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Development and application of thermal runaway criteria

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Abstract

Development and application of thermal runaway criteria

Safe operation of thermally sensitive chemical reactors remains a crucial engineering issue. Thermal runaway can result in serious consequences, such as the explosion of the reactor, therefore; engineers must know about reactor runaway in detail, and they must know the possible causes and consequences. Thermal runaway occurs mainly due to loss of temperature control, but many chemical accidents initiated by thermal runaway can be foreseen by an appropriate analysis of thermal process data. So-called thermal runaway criteria can be used to predict the development of reactor runaway which can be geometric-, stability- and sensitivity-based methods. Unfortunately, these runaway criteria are not frequently applied in the industrial practice.

Runaway criteria classify the different states of a reactor operation as non-runaway or runaway based on a critical equation. However, these runaway criteria indicate the development of thermal runaway in different states, and there is no a fully general method or theory which can be applied with the highest reliability and with the shortest indication time for every reactor and reaction system. Each criterion has its truth about the runaway. Despite of it I developed two new thermal runaway criteria (*Modified Slope Condition, MSC, Modified Dynamic Condition, MDC*), and their performances were compared with the most frequently applied runaway criteria based on their reliability and their indication time. MDC criterion came out as the most reliable while the indication time is in the midfield. Since runaway criteria do not consider system specifics (such as Maximum Allowable Temperature, or maximum process pressure), I applied a genetic programming-based methodology to identify system-specific critical equations, which outperforms the conventional criteria.

As it was mentioned, runaway criteria can be applied to predict the development of runaway, hence; I applied criteria in offline and in online tasks. Offline tasks mean for instance the design phase of a reactor and/or its operation, and I applied runaway criteria to optimize the operation of semi-batch reactors where runaway states are prohibited.

In case of online application I present an investigation of a reactor operation with Nonlinear Model Predictive Controller, where runaway criteria are considered to improve the safeness of reactor operation. I proposed a control structure which can be useful in case of optimal operation of fed-batch reactors with highly exothermic reactions.

Kivonat

Reaktorelfutási kritériumok fejlesztése és alkalmazása

Termikusan érzékeny reaktorok biztonságos üzemeltetése mindig kulcsfontosságú mérnöki feladat lesz. Termikus elfutás bekövetkezése súlyos következményekkel járhat, mint például a reaktor felrobbanása. Ezért, a mérnököknek részleteiben ismernie kell a reaktorelfutás jelenségét, és ismernie kell a lehetséges okokat és következményeket. Termikus elfutás azért következik be, mert nem tudjuk megfelelően kézben tartani a reakcióhőmérsékletet, azonban ezek az üzemzavarok előre jelezhetőek úgynevezett reaktorelfutási kritériumokkal. Azonban, ezek a módszerek még nem terjedtek el ipari körülmények között, általában csak az adiabatikus hőmérséklet emelkedést veszik alapul (gyógyszeripar), vagy alaposan túltervezik a hűtő kapacitást a megfelelő üzemvitel biztosításához. Ezek a módszerek geometriai-, stabilitás vagy érzékenység vizsgálatokon alapulnak.

Az elfutási kritériumok alapján eldönthető egy-egy adott állapotról, hogy az a biztonságos, vagy pedig az elfutásos zónába tartozik. Azonban a különböző elfutási kritériumok különböző állapotokat tekintenek elfutottnak, és nem létezik olyan teljesen általános összefüggés vagy elmélet, amely minden reaktor és reakciórendszeren egyértelműen alkalmazható a legnagyobb megbízhatósággal és a legrövidebb előrejelzési idővel. Kidolgoztam két új elfutási kritériumot („Modified Slope Condition”, MSC, és „Modified Dynamic Condition”, MDC), amelyek teljesítményét összehasonlítottam az irodalomban található, leggyakrabban alkalmazott elfutási kritériumokkal. MDC kritérium bizonyult az adott esettanulmányok vizsgálata során a legmegbízhatóbbnak, valamint jelzésidőben a középmezőnyben végzett. Azonban, ezen összefüggések nem veszik figyelembe a különböző rendszerspecifikációkat (mint például a maximálisan megengedett hőmérsékletet, nyomást), így egy genetikus programozáson alapuló módszert alkalmaztam kritikus összefüggések identifikálására, ahol már a különböző specifikációkat figyelembe tudtam venni.

Mivel az elfutási kritériumok jelezni tudják az elfutás bekövetkezését, így felhasználtam azokat különböző offline és online feladatokban. Offline feladat esetén a kritériumot reaktor üzemeltetés tervezésére használtam fel, ahol rátáplálásos reaktor esetében meghatároztam az optimális rátáplálási trajektóriát.

Online feladatok elvégzése esetében pedig az elfutási kritériumokat nemlineáris modell prediktív szabályozó algoritmusba implementáltam, így növelve a rátáplálásos reaktorok üzemeltetésének biztonságát.

Auszug

Entwicklung und Anwendung von Kriterien des Reaktorentlaufens

Die sichere Betriebsführung thermisch sensibler Reaktoren wird immer eine essentielle ingenieurtechnische Aufgabe sein. Das Auftreten eines thermischen Entlaufens kann mit schwerwiegenden Folgen, wie zum Beispiel die Explosion des Reaktors, einhergehen. Deshalb müssen die Ingenieure die Erscheinung des Reaktorentlaufens im Detail und die möglichen Ursachen und Folgen kennen. Das thermische Entlaufen tritt meist aus dem Grund auf, weil wir die Reaktionstemperatur nicht entsprechend handhaben können, diese Havarien können jedoch mit den sogenannten Kriterien Reaktorentlauf im Voraus angezeigt werden. Aber diese Methoden wurden unter Industrieverhältnissen noch nicht verbreitet. Diese Methoden basieren auf geometrischen, Stabilitäts- oder Sensibilitätsuntersuchungen.

Durch die Kriterien Reaktorentlauf wird über je einen gegebenen Zustand entschieden, ob er entlaufen ist oder nicht. Durch die verschiedenen Kriterien Reaktorentlauf werden verschiedene Zustände als entlaufen angesehen, und es gibt keinen einzigen allgemeinen Zusammenhang oder Theorie, der oder die mit der größten Zuverlässigkeit und mit der kürzesten Voranzeigezeit für alle Reaktoren oder Reaktionssysteme angewendet werden kann. Ausdrücklich zwei Kriterien Rektorenentlauf („Modified Slope Condition", MSC, und „Modified Dynamic Condition", MDC), habe ich untersucht, deren Leistung ich mit den in der Literatur auffindbaren häufigsten Kriterien Reaktorentlauf verglichen habe. Das Kriterium MDC erwies sich während der Prüfung der gegebenen Fallstudien als dasjenige, das am meisten zuverlässig ist, es war auch nicht das Letzte bezüglich der Voranzeigezeit. Aber durch diese Zusammenhänge werden die verschiedenen Systemspezifikationen (wie zum Beispiel die maximal zulässige Temperatur) nicht berücksichtigt, deshalb habe ich eine Methode auf der Basis Genetischer Programmierung für die Identifizierung kritischer Zusammenhänge verwendet, wo ich die verschiedenen Spezifikationen berücksichtigen konnte.

Im Fall der Lösung von Onlineaufgaben habe ich die Kriterien Reaktorentlauf in den Nichtlinearen Prädiktiven Regelungsalgorithmus implementiert, wodurch die Sicherheit der Betriebsführung von Speisereaktoren erhöht wird.

Contents

List of Notations

Mathematical symbols

a_i	slope of linear equation
A	heat transfer area [m^2]
B^{dos}	Volume flow rate [m^3/s]
c	concentration [$kmol/m^3$]
c_m	maximum concentration [$kmol/m^3$]
c_i^{aq}	concentration of i component in aqueous phase [$kmol/m^3$]
c_i^{org}	concentration of i component in organic phase [$kmol/m^3$]
c_0	inlet concentration [$kmol/m^3$]
c_p	heat capacity [kJ/kg K]
d	reactor diameter [m]
e	control error [K]
Da	Damköhler number
H_0	Hammett's acidity function
E	activation energy [kJ/kmol]
F	feed rate [m^3/s]
F_j	coolant feed rate [m^3/s]
FP	false positive
FN	false negative
Ex	exothermicity number
I	runaway indication
k_0	preexponential factor
m	material balance equation
m_i	molar distribution coefficient of component
m_{H0}	Hammett's reaction rate coefficient
MAT	maximum allowable temperature [°C | K]
n_i	mole of component i [kmol]
$n_{P,max}$	maximum possible mole of product [kmol]
I	penalty indices
ITHI	inherent thermal runaway hazard index
MF	material factor

MTSR	Maximum Temperature of Synthesis Reaction [°C | K]
p_i	model parameters
P	pressure [Pa]
Pr	probability
PST	process safety time [hr]
PST_c	critical process safety time [hr]
q_{gen}	generated heat flow [J/s]
q_{rem}	transferred heat flow [J/s]
r	reaction rate [kmol/m^3 s]
r_c	derivative of reaction rate with respect to c
r_T	derivative of reaction rate with respect to T
R	gas constant [kJ/kmol K]
RD	relative deviation [%]
RI	risk index
Ry	reactivity number
S	severity
t	time [s | hr]
t_{dos}	dosing time [s]
TMR_{ad}	Time to Maximum Rate under adiabatic conditions [s]
T_c	critical or cooling temperature [K]
T_p; T	process temperature [K]
T_{ta}	target temperature [K]
T_w	wall temperature [K]
TP	true positive
TN	true negative
u	input
U	overall heat transfer coefficient [kW/K m^2]
UA	heat transfer parameter [kW/K]
V	reactor volume [m^3]
V_{dos}	dosing volume [m^3]
V_j	jacket volume [m^3]
w	weighting factor
Wt	Westerterp number
X_{ac}	accumulated reagent

x	conversion
z’	dimensionless length
$\underline{J}$	Jacobian matrix
$\underline{I}$	identity matrix

Greek letters

α	$UA/(V\rho c_p)$ [1/h]
β	$\Delta H_r/(\rho c_p)$ [m^3 K/kmol]
γ	kinetic parameter
δ	E/R [K]
ψ	Semenov number
ε	relative volume increase
ρ	density [kg/m^3]
λ	eigenvalue
τ	residence time [s | hr]
ΔT_{ad}	adiabatic temperature rise [K]
ΔH_r	reaction heat [kJ/kmol]

1 Introduction

The worst consequence of a thermal runaway (which is thermal explosion) shows that process engineers must have a detailed knowledge about this phenomenon. As the reader will see in the literature survey, there are many examples for accidents occurred due to thermal runaway resulted in lethal damage, and the last accident occurred in the recent past, in 2012. This is my motivation to work on this field, I would like to get a deep knowledge about thermal safety and I would like to develop a reliable method for the safe operation of reactors carrying out exothermic reactions.

My dissertation starts with a review about thermal runaway (see Section 1), including: the possible cause and consequences of reactor runaway, the prevention steps, thermal risk assessment methods. The main key in runaway prevention despite the inherently safer design is the development of an appropriate early warning detection system. Thermal runaway criteria can be used to predict the development of reactor runaway, and I present clearly the theories behind them (see Section 2.4). The advantages and disadvantages of Safety Boundary Diagrams (Westerterp diagram) are presented in detail in Section 2.5. Different mitigation methods to moderate the consequences of reactor runaway are presented. My work on this field starts at Section 3. I present the derivation of two new thermal runaway criteria (Modified Slope - MSC, and Dynamic Conditions – MDC) which came out as a result in the systematic analysis of literature runaway criteria (see Section 5). I evaluated and compared their performance based on their reliability and earliness, which are the two main expectations from a runaway criterion, to the performance of widely applied criteria from literature. The presented general runaway criteria investigate the reactor states but they do not consider any system specific, such as maximum allowable temperature (MAT). I used genetic programming to develop system specific runaway criteria (see Section 6). For further investigation in applicability of runaway criteria I used these criteria in the task of feeding trajectory optimization offline and online. I proposed a Model Predictive Control-based control scheme for the operation of semi-batch reactors (see Section 7-8).

In the following sections under literature survey my name and my work may appear, because I would like to show my contribution on this field in a unified environment. In later sections these works will be presented in detail.

2 Theoretical background

Safety assessment is always a crucial point in chemical plant design and operation due to the complexity of modern, highly integrated plants, and it requires deep knowledge of all process units and all the interactions between them. It is necessary to have information about every important physical and physico-chemical properties of every component which occurs or can occur in the system [1]. Also process safety regulations have been getting stricter in recent decades, and they cover every process unit and step on every level in modern chemical technology. These increasing requirements from process safety system triggered significant progress in process safety management that makes possible to avoid unnecessary events in nowadays fully integrated technologies which should operate in a hectic business environment, which require more flexible technologies than ever. However, due to evolutionary changes in the industry, new hazardous events occur, which are more related to organization, safety culture, and lack of knowledge and awareness [2].

It is well-known that certain operating conditions, so certain values of the parameters can cause the system become really sensitive to values of the initial or operating parameters. In sensitive region of the system, very small change in initial condition leads fully different trajectories with respect to pressure, temperature, concentrations, etc. It is more interesting if an exothermic reaction is carried out, where runaway can occur as a result of small changes. Thermal reactor runaways are characterized by a rapid increase in the temperature and pressure due to continuously increasing rate of heat generation. The rate of heat generation increases exponentially with the temperature, contrarily the removed heat increases only linearly with it. The risk of thermal runaway occurs is actually the risk of losing the control of chemical reactions which take place in the system (e.g. triggering a runaway reaction). A reaction runaway may have multiple consequences where the worst case is the explosion of the reactor [3].

During thermal runaways some of the components can vaporize or decomposition can occur due to the elevated temperature, which increases the pressure in the process unit [4]. In the worst case it leads to a Boiling Liquid Expanding Vapor Explosion (BLEVE). If the pressure increase rate is higher than the discharge rate, the reactor will explode due to the high pressure [5]. In less catastrophic cases prevention of the development of thermal runaway should be avoided because so-called hot-spots cause early deactivation of the catalyst and/or quality

drop. Hence, the determination of stabile operating regimes of a reactor is a crucial step in process design and operation [6]. 12% of BLEVE type accidents occurred due to runaway reactions, also from 1926 to 2004 6 BLEVE type accidents occurred due to runaway led to 19 death and 171 injured people [7].

Knowledge about the phenomenon of thermal runaway has improved a lot lately, but regretfully that knowledge is not fully integrated into the practice, and it causes some serious failures and process malfunctions nowadays. Thermal runaway is responsible for 26.5% of the petrochemical accidents [8], and reactor runaway was responsible for 25% of the accidents in French industry [9]. There were many lethal or non-lethal accidents due to thermal runaway in the recent past. The Seveso-disaster in 1976 is the prime example of the importance of knowing particularly the phenomenon of thermal runaway. In this disaster a toxic cloud was released into the atmosphere through a rupture disk poisoning almost 37000 people [10]–[12]. In 1990, in Stanlow a 15 m^3 batch reactor at Shell plant producing 2,4-difluoro-aniline had a runaway reaction leading to an explosion, where the entire plant was destroyed [13], [14]. In 1996 a runaway reaction occurred in a batch reactor creating high pressure that led to rupture of the vessel [15]. In 1997, Ohio, an explosion occurred in a resins production unit, where one worker died and four employees injured [16]. In 1998, in New Jersey a violent explosion and fire occurred due to a reactor runaway injuring nine employees [17]. In 2001 a destructive explosion occurred in an acrylic resin manufacturing plant in Taiwan at the Fu-Kao Chemical Plant as a result of runaway reaction. A batch reactor carrying out polymerization reactions exploded where more than 100 people were injured and one person died. The catastrophic explosion damaged and destroyed the nearby plants and buildings, which is shown in Figure 2.1 [18].

Now it is clear that we have to deal with thermal runaway to avoid more or less catastrophic incidents, and we must “learn from history or you are doomed to repeat it”. The first aspect is always the safety, which can be realized through studying the phenomenon of thermal runaway in detail. My goal with this review is to emphasize that engineers should never forget about that the safety has much higher priority than income despite the frequency of accidents in chemical processes are decreasing. Especially on the field of thermal safety, where the ignorance and the irresponsibility can result in serious and unfortunately, sometimes lethal consequences.

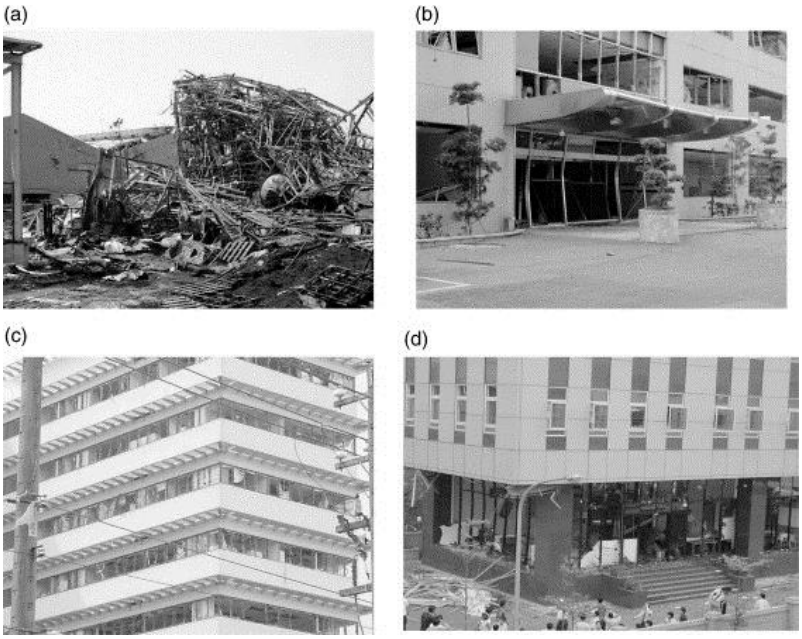

Figure 2.1 Explosion of Fu-Kao chemical plant [18]

Beside the well-designed reactor an appropriate, reliable and early warning detection system should be developed for safe reactor operation. If it is done, we have to prepare the system and operators for emergency cases, so we must design appropriate safety actions to moderate the consequences of thermal runaway.

