of the EU-countries have revealed that, within the total number of around 2000 batch and semi-batch reactors installed, an average of about 110 runaways occur annually **[9]**. In Germany about 13.75% of the accidents in the process industry were caused by chemical reactions **[10]**. An important analysis was also conducted in 1989 by Barton and Nolan **[11]**. They highlighted 189 accidents that occurred in the UK chemical industry between 1962 and 1987. **Figure 1.1** shows the contribution of different reaction types to the total number of exothermal runaway reactions **[12]**.

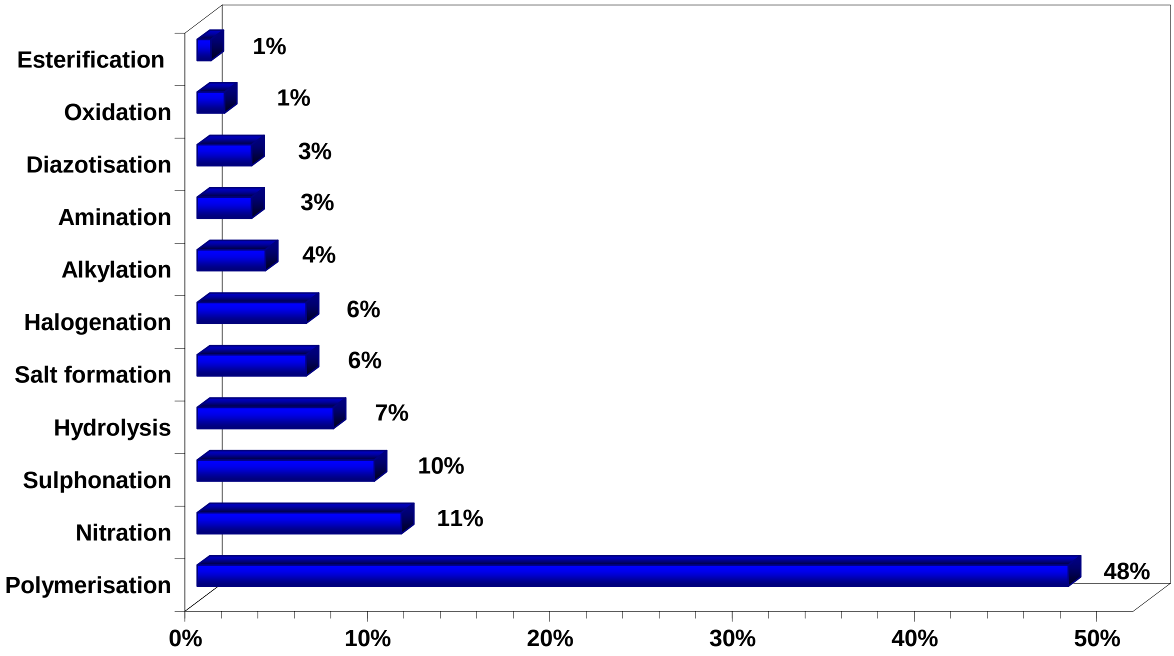

Figure 1.1 *Percentage of incidents per specified chemical process*

The above statistical evidence shows that the potential for loss of control and hence runaway reactions is very high. Polymerisation reactions contribute most (48%) and esterification reactions least (1%).

Another statistical study showed that at least 60% of batch reactor incidents could probably be avoided, if a proper design of the reactor plant and safe operating conditions had been adhered to. **Table 1.1** presents a comparison of three different studies **[13]**.

Table 1.1 *Prime causes of batch reactor incidents*

Incident cause	**Barton and Nolan (1987)**	**Barton and Nolan (1989)**	**Etchells (1993)**
	1962-1984	**1962-1987**	**1986-1990**
Thermo-reaction chemistry	21.4%	20.1%	14.8%
Raw material quality	7.9%	8.9%	9.8%
Maintenance/other factors	22.3%	21.3%	22.2%
Temperature control	22.2%	18.9%	13.9%
Loss of mixing/agitation	9.5%	10.1%	13.1%
Mischarging of reactants	16.7%	20.7%	26.2%
Incident rate (1/month)	0.46	0.54	2.03

The last row in table indicates that the number of incidents per month increased but, in reality, this merely demonstrates the improvement of reporting methods. These surveys also proved how important it is to control temperature in batch reactors.

The principal causes of exothermic runaway incidents are:

- Inadequate maintenance – 21.9%
- Human factors (mischarging) – 21.2%
- Little or no study of the reaction chemistry and thermochemistry – 18.7%
- Cooling system failures - 18.3%
- Stirrer failures - 10.3%
- Mistakes made as a consequence of raw material quality – 8.9%

Other but also important factors responsible for exothermic incidents are:

- Poorly designed reactors
- Underrated control systems
- Inadequate procedures and training

A study conducted by the Health and Safety Executive (HSE) shows the same trend. Special attention should be paid to the following critical points: mischarging (23%), little knowledge of reaction chemistry (18%) and inadequate temperature control (15%).

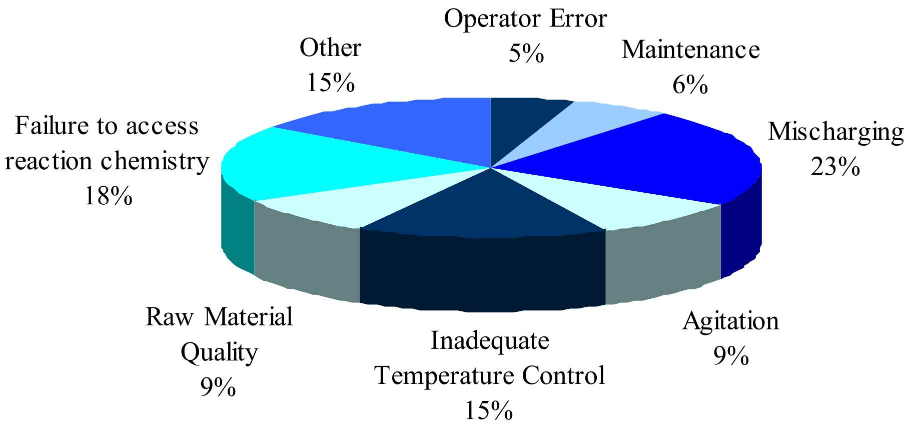

Figure 1.2 *Main causes of runaway reactions in UK (Chemical Industry) [1986-2000]*

In 2002, the U.S. Chemical Safety and Hazard Investigation Board (CSB) published a report containing the results of investigations on 167 reactive chemical incidents that occurred in the U.S. between 1980 and 2001. The results of these investigations are presented in **Appendix C**. These accidents caused 108 deaths and millions of dollars in property damage. About 35% of the incidents were caused by runaway reactions. Chemical reactors constituted the highest share of equipment involved in accidents triggered by reactive chemicals. The next highest share of equipment affected is storage equipment and other process equipment with a contribution of 22%. About 70% of accidents occurred in the chemical industry and the remaining 30% occurred in other industries that use bulk quantities of chemicals, such as waste processing and petroleum refining. The manufacture of fine, intermediate organics and plastic, rubbers and resins in batch reactors had the highest share of incidents reported. Nearly 70% of all analyzed accidents were caused by exothermal reaction. The highest contributions were made by decomposition reactions (26%) and polymerization reactions (10%).

According to the HSE, 269 accidents were reported between 1986 and 2000 and currently there are 10-20 incidents reported every year. Although fatalities and injuries are very rare, there nonetheless exists a high potential for injury in some cases.

In the European Union, the Major Accident Hazard Bureau (MAHB) established the Major Accident Reporting System (MARS). At present (January 2007), the MARS database contains around 600 reported accidents. According to the research presented in **[14],** a total number of 132 accidents related to reactive chemical incidents (exothermic runaway reactions) can be identified. The list of these accidents with a short overview is presented in **Appendix B.** The statistical analysis presented in **Table 1.2** confirmed the results of investigations performed by HSE, CSB and ZEMA.

Table 1.2 *Number of runaway accidents in the MARS databank with indication of technical and physical causes*

Technical and physical causes	Total	%
Unexpected reaction	30	22.9
Runaway reaction	21	16
Component failure	13	9.9
Vessel failure, containment equipment failure	12	9.2
Electrostatic accumulation	9	6.9
Failure of control / monitoring device	7	5.3
Loss of process control	6	4.6
Corrosion / fatigue	6	4.6
Blockage	4	3.1
Utilities failure (electricity, gas, water, steam etc.)	4	3.1
Natural event (earthquake, temperature etc.)	3	2.3
Other	3	2.3
Transport accident	1	0.8

1.3 Lessons learnt

The use of hindsight from the analysis of accidents reported in the aforementioned databases plays an important role in improving process safety. The most common issues involve flaws in either process analysis, design of safety measures and control systems and management procedures. All these issues are very important and therefore should be considered by safety engineers.

The study of past accidents can help avoid the recurrence of similar situations. **Table 1.3** summarizes the statistical data presented in **Chapter 1.2**. The most important conclusions confirm how important runaway reaction control is and how much there is still left to be done for safety and chemical engineers.

Table 1.3 *Statistics on the importance of runaway reactions (multiple causes are possible)*

Runaway reaction related characteristics	**Fraction**	**Source**
Chemical manufacturing (industry)	70%	[3]
Runaway accidents due to inadequate engineering design	60%	[13]
Runaway reactions - polymerization	48%	[12]
Fires and explosions due to runaway reactions	42%	[3,5]
Runaway major chemical plants accidents	26,5%	[4]
Fine and intermediate organics	26%	[13]
Batch reactors and storage tanks involved in runaway accidents	25%, 22%	[3]
Decomposition and polymerization	26%, 10%	[3]
Lack of proper understanding of the process chemistry	18%	[HSE]
Runaway major accidents in Germany	13,75%	[10]

Despite the large amount of literature and organizations that deal with runaway reaction phenomena, the topic still demands a lot of work. The most important area seems to be the chemical manufacturing industry, especially regarding batch reactors (70%) and the manufacture of fine and intermediate organics (26%). The prevention and protection systems installed have to be more reliable in order to avoid accidents such as fires or explosions (42%). More attention has to be paid to decomposition and polymerization reactions, which have the highest potential to runaway (26% and 10% respectively). It is also essential to have a thorough understanding of process chemistry and thermochemistry (18%). Finally, an adequate engineering design for heat transfer, adequate control systems and operational procedures including training must be guaranteed.

2

Batch and semi-batch reactors – hazards and safety

2.1 Batch and semi-batch reactor hazards

Batch reactors are operated by a wide variety of firms because of their convenience and flexibility. In most cases they are quite small (about 20-1000 litres in small industrial plants) but the number of reactions or chemicals can be quite large. The size of batch reactors in large plants ranges from 38.000 to 76.000 litres. The same batch reactor allows one to carry out many different reactions **[15]**. Frequently, these reactions are exothermic and loss of control, the most critical event of which is operational cooling failure, can lead to a temperature increase and thermal runaway as a consequence of this reaction.

In the case of batch reactors, where the rate of reaction, and thereby the rate of heat production, varies with time, runaway reactions can be very problematic **[16]**. The task of designing apparently simple batch reactors with their operating, control and safety systems can be very difficult if all the time-dependent parameters are considered. The problem is aggravated additionally, if the same reactor has to carry out different chemical processes. Therefore, it is necessary to adjust the safety system to each reaction in order to avoid thermal runaway.

2.1.1 Batch and semi-batch reactors

Batch reactors are characterized by the fact that neither a reactant is added, nor is a product removed during the reaction. Any reaction being carried out with this constraint, regardless of any other reactor characteristic, is considered batch. The batch operations are characterized by:

- well mixed tank contents,
- a reaction that does not occur in any appreciable degree until filling and start-up procedures are complete, and
- a reaction that stops when quenched or emptied.

The main advantages of a batch reactor are:

- the simple construction (cylindrical tank with charging nozzles and access for inserting agitators, coils, or other internal devices and for cleaning),
- the small instrumentation and cost (when small quantities of different materials are to be made using the same equipment or when products are highly regulated such as pharmaceuticals **[17]**),
- the ease at which they can be scaled up (beneficial when time-to-market is important), and
- the flexibility of operation (used in the production of fine and speciality chemicals).

Although the operation of batch reactors demonstrates a high degree of flexibility, batch processes are usually very complex with strong nonlinear dynamics and time-varying parameters. Therefore they require continual safeguarding and corrections by the operator or automatic devices. Due to the small amounts produced and the variety of processes, obtaining a complete understanding of the reactor dynamics is often not economically feasible. This lack of knowledge gave rise to a number of accidents, see **Chapter 1.** The study of accidents also shows that batch units are more frequently involved in accidents than continuous reactors. This fact highlights, perhaps more so than any other, the necessity of investigations on safety systems for batch reactors. The main disadvantage of a batch reactor is in the labour costs, which include the time taken to:

- fill the reactor,
- heat the reactor contents to the initial temperature,
- cool it after completion of the reaction,
- discharge the reactor contents, and

- clean the reactor for the next batch (required between runs for emptying and filling the tank).

These procedures increase the overall labour costs per unit of production.

An attractive way to reduce any potential hazard is to use semi-batch reactors instead of batch reactors. With this type of operation, the reactor is initially charged with one reactant and then the other reactants are subsequently added to the vessel. This makes it possible to control the reaction rate by varying the amount of reactant introduced and hence the heat production. Therefore, semi-batch reactors are used for highly exothermic reactions. Furthermore, the addition of reactants in small increments enables one to control the distribution of the product and the evolution of the reaction with time. In addition, the removal of the product increases both conversion and selectivity.

These systems also have disadvantages. Under certain circumstances, when the initial temperature is too low, the added reactants will not react immediately and will accumulate, after which the combination of increasing concentration and gradual temperature rise may lead to a runaway **[18]**. A safe operation of a semi-batch reactor is therefore based on the prevention of accumulation of reactants in the system. Consequently, this reactor type should be operated with a temperature high enough to maintain a reaction rate that is approximately equal to the feed rate. A semi-batch reactor has similar disadvantages as the batch reactor. However, when comparing these reactors, a semi-batch reactor seems to be the safer solution. Other disadvantages of the batch and semi-batch reactors are dependent on the particular type of reaction, such as whether the reaction is in parallel or in series.

2.1.2 Thermal runaway

The statistics presented in the first chapter showed that a considerable number of accidents in the industry can be attributed to runaway reactions. A basic understanding of a runaway reaction can be drawn from the thermal explosion theory according to Semenov **[18]**. This theory deals with the competition between the heat generation from an exothermic reaction and its removal from the reaction mass to, for instance, a cooling jacket or a cooling coil, or both. A thermal runaway may be initiated if the heat generated by a chemical reaction exceeds the heat removed by the cooling systems (c.f. **Figure 2.1)**.

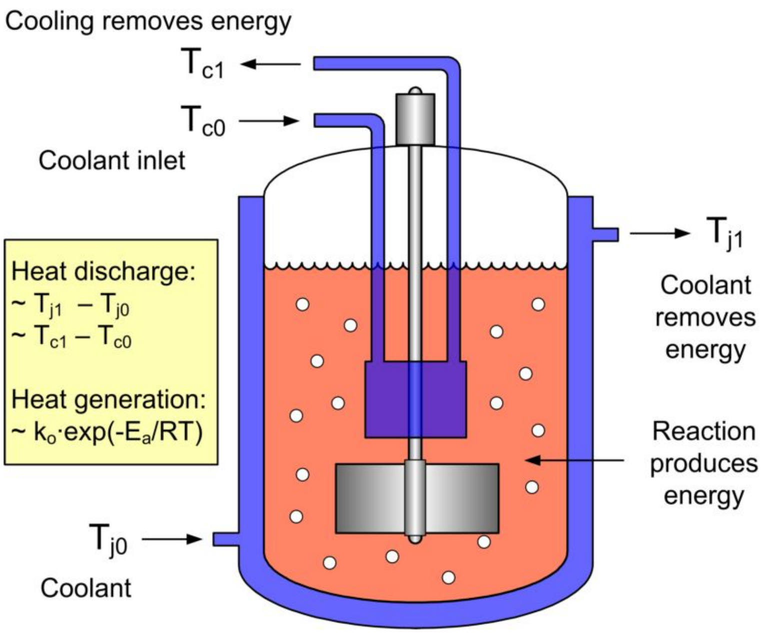

Figure 2.1 *Batch reactor with cooling jacket and cooling coil*

The surplus heat increases the temperature of the reactor contents, which causes the reaction rate to increase. Subsequently, the exothermal reaction produces heat at a much faster rate. Consequently, a runaway reaction occurs along the following lines: as the temperature rises, the rate of heat loss to the cooling system increases linearly with the temperature (Newtonian cooling) and is given by:

$$\dot{Q} = -U \cdot A \cdot (T - T_C) \tag{2.1}$$

where: $\dot{Q}_c$ = heat flow (rate) removed by the cooling system [W]; U = overall heat transfer coefficient [W/(m^2 K)]; A= surface area for heat transfer [m^2]; T = reactor contents temperature [K]; T_c = coolant temperature [K].

In contrast, the rate of heat generation increases exponentially with the temperature according to the Arrhenius equation:

$$k = k_0 \cdot \exp(-E_a / R \cdot T) \tag{2.2}$$

where: k is the reaction rate constant or velocity constant; k_0 is the pre-exponential factor or frequency factor (its dimension depends on the order of the reaction kinetics); E_a is the activation energy [J/mol]; R is the universal gas constant [8.314 J/mol K], and T is the absolute temperature in [K].

Therefore, thermal runaway starts slowly but then tends to accelerate, until eventually it can lead to a thermal explosion. Possible operational regimes are shown in **Figure 2.2**, where the ideal cooling regime is marked by A. Regime B is only metastable and at C the reaction cannot be controlled any more.

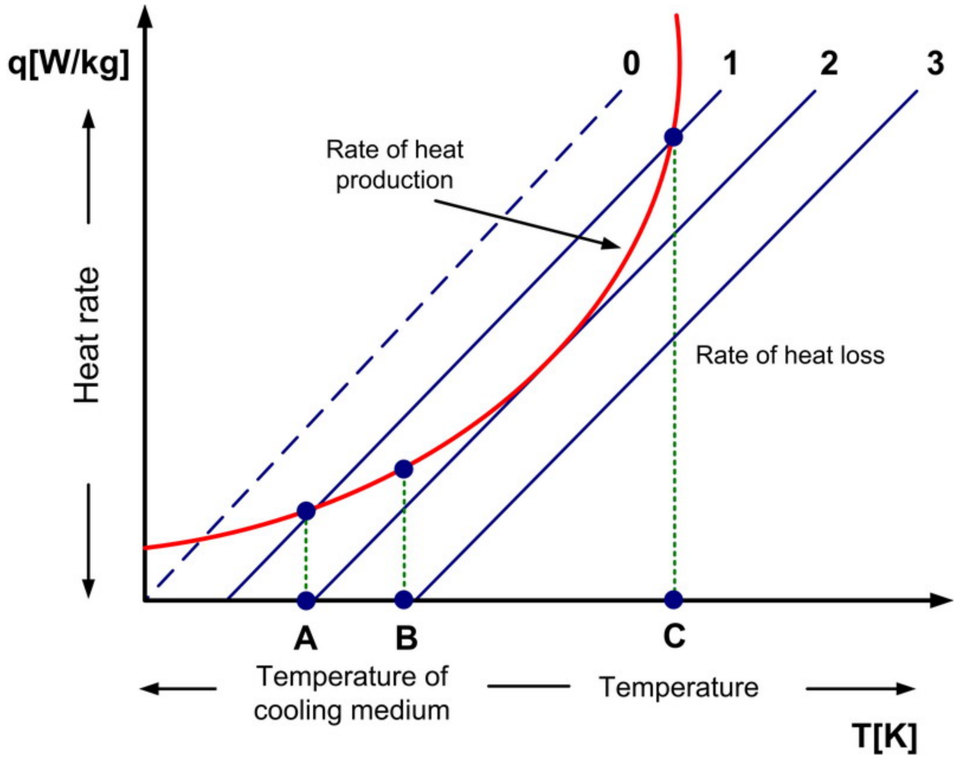

Figure 2.2 *Self heat rate and heat transfer of a reaction with cooling*

In the first case, the rate of heat loss (line 1) intersects the exponential heat production curve at two points (A and C). Point A represents a stable situation which can be illustrated by comparing it to an increase in temperature at point B. At this point, the rate of heat loss due to cooling is greater than the rate of heat production and the temperature will return to point A. Point C is unstable and any slight increase in temperature will cause an increase in the rate of heat production not matched by the rate of heat loss and a runaway will occur. At this moment an emergency cooling system, could be of help (line 0). It should cool down the reactor contents and consequently stop the runaway reaction.

Line 2 represents the situation where the heat production is equal to heat removal. A slight decrease in temperature will cause the reaction to fade away, whilst a slight increase in temperature will produce a runaway. The equilibrium is not stable. Both cases are highly probable.

Line 3 represents situation where the rate of heat loss is always less than the rate of heat production and a runaway reaction will always occur.

Additionally, since the rate of heat loss is dependent on the heat transfer coefficient and area, a decrease in either will lead to a decrease in the slope of the cooling line and a reduction in the rate of heat loss from the reactor.

A further very important problem is that the amount of heat produced increases proportionally to the volume of the reactor content (cube term - [m^3]), whereas the cooling capacity varies in proportion to the surface area of the cooling system (square term - [m^2]). This is very important for scaling up, where a small increase in volume may lead to an inadequate design of the cooling system and therefore the possibility of a loss of control.

The quantities which have to be considered in specifying safe operating conditions for batch reactors are therefore:

- heat of reaction,
- heat capacity,
- rate of heat production,
- rate of heat removal,
- heat transfer properties of the reaction mixture,
- dependence of reaction kinetics on reactant concentration,
- factors which affect accumulation,
- temperature range in which decomposition occurs,
- amount and rate of gas evolution, and
- effects of mischarging, impurities.

Furthermore, all of this data can be affected by many factors. One of them is the degree of mixing which affects at least two of the quantities measured, the reaction rate and heat transfer behaviour. Where the reaction mass is well mixed, the temperature in the whole reactor is uniform and the integral reaction rate increases. Where thermal control is lost (the worst case being a total loss of the cooling system), exothermic reaction will occur without a significant heat loss i.e. almost adiabatically, see **Figure 2.3.** The temperature will rise until the maximum available has been reached. This can be calculated from:

$$T_{max} = T_s + \Delta T_{ad} \tag{2.3}$$

where T_s is the starting temperature of the reaction and ΔT_{ad} is the adiabatic temperature increase, which can be calculated from:

$$\Delta T_{ad} = \frac{(-\Delta H_R) \cdot c_{A0}}{(-\nu_A) \cdot \rho \cdot c_p} \tag{2.4}$$

where ΔH_R is the enthalpy of reaction in [kJ/kg], c_{A0} is the concentration of limiting reactant in [kmol/m^3], c_p is the specific heat capacity in [kJ/kmol K], ν_A is the stoichiometric coefficient, ρ is the density of the reactor contents in [kg/m^3].

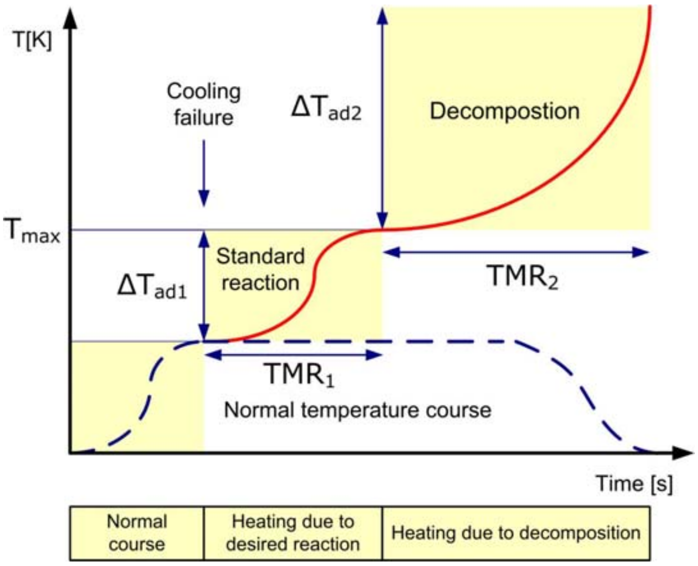

Figure 2.3 *Thermal scenario for a runaway in a batch reactor from* ***[19]***

The adiabatic temperature rise is one of three characteristic numbers. It provides direct information of the exothermic effect of the chemical reaction and gives the maximum increase in temperature that can be attained. This increase takes place when the substance or reacting mixture decomposes (ΔT_{ad2}) or fully reacts under adiabatic conditions (ΔT_{ad1}) and, in consequence, leads to thermal runaway (desired reaction). Medium and high temperature increases **(Table 2.1)** must be assessed with regard to the probability of an accident occurring. In general, the batch reactor can be applied only for reactions with a low adiabatic temperature increase. For exothermic reactions not satisfying this requirement, a semi-batch reactor is used.

Table 2.1 *Classification of the adiabatic temperature increase* ***[16]***

Adiabatic temperature increase ΔT_{ad} (K)	**Impact**
> 200	High
$50 < \Delta T_{ad} < 200$	Medium
< 50	Low (the boiling point is not exceeded)

Due to the fact that T_{max} is reached quickly when cooling fails, the time left for intervention is more or less determined by the dynamics of the reaction. The time to thermal explosion is referred to as the time of the maximum rate under adiabatic conditions (TMR); it is also called induction time. This parameter depends on the reaction kinetics as well as the temperature at which it is evaluated and can be predicted using the following formula **[17]**:

$$\mathrm{TMR_{ad}} = \frac{c_p \cdot R \cdot T_0^{\,2}}{\dot{q}_0 \cdot E_a} \tag{2.5}$$

where c_p is the specific heat capacity in [J/kg K], R is the universal gas constant [8.314 J/mol K], E_a is the activation energy in [J/mol], T_0 is the start temperature in [K], and $\dot{q}_0$ is the corresponding heat release rate in [W/kg].

Time to maximum rate TMR_2 corresponds to T_{max} or the temperature reached at the end of standard reaction and TMR_1 corresponds to T_s, or the temperature at the start of reaction (c.f. **Figure 2.3**). The latter gives an indication of the time available for triggering emergency measures once the deviation has occurred.

The second characteristic number is the Damkoehler (Da) number. This number represents the ratio of the characteristic reaction time to the kinetic time constant of the reaction. Therefore it is a measure for the reaction time. The characteristic times are specific for each reactor type. For ideal reactors, it is the reaction time for the batch reactor, the feed time for semi-batch reactor and the mean residence time for both continuous types. The value of the Damkoehler number can vary from 0.01 for slow batch reactors to 100 and more for semi-batch processes or continuous manufacturing with high mean residence times.

$$\mathrm{Da_I} = \frac{(-\nu_A) \cdot r_0 \cdot t_{ch}}{c_{A0}} \tag{2.6}$$

The third characteristic number, the modified Stanton (St) number, combines all relevant parameters which determine the cooling capacity of the reactor. This number ranges from 3 for plant scale reactors to 20 for laboratory equipment.

$$St = \frac{U \cdot A \cdot t_{ch}}{c_p \cdot V \cdot \rho} \tag{2.7}$$

Large batch reactors without cooling systems are working near to adiabatic conditions unless a trip system, based on emergency cooling is activated. When considering decomposition reactions, it is important to understand that decomposition can occur at all temperatures. As the temperature is reduced, the decomposition slows down but does not stop.

The consequence of such a reaction is often a loss of the process containment. Depending on material properties, process conditions and reactor design, this can lead to hazardous situations such as fires, explosions, missiles or toxic hazards. If the materials are toxic, this can pose a hazard to both operators and off-site personnel. Furthermore, if the materials are environmentally damaging, this can also pose a widespread environmental hazard.

2.1.3 Reactive systems

The main hazard posed by exothermal reactions is associated with the generation of heat and consequent pressure built-up due to degassing or evaporation. This pressure can be developed in three different ways:

- The exothermic reaction increases the temperature of reactor content to above its boiling point at nominal operating conditions causing the pressure to rise – **vapour pressure system**.
- Gas production as a result of an exothermic reaction can cause pressurisation – **gassy system.**
- The exothermic reaction produces both gas and vapour – **hybrid (gas + vapour) system.**

These categories have a significant meaning in terms of either pressure relief systems or passive trip systems and are reviewed below. **Figure 2.4** shows the characteristic temperature changes for the three systems, according to the Health and Safety Executive (HSE).

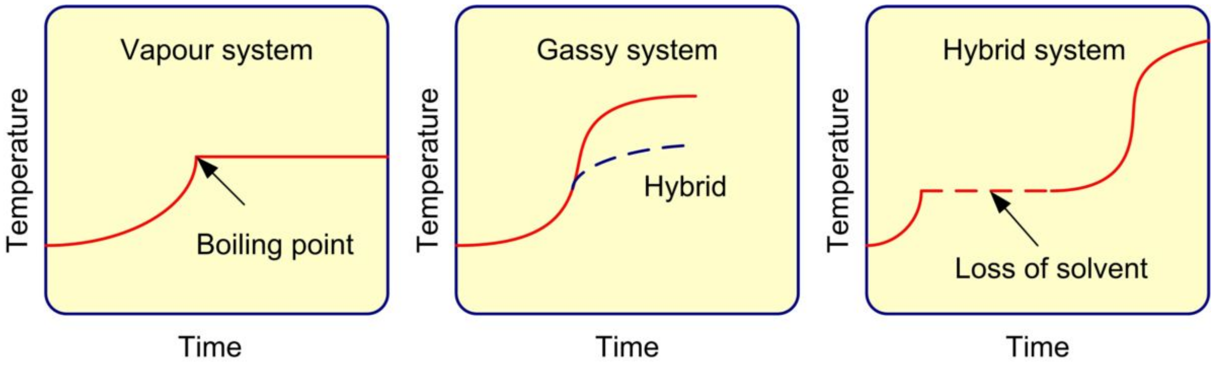

Figure 2.4 *Runaway reaction categories – vapour, gassy and hybrid*

Vapour pressure system

In this type of reaction, there is no permanent gas generation. The pressure increases as the temperature of the reaction mixture increases due to the progress of chemical conversion (evaporation of the reactants, products and/or inert solvent). In that case, it is not the peak rate but the rate of temperature rise that determines the design parameters of the relief system such as the diameter of a relief valve. Boiling point is thus attained before potential gaseous decomposition (i.e. the heat of reaction is removed by the latent heat of vaporization). After relief system activation, the reaction is tempered by vaporization and, additionally, in the case of the passive trip system, by internal cooling coils **(Figure 2.5, Case A and B)**. The pressure inside the reactor is equal to the vapour or atmospheric pressure. Such vapour pressure systems can be approximated by the well known Clausius-Clapeyron relationship or Antoine's equation **(Equation 2.5)**.

$$\ln P_v = A + \frac{B}{T} \tag{2.8}$$

where P_v is vapour pressure, A and B are constants and T is the absolute temperature. An ideal example of this reaction type is the esterification of methanol and acetic anhydride.

Gassy system

The pressure increase is caused by the production of non-condensable gassy products. These gases may be produced by the decomposition of reactants. The exothermic heat release is retained in the reaction mass because the cooling potential of volatile materials is not available. Due to that, both the maximum temperature and maximum gas generation rate can be attained during system activation. Gaseous decomposition reactions occur without tempering and the total pressure in the reactor is equal to the gas pressure. The main parameter for dimensioning relief devices is the maximum rate of pressure rise. For the pressure of non-condensable, ideal gas law is approximately obeyed.

$$P_g = \frac{m_g \cdot R \cdot T}{M_{wg} \cdot V_g} \tag{2.9}$$

where P_g is gas pressure, m_g is mass of gas, M_{wg} is molecular mass of gas, Vg is volume of gas, R is ideal gas constant and T is the absolute temperature.

A survey within the chemical industry shows that gassy reaction systems predominate due to established processes such as nitrations, diazotizations, sulphonations, and many other reaction types. Very few vapour pressure systems can be identified that also generate a permanent gas – hybrid reaction. A good example of gassy systems is the decomposition reaction of ammonium peroxydisulphate.

Hybrid (gas + vapour) system

This system is a combination of the two previous systems. The pressure increase is caused by the production of gassy non-condensable products as well as by evaporation. Gaseous decomposition reaction occurs before boiling and the reaction is still tempered by vapour stripping. The total pressure in the system is the summation of the vapour pressure and gas partial pressure **(Equation 2.7)** and is called Dalton's law of partial pressure.

$$P_{tot} = P_v + P_g \tag{2.10}$$

where P_{tot} is total pressure, P_v is vapour pressure and P_g is gas pressure.

In this case, the principal parameters in determining the venting diameter are the rates of temperature and pressure rise. A tempered reaction contains volatile fluid that vaporizes during the relieving process through the venting system. This vaporization removes energy which is evolved by exothermic reaction and tempers a rise in the temperature rate. An example of this type of reaction systems is the decomposition of hydrogen peroxide.

In order to prove the feasibility of the design of the passive trip system, its effectiveness for these different reaction systems will be demonstrated. The choice of the system has considerable influence on the activation and functioning of any pressure relief system, including the passive trip system. For instance, in the case of some hybrid and all vapour pressure reaction, the relief system activation will temper the reaction by losing enough heat through vaporization in order to maintain temperature and pressure at a safe level **(Figure 2.5, Case A)**. In the case of passive trip activation, there is an additional cooling effect which enables one not only to maintain a constant temperature and pressure in the system but also to reduce them and bring the reaction to a stand-still **(Figure 2.5, Case B)**.

In hybrid systems that do not temper and gassy systems, there is negligible or sometimes no control of temperature due to pressure relief. The control of temperature in the reactor could be achieved by the use of emergency cooling, such as the passive trip system **(Figure 2.5, Case B)**. In the case of relief venting, the temperature continues to rise and the rate of reaction continues to increase even after the relief device has opened and the pressure is held constant **(Figure 2.5, Case C)**. In such systems, the maximum rate of material discharge the relief vent devices have to safely cope with is determined by the maximum rate of the runaway reaction.

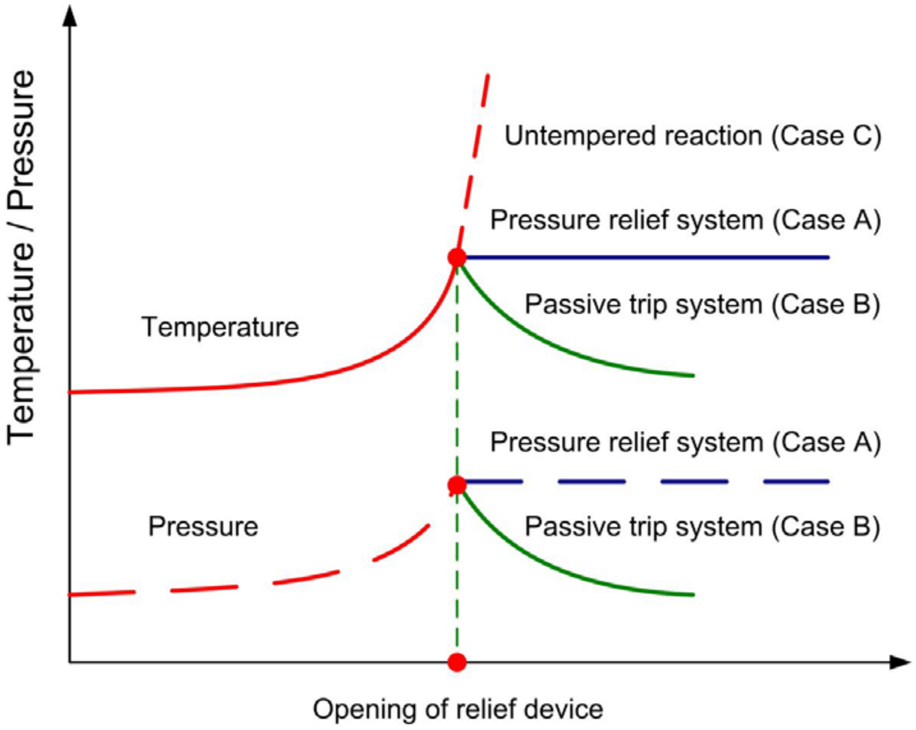

Figure 2.5 *Diagram of tempering of runaway reaction*

There are a lot of vent sizing methods, such as Richter and Turner **[22]**, and these have provided methods for sizing batch reactor relief systems. A large number of them were also elaborated by Fauske **[23]** and DIERS **[24]**. There is a wide range of theoretical work on vent sizing, which, unfortunately, to a large extent lacks experimental verification, if two-phase flow is involved. Therefore, the application of safety factors in the design of vent areas is necessary.