2.1 Cause and consequence of thermal runaway

The safe operability of chemical reactors is highly dependent on the appropriate design of safety as well as control systems of technologies. Barton and Nolan investigated case histories (169 cases) from 1962 to 1987. Based on their review thermal runaway accidents occur due to the following causes [19], [20].

- a basic lack of understanding of the process chemistry and thermochemistry (e.g. no appreciation of the heat of reaction, unintended reactions and autocatalysis occurred, product mixture decomposed, low material quality, etc.);
- inadequate engineering design for heat transfer;
- inadequate control systems and safety back-up systems (e.g. loss of cooling water which was not monitored, wrongly positioned probe of temperature measurement, thermocouples coated result in slow response, etc.);
- inadequate operational procedures and operator training (e.g. starting the reactor at low process temperature, mischarging of reactants, inadequate mixing, poor communication between operators, etc.).

Rim Saada et al. studied thirty cases from 1988 till 2013, and they also classified the possible causes that lead to a runaway situation. The classification consists of "Technical and Physical Causes" and "Human and Organisational Causes". Under technical and physical causes five cases were due to mischarging the reactor. This includes charging chemicals or catalysts in inappropriate order and addition of incorrect amount of chemicals. Four cases have been caused due to agitator failures. In some cases trace quantities of impurities caused runaway phenomena. Four incidents occurred due to poor plant design, and five other cases were caused as a result of wrong process control. Under human and organisational causes thirteen incidents were due to operator errors. Operators do not understand the basics of chemistry and thermodynamics, and in some cases the operators decide on their own without discussing it with the technical advisor. In one case the reactor was operated outside the safety limits. Inadequate training, absence of supervision, an increase in work load, failure to follow standard operating procedures and incorrect opening/closing of the valves resulted in incidents too. Poor management in process operation also resulted in 11 incidents in the investigated time. Based on their systematic evaluation, twenty-one people died and 393 people injured directly due to thermal runaway. Their research indicated that lessons have not been learnt from the consequences of thermal runaways [21]. Different case studies about reactor runaway accidents with causes and consequences is shown in [17], [22]–[24].

In a better scenario the consequence of a runaway is only a low quality product; in a worse case the reactor physically explode result in a release of large quantities of flammable, toxic and hazardous materials. Liu et al. showed a flowchart of runaway accident sequences shown in Figure 2.2 [25].

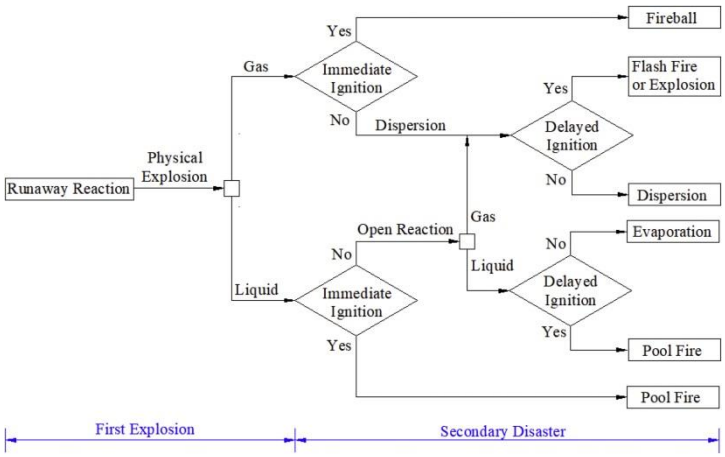

Figure 2.2 Flowchart of runaway accident sequences [25]

If the gas phase with high concentration is ignited immediately a fireball occurs, otherwise, it spreads around the reactor. The gas phase will diffuse and dilute may result in a vapour cloud explosion or forming a potential toxic cloud. If the liquid phase is ignited immediately a pool fire occurs, otherwise, the reactants may continue the reaction. The residual liquid phase may ignites and result in a pool fire or it forms aspiration hazard [25]. The size of endangered area can be efficiently estimated based on CFD simulations [5], [26], [27].

2.2 Prevention of reactor runaway

Prevention of reactor runaway begins in the design phase. As it is shown in Section 2.1 a detailed knowledge about the chemicals and its thermophysical properties is necessary for safe operation. Detailed kinetic information about the possible reactions is necessary for the appropriate design of the reactor. However, we must calculate with plant-model mismatch, we never can be confident with that the developed model is adequate in non-runaway and especially in runaway situations. First phase of prevention is the appropriate design of the reactor system and operating conditions.

Engineers must perform inherently safer design (ISD), which is about to prevent human error and invalidation of facility to reduce the risk of a process by ways of minimizing, substituting, moderating and simplifying. Four classes is mentioned as strategies toward ISD [28]:

- Inherent: Eliminating the hazard by using materials and process conditions which are non-hazardous.
- Passive: Eliminating or minimizing the hazard by process and equipment design features which reduce either the frequency or consequence of the hazard without the active functioning of any device.
- Active: Using controls, safety interlocks, emergency shutdown systems, mitigation devices to detect potentially hazardous process deviations and to take corrective actions.
- Procedural: Using operating procedures, administrative checks, emergency response, and other management approaches to prevent incidents, or to minimize the effects of an accident.

Apart from the offline investigations, also online prevention measures are necessary to detect any unexpected situation leading to a runaway scenario. An early warning detection system is indispensable to detect unexpected dangerous situations. Online applicable thermal runaway

criteria are excellent soft-sensors, which can predict the development of thermal runaway and the criteria are able to distinguish between dangerous and non-dangerous reactor states. Therefore, a robust safety criterion is an essential element of any Early Warning Detection System (EWDS). EWDS is necessary to detect and evaluate unexpected dangerous situations. We must provide sufficient time for a protection system or the plant operator to perform the necessary steps to stop or to moderate the undesired effects of runaway development. There are several time indices which can be applied to measure how far the system from a runaway state is. A good review about these time indices can be found in [6]. These indices are:

- Time of occurrence: the time when fault occurs;
- Reaction time: the minimum time required to execute a response step;
- Execution time: measured execution time of the system;
- Response time: the time between the detection of initiating event and the response of the system;
- Safety reaction time: the time needed to sense a problem and initiate a safety shutdown to the control element;
- Time-in-alarm: the time between timestamps of alarm and return-to-normal events;
- Irreducible minimum: the minimal time of response, usually approximately 100 ms;
- Process Safety Time (PST): PST is the period of time in which the process can be operated without protection and without undesired event occurs. Varga and Abonyi introduced how PST can be determined in case of highly exothermic reactions in [29];
- Time of no Return: after this time it is impossible to cool the reactor [3].

The safety steps to moderate the consequences of runaway can be an opening a pressure relief valve, full cooling or quenching (i.e., addition of inhibitor or cold inert liquid as well as dumping of the reactor content into a cold catch tank) [30].

2.3 Methods to evaluate thermal risks

The goal is always to reduce thermal risks, for which we have to answer some questions. If we are prepared for the worst-case scenario then heavy consequences can be prevented. Therefore, a systematic assessment procedure is based on the cooling failure scenario assuming adiabatic conditions. In adiabatic case the process temperature can rise to the highest. Based on the characteristic temperature levels arising from the scenario, criticality classes were defined by F. Stoessel [3]. The representation of worst-case scenario as a cooling

failure were introduced by Gygax [31], and he made a scenario for thermal assessment, which can be seen in Figure 2.3.

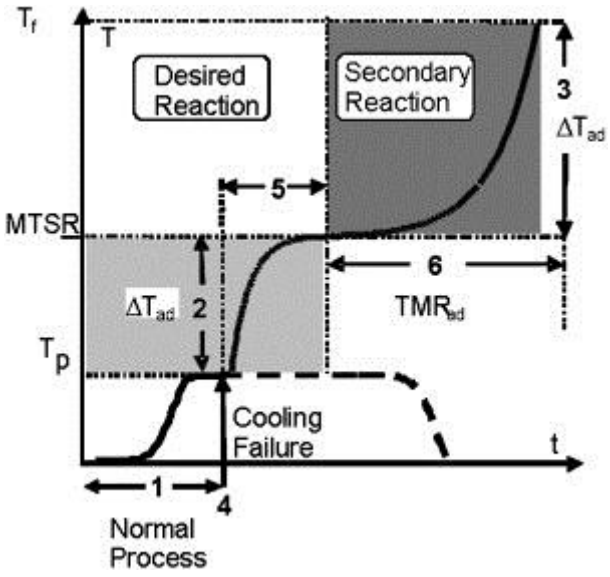

Figure 2.3 Runaway scenario, where numbers represent the six key questions [32]

In [33] a good description of Figure 2.3 can be found. The process is at temperature T_p when a cooling failure occurs. Since the reaction is exothermic, in adiabatic case, the presence of unreacted reagents will react increasing the reactor temperature with the adiabatic temperature rise (ΔT_{ad}). The most crucial time for a cooling failure is when the accumulation of unreacted reagent is at maximum. Maximum Temperature of Synthesis Reaction (*MTSR*) is introduced for describing the possible reactor temperatures during the operation. At *MTSR* secondary reactions might be triggered, and the secondary reaction will increase further to a final temperature (T_f). The duration of reaction runaway can be estimated by calculating the Time to Maximum Rate adiabatic parameter (TMR_{ad}).

MTSR can be calculated based on the degree of accumulation of unconverted reagents and the adiabatic temperature rise at the given instant.

$$MTSR = T_p + X_{ac}\Delta T_{ad,rx} \tag{2.1}$$

TMR_{ad} can be calculated based on the following formula using the initial heat release rate of the reaction.

$$TMR_{ad} = \frac{c_p' R T^2}{q_{gen} E} \tag{2.2}$$

Gygax formulated six key questions which helps for the assessment of thermal risk, which were refined for easier understanding [33]. The key questions are the following:

1. What is the heat evolution rate as a function of time of the operating process to be coped with by the operational equipment? So can the process temperature be controlled by the cooling system?
2. What temperature can be reached when the desired process runs away, assuming adiabatic conditions for a cooling failure?
3. What temperature can be attained after runaway of the secondary reaction?
4. Which is the most critical instant for a cooling failure? So at which time does the cooling failure have the worst consequences?
5. How fast is the runaway of the desired reaction?
6. How fast is the runaway of the decomposition starting at MTSR?

For thermal risk assessment Stoessel proposed a quantitative method for describing the severity and probability of the runaway, which are described in Table 2.1 and in Table 2.2. For defining the probability of runaway an extended Table can be found in [32].

Table 2.1 Assessment criteria for the severity of a runaway reaction [32]

Severity	**ΔT_{ad}**	**P**	**Extension**
Catastrophic	>400	$>P_{test}$	>Site
Critical	200-400	$P_{max}<P<P_{test}$	Site
Low	50-200	$P_{set}<P<P_{max}$	Plant
Negligible	<50	$P<P_{set}$	Equipment

Table 2.2 Assessment criteria for the probability of loss of control of a runaway reaction [32]

Probability	**Controllability**	**TMR_{ad} [hr]**
Frequent	Unlikely	<1
Probable	Difficult	1-8
Occasional	Marginal	8-24
Seldom	Feasible	24-50
Remote	Easy	50-100
Almost impossible	Not a problem	>100

In addition Stoessel formulated 5 criticality classes based on the relative order of four specific temperature levels, ranging from the least critical (1-2) to the most critical (3-5) presented in Figure 2.4 [34]. The four specific temperature levels are the following:

- The process temperature (T_p): the initial temperature in the cooling failure;
- Maximum temperature of synthesis reaction (*MTSR*): it depends on the degree of accumulation of unconverted reactants;
- Temperature at which TMR_{ad} is 24 hours (T_{D24}): it is the highest temperature at which the thermal stability of the reaction mass is unproblematic;
- Maximum temperature for technical reasons (*MTT*): it can be a boiling point in an open system, or it can be a temperature at the maximum permissible pressure in a closed system.

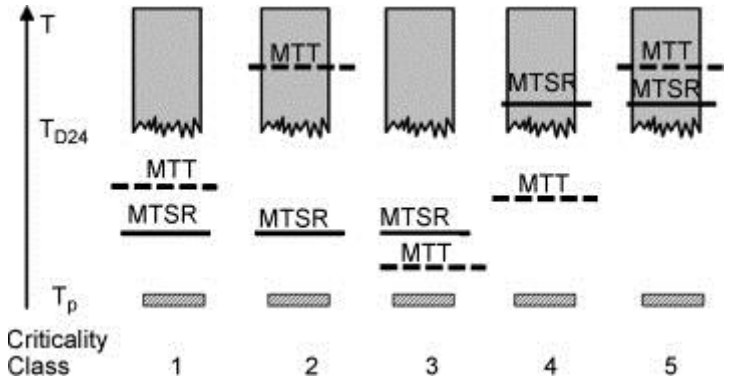

Figure 2.4 Criticality classes of scenario [32]

The criticality classification is a useful tool for the risk assessment and also for the choice and definition of adequate risk reducing measures. In Class 1 and Class 2 the loss of control of the

main reaction does not trigger secondary reactions and also the technical limit is not reached. In Class 3 the technical limit is reached and may serve as a safety barrier, but the secondary reactions are not triggered. In Class 4 the secondary reactions could be triggered, but the technical limit may serve as a barrier. In Class 5 the secondary reactions are triggered and the technical limit is reached as the runaway is too fast for a safety barrier to be efficient [32].

Juncheng et al. improved and applied the earlier mentioned classifications, and they developed inherent thermal runaway hazard index (*ITHI*), which is calculated by multiplying the material factor (*MF*) and risk index (RI) [35].

$$ITHI = MF \cdot RI \tag{2.3}$$

Risk index is calculated based on the severity of runaway reaction and the probability of the runaway reaction.

$$RI = S \cdot Pr \tag{2.4}$$

Material factor (*MF*) is calculated based on the initial reaction temperature (T_{onset}), and Max power density (*MPD*), where *MF* is limited in [1,2]. *MPD* is the function of heat of decomposition and the maximum reaction rate.

$$MF = 1 + \frac{I_{T_{onset}} \cdot I_{MPD}}{16} \tag{2.5}$$

where $I_{T_{onset}}, I_{MPD}$ are penalty indexes. Severity and probability of runaway reactions are determined based on quantitative intervals based on different penalty parameters, which parameters can be found in [35].

2.4 Reactor runaway criteria

Reactor runaway criteria can be applied to define the boundaries of safe and unsafe regimes through distinguishing the runaway and non-runaway states. This feature allows to apply criteria in off-line tasks (like process design, optimization) and in on-line tasks too (like early warning). Therefore, thermal runaway criteria are applicable in the design and operation of chemical reactors [36]. A brief history about the reactor runaway criteria until 2006 can be found in [37].

Thermal runaway criteria can be classified into three types, which are geometry-based criteria, stability-based criteria and sensitivity-based analysis can be performed to define runaway boundaries, which are presented in the following Sections 2.4.2-2.4.4. Section 2.4.1 presents a simple mathematical model of a tubular reactor (or batch reactor), on which the derivation of runaway criteria can be practiced easily.

2.4.1 Mathematical model

A first order reaction carried out in a batch reactor is presented in this section which will provide as a base for presentation of thermal runaway criteria. The reactor was considered as perfectly mixed so the following differential equations can be written to describe the dynamical behaviour:

$$\frac{dc}{dt} = -r \tag{2.6}$$

$$\frac{dT}{dt} = q_{gen} - q_{rem} \tag{2.7}$$

$$q_{gen} = \beta r \tag{2.8}$$

$$q_{rem} = \alpha(T - T_w) \tag{2.9}$$

Where

$$r = \exp\left(\gamma - \frac{E}{RT}\right) c \tag{2.10}$$

$$\alpha = 5\frac{l}{h}, \beta = 180\frac{m^3 K}{kmol}, \gamma = 20, \frac{E}{R} = 6600K, c_0 = 1\frac{kmol}{m^3}, T_0 = 300\ K \tag{2.11}$$

Figure 2.5 shows how the presented model Eq. (2.6)-(2.11) is sensitive to the wall temperature, and it presents the development of thermal runaway. The wall temperature is

increased from 310 K by 5 K steps, but the maximum process temperature increases are much higher, hence; we must strive to avoid the sensitivte region in operation.

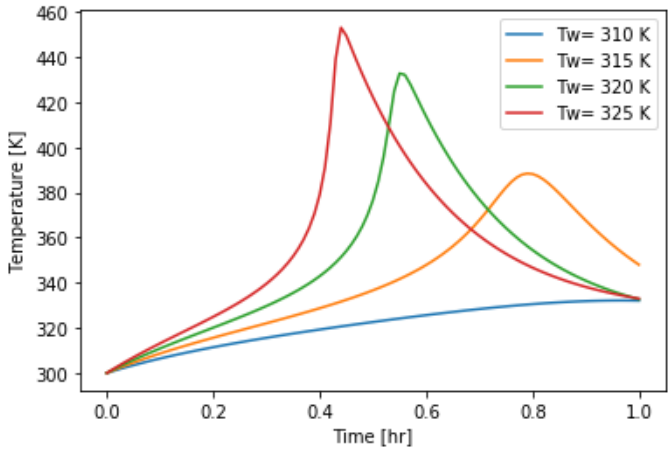

Figure 2.5 Sensitivity of the reactor model with respect to wall temperature

2.4.2 Stability-based criteria

The state of the system can be considered stable if after a small disturbance the system returns to initial state and during the transient behaviour the state of the reactor stays close to that initial state. This theory can be used to investigate reactor runaway since in case of runaway reactions similar situation occurs, where the positive feedback in the temperature and reaction rate relationship can result in the development of runaway. That first state of the system, when runaway is occurred can be considered as unstable state, from which the reactor cannot go back to the initial state. Numerous stability-based runaway criteria were proposed to indicate the development of thermal runaway, which are now presented in the following section.

2.4.2.1 Semenov-criterion

First pioneer work in the field of reactor runaway was done by Semenov, which work laid the groundwork for further researches. This section is written based on [3], [38], [39]. Semenov considered an exothermal reaction with zero-order kinetics. Semenov-diagram presents the heat-release in reaction and the removed heat by heat transfer as a function of temperature.