The knowledge of chemical reactor systems is of paramount importance for the protection strategy to be adopted. On this basis, it can be decided whether the system is gassy, vapour or hybrid and tempered or untempered **(Figure 2.6)**. This information is one of the main factors for safety system design.

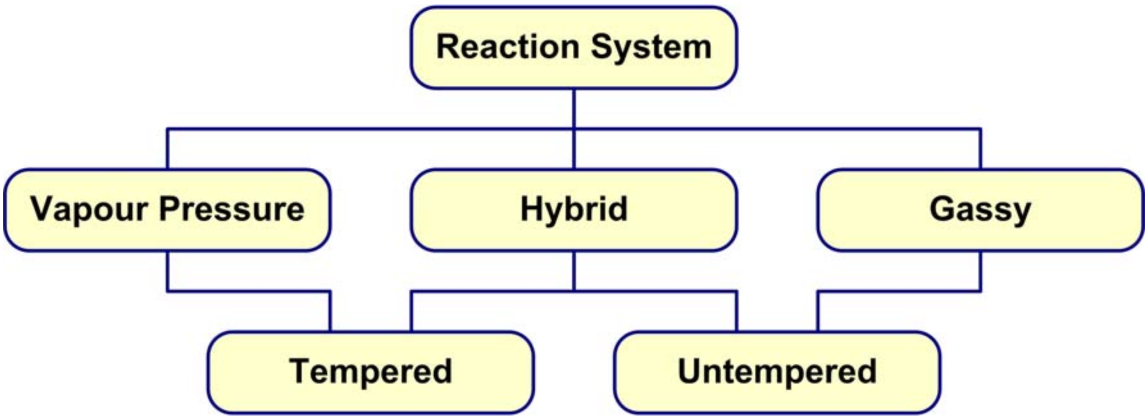

Figure 2.6 *Reactivity categories from **[24]***

2.2 Batch and semi-batch reactors safety development

The process industry has made major improvements in safety performance over the last half century. A huge progress can be observed in prevention measures, but much more obvious improvements have been made to protection systems such as critical alarms, automatic safety instrumented systems (SIS), emergency relief systems, active quenching (inhibition), emergency dumping (drown out), and manual intervention. However, there is still a need for additional levels of protection and hence increases in the quality and amount of safeguards are clearly justified. In order to improve the reliability of the safety systems, fault tree analyses are appropriate and recommended. Therefore a reliability analysis of frequently used trip systems for chemical batch reactors was performed, see **Chapter 3**.

2.2.1 Layers of protection

Chemical batch reactors with hazardous processes and materials should be designed with multiple layers of protection **[25]**. These should protect people, the environment, and property from the hazard associated with the chemical processes. While we can design more reliable equipment and motivate people to reduce mistakes, we can never completely avoid failures. The famous statement made by Trevor Kletz that “an accident recurs” **[26]** is always true in spite of all possible measures taken in the chemical process industry. Therefore, it is very important to use multiple layers of protection in order to reduce risk **(Figure 2.7, Case 1)**. Nevertheless, there is always a small probability that all layers of protection will fail simultaneously and an accident will occur. For instance, the deterioration of a management system, maintenance of equipment or training will reduce the reliability of protection layers and consequently the risk will be increased **(Figure 2.7, Case 2)**. Here the passive strategy can be helpful. In the case of a properly designed passive system, it could reduce the risk **(Figure 2.7, Case 3)**. Furthermore, an inherently safer design **[27]** can reduce the need for layers of protection. If the magnitude of the potential consequence of an accident could be reduced sufficiently, it may eliminate the need for protection layers entirely **(Figure 2.7, Case 4)**.

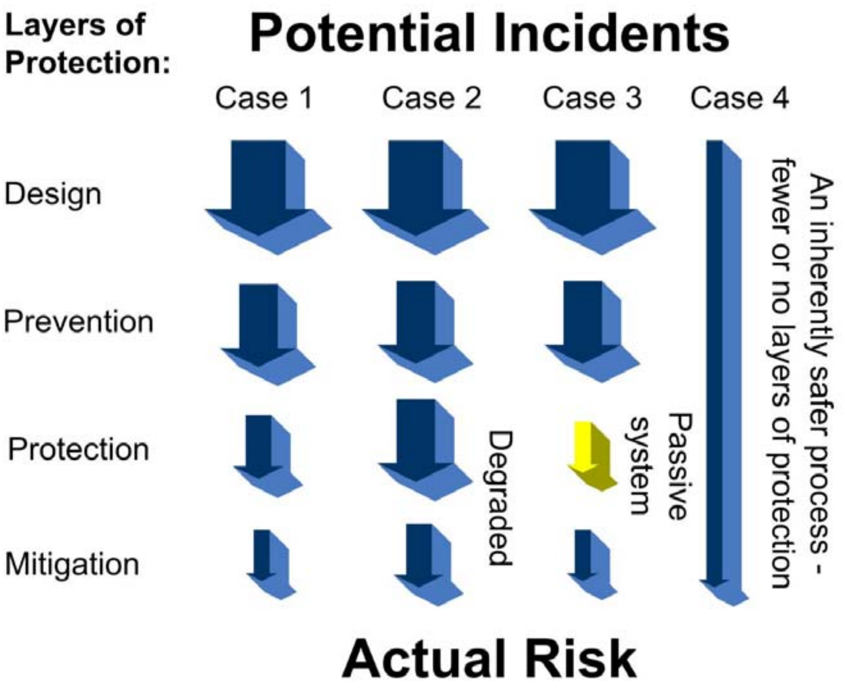

Figure 2.7 *Layers of protection for chemical processes*

In scientific literature concerning regulations and standards, we can find many similar terms for safety systems, such as layer of protection, safety barrier, safety function etc. It is therefore practical to distinguish between the safety functions and safety systems that carry out these functions. There are many ways in which safety systems may be classified. One of them is classification according to their functions: prevention, protection and mitigation (LOPA). Safety systems can also be classified by several criteria, some of them being active versus passive or physical / technical versus human / operational. One of the methods used to classify safety systems is shown in **Figure 2.8**.

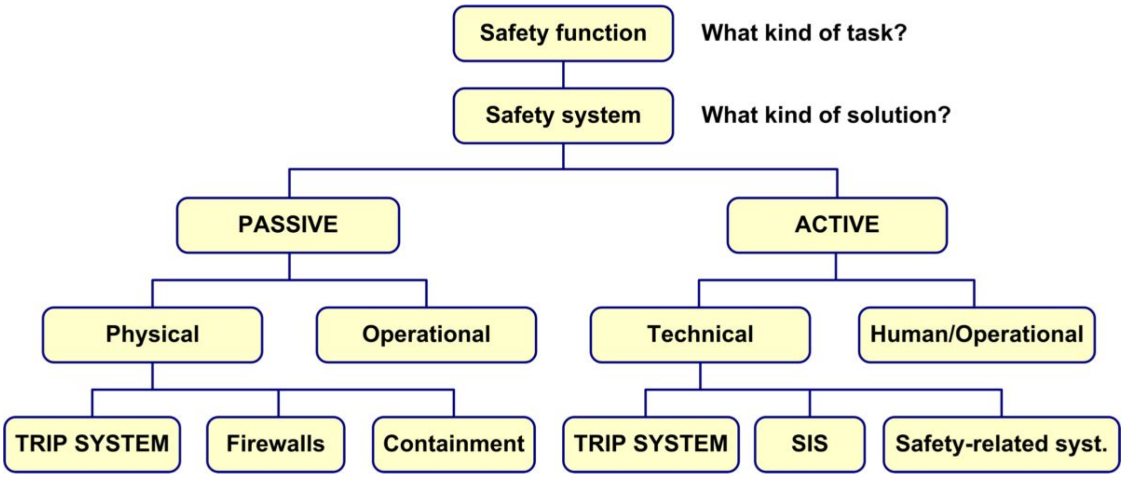

Figure 2.8 *Classification of safety systems*

Safety strategies applied to a chemical process can be placed into four main categories:

- **Inherent:** eliminate or reduce the hazard by using less hazardous materials and conditions, or naturally occurring safety directed phenomena, such as self stabilisation.
- **Passive:** control or minimization of the hazard using design features that reduce either the frequency or consequence of incidents using no active components.
- **Active:** incident control or mitigation using controls, safety interlocks, or emergency shutdown systems in order to detect hazards and thus enable appropriate action to be taken.
- **Procedural:** operating procedures, emergency response, administrative checks and other management systems that are used to prevent incidents, to detect incidents in time, or to reduce the magnitude of damage resulting from an incident.

Safety strategies belonging to passive and inherent categories are generally considered to be the most robust and reliable. They depend on the physical and chemical properties of the system, rather than on the successful operation of equipment, safety devices or procedures. Inherent and passive safety concepts are often confused but, in reality, they are quite different. For instance, the inherent solution to the batch reactor will either eliminate the hazard or reduce the potential magnitude of an incident associated with the hazard sufficiently so that it cannot cause significant damage. Passive safety strategies do not necessarily eliminate the hazard, but prevent damage and injury by eliminating or reducing exposure of people to the hazardous conditions without the active functioning of any components. The passive trip system is a good example **[28]**. In the case of an operating cooling system failure and possible reaction runaway, it performs its function of preventing damage and injuries simply by being present. There is no need for any active devices or person to perform their function.

As mentioned before, in order to achieve the safe operation of chemical reactors that process exothermic reactions, a combination of four layers of protection is required **[25]**, **(Table 2.2)**.

Table 2.2 *Layers of protection for process industry* **[26]**

Layer of protection	Classification of safeguards	Functional requirements
Design - Layer 1	1. Chemical process design	Normal operation with control of operational design conditions (considering start-up and shut-down).
Prevention - Layer 2	1. Process control systems 2. Alarm systems 3. Operator response	To stop the runaway reaction from occurring and to reduce the frequency of its possible scenario.
Protection - Layer 3	1. Critical alarms 2. Automatic SIS 3. Emergency relief systems Active quenching (inhibition) Emergency dumping (drown out) 6. Manual intervention **7. Passive systems**	To slow down development of runaway scenario and reduce the probability and severity of its consequences.
Mitigation - Layer 4	1. Active protection systems Community emergency response	To limit and mitigate on and off-site consequences of reactants release.

Figure 2.9 presents the functioning of layers of protection and interactions between them **[30]**.

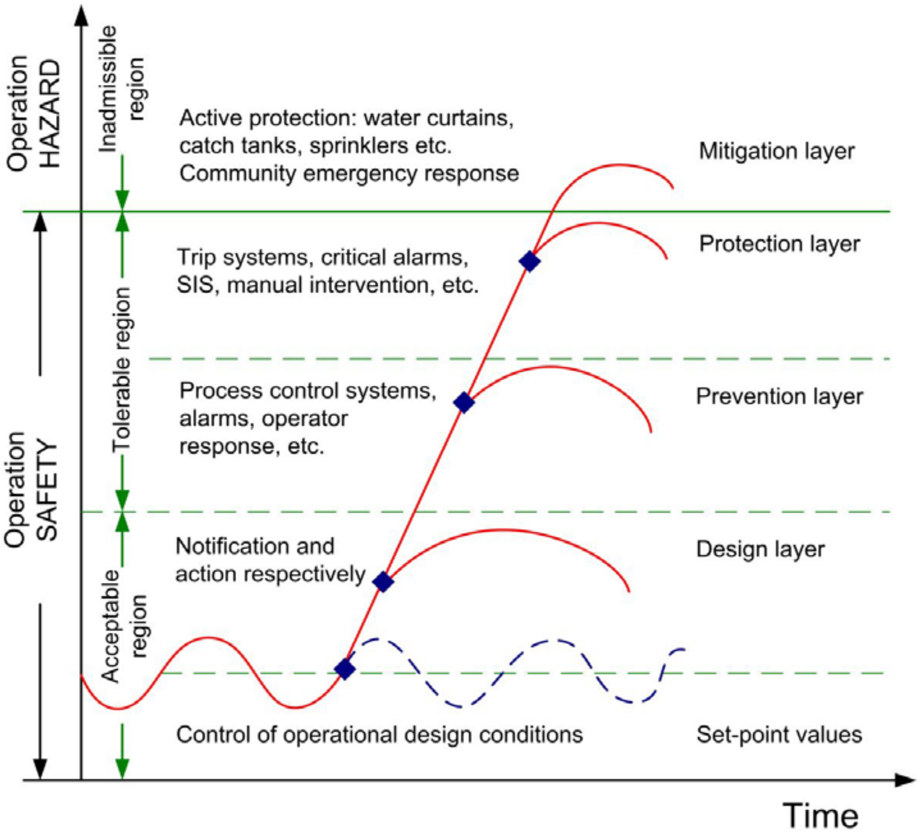

Figure 2.9 *Layers of protection for process industry*

The first design layer is the most important one and should always be implemented at the earliest possible stage, such as during the selection of processes, plant layout, facility siting etc. If operational design conditions are held constant and there are no deviations in the process, there will be no need to employ prevention, protection and mitigation layers.

As was presented in the table, the purpose of prevention is to reduce the probability of accidental releases. The ideal result of a successful prevention effort is that a runaway reaction does not occur. In reality, prevention can succeed only in reducing the probability of a runaway to a reasonable minimum. The main role of prevention is the choice of the right operating conditions such as:

- the degree of mixing (mixing rate),
- the capacity of the cooling system,
- the temperature of the coolant,
- the dosing rates of the reactant(s) etc.

Automatic control systems also play a vital role, and these include the use of an independent hardwired alarm and trip system based on Safety Integrity Level analysis **[31]**.

When preventive measures fail, then a second function of control concerns protection from reaction runaway. Protection means that the runaway onset must be detected, contained and neutralized or suppressed before the reactor content escapes into the environment. The protection can be considered as inartistic or extrinsic. Some examples of this are:

- critical alarms,
- Safety Instrumented Systems (SIS) which use realized functions of shut down or emergency shutdown of reactor and physical protection systems like diking, flares and scrubbers,
- relief systems (rupture discs, relief valves),
- active quenching (inhibition) **[12]**,
- emergency dumping (drown out),
- passive systems (passive trip system).

If the reactor protection fails or is deficient, the system will release chemicals in the form of vapour or gas into the environment. The consequences of such a release can be reduced by the effective activation of the fourth layer of protection and this mitigation equipment can reduce the concentration of released chemicals to below a harmful level. For chemical reactors, there are technical systems used such as water sprays, steam curtains, barriers for dispersion and different alarms and communication systems.

Although the prevention of accidents clearly has the highest priority, prevention alone is not enough as major accidents do happen. The most efficient method of dealing with a major accident is the protection layer with its most commonly used technique: emergency relief venting. Unfortunately, this method is not so reliable due to the risk connected with inadequate vent sizing and failures **[32, 33, 34]**. There are many other methods for reactor protection, but all of them require external energy sources, which can always fail. Passive trip systems were also mentioned as a final safeguard. These methods are not so commonly used but they have a big potential to overcome some of the inherent disadvantages of active systems. The passive trip system investigated here is patented **[28]** and may be used in batch, semi-batch, and possibly in continuous processes using cascades of reactors. It can also be applicable to the storage of self-reactive substances in devices either barrels. The exact description of the system will be given in **Chapter 4**.

The main hazard posed by exothermal reactions is pressure generation and the consequent loss of the process containment (fires, missiles, explosions, toxic hazards). Furthermore, there are other important effects such as loss of productivity, loss of market share, environmental clean-up costs, costs of rebuilding the damaged plant and, as a further consequence, a negative perception of the company. Any of the above mentioned consequences would be reason enough to investigate new methods for the protection of chemical reactors.

2.2.2 Passive and inherent safety aspects

Both inherent and passive strategies relate to the basic process technology and design and should always be considered and implemented in the design life cycle. The main intention of these strategies is to eliminate hazards or at least to minimize their degree. Even after all the above efforts, the remaining or residual spectrum of various risks will still remain together with the question “how safe is safe enough?” **[27]**.

As far as possible, chemical reactors should be designed to be inherently safe. This is the first step in safety, and techniques such as the use of low-pressure designs and low capacities are obviously the most desirable route to follow wherever possible. According to the Chemical Process Safety Centre, there are four important strategies for inherent safety: minimize, substitute, moderate and simplify **[35]**.

Inherently safer plants in reactor systems equipped with passive systems

Kletz **[27]** and later Englund **[36]** have both given details of inherently safer plants involving reactors. They emphasized the importance of friendly plants. When designing reactors for safety, the following should be considered:

1. A very good understanding of reaction kinetics (safe conditions for operation of exothermic reaction).
2. The replacement of batch reactors with continuous (reduction of resident mass of hazardous substances) and, if possible, easier temperature control, although this is only feasible for large quantities.
3. The production and consumption of hazardous materials in situ as hazardous shipping and storing should be avoided.
4. The use of high purity materials that can reduce the amount of waste materials.
5. Designing the reactor for the highest possible pressure in order that thermal explosion and release to environment can be avoided.
6. Limiting the total possible charge to a batch reactor by using a feed tank of limited capacity.
7. Limiting the maximum or minimum temperature attainable in the reactor by properly designed operating or passive cooling systems.
8. Reducing and simplifying the inventory by tubular reactors application (no moving parts).

9. Mass transfer is often the rate-limiting step in gas-liquid reaction. Novel reactor designs that increase mass transfer can reduce reactor size and improve yields.

Metrics for passive and inherent safety

How can we measure passive and inherent safety? Such questions must be answered in order to perceive the significance of these strategies. It is evident that the development of new technologies could be more easily obtained when the costs and potential benefits of a new technology (including economics, environment, and safety) can be measured. However, this is not a simple task as chemical processes usually involve multiple hazards and, therefore, the tools for measuring inherent and passive safety should be available. The engineers are beginning to understand and recognize the value of these strategies.

One of the most practical methods used for passive and inherent safety identification is the analysis of the potential consequences of accidents. For instance, the consequences of a thermal explosion in the reactor might take into consideration the safety distances from the reactor that results from a fire, explosion or toxic release. This analysis helps us to understand the benefits of inherent and passive strategies and highlights where improvements can be made.

Another method to measure inherent and passive safety is risk indices. They usually measure a single aspect and it is necessary to use several indices to understand what characterises the overall process. The most popular are the Dow Fire and Explosion Index and the Dow Chemical Exposure Index **[33, 34]**. Unfortunately, they only focus on the inherent safety and only on such areas as fires, explosions and toxic hazards.

Some work has already been done on the development of an overall inherent safety index (Loughborough University, VTT in Finland), **[35]**. These indices take more phenomena into account, such as inventory, flammability, explosiveness, toxicity, temperature and pressure).

Passive and active layers of protection - process intensification

The term "process intensification" was developed to describe a kind of thinking about the process unit operations **[36].** This approach led to the prospect of much smaller chemical plants that would be significantly cheaper and safer than existing ones. While a smaller process may not eliminate all hazards, it can frequently have a positive influence on making effective passive mitigation measures for the process more feasible and cost effective. Blast-resistant enclosures, bunkers or dikes can be considered as a common example of passive mitigation systems. In the case, when an explosion occurs, the process equipment within the enclosures can be damaged, but nobody will be injured and the environment and other property will be safe. Such a type of protection systems may be practical for small equipment but is very expensive for large equipment. Additionally, the enclosure not only has to be much bigger but also much stronger for bigger tanks because of the magnitude of the explosion potential. In this instance, two different approaches to the problem have to be taken into account:

- **Safety** – very efficient protection systems of the plants, but more expensive.
- **Economy** – less efficient protection systems, but not so expensive.

Here the question arises: what is more important? Both these factors have an important influence on the environment, human beings and chemical plants. However, the application of some protective systems such as emergency quenching, which is used to protect against a runaway reaction, can be restricted. If the temperature in the reactor exceeds a threshold pressure, the content of the reactor will be rapidly discharged to another tank containing an inhibitor. Such a system can easily be applied to a small reactor but for a bigger one it could be questionable. A small tank can be emptied into the quench tank in a few seconds and the reaction will be inhibited but, in the case of a large reactor, emptying can take many minutes and it may be not possible to prevent runaway in time.

For a passive cooling system, there are no technical restrictions. The emergency cooling system can be easily adjusted to every reacting system and, if every device and parameters are correctly dimensioned, the runaway reaction can be prevented. Hence, the only barrier will be the cost of the emergency cooling tank.

Batch reactors are often protected from overpressure by active devices such as relief valves. These devices open at a set pressure and allow gas and liquid to escape in order to limit the pressure. A few years ago, relief devices would simply discharge into the atmosphere. Nowadays such situation is unacceptable and the reactor content must be discharged to a collection-and-treatment system, unless totally innocuous, which is rare.

Chemical process safety has to be taken into account together with the criteria for process and plant design. During chemical plant design and operation, there are a lot of requirements which have to be fulfilled. These are related to the following groups:

- **Workers** (long-term health, employment etc.)
- **Owners** (costs, capital investment, etc.)
- **Customers** (cost, quality of products, etc.)
- **Neighbours** (environmental impact, health and safety)
- **Government** (regulations and laws)

In order to meet all of them, the engineer must optimize the design of the plant. Process intensification is likely to play a very important role in the future since all modern prevention and protection strategies are more efficient and cheaper for smaller plants. Process plants will then be more safe, more economically competitive and more environmental friendly.

2.2.3 Trip systems

In general, trip systems are used to protect the equipment or plant against certain hazardous situations by shutting the whole or part of it down if particular parameters go outside the specified limits. For the protection of batch reactors against exothermic runaway reactions, there are many old and few new practical solutions available. These include, in the first place, the most common emergency relief venting, then physical containment, secondary emergency cooling, quenching or reaction inhibition, emergency dumping and the concept of the passive trip system. For these systems a reliability analysis was made. The new passive concept for batch reactor protection was compared with the most popular trip systems. The results of this analysis are discussed in the next chapter.

All of these systems have many limitations and the possible application of any one of them depends mainly on the reaction type and thus a brief description and characterization of these techniques is presented below.

a) Pressure relief system

The venting of the reactor contents is one of the most frequently used safety measures against pressure increase. The main effect of pressure relief is temperature stabilisation due to the heat removed by evaporation (vapour reactions). However, this system has some problems:

- restrictions due to environmental protection (release of chemical substances to the atmosphere) and containment of the ejected material needed,
- the difficulty of finding the size of the relief valve (two-phase flow and starting pressure for venting, and
- the fact that it is ineffective for low vapour pressure systems.

The adequate function of a particular vent also depends upon many factors:

- the accuracy of the kinetic data,
- the accuracy of physical properties of the reactants,
- the accuracy of the design of the safety device, and
- the accuracy in determining the initial conditions.

b) Inhibition trip system

The use of small quantities of active quenching agents that are capable of stopping runaway reactions is called inhibition **[12]**. An inhibitor or diluent is usually placed in an emergency tank and it is pressurized to allow for fast injection, when required. The type of inhibitor or diluent depends generally on the reacting system under investigation. The addition of such an inhibitor modifies the reaction rate expression and thus the reaction slows down. The polymerization of vinyl compounds is a good example of this. After the detection of a runaway reaction, an inhibitor such as tertiary butyl catechol is added. It can stop reactions by removing free radicals, which propagate runaway reaction. This method seems to be very effective but there are still many limitations, such as:

- the lack of inhibiting species for many exothermal reactions (e.g. decomposition),
- non effective injection systems,
- problems with effective detection of abnormal behaviour,
- non effective mixing of agents in the reactor (hot spots),
- the high price of inhibitors,
- the necessity of laboratory studies,
- the lack of sufficient free volume in the reactor.

c) Emergency Dumping System

The dumping of the reactor contents is a very old method. The reaction mixture is dumped into a vessel which contains water or other cold diluents. Sometimes the dumping system is combined with the inhibition system and the inhibitor is added to the dumping vessel. This method requires a good understanding of the reacting system and technical installation to perform dumping. The dumping system has some disadvantages, such as the loss of products and expensive equipment but, conversely, it also has many advantages:

- the reactor is not subjected to pressure,
- there is no discharge to the environment,
- the mixture can be disposed of later and expensive reactants can potentially be recovered.

d) Passive trip system

A passive trip system can be approximated as a combination of pressure relief system and emergency cooling system. Therefore, it can be applied to all reactive systems and successfully reduce both temperature through vaporization and by cooling coils, and pressure by relief. It has many advantages in comparison to other trip systems which will be proved in this work. The detailed description of passive trip system can be found in **Chapters 3** and **4**.

Summary of trip systems

There are many different ways in which trip systems function. Each of them can influence one or several parameters that play important roles in batch reactor protection. The main parameters which can have a substantial influence on the successful operation of a trip system are part of the reaction rate equation (Arrhenius), the heat transfer equation for emergency cooling and the Clausius-Clapeyron equation (assuming ideal gas). These are presented in **Table 2.3**:

Table 2.3 *The influence of trip systems activation on crucial process parameters*

Equation / Trip System	**Pressure relief**	**Inhibition**	**Dumping**	**Passive**
$\text{Rate}(k) = k_0 \cdot \exp(-E_a / R \cdot T)$	2) **T** ↓	1) **k_0** ↓ Reaction slows down	2) **T** ↓ 3) **k** ↓	2) **T** ↓ 3) **k** ↓
$\text{Cooling}(\dot{Q}_c) = -U \cdot A \cdot (T - T_c)$	-----------	------------	1) **T** ↓	1) **T** ↓
$\text{Pressure}(P) = (n \cdot R \cdot T) / V$	1) **P** ↓ 2) **T** ↓	2) **T, P** stabilisation	1) **P** ↓	1) **P** ↓

where k_0 is the reaction rate constant (pre-exponential factor), T the temperature, E_a the activation energy, R the gas constant, U overall heat transfer coefficient, A the surface area available for heat transfer, T_c coolant temperature, n the number of moles of gas and V is the volume of gas or vapour.

The reduction of process parameters presented in the table is highlighted with an arrow. The numbers preceding the process parameters from 1 to 3 indicate the sequence of interactions. The same number preceding two different parameters means simultaneity.

Temperature and pressure reduction are classified in the first place for both dumping and a passive system. In the case of a pressure relief system, the pressure relief plays the main role. The reduction of pre-exponential factors is for these systems in the last position, contrary to the inhibition system, where reduction of this parameter (k_0) is of great importance. The injection of an inhibitor slows down the reaction and stabilizes both temperature and pressure.

3

The reliability study of different trip systems

3.1 Trip systems under investigation

Trip systems belong to the principal types of protective systems. They are used for shutting down plants or parts of them e.g. reactors, if a hazard condition is detected. The choice of the trip system and necessity of using it depends on design philosophy. The most common types of trip systems include flow, pressure, temperature, level or limit switches. The chemical reactors used for exothermic reactions are, amongst others, equipped with trip systems. As mentioned before, these may, for example, be based on the fast injection of a reaction inhibitor or the fast dumping of the reactor contents into a knock-out tank. The measures enumerated are active, in that they require a number of components (e.g. sensors, pumps, valves etc.) to function in order to be successful. The availability of trip systems, i.e. their probability of functioning on demand, largely depends on their degree of redundancy. However, there is a limitation to increasing their availability by raising their degree of redundancy. This is imposed by the possibility of the occurrence of common cause failures **[41]**. Nevertheless, the availability of a trip system may be elevated further if, instead of a higher redundancy, a passive system is used **[42]**. In order to demonstrate this, four different trip systems, among them a passive one, are described and analyzed using fault tree analysis **[43]**. In performing the comparison, only the trip systems as such are considered. Possible additional safety measures either engineered or by operator intervention, which is often provided for, are disregarded in order to create a sound basis for comparison. Potential failures of instrument air, normally counteracted by fail-safe positions of the affected components, are not treated either. No consideration is given to the expected frequencies of demand of the systems, since only the trip function is of interest here.

3.1.1 Emergency Dumping System

The emergency dumping system presented in **Figure 3.1** belongs to a nitration reactor for producing hexogen **[44, 45]**. The reactor temperature is measured by sensor TE2. In case of a temperature rise above the set-point of temperature switch TSH2, the hexamine supply to the reactor is cut by stopping motor M1. Should the temperature increase not be contained by this measure and the set-point of temperature switch TSHH2 be reached, the reactor contents is discharged via discharge valve DV1 into the knock-out tank. In order to achieve this, the solenoid valve SV1 activating the discharge valve DV1 as well as that itself have to open and the stirrer motor M2 has to start. Weekly inspections by the operator ensure that the knock-out tank is always filled.

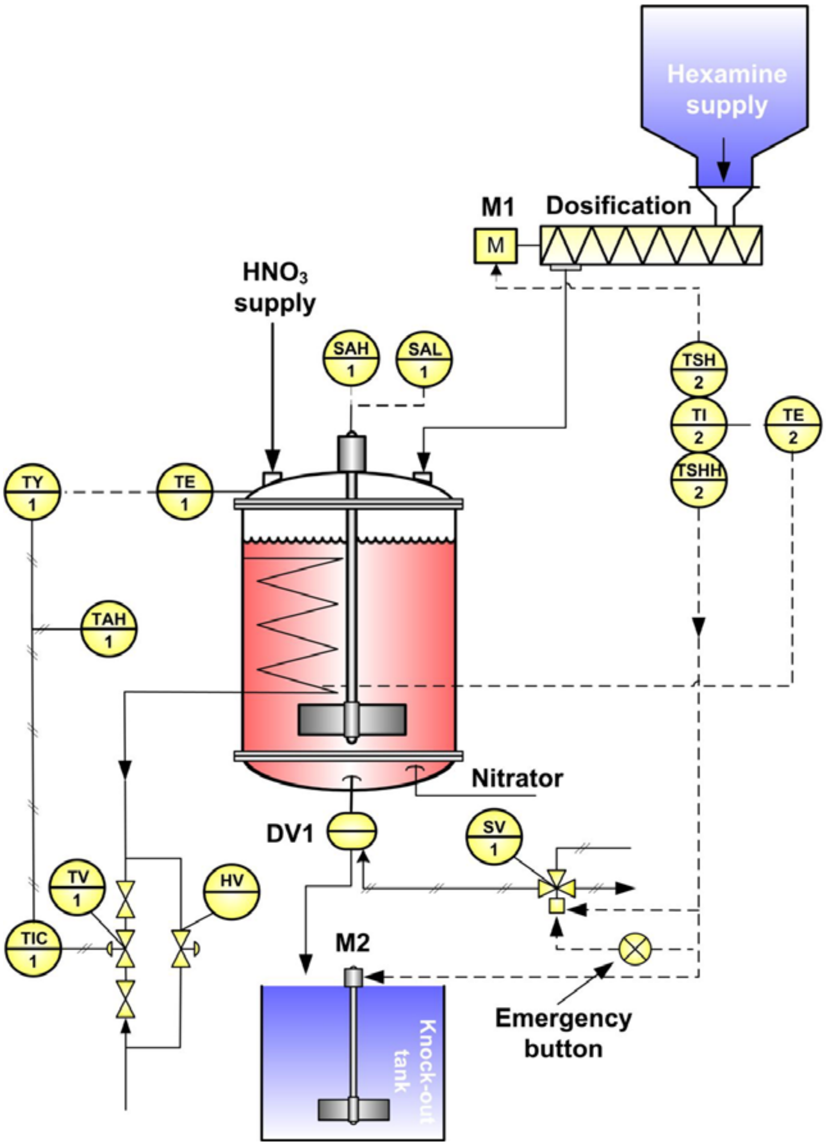

Figure 3.1 *Emergency dumping system*

3.1.2 Inhibition trip system

A reactor with an inhibition trip system is shown in **Figure 3.2**. It is equipped with an injector vessel containing the inhibitor. In case the temperature is too high, temperature switch TSH opens valve AV 5 and the inhibitor is injected into the reactor by a pressure blanket inside the injector vessel. Redundantly, pressure switch P1 opens valve AV 2 due to the pressure increase associated with a rising temperature and the reactor contents is relieved into the catch tank. Sufficient pressure in the injector vessel is ensured by weekly inspections of the pressure sensor P4 and the corresponding operator action, if required.

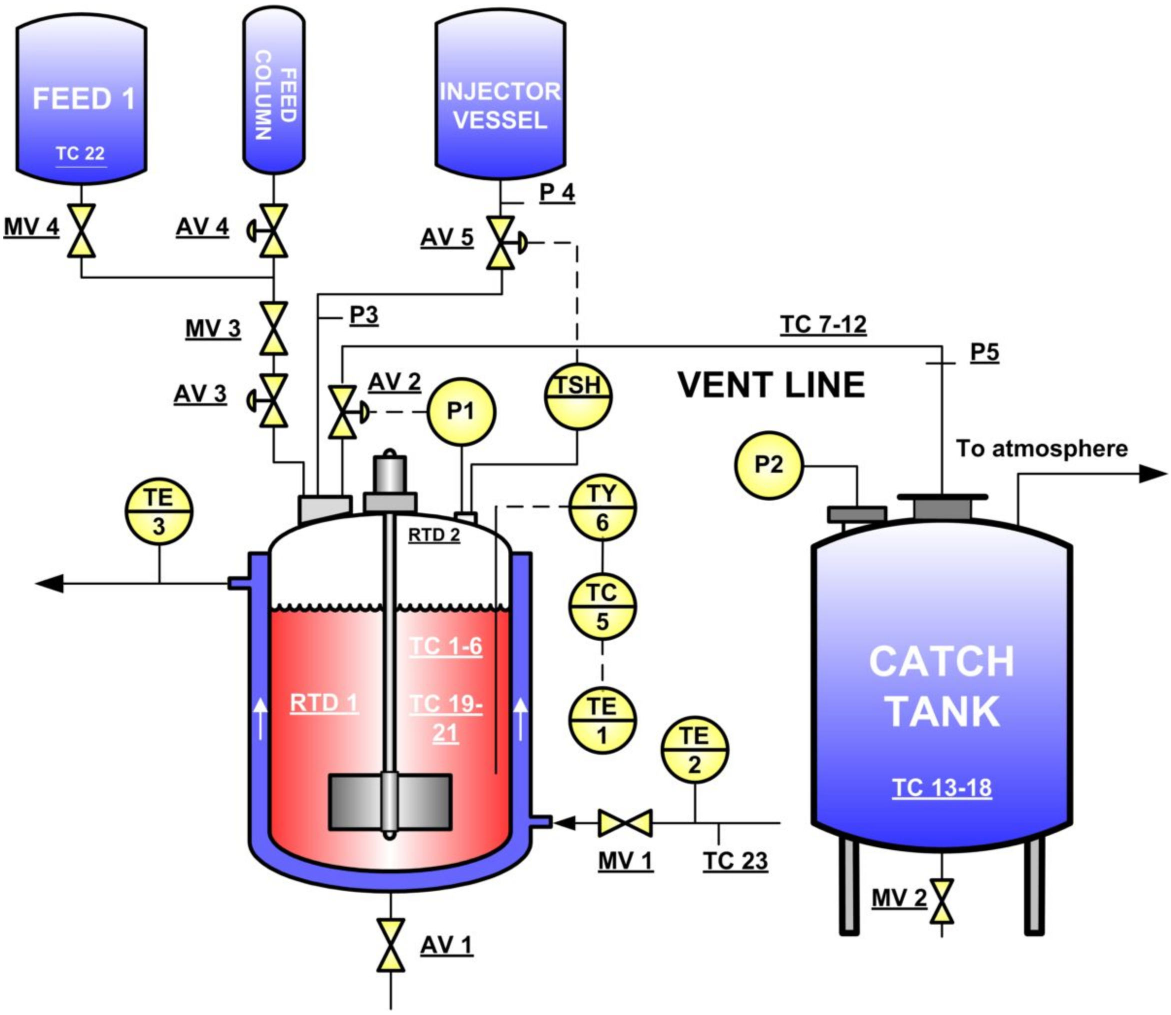

Figure 3.2 *Inhibition trip system – HSE pilot plant diagram* **[12]**

3.1.3 Pressure relief system

A standard reactor used in the chemical industry for synthesis reactions is shown in **Figure 3.3**. Reactants A and B are introduced in controlled quantities into the reactor. A catalyst is continuously supplied and both the temperature and the pressure increases are measured. The protective trip system consists of the safety valve SV1 and the relief system made up of pressure switch PSHH1, relay I, and pneumatic valve AV1. The "safe place" for relief is considered to be a knock-out tank equal to that in **Figure 3.1**.

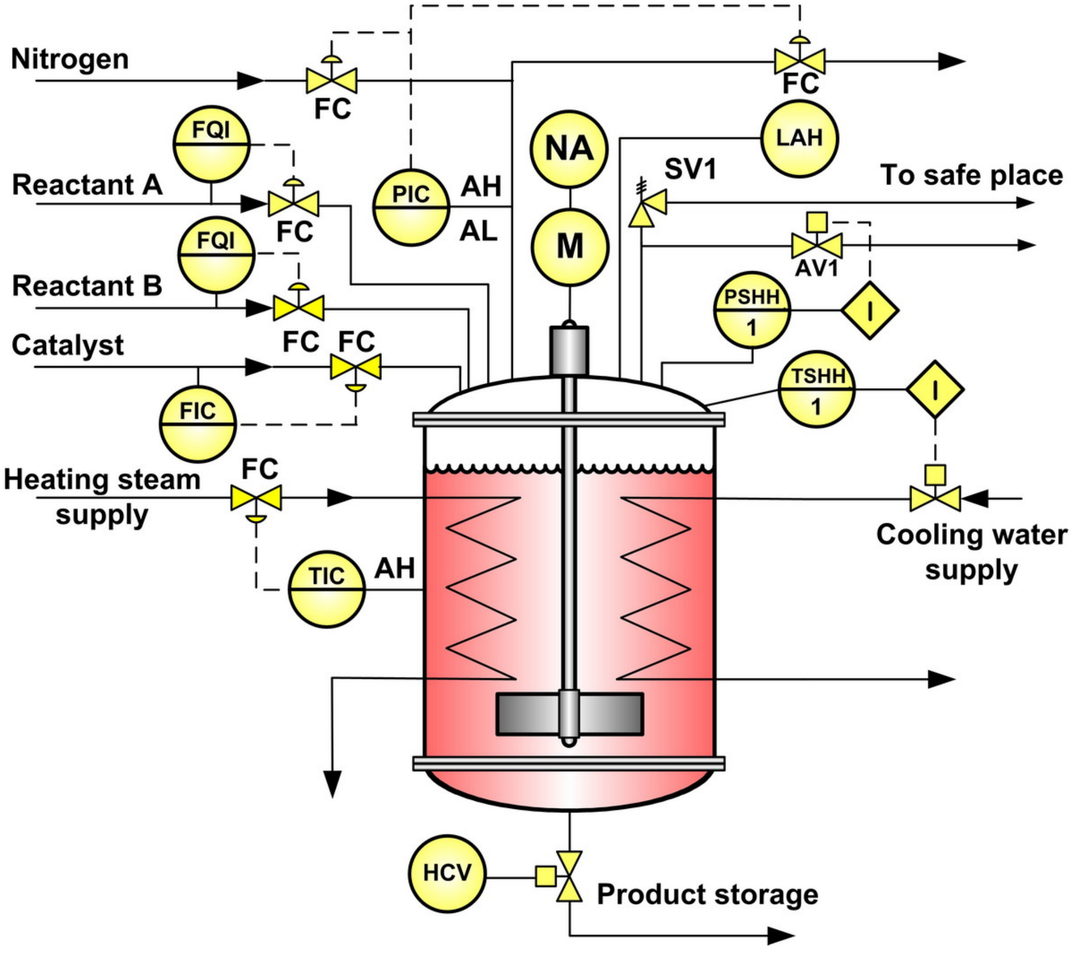

Figure 3.3 *Pressure relief system*

3.1.4 Passive trip system

A passive trip system **[28, 42]** is shown in **Figure 3.4**. It provides emergency cooling and works as follows. The pressure increase which accompanies a runaway reaction is used for driving the coolant from the emergency coolant supply tank (ECST) through the coil inside the reactor. During normal reactor operation, the coolant is separated from the reactor contents and the cooling coil by two bursting discs. If the pressure increases above the set-point of bursting disc BD 1 this will rupture and the pressure is relieved by opening the pipe to the emergency coolant supply tank. Rupture disc BD 2 then bursts as well, thus allowing the coolant to be forced through the cooling coil. The reactor contents is cooled down and the reaction is stopped. With appropriate dimensioning this occurs before the substances escape from the system. Hence, a receiving tank for vented substances becomes unnecessary. There is a sufficient margin for the onset pressure of relief so that the system even works if the rupture discs open below or above their set points, which is their most frequent failure mode.

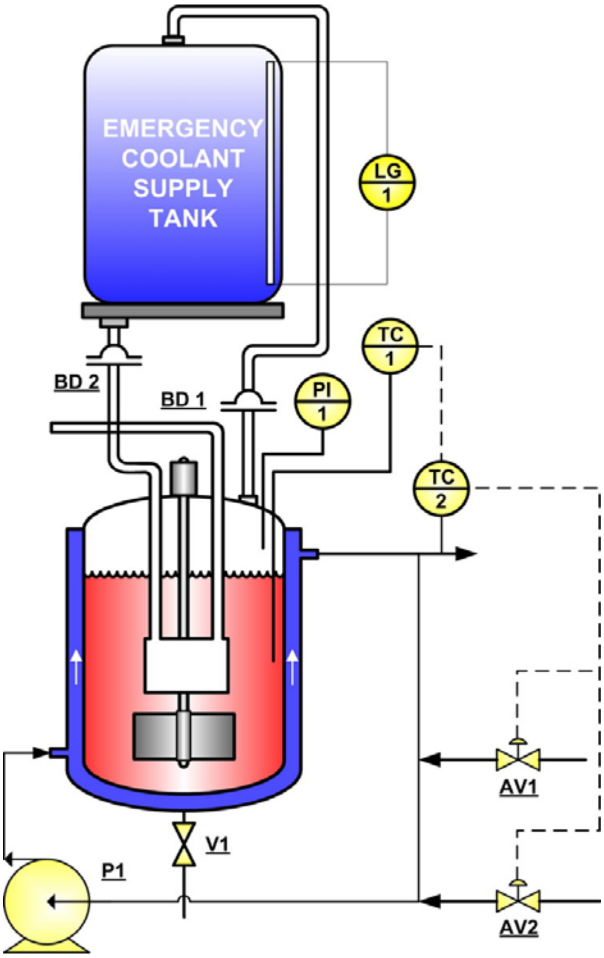

Figure 3.4 *Passive trip system*

3.2 Fault tree analysis

Fault tree analysis **[43]** was used to investigate presented systems. Their unavailabilities, i.e. their probabilities of not functioning if demanded, were calculated using a program written in FORTRAN. The fault trees for the top event “Failure of protective trip system” for each of the systems are shown in **Figures 3.5-3.8**.

Emergency dumping system

The corresponding fault tree is shown in **Figure 3.5**. The following assumptions were made in its elaboration: the trip is only successful if the hexamine supply is cut in addition to successful dumping, dumping is only successful if the stirrer motor M2 starts and thus provides sufficient initial mixing with the contents of the knock-out tank (although continuous operation of M2 is not deemed necessary), the relay represents the signal processing which converts the demand for opening into the activation signal for solenoid valve SV1.

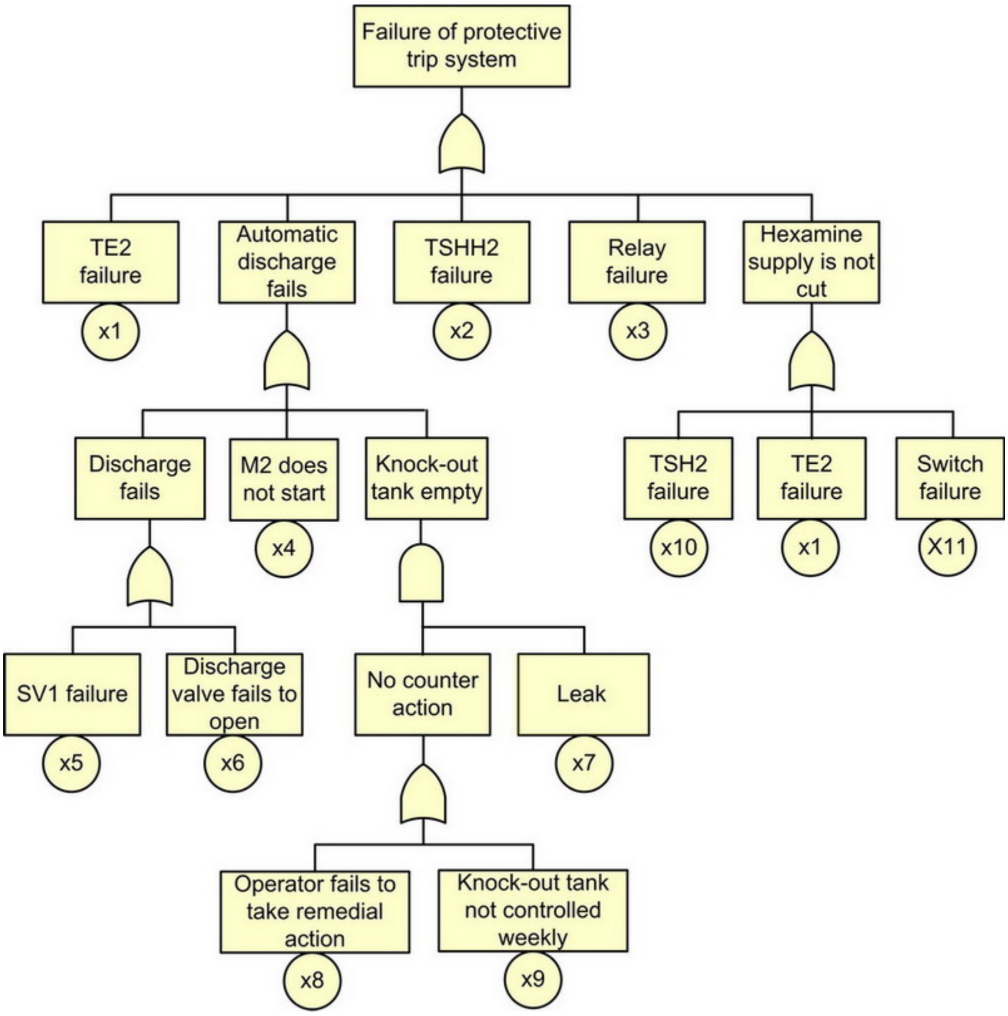

Figure 3.5 *Fault tree for the emergency dumping system*

Inhibition trip system

The fault tree for the inhibition trip system is given in **Figure 3.6**. In the following analysis, the assumption was made that either successful inhibition or relief into the catch tank will bring about a safe state. The system is redundant.

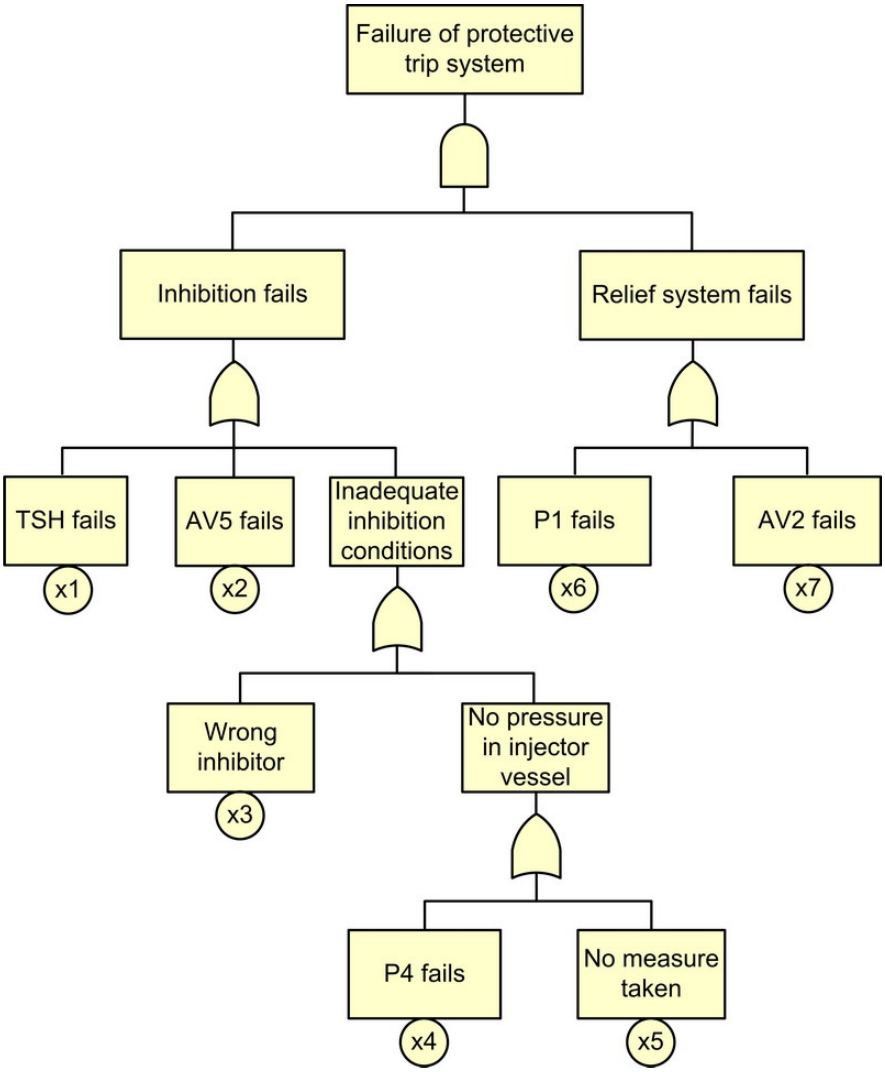

Figure 3.6 *Fault tree for the inhibition trip system*

Pressure relief system

The fault tree for the pressure relief system is presented in **Figure 3.7**. The following assumptions were made: relief is only successful if the stirrer motor M2 starts and thus provides sufficient initial mixing with the contents of the knock-out tank (although the continuous operation of M2 is not deemed necessary), the relay represents the signal processing which converts the demand for opening into the activation signal for valve AV1.

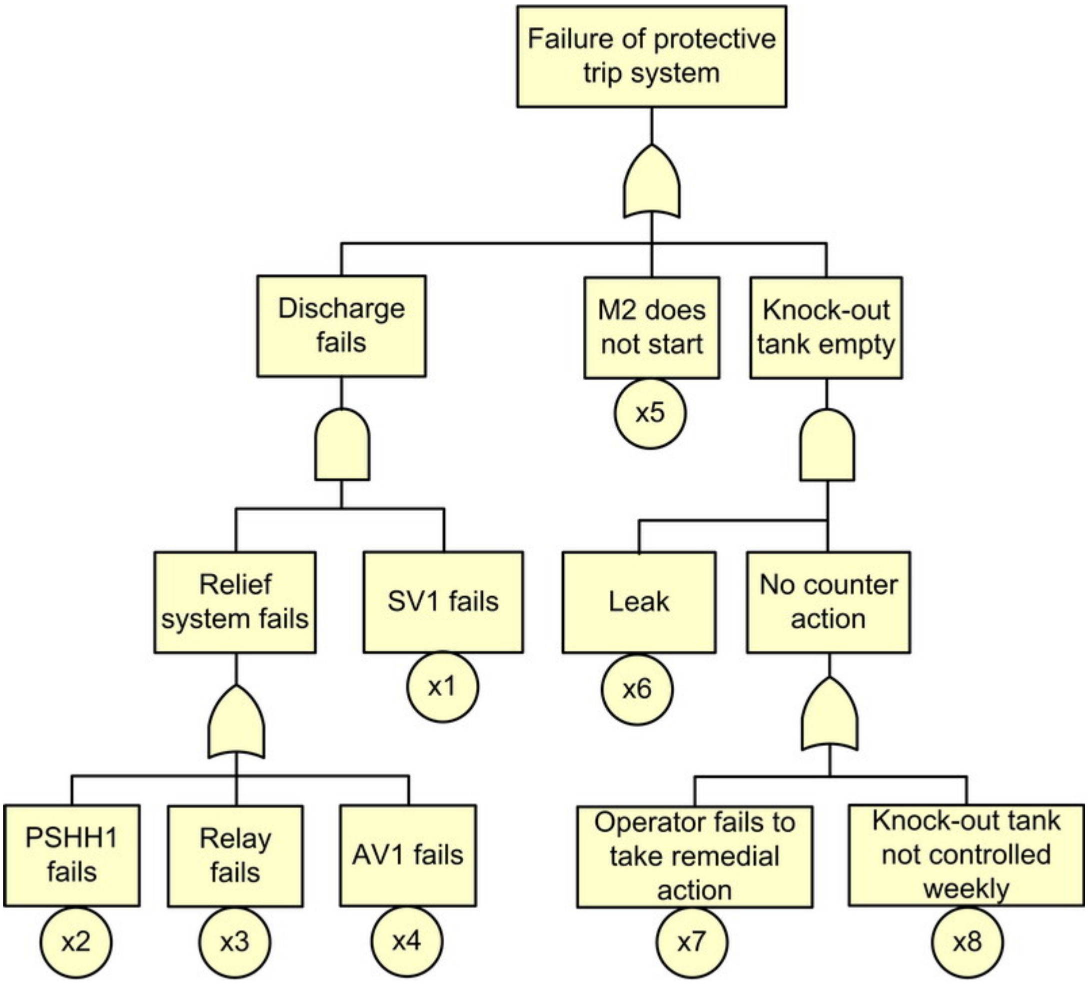

Figure 3.7 *Fault tree for the pressure relief system*

Passive trip system

The fault tree for the passive trip system is shown in **Figure 3.8**. The following assumptions were made in its elaboration: the trip function is only successful if both bursting discs open and the emergency cooling supply tank is filled with the coolant. The lack of coolant can be caused by a leak and failure of level control LG1 or operator can fail to take action.

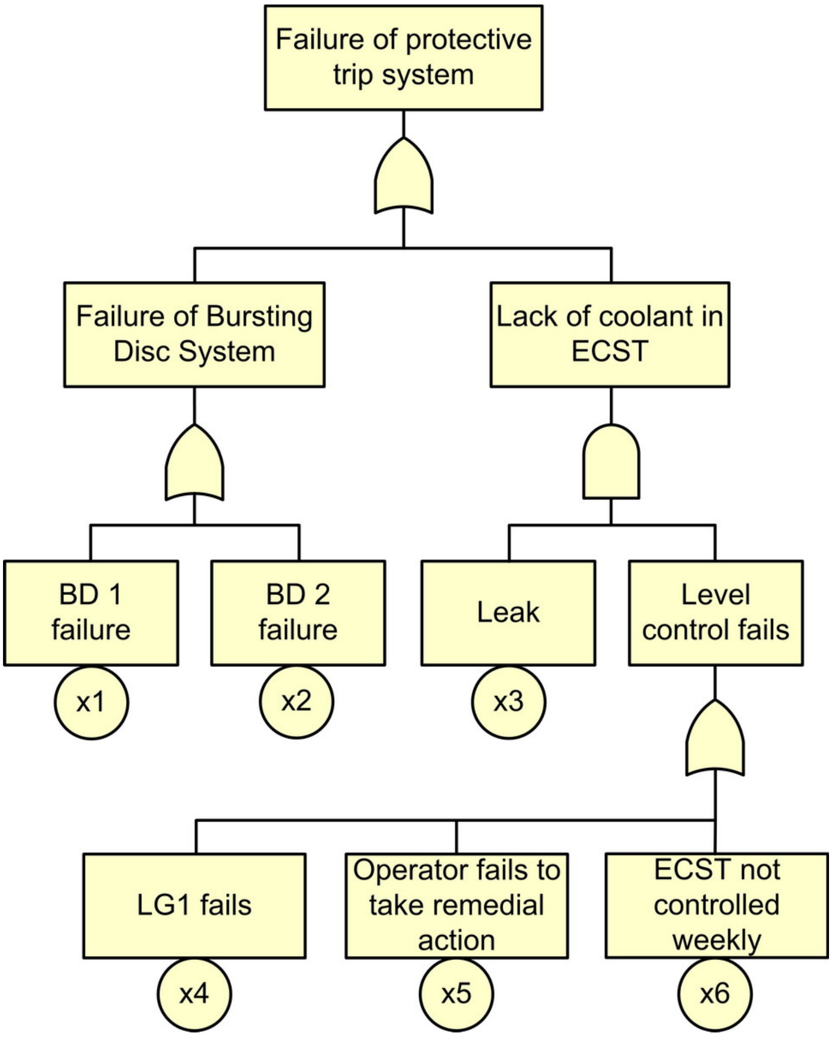

Figure 3.8 *Fault tree for the passive trip system*

3.3 Reliability study and test intervals

The reliability data and test or inspection intervals for the evaluation of the fault trees are given in **Table 3.1**. The former are based on **[46]** and the following investigation. Both the median and the 90% uncertainty factor K_{95} for a log-normal distribution of the failure rates are provided **[47]**. Probabilities for human error in operator actions are represented by rectangular distributions **[48]** whose width is assessed on the basis of information contained in **[35]**. The values for test and inspection intervals were derived from indications by plant owners.

Table 3.1 *Reliability data and test/inspection intervals*

[a] upper probability limit, [b] lower probability limit, [c] taken as 0.1% of the safety valve failure rate, replacement after 2 years

System	Fault tree variable	Type of component/failure mode	Median of failure rate λ in 10^{-6}/hr	Uncertain-ty factor K_{95}	Test/in-spection interval θ in hrs
Emergency dumping system	x_1	temperature sensor	27.8	1.5	720
	x_2	temperature switch	60.4	1.5	720
	x_3	relay	0.30	3.0	720
	x_4	stirrer motor does not start	1.00	3.3	168
	x_5	solenoid valve	1.92	8.4	168
	x_6	discharge valve fails to open	17.8	2.2	168
	x_7	leak (includes all modes of fluid loss)	1.50	8.4	168
	x_8	operator fails to take remedial action	0.05[a]	0.002[b]	
	x_9	knock-out tank not controlled weekly	0.05[a]	0.002[b]	
	x_{10}	temperature switch	60.4	1.5	720
	x_{11}	remotely operated switch	9.2	1.7	168
Inhibition trip system	x_1	temperature sensor	27.8	1.5	17500
	x_2	relief valve does not open	17.8	2.2	17500
	x_3	wrong inhibitor	0.05[a]	0.002[b]	
	x_4	pressure switch	0.93	8.4	720
	x_5	no measure taken	0.05[a]	0.002[b]	
	x_6	pressure switch	0.93	8.4	720
	x_7	relief valve does not open	17.8	2.2	168
Pressure relief system	x_1	safety valve does not open	1.13	8.4	17500
	x_2	pressure switch	0.93	8.4	720
	x_3	relay	0.30	3.0	720
	x_4	relief valve does not open	17.8	2.2	168
	x_5	stirrer motor does not start	1.00	3.3	168
	x_6	leak (includes all modes of fluid loss)	1.5	8.4	168
	x_7	operator fails to take remedial	0.05[a]	0.002[b]	

		action			
	x_8	knock-out tank not controlled weekly	0.05[a]	0.002[b]	
Passive trip system	x_1	bursting disc does not open	0.001	8.4	17500
	x_2	bursting does not open	0.001	8.4	17500
	x_3	leak (includes all modes of fluid loss)	1.5	8.4	168
	x_4	level gauge	6.7	1.7	168
	x_5	operator fails to take remedial action	0.05[a]	0.002[b]	
	x_6	emergency coolant supply tank not controlled weekly	0.05[a]	0.002[b]	

The time averaged unavailabilities for components subject to periodical tests or inspections every θ hours were calculated under the assumption that the duration of functional tests is negligible and that repair, if needed, restores the original properties of the component ("as good as new hypothesis"). This leads to:

$$\bar{u} = 1 + \frac{1}{\lambda \cdot \theta} \cdot \left(e^{-\lambda \cdot \theta} - 1\right) \tag{3.1}$$

where $\bar{u}$ is the time averaged unavailability, λ the failure rate in 1/hr, and θ the time interval between functional tests in hrs.

3.4 Results and conclusions

Characteristic distribution parameters for the time averaged unavailabilities obtained for the four trip systems are given in **Table 3.2**.

Table 3.2 *Time averaged unavailabilities of the investigated systems*

System	**5th percentile**	**Expected value**	**95th percentile**
Emergency dumping system	$4.5 \cdot 10^{-2}$	$5.7 \cdot 10^{-2}$	$7.1 \cdot 10^{-2}$
Inhibition trip system	$3.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$2.1 \cdot 10^{-3}$
Pressure relief system	$4.8 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$	$4.1 \cdot 10^{-4}$
Passive trip system	$9.9 \cdot 10^{-6}$	$6.1 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$

The analysis of the underlying minimal cut sets **[38]** shows the following:

Emergency dumping system

Key contributors to the unavailability are the failures of instruments TE2, TSH2, and TSHH2. An introduction of redundant instrumentation would reduce the expected value of the time averaged unavailability of the system to $2.1 \cdot 10^{-3}$.

Inhibition system

The most important contributions to its unavailability stem from the minimal cut sets x_1x_6, x_1x_7 and x_2x_6, x_2x_7. Since the system is already redundant, the gain from further redundancies would most likely be limited by common cause failures **[41]**.

Pressure relief system

The main contribution to its unavailability stems from the failure of the stirring motor to start. Since the system is already redundant and highly available, the reduction by further redundancies would most likely be limited by common cause failures **[41]**.

Passive trip system

Its unavailability is dominated by the failure probability of the bursting discs, which, based on the chosen failure rate and period between replacements, amounts to $2.3 \cdot 10^{-5}$, a value which lies within the range indicated in **[35]**. If the lower limit given there, i.e. a failure probability of 10^{-5}, were used, the time averaged unavailability of the passive system would drop to $3.5 \cdot 10^{-5}$. The frequency of testing/inspection plays a subordinate role for unavailability. Placing the outlet of the emergency coolant tank above the upper coolant level would make rupture disc BD2 superfluous and hence further reduce the time averaged unavailability to $1.8 \cdot 10^{-5}$.

The choice of the test or inspection intervals has a considerable impact on the unavailabilities of the active trip systems. Hence, it is difficult to make a fair comparison. However, in practice, the operator is not free in his choice. For example, the inhibitor and corresponding systems cannot be tested too frequently, because a test involves the loss of the inhibiting substance. The times selected represent a compromise between frequent tests, which lower the unavailability, and operational requirements, which imply avoiding interferences of production and costs caused by tests and inspections.

Overall, the passive system showed the lowest time averaged unavailability and the best technical properties. Its unavailability is dominated by the failure rates assigned to the bursting discs. Test intervals and inspections play a minor role. If the design is made properly, even the most frequent failure mode of bursting discs, i.e. not rupturing exactly at the specified set-point, does not affect its effectiveness so that low failure rates are warranted. Hence, the passive system proves to be superior to those involving the necessity of the functioning of active components. This is true especially since it does not require a redundant design in order to reach a high level of availability and will therefore not be affected by potential common cause failures.

4

The Passive Trip System as a method of reactor protection

4.1 Working principle of the Passive Trip System

The passive trip system is patented and applies to the process and equipment for emergency cooling and pressure relief of the facilities for exothermal reactions **[28, 42]**. It can be also applied together with a conventional safety system such as pressure relief systems or as an independent safety system for facilities like manufacturing, storage or transport of substances, which are able to react with the heat evolution (exothermal reactions).

The general principle of operation of the passive cooling system is as follows. The pressure increase which accompanies the runaway reaction, either because gaseous reaction products are generated and/or the reactor contents starts to boil, is used for driving the reactor cooling. In order to achieve this, a reactor **(Figure 4.1, 4.2)** was equipped with an emergency coolant supply tank. This tank was installed above the reactor and connected to a cooling coil passing through the reactor. During normal reactor operation, the coolant is separated from the reactor contents and from the cooling coil by two bursting discs. If the pressure increases above the set-point of bursting disc no. 1, it will rupture and the pressure is relieved by opening the pipe to the emergency coolant supply tank. At the same time, the coolant is forced through the cooling coil and thus cools down the reacting mixture. In this way, the reactor contents are cooled in time and both the temperature and the pressure are reduced until the reaction comes to a stand-still. This will normally occur before substances from inside the reactor escape. Hence, a receiving tank for vented substances becomes unnecessary.

In the figures seen below, arrows show the direction of fluid flow. Under normal working conditions **(Figure 4.1)**, the reactor is cooled by the continuous circulation of coolant through the reactor jacket. The emergency cooling system is not active, since the coolant is withheld from the cooling coil by the bursting discs. Should the operational cooling system fail or a runaway be initiated for other reasons e.g. stirrer failure, the passive trip system is activated **(Figure 4.2)**. The pressure build-up in the reactor, will then open bursting disc no. 1 and pressurize the emergency system. This opens bursting disc no. 2 and makes the coolant flow through the coil inside the reactor. Pressure is relieved, evaporation and forced cooling cool the reactor content down and the reaction comes to a stand-still. Hence the hazard (increase of pressure) is used for its combat.

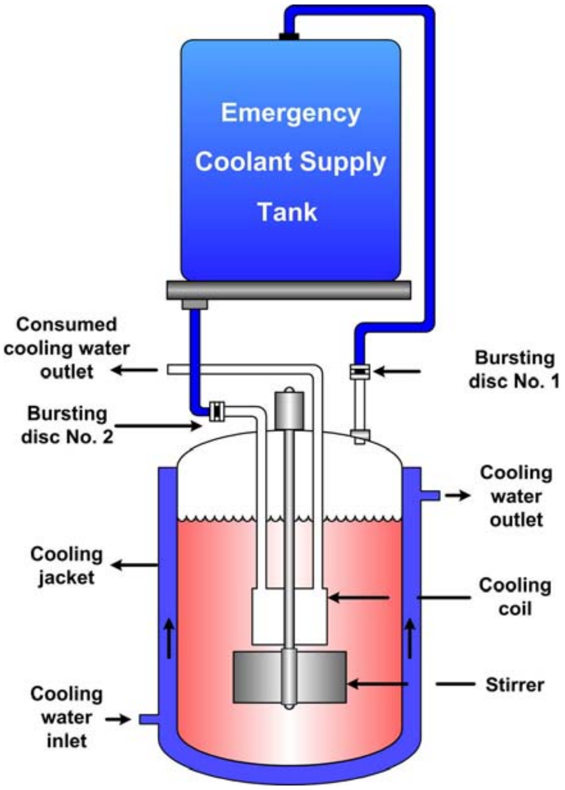

Figure 4.1 *Normal working conditions*

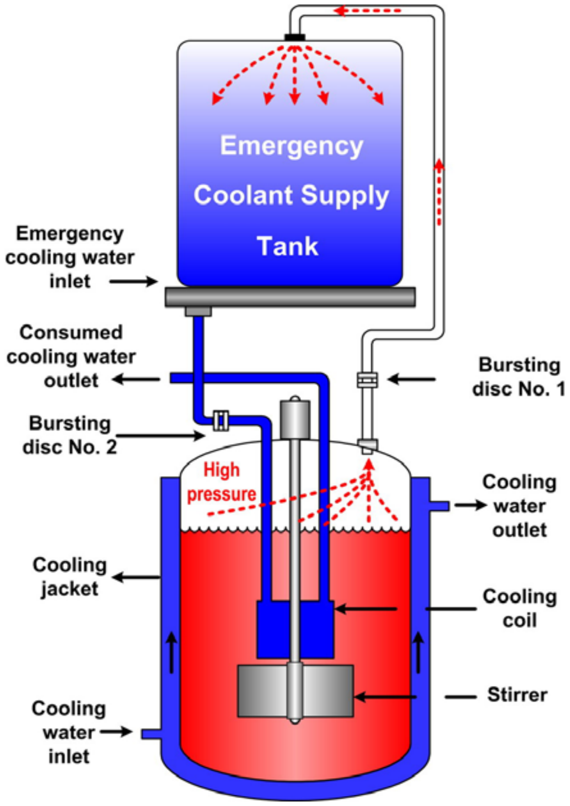

Figure 4.2 *Emergency working conditions*

For passive trip system simulation, visualisation and documentation 3-dimensional model and dynamic visualisation were performed [ACHEMA 2006].

4.2 Experimental demonstration of the feasibility of the Passive Trip System

For passive trip system development and design, a 3-dimensional model was constructed, see **Figure 4.3**. The laboratory scale batch reactor, type III manufactured by Büchi AG, was used to build the passive trip system. In order to demonstrate the feasibility this reactor was equipped with an emergency coolant supply tank (1). This tank was installed above the reactor and connected by pipes (2) to a cooling coil (3) passing through the reactor During normal reactor operation the coolant is separated from the reactor contents and the cooling coil by two bursting discs or permanent valve (4, 5). **Figure 4.4** shows the realization of the project.