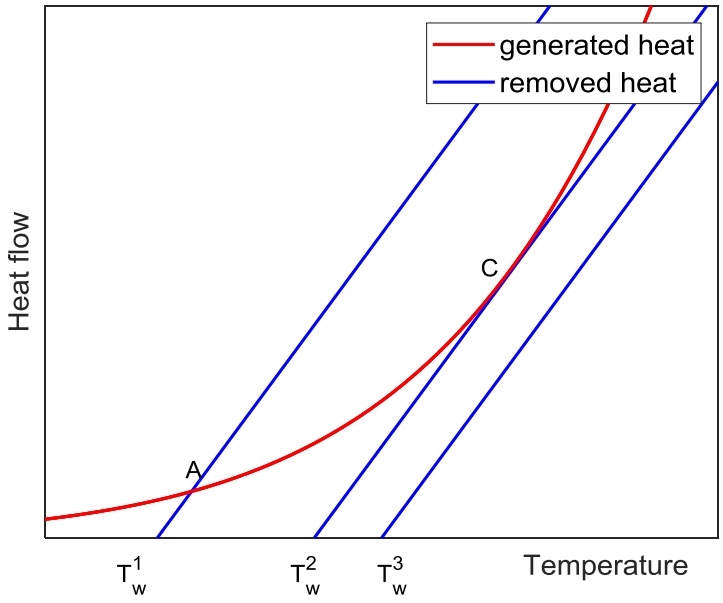

Figure 2.6 Semenov-diagram

Figure 2.6 presents the relationship between the generated and removed heat, where the generated heat varies exponentially with process temperature, while the removed heat varies linearly with it. Two essential points draw attention in Semenov-diagram, which are marked as A and C, and the different cooling agent temperatures are marked as T_w^1, T_w^2 and T_w^3. In *A* we can respect a stable operating point since if the cooling temperature is lower than T_w^2, the process temperature will decrease due to the higher removed heat until *A*, and no self-ignition occurs. If the cooling temperature is higher than T_w^2 self-ignition occurs since the generated heat is always higher than the removed heat. Therefore, *C* point represents the critical point in case of a higher cooling temperature, where the generated heat curve is tangent at one point to the removed heat line. The belonging cooling temperature is considered as critical, or as the lowest temperature of self-ignition. In this point a little increase in cooling agent temperature the cooling line will have no intersection between the generated and removed heat curve leads to the runaway of reaction.

For the aim of avoiding thermal runaway it is necessary to operate the reactor far away from critical conditions. Based on the Semenov-diagram and further investigation of the critical point a runaway criterion can be derived. In the critical point the generated and removed heat, and also their derivatives with respect to temperature equals, this can be written as Eq. (2.12) -(2.15) presents. Since the reagent consumption is neglected, the reaction rate varies only with temperature, hence the partial derivative of the reaction rate can be considered.

$$q_{gen} = \mathrm{q}_{rem} \tag{2.12}$$

$$\beta r = \alpha(T_c - T_w) \tag{2.13}$$

$$\frac{dq_{gen}}{dT} = \frac{d\mathrm{q}_{rem}}{dT} \tag{2.14}$$

$$\beta r_T = \alpha \tag{2.15}$$

Dividing the Eq. (2.13) and (2.15) the following critical equation is the result:

$$\frac{r}{r_T} = \frac{RT_c^2}{E} = (T_c - T_w) = \Delta T_c \tag{2.16}$$

Eq. (2.16) presents that there is a minimal temperature difference between the process and cooling temperature to keep the reaction operation stable. Semenov-diagram helps us to formulate the runaway criterion, because the critical temperature difference is always satisfied when the temperature is below the critical temperature value.

$$(T - T_w) \leq \frac{RT_c^2}{E} \tag{2.17}$$

From Eq. (2.17) the critical temperature can be calculated by solving the quadratic equation.

$$T_c = \frac{1 - \sqrt{1 - \frac{4RT_w}{E}}}{\frac{2R}{E}} \cong \frac{2\left(\frac{RT_w}{E}\right) + 2\left(\frac{RT_w}{E}\right)^2 + 4\left(\frac{RT_w}{E}\right)^3 \ldots}{\frac{2R}{E}} \tag{2.18}$$

If we consider only the first two terms on the right side, the following runaway criterion (Semenov-criterion) can be derived:

$$(T - T_w) \leq \frac{RT_w^2}{E} \tag{2.19}$$

We pay tribute to the Semenov-number, which is the ratio of dimensionless reaction heat parameter and the heat transfer, as follows:

$$\psi = \frac{(-\Delta H_r)kc^n}{UA}\frac{E}{RT^2} \tag{2.20}$$

For very large activation energies the following criterion can be defined, mentioned in the literature as Semenov-criterion (where *e* is the natural number):

$$\psi < \frac{1}{e} = \psi_c \tag{2.21}$$

This equation is determining in the research field of thermal ignition, because the following researches focus on how to determine the critical Semenov-number in more realistic cases, like without neglecting the reactant consumption.

However, we are going to present the runaway criteria without investigating the concrete value of Semenov-numbers in the following sections, instead we are going to present the base theory. Critical states (temperature, concentration, etc.) can be defined though, and the critical Semenov-numbers can be calculated from these variables.

2.4.2.2 Van Heerden and "Practical Design" criterion

Berty clearly presented the theory behind Van Heerden criterion, which is often called as "Slope Condition" [40], [41]. In a steady-state operation the generated and removed heat are equal. It is evident also that the heat generation and heat removal rate increases with temperature, but the generated heat increases exponentially. If there is any disturbance in the reactor temperature the heat removal rate should increase faster with temperature than the generated heat, it would prevent temperature runaways. Mathematical form of the criterion is the following:

$$\frac{dq_{gen}}{dT} \leq \frac{dq_{rem}}{dT} \tag{2.22}$$

The area of sensitive domain was defined by Van Heerden in 1953 [40]. Perkins assumed zero order kinetics to define a safe boundary. Considering Eq. (2.22) and Eq. (2.12) the following criterion can be defined:

$$T - T_w \leq \frac{R\mathrm{T}^2}{E} \tag{2.23}$$

Bashir et al. derived the same criterion investigating the inflection point in a geometric plane [42], stating that the calculated maximum temperature in Eq. (2.23) is the limiting value for runaway at the inflection point.

2.4.2.3 Gilles-Hoffmann criterion

Gilles and Hoffmann in 1961 recognized the "Dynamic Condition", which is the condition that sets the limits to avoid rate oscillation. Criterion is stated as the increase of heat removal rate with the increase of temperature must be larger than the difference between heat generation rate increase due to temperature alone and reaction rate decrease due to the concentration drop alone [41], [43].

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \leq \frac{dq_{rem}}{dT} \tag{2.24}$$

where m is the material balance function.

2.4.2.4 Lyapunov-stability in geometric- and phase-plane

Szeifert et al. proposed to use Lyapunov's indirect method to forecast reactor runaway [44], [45]. The stability analysis of a system defined by a set of nonlinear differential equations of the state variables applying Lyapunov's indirect method is reduced to an eigenvalue analysis of the Jacobian matrix.

$$\boldsymbol{J} = \frac{\partial f}{\partial x} \tag{2.25}$$

If real part of each eigenvalues of the Jacobian matrix is negative then the model is stable, but if any of these are positive then system is unstable at the investigated operating point. Lyapunov-stability can be performed in geometric- and in phase-plane too. The spatial stability criterion is always more conservative, because the stability in phase space always follows from the spatial stability while inversely does not.

In 2008 López-García et al. proposed to investigate the steady-state solutions with a perturbation model, because the dynamic study is essential to guarantee the thermally stable operation. The method is based on the linearization of the perturbation model which result in the analysis of the eigenvalues of Jacobian matrix [46]. Vajda and Rabitz similarly investigated the perturbation model earlier in 1992, but they investigated the sensitivity of maximum values of eigenvalues of the Jacobian matrix [47].

For investigating the dynamics of a system, Hopf-bifurcation analysis was suggested, which is based on investigating the eigenvalues too. If the real part of a complex-conjugate pairs of the

Jacobian matrix becomes positive then bifurcation occurs, and that means reactor runaway may develop [48]–[54].

2.4.2.5 Strozzi-Zaldivar criterion (Divergence criterion)

Strozzi and Zaldivar investigated the phase-space volume contractions during the reactor operation based on investigating the Lyapunov-exponents and the divergence of the system [55]. It has been shown that the divergence criterion can be applied for developing safety boundary diagrams to distinguish the runaway and non-runaway states for several types of reactors (batch reactor, BR, semi-batch reactor, SBR, continuous stirred tank reactor, CSTR) and for multiple reactions, also with and without of a control system [56].

Strozzi and Zaldivar provided the following derivation of their runaway criterion [55]. According to the Liouville's theorem, contraction of a state space volume of a d-dimensional dynamical system can be defined based on its divergence [57].

$$\frac{dV(t)}{dt} = \int div\, F[x(t)] dx_1(t) \dots dx_d(t) \tag{2.26}$$

where the divergence of the system can be calculated as

$$div\, F[x(t)] = \frac{\partial F_1[x(t)]}{\partial x_1(t)} + \frac{\partial F_2[x(t)]}{\partial x_2(t)} + \dots + \frac{\partial F_d[x(t)]}{\partial x_d(t)} \tag{2.27}$$

Assuming that the d-dimensional volume is small enough that the divergence of the vector field is constant over V(t), then

$$\frac{dV(t)}{dt} = V(t)\, div\, F[x(t)] \tag{2.28}$$

Integrating Eq. (2.28) the initial phase-space volume V(0) changes with time as

$$V(t) = V(0) exp\left(\int_0^t div\, F[x(t)] d\tau\right) \tag{2.29}$$

Hence the change rate of the state-space volume is given by the divergence of the system, which is locally equivalent to the trace of the Jacobian of F. The expansion and contraction of the state-space volume, so that the divergence of the investigated system, are in relation with runaway and non-runaway situations. Practically it means that if the state variables drift off for a small perturbation then the system is unstable. In case the divergence is negative there

will be no runaway, although if the divergence is positive, runaway will develop. Therefore, the proposed runaway criterion is the following:

$$div\, F[x(t)] \leq 0 \tag{2.30}$$

Copelli et al. modified the original divergence criterion, and they proposed to disregard all contributions arising from extent-of-reactions that are not related to heat evolution. Other state variables can generate a strong state-space volume contraction that is not related to the development of runaway which may leads to the failure of divergence criterion in predicting reactor runaway. It means that for example the components which are not reactant are neglected when evaluating the modified divergence of the system [58], [59].

Strozzi et al. also investigated the Lyapunov-exponents to define sensitivity. Lyapunov-exponent can monitor the behaviour of two neighbouring points of a system in a direction of the phase space as a function of time: If the Lyapunov-exponent is positive, then the points diverge from each other, if the exponent becomes negative, then the points converge. Lyapunov-exponents are related to the eigenvalues of the Jacobian matrix, since it averages the real parts of all eigenvalues along a trajectory [60], [61]. Although the Lyapunov-exponents can underestimate the runaway boundary for like autocatalytic reactions, because it uses the integral over time which is slow to respond to fast change. Therefore, Strozzi et al. proposed to apply divergence criterion [55]. Kähm et al later investigated the Lyapunov-exponents not in sensitivity context, but investigating the values of it. If the Lyapunov-exponent becomes positive, an unstable process is present [62]–[64].

We can calculate the divergence online, without needing to know the differential equations of the system by using the theory of embedding. State space reconstruction is a possible technique to address this problem using time delay embedding vectors of the original measurements (i.e., temperature or pressure measurements) [65], [66]. Although there is several methods of reconstruction, but there is no a priori method to decide which one is the best. In [67] Zaldivar et al. tested several methods: time delay embedding vectors; derivative coordinates and integral coordinates, but the results were similar and they used derivative coordinates because of their clear physical meaning. There are two reconstruction parameters: the embedding dimension, and the time delay. The embedding dimension is the dimension of the state space required to unfold the system from the observation of scalar signals, whereas the time delay is the lag between data point in the state space reconstruction [66].

Guo et al. developed an adiabatic criterion based on the divergence of an adiabatic model of the reactor system with zero feed rate result in a more strict runaway criterion [68], [69].

Walter Kähm developed a stability criterion based on the original divergence criterion, which is based on the difference between the divergence of the Jacobian matrix of the investigated reactor system variables and the correction function. The correction function is derived as a function of the divergence of the Jacobian at the previous time step; Damköhler number; Barkelew number; Arrhenius number and the Stanton number. They introduced this stability criterion, because divergence criterion may over predict the thermal runaway potential of the system. The derivation is based on a linear approximation of the divergence [59], [62], [70]. The proposed stability criterion is successfully generalized for multiple reactions [71].

2.4.2.6 Modified Dynamic and Slope Condition

I would like to mention our recently developed runaway criteria in this Section in advance, so it is classed and presented with the other stability-based criteria. The reader can learn about the development steps in Section 5.

Kummer and Varga investigated the most frequently applied criteria and derived two new criteria as a result [72]. Eq. (2.31) presents the Modified Slope Condition (MSC) and Eq. (2.32) presents the Modified Dynamic Condition (MDC). We investigated three different reaction systems (single reaction with a reagent, two parallel reactions, and an autocatalytic reaction system) to validate the Modified Dynamic and Slope Condition criteria, which in the reliability and the time of indication were compared. MDC did not miss any thermal runaway development, but the performance of MSC is compatible with the investigated ones.

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c \leq \frac{dq_{rem}}{dT}\left(1+\frac{q_{gen}}{q_{rem}}\right) \tag{2.31}$$

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \leq \frac{q_{gen}}{q_{rem}}\frac{dq_{rem}}{dT} \tag{2.32}$$

2.4.3 Geometry-based criteria

Several reactor runaway criteria exist based on a geometric characterization of temperature trajectories, which will be presented in this section. Advantages of inflexion-based criteria (Thomas and Bowes-, Adler and Enig criterion) and adiabatic criterion is that it requires only a temperature profile or trajectory to evaluate the reaction states, although without

investigating the states on a prediction horizon the runaway indications probably occurs lately. Inflection-based criteria do not give information about the intensity of the reactor runaway. Van Welsenaere and Froment criterion is quite conservative though and indicates reactor runaway quite early, but a model of the reactor system is required for the application.

2.4.3.1 Thomas and Bowes criterion

Thomas and Bowes proposed to indicate reactor runaway as the situation in which an inflexion point appears before the temperature maximum in the geometric plane (in versus time or length). It means that the reactor operation stays controllable if the following statements are satisfied [73], [74].

$$\frac{d^2T}{dt^2} < 0 \; while \; \frac{dT}{dt} > 0 \tag{2.33}$$

Dente and Collina in 1964 independently proposed the same criterion [74].

2.4.3.2 Adler and Enig criterion

Adler and Enig found it more convenient to work in a phase-plane (in temperature-conversion) than in the geometric plane. To indicate reactor runaway an inflexion point must appear before the temperature maximum in the phase-plane. It means that the reactor operation stays controllable if the following statements are satisfied, where x is the conversion [75].

$$\frac{d^2T}{dx^2} < 0 \; while \; \frac{dT}{dx} > 0 \tag{2.34}$$

2.4.3.3 van Welsenaere and Froment criterion (or Maxi criterion)

van Welsenaere and Froment determined critical conditions based on the locus of temperature maxima in the temperature-conversion plane. This criterion can be eliminated based on obtaining the relation between maximum process temperatures evolving at different cooling agent temperatures [76].

$$\frac{dT}{dx} > 0 \qquad \frac{dc_m}{dT_m} > 0 \tag{2.35}$$

2.4.3.4 Adiabatic criterion

A frequently applied runaway criterion (even in industrial application) is that the process temperature evolving under adiabatic conditions (so the MTSR) cannot exceed the Maximum Allowable Temperature [77].

$$T_p + \Delta T_{ad} = MTSR \leq MAT \tag{2.36}$$

2.4.4 Sensitivity-based criterion (Morbidelli-Varma criterion)

Varma et al. wrote an excellent book about the parametric sensitivities in chemical systems [74]. The analysis of how a system responds to changes in the parameters is called parametric sensitivity [74]. In the context of chemical reactors Bilous and Amundson performed a pioneer work on the field of parametric sensitivity, where the researchers showed how the maximum temperature along the reactor length varies with the ambient (cooling) temperature [78]–[80]. The result of a similar analysis can be seen in Figure 2.5. Sensitive regions of operations should be avoided because its performance becomes unreliable and changes sharply with small variations in parameters. Although some experimental studies are available in the literature [81], [82], it is difficult to perform wholesome investigations about the reaction systems (not to mention the industrial systems), because these systems involve many parameters affecting the behaviour of the reactor. Therefore, model based investigations are necessary. For the aim of investigation the sensitivity of reactors we should define valuable outputs (dependent variables), and valuable inputs (independent variables). Dependent variables can be investigated in geometric- or/and in phase-plane, which can be for example productivity, process temperature, process pressure etc. Input variables typically are initial conditions, operating conditions and geometric parameters of the system.

Morbidelli and Varma used the fact that near the explosion (runaway) boundary the system behaviour becomes sensitive to small changes in some of the input or initial parameters, and they defined the boundary between runaway and non-runaway zone based on this sensitivity concept. The first-order local sensitivity or absolute sensitivity of the dependent variable (**y**) with respect to the input parameters ($\boldsymbol{\phi}$) can be calculated based on the following form:

$$s_{\boldsymbol{\phi}}^{\boldsymbol{y}} = \frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\phi}} \tag{2.37}$$

Another quantity related to local sensitivity is the normalized sensitivity, which can be defined as:

$$S_{\phi}^{y} = \frac{\boldsymbol{\phi}}{\boldsymbol{y}} \frac{\partial \boldsymbol{y}}{\partial \boldsymbol{\phi}} = \frac{\partial \ln \boldsymbol{y}}{\partial \ln \boldsymbol{\phi}} = \frac{\boldsymbol{\phi}}{\boldsymbol{y}} s_{\boldsymbol{\phi}}^{\boldsymbol{y}} \tag{2.38}$$

The advantage of normalized sensitivity is that it normalizes the magnitudes of the input parameter $\boldsymbol{\phi}$ and the variable $\boldsymbol{y}$.

In Morbidelli-Varma criterion the parametrically sensitive region of the system or criticality for thermal runaway to occur is defined as that where the absolute value of the normalized sensitivity of the temperature maximum reaches its maximum [83]–[85]. Lacey [86] and Boddington et al. [87] independently proposed to use the sensitivity maximum of the temperature maximum with respect to Semenov number, to define the critical conditions for thermal explosion, but Morbidelli and Varma generalized this criterion considering other physicochemical parameters of the reacting system in the definition of the sensitivity.