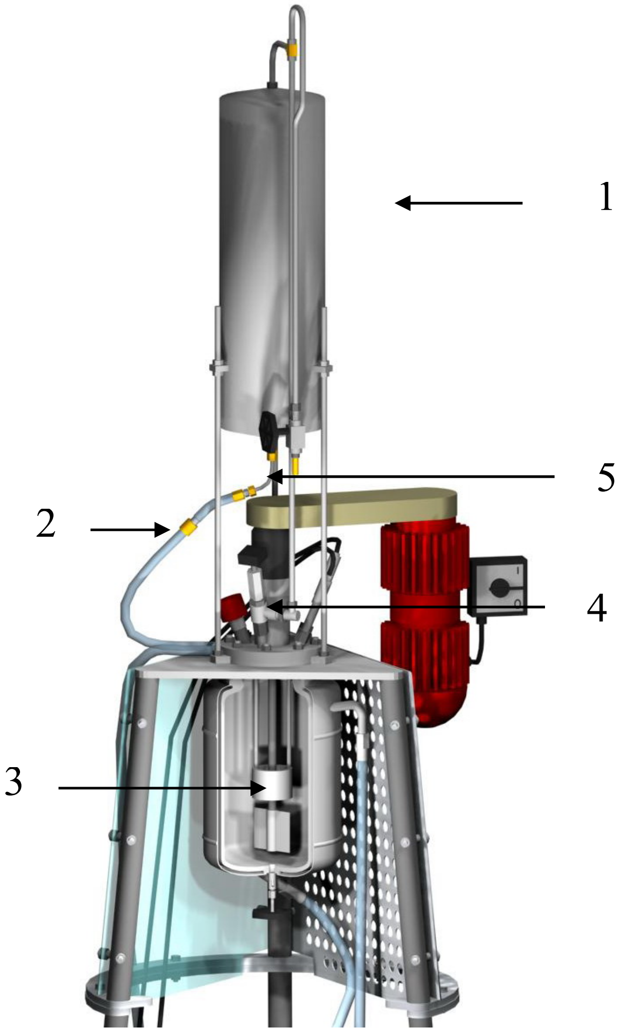

Figure 4.3 *Passive trip system (3D-model)*

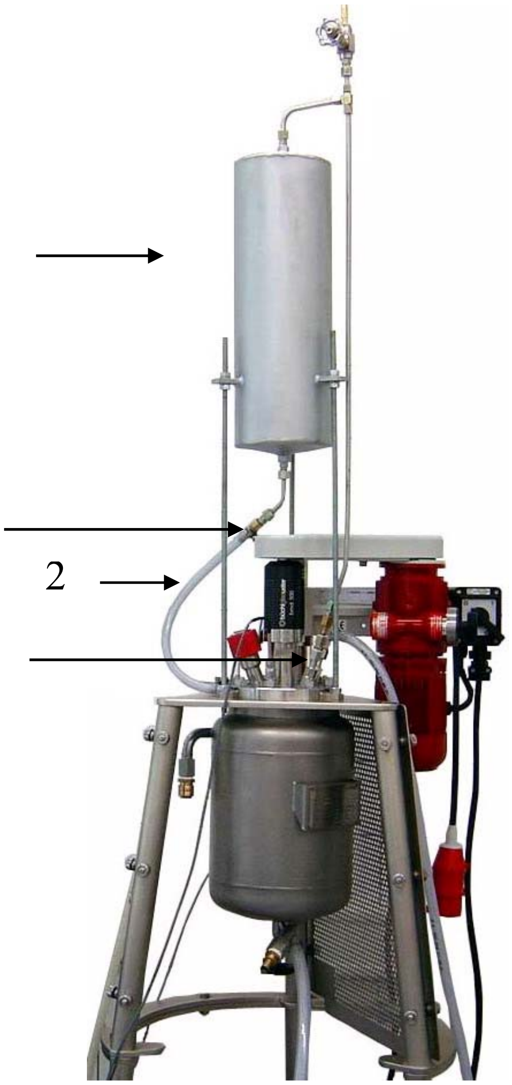

Figure 4.4 *Passive trip system (realization)*

The main components of the passive system are an emergency coolant supply tank, a cooling coil and bursting or other relief devices, see **Figure 4.5.**

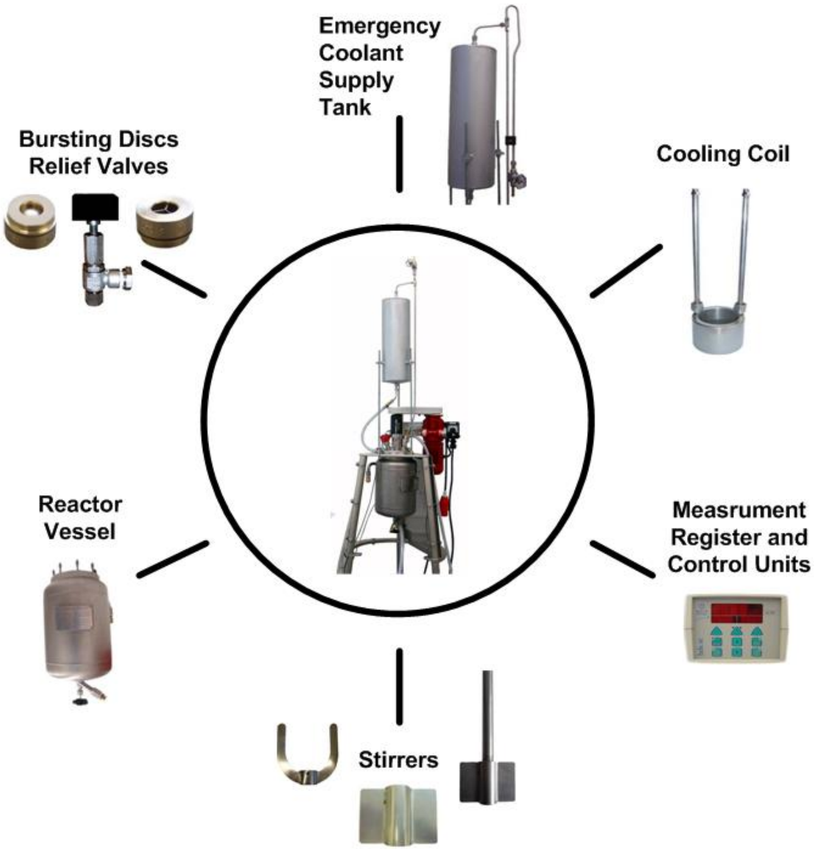

Figure 4.5 *Passive cooling system components*

Reactor vessel, stirrers, measurement register and control units belong to the standard batch reactor equipment. Their detailed specification is presented in **Table 4.1**.

Table 4.1 *Specification of the reactor*

Description	**Value / Type**
Capacity of the reactor	0.01 m^3
Capacity of jacket cooling system	0.0015 m^3
Stirrer	Blade
Max. pressure	20 bar
Max. temperature	250°C
Inner diameter of the reactor	0.207 m
Safety valve	20 bar
Material	Stainless steel 1.4571
Pressure indicator and recorder	Digital measurement instrument with display
Temperature indicator and recorder	Digital measurement instrument with display

A detailed size specification of the passive trip system is presented in **Table 4.2**. The remaining design parameters depend on the reacting systems.

Table 4.2 *Specification of the passive trip system*

Description	Capacity	Diameter	Length	Thickness
Emergency cooling tank	0.01 m^3	0.16 m	0.45 m	0.001 m
Bursting discs	-	0,00635 m	-	Depends on material
Permanent relief valve	-	0,00635 m	-	-
Cooling coil	0.001 m^3	0.00635 m	2.1 m (modelling)	0.001 m

Emergency cooling tank

The emergency coolant supply tank was designed according to simulations executed for several reacting systems. A nine litre cylindrical tank was built (1), and with the help of three supports (2), installed above the reactor. In order to render filling and emptying operations a hand-operated valve (3) was installed at the bottom of the coolant tank. The outlet of a coolant (4) was fitted at the bottom of the tank and connected with the reactor using 6 mm diameter pipe (5). To prevent the coolant from flowing out, before the trip system activation, a bursting disc was installed (6). On the pipe connecting inlet site of a coolant tank with the vapour phase of reactor, the permanent relief valve (7) was installed. The emergency cooling tank is designed according to existing standards for pressure vessels.

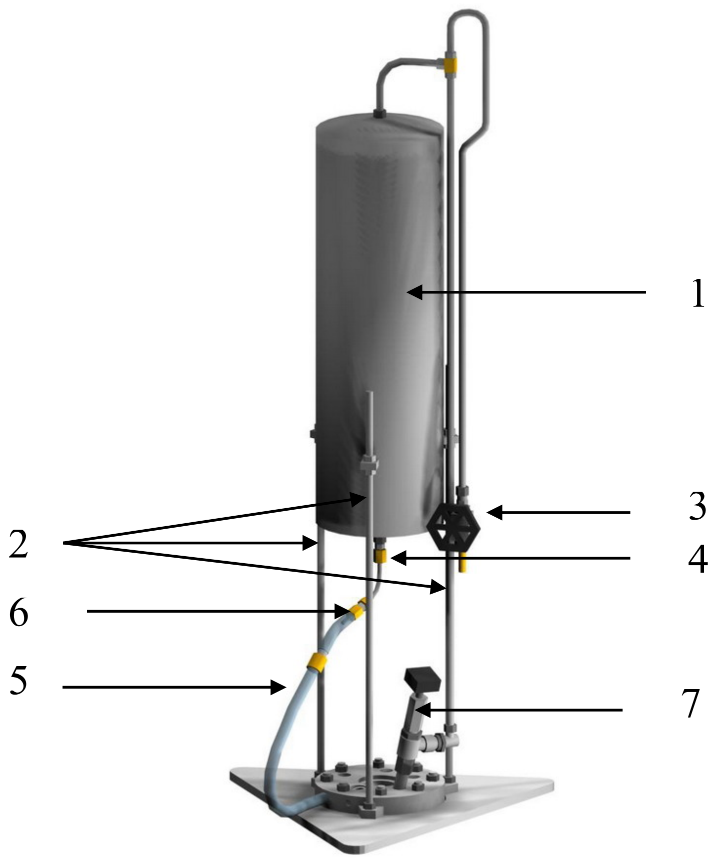

Figure 4.6 *Emergency coolant tank*

Bursting and relief devices

Bursting discs were chosen in the original design for availability reasons. In order to avoid the consumption of many bursting discs during experimentation, a special valve was designed to replace bursting disc no. 1, whilst bursting disc no. 2, which only has to prevent the water from flowing out, was replaced by a thin metal foil. A conventional safety valve **(Figure 4.7)** was modified by application and adjustment of a strong permanent magnet (1) and two stainless steel screws (2, 3) see **Figures 4.8 - 4.10**. The forces of springs (4) inside the valve were measured and a permanent magnet sufficiently strong to overcome them was installed. Once the safety valve opens it is held open by the magnet. Apart from saving bursting discs, the device enables one to use different set points for the opening pressure in search for optimal operating conditions for the emergency cooling system. The set-point pressure adjustment for a valve takes a few seconds and by this specific design enables one to set opening pressures between 0,1 – 4 bar above atmospheric pressure.

Figure 4.7 *Conventional relief valve*

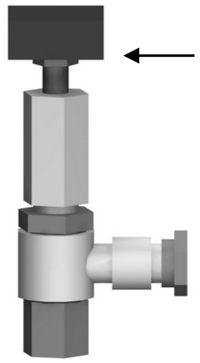

Figure 4.8 *Permanent relief valve (3D-model)*

Figure 4.9 *Permanent relief valve (realization)*

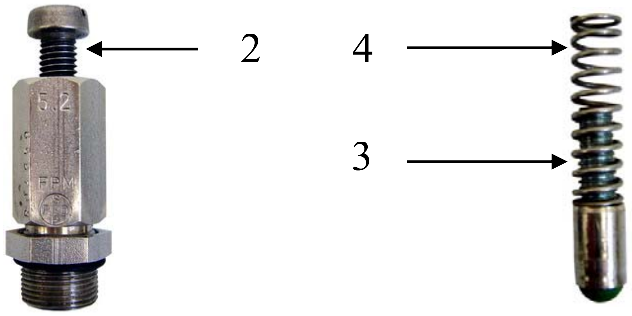

Figure 4.10 *Components of the permanent relief valve*

Cooling coil

The cooling coil of straight tube type, manufactured and recommended by Büchi AG, was used to develop the passive cooling system. The geometry and specification of a cooling coil is shown in **Figure 4.11**. The coil has a simple cylindrical geometry which enables effective heat transfer and does not cause a significant decrease of the volume of the reactor.

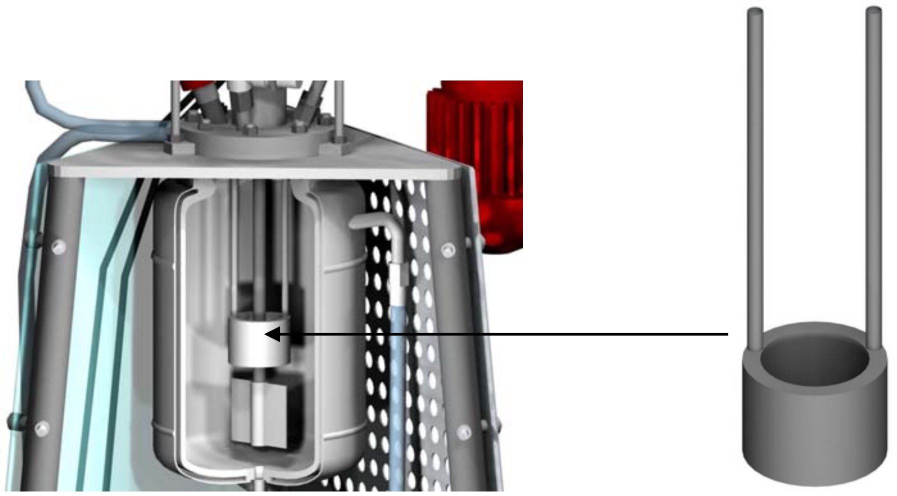

Figure 4.11 *Cooling coil*

4.3 Choice of design parameters

The first step of designing a passive trip system is to understand the runaway reaction mechanism. Of crucial interest are properties, such as reaction kinetics, chemistry and especially thermo-chemistry.

The most important requirement for an effective passive trip system is the choice of coolant quantity (the size of emergency coolant tank) capable of moderating or halting the runaway reaction. There are no restrictions for the application of a passive trip system to any exothermal reaction. The tank size depends only on the reaction investigated. In order to guarantee efficient cooling and thus a halting of heat development, appropriate design parameters have to be selected. This has a vital influence on the successful trip function and will be investigated. For reasons of vessel certification some of the design parameters are fixed. The cooling coil has, for instance, a fixed diameter of 0.00635 m and a wall thickness of 0.001 m (the reactor is certified pressure vessel, which may not be modified). The crucial parameters which influence the efficiency of the passive trip system are:

- Capacity of the emergency coolant supply tank
- Cooling coil dimension (diameter, length, wall thickness, material)
- Coolant characteristics (type, temperature, amount)
- Relief device characteristics (response pressure, diameter)

The main problems in designing the passive trip system are:

- Lack of case-specific kinetics for chemical reactions
- Bursting discs do not open at an exact pressure
- Uncertainties connected with the transfer of measured data under laboratory conditions to real plants
- Insufficient knowledge on runaway reactions mechanisms and thermo-chemistry

5

Laboratory investigations

The experimental work was carried out in the safety laboratory at the Otto-von-Guericke-University. In this chapter, equipment and procedures relevant for the passive trip system experiments are described. The experimental setup and procedure in the experimental runs are described in **Sections 5.1 and 5.2**. **Section 5.3** describes reacting systems investigated and presents experimental results. The analysis of them is presented in **Section 5.4**.

5.1 Experimental setup

The identification of hazardous scenarios, reactions etc., is often very difficult without experimental testing. The scale of experiments and equipment used at this stage should be such that a potential runaway can be contained **[49]**.

The experiments with different exothermal reactions were carried out in the batch reactor described in the previous chapter using the experimental setup of **Figure 5.1**. The reactor is equipped with the emergency cooling system (1), pressure and temperature sensors (2), water bath (3), pressure and temperature digital meters (4), and the computer (6). The temperature and pressure signals from the sensors are continuously transferred to the digital meters and from there to the computer, where they are registered in the graphical and numerical form. The passive trip system was designed, performed and installed in the Department of Process Design and Safety. Preliminary tests were then carried out. In the beginning, water was used to test the system. When the tests brought satisfactory results, a second medium, methanol, was applied. Due to the low boiling point (64°C), it was very easy to heat the reactor contents and observe the system. The test results for this were also satisfactory. Thereafter, the test facility was prepared for experiments with exothermal reactions.

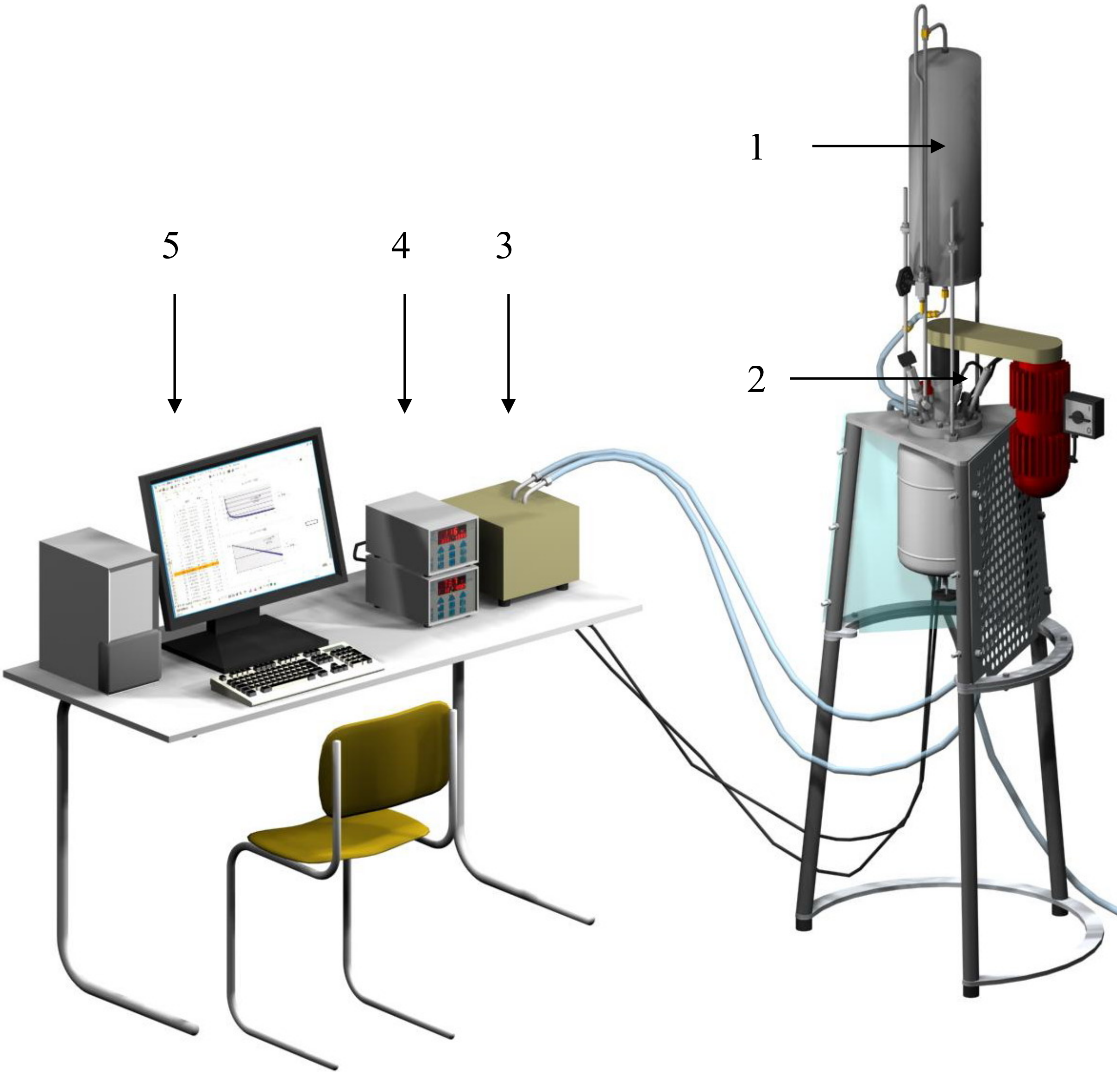

Figure 5.1 *Experimental Setup*

5.2 Experimental procedure

For the visualisation and documentation of the experimental procedure, a 3-dimensional dynamic presentation was performed, see **Appendix G**. The experimental procedure included preparing the system and carrying out the experiments themselves. Due to different conditions and reacting systems, a full preparation of the system was always necessary. The preparation of the system consists of the following steps:

- cleaning and assembling the passive trip system and the reactor,
- control and start of computer and registry devices,
- control of the safety valve,
- set of the permanent relief valve - activation pressure,
- filling the emergency cooling tank with the coolant (water),
- pressure tests and control of the set-pressure for relief devices,
- preparing emergency measures like additional cooling, ice, etc.

The procedure for preparing an experiment is as follows:

- the emergency cooling tank is filled with a coolant,
- the reactants are prepared by using graduated flasks,
- the agitation and registry devices are switched on,
- the reactor is filled with reactants through the top,
- the reactor contents is heated until the required starting temperature is reached,
- the reactor is closed and its contents is mixed by stirring,
- the reaction starts,
- the operating cooling system (the reactor jacket) is stopped in order to simulate a cooling system failure.

The evolutions of pressure and temperature can be observed by the registry units and saved by the computer software BLS 2 (Büchi AG). After the passive trip system operation, the experiment is finished. For a new experiment the above steps have to be repeated.

5.3 Laboratory investigations

In order to show the feasibility of the design of the passive trip system, its effectiveness for different realistic reaction systems must be demonstrated. Based on the DIERS classification the following three systems were chosen (c.f. **Chapter 2**):

- vapour system – the pressure increases as the temperature of the reaction mixture increases by a progressing chemical conversion (evaporation of the components),
- gassy system – the pressure increase is caused by the production of permanent gassy products, for example due to a decomposition reaction, and
- hybrid system – a combination of the two previous systems; the pressure increase is caused by both the production of gassy products and evaporation.

From each group a representative reaction was chosen. The first group is represented by the esterification of methanol and acetic anhydride, the second by the decomposition of hydrogen peroxide (temperature initiated) and the last one by the decomposition of hydrogen peroxide in the presence of catalyst. Depending on the reacting system, different safety parameters have to be taken into account. The main intrinsic safety parameters are presented in **Table 5.1**.

Table 5.1 *Intrinsic safety parameters for chemical reactions*

Kinetic	**Thermodynamic**	**Physical**
Reaction rate constant [k_0]	Reaction enthalpy [ΔH_r]	Heat capacity
Activation energy [E_a]	Adiabatic temperature and pressure rise [ΔT_{ad}, ΔP_{ad}]	Thermal conductivity
Time to maximum rate [TMR]	Quantity of gas generated	
Onset of exothermicity		
Reaction order [n]		
Rate of vessel pressure rise		

The data enable one, for example, to evaluate temperatures and pressures, as well as their evolution with time. However, for the vast majority of batch operations employed in the pharmaceutical and speciality chemicals industries, reliable thermodynamic and kinetic data are scarce.

For all experiments, the operating cooling failure was considered as a cause of runaway. Due to this failure, a runaway reaction was triggered. When the pressure reached the set-point of the relief device, the passive trip system was activated. Furthermore the influence of stirrer failure on the passive trip system efficacy was investigated. In the next sections, the passive trip system experiments will be presented. In addition to this, an experimental comparison of the same scenarios with and without trip system will be presented.

5.3.1 Esterification reaction between methanol and acetic anhydride

The kinetic data for this reaction have been published by several authors; see Duffield and Nijsing **[45]**, Wright and Rogers **[46]**, Singh **[47],** Friedel and Wehmeier **[48]**. The reaction progresses according to the following stoichiometric formula:

$$(CH_3CO)_2O_{(l)} + CH_3OH_{(l)} \xrightarrow{T_s \approx 25°C} CH_3COOCH_{3(l)} + CH_3COOH_{(v,l)} \qquad (5.1)$$

The reaction is very slow, which enables one to easily observe and record all changes in the system. The esterification reaction is irreversible and proceeds with stoichiometric quantities of the reactants. Its reaction products are acetic acid and acetic methyl ester. Both reactants and the products of reaction are in the liquid phase. Their physical and chemical properties are presented in **Appendix E**. The reaction (without catalyst) starts slowly at 25-30°C and becomes more rapid above 70-80°C. Due to the low boiling point, the methanol vaporizes first. The main kinetic and thermodynamic data for a molar ratio of methanol/acetic anhydride 2:1 mol/mol are presented in **Table 5.2**:

Table 5.2 *Kinetic data for esterification of acetic anhydride reaction*

Parameter	Value
Reaction rate constant	$k_0 = 8.97 \cdot 10^6$ m^3 /(kmol s)
Energy of activation	$E_a = 73752$ kJ/kmol
Enthalpy of reaction	$-\Delta H_r = 66300$ kJ/kmol

Figure 5.2 shows the pressure and temperature history of noncatalysed esterification reaction, which was carried out in the Dewar Calorimeter **[DynoChem]**. At the beginning, the reactor contents were heated to a temperature of 24°C in order to slowly start the runaway reaction. Due to the low reaction rate, the temperature and pressure increased very slowly. Two hours later, the temperature 60-70°C was reached. The reaction became very fast and, after full conversion of the limited reactant, reached a temperature of almost 180°C and a pressure of 20 bar.

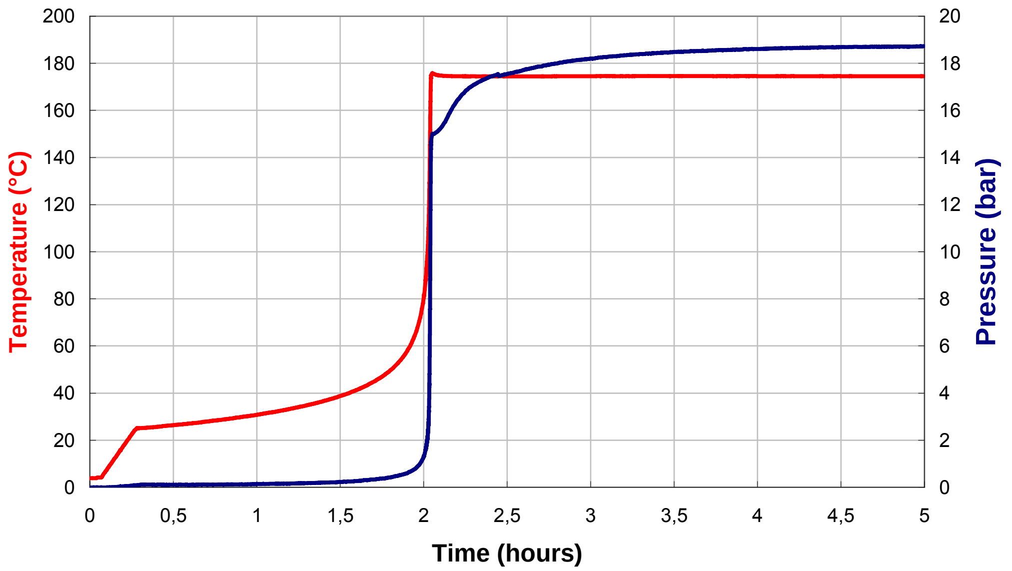

Figure 5.2 *Esterification of acetic anhydride with methanol (Mol ratio 2:1)* **[54]**

Figure 5.3 presents the experimental result of the esterification reaction. The initial temperature of the process was 30°C. Other conditions were a reactor filling level of 80% and a molar ratio of reactants of 1:1. After three hours, when the pressure reached 2.3 bar, the passive trip system was activated. The pressure decreased to atmospheric pressure and the temperature by 25°C. The reaction came to a standstill.

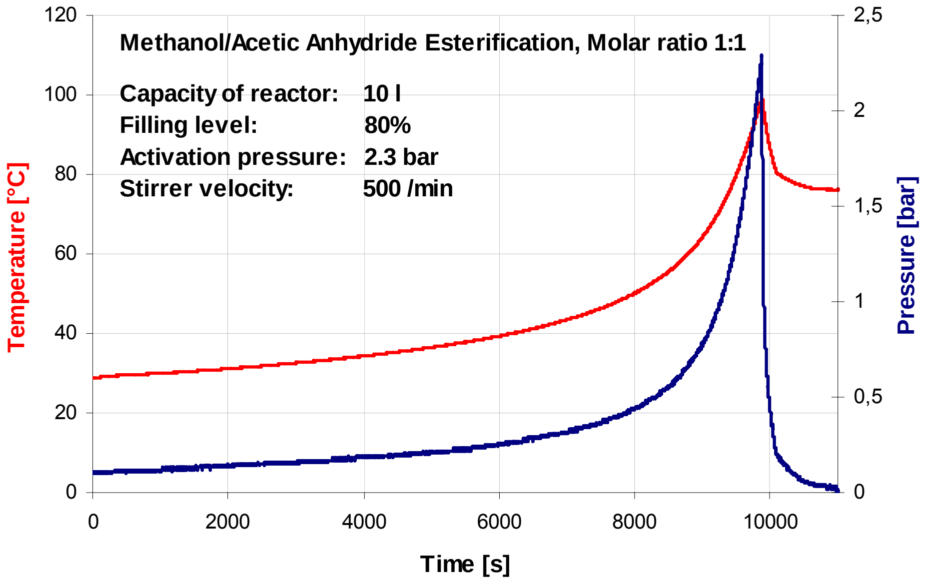

Figure 5.3 *Temperature and pressure profile for esterification reaction*

In order to show the feasibility of the passive trip system, the same reaction but without activation of the passive trip system was carried out, see **Figure 5.4**. The safety valve opened at the same pressure as in the first case (2.3 bar) but, since there was no emergency cooling, the temperature still increased. A short moment after relief, the pressure decreased to 1.4 bar but, due to a very high temperature and the vaporization rate of reactants, it started to increase again. **Figure 5.5** provides a more detailed look around the point of the passive trip system activation. It presents this case 5 minutes before and 5 minutes after pressure relief. Finally the runaway reaction was successfully stopped by the operational cooling system, which was activated manually.

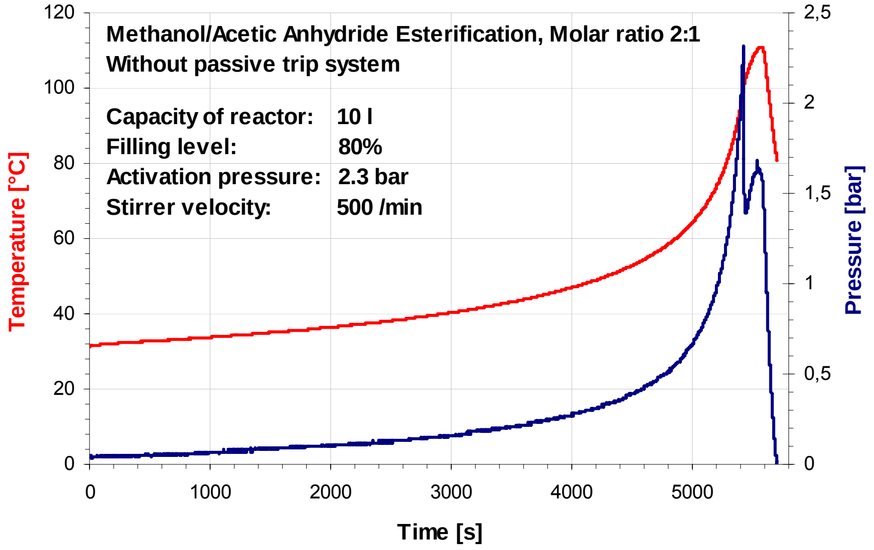

Figure 5.4 *Temperature and pressure profile for esterification reaction (without passive trip system)*

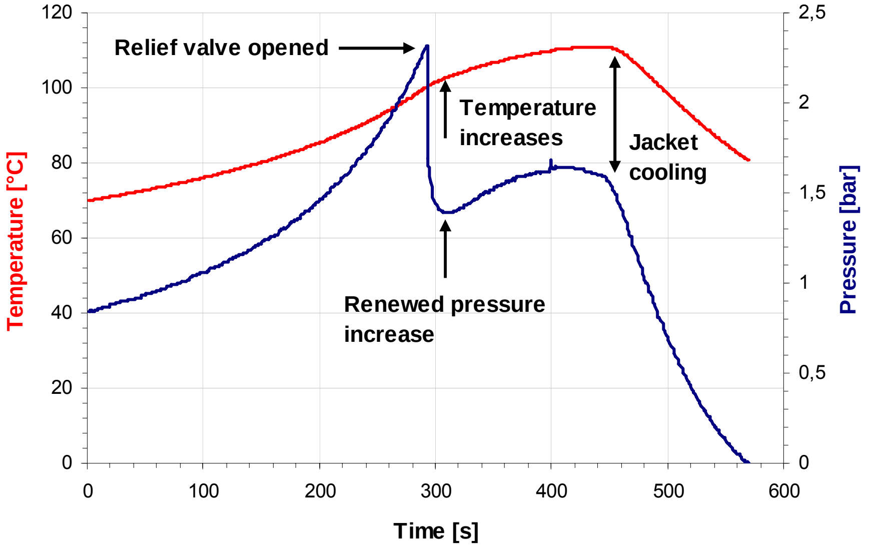

Figure 5.5 *Enlarged fragment of* ***Figure 5.4***

The next experiment **(Figure 5.6)** presents the same reaction conditions but for another activation pressure of the trip system – 2.4 bar. Furthermore, it was assumed that during the reaction course the operating cooling system would be restored. Therefore, at a temperature of 52°C and a pressure of 0.6 bar, the jacket cooling system was activated. A momentary decrease in the temperature and pressure could be observed. However, the operating cooling system was not sufficient and, due to the very high reaction rate the runaway reaction began again. The pressure reached the set-point and the trip system was initiated. The runaway reaction was then stopped successfully.

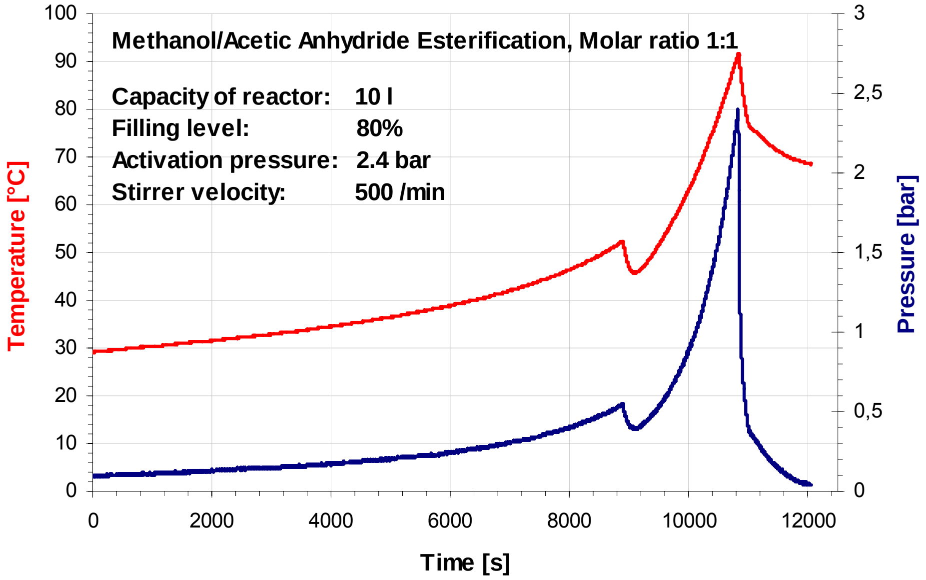

Figure 5.6 *Temperature and pressure profile for esterification reaction (with passive trip system)*

Figure 5.7 presents the case of reduction of stirrer revolutions and finally the stirrer failure. The initial temperature of the process was 25°C. Other conditions were a reactor filling level of 80% and molar ratio of reactants 2:1. The time to the passive trip activation was approximately 1.5 hours. By that time, the stirrer revolutions were reduced from 500 to 250 and, a short time before the activation of the passive trip system, the stirrer was turned off. Due to the reduction of revolutions, the reaction slowed down. Furthermore, as a consequence of stirrer failure, the emergency cooling system became less effective. The reactor content was not mixed well and therefore the heat transfer between coolant and reactants was limited. Usually the simultaneous failure of two operational systems, i.e. the simultaneous occurrence of two initiating events, is highly improbable and therefore normally not considered (an exception are events causing several dependent failures, e.g. failure of electric supply).

Finally, the stirrer was activated and the cooling effect of the trip system was significantly improved.

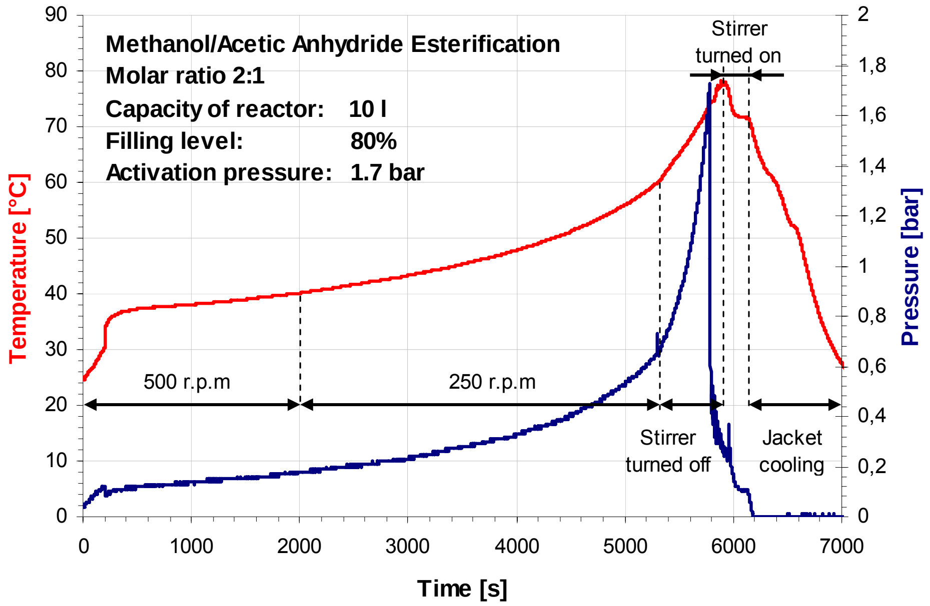

Figure 5.7 *Temperature and pressure profile for esterification reaction*

5.3.2 H_2O_2 decomposition – temperature initiated

Hydrogen peroxide is a frequently used reactant in the chemical industry and it is one of the most powerful oxidizers known. Hydrogen peroxide oxidative power, and the gas and heat generated by its decomposition, are responsible for the large majority of hazardous situations that arise during its storage, handling and use. Hydrogen peroxide is generally supplied in aqueous solutions (industrial concentration are 27.5% - 70%).

The normal rate of decomposition for commercially supplied hydrogen peroxide is very low (1% loss per year) **[55]**. However, significantly faster decomposition can be triggered by even very small amounts (less than 1 ppm) of soluble impurities, or by contact with incompatible rough surfaces.

The reaction was carried out in the liquid phase using the following concentrations of hydrogen peroxide: 3, 6, and 12%. The decomposition was initiated by an external heat source. The temperature was kept below the boiling point of the solution. Therefore, the only product of decomposition was oxygen, since hydrogen peroxide solutions vaporize above

100°C. The filling level of the reactor was 50%. The number of stirrer revolutions was varied between 300 and 1200 rpm.

The reaction progressed according to the following stoichiometric formula:

$$H_2O_{2(l)} \xrightarrow{90°C/MnO_2} H_2O_{(v,l)} + \frac{1}{2}O_{2(g)} \tag{5.2}$$

The products of H_2O_2 decomposition are water and oxygen. The physical and chemical properties of reactant, products and catalyst are presented in **Appendix E**. The reaction kinetic data were adopted from Duffield and Nijsing **[50]** and are presented in **Table 5.3**.

Table 5.3 *Kinetic data for hydrogen peroxide decomposition*

Parameter	Value
Reaction rate constant	$k_0 = 1.5 \cdot 10^{12}$ 1/s
Energy of activation	$E_a = 12833$ kJ/kmol
Enthalpy of reaction	$-\Delta H_r = 2.79\ 10^3$ kJ/kg

Figure 5.8 shows the pressure and temperature history for 3 wt-% hydrogen peroxide solution. The filling level of the reactor was 5 litres. The reaction started slowly at a temperature of 68°C and took approximately 1.5 hours until the passive trip system was activated. The permanent relief valve opened at 3 bar, thus activating the passive trip system. The pressure decreased to atmospheric pressure and the temperature by 15°C.

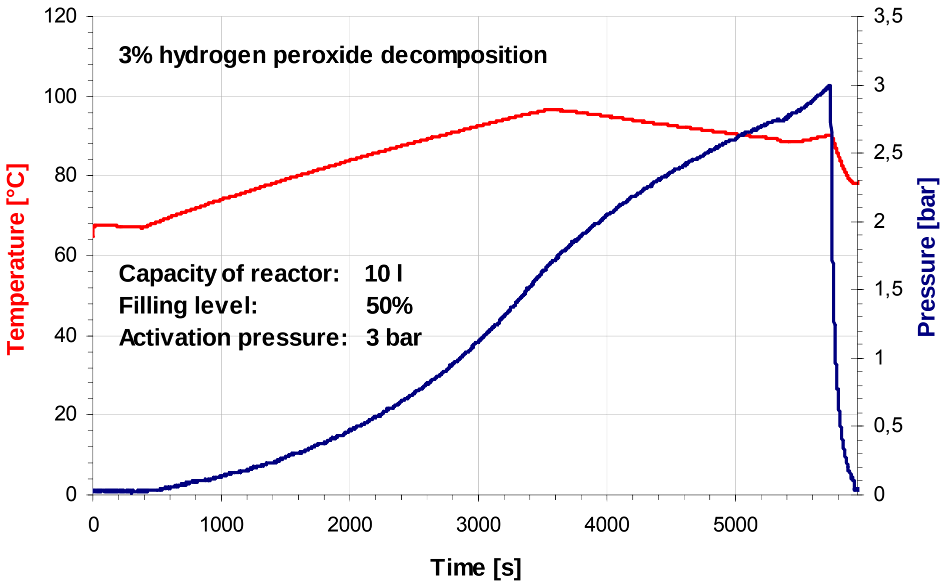

Figure 5.8 *Temperature and pressure profile for hydrogen peroxide decomposition - 3%*

For 6 wt-% hydrogen peroxide solution **(Figure 5.9)** the reaction was significantly faster. The passive trip system was activated at a pressure of 3.5 bar and at a temperature of about 98°C. The pressure decreased to the ambient pressure but, due to the failure of the permanent relief valve, increased again due to oxygen generation. The pressure reached 0.7 bar and, due to the fact that the reactant was consumed, it was stopped. Hence the reaction did not present a runaway hazard as the pressure relief and operational cooling were actuated. The reaction came to a standstill. **Figure 5.10** presents the fragment of this curve for a 10 minute time period after passive trip system activation.

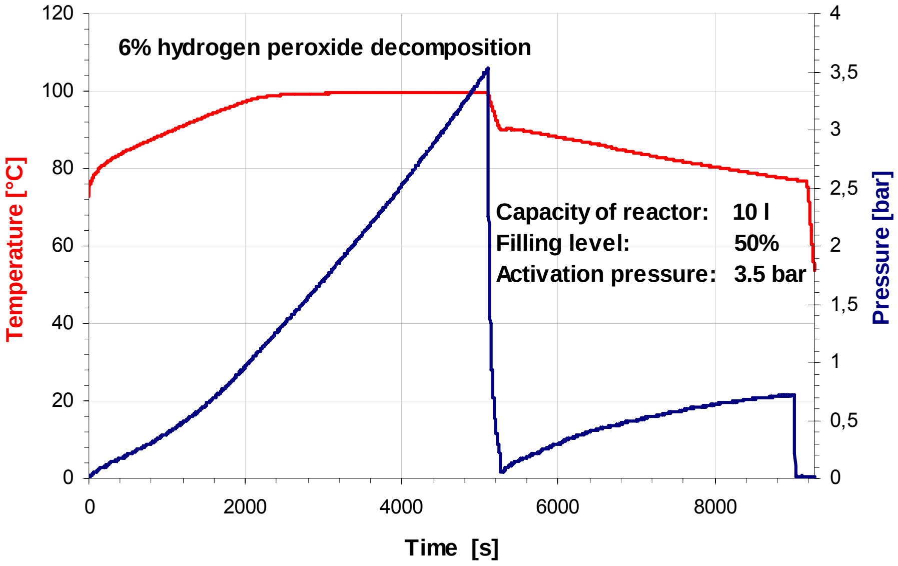

Figure 5.9 *Temperature and pressure profile for hydrogen peroxide decomposition -6%*

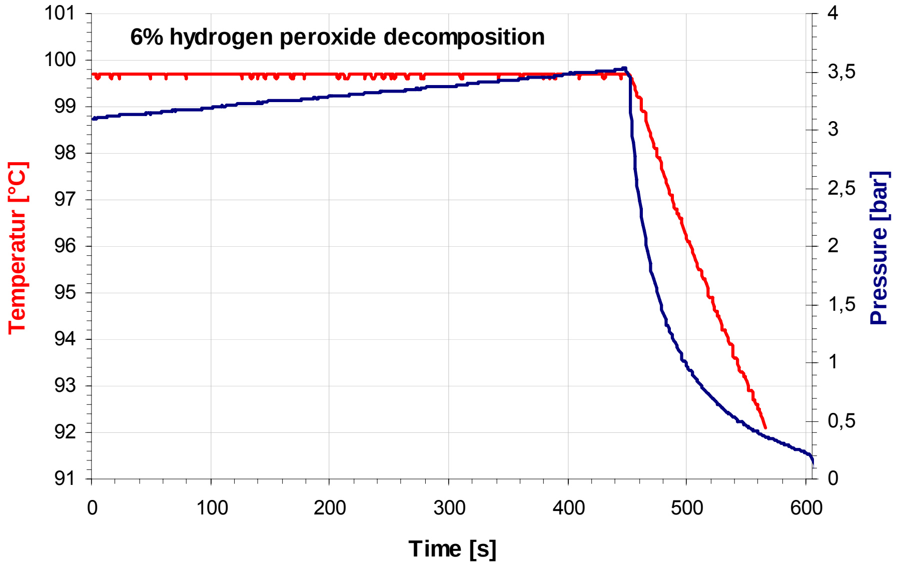

Figure 5.10 *Enlarged section of* ***Figure 5.9***

The third experiment **(Figure 5.11)** was carried out for 12 wt-% hydrogen peroxide solution. Due to safety precautions, the set pressure of the permanent safety valve was reduced to 3.2 bar. The reaction started at 60°C and reached a maximum temperature of 99°C and a maximum pressure of 3.2 bar. At this point, the passive trip system responded and both the pressure and the temperature were reduced. In order to prove whether or not the decomposition reaction could be initiated again, the permanent safety valve was closed for a moment. Consequently, an increase of the pressure by 0.5 bar could be observed but, due to the high conversion of hydrogen peroxide, the temperature did not increase and the reaction was successfully stopped.

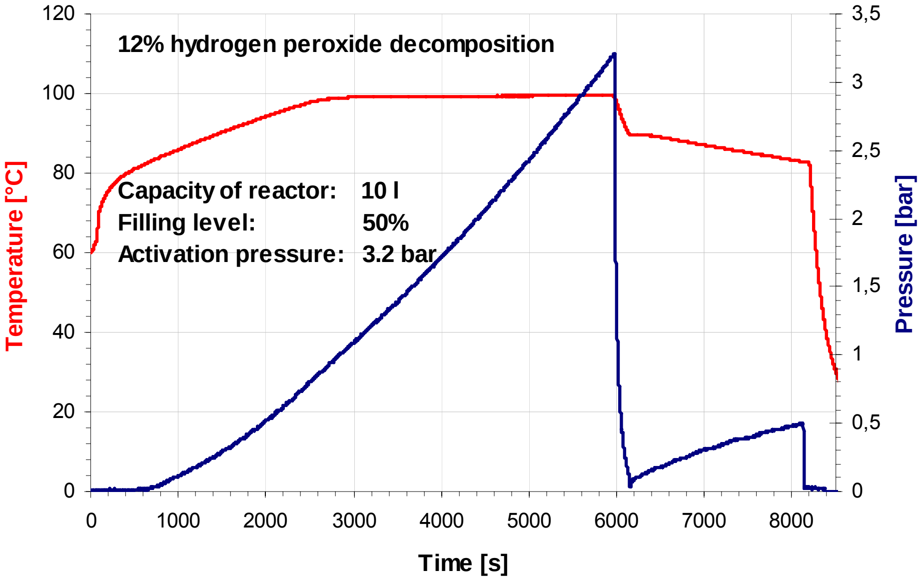

Figure 5.11 *Temperature and pressure profile for hydrogen peroxide decomposition -12%*

5.3.3 H_2O_2 decomposition - on MnO_2 catalyst

The third reaction investigated was the decomposition of hydrogen peroxide catalyzed by manganese dioxide (MnO_2). The temperature at the beginning was 60-70°C. The experiments were carried out in the liquid phase using 1, 1.5 and 2% solutions of hydrogen peroxide. The reaction is very fast and is characterized by a violent gas generation. The products of this reaction are only water and oxygen and the catalyst can easily be separated from the water solution. The filling level of the reactor was 70% and the agitation rate was varied between 300 and 1200 rpm.

Figures 5.12-5.16 show the pressure and temperature history of the reactor equipped with a passive trip system for different hydrogen peroxide solutions. Other conditions were a reactor filling level of 70%, a temperature at the beginning T_{pr} = 60-61°C, a mass of catalyst 0.0175 kg and an agitation rate of 400 rpm.

Figure 5.12 presents the temperature and pressure history for 1 wt-% hydrogen peroxide solution. The reactor filling level was 70%. The reaction started at 60.7° C. After 82 seconds, the reaction reached a temperature of 62.4°C and a pressure of 3.9 bar. At this moment, the passive trip system was activated and both the pressure and the temperature dropped. Hence, because there was no further increase in either pressure or temperature, the danger of a runaway reaction was avoided. The atmospheric pressure was reached and the temperature dropped by 6°C.

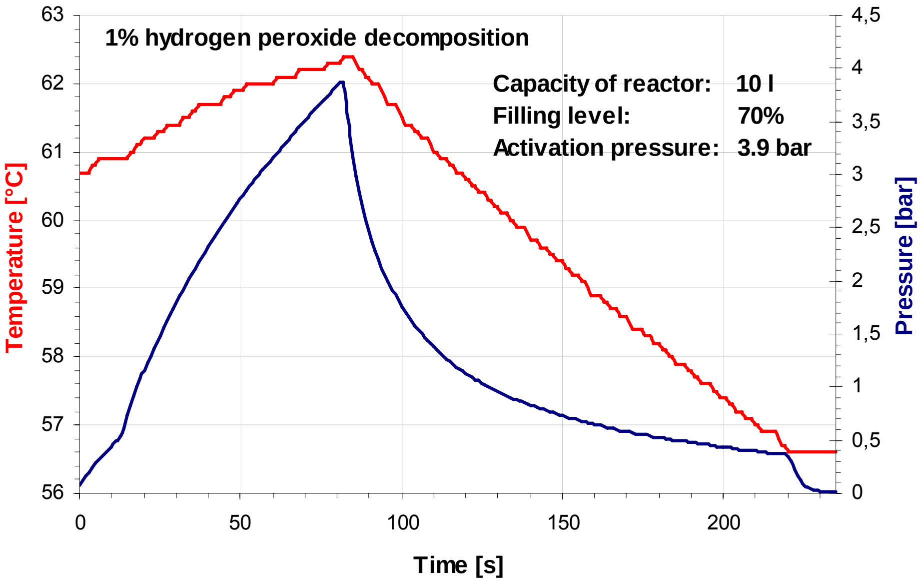

Figure 5.12 *Temperature and pressure profile for hydrogen peroxide decomposition -1%*

A similar scenario for higher concentration of hydrogen peroxide is presented in **Figure 5.13**. The reaction started at the same temperature and reached the set pressure of the trip systems after 60 seconds. In that case the emergency cooling system was also effective and stopped the runaway reaction.

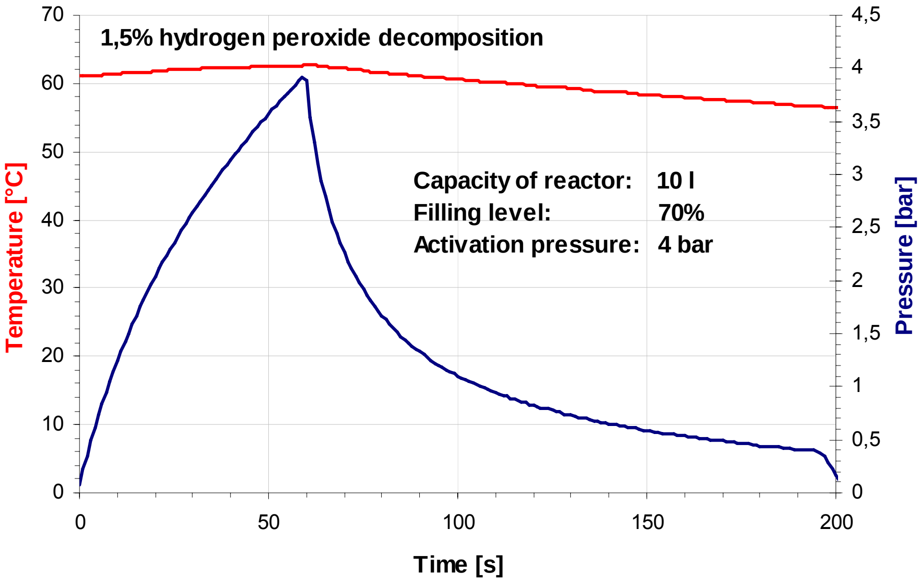

Figure 5.13 *Temperature and pressure profile for hydrogen peroxide decomposition -1.5%*

The third case **(Figure 5.14)** proved again that the passive trip system is able to stop fast decomposition reactions for different concentrations of hydrogen peroxide. Due to a lower temperature at the beginning, the reaction reached the set pressure of the trip system after 74 seconds. The pressure and temperature decreased and the reaction came to a standstill.

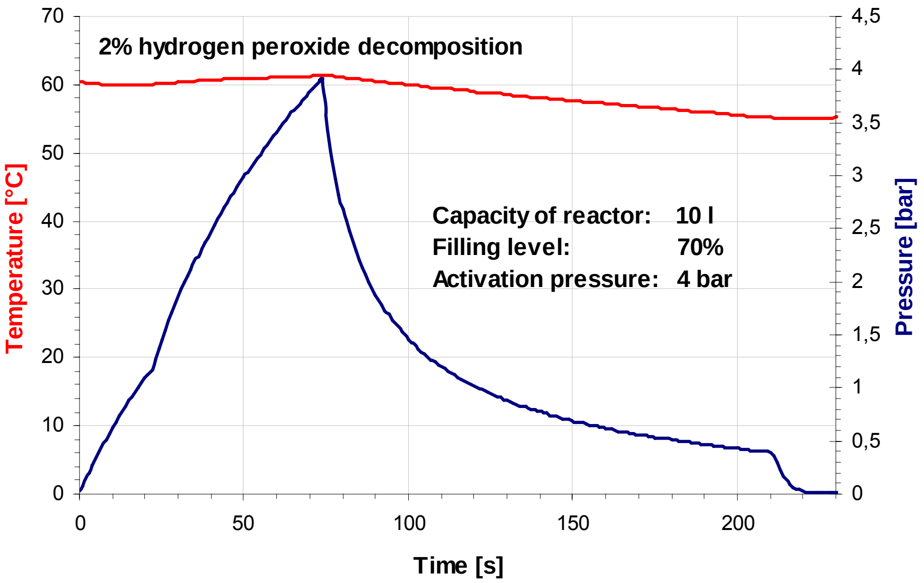

Figure 5.14 *Temperature and pressure profile for hydrogen peroxide decomposition -2%*

In order to show the feasibility of our system, the experiments were carried out with pressure relief but without the emergency cooling system. The diameter of the relief valve was the same as that of the permanent valve. **Figure 5.15** proves that, even though the pressure dropped very quickly, the temperature was still increasing and had the potential to initiate secondary reactions. **Figure 5.16** presents the same experimental conditions. The oxygen produced was relieved through the safety valve but, every time the atmospheric pressure was reached, the relief valve was closed again. The amount of gas produced was so high that even after three relief activations the pressure and temperature were still increasing. At the end the reaction was cooled down by the operational cooling system.

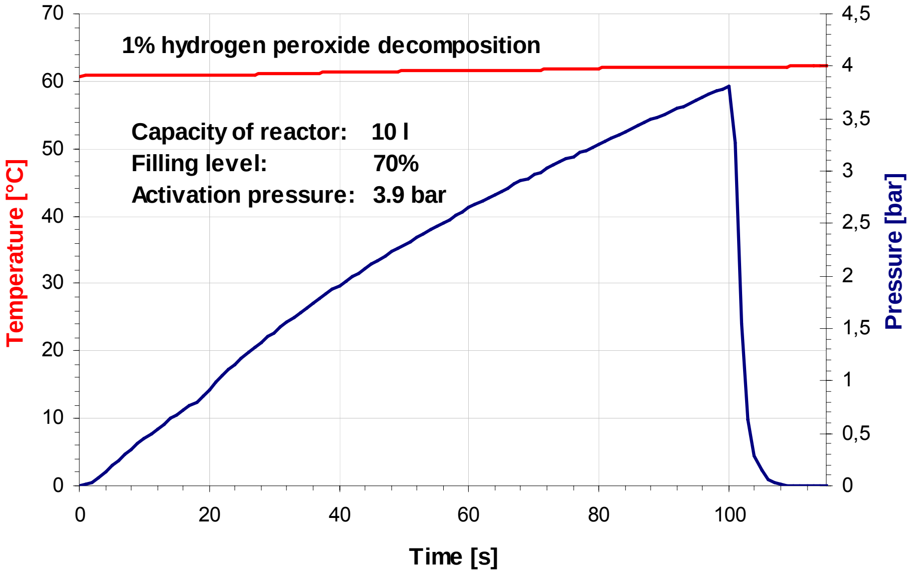

Figure 5.15 *Temperature and pressure profile for hydrogen peroxide decomposition -1%, without passive trip system*

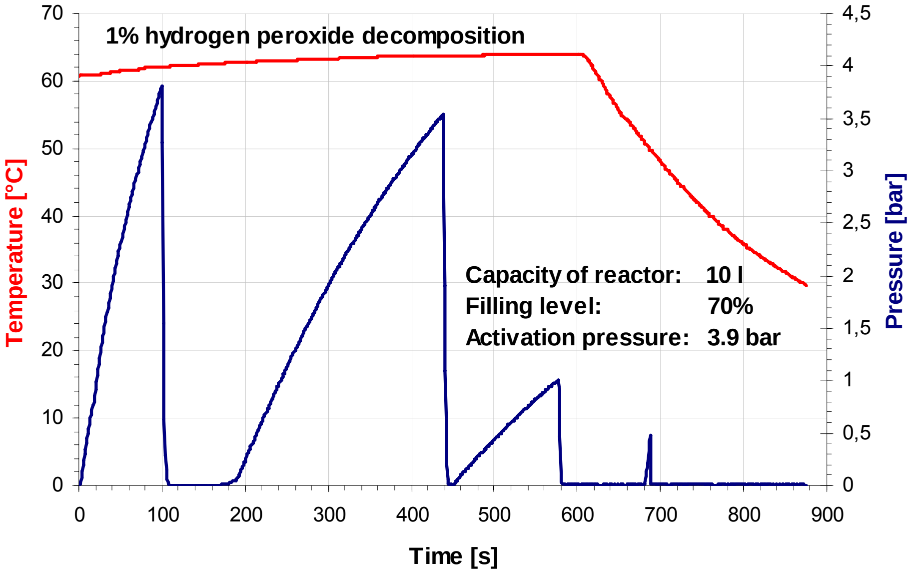

Figure 5.16 *Temperature and pressure profile for hydrogen peroxide decomposition -1%, without passive trip system*

5.4 Concluding remarks

The aim of the experiments was to determine whether the passive trip system can successfully halt the runaway reactions under various conditions. The results of these experiments are clear. Three different reactions have been examined and the results showed that the system is able to halt vapour, gassy and hybrid reactive systems.

The first reaction, esterification of acetic anhydride, was carried out for different concentrations of methanol and acetic anhydride. The effect of the degree of mixing on the passive trip system effectiveness was also studied. The failure of the operating cooling system was assumed in every case. Furthermore, the case of stirrer failure was investigated. It affects the process itself and can also lead to accumulation or cause hot spot formation. Concerning the trip system, the failure of the stirrer will affect the heat distribution inside the reactor and consequently reduce the effectiveness of its safety function.

The second reaction investigated concerned the decomposition of hydrogen peroxide. In the first case, the reaction was induced by a temperature increase and, in the second, by the addition of a catalyst. The decomposition rate of a catalyzed reaction was much higher than that of the noncatalysed one. The passive trip system was investigated for different concentrations of hydrogen peroxide and for different set points of trip system activation. In every case, successful trip operation could be observed. Additionally, the tests were carried out without a passive trip system. They have proved that pressure relief alone through the trip system coil cannot avoid temperature increase and consequently a runaway reaction. Hence, the coolant is essential for success.

These experiments show that the application of a passive trip system to vapour, gassy and hybrid reactive systems is a feasible method. With its help, the development of runaway scenarios can be avoided. However, a very important obstacle for investigations of exothermal reactions seems to be the lack of case-specific reaction kinetic data.

6

Modelling of the Passive Trip System

6.1 Numerical modelling

In parallel to the experimental demonstration of the feasibility of the system, a computer program was also written. This serves**,** amongst other things, to optimise the important system parameters such as the set-point pressure of the bursting disc, the diameter of the cooling coil and the quantity of the coolant according to the reaction in question. In order to build the mathematical model of the passive trip system, a set of energy and mass balance equations were written in order to state the fundamental aspects of the program used to simulate the system. The program had been developed focusing mainly on the dynamics of an exothermal reaction and dynamics of the heat transfer from the reaction to the cooling liquid. Depending on the reaction type and their products, the system consisted of five or six first order non-linear differential equations. The description of the mathematical model is presented in **Appendix D**. The program can easily be adapted to any other reactor configuration and size if the necessary modifications are introduced.

6.1.1 Comparison – Experiments vs. Modelling

In order to optimize the functioning of the passive trip system and to verify the experimental results, the simulations were carried out using a computer program. **Figures 6.1** and **6.2** present the comparison of numerical and experimental analyses. The first reaction investigated is the esterification of acetic anhydride with methanol and the second one the decomposition of hydrogen peroxide. The description of both processes was presented in **Chapter 5**. The process parameters for numerical simulations are presented in **Appendix D**, **Table 10.3**.

Some assumptions were made in the development of a mathematical model to describe the dynamics of batch reactor and cooling process behaviour. First of all, it was assumed that the reactor was perfectly mixed. The physical parameters of reactants and products, such as density, viscosity or specific enthalpy were assumed to be constant. The parameters regarding heat transfer such as heat conduction were found in VDI-Heat Atlas **[56]**. Assuming that vapour is in equilibrium with liquid, partial pressures of reactants and products were calculated using the following formula:

$$P_i = P_i^0 \cdot \alpha_i = P_i^0 \cdot \gamma_i \cdot x_i \tag{6.1}$$

where P_i is the partial vapour pressure of component i (mmHg), $P^0{}_i$ is the vapour pressure of component i (mmHg), α_i is the activity of component i, γ_i is the activity coefficient of component i and x_i is the mole fraction of component i in the liquid phase.

Afterwards the Clausius-Clapeyron equation was used **[57, 58]**. This relationship can be less accurate at very low temperatures **[59]** but since the temperatures during runaway simulations are high, it can be applied to the passive trip system.

$$\frac{d \ln P_i}{dT} = \frac{\Delta H_i}{R \cdot T^2} \tag{6.2}$$

where T is the temperature (K), ΔH_i is the enthalpy of vaporization of component i (kJ/mol), and R is the gas constant, 8.314 (J/mol K).

Figure 6.1 presents experimental and model calculations results for the esterification reaction.

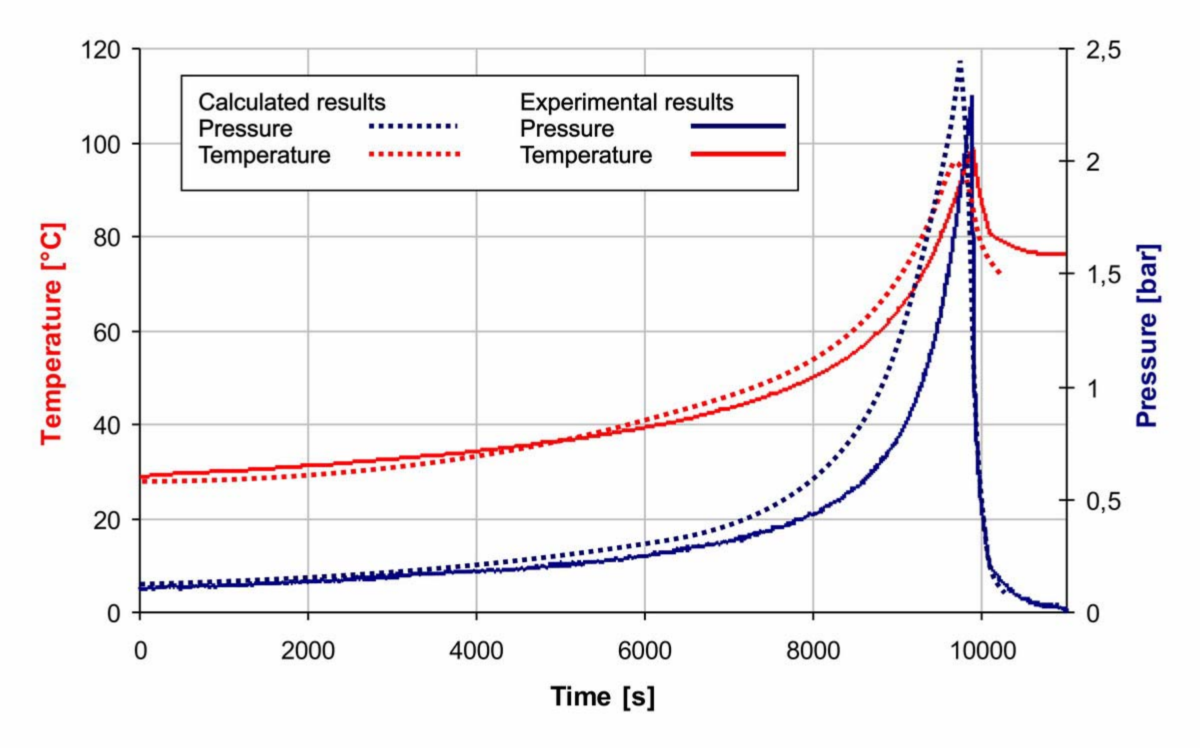

Figure 6.1 *Comparison of experimental and calculate results for the esterification reaction*

It can be seen that there is some discrepancy between the simulation trends and the experimental results. The magnitude of the initial pressure and temperature increase observed in the experiments is less than that in the simulations. A vital role was played here by kinetics, which was adopted from the other authors **[50], [51], [52], [53]**. Nevertheless, the overall agreement at the end of the simulation is very good, despite discrepancies in the initial phase. The mathematical model can be considered adequate for the purposes of the passive trip system simulations. In both cases, the emergency cooling system responded at the same pressure and temperature level, but not at exactly the same time. The introduction of case-specific kinetic data and correction factors for heat losses would improve the evolutions of pressure and temperature. The results of the laboratory-scale experiments were found to be quantitatively consistent with the simulated temperature-time and pressure-time curves.

Figure 6.2 shows the decomposition of 6% hydrogen peroxide solution without a catalyst. It can be observed that the pressure increases linearly and temperature exponentially and that both the numerical temperature and pressure increase at a slightly faster rate than the experimental one.

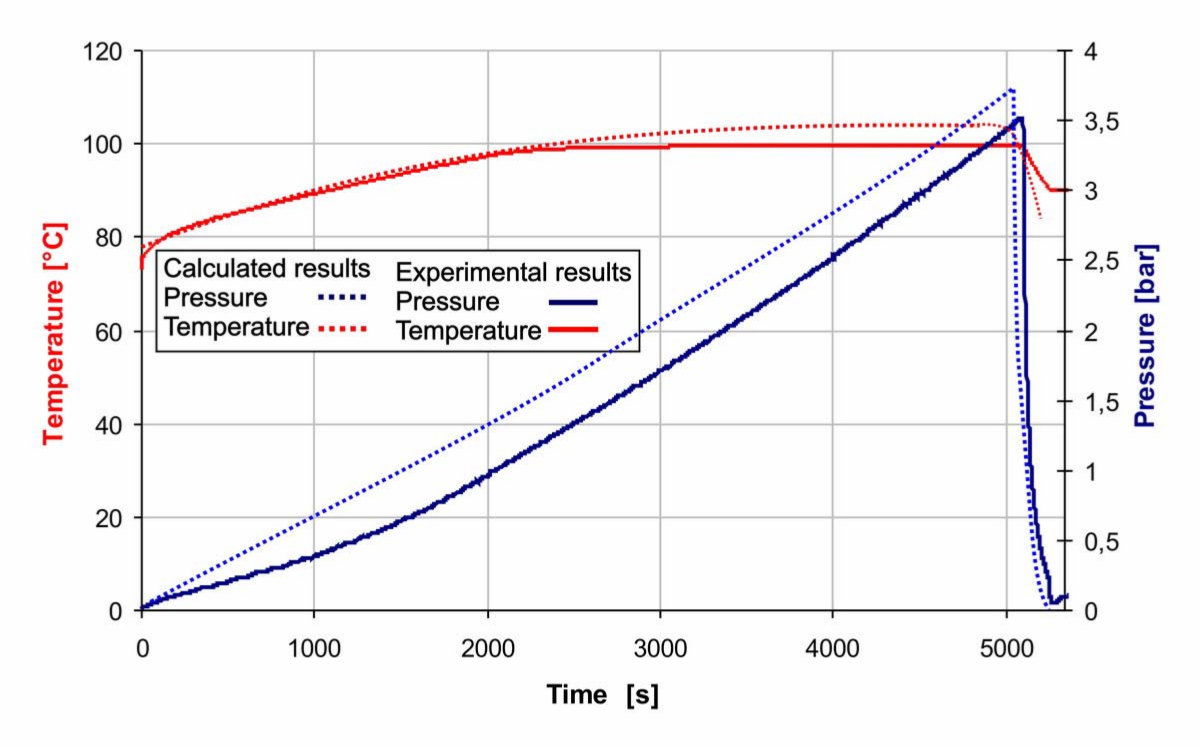

Figure 6.2 *Comparison experiment vs. model calculations for the decomposition of hydrogen peroxide*

To conclude, the results of the laboratory-scale experiments were found to be quantitatively consistent with the simulated temperature/pressure-time curves. In order to obtain an accurate model, many considerations had to be fulfilled. Different parameters for the reaction and the system had to either be calculated or found in existing literature. Nevertheless, good results can also be obtained only from using approximated data.

6.1.2 Possible modifications in the system

The operation of the passive trip system depends on many design and process parameters which can determine whether or not the trip will be successful. The computer program allows variations of these parameters in order to optimize its design. The most important parameters are:

- the capacity of emergency cooling tank (coolant quantity),
- the cooling coil dimension (length, diameter, wall thickness, material, geometry),
- the relief devices characteristic (set pressure, diameter), and
- the coolant characteristic (type, temperature).

Some of these parameters, such as the cooling coil dimension or coolant type, were fixed but all of them could be varied using the FORTRAN program. The variations of parameters such as the coolant quantity, activation pressure of trip system, cooling coil length and diameter, and their influence on temperature and pressure history are presented below, see **Figures 6.3-6.10**. The esterification of acetic anhydride as a very slow reaction was also investigated.