Jiang et al. proposed to apply the absolute sensitivity in the following form: Safe operating conditions can be defined by the temperature sensitivity value which is less than one in the whole interval except in the initial point. The boundary between runaway and stable condition is established by the maximum value of the sensitivity function which equals one, so as:

$$\max\left(s_{\boldsymbol{\phi}}^{\boldsymbol{y}}\right) = 1 \; (except \; t = 0) \tag{2.39}$$

They explained it through analysing the maximum values of absolute sensitivities, and noting that lower sensitivity values mean less sensitive systems. Practically they just made a threshold to make the system safer and the criterion stricter [36].

2.4.5 Data modelling approach-based prediction of thermal runaway

Runaway criteria were developed using data-mining tools, where data were generated based on the model of the reactor system. In [88] a decision-tree based approach is developed to distinguish between runaway and non-runaway situation, where the case study is an industrial reactor producing phosgene. A similar approach is presented in [89], where binary decision diagrams and linear classifiers were applied to diagnose the fault. They detected runaway criteria based on dynamic thresholds evaluated by investigating temperature characteristics [90]. The major drawback of these criteria, that a huge amount of process simulations should be performed to obtain the necessary amount of data. Moreover, the results are burdened with

parameter uncertainty. However, the resulted decision-tree can be easily understood by a process operator, and the most appropriate safety actions can be determined for any of the runaway states.

2.5 Safety Boundary Diagrams

In case of operation of batch and semi-batch reactors (SBR) carrying out exothermic reactions safety boundary diagrams can give an efficient support for safe operation. Westerterp et al. had a lot of pioneer work on this field, also a dimensionless number is called as Westerterp-number (*Wt*, earlier Cooling number, *Co*, [91]) and the safety boundary diagram often mentioned as Westerterp-diagram. Hugo and Steinbach have observed that an accumulation of the non-converted component in SBR may cause runaway events, and also investigated how the maximum process temperature varies in case of a breakdown of cooling [92], [93]. Westerterp et al. generalized the concept of avoiding reagent accumulation through safety boundary diagrams. They investigated heterogeneous liquid-liquid and homogeneous reactions too [94]–[96]. The proposed safety boundary diagram can be applied generally, hence most of the recent articles use the same general reactor and homogenous reaction system for further investigations [97]. Of course, laboratory experiments were also performed to investigate the safety boundary diagrams, a detailed work about the thermally safe operation of a nitric acid oxidation in SBR can be found in [98], [99]

In ideal cases the reaction rate equals the feed rate, means that the dosed reagent reacts away immediately avoiding the reagent accumulation. In that case the reactor temperature follows a trajectory called the target temperature, which can be estimated with the following equation. Derivation of this equation can be seen in [100].

$$T_{ta} = T_c + \frac{1.05\ \Delta T_{ad,0}}{\varepsilon[Wt(1+\varepsilon\theta)+R_H]} \tag{2.40}$$

where T_c is the cooling temperature, $\Delta T_{ad,0}$ is an initial adiabatic temperature rise, ε is the relative volume increase, Wt is Westerterp number, θ is dimensionless time, R_H is the ratio of heat capacities of the dispersed and the continuous phase.

If the dosing is completed Eq. (2.40) can be used to define the target temperature beside θ=1. At the target temperature the reaction rate is high enough for avoiding reagent accumulation, so the reactor is operated safely. Therefore, reactor runaway occurs if the process temperature exceeds the target temperature.

Three zones can be distinguished based on the evolution of temperature and concentration trajectories in SBRs, which are: marginal ignition (MI, or no ignition), thermal runaway (TR) and QFS (quick onset, fair conversion, smooth temperature profile) zones, as it can be seen in Figure 2.7. In the marginal ignition the reactor temperature is always much lower than the target temperature, the reaction does not ignite; hence the accumulation is too high for safe operation. In the thermal runaway zone the process temperature exceeds the target temperature, also reaches much higher values than the target temperature because of the accumulated reagent abrupt ignites the reaction behaving closely to a batch operation. In QFS zone the process temperature trajectory is very close to the target temperature trajectory, because the fed reagent reacts almost immediately, which is the goal in the operation.

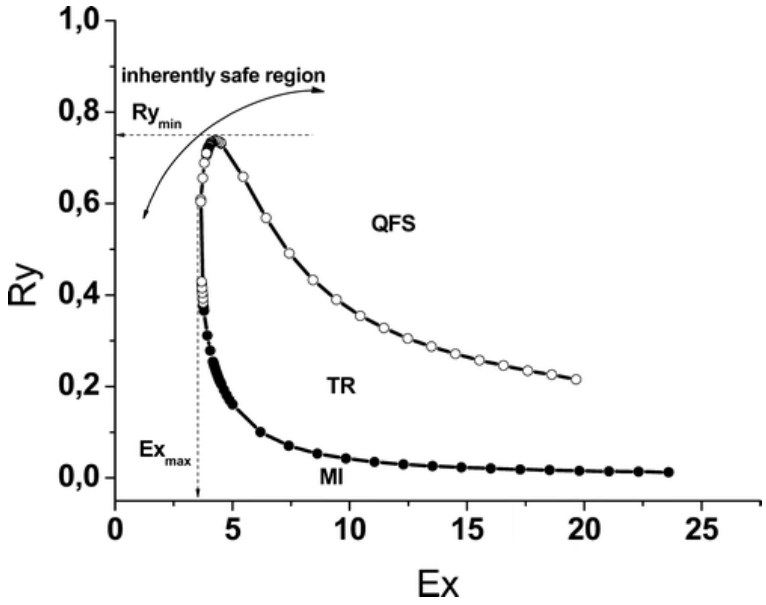

Figure 2.7 Safety boundary diagram [100]

The three zones are characterized by two dimensionless number, exothermicity (*Ex*) and reactivity (*Ry*), which are defined as follows:

$$Ex = \frac{\Delta T_{ad,0}(E/R)}{T_c^2 \varepsilon (R_H + Wt)} = \frac{\Delta \gamma_{ad,0} \gamma}{\beta_c^2 \varepsilon (R_H + Wt)} \tag{2.41}$$

$$Ry = \frac{Da(T_R) exp\left(\gamma\left(1 - \frac{1}{\beta_c}\right)\right)}{\varepsilon (R_H + Wt)} \tag{2.42}$$

where T_c is the cooling temperature, $\Delta T_{ad,0}$ is an initial adiabatic temperature rise, E is activation energy, R is the gas constant, ε is the relative volume increase, Wt is Westerterp number, θ is dimensionless time, R_H is the ratio of heat capacities of the dispersed and the

continuous phase, $\Delta\gamma_{ad,0}$ is dimensionless adiabatic temperature rise, γ is the Arrhenius number, β_c is the dimensionless cooling temperature, *Da* is the Damköhler number.

The exothermicity numbers presents the ratio of the maximal power generated due to the reaction and the cooling abilities. The reactivity number presents the ratio of the reaction rate and the cooling rate. The boundary line indicates the case where the process temperature does not exceed the target temperature, only touches it [101]. The boundary diagrams and the boundary lines depend on the value of the Westerterp-number (*Wt*) and the ratio of heat capacities of (R_H).

Westerterp-number presents the cooling ability related to the heat capacity of the reactor content at the beginning of the process. Dosing time is also appears in this dimensionless number considering the rate of heat evolution. Westerterp-number can be calculated as follows:

$$Wt = \frac{(UA)_0 t_{dos}}{\varepsilon\left(V\rho c_p\right)_0} \tag{2.43}$$

where U_0 is the initial heat transfer coefficient, A_0 is the initial heat exchange surface, t_{dos} is the dosing time, ε is the relative volume increase.

The Westerterp-number is the key parameter to determine the difference between the behaviour of the large scale, industrial reactor and the laboratory reactor [102]. There is an inherently safe region, as it can be seen in Figure 2.7. They determine the maximum of the exothermicity values below which the heat evolution is always too low, hence reactor runaway does not develop. There is also a minimum reactivity value above which reagent accumulation does not occur because of the high reaction rate, hence reactor runaway does not develop either [30]. These specific values determine unambiguously the inherently safe region. Boundary diagram safety criterion (BDSC) is based on comparing the reactivity and exothermicity numbers to the maximal exothermicity and minimal reactivity numbers, for further information see [100]. The safety boundary diagrams can be easily used for an existing reactor to identify thermally safe operating conditions without solving the mathematical model of the reactor. Also the Westerterp-diagram can be easily used to scale up reactors [103], [104], and also a kinetics-free approach can be found in [105]. Flowchart for designing thermally safe operating conditions based on safety boundary diagrams can be found in [101], [106].

Although the Westerterp-diagram is understandable and easy to use, there is no direct information about the maximum process temperatures evolving during the reactor operation in the QFS zone, which always should be checked, because the reactor system may cannot stand it (maximum process temperature exceeds MAT), or the cooling capacity may be not high enough to transfer the developing reaction heat. Maestri and Rota introduced Temperature Diagrams (TD), which can be applied next to the Westerterp-diagram. TDs allow for bounding the maximum process temperature as a function of exothermicity or reactivity numbers [107]–[109].

Ni et al. considered second reaction region too through including the MAT value in the development of safety boundary diagram, as it can be seen in Figure 2.8. EG curve represents the marginal ignition, runaway region is located between EG and EF. QFS region is located between ABCD and EG curves, and the second reaction region is above ABCD curve [110]. They also successfully applied this method for an autocatalytic reaction system, where the autocatalytic behaviour was defined as parallel reactions, and for this they proposed a modified Exothermicity and reactivity number [111].

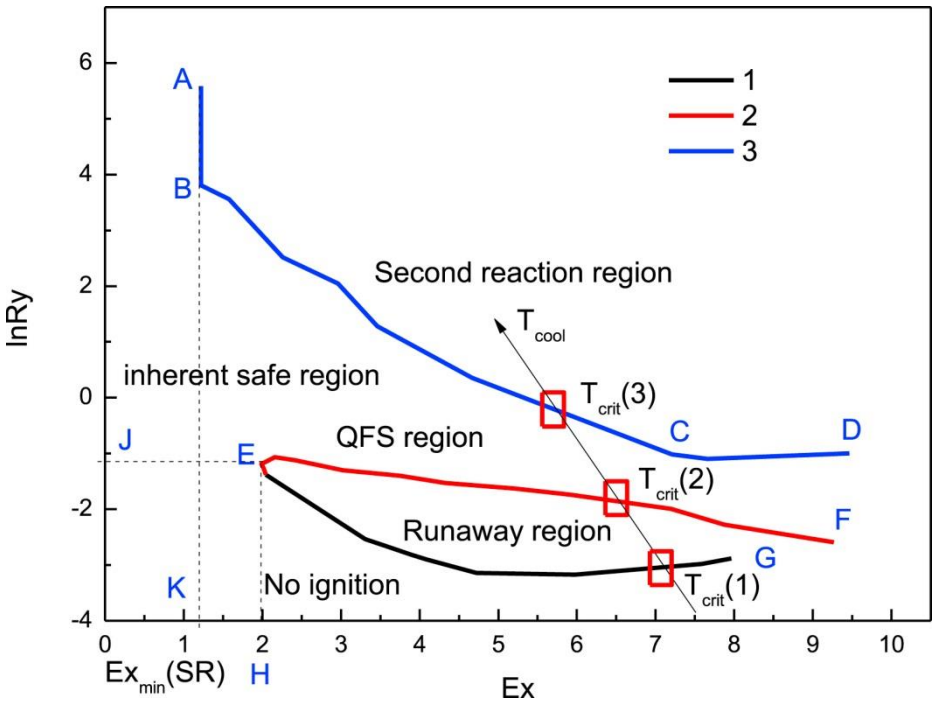

Figure 2.8 Safety boundary diagram considering MAT [110]

Maximum temperature of synthesis reaction (MTSR) is an important criterion for reactor design and process hazard assessment, because in case of a cooling failure this parameter gives information about the evolving process temperatures. For safety reasons it should be

lower than the MAT. Guo et al. investigated process malfunction in detail [112]. Bai et al. applied MTSR values instead of process temperatures for comparing it with the target temperature values to build safety boundary diagrams result in a safer reactor operation. Their criterion is denoted as Maximum temperature of a synthesis reaction criterion (MTSRC) [113]. Flowcharts for designing thermally safe operations considering MTSR values can be found in [113]–[115]. A more generalized method for including and investigating the maximum process temperatures developing at given operating parameters are proposed in [116]. Guo et al. proposed an artificially defined constant temperature, which can be calculated as follows:

$$T_n = T_c + \frac{n\,\Delta T_{ad,0}}{\varepsilon[Wt + R_H]} \qquad n \geq 1.05 \tag{2.44}$$

T_n gives information about the *MTSR* values evolving at a specific operation conditions, for example at n=2 the given T_2 points in SBD can be seen in Figure 2.9, where MTSR values equals T_2 [116].

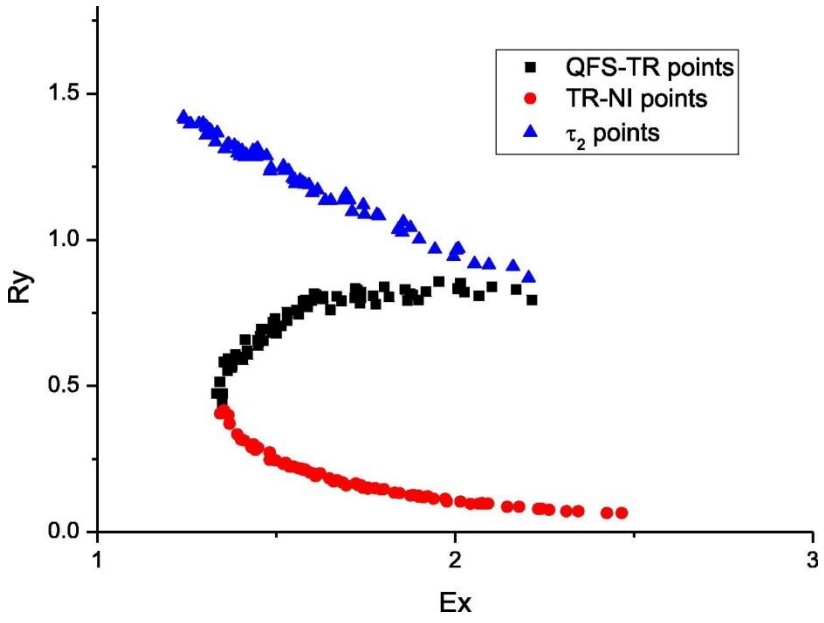

Figure 2.9 Extended Boundary Diagram [116]

Recently a multi-feature recognition (MFR) criterion based on pattern recognition was proposed to develop safety boundary diagrams [117].

The presented methods are great and easy to use, but it requires constant feed rate of reagents. However, if we would like to maximize the productivity or other efficiency metrics the feeding rate should be varied in time. In our humble opinion safety boundary diagrams should

be used to define the suitable initial conditions, so to define initial process temperature, flow rate of cooling agent and reagents. The whole concept of SBDs is to avoid the accumulation of reagents, but as the reactor temperature increases the feed rate of reagents can be increased where accumulation will not happen.

2.6 Safety equipment/actions to moderate serious consequences

In case we have the most reliable criterion which can be achieved to forecast runaway, the next step is to prepare our system to decrease the effect of runaway development. When runaway occurs and it cannot be handled in normal operations it is necessary to stop the reaction, so we can avoid undesired scenarios. In such a situation, shutdown of the reactor is performed by some safety interlock or emergency shutdown system. When pressure increases too high a commonly applied mitigation system is using a pressure relief valve which directs the flow to a known location, in this way the pressure can be decreased. However, some consideration always must be given to the direction and location of the end of the vent line. During venting, the discharge may be passed to: a vent stack; a quench tank; a liquid/vapour separator; a scrubber; an incinerator; or a flare stack [118].

Thermal runaways can be stopped for example by shut-off of feed; direct removal of heat; increasing the heat removing or dumping (so dropping the reactor charge into a quench vessel which contains a quench liquid). Thermal runaways can be inhibited by adding cold diluents to decrease the temperature or by adding a chemical reaction inhibitor [119]. A necessary requirement of inhibitors is that it is effective at small injection quantities and it can be easily injected into the system. The inhibiting agent must be well distributed in the reacting medium otherwise it cannot prevent reactor runaway. Also there is a need for a reliable detection of the runaway triggers [120], and the time of the detection is also a crucial factor, because we need time to perform some safety actions and to affect the reactor operation.

Simulations are not negligible in such a task, because with these tools we are able to fast and quantitatively evaluate the backup safety systems, and we are able to choose and plan the proper system for moderating the runaway reaction. Dynamic Simulator-based works about evaluating the consequences of malfunction can be found in [121]–[126].

2.7 Application examples of runaway criteria

This section provides some topics in the application of thermal runaway criteria, which are mainly considered in the design of the reactor, the process control and the inhibition of runaway.

2.7.1 Comparison of reactor runaway criteria

Each runaway criterion can be applied to define the runaway limits in every type of reactor, so in batch-, semi-batch-, tube-, and in continuous stirred tank reactors since these criteria are general from this aspect. There are several study on investigating the commonly applied runaway criteria, and their relationships are presented, for instance in [45], [72], [127], [128]. Szeifert et al. derived that for the Mathematical model introduced in Section 2.4.1. The Adler and Enig criterion equals Lyapunov-stability in phase plane (1^{st} group); Gilless-Hoffmann criterion equals Lyapunov-stability in geometric-plane and Thomas-Bowes criterion equals Van Heerden criterion (2^{nd} group) [45]. In additional Kummer et al. showed that the Divergence criterion equals Gilless-Hoffmann criterion and Lyapunov-stability in geometric plane (3^{rd} group) on the same mathematical model. Since the investigations included only a batch reactor model, the classifications are surely true only for the batch cases. The connection between runaway criteria in other types of reactors should be discussed in the future. The critical curves distinguishing the runaway and non-runaway regimes are shown in Figure 2.10 presenting how these criteria indicate runaway in order. There is a definition to compare criteria to each other, which is conservativeness. A more conservative criterion allows lower temperature gradients and increment. Based on Figure 2.10 Maxi criterion is one of the most conservative, and MSC is one of the less conservative criteria.