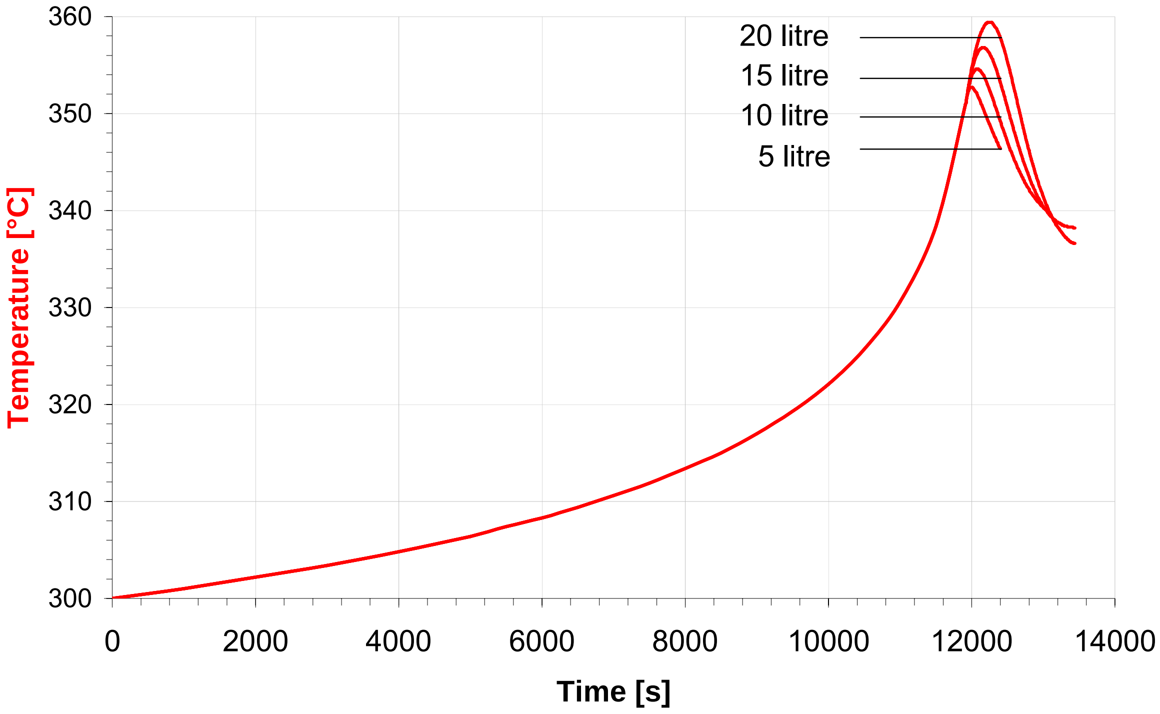

Figure 6.3 *Temperature as a function of time for different coolant quantities*

The passive trip system responded at a pressure of 1.6 bar. As shown in **Figure 6.3** the effectiveness of cooling increased as the amount of water increased. The reactor contents can already be effectively cooled down by the use of 10 litres of coolant. The next figure highlights the pressure history for the same variations. It can be observed that the pressure peak is higher in the cases where more coolant is applied. It can be easily explained in that more coolant means that the fluid takes longer to go through the cooling system until the emergency cooling tank is empty and the ambient pressure reached. Of course, parallel to the passive trip system operation, the reaction progresses, thus increasing pressure and temperature.

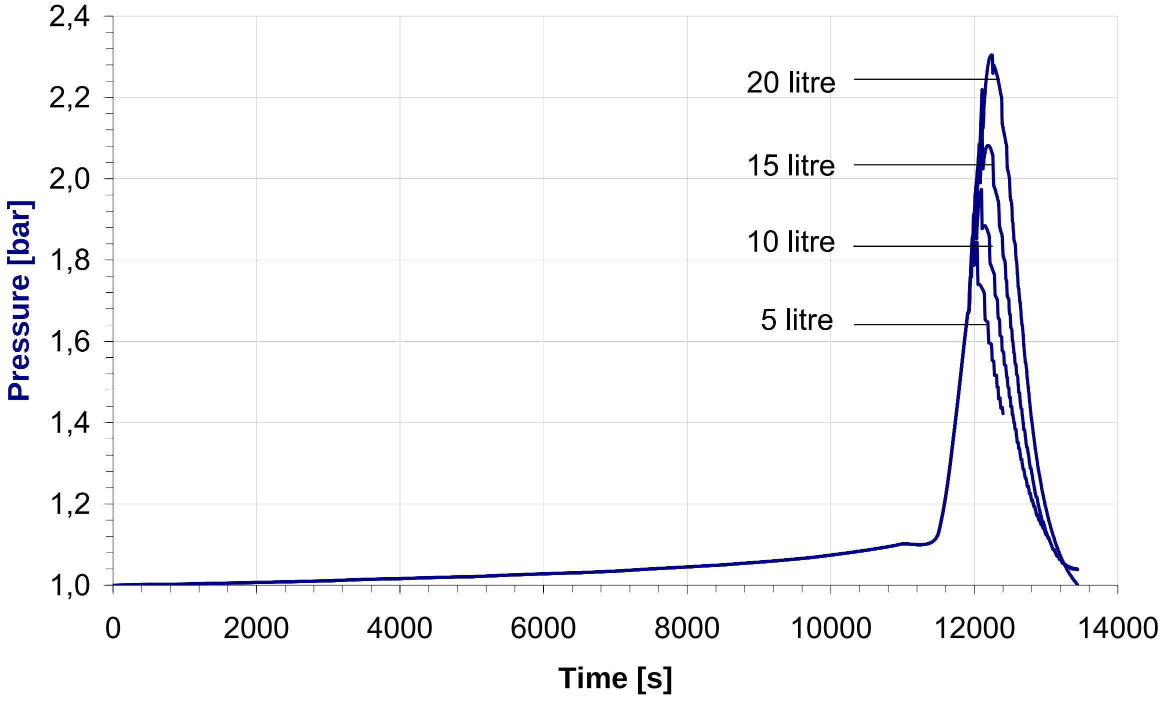

Figure 6.4 *Pressure as a function of time for different coolant quantities*

In **Figures 6.5** and **6.6** the variations of activation pressure for the system are presented.

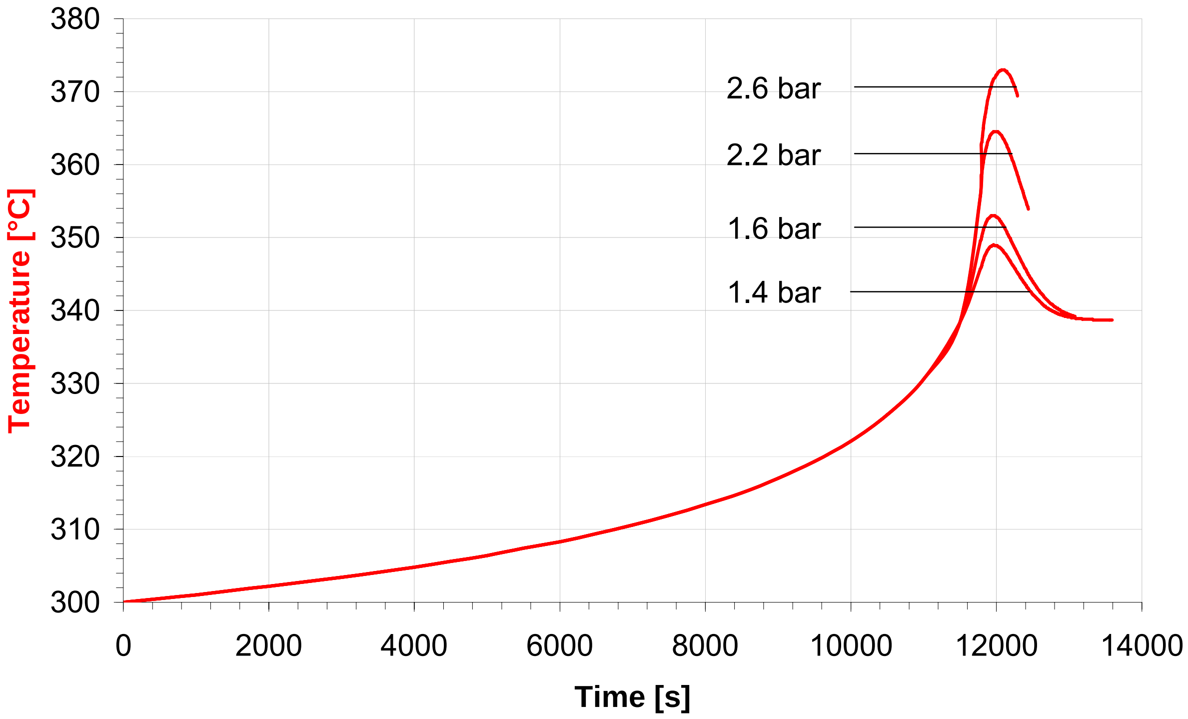

Figure 6.5 *Temperature as a function of time for different triggering pressure setpoints*

The main conclusion is that for higher activation pressures the velocity of coolant can be too high and hence the consumption of the coolant too fast in order to stop the runaway. The system seems to be most effective in the range of 1.4 - 2.2 bar.

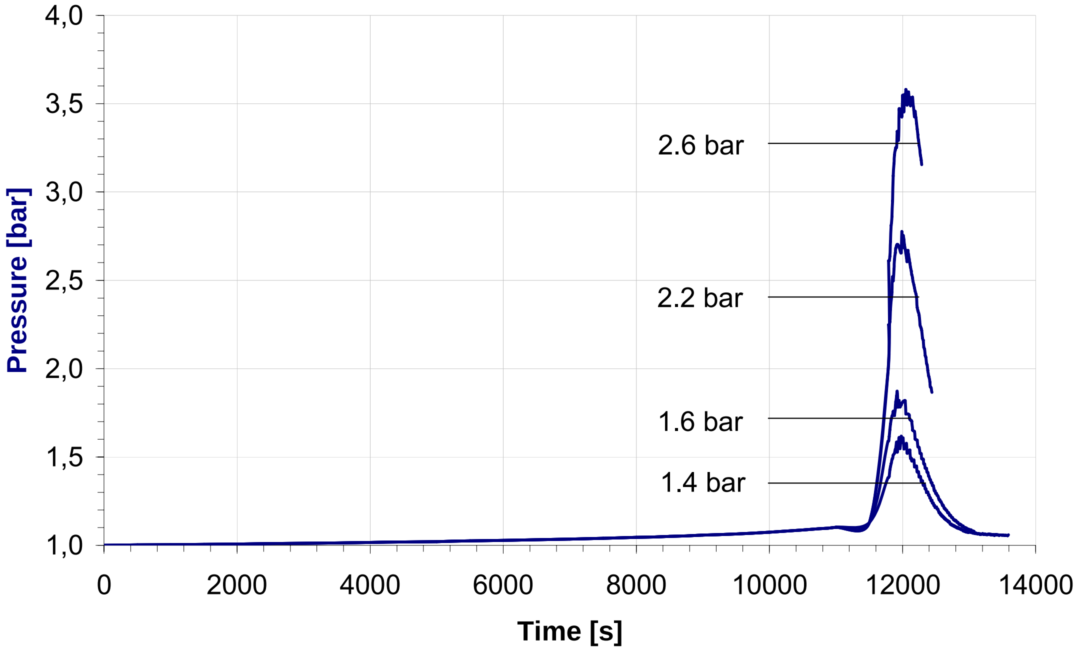

Figure 6.6 *Pressure as a function of time for different triggering pressure setpoints*

The next varied parameter was cooling coil length (c.f. **Figures 6.7** and **6.8**).

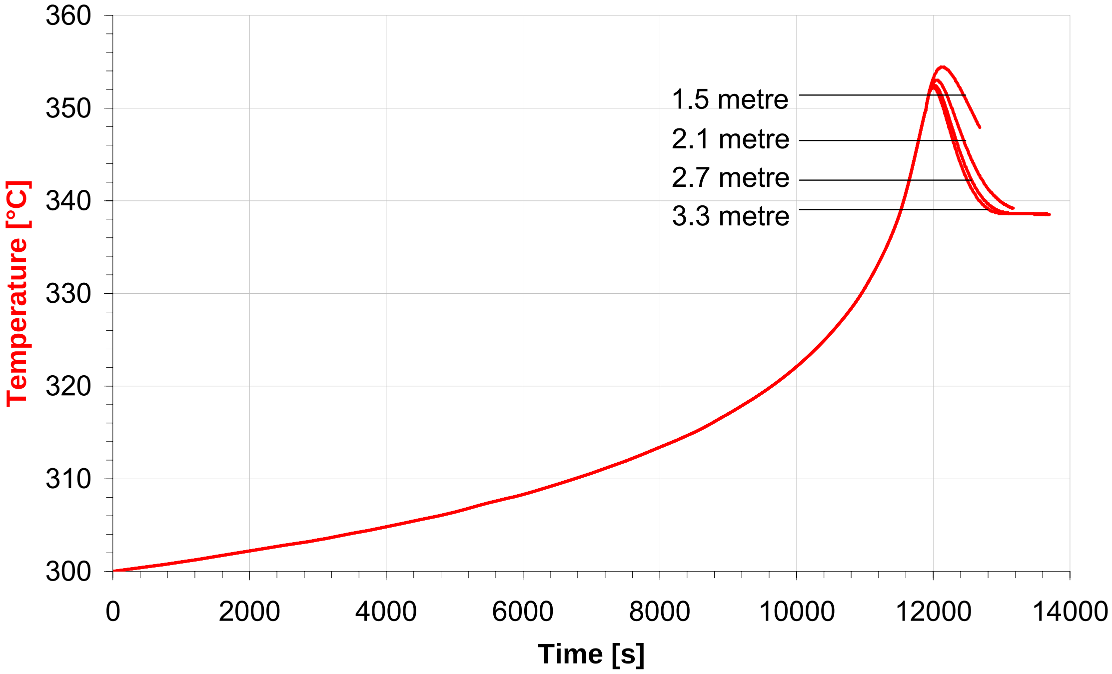

Figure 6.7 *Temperature as a function of time for different cooling coil lengths*

A longer cooling coil means a larger heat transfer surface and therefore better cooling effect. For ten litres of coolant, a cooling coil longer than 2 metres seemed to be a good choice. Both the temperature and pressure were sufficiently reduced.

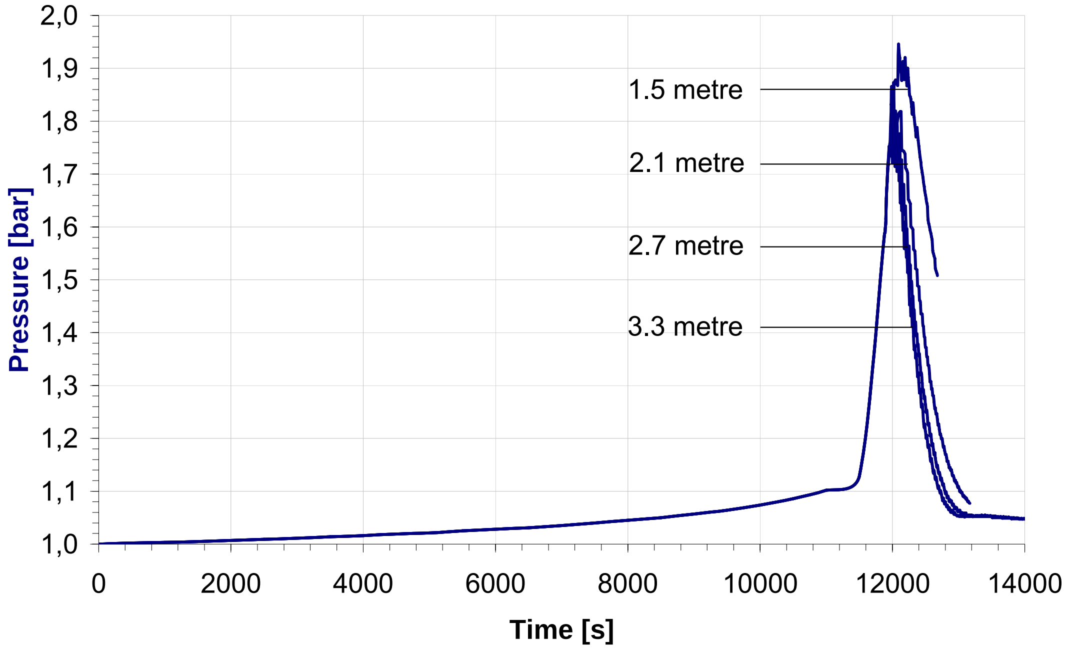

Figure 6.8 *Pressure as a function of time for different cooling coil lengths*

The diameter of a cooling coil has tremendous influence on the cooling efficiency, see **Figures 6.9** and **6.10**.

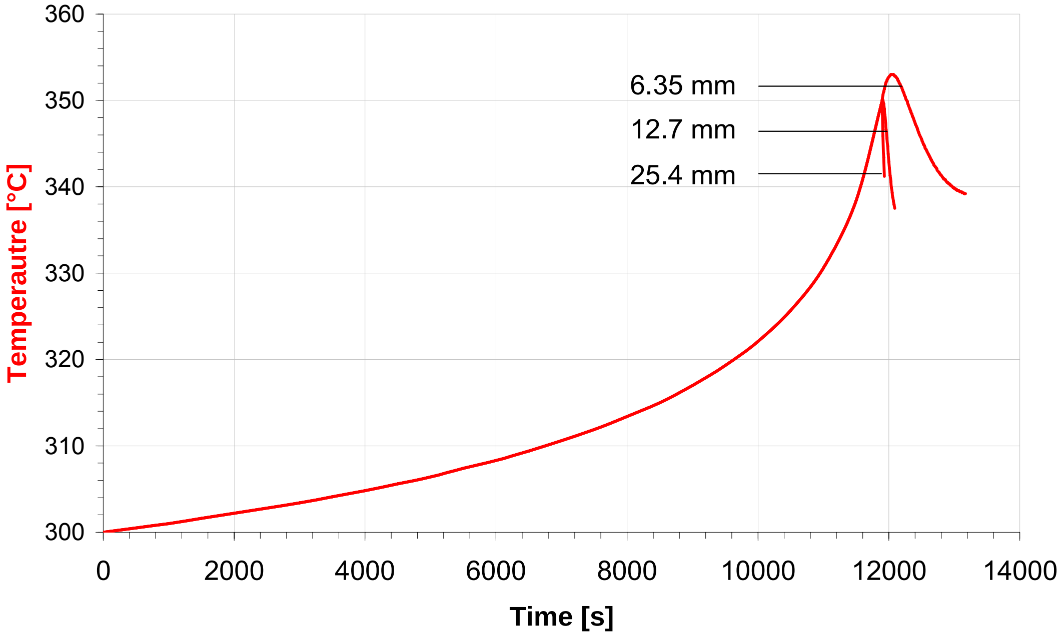

Figure 6.9 *Temperature as a function of time for different cooling coils diameters*

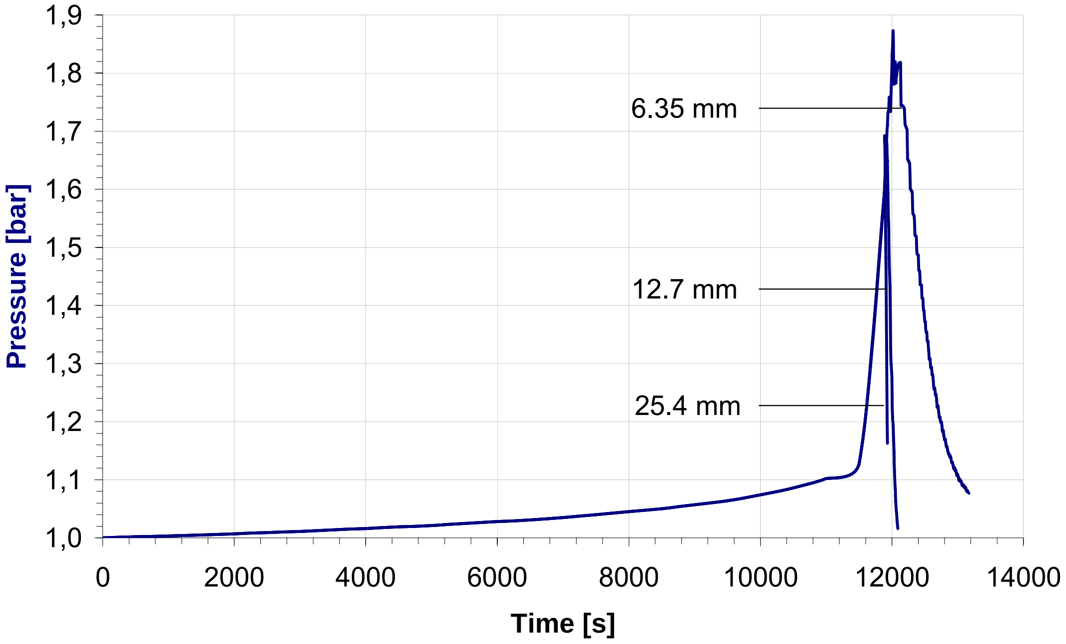

Figure 6.10 *Pressure as a function of time for different cooling coil diameters*

It can be seen that for too big diameters the cooling effect decreases. This is the result of a very high mass coolant flow. The best choice seems to be the cooling coil with a diameter of 12.7 mm. In this case, the response time is very good and it does not limit the end pressure and temperature reached. For the smaller diameter of 6.35 mm, cooling takes longer but, nonetheless, the end temperature is still higher than in the case before.

The FORTRAN program allows the variations of many other parameters such as:

- the temperature at the beginning of reaction,
- the pressure at the beginning of reaction,
- the temperature of coolant,
- the concentration of the reactants,
- the filling level of the reactor,
- the number of cooling coils.

The variations of these aforementioned parameters enable one to find the optimum design.

The experimental results indicated that the activation pressure of the passive trip system was the most important parameter for the success of a trip in controlling a runaway.

6.2 Theoretical application of the passive trip system

The passive trip system was investigated both experimentally and numerically at laboratory scale but, since its intended application is to large-scale reactors, a program able to simulate the real conditions in the industrial scale was also written. The Seveso batch plant for the manufacture of 2,4,5-trichlorophenol (TCP) from 1,2,4,5-tetrachlorobenzene was found to be a good application **[60, 61]**. It was adapted to the problem of reactor trip in **[62].** If the passive trip system is able to stop such a runaway reaction, which sparked the first campaign about the safety of process plants 32 years ago, this would be the best proof of its feasibility.

6.2.1 Process description

2,4,5 Trichlorophenol is used for manufacturing herbicides, antiseptics or as a fungicide in paper and pulp mills. The process used for its production is carried out in a batch reactor at a pressure of approximately 19 bar using methanol as a solvent.

A total amount of 1400 kg of the feed, 1,2,4,5-tetrachlorobenzene (TCB), is suspended in a mashing-tub together with 3.8 m^3 of methanol (CH_3OH) and 0.05 m^3 of sodium hydroxide. The suspension is introduced into the reactor and heated to 141°C. After that, a total quantity of 0.775 m^3 of a 50% aqueous solution of sodium hydroxide (NaOH) is added to the process over a time period of 60 minutes. The subsequent time for reaction amounts to 13.5 hrs. The reaction is exothermal and is held at a temperature of 155°C by a cooling system once it has been started up by heating the mixture with steam of 156°C.

The initial volume of the reactor contents amounts to 4825 l reaching 5600 l after the addition of the sodium hydroxide lye, which is fed into the reactor at a temperature of 25°C.

It is well known that during the process the highly toxic dioxin (TCDD) is produced, albeit in minute quantities, as long as the nominal range of the reaction parameters is maintained. A deviation of the reaction parameters was the cause of the Seveso accident **[63]**, in which an estimated quantity between 0.45 and 3 kg of TCDD was released into the environment.

The reaction network of the important steps (up to the formation of tetrachlorophenolate) is shown in **Figure 6.11**.

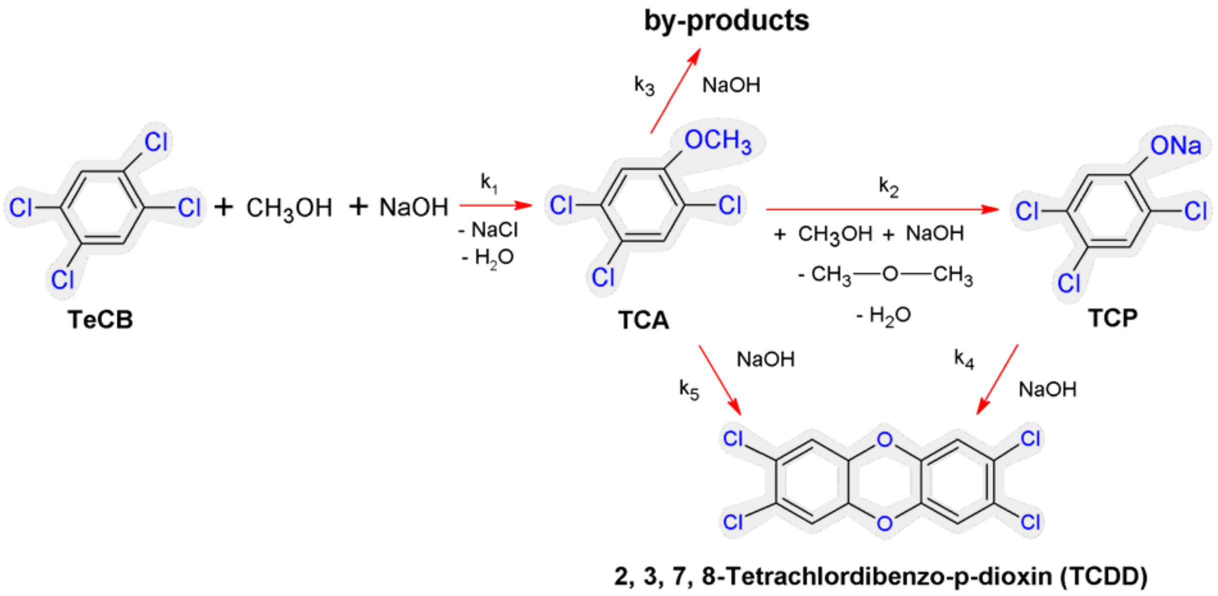

Figure 6.11 *Reaction network for the synthesis of TCP according to the Boehringer process* **[60, 61]**

The parameters required for describing the reactions mathematically are given in **Table 6.1**.

Table 6.2.1 *Kinetic data for the reactions of* ***Figure 6.11***

Reaction i	$\Delta H_{R,j}$ in kJ/mol	k_i (428 K) in $m^3/(mol\ s)$	$E_{a,j}$ in kJ/mol
1	-112	$2.17 \cdot 10^{-7}$	64.8
2	-50.5	$7.70 \cdot 10^{-8}$	146.5
3	-50.5	$7.92 \cdot 10^{-9}$	194.3
4	not determined	$7.90 \cdot 10^{-14}$	240
5	not determined	$2.70\ 10^{-13}$	220

The reaction network and parameters stem from co-operation of the authors of **[60, 61]** with the Boehringer Company. Simulations based on them agree with the experimental results obtained in a 10 l laboratory reactor and values measured in production as shown in **[60, 61]**. The substances involved in the process and their relevant properties are given in **Table 6.2**.

Table 6.2 *Substances of the process and relevant properties ([a] assumed values; [b] calculated according to [65], [c] NaOH only)*

No. i	Substance	Chemical formula	Molar mass M_i [kmol/kg]	Heat capacity c_p in J/(kg K)
1	1,2,4,5 Tetrachlorobenzene (TeCB)	$C_6H_2Cl_4$	215.9	937.9
2	2,4,5 Trichloroanisole (TCA)	$C_7H_5Cl_3O$	211.4	953.3[b]
3	2,4,5 Trichlorophenolate (TCP)	$C_6H_2Cl_3ONa$	219.42	884.8[b]
4	2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD)	$C_{12}H_4Cl_4O_2$	321.97	889.9[b]
5	Miscellaneous by-products	-	200[a]	700[a]
6	Aqueous solution of sodium hydroxide (50%)	$NaOH+H_2O$	40.0[c]	3274.0
7	Methanol	CH_3OH	32.04	2541.0

6.2.2 Passive trip system simulations

The process model described in **[60, 61]** is used. The reactor model was extended in [62] by an operational cooling and heating system and its control. This extended version forms the basis of the present treatment. The underlying concept is that of a well stirred reactor **[64]**. The resulting system of first-order differential and algebraic equations is given in **Appendix F**. It is solved by a second order Runge-Kutta scheme with adaptive time steps.

The passive trip system described in **[42]** was applied to this reactor and a mathematical model of the trip system **[Appendix E]** was combined with mathematical model of Seveso reactor **[Appendix F]**.

In order to investigate the feasibility of the trip function, the failure of the operational cooling system was assumed. The design parameters of the passive trip system such as the quantity of coolant, pressure set-point for trip activation, time of cooling failure and size of cooling coil were varied in order to optimize the emergency cooling operation. Some results of those simulations are presented in figures below.

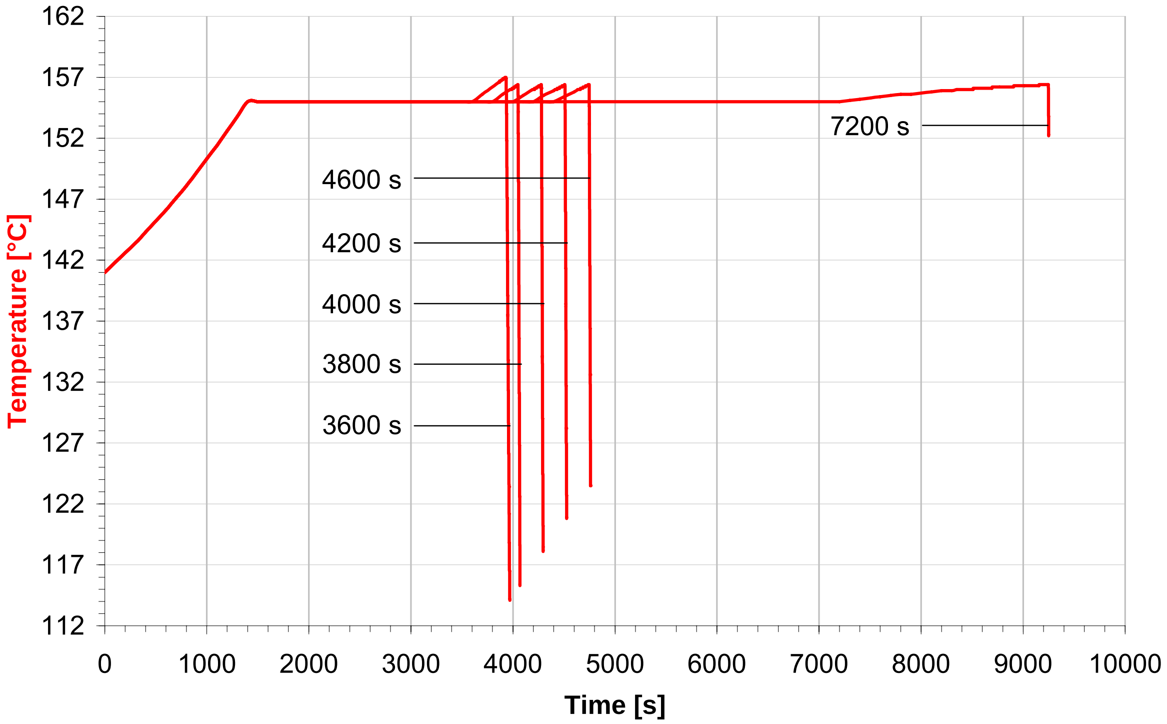

Fig. 6.12 *Temperature profiles for different moments of cooling failure (time after start of reaction)*

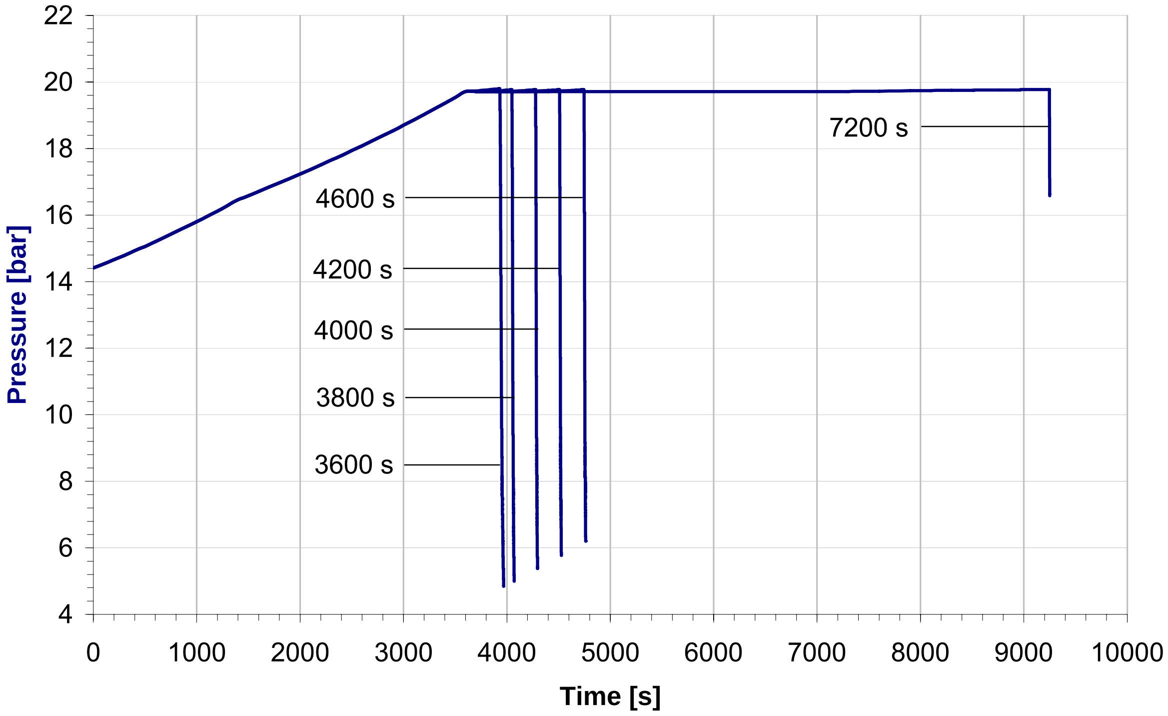

Fig. 6.13 *Pressure profiles for different moments of cooling failure (time after start of reaction)*

The passive trip system is most effective 1 hour after the start of reaction. Its effectiveness decreases with the time and consequently its initiation 2 hours after the start of reaction would not stop runaway reaction.