For the purpose of online application if there is no an adequate model of the reactor system the Thomas-Bowes criterion and Strozzi-Zaldivar criterion have advantages since these do not need models to perform. Thomas-Bowes criterion searches for inflection points in the temperature trajectory and the divergence of the system can be estimated based on phase-space reconstruction techniques. That is the one of the reason that divergence criterion is really popular in this field. However, as the industry opens to the application of models and its advantages the other runaway criteria can be easily derived too for industrial application. It would be really important since the divergence criterion may be too conservative for some type of reactor operation decreasing the potential possibility for maximizing the efficiency [129].

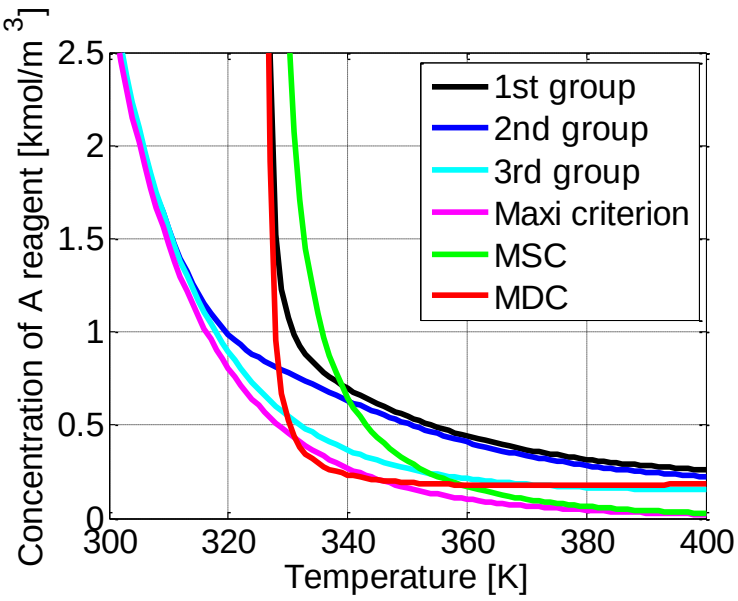

Figure 2.10 Critical curves of runaway at Case study presented in Section 2.4.1 (T_w=310 K) [72]

2.7.2 Reactor operation design

Since runaway criteria characterize the runaway and non-runaway regimes in the state-space, possible reactor operations can be designed based on it to avoid the development of reactor runaway. In [45] the design diagram for the methanol synthesis reactor is shown where the runaway boundaries are defined based on the Lyapunov's indirect method. Runaway criteria are widely applied in the literature to define the alarm and onset temperatures for a reactor operation, [127], [130].

2.7.3 Process control

Adequate models of reactors can be used for a nonlinear model predictive control (NMPC) [131]. NMPC can be a suitable tool to handle nonlinear processes and is gaining more attention because it can capture detailed nonlinear dynamics of the system throughout the entire state space [132], [133]. NMPC is an excellent tool for the control of reactors which perform potential runaway reactions, because with such a tool we can predict the development of reactor runaway. Thermal runaway criteria (Modified Dynamic Condition and Strozzi-Zaldivar criterion) were implemented successfully in NMPC to reliably indicate the development of runaway. One of the most important steps in using MPC to predict runaway is that we must capture the essence of runaway, and we developed a process safety time based method for defining the length of prediction horizon in which the development of runaway can be caught [134].

Different stability analyses to predict the development of thermal runaway were successfully implemented in NMPC, such as the batch simultaneous model-based optimization and control (BSMBO&C) algorithm. This algorithm is an extension of NMPC and dynamic real-time optimization (DRTO) techniques, which use a Boolean term that penalizes the objective function when the controller system is close to thermal runaway [135]. Specific classes of deterministic NMPC/DRTO frameworks can identify reactor runaways under parameter uncertainty too [136]. Strozzi-Zaldivar criterion can be too strict; hence, it is not suitable to analyse the stability of semi-batch reactors in some cases [137]. Kähm-Vassiliadis criterion for exothermic batch reactors was introduced to overcome this problem, and the proposed stability criterion can be successfully applied in batch reactor control to perform highly exothermic reactions [62]. Their stability criterion was applied to an industrial case study and they considered the parameter uncertainty during the process control [138]. Lyapunov exponents as an indicator of stability were successfully realized in NMPC to control batch reactors [139]. The operation of an industrial semi-batch polymerization reactor was optimized by considering a cooling system failure [77]. The interaction between control and safety systems was also studied, where an LMPC (Lyapunov-based MPC) system was integrated with the activation of a safety system in a CSTR to avoid thermal runaway [140]. Recently, two new NMPC-based methods were introduced to solve the closed-loop dynamic optimization problems, which were tested on a semi-batch reactor with potential runaway reactions, where the adiabatic temperature rise was considered to avoid reactor runaway. The first method is based on an adaptive backing off of their bounds along the moving horizon with a decreasing degree of severity. The second method is a chance-constrained control approach, which considers the relation between the uncertain input and the constrained output variables. Both methods consider the unexpected disturbances in advance, which results in a robust control approach [141].

2.7.4 Runaway prediction and inhibition

There are several studies about the investigation of shortstopping of thermal runaway, where they analysed the effect of location of temperature probe, the location and amount of cold diluent injection and the rotational speed while some of them used a runaway criterion to monitor the process [142]–[149]. Jiang et al. investigated the effect of stirring speed, flow rate of cooling agent and the addition of inhibitor. They used divergence criterion to investigate the effect of location of the temperature probe and showed that how this location influences

the detection time of runaway [150]. Russo et al. connected the EWDS system (runaway criterion) with the action of protection [151].

2.8 Future directions

The goal is clearly the industrial application of the presented methods and tools in process design and operation to improve thermal safety while we increase the productivity. In order to fulfil our goal we must extend our knowledge on some field. As we have seen it the runaway develops if somehow the balance between generated and removed heat is upset, and most of runaway criteria are based on it. Removed and generated heat are function of other variables such as concentrations, kinetic parameters, heat transfer parameters, etc., which can vary in time; moreover, these values may not be correctly identified, we cannot know it surely. One of the main issues is the problem of uncertainty from the viewpoint of thermal runaway indication, as we should focus on how the uncertainties affect the detection time of the reactor runaway. Besides, we should perform some researches on how we can eliminate all types of uncertainty and develop a robust runaway indication/forecast tool.

There is no 100 % guarantee that in every case we can indicate the development of runaway, and we can avoid it with the available safety actions. We always must be prepared to moderate the consequences of thermal runaway; hence we must complete detailed researches on how we can mitigate effectively runaway reactions in laboratory and pilot-plant experiments. For this purpose also process simulators can be applied to quantitatively evaluate the mitigation systems.

For industrial applications we should investigate industrial case studies to present how these systems can be designed in detail from the basic information we have, where the design consists of the equipment-, process-, control- and mitigation system design.

For the purpose of gaining more information about thermal runaway CFD simulations and studies should be continued. In most studies the hydrodynamic conditions, flow patterns are neglected, but in fact it can have a high impact on the runaway development. Moreover, CFD simulators can be applied to identify local temperature hot-spots in mixed tank or in a fixed-bed reactor to moderate the consequences.

2.9 My role in the research of thermal runaway

In Section 2.1-2.7 I shortly presented the main research works and directions about thermal runaway, and as we experienced during the reading the research area is diversified. It takes a lot of time to leave a footprint in each research area, and I have not had enough time for it. However, I added my values to the research topic about reactor runaway criteria and its application possibilities.

Based on the literature survey one of my goals is the detailed investigation of thermal runaway criteria. For this purpose I derived the most popular runaway criteria for some general case studies (Section 3-4), and as a result I developed two new thermal runaway criteria (namely Modified Dynamic and Slope Condition). The performance of MSC and MDC are almost the same as the mentioned ones in Section 2.4. Moreover, as the reader will see in Section 5 the reliability of the proposed new criteria can be higher.

Runaway criteria analyses "only" the different reactor states and decides based on that if runaway may occur or not. However, there are cases when the applied runaway criterion indicates runaway but these indicated states do not cause any problem in the process. It can be obtained if the applied criterion is too conservative for the application. My second goal is to develop system-specific runaway criteria, which I performed based on genetic programming methodologies. The identified critical equations outperform the criteria found in literature (see Section 6). As it was told before the main goal and the big result later would be the industrial application of runaway criteria, but unfortunately it is not widespread at all. For this purpose I investigated the applicability of runaway criteria in offline and online tasks for optimal reactor operation, for further information please see Section 7-8.5.

3 Case studies

Seven case studies were used to investigate the phenomenon of reactor runaway in this thesis starting with a simple one-way reaction with one reagent carried out in a batch reactor to a complex one with three reactions carried out in semi-batch reactor. This section provides the model system of these case studies classed for offline and online applications. The mathematical models for offline applications were solved in MATLAB 2011, and for online applications were solved in MATLAB 2019a using third-order Runge-Kutta method. The simulations were carried out on a DELL OPTIPLEX 790 Desktop PC with an Intel® Core™ i7-2600 processor.

3.1 Investigated case studies in the literature

This section provides information about what type of model systems were used for the development of runaway criteria, and as it can be seen in *Table 3.1*, new runaway criteria were investigated with a general reaction system carried out in an ideal batch or tubular reactor. Therefore, in the first investigations I used general models (see Section 5-6).

Table 3.1 Investigated model system in case of presenting new criterion (PSR-batch reactor, ITR – ideal tubular reactor, DITR – dimensionless ideal tubular reactor)

Criterion	Reaction model	Reactor model	Reference
IPP	General reaction system: single reaction	PSR	[75]
IG		ITR	[76]
Maxi		ITR	
PD		ITR	[42]
GH		CSTR	[43]
SZ		PSR/DITR	[55]
LG		PSR/DITR	[45]
LPP		PSR/DITR	
WT_SBD		SBR	[99]
VH	General diagram of removed and generated heat in function of temperature	-	[40]
	specific industrial reactor	TR	

For the purpose of analysing runaway criteria (in this thesis), three types of reaction (single , parallel and autocatalytic reaction) schemes are carried out in tubular reactors with different

kinetic and thermodynamical parameters, which are the following: α ($UA/(V\rho c_p)$) related to the heat transfer coefficient, β ($-\Delta H_r/(\rho c_p)$) related to the heat of reaction, γ which is related to the reaction rate constant and δ (E/R) related to the activation energy of each reaction step in the mechanism. Based on our experience minimum and maximum values for α and β parameters are calculated and shown in *Table 3.2*. The heat transfer coefficient for liquid-liquid systems can change between 400 and 1000 W/(m^2K), and other typical values can be seen in [152]. Specific heat transfer surface is lower at tank reactors, and it is higher at tubular reactors. Reaction enthalpy can vary in a wide interval, some values for exact case studies can be seen in *Table 3.3* through β. Based on the previous parameter regions the interval of α and β parameters can be determined, which delimits the parameters of reactors in industrial practice.

Table 3.2 Usually investigated interval of applied parameters

Parameter	Unit	Lower	Higher
U	W/(m^2K)	400	1000
A/V	m^2/m^3	1	100
rhocp	kJ/(m^3K)	4000	1600
-ΔHr	kJ/kmol	10000	400000
β	m^3K/kmol	2.5	250
α	1/h	0.1	62.5

Some references were collected to show that the considered kinetic parameters in each investigated case study are in the interval of real reaction systems. The references with every relevant information can be seen in *Table 3.3*.

Table 3.3 Kinetic and thermodynamical parameters of reference case studies (BR – batch reactor, SBR – semi batch reactor, CSTR – continuous stirred tank reactor, TR – tubular reactor)

	Reaction scheme / Reactor type	**Case study**	**δ [1/K]**	**γ [-]**	**Reaction Order**	**α [1/h]**	**β [m^3K/kmol]**	**Reference**
1	single reaction / BR	esterification of acetic anhydride and methanol	8606	18	1;1	n.a.	29.5	[25]
2	single reaction / SBR	nitration of 4-cholorobenz otrifluoride	10496	29	1;1	0.7	72.5	[58]
3	equilibrium reaction / BR	PAA synthesis	6958	20	1;1	n.a.	5.6	[153]
			7266	20	1;1		-5.6	
	single reaction / BR		not Arrhenius type				33.1	
6	autocatalytic reaction / BR	esterification of 2-butanol and propionic-anhydride	9502	25	0.81;0.81; 0.9	n.a.	26.3	[143]
			9862	25	0.69;0.79; 1.4			
7	single reaction / SBR	oxidation of 2-octanol	11300	12	1;1	0.3	77.6	[154]
	single reaction		12000	23	1;1		252.3	
8	single reaction / CSTR	acetic anhydride hydrolysis	11244	24	1;1	n.a.	27.4	[49]
9	equilibrium reaction / TR	phosgene reaction	not Arrhenius type			279.3	13406.8	[88]
10	single reaction / TR	nitrobenzene hydrogena -tion	not Arrhenius type			15.0	238	[155]

3.2 Case studies for criterion developments and offline applications

Section 3.2.1 and 3.2.2 presents the applied model system for the investigation of thermal runaway criteria. Model systems in Section 3.2.1.1-3.2.1.3 are used for criteria developments and performance analysis, whose results are in Section 5. Model systems in Section 3.2.1.1 and 3.2.1.4 are used for genetic programing-based criterion development, whose results are

presented in Section 6. For offline applications the production of 2-octanone was used as a case study, presented in Section 3.2.2.

3.2.1 General models

Parameter sensitive models are presented in Section 3.1-3.3 as the basic of the evaluation of all runaway criteria. The reactor is considered as a tube reactor with ideal plug flow condition. The dimensionless model is based on the following simplifications:

- the flow in the reactor is ideal, plug flow;
- density and heat capacity of reaction mixture are constant;
- heat transfer coefficient does not depend on flow conditions;
- wall temperature is constant.

Please notice that the behaviour of an ideal tubular reactor and a batch reactor can be described with the same model system, but in the first case the independent variable is the dimensionless length while in the other case it is the time.

3.2.1.1 Mathematical model of case study I. (CS1)

The first case study (CS1) was presented earlier in Section 2.4.1.

3.2.1.2 Mathematical model of case study II. (CS2)

In the second case study (CS2) we consider two parallel reactions, which can be described by the differential equations (3.3) and (3.4). Multiple reactions can strongly influence the thermal behaviour of the reactor, so they influence the critical curves too.

$$A \overset{r_1}{\rightarrow} C \tag{3.1}$$

$$B \overset{r_2}{\rightarrow} D \tag{3.2}$$

$$\frac{dc_j}{dt} = -r_j \; where \; j = \{A; B\} \tag{3.3}$$

$$\frac{dT}{dt} = \sum_{i=1}^{2} \beta r_i - \alpha(T - T_w) \tag{3.4}$$

Where

$$r_i = \exp\left(\gamma_i - \frac{\delta_i}{T}\right) c_i \tag{3.5}$$

$$i = \{1; 2\} \quad \alpha = 5\frac{1}{h}, \beta = [100\ 70]\frac{m^3 K}{kmol}, \gamma = [19\ 20] \tag{3.6}$$

$$\delta = [6200\ 6800]K, c_0 = [1\ 1]\frac{kmol}{m^3}, T_0 = 320\ K \tag{3.7}$$

The model is parameter sensitive which can be seen in Figure 3.1 and Figure 3.2, therefore the model is applicable in studying runaway criteria.