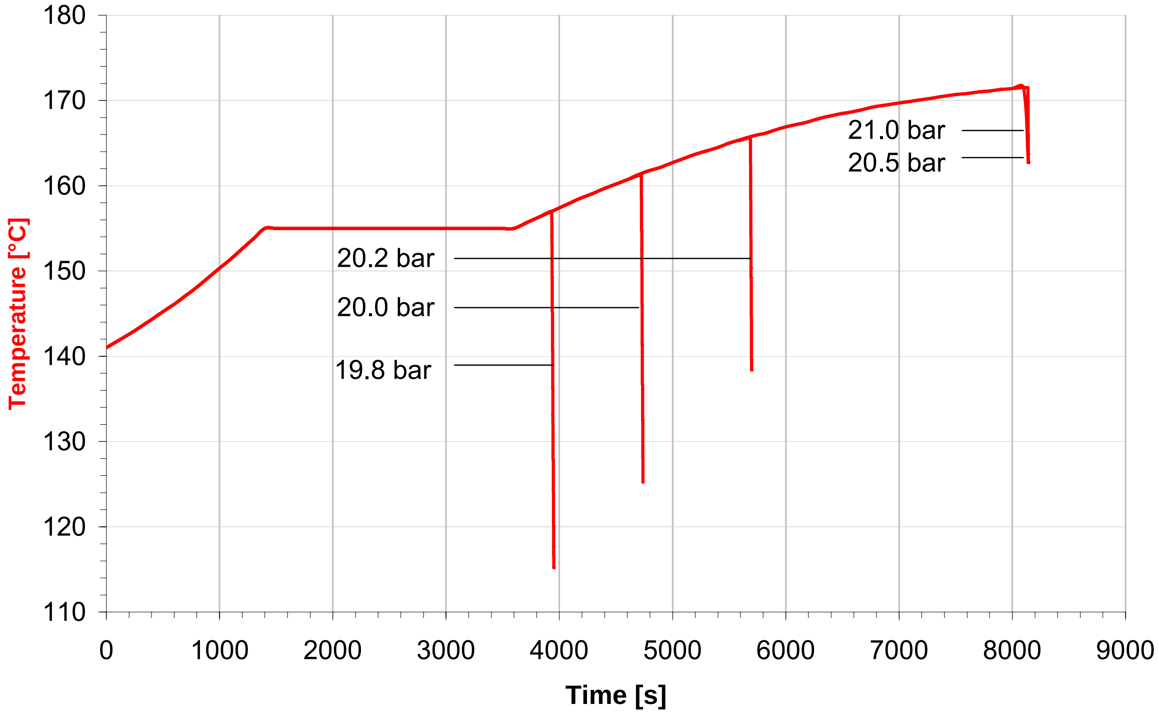

Fig. 6.14 *Temperature profiles for different set points of bursting device*

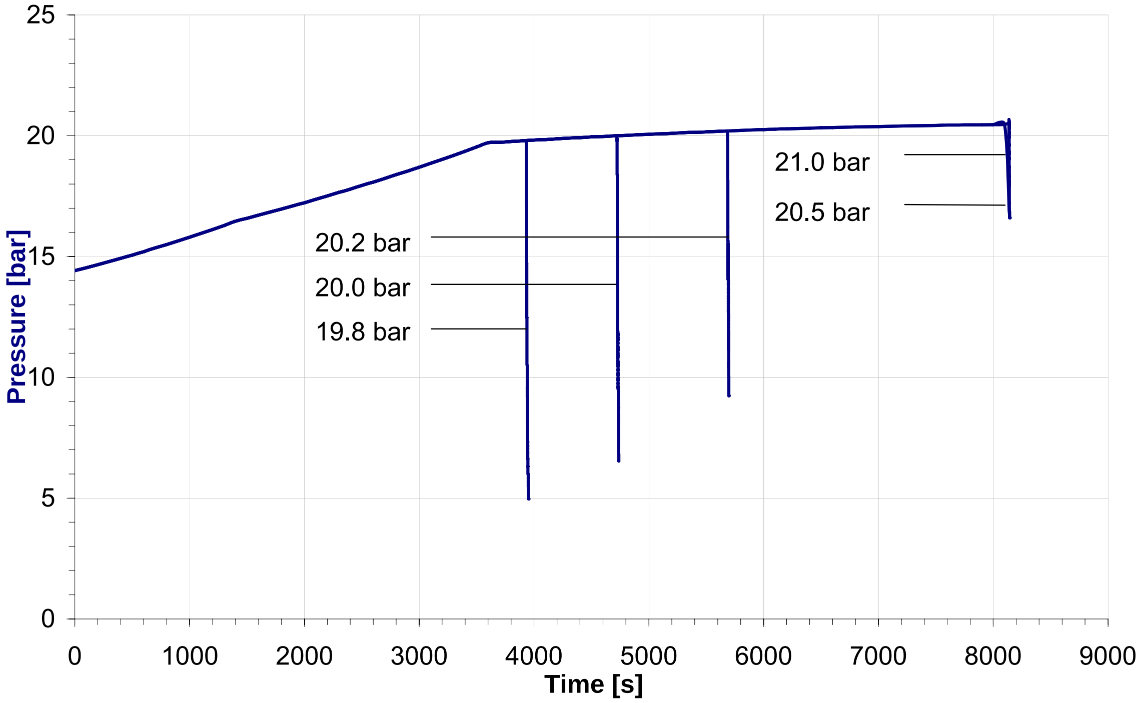

Fig. 6.15 *Pressure profiles for different set points of bursting device*

The system seems to be most effective at a set-point pressure of 19.8 bar but this efficacy decreases rapidly at higher pressures.

The feasibility of the passive trip system application to the SEVESO batch plant was confirmed. The system would have been able to reduce both the temperature and pressure to safe levels, thus avoiding the evolution of a runaway reaction. The most important issue concerning the application of the passive trip system to pilot-scale or large-scale reactors is the effect of scale. The fact that the mass of the fluid increases linearly with the reactor volume, but the heat transfer area does not, has to be taken into account at the simulation and design stage. In scaling up from the laboratory 10 litre batch reactor to the industrial 8000 litre reactor, there were some significant differences such as the relative heat loss, agitation efficiency or the pressure set-point of the bursting disc.

6.3 CFD modelling of the passive trip system

Due to the hazardous nature of runaway reactions, some factors can not be exactly studied with laboratory scale experiments. Furthermore, the modelling of such systems with a zero-dimensional code does not take into account all of the important factors. Recent developments in CFD (computational fluid dynamics) allow for carrying out virtual experiments in three dimensions. There is not much commercial CFD software which specializes in the modelling of chemical reactors but the most popular are: Comsol **[66]** and Fluent **[67]**.

CFD is a method of predicting fluid flow, heat and mass transfer, chemical reactions and other related phenomena (e.g. boiling, vaporization) by solving a set of appropriate partial differential equations that describe these processes – mass, momentum and energy balances. CFD simulations are very useful for modelling and designing processes, particularly in the industrial scale **[68]**. The work on CFD-models consists mainly of three steps: preprocessing, solution, postprocessing and will be presented in this sequence.

6.3.1 Preprocessing – MixSim, Gambit and TGrid

The commercial grid-generation tools MixSim 2.0, Gambit 2.2.30 and TGrid 3.6.8 (Fluent Inc., USA) have been used to create the geometry of the passive trip system and generate the grids. The preprocessing consists of four main steps:

1. Building of the reactor, stirrer, and cooling coil geometries
2. Verification of the above mentioned geometries
3. Volume generation
4. Mesh generation

The geometry consists of a flat-bottomed cylindrical vessel (diameter D equal 0.16 m, and height H equal 0.45 m) without baffles, which is agitated by a stirrer. The emergency cooling process is performed by a cylindrical cooling coil.

About 300.000 computational cells are applied for the simulation. It must be pointed out that an adequate number of cells is crucial for the accuracy of CFD calculations. **Figure 6.16** presents the technical drawing of the batch reactor under investigation. The geometries performed in MixSim, Gambit and TGrid are presented in **Figures 6.17 – 6.18**.

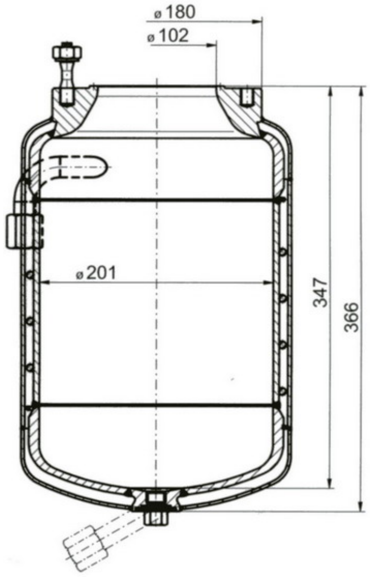

Fig. 6.16 *Reactor vessel – technical drawing*

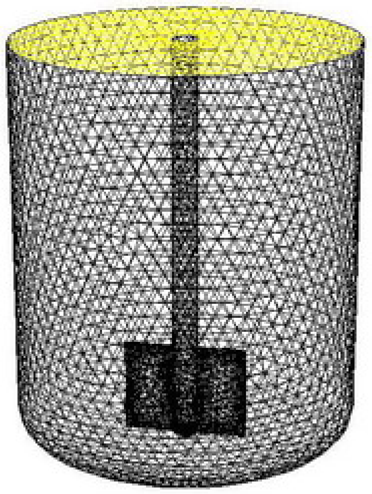

Fig. 6.17 *Reactor vessel - MixSim*

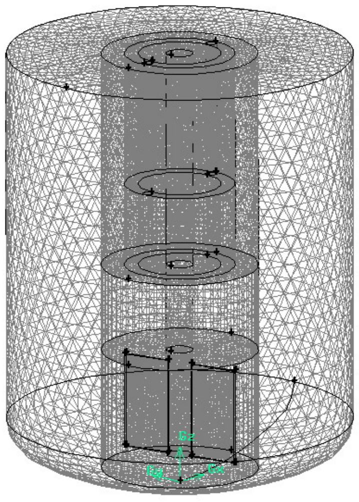

Fig. 6.18 *Reactor vessel - Gambit, TGrid*

The geometry of the cooling coil has been simplified, see **Figures 6.19-6.20**. The grids of the cooling coil placed close to the connections between pipes and a tube were notably refined in order to ensure good quality of the grids, see Figure **6.21.**

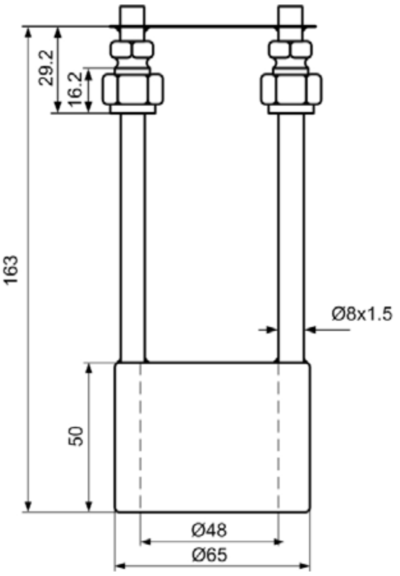

Fig. 6.19 *Cooling coil – technical drawing*

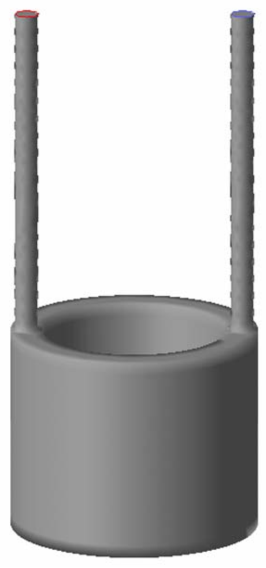

Fig. 6.20 *Cooling coil*

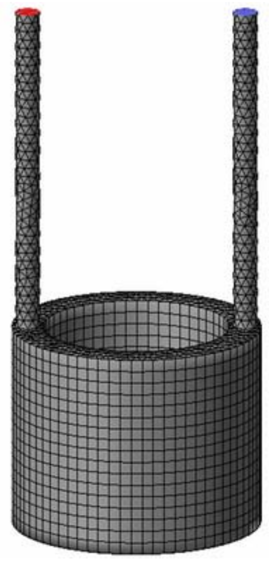

Fig. 6.21 *Cooling coil - grids*

Based on several trials, it was established that the number of cells for each grid and their quality is sufficient for our model. In the next step the geometry of the passive trip system was exported to the CFD software Fluent.

6.3.2 Solution – Fluent

Fluent solutions are transient and thus require a time stepping procedure to solve the problem. Subsequently each time step needs to be converged in flow velocity and especially energy balance. The stability of the solution results in very small time steps, thus requiring a lot of them. The "Reynolds stresses" appearing in a momentum balance equation have been modelled by employing the Bussinesq hypothesis and the standard k-ε turbulent model **[69, 70].** The stirrer movements were modelled by using a "multiple reference frame" (MFR) approach. The finite volume method was employed and CFD simulations were carried out. Since the reactor and its equipment are symmetrical and the geometry was simplified by cutting it off, significant reduction of computing time could be achieved. For the esterification reaction of acetic anhydride with methanol the user defined function (UDF) was created. The kinetic expression and other related data were adopted from earlier studies. The properties of components and products were found in **[71]**.

6.3.3 Postprocessing

The elaborated CFD model was built in order to simulate an operation of a laboratory scale reactor equipped with a passive trip system in both normal operation and operation after operational cooling failure. Due to the high computational requirements of the models applied to the problem, only flow and mixing simulations were performed. Nevertheless, this approach presents a good basis for further investigations of the model of the passive trip system.

Modelling of such complex systems as this one is a very difficult task, since the physics and the computational resources are still very limiting and computational requirements are high. The complexity of the problem results from:

- complex geometry (cylindrical reactor, cooling jacket, cooling coil, stirrer)
- flow generated by a rotating stirrer
- heat transfer combined with a flow (cooling coil, cooling jacket)
- two-phase flow
- phase change
- chemical reaction (exothermic)

The results presented in this chapter can be very useful for continuing and extending the application of CFD to passive trip systems and the approach used here can also be generalized for different reacting systems and different reactor geometries. Approximations employed using the MRF method lead to very good results, which are presented in **Figures 6.22 – 6.23.**

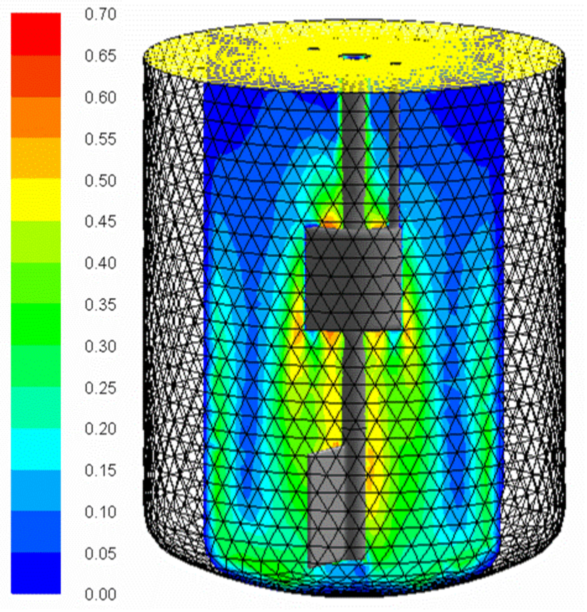

Fig. 6.23 *Contours of velocity magnitude (m/s) – 3D model*

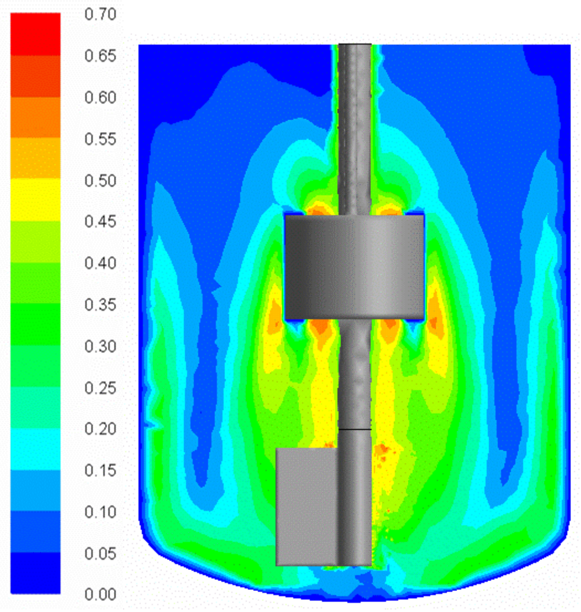

Fig. 6.24 *Contours of velocity magnitude (m/s) – 3D model*

The results show that placing the cooling coil above the stirrer has a considerable influence on the mixing process, see **Figures 6.24 – 6.25**.

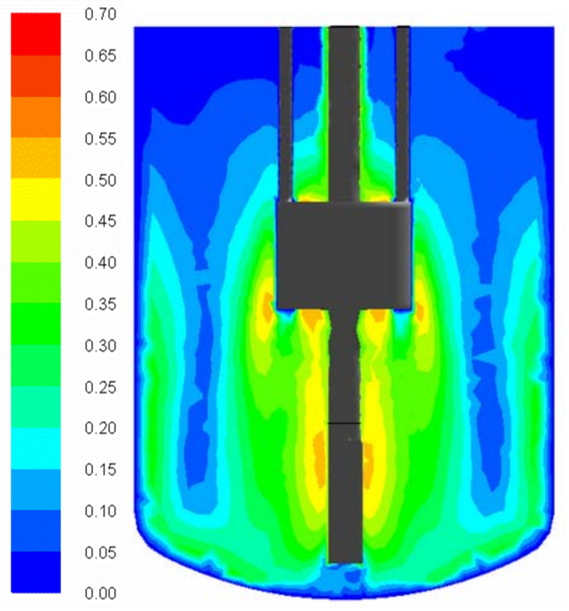

Fig. 6.24 *Contours of velocity magnitude (m/s) – 3D model*

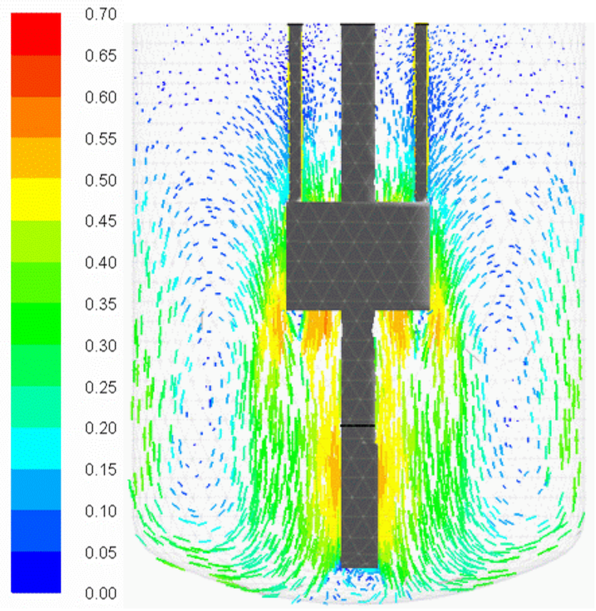

Fig. 6.25 *Velocity vectors colored by velocity magnitude(m/s) – 3D model*

7

Summary, conclusions & outlook

7.1 Summary

The passive trip system was investigated theoretically, experimentally and numerically. In the beginning, in **Chapter 1**, the demand for investigations on safety systems for batch and semi-batch reactors was examined. The statistical study revealed that the topic still requires a lot of research, especially due to the relatively large number of accidents involving these reactors.

Moreover, hazards related to chemical batch and semi-batch reactors, such as runaway reactions, were investigated in **Chapter 2**. In addition to this, safety systems and safety strategies such as passive, active or inherent were discussed in detail and a layer of protection analysis (LOPA) was identified as a suitable tool to achieve the safe operation of chemical reactors processing exothermic reactions.

In the next step, the reliability study of the most frequently used chemical reactor trip systems for chemical reactors was carried out. Three active trip systems were compared with the passive one. The passive system demonstrated the lowest unavailability ($6.1 \cdot 10^{-5}$) and the best technical properties, as shown in **Chapter 3**.

Chapter 4 presented the working principle and technical design of the PTS. For its simulation, visualisation and documentation, a three-dimensional model was used. It was created in 3D Studio Max software and then an animation which presented the working principle and the experimental procedure was prepared. For the aim of teaching, a video presentation with a real experiment was also made.

In addition to the creation of a computerised model, the system was also built and laboratory investigations were carried out, see **Chapter 5**. Before each investigation, preliminary calculations were performed. In the course of the experiments, the feasibility of applying the passive trip system to different chemical systems such as gassy, vapour and hybrid was examined and the results proved that the system is able to halt all of the above mentioned reactive systems.

The preparation of these experiments was carried out using a zero-dimensional program written in FORTRAN. The crucial design and process parameters were optimized and a comparison between experimental and numerical results was carried out. The results of the laboratory-scale experiments were found to be quantitatively consistent with the simulated temperature-time and –pressure curves. Variations of different parameters and their influence on the trip function were investigated. The results indicated that the set-point pressure of the bursting disc is an important parameter for the success of a trip in controlling a runaway, as presented in **Chapter 6**.

Furthermore, the plausibility of applying the passive trip system to an industrial reactor was also investigated. A FORTRAN program was used to carry out a simulation of a process for the production of TCP. The main conclusion was that the passive trip system would have avoided even a major accident, such as that in Seveso, in 1976.

Finally, the CFD technique was applied to the modelling of the passive system. The commercial tools MixSim, Gambit and TGrid were used to create the geometry and a mesh of a reactor with a stirrer and a cooling coil. After that, the geometry was imported to the Fluent software. The simplified case of the mixing operation was defined and simulated.

The possibility of taking advantage of passive features, such as the natural driving force of gravity, the pressure build-up during runaway or the operation of bursting discs, were examined and the feasibility of the passive trip system was proved. It can potentially be applied not only in a laboratory or pilot scale, but also at an industrial scale. The scale up process is not a simple task but the use of modern simulation techniques makes this process more feasible.

7.2 Implications for industrial application

Some suggested industrial applications of the passive trip system include the following:

- batch and semi-batch reactors,
- storage facilities, and
- continuous reactors in series.

However, the most adequate applications are batch and semi-batch reactors. As already mentioned in **Chapter 1,** batch processes are most frequently involved in accidents compared to a continuous one.

During investigations on the topic many factors and parameters were taken into account. Some of them helped design the safety system and could potentially be very helpful in industrial applications. For instance, in order to increase the heat transfer parameter, helical coils are recommended. One of the main advantages in the use of helical coiled tubes lies in the fact that the considerable length of the tubing may be contained in a space saving configuration. Heat transfer coefficients and mass transfer coefficients are higher in helical coiled tubes than straight tubes. When fluid flows through a curved pipe, the presence of curvature generates the centrifugal force that acts at a right angle to main flow and results in secondary flow. The strength of the secondary flow depends on the curvature of the surface.

Furthermore, an application of other coolants than water would also influence a heat transfer coefficient. These factors can improve the functioning of the passive trip system and have to be taken into account at the scale up stage.

A fundamental issue in applying the passive trip system to industrial use is the scale up of the emergency cooling tank, cooling coil and reactor. Even a very small increase in the volume of the reactor can lead to an inadequate design of the cooling coil and the coolant tank. Consequently, the trip function will fail and an incident may occur. The problem arises from the fact that the amount of heat produced increases proportionally to the volume of the reactor content (m^3), whereas the cooling capacity varies in proportion to the surface of the cooling coil (m^2).

Due to economical and environmental factors, only water and a straight tube cooling coil were applied. Even so, the application of the aforementioned improvements will not create any crucial changes and, in laboratory-scale experiments, the influence of them is negligible.

7.3 Advantages of the PTS and future research

As already discussed in **Chapter 1**, many industrial accidents caused by chemical reactions still happen today in the process industries. In the aftermath of that, new additional technical measures, which are mostly active, have been developed and applied. Consequently, the growing complexity of the process installations, where more and more products are produced, became a huge problem. Here, a new solution for the protection of chemical reactors as an alternative to active systems was proposed and tested. It does not rely on an energy supply from outside, pump functioning or generally PLC systems and therefore is much more reliable. The essence of the passive approach is the avoidance of hazards in the case of runaway reactions. At present, the system is in successful operation in the safety laboratory at the Otto-von-Guericke-University. Passive trip systems have many advantages as compared with active ones, such as:

- higher availability (SIL 4),
- quicker response in time (dependent on runaway incipient point),
- huge sensitivity on deviation in the system,
- automatic response on deviation in the system,
- simplicity of the system (cheaper and easier maintenance),
- water ingress into reactor is not possible,
- high reliability performance (high reliability of bursting discs),
- since the pressure which produces the problem is used as a driving force it cannot fail.

These capabilities of the proposed solution provide the safety assurances needed at present for many installations worldwide. In spite of many advantages, the system has also some weaknesses, which have to also be presented. These are aspects such as:

- energy loss during operation, which is, however, partly enhancing mixing,
- longer pipes are needed,
- more space is required,
- the cost of additional tanks and pipes,
- the difficulties by dimensioning for different reactive systems (e.g. lack of reaction kinetic data).

Fortunately, these disadvantages are mostly related to equipment costs and the safety of a chemical reactor should not be compromised for economic reasons.

However, contrary to the passive system, active safety instrumented systems have many disadvantages:

- an increased number of shutdowns and start-ups,
- instruments may be susceptible to the weather conditions, such as water ingress or corrosion,
- high complexity (higher maintenance costs),
- adding safety systems may reduce the risk from specific hazards but creates an infrastructure which has a higher chance of an accident and exposes more people to its effects.

Despite the advantages resulting from this thesis, the passive trip system can still be improved. The most important issues which should be investigated in the future are:

- three-dimensional modelling of the reactor and emergency cooling for the purpose of optimisation,
- the development of the passive trip system integrated with the passive inhibition,
- the application of CFD for modelling of the passive trip system integrated with passive inhibition,
- the application of the other cooling coil types,
- the application of other coolants.

8

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9

Nomenclature & Abbreviations

Latin letters

A	cross section area	[m^2]
C	concentration	[$kmol/m^3$]
c_p	specific enthalpy	[kJ/(kmol K)]
D	diameter	[m]
E_a	activation energy	[kJ/kmol]
f_r	friction factor	[-]
G	wall thickness	[m]
H_v	heat of vaporization	[kJ/kg]
k_0	pre-exponential factor (2order)	[m^3/(kmol s)]
L	length	[m]
M	molar mass	[kmol/kg]
	motor	
m	mass	[kg]
n	number of moles, reaction order	[-]
N	number	[-]
Nu	Nusselt number	[-]
P	pressure	[Pa]
Pr	Prandtl number	[-]
P_{BD}	Activation pressure of BD	[Pa]
Q	heat output rate	[W]
r	rate of reaction	[mol/s]
R	universal gas constant	[kJ/(kmol K)]
Re	Reynolds number	[-]
Ro	density	[kg/m^3]

t	time	[s]
T	temperature	[°C]
U	overall heat transfer coefficient	[W/(m^2 K)]
V	volume	[m^3],
u	velocity	[m/s]
$\bar{u}$	time average unavailability	[-]
X	volume fraction	[-]

Greek letters

α	heat transfer coefficient	[W/(m^2 K)]
ΔHr	reaction enthalpy	[kJ/kmol]
ΔT_{ad}	adiabatic temperature rise	[kJ/kmol]
λ	heat conductivity	[W/(m K)]
λ	failure rate	[1/hr]
ν	stoichiometric coefficient	[-]
ρ	density	[kg/m^3]
θ	time interval between functional tests	[hr]

Indices

A	limiting component
abs	absorbed
ad	adiabatic conditions
atm	atmospheric
CC	Clausius-Clapeyron
ch	characteristic
c	cooling, cooling coil
f	final
g	gaseous products
v	vapour products
G	thickness
i	component i

in	inlet
L	liquid phase
max	maximum
out	outlet
pr	process
R	reactor
rmv	removed
R	chemical reaction
s	parameter at the start
tot	total
v	vapour
0	initial or reference state

Abbreviations

AV	automatic valve
BD	bursting disc
BR	batch reactor
CSB	Chemical Safety Board
CFD	computational fluid dynamics
CSTR	continuously stirred tank reactor
DA	Damkoehler number
DIERS	Design Institute for Emergency Relief Systems
DV	discharge valve
ECST	emergency coolant supply tank
HSE	Health and Safety Executive
I	relay
LG	level gauge
LOPA	Layer of Protection Analysis
MAHB	Major Accident Hazard Bureau
MARS	Major Accident Reporting System
MFR	multiple reference frame
P	pressure switch
PSH	pressure switch high

PSHH	pressure switch high high
PTS	passive trip system
SAL	switch alarm low
SAH	switch alarm high
SBR	semi-batch reactor
SIL	Safety Integrity Level
SIS	Safety Instrumented System
SV	safety valve
TCB	1,2,4,5 - tetrachlorobenzene
TCP	2,4,5 - trichlorophenol
TCDD	2,3,7,8 – tetrachlorodibenzo-p-dioxin
TE	temperature sensor
TSH	temperature switch high
TSHH	temperature switch high high
TMR	time to maximum rate
UDF	user defined function
ZEMA	Zentrale Melde- und Auswertestelle für Störfälle und Störungen in Verfahrenstechnischen Anlagen, UBA, Berlin

10

Appendices

10.1 Appendix A – Common Accident Databases

Table 10.1 *List of common accident databases (Germany, EU Countries and USA) [3, 4]*

Data Source (a)	Organization	Years Searched	Description	Availability
KAS	Guides and reports adopted by the SFK and TAA	1999–Present	Includes fire and explosion incident reports	www.sfk-taa.de/ http://www.kas-bmu.de/
DECHEMA	Description of non reportable accidental events (near misses)	1978-present		http://www.dechema.de/deutsch/dechema/pages/dechge4.htm http://fach-for.dechema.de/sicherheitstechnik/deutsch/fa/ahag2/schaden/index.html
MARS	Information on major accident hazards	1982-Present	15 local databases in each Member State of the European Union	http://mahbsrv.jrc.it/mars/Default.html
ORPS	Chemical occurrences (events and conditions) reported at DOE facilities	1992- Present	Analysis of occurrences, causes, corrective actions, and lessons learned as well as some statistical analysis of chemical safety performance	http://www.dne.bnl.gov/etd/csc/
NTSB	Hazardous Materials Accidents - National Transportation Safety Board Reports	1997-Present	A list of hazardous materials accident reports	http://www.ntsb.gov/Publictn/Z_Acc.htm
FACTS (TNO)	FACTS, a database containing more than 22000 descriptions of serious accidents involving hazardous materials that caused, or could have caused,		Accident prevention by analyzing former accidents. Research on safety methods, accident mechanisms,	http://www.factsonline.nl/FRIENDS2006update/tabid/188/Default.aspx

	severe damage and danger		equipment, reaction of chemicals, emergency response and cost reduction Investigating the risks that are involved with the handling of hazardous materials	
USCG NRC	Data on release notifications of oil and hazardous substance reports to NRC or EPA regional offices	1982-Present	Extensive range of incidents, including those resulting in a chemical release from a reactive incident All states and localities included	http://www.nrc.uscg.mil/
OSHA IMIS	Records of workplace inspections, including those prompted by accidents where a worker is injured	1984-Present	Information from OSHA field inspections, a third party More accurate description of impacts on employees and contractors Keyword indexing allows for easy search and retrieval	www.dol.gov
EPA ARIP	Responses to questionnaires sent by EPA from facilities that have had significant releases; purpose is to learn about causes and consequences of hazardous material incidents	1986-Present	Supplements NRC reports for more significant events Additional information on causal factors, consequences, and company safety programs. Data are easily analyzed for common causes Includes all states and localities	http://yosemite.epa.gov/OSWER/Ceppoweb.nsf/content/ds-epds.htm
EPARMP Info	Data about chemical releases resulting in specific impacts covered under RMP regulation (40CFR 68)	1994-Present	Provides further information about major events involving specific listed chemicals More accurate data on impacts, causal factors, and corrective actions Includes all states and localities	http://yosemite.epa.gov/oswer/Ceppoweb.nsf/content/RMPoverview.htm

IChemE Accident Database	Reports about chemical incidents around the world from official government sources, the news media, and company reports	1980-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders Contains lessons learned from 3,000 incidents	http://www.icheme.org/she/accident_db.html http://www.environment97.org/framed/icheme/accident1.htm
HSE MHIDAS	Information taken from public domain sources worldwide; however, majority of the 7,000 incidents occurred either in UK or US	1985-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders	http://www.hse.gov.uk/infoserv/mhidas.htm
U.S. Fire Administration NFIRS	Response data submitted by local fire departments	1980-Present	Includes fire and explosion incidents with no/little release, incidents resulting in property damage only, and near-misses if fire department was called	http://www.usfa.dhs.gov/fireservice/nfirs/
CSB CIRC	Initial reports about chemical incidents around the world from official government sources, news media, and eyewitnesses	1998-Present	Scope is beyond incidents reported to or investigated by regulatory agencies or first responders includes domestic and international incidents	http://www.chemsafety.gov/circ/

(a) **KAS** = Commission on Process Safety; **DECHEMA** = Society for Chemical Engineering and Biotechnology; **ORPS** = US Department of Energy's Occurrence Reporting and Processing System; **NTSB** = National Transportation Safety Board; **FACTS** = Database for accidents with hazardous materials ;**MARS** = Major Accident Reporting System; **ARIP** = Accidental Release Information Program; **CIRC** = Chemical Incident Reports Center; **HSE** = Health and Safety Executive, United Kingdom; **IChemE** = Institution of Chemical Engineers; **IMIS** = Integrated Management Information System; **MHIDAS** = Major Hazard Incident Data Service; **NFIRS** = National Fire Incident Reporting System; **NRC** =National Response; Center; **RMP** = Risk Management Program;

10.2 Appendix B – Major accidents involving chemical reactive substances

Table 10.2 *Study of major accidents involving chemical reactive substances* ***[11]***

Accident	Chemical description	Main features of accident
001	Acid-base reaction; NaClO + acid waste	Tanks connected erroneously; blocked valve due to crystals formation
002	Ethylene oxide reacted with ancillary equipment	Leakage; possible hot spot in column
003	Ethylene oxide reacted with moisture to form non-volatile polyethylene glycols in the insulation material which auto-oxidized	Leakage in weld due to fatigue
004	Phenol crystallization	Lack of pipe heating led to blockage
005	$TiCl_4$ reacted with water	Control system not disconnected during maintenance led to tank overflow; external operators did not know way out
006	Ethylene mixed with air, oxygen started decomposition of ethylene	Incorrect purging of installation
007	Decomposition of nitro compounds due to temperature raise	Climatic conditions lead to freezing of waste condensate
008	Unexpected formation of methylnitrate in tank containing chlorine residuals	Introduction of hydrogen chloride contaminated with methanol
009	Decomposition of 1-nitro-anthraquinone	Unknown catalytic effect of impurities (inorganic salts)
010	TiCl4 reacted with water from cooling circuit	Leakage in cooling circuit made water become in touch with TiCl4; leakage due to corrosion for incorrect cleaning procedures
011	Self ignition of substances in storage area	Unexpected unstable behaviour of substance
012	Mixture formaldehyde/air exploded due to a temperature increase	Welding operation in a tank containing flammable mixture provoked explosion
013	Mixture of Zinc powder and air	Explosion due to hitting equipment with a hammer generating a hot nucleus of zinc powder
014	NaClO + HClO releasing chlorine	Labels of tanks had been interchanged
015	Decomposition of crystallized hypophosphorous acid; formation of explosive air/phosphine mixture	Formation of crystalline incrustration in tank; failure in steam supply line
016	Flammable vapours ignited	Excessive heating from worn bearing of the agitator
017	Mixture of methanol, methylacetate and air ignited	Wrong maintenance procedures
018	Crystalline SO3 formed due to contact between oleum and ammonium sulphate	Introduction of air increased pressure in blocked pipe
019	Acid mixture in contact with water generated release of nitrous gases	Storage tank not properly emptied, cleaning water reached tank
020	NaClO + acid releasing chlorine	Label mismatch, tank used for NaClO was exceptionally loaded with acid, then forgotten
021	Self ignition of substances in storage area for wastes	Unexpected unstable behaviour of substance
022	Ferric chloride sulfate + sodium chloride	No verification of vessel contents

	released chlorine	
023	Decomposition of H_2O_2 due to presence of impurities	Ventilation pipe used for safe drainage of H_2 blocked, possibility of product backflow
024	Aqueous caustic soda solution ţ alkyl residues generating flammable gases	The container had been sealed infringing operating instructions
025	Uncontrolled formation of phenylphosphine	Unexpected unstable behaviour of substance
026	Flammable vapours ignited	Ignition due to lightning with halogen lamp in highly flammable tank
027	Ignition of polyvinylpyrrolidine	Oxidation and ignition due to atmospheric air feed instead of nitrogen
028	Release of polychloroacetone	Faulty pipe connection
029	Release of phenol-water solution	Operator erroneously opened valve
030	Mixture of air/styrene vapours ignited	Mixture ignited due to static electricity
031	Release of acetylene and decomposition products	Leakage of pipe
032	Release of SO2 due to different exothermic reactions	Wrong storage procedures; no toxic detectors
033	Decomposition of fertilizers producing NOx vapours due to wrong mixture of products containing Cu and Cl	Wrong process analysis
034	Ignition of air/ethyl alcohol mixture	Mixture ignited due to static electricity
035	Ignition of flammable materials due to overheating	Wrong storage procedures
036	Explosion of mixture of volatile elements and fuel-oil	Unexpected unstable behaviours of substance
037	NaClO + HCl releasing chlorine	Tank rupture; pipe containing uncompatible materials broke as well
038	Fire of sodium dichlorisocyanurate associated with the release of chlorine	Rupture of bag, product reached drainage, ignited in touch with wastes and oils
030	Decomposition of fertilizers	Wrong storage procedures
040	Decomposition of H2O2 due to presence of impurities	Control failure + human error; valves opened that should have been closed
041	Release of hydrochloric acid and sulphur dioxide due to mixture of sulphur chloride and water	Operator cleaned tank with water
042	Spontaneous burning of pyrophoric iron sulphides deposit	No verification of vessel contents
043	NaClO + HCl releasing chlorine	Chemicals picked from wrong container
044	Trichloromethylsilane + water releasing chlorine	Operator mixed wrong chemicals
045	Isocyanuric acid + water	Label mismatch
046	Ignition of sodium chlorate + combustible substances in storage area	Wrong storage procedures
047	Explosion of sodium hydroborate	Unexpected unstable behaviour of substance
048	Sulphuric acid + sodium bisulphite released SOx	No verification of vessel contents, wrong chemical used
049	Release of SO_2	Wrong handling of chemical drum
050	Spontaneous combustion of sodium dichloroisocyanurate polluted with organic compounds	Wrong storage procedures; hazard was foreseen but no measures put in place
051	Ethoxyalkylphenol + water	Operator mixed wrong chemicals
052	Water + benzoil chloride	Leakage due to failure of joint in condenser