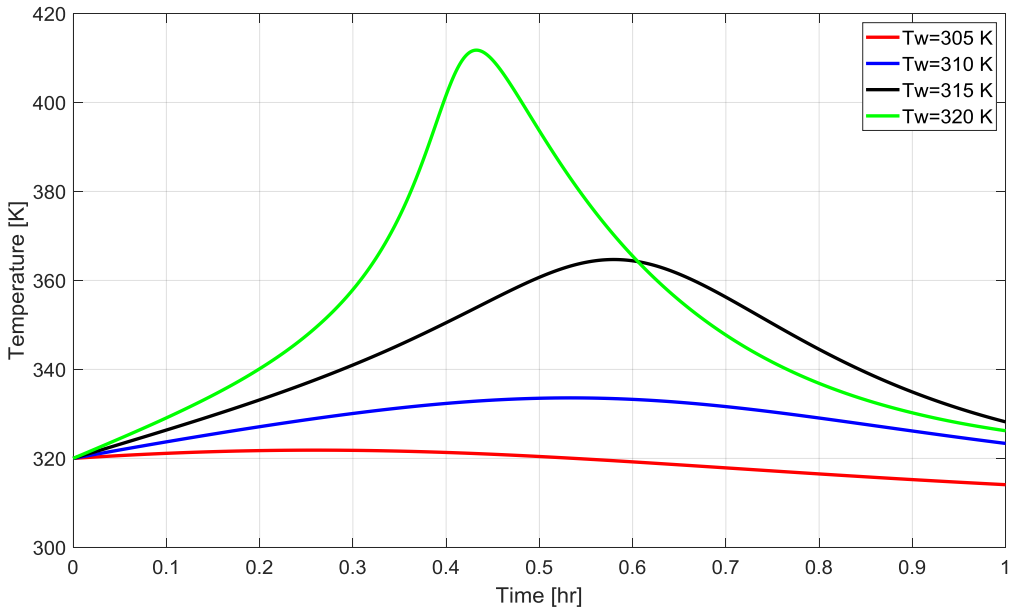

Figure 3.1 Temperature profiles (CS2)

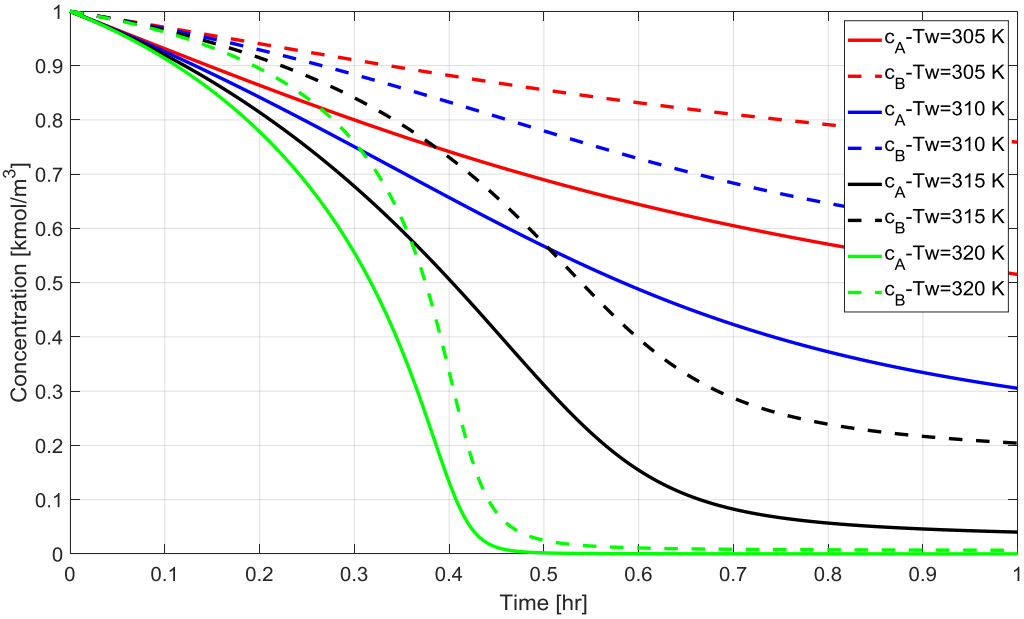

Figure 3.2 Concentration profiles (CS2)

3.2.1.3 Mathematical model of case study III. (CS3)

The third case study (CS3) is an autocatalytic reaction system considers one reaction, but the product catalyses the reaction. Autocatalytic reactions are considered hazardous because they give rise to sudden heat evaluation. The sudden heat evolution stems from the nature of reaction kinetics. For this is reason it is worth to use autocatalytic systems to analyse runaway criteria. The following differential equations describe the system:

$$A \overset{r_1}{\rightarrow} C \tag{3.8}$$

$$A + C \overset{r_2}{\rightarrow} 2C \tag{3.9}$$

$$\frac{dc_j}{dt} = -\sum_{i=1}^{2} r_i \ \ where\ j = \{A\} \tag{3.10}$$

$$\frac{dT}{dt} = \sum_{i=1}^{2} \beta_i r_i - \alpha(T - T_w) \tag{3.11}$$

Where

$$r_1 = \exp\left(\gamma_1 - \frac{\delta_1}{T}\right) c_1 \tag{3.12}$$

$$r_2 = \exp\left(\gamma_2 - \frac{\delta_2}{T}\right) c_1 c_2 \tag{3.13}$$

$$i = \{1; 2\} \quad \alpha = 5\frac{1}{h}, \beta = [100\ 140]\frac{m^3 K}{kmol}, \gamma = [14\ 20] \tag{3.14}$$

$$\delta = [4000\ 6000]\ K, c_0 = [1\ 0]\frac{kmol}{m^3}, T_0 = 300\ K \tag{3.15}$$

The model is parameter sensitive which can be seen in Figure 3.3 and Figure 3.4, therefore the model is also applicable in studying runaway criteria.

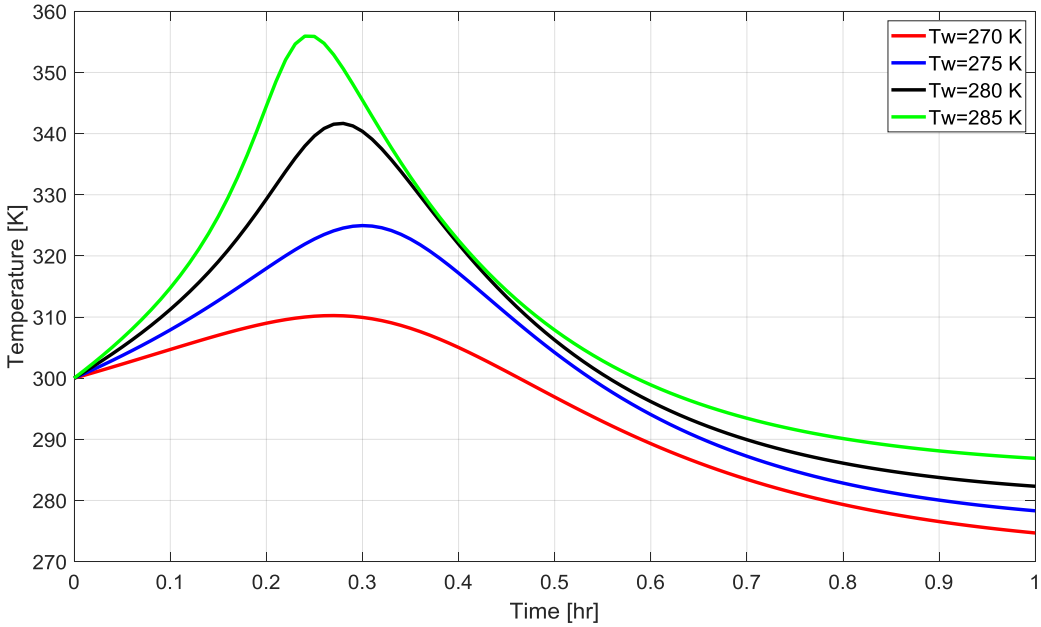

Figure 3.3 Temperature profiles (CS3)

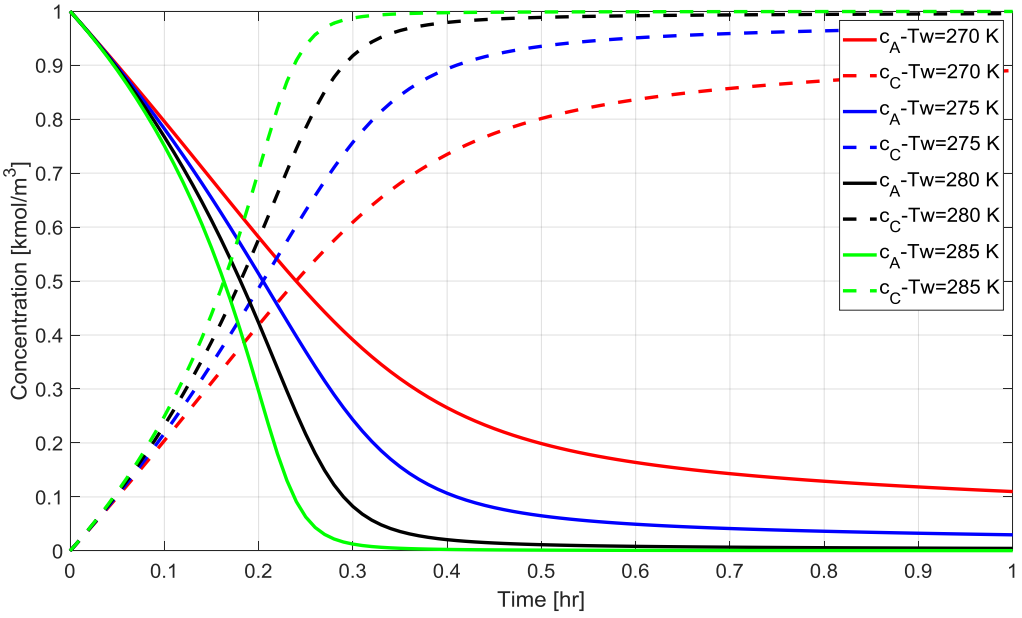

Figure 3.4 Concentration profiles (CS3)

3.2.1.4 Mathematical model of CSTR (CS4)

The case study (CS4) considers a one way reaction including one reagent, where reaction is the following:

$$A \xrightarrow{r} C \tag{3.16}$$

The following differential equations can be written to describe the behaviour of this kind of reactor:

$$\frac{dc_A}{dt} = \frac{1}{\tau}\left(c_{A,in} - c_A\right) - r \tag{3.17}$$

$$\frac{dT}{dt} = \frac{1}{\tau}(T_{in} - T) + \beta r - \alpha(T - T_w) \tag{3.18}$$

Where

$$r = \exp\left(\gamma - \frac{\delta}{T}\right)c \tag{3.19}$$

$$\alpha = 5\frac{1}{h}, \beta = 180\frac{m^3K}{kmol}, \gamma = 20, \delta = 6600\ K, c_0 = 1\ \frac{kmol}{m^3}, T_0 = 300\ K \tag{3.20}$$

3.2.2 2-octanone production process (2OCT)

Production of 2-octanone is based on oxidation of 2-octanol with nitric acid carried out in a semi-batch reactor. In this reactor a parameter sensitive, highly exothermic reaction is carried out. The model is determined in [154] and [156] in detail. A short introduction is given about this model, and the simplified reaction mechanism is the following:

$$A + B \rightarrow 2P + B \tag{3.21}$$

$$P + B \rightarrow X \tag{3.22}$$

where A is 2-octanol, B is nitrosonium ion, P is 2-octanone, and X is byproducts. The calculation of reaction rates are based on the following equations:

$$r_1 = \varepsilon_{aq} \cdot k_{eff,1} \cdot m_A \cdot c_A^{org} \cdot c_B^{aq} \tag{3.23}$$

$$r_2 = \varepsilon_{aq} \cdot k_{eff,2} \cdot m_P \cdot c_P^{org} \cdot c_B^{aq} \tag{3.24}$$

where the effective calculation rates are calculated by the following equations:

$$k_{eff,i} = k_{eff,i}^0 \cdot exp\left(-\frac{E_{A,eff,i}}{RT^R} - m_{H_{0,eff,i}} \cdot H_0\right) \tag{3.25}$$

The following ordinary differential equations describe the concentration and temperature trajectories during the operation:

$$\frac{d\left(V^R \cdot c_A^{org}\right)}{dt} = B^{R,in} \cdot c_{A,in} - r_1 \cdot V^R \tag{3.26}$$

$$\frac{d\left(V^R \cdot c_B^{aq}\right)}{dt} = V^R \cdot (r_1 - r_2) \tag{3.27}$$

$$\frac{d\left(V^R \cdot c_P^{org}\right)}{dt} = V^R \cdot (r_1 - r_2) \tag{3.28}$$

$$\frac{d\left(V^R \cdot c_X^{org}\right)}{dt} = V^R \cdot r_2 \tag{3.29}$$

$$\frac{d\left(V^R \cdot c_N^{aq}\right)}{dt} = -V^R \cdot (r_1 + r_2) \tag{3.30}$$

$$\frac{dT^T}{dt} = \frac{1}{HC^R} \cdot (Q_r + Q_{in}^R - Q_{cool} + Q_{stir} - Q_{loss}) \tag{3.31}$$

$$\frac{dT^C}{dt} = \frac{1}{HC^C} \cdot \left(Q_{in}^C + Q_{cool}\right) \tag{3.32}$$

Figure 3.5 shows the reactor operation with and without reactor runaway pointing out the sensitivity of the model system, where runaway occurred as a result of different feeding trajectory.

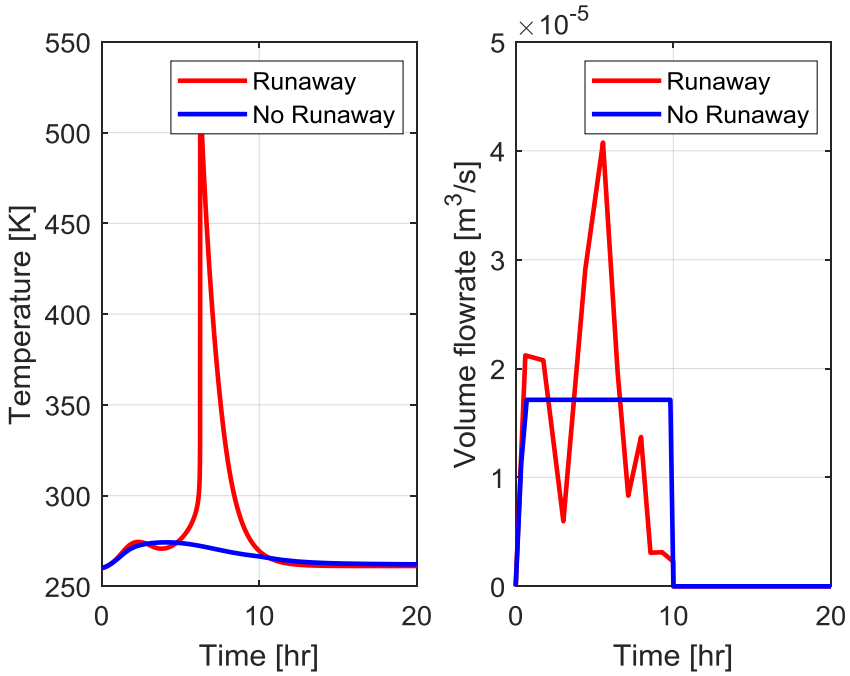

Figure 3.5 Temperature and feeding trajectories (runaway and no runaway)

3.3 Case studies for online applications

Section 3.3.1 and 3.3.2 present the applied model system for investigating the applicability of runaway criteria online in reactor operation. I investigated that how semi-batch reactors can

be optimally controlled while the reactor mains in the safe operating regime during the whole operation. The control scheme first was investigated with a general model (Section 3.3.1), and its results are in Section 8. Then an extended control scheme was investigated on Williams-Otto process (Section 3.3.2), and its results are in Section 8.5.

3.3.1 General model

A second-order reaction was chosen as a case study, since in industrial practice the second and higher order reactions occur frequently. Reaction kinetic and reactor parameters were chosen based on our earlier investigation, so the chosen parameters fit in the possible region of practical values [72]. In the process model $A + B \rightarrow C$ second order reaction is considered, in which the reaction rate is expressed with the following equation:

$$r = kc_A c_B = k_0 exp\left(-\frac{E_A}{RT_R}\right) c_A c_B \tag{3.33}$$

The following differential equations describe the dynamic behaviour of the system.

$$\frac{dV}{dt} = F \tag{3.34}$$

$$\frac{dn_A}{dt} = Fc_{in,A} - Vr \tag{3.35}$$

$$\frac{dn_B}{dt} = -\frac{dn_C}{dt} = -Vr \tag{3.36}$$

$$\frac{dT_R}{dt} = \frac{F\rho c_p(T_{in} - T_R) + (-\Delta H_r)Vr - UA\left(T_R - T_j\right)}{V\rho c_p} \tag{3.37}$$

$$\frac{dT_J}{dt} = \frac{F_J\left(\rho c_p\right)_J\left(T_{J,in} - T_J\right) + UA\left(T_R - T_J\right)}{\left(V\rho c_p\right)_J} \tag{3.38}$$

$$UA = UA_0\left(1 + \frac{V_{dos}}{V_0}\right) \tag{3.39}$$

The kinetic, reactor geometry and material parameters are presented in Table 3.4, and operating parameters are presented in Table 3.5. Reactor constructional parameters are from [157].

Table 3.4 Parameters and initial conditions of the case study

Parameter		Value	Unit
k0	pre-exponential factor	$1.465 \cdot 10^7$	$\frac{m^3}{kmols}$
$\frac{E_A}{R}$	activation energy	8500	K
ΔH_r	reaction heat parameter	-350000	$\frac{kJ}{kmol}$
MAT	Maximum Allowable Temperature	100	°C
UA_0	initial heat transfer parameter	1.85	$\frac{\text{kW}}{°C}$
V_0	initial reagent volume	0.5	m^3
V_J	jacket volume	0.41	m^3
ρc_p	liquid property in reactor	4800	$\frac{\text{kJ}}{m^3 °C}$
$(\rho c_p)_J$	cooling agent property	4183	$\frac{\text{kJ}}{m^3 °C}$

Table 3.5 Reactor operation parameters

Parameter		Value	Unit
F_j	coolant flow rate	4	$\frac{m^3}{hr}$
$n_{A,feed}$	feed moles of *A* reagent	5	kmol
n_{A0}	initial moles of *A* reagent	0	kmol
n_{B0}	initial moles of *B* reagent	5	kmol
$c_{in,A}$	feed concentration of *A* reagent	5	$\frac{\text{kmol}}{m^3}$
T_{R0}	initial reactor temperature	25	°C
T_{J0}	initial jacket temperature	25	°C
T_{in}	reagent feed temperature	25	°C
T_{Jin}	coolant feed temperature	25	°C

3.3.2 Williams-Otto Process

The Williams-Otto process (WOP) has been used for years to test different control and optimization algorithms [35]. We optimize the fed-batch version of this process as presented in [158]. In the Williams-Otto process three exothermic reactions occur, which are presented in Eqs. (3.40)-(3.42) followed by the equation of reaction rates.

$$A + B \rightarrow C \qquad r_1 = k_{0,1} exp\left(-\frac{E_1}{RT}\right) c_A c_B \tag{3.40}$$

$$B + C \rightarrow P + E \qquad r_2 = k_{0,2} exp\left(-\frac{E_2}{RT}\right) c_B c_C \tag{3.41}$$

$$C + P \rightarrow G \qquad r_3 = k_{0,3} exp\left(-\frac{E_3}{RT}\right) c_C c_P \tag{3.42}$$

Component *A* is preloaded and component *B* is continuously fed into the reactor. The desired product is component *P*, and two co-products can be formed: components *E* and *G*. The following differential equations (Eq. (3.43)-(3.46)) describe the dynamical behaviour of the reactor system:

$$\frac{dc_i}{dt} = \frac{F^{in}}{V_R}\left(c_i^{in} - c_i\right) + \sum_{l=1}^{N_R} v_{il} R_l \;\; i = 1 \ldots N_C \tag{3.43}$$

$$\frac{dV_R}{dt} = F^{in} \tag{3.44}$$

$$\frac{dT_R}{dt} = \frac{4U}{D_R \sum_{i=1}^{N_C} c_i cp_i}\left(T_j - T_R\right) + \frac{F^{in} \sum_{i=1}^{N_C} c_i^{IN} cp_i}{V_R \sum_{i=1}^{N_C} c_i cp_i}\left(T^{in} - T_R\right) - \frac{\sum_{l=1}^{N_R} \Delta H_{r,l} R_l}{\sum_{i=1}^{N_C} c_i cp_i} \tag{3.45}$$

$$\frac{dT_j}{dt} = \frac{4UV_R}{D_R V_j \rho_j cp_j}\left(T_R - T_j\right) + \frac{F_j}{V_j}\left(T_j^{in} - T_j\right) \tag{3.46}$$

The kinetic parameters, component properties and reactor constructional and operating parameters are summarized in Table 3.6-Table 3.8. The parameters will be handled as nominal hereinafter. The constraints are defined in Table 3.8, such as the MAT, and maximum feed rates of the reagent and cooling agent.

Table 3.6 Kinetic and thermodynamic parameters of reactions [159], [160]

Parameter		**Value**	**Unit**
Pre-exponential factors	$k_{0,1}$	$1.3833\ 10^5$	$\frac{m^3}{kmol\ s}$
	$k_{0,2}$	$6.0098\ 10^7$	
	$k_{0,3}$	$2.2288\ 10^{11}$	
Activation energies	$\frac{E_1}{R}$	6450	K
	$\frac{E_2}{R}$	8778.5	
	$\frac{E_3}{R}$	11155	
Heat of reactions	$\Delta H_{r,1}$	$-1.851\ 10^5$	$\frac{kJ}{kmol}$
	$\Delta H_{r,2}$	$-2.5765\ 10^5$	
	$\Delta H_{r,3}$	$-5.053\ 10^5$	

Table 3.7 Component properties [159], [160]

Component	**Molecular weight [kg/kmol]**	**Specific heat [kJ/kmolK]**
A	142	321.204
B	60	127.14
C	202	352.288
E	81	166.212
P	181	426.617
G	383	844.132
		[kJ/kgK]
Cooling agent (water)	18	4.186

Table 3.8 Reactor constructional and operating parameters [159], [160]

Parameter	Value	Unit
d	1	m
h	3.5	m
V_j	0.8236	m^3
U	0.8	$\frac{kW}{m^2}$
c_{in}	1	$\frac{kmol}{m^3}$
$T_{in,R}$	298	K
$T_{in,j}$	298	K
$c_{0,A}$	1	$\frac{kmol}{m^3}$
V_0	0.5	m^3
$T_{0,R}$	312	K
$T_{0,J}$	308	K
F_{max}	1e-3	$\frac{m^3}{s}$
$F_{j,max}$	1e-2	$\frac{m^3}{s}$
MAT	335	K

4 Derivation of the applied runaway criteria

Here I present some of the derivations behind the application of thermal runaway criteria to obtain the critical equations. The investigated runaway criteria are Practical Design criterion (PD), inflection point in phase-plane (IPP), Lyapunov-stability in phase-plane (LPP), Maxi criterion, inflection in geometric-plane (IG), Van Heerden criterion (VH), Gilless-Hoffmann criterion (GH), Lyapunov-stability in geometric-plane (LG), and Strozzi-Zaldivar criterion (SZ).

The aim of this section is to present how the runaway criteria can be applied and derived analytically if it is necessary, hence I only present it on the first to four case studies (Section 3.2.1.1-3.2.1.4). I could present the derivation steps for the other case studies too (Section 3.2.2-3.3.2), but that would not have much information content, so it would just increase the number of pages. Everyone can derive these based on the information presented in this section.

4.1 Inflection point in geometric plane

For the first case study (CS1, Section 2.4.1) inflection point in geometric plane can be obtained by differentiating Eq. 2.7 with respect to *t* and equalling with zero (Eq. 4.1). After the substitutions and the rearranging Eq. 4.2 critical equation is resulted.

$$\frac{d^2T}{dt^2} = \beta\left(r_c\frac{dc}{dt} + r_T\frac{dT}{dt}\right) - \alpha\frac{dT}{dt} = 0 \tag{4.1}$$

$$r_T \leq \frac{\alpha}{\beta} + \frac{rr_c}{\beta r - \alpha(T - T_w)} \tag{4.2}$$

For the second case study (CS2, Section 3.2.1.2) we need to differentiate Eq. 3.4 with respect to *t* and it needs to be zero at critical conditions, as Eq. 4.3 presents.

$$\frac{d^2T}{dt^2} = \sum_i \beta_i\left(r_{i,c_j}\frac{dc_j}{dt} + r_{i,T}\frac{dT}{dt}\right) - \alpha\frac{dT}{dt} = 0 \tag{4.3}$$

After substitutions and rearrangement we obtain the following critical equation:

$$\sum_i \beta_i r_{i,T}\frac{dT}{dt} - \sum_i \beta_i r_{i,c_j} r_i \leq \alpha\frac{dT}{dt} \tag{4.4}$$

For the third case study (CS3, Section 3.2.1.3) we need to differentiate Eq. 3.11 with respect to *t* and it needs to be zero at critical conditions, as Eq. 4.5 presents.

$$\frac{d^2T}{dt^2} = \sum_i \beta_i \left(\sum_j r_{i,c_j} \frac{dc_j}{dt} + r_{i,T} \frac{dT}{dt} \right) - \alpha \frac{dT}{dt} = 0 \tag{4.5}$$

If we divide Eq. 4.5 with *dT/dt* after a rearrangement we obtain the following equation:

$$\sum_i \beta_i r_{i,T} + \sum_i \beta_i \left(\sum_j r_{i,c_j} \frac{dc_j}{dT} \right) \leq \alpha \tag{4.6}$$

4.2 Inflection point in phase-plane

Based on this theory runaway occurs if an inflection point appears on the temperature profile in the conversion-temperature (*x*-*T*) phase-plane, so if the second derivative equals zero. For the first case study (CS1, Section 2.4.1) inflection point in phase plane can be obtained if we differentiate Eq. 4.7 with respect to *x* and equalling it with zero (Eq. 4.8). After substitution and a rearrangement we obtain Eq. 4.10 critical equation.

$$\frac{1}{c_0}\frac{dT}{dx} = \beta - \frac{\alpha}{r}(T - T_w) \tag{4.7}$$

$$\frac{d^2T}{dx^2} = \left(\beta - \frac{\alpha}{r}(T - T_w) \right) \frac{d}{dx} = \frac{d}{dx}\left(\frac{T - T_w}{r} \right) = 0 \tag{4.8}$$

$$\frac{d}{dx}\left(\frac{T - T_w}{r} \right) = \frac{\frac{dT}{dx} r - (T - T_w)\left(r_x + r_T \frac{dT}{dx} \right)}{r^2} = 0 \tag{4.9}$$

$$r_T \leq \frac{r}{T - T_w} + \frac{r r_c}{\beta r - \alpha(T - T_w)} \tag{4.10}$$

For the second case (CS2, Section 3.2.1.2) it is an interesting problem since in this case I have one dependent variable (process temperature) and two independent variables (two conversions of the reagents). I guess I can choose from three possibilities. The first is that we consider only the conversion of the key component, the second is that we consider the conversion of each reagents independently, and the third one is that we try to merge the conversions. I choose the third one so I can say that there is a runaway if inflection points appear in the

temperature profile with respect to the sum of the conversions. Otherwise, I was not able to solve the criterion for CS2 analytically, so I used numerical solution.

For the third case (CS3, Section 3.2.1.3) we need to differentiate Eq. 4.11 with respect to *x* and we need to equal that with zero.

$$\frac{1}{c_0}\frac{dT}{dx} = \frac{\sum_i \beta_i r_i - \alpha(T - T_w)}{\sum_i r_i} \tag{4.11}$$

$$\frac{d^2T}{dx^2} = \left(\sum_i \beta_i \left(r_{i,x} + r_{i,T}\frac{dT}{dx}\right) - \alpha\frac{dT}{dx}\right)\sum_i r_i - \left(\sum_i r_{i,x} + r_{i,T}\frac{dT}{dx}\right)\frac{dT}{dt} = 0 \tag{4.12}$$

After substitutions and some formal rearrangement we obtain the following critical equation.

$$\sum_i \beta_i r_{i,x}\left(\sum_i r_i\right) + \sum_i \beta_i r_{i,T}\frac{dT}{dt} - \sum_i r_{i,x}\frac{dT}{dt} - \sum_i \frac{r_{i,x}}{\sum_i r_i}\left(\frac{dT}{dt}\right)^2 \leq \alpha\frac{dT}{dt} \tag{4.13}$$

4.3 Maxi criterion

I am going to present the derivation of Maxi criterion for the first case study (CS1, Section 2.4.1). We need to know where the temperature reaches the maximum (T_m) with respect to the conversion (Eq. 4.14), and we need to know in these points the maximal concentration (Eq. 4.16), which can be derived from the maximal reaction rate (Eq. 4.12).

$$\frac{dT}{dx} = 0 = c_0\left(\beta - \frac{\alpha}{r_m}(T_m - T_w)\right) \tag{4.14}$$

$$r_m = exp\left(\gamma - \frac{E}{RT_m}\right)c_m \tag{4.15}$$

$$c_m = \frac{\alpha}{\beta}\frac{(T_m - T_w)}{exp\left(\gamma - \frac{E}{RT_m}\right)} \tag{4.16}$$

In fact Eq. 4.16 presents a Maxi function and we call an operation critical if the process temperature exceeds the temperature at the maximum of c_m. We can generalize it through defining an equation presenting the maximum values (Eq. 4.17).

$$\frac{dc_m}{dT_m} = 0 = \frac{d}{dT_m}\left(\frac{(T_m - T_w)}{exp\left(\gamma - \frac{E}{RT_m}\right)}\right) \tag{4.17}$$

$$\frac{dc_m}{dT_m} = exp\left(\gamma - \frac{E}{RT_m}\right) - \frac{E}{RT^2}exp\left(\gamma - \frac{E}{RT_m}\right)(T_m - T_w) = 0 \tag{4.18}$$

$$T_m - T_w = \frac{RT_m^2}{E} \tag{4.19}$$

We should wonder about Eq. 4.19 since this form appears again and again if the reader still remembers. On the other hand if we rearrange Eq. 4.19 and substitute it into Eq. 4.16 we get Eq. 4.20 and Eq. 4.21, the desired form of our critical equation.

$$c_m = \frac{\alpha}{\beta}\frac{\frac{RT_m{}^2}{E}}{exp\left(\gamma - \frac{E}{RT_m}\right)} \tag{4.20}$$

$$r_T \leq \frac{\alpha}{\beta} \tag{4.21}$$

It is worth noting that Eq. 4.21. equals with Eq. 4.22, which is much easier to handle.

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c \leq \frac{dq_{rem}}{dT} \tag{4.22}$$

For the second to fourth case study (CS2, CS3, CS4, Section 3.2.1.2-3.2.1.4) I used Eq. 4.22 to define the critical equations. For CS2 and CS3 Eq. 4.23 presents the derived critical equation.

$$\sum_i \beta_i r_{i,T} \leq \alpha \tag{4.23}$$

For the CS4 we need to derive Eq. 3.18 which results in the critical equation of Eq. 4.24.

$$r_T \leq \frac{\alpha + \tau^{-1}}{\beta} \tag{4.24}$$

4.4 Van Heerden criterion

For the first case (CS1, Section2.4.1) the derivation of VH criterion is presented in Eq. 4.25-4.27, for this derivation we have to derive the terms of Eq. 2.7 with respect to *T*.

$$\frac{dq_{gen}}{dT} \leq \frac{dq_{rem}}{dT} \tag{4.25}$$

$$\beta\left(r_T + r_c\frac{dc}{dT}\right) \leq \alpha \tag{4.26}$$

$$r_T \leq \frac{\alpha}{\beta} + \frac{rr_c}{\beta r - \alpha(T - T_w)} \tag{4.27}$$

For the second case study (CS2, Section 3.2.1.2) we have to derive the terms of Eq. 3.4 with respect to *T*.

$$\sum_i \beta_i\left(r_{i,T} + r_{i,c_j}\frac{dc_j}{dT}\right) \leq \alpha \tag{4.28}$$

After substation and rearrangement we obtain the following critical equation:

$$\sum_i \beta_i r_{i,T}\frac{dT}{dt} - \sum_i \beta_i r_{i,c_j} r_i \leq \alpha\frac{dT}{dt} \tag{4.29}$$

For the third case study the methodology is the same, we have to derive the terms of Eq. 3.11 with respect to *T*.

$$\beta_1\left(r_{1,T} + r_{1,c_A}\frac{dc_A}{dT}\right) + \beta_2\left(r_{2,T} + r_{2,c_A}\frac{dc_A}{dT} + r_{2,c_C}\frac{dc_C}{dT}\right) \leq \alpha \tag{4.30}$$

After substituting and a rearrangement we obtain the following critical equation:

$$\sum_i \beta_i r_{i,T} + \sum_i \beta_i\left(\sum_j r_{i,c_j}\frac{dc_j}{dT}\right) \leq \alpha \tag{4.31}$$

In case of the fourth case study (CS4, Section 3.2.1.4) I used numerical differentiating method for the evaluation of the VH criterion.

4.5 Gilless-Hoffmann criterion

For the first case study (CS1, Section 2.4.1) the derivation of GH criterion is presented in Eq. 4.32-4.33, where we need to derive the terms of Eq. 2.7 with respect to *T*, and we need to derive Eq. 2.6 with respect to *c*.

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \leq \frac{dq_{rem}}{dT} \tag{4.32}$$

$$\beta r_T - r_c \leq \alpha \tag{4.33}$$

For the second case study (CS2, Section 3.2.1.2) the methodology is the same, we need to use Eq. 3.4 and Eq. 3.3 for the differentiation procedure. The difference is that we need to consider both mass balance functions of the reagents for the differentiation, the critical equation is presented in Eq. 4.34. For the third case study (CS3, Section 3.2.1.3) the methodology is almost the same, but since it is an autocatalytic reaction, we need to consider that the increase in concentration of product contributes to the runaway (eq. 4.35-4.36).

$$\sum_i \beta_i r_{i,T} - \sum_i r_{i,c_j} \leq \alpha \tag{4.34}$$

$$\frac{\partial\left(\sum_i \beta_i r_i - \alpha(T - T_w)\right)}{\partial T} + \frac{\partial(-r_1)}{\partial c_A} + \frac{\partial(-r_2)}{\partial c_A} + \frac{\partial(r_2)}{\partial c_C} \leq 0 \tag{4.35}$$

After solving Eq. 4.35 and a rearrangement we obtain the following critical equation:

$$\sum_i \beta_i r_{i,T} - \sum_i \sum_j r_{i,c_j} \leq \alpha \tag{4.36}$$

4.6 Practical Design criterion

For the first and fourth case study (CS1, Section 2.4.1, CS4, Section 3.2.1.4) this is just a formal transformation of Eq. 2.23, as it is presented in Eq. 4.37-38. If we have more than one reaction we need to calculate the sum of the reaction rates and their derivatives (CS2, Section 3.2.1.2, CS3, Section 3.2.1.3), as it is presented in Eq. 4.39.

$$T - T_w \leq \frac{R\mathrm{T}^2}{E} \equiv \left(\frac{r}{r_T}\right) \tag{4.37}$$

$$r_T \leq \frac{r}{T - T_w} \tag{4.38}$$

$$\sum_i r_{i,T} \leq \frac{\sum_i r_i}{T - T_w} \tag{4.39}$$

4.7 Lyapunov-stability analysis in geometric plane

For the derivation of Lyapunov-stability we need to calculate the eigenvalues of the Jacobian-matrix of the model system. For the first case study (CS1, Section 2.4.1) the Jacobian-matrix is presented in Eq. 4.40. The calculation of eigenvalues leads to a quadratic equation (Eq. 4.41-4.42).

$$\underline{\underline{J}} = \begin{bmatrix} -r_c & -r_T \\ \beta r_c & \beta r_T - \alpha \end{bmatrix} \tag{4.40}$$

$$(-r_c - \lambda)(\beta r_T - \alpha - \lambda) + r_c r_T \beta = 0 \tag{4.41}$$

$$\frac{-(r_c + \alpha - \beta r_T) + \sqrt{(r_c + \alpha - \beta r_T)^2 - 4\alpha r_c}}{2} = \lambda_{1,2} \tag{4.42}$$

The real parts of the eigenvalues should be below zero. In Eq. 4.42 the first term is the determining since the term under the square root is much lower. It means that if the first term is positive then the eigenvalues are negative, so the system is stable. After formal transformation of the first term we obtain the following critical equation:

$$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta} \tag{4.43}$$

For the second and third case study I calculated the eigenvalues numerically.

4.8 Lyapunov-stability analysis in phase-plane

For the first case study (CS1, Section 2.4.1) the stability analysis in phase-plane becomes simpler since the number of state variables is only one. We need to differentiate Eq. 4.44 with respect to *T* and it needs to be less than zero. The derivation is presented in Eq. 4.44-4.47.

$$\frac{1}{c_0}\frac{dT}{dx} = \beta - \alpha\frac{(T - T_w)}{r} \tag{4.44}$$

$$\frac{d}{dT}\left(\beta - \alpha\frac{(T - T_w)}{r}\right) \leq 0 \tag{4.45}$$

$$-\frac{\alpha}{r^2}\left(r - (T - T_w)\left(r_T + r_x\frac{dx}{dT}\right)\right) \leq 0 \tag{4.46}$$

$$r_T \leq \frac{r}{T - T_w} + \frac{r r_c}{\beta r - \alpha(T - T_w)} \tag{4.47}$$

At the second case study (CS2, Section 3.2.1.2) we struggle with the same problem as in Section 4.2 since we have more than one dependent variable (the conversions), but I applied the same methodology, so I considered the sum of the conversions. We can guess that, but I was not able to solve the criterion for CS2 analytically, so I used numerical solution.

For the third case study (CS3, Section 3.2.1.3) we need to differentiate Eq. 4.48 with respect to *T*.

$$\frac{1}{c_0}\frac{dT}{dx} = \frac{\sum_i \beta_i r_i - \alpha(T - T_w)}{\sum_i r_i} \tag{4.48}$$

$$\frac{1}{dT}\frac{dT}{dx} = \left(\sum_i \beta_i \left(r_{i,T} + r_{i,x}\frac{dx}{dT}\right) - \alpha\right)\sum_i r_i - \left(\sum_i r_{i,T} + r_{i,x}\frac{dx}{dT}\right)\frac{dT}{dt} = 0 \tag{4.49}$$

After substitutions and some formal rearrangement we obtain the following critical equation.

$$\sum_i \beta_i r_{i,x}\left(\sum_i r_i\right) + \sum_i \beta_i r_{i,T}\frac{dT}{dt} - \sum_i r_{i,x}\frac{dT}{dt} - \sum_i \frac{r_{i,x}}{\sum_i r_i}\left(\frac{dT}{dt}\right)^2 \leq \alpha\frac{dT}{dt} \tag{4.50}$$

For the fourth case study (CS4, Section 3.2.1.4) I evaluated the criterion numerically.