053	Tosyl isocianate + metal container released H_2S, HCl, sawdust added as inhibitor but did not work	Wrong operation procedures; addition of sawdust to inhibit reaction did not work
054	Sodium chloride + ferric chloride	NaClO introduced erroneously in tank containing $FeCl_3$
055	Dust cloud ignition	Chemical reacted with container material; blockage of aerosol outlet
056	Decomposition of 2-azo-bis methylburtyronitrile	One plate of the dryer was broken; excessive heating over safe temperature
057	Release of HCN	Wrong process analysis
058	Reaction of water + toluene diisocyanate	Leakage
059	$KMNO_4$ + ethanol solution	No verification of compatibility of mixture
060	Benzoyl chloride + methanol released HCl	Verification of compatibility of mixture inadequate
061	Release of SO_2	Accumulation of product in equipment; improvement of agitation systems required
062	Trichloromethylbenzol reacted with humidity releasing HCl	Wrong connections
063	Formation of polymer of ethylene oxide	Valve blockage
065	Release of vapours and ignition due to welding	Wrong procedures for maintenance
066	Ignition of vapours	Wrong application of foam; compatibility of auxiliary services
067	Decomposition of azodibutyronitrile	Unexpected unstable behaviour of substance
068	Mixture of H_2, light hydrocarbon gases and CO ignited by pyrophoric carbon deposits	Wrong maintenance procedures
069	Ignition of different materials accumulated	Long overheating of materials; wrong tests to determine thermal stability
070	Ignition of unstable residues containing nitrotoluenes and nitrocresols	Wrong management and maintenance, failure of tests for stability
071	Mixture of water with SO_3 releasing H_2SO_4	Erroneous introduction of water, no verification of vessel contents
072	Sodium chloride + epichlorydrin generated an exothermic reaction	No verification of vessel content
073	SCl_2 + water releasing SO_2	Monochlorobenzene by supplier contaminated with water
074	Release of hydrogen sulphide gas, formed when waste chemicals were mixed	Wrong process analysis
075	Ignition of metholate	Operator forgot to switch off heater, lead to overheating
076	Ignition of solvent vapours, acetone, methanol	Static electricity from polyethylene bags
077	Powdered pharmaceutical product ignited	Static electricity, wrong process analysis
078	Explosion of highly flammable liquids	Teflon coating worn out, metal-to-metal contact generated the explosion
079	Explosion of methanol vapours/air mixture	No inertization, monitoring of flammables, explosive or smoke detectors
080	Nitric acid + formic acid	Wrong connections; mistaken tank
081	Explosion of different solvents	Unknown catalytic effect of impurities (inorganic salts)
082	Release of flammable hydrocarbons + NaOH solution	Human error during diluting mixture; flammable reached zone of welding work; stop of electricity

		supply induced explosions in other zones
083	Ignition of acrylonitrile, vinyl acetate polymers	Accumulation of product in equipment; ignition due to friction generating sparks
084	Explosion involving thioridazine hydrochloride	Residues from previous process, incomplete cleaning of vessel; ignition due to static electricity; no investigation of previous incidents
085	Release of PCl_3 in contact with water generates HCl and phosphines which self-ignited	Wrong connections; reaction with rain water; extinguishing with water increased HCl cloud
086	Decomposition of organic peroxides	Overheating; incorrect procedures for heating; control and management failures
087	Flammable vapours ignited due to self heating	Wrong process analysis; no flame arrestors installed
088	$TiCl_4$ and $AlCl_3$ water pressure increase and HCl release	Deposit of $AlCl_3$ and $TiCl_4$ formed in tube
089	Decomposition of NO_2 due to overheating	Overheating due to pump bearing; pumps inadequately cooled
090	Polymer waste explosion	Operators not aware of possible flammables inside vessel
091	Ignition of flammable materials	Leakage + ignition due to welding operations
092	Phenol-formaldehyde polymerization	Mischarging; operator error, lack of training
093	Polyvinyilchloride polymerization	Supplies failure
094	Epichlorhydrine polymerization	Cooling failure
095	Copper phthalocyanine + chlorosulfonic acid	Dosing failure; no interlock between sensors
096	Azo compounds for paints	Agitation failure; operation error restarting agitation
097	Nickel-metal + nitric acid	Cooling failure
098	Ketone-colons manufacture, dimethylaniline chloroform, phosgene and dyphenilketone	Dosing failure; erroneous use of water
099	Unknown, dymethilsulphate involved	Dosing failure; operator error
100	Azo compounds for paints	Impurities/contamination
101	Azo compounds for paints	Impurities/contamination
102	Resin synthesis (maleic anhydride, lithium hydroxide)	Mischarging; control system erroneously programmed
103	Production of dimethyl phosphorochloridothioate and diethylphosphorochloridothioate	Dosing failure; insufficient cooling
104	Polyvinyilchloride polymerization	Pressure increase due to unknown reasons; safety valve did not work
105	Unknown, involved SO_2	Impurities/contamination; presence of water unnoticed
106	Polyvinyilchloride polymerization	Supplies failure; inhibition did not work
107	Polyvinyilchloride polymerization	Dosing failure; rupture disk broken releasing gas in atmosphere
108	Fine chemical production (sodium borohydride)	Pressure increase due to unknown temperature rise, breaking down process intermediate; reactor was on stand by
109	Synthesis of 3-methylthioaniline	Dosing failure; inversion of order in reactants
110	Styrene polymerization	Supplies failure; false indication in control room
111	Various chemicals for production of textile	Mischarging; wrong pH control

	and plastic industries; emulsion oil and water	
112	Production of zirconium sponges (involving Mg)	Impurities/contamination
113	Synthesised active ingredients for the pharmaceutical industry,	Dosing failure; wrong working procedures; unexperienced worker
114	Production of pectines	Dosing failure
115	Phenol-formaldehyde polymerization	Supplies failure; wrong working procedures
116	Phenol-formaldehyde polymerization	Dosing failure; wrong working procedures
117	Pharmaceutical synthesis (p-clorobenzaldehyde instead of o-cloronitrobenzene)	Mischarging; labelling mismatch from supply
118	H_2O_2 + alcohol vapour	Impurities/contamination; bursting disks did not work; no investigation of previous similar incidents
119	Fertilizers production	Impurities/contamination
120	o-Nitrobenzylnitrate was produced instead ofo-nitrobenzaldehyde	Impurities/contamination; dumping system did not operate
121	Difluoronitrobenzene contaminated with water	Impurities/contamination; decomposition T of intermediates were known, but unexpected that the presence of water could generate such T raise
122	Ethylene production	Unknown causes for the runaway; isolation and dump valves did not work; hot carbon particles generated during the fire ignited vapours
123	Unknown (involved ethanol and Ni Raney)	Cooling failure; control failure; pyrophoric nickel as source of ignition
124	Dosing failure involving H_2O_2	Dosing failure; operator error; failure of quenching system
125	Hydrogen explosion	Leakage; ignition due to static electricity; agitator failure; no study of previous incidents; failure of bursting disk
126	Manufacture of bulk fine chemicals (1-methyl-2-fromyl-1-Nitroimidazole)	Unknown; wrong laboratory analysis procedures; accident during change of scale trials
127	Isopropyl alcohol recovery	Unknown; potential for runaway not detected previous to production
128	Phtalocyamines process unit	Dosing failure; operator error; no monitoring of pH; pressure relief system inadequate
129	Production of chemicals to reduce grease	Mischarging; wrong chemicals; inexperienced operator; no emergency measures available
130	Polyvinyilchloride polymerization	Mischarging; operator error; extra cooling didn’t work; formation of corrosive substance attacked reactor wall; sprinkler system worked
131	Polymerization of dicyclopentadiene	Mischarging; wrong working procedures; inadequate training
132	Production of ferric chloride	Dosing failure; no pH monitoring; wrong working procedures

10.3 Appendix C – Statistics for runaway incidents

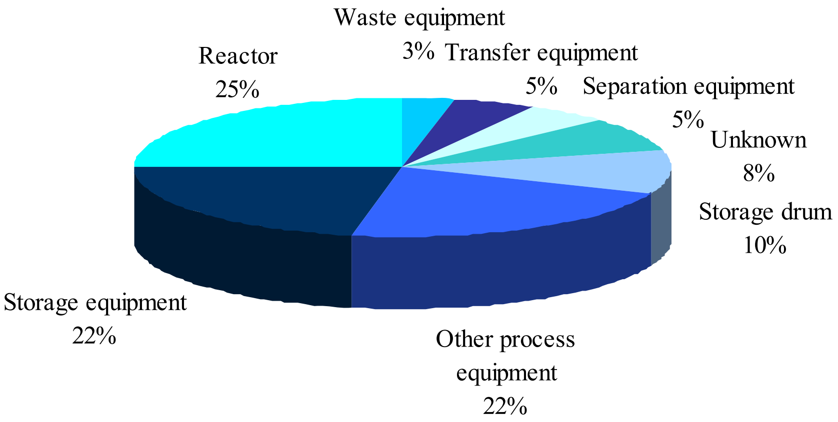

Figure 10.1 *Equipment involved in incidents, 1980-2001*

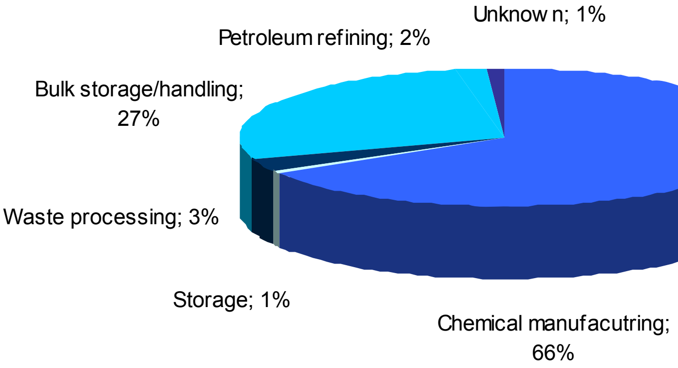

Figure 10.2 *Industry profiles, 1980 – 2001 (CSB)*

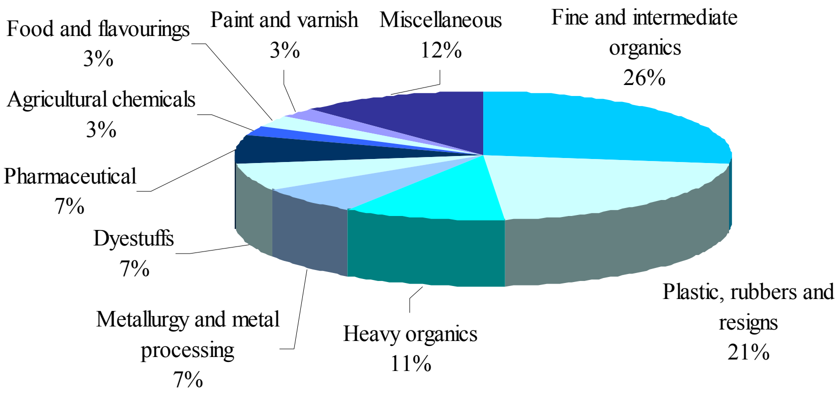

Figure 10.3 *Specific manufacturing industries (189 incidents)*

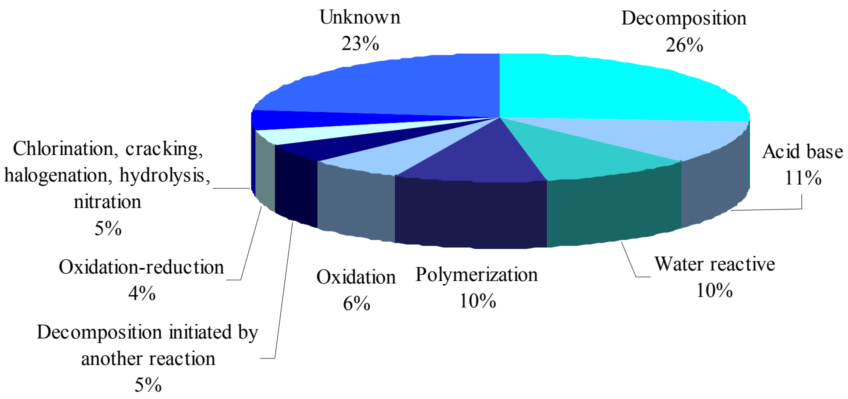

Figure 10.4 *Types of exothermal runaway reaction*

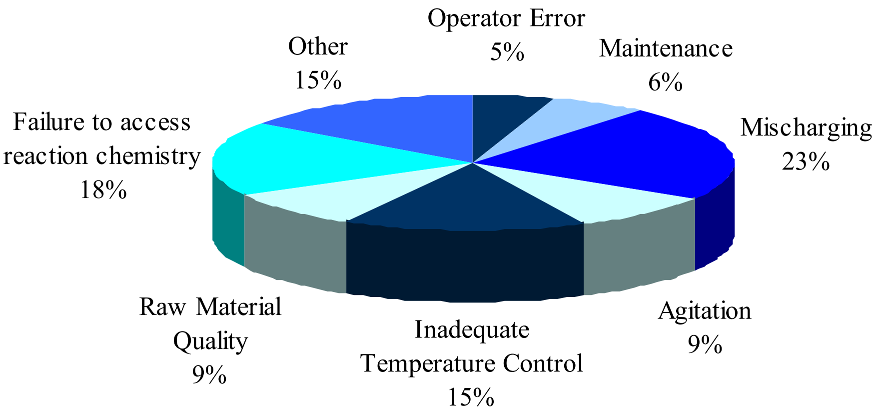

Figure 10.5 *Main causes of Runaway Reactions in UK (Chemical Industry) [1986-2000]*

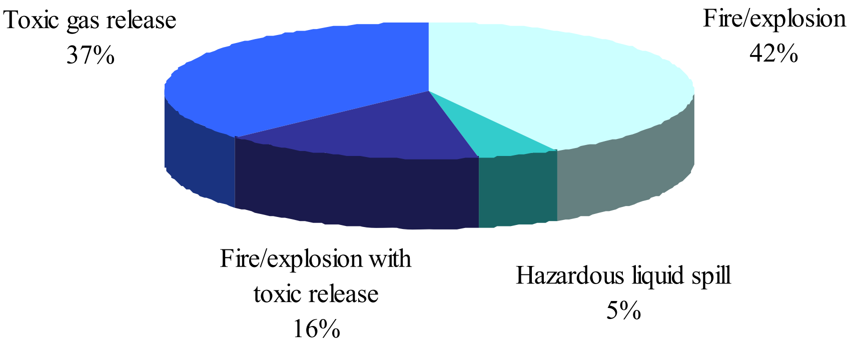

Figure 10.6 *Consequences of runaway reactions*

10.4 Appendix D – Mathematical modelling

10.4.1 System of equations for esterification of acetic anhydride

In what follows the model for treating the passive trip system is presented using the esterification reaction as an example. The procedure is analogous for the other reactions.

Mass balance of the liquid phase in the reactor

The change of the mass of liquid in the reactor is produced either by de-gassing or evaporation or both, as described by the following equation.

$$\frac{dm_l}{dt} = -\frac{dm_g}{dt} - \frac{dm_v}{dt} \tag{10.1}$$

Mass balance of the gas production

Eq. 10.2 gives the change of the mass of gas with time. For the vapour system, which does not produce gas, we have

$$\frac{dm_g}{dt} = 0 \tag{10.2}$$

Mass balance of vapour

The heat generated by the reaction serves to both heat up the reactor content and to finally evaporate it. This is reflected by the following equation

$$\frac{dm_v}{dt} = \frac{k_0 \cdot e^{-\frac{E_A}{RT}} \cdot c_1 \cdot c_2 \cdot H_R \cdot V - m_l \cdot c_p \cdot \frac{dT}{dt}}{H_V} \tag{10.3}$$

Change of temperature in time

The energy balance is contained in eq. (10.4). $\dot{Q}_{cool}$ is the cooling power of the emergency cooling system. Before its response it is equal to 0, afterwards it is represented by eq.(10.5). Its left hand side becomes equal to zero as soon as the boiling temperature is reached; the latter is approximated using the well-known equation of Clausius-Clapeyron.

$$\frac{dT}{dt}=\frac{k_0\cdot\exp\left(-\frac{E_A}{R\cdot T}\right)\cdot c_1\cdot c_2\cdot H_R\cdot V-H_V\cdot\frac{dm_v}{dt}-\dot{Q}_{cool}}{m_L\cdot c_p} \qquad (10.4)$$

Heat removal after trip system response

$$\dot{Q}_{cool}(t)=\dot{m}\cdot c_{p,c}\cdot\left(T-T_{c,in}\right)\cdot\left[1-\exp\left(-\frac{s(t)\cdot P\cdot U}{\dot{m}\cdot c_{p,c}}\right)\right] \qquad (10.5)$$

Where $\dot{m}$ is the coolant mass flow, T the reactor temperature, $T_{c,in}$ the coolant inlet temperature, $c_{p,c}$ the therml capacity of the coolant, U the global coefficient of heat transfer, P the parameter of the cooling coil and s(t) the distance the coolant has been introduced, which is obtained from eq.(10.7).

Emergency coolant acceleration

The accelerating force is the difference between internal and external pressure multiplied by the cross-section area of the coolant coil pipe. Opposed to it is the force produced by the friction of the coolant flow, i.e.

$$\frac{dv_c}{dt}=\frac{A_c\cdot\left(P-P_{atm}\right)-\frac{1}{2}\cdot A_c\cdot f_r\cdot v_c^2\cdot\rho_c\cdot\frac{L_c}{d_c}}{m_c} \qquad (10.6)$$

Using eq. (10.6) one obtains the distance of introduction of the coolant by

$$s(t)=\int_0^t v_c(t')\,dt' \qquad (10.7)$$

Mass balance of the acetic anhydride

The concentration of acetic anhydride changes with time according to a second order reaction kinetics, i.e.

$$\frac{dc_1}{dt}=-k_0\cdot\exp\left(-\frac{E_A}{R\cdot T}\right)\cdot c_1\cdot c_2\cdot V \qquad (10.8)$$

Mass balance of methanol

The concentration of methanol changes with time in analogy with eq. (10.8), i.e.

$$\frac{dc_2}{dt} = -k_0 \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \cdot c_1 \cdot c_2 \cdot V \qquad (10.9)$$

Documentation of the equations not defined here, can be find in the table 10.3.

10.4.2 Algorithm

Figure 10.6 presents the algorithm of the FORTRAN program for modelling the passive trip system. The algorithm was performed in a flowchart form and enables one to follow important steps through calculations of the passive trip system.

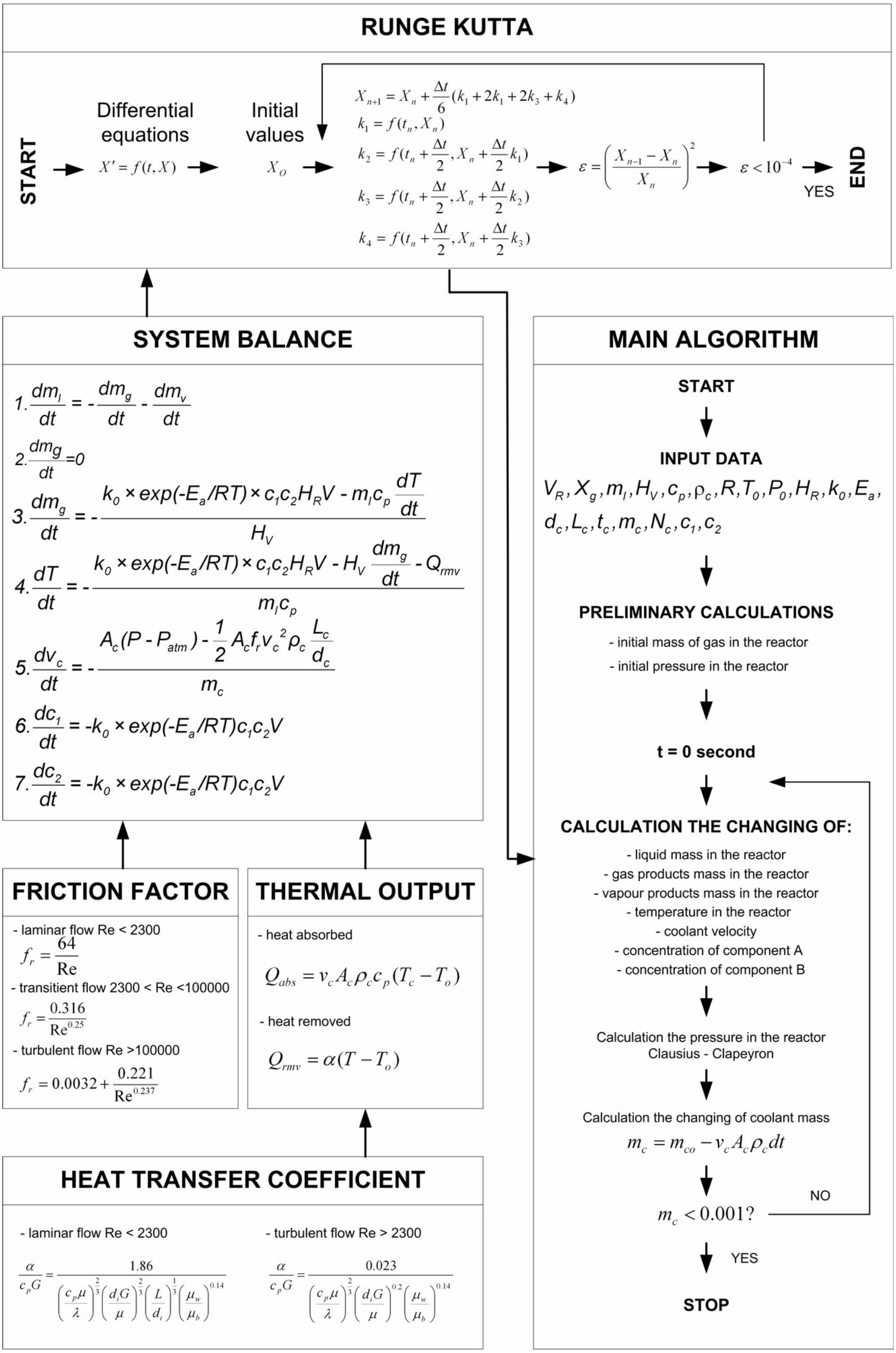

Figure 10.6 *Algorithm for FORTRAN program*

10.4.3 Process parameters

Table 10.3 *Process and system parameters for numerical simulation (esterification)*

Symbol	Passive trip system data	Unit	Value
V_R	Reactor volume	[m^3]	0.01
D_c	Diameter of the cooling coil	[m]	0.00635
L_c	Length of the cooling coil	[m]	2.1
G_c	Thickness of the cooling coil wall	[m]	0.001
N_c	Number of cooling coils	[-]	1
P_{BD}	Activation pressure of BD	Pa	$1 \cdot 10^5$ - $4 \cdot 10^5$
	Initial parameters		
m_l	Mass of the liquid in reactor	[kg]	7.96
x_g	Volume fraction of the gas space	[-]	0.11
c_1	Concentration of acetic anhydride	[$kmol/m^3$]	10.58
c_2	Concentration of methanol	[$kmol/m^3$]	24.8
m_c	Mass of the coolant	[kg]	10
	Material data		
Hv	Specific enthalpy of vaporization	[kJ/kg]	648.4
c_p	Specific enthalpy	[kJ/(kg K)]	2.55
ρ	Density	[kg/m^3]	900.8
R	Specific gas constant	[J/kg K]	259.49
	Reaction parameters		
ΔHr	Specific enthalpy of reaction	[kJ/kg]	650
k_0	Pre-exponential factor	[1/s]	$8.96 \cdot 10^6$
E_a	Activation energy	[kJ/kmol]	73752
T_0	Work temperature	[K]	300
T_{cc}	Temperature for CC equation	[K]	293
P_{cc}	Pressure for CC equation	[Pa]	10^5

10.5 Appendix E – Material properties

10.5.1 Esterification of acetic anhydride

Table 10.4 *Properties of reactants and products in esterification reaction*

Parameter / Reactant	**Acetic Anhydride**	**Methanol**	**Acetic Acid**	**Methyl acetate**
Formula	$(CH_3 CO)_2O$ $C_4H_6O_3$	CH_3OH CH_4O	CH_3COOH $C_2H_4O_2$	CH_3COOCH_3 $C_3H_6O_2$
Molar mass [kg/kmol]	102.01	3.04	60.05	74.08
- UEL (%)	10.1	36,5	16	12.1
- LEL (%)	2.7	6	5.4	2.9
Flash point (°C)	49	12	39	N/A
Autoignition (°C)	316	385 - 470	427	N/A
Vapour density	3.52	-	2.1	2.56
Vapour pressure mm Hg at 25°C (kPa)	0.68	16.9	2.07	28.8
Melting point (°C)	-7.3	-97,8	16.7	-20,8
Boiling point (°C)	139	64,5	117.9	141.1
Density (kg/m^3)	1082	795	1049	933
Specific enthalpy of formation (kJ/mol)	-624.4	-239.1	-484.5	-445.8
Specific enthalpy of vaporization (kJ/kg)	506.244	1101	395	-
Specific heat capacity c_p (kJ/(kg K))	1.670	2.496	1.997	2.119

10.5.2 Decomposition of hydrogen peroxide

Table 10.5 *Properties of reactants and products in a decomposition of hydrogen peroxide*

Parameter / Reactant	**Hydrogen peroxide (30%)**	**Water**	**Oxygen**	**Manganese dioxide**
Formula	H_2O_2	H_2O	O_2	MnO_2
Molar mass (kg/kmol)	34.02	18	32	86.94
- UEL (%)	N/A	not appl.	N/A	not appl.
- LEL (%)	N/A	not appl.	N/A	not appl.
Flash point (°C)	N/A	not appl.	N/A gas	not appl.
Autoignition (°C)	316	not appl.	N/A	not appl.
Vapour density	3.52			not appl.
Vapour pressure mm Hg at 20°C (kPa)	24	2.32		not appl.
Melting point (°C)	-25	0	-219	535
Boiling point (°C)	106	100	-181	not appl.
Density (kg/m^3)	1110	1000		5080
Enthalpy of formation (kJ/mol)	-241814	-285.83	0	-520
Enthalpy of vaporization (kJ/mol)	51.6	40.65	6.82	-
Specific heat capacity c_p (J/(mol K))	89.1	75.3	29.4	54.1

10.6 Appendix F – Seveso process and reactor model

TeCB

$$\frac{dn_1}{dt} = -k_1\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A1}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_1\cdot n_6}{V} \qquad \text{(Eq. 10.10)}$$

TCA

$$\frac{dn_2}{dt} = k_1\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A1}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_1\cdot n_6}{V} - k_2\left(428\ \ K\right)$$

$$\cdot\exp\left[-\frac{E_{A2}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V} - k_3\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A3}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right] \qquad \text{(Eq. 10.11)}$$

$$\cdot\frac{n_2\cdot n_6}{V} - k_5\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A3}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}$$

TCP

$$\frac{dn_3}{dt} = k_2\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A2}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}$$

$$-k_4\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A4}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_3\cdot n_6}{V} \qquad \text{(Eq. 10.12)}$$

TCDD

$$\frac{dn_4}{dt} = k_5\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A5}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}$$

$$+k_4\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A4}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_3\cdot n_6}{V} \qquad \text{(Eq. 10.13)}$$

By-products

$$\frac{dn_5}{dt} = k_3\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A3}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V} \qquad \text{(Eq. 10.14)}$$

NaOH

$$\begin{aligned}\frac{dn_6}{dt} = &-k_1\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A1}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_1\cdot n_6}{V}-k_2\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A2}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\\ &\cdot\frac{n_2\cdot n_6}{V}-k_3\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A3}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}-k_5\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A5}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\\ &\cdot\frac{n_2\cdot n_6}{V}-k_4\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A4}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_3\cdot n_6}{V}+\frac{\rho_6\cdot\dot{V}_{in}}{2\cdot M_6}\end{aligned}\tag{Eq. 10.15}$$

CH₃OH

$$\begin{aligned}\frac{dn_7}{dt} = &-k_1\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A1}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_1\cdot n_7}{V}\\ &-k_2\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A2}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_7}{V}\end{aligned}\tag{Eq. 10.16}$$

Process energy balance

$$\begin{aligned}&\left(C_R+\sum_{i=1}^{5}M_i\cdot c_{pi}\cdot n_i+2\cdot c_{p6}\cdot M_6\cdot n_6+c_{p7}\cdot M_7\cdot n_7+C_P\right)\cdot\frac{dT}{dt}=k_1\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A1}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\\ &\frac{n_1\cdot n_6}{V}\cdot\left|\Delta H_1\right|+k_2\left(428\ \ K\right)\cdot\exp\left[-\frac{E_{A2}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}\cdot\left|\Delta H_2\right|+k_3\left(428\ \ K\right)\cdot\\ &\exp\left[-\frac{E_{A3}}{R}\cdot\left(\frac{1}{T}-\frac{1}{428}\right)\right]\cdot\frac{n_2\cdot n_6}{V}\cdot\left|\Delta H_3\right|-\rho_6\cdot c_{p6}\cdot\dot{V}_{in}\cdot\left(T-T_{in}\right)+\frac{\rho_6}{2\cdot M_6}\cdot\dot{V}_{in}\cdot\left|\Delta H_{mix}\right|-\dot{Q}_{cool}-\dot{Q}_{loss}\end{aligned}\tag{Eq. 10.17}$$

- Feed

$$\dot{V}_{in}=\frac{V_f-V_i}{T_d}$$

- Heat capacity C_P (accounts for heat capacity of residual products, which produces an increase of the total heat capacity from 15600 kJ/kg to 20100 kJ/kg after feed)

$$C_P=116.82\cdot\left(n_{7,i}-n_7\right)$$

- Heat loss from the reactor (which varies with reaction temperature and amounts to 21 kW at 155°C)

$$\dot{Q}_{loss}=0.15556\cdot\left(T\text{-}293.15\right)$$

Coolant energy balance and PI controller

$$\dot{Q}_{cool} = \dot{m} \cdot c_{p,w} \cdot \left(T - T_{c,in}\right) \cdot \left[1 - \exp\left(-\frac{A \cdot k_w}{\dot{m} \cdot c_{p,w}}\right)\right] \qquad \text{(Eq. 10.18)}$$

$$\frac{d\dot{m}}{dt} = \frac{K_1}{\tau} \cdot \left(\dot{Q} - \dot{Q}_{cool}\right) + \frac{K}{\tau} \cdot s_h \qquad \dot{m}\left(t^*\right) = a \qquad \text{(Eq. 10.19)}$$

$$\frac{ds_i}{dt} = \frac{K_0}{p_i} \cdot \left(u_c - K_{mV/T} \cdot T\right) \qquad s_i(0) = 0 \qquad \text{(Eq. 10.20)}$$

$$s_h = k_c \cdot \left(u_c - K_{mV/T} \cdot T\right) + s_i \qquad s_h(0) = 0 \qquad \text{(Eq. 10.21)}$$

Table 10.6 *General process conditions*

k_w	heat transfer coefficient	0.5 kW/(m^2 K)
A	area for heat exchange	12 m^2
T_{in}	temperature of sodium hydroxide feed	25°C
ΔH_{mix}	enthalpy of mixing (NaOH/TeCB)	-30 kJ/mol
V_i	initial volume	4825 l
V_f	final volume	5600 l
T_d	dosification period for NaOH	60 min
$n_{1,i}$	tetrachlorobenzene (TeCB) (initial quantity)	6161 mol
$n_{4,i}$	miscellaneous by-products (initial quantity)	368 mol
$n_{6,i}$	sodium hydroxide (initial quantity)	950 mol
$n_{7,i}$	methanol (initial quantity)	93827 mol
ρ_6	density 50% aqueous solution of sodium hydroxide	$1521.7 \cdot 10^{-3}$ kg/l
ρ_7	density of methanol	$773.2 \cdot 10^{-3}$ kg/l
C_R	heat capacity of the reactor	6800 kJ/K

Table 10.7 *Cooling system including control*

$\dot{Q}$	net heat generation (reaction+mixing-$\dot{Q}_{loss}$-feed)	kW
$T_{c,in}$	coolant inlet temperature	20°C
$c_{p,w}$	coolant heat capacity (water)	4.179 kJ/(kg K)
a	coolant/steam mass flow at time t* (when T = 428.15K is reached)	2 kg/s
τ	cooler time constant	100.0 s
K	cooler gain	5.0 kg/(s·mV)
u_c	command signal	428.15 mV
k_c	proportional gain	10.0
$K_{mV/T}$	gain of temperature in mV transducer	1.0 mV/K
K_0	gain	10.0
K_1	gain	1 kg/(s·kW)
p_i	integrator coefficient	5.0 s

10.7 Appendix G – Three-dimensional visualisation of the PTS

The visualization of the passive trip system is available on request. The movie can be opened with any video player.

Figure 10.7 *Visualisation of the passive trip system*

11

Curriculum vitae

Personal data

Name:	Dariusz Jabłoński
Date of birth:	February 23, 1977
Birth place:	Łowicz, Poland

Education

1992 – 1996	Grammar school name Józef Chełmoński in Łowicz, Poland
1996 – 2001	Process Engineering Studies - Technical University in Łódź, Poland
2002 – 2005	Doctoral Studies – Otto-von-Guericke-University in Magdeburg

Professional Experience

2001 – 2002	Research worker - Technical University in Łódź, Poland
2005 – 2008	Research worker - Otto-von-Guericke-University in Magdeburg

Publications

- Jablonski D. and Markowski A.S., Die Beurteilung von Domino-Effekten in Folge schwerwiegender industrieller Störfälle, Fachzeitschrift ATEST – Arbeitschutz, 2001.
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