4.9 Strozzi-Zaldivar (divergence) criterion

For the first case study (CS1, Section 2.4.1) the divergence of the model system is the sum of the trace of the Jacobian-matrix (Eq. 4.51):

$$\frac{\partial(-r)}{\partial c} + \frac{\partial\left(\beta r - \alpha(T - T_w)\right)}{\partial T} \leq 0 \tag{4.51}$$

After solving Eq. 4.52 and a rearrangement we obtain the following critical equation:

$$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta} \tag{4.52}$$

For the second to fourth case study the methodology is the same and easy to derive using the balance equations, the derived critical equations are presented in Eq. 4.53-4.55 respectively.

$$\sum_i \beta_i r_{i,T} \leq \alpha + \sum_i r_{i,c_j} \tag{4.53}$$

$$\sum_i \beta_i r_{i,T} - \sum_i \sum_j r_{i,c_j} \leq \alpha \tag{4.54}$$

$$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta} + \frac{2}{\beta\tau} \tag{4.55}$$

Great, we have derived a lot of critical equations, especially for the case of batch reactors. I would like to summarize the derived critical equations for the first case study (CS1, Section 2.4.1) in *Table 4.1*. As we can see, some of the runaway theories result in the same critical equations, which mean that these runaway criteria indicate the development of runaway at the same states of operation. This is clearly visible in this table, but if the reader devotes a few minutes for it, you can see that it is true for the other reaction systems carried out in batch reactors too (CS2-CS3, Section 3.2.1.2-3.2.1.3). The same critical conditions are classed into groups as it is presented in *Table 4.1*. Unfortunately my investigation does not cover that if this classification is true or not for other reactor types too (CSTR, SBR), but it really should be the task of a future work since it is a really interesting question.

Table 4.1 Critical equations according to different criteria for CS1

Criterion	**Derived critical curves for CS1**	
PD	$r_T \leq \frac{r}{T - T_w}$	-
IPP, LPP	$r_T \leq \frac{r}{T - T_w} + \frac{r r_c}{\beta r - \alpha(T - T_w)}$	1st group
Maxi criterion	$r_T \leq \frac{\alpha}{\beta}$	-
IG, VH	$r_T \leq \frac{\alpha}{\beta} + \frac{r r_c}{\beta r - \alpha(T - T_w)}$	2nd group
GH, LG, SZ	$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta}$	3rd group

5 Completion of thermal runaway criteria: Two new criteria to define runaway limits

All the introduced criteria (see in Section 4.) were investigated in three general case studies, with different reaction systems, which were introduced in Section 3.2.1.1-3.2.1.3. An irreversible reaction system including one reagent, a parallel reaction system including two reagents, and an autocatalytic reaction system are considered in our investigation.

The most relevant thermal runaway criteria found in literature (see in Section 4.) have been systematized based on the similarities and differences between them. My goal is to determine new runaway criterion which can be applied as a transitional criterion between the strictest and the softest criteria in different cases. The proposed criteria are analysed compared to the most relevant existing criteria. Early detection of runaway comes from the strictness of applied runaway criterion. An early runaway indication is good only if there is really any possibility of the development of hazard event, otherwise it just decreases efficiency of production. Therefore, thermal runaway indications were analysed to qualify runaway criteria through different case studies. The novel of this work is the two new general reactor runaway criteria, whose performances from the viewpoint of earliness and reliability were compared to the existing criteria.

5.1 Analysis of derived critical curves

It is worth to note that all of the derived critical equations consist of the same terms and the sum of these terms (see *Table 4.1*). In *Table 5.1* all the investigated runaway criteria according to the terms of derived critical equations are sorted into groups.

Table 5.1 Runaway criteria in function of derived critical equation terms

Terms of derived critical equations	$\frac{\alpha}{\beta}$	$\frac{r}{T-T_w}$	$\frac{r_c}{\beta}$	$\frac{rr_c}{\beta r-\alpha(T-T_w)}$
$\frac{\alpha}{\beta}$	Maxi criterion	I.	GH, LG, SZ	VH, IG
$\frac{r}{T-T_w}$	I.	PD	II.	IPP, LPP

As it can be seen in *Table 5.1* there are some gaps (grey cells) because none of the existing criteria is based on the sum of those specific terms. There is two more possibility in combination of the terms result in new critical curves (Eq. (5.1) and (5.2)):

$$r_T \leq \frac{r}{T - T_w} + \frac{\alpha}{\beta} \tag{5.1}$$

$$r_T \leq \frac{r}{T - T_w} + \frac{r_c}{\beta} \tag{5.2}$$

General form of the new critical curves can be described with the following equations:

$$\beta r_T = \left.\frac{\partial q_{gen}}{\partial T}\right|_c \tag{5.3}$$

$$\alpha = \frac{dq_{rem}}{dT} \tag{5.4}$$

$$\beta r = q_{gen} \tag{5.5}$$

$$\alpha(T - T_w) = q_{rem} \tag{5.6}$$

After the substitutions of Eq. (5.3)-(5.6)into Eq. (5.1)-(5.2) the general form of new criteria are presented in Eq.(5.7)-(5.8). The first criterion is called as Modified Slope Condition (MSC), and the second criterion is called as Modified Dynamic Condition (MDC).

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c \leq \frac{dq_{rem}}{dT}\left(1 + \frac{q_{gen}}{q_{rem}}\right) \tag{5.7}$$

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \leq \frac{q_{gen}}{q_{rem}}\frac{dq_{rem}}{dT} \tag{5.8}$$

Runaway can occur only if the generated heat is higher than the heat removed, and since the derivatives of removed heat with respect to temperature is multiplied with the ratio of generated and removed heat, this results a less strict criterion than for example the “Practical Design” criterion and Strozzi-Zaldivar criterion.

5.2 Derivation of critical curves for MSC and MDC

In case of CS1 (Section 3.2.1.1) the derived critical curves of MSC and MDC are presented in Eq. 5.1 and Eq. 5.2 respectively. In case of CS2 and CS3 (Section 3.2.1.2) the derived critical curves of MSC and MDC are presented in Eq 5.9 and in Eq. 5.10 respectively.

$$\sum_i \beta_i r_{i,T} \leq \alpha + \frac{\sum_i \beta_i r_i}{T - T_w} \tag{5.9}$$

$$\sum_i \beta_i r_{i,T} - \sum_i r_{i,c_j} \leq \frac{\sum_i \beta_i r_i}{T - T_w} \tag{5.10}$$

5.3 Critical curves in concentration-temperature plane

Runaway criteria can be compared to each other in concentration and temperature phase plane based on the critical curves resulted by each criteria. Critical curves were calculated by equating the left- and right-hand side of critical equations. Along the points on critical curve the criterion will indicate the runaway development. *Figure 5.1-Figure 5.3* show the critical curves of runaway criteria calculated for the case studies CS1-CS3. Concentration of reagent "A" does not affect the critical curves at CS1 and CS3, therefore PD' critical curves cannot be represented in such a plane. In CS2 and CS3 the generated heat is influenced by the concentration of two components. In *Figure 5.2* and *Figure 5.3* the evolution of critical curves due to concentration variations can be seen. Concentration of "B" reagent was varied from 0.5 kmol/m^3 (solid line) to 1 kmol/m^3 (dashed line), which caused relevant difference in critical curves. Higher "B" reagent concentration results that the runaway criteria is going to indicate runaway at lower operating temperature. It is logical since the higher concentration causes higher reaction rate result in more generated heat.

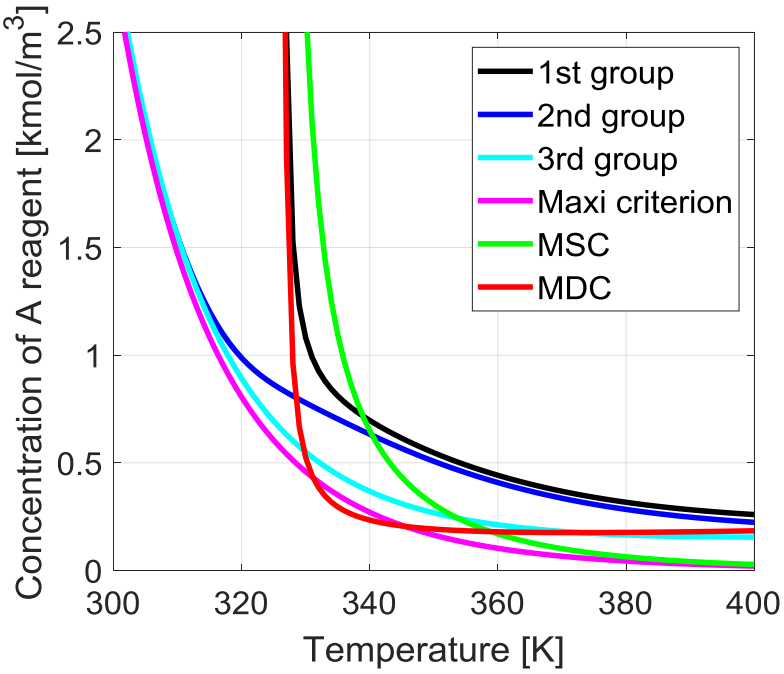

Figure 5.1 Critical curves of runaway at CS1 (T_w=310 K)

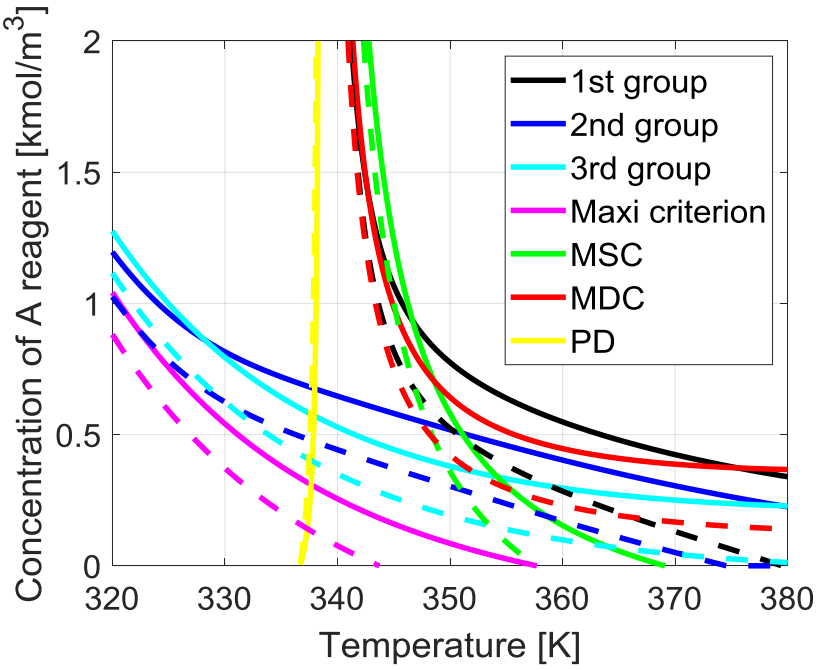

Figure 5.2 Critical curves of runaway at CS2 (T_w=320 K, solid line: c_B=0.5 kmol/m^3, dashed line: c_B=1 kmol/m^3)

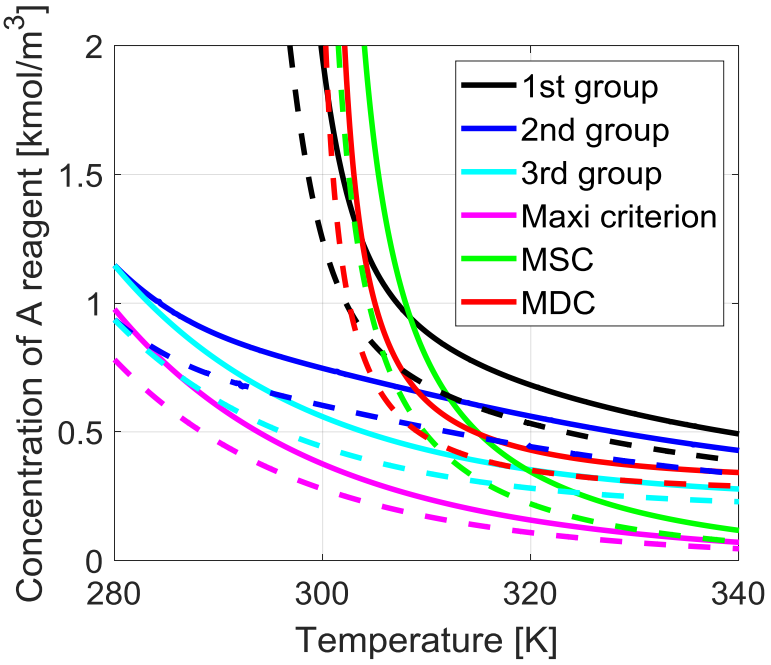

Figure 5.3 Critical curves of runaway at CS3 (T_w=280 K, solid line: c_B=0.5 kmol/m^3, dashed line: c_B=1 kmol/m^3)

There are relevant differences between critical curves investigating simple systems too, each criteria indicates thermal runaway at different points on the phase plane. But how can we decide that which criterion indicates runaway development correctly? There is no adequate solution to define the exact critical curve of runaway zone; therefore it is difficult to tell how a new reactor runaway criterion performs. A possible evaluation strategy for new criterion is

that a branch of existing criteria are implemented in the current case study and we can state, that the reactor is in a runaway zone if the most of the different criteria indicate reactor runaway. *Figure 5.1-Figure* 5.3 show seven different critical curves, and one by one indicates runaway at different reactor states. If at least four criteria indicate runaway, then that condition is considered as a runaway condition. *Figure 5.4-Figure 5.6* show different temperature profiles in the function of conversion, which characterize the boundaries at a specific number of indications (NoI).

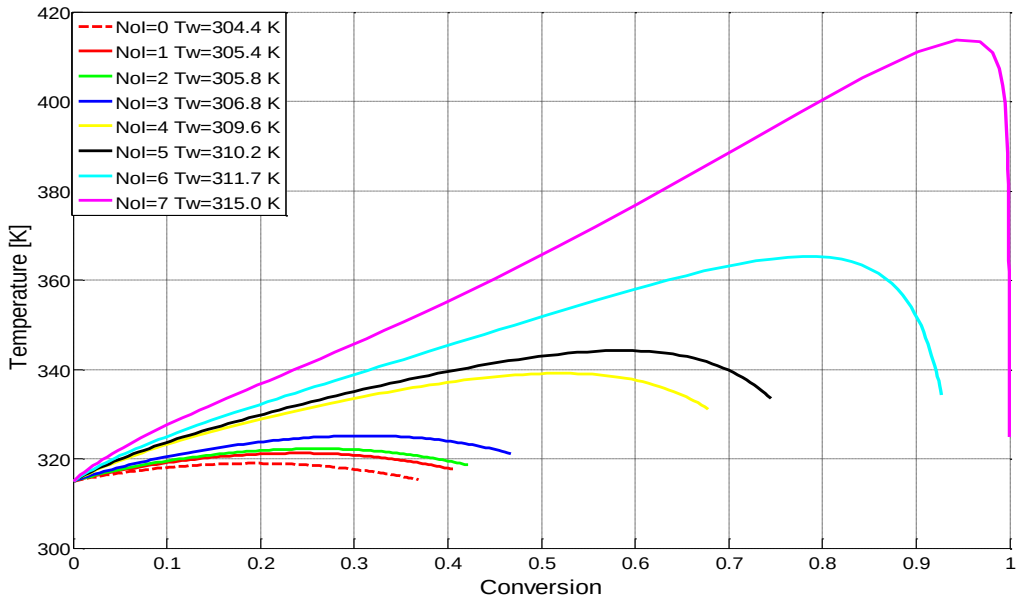

Figure 5.4 Temperature profiles with respect to number of indications (NoI) at CS1

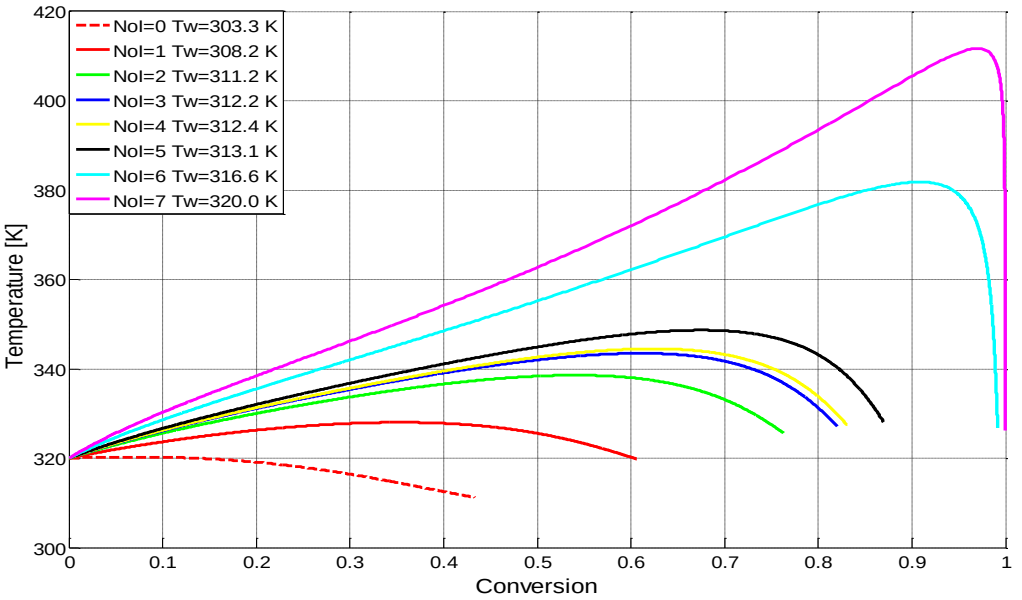

Figure 5.5 Temperature profiles with respect to number of indications (NoI) at CS2.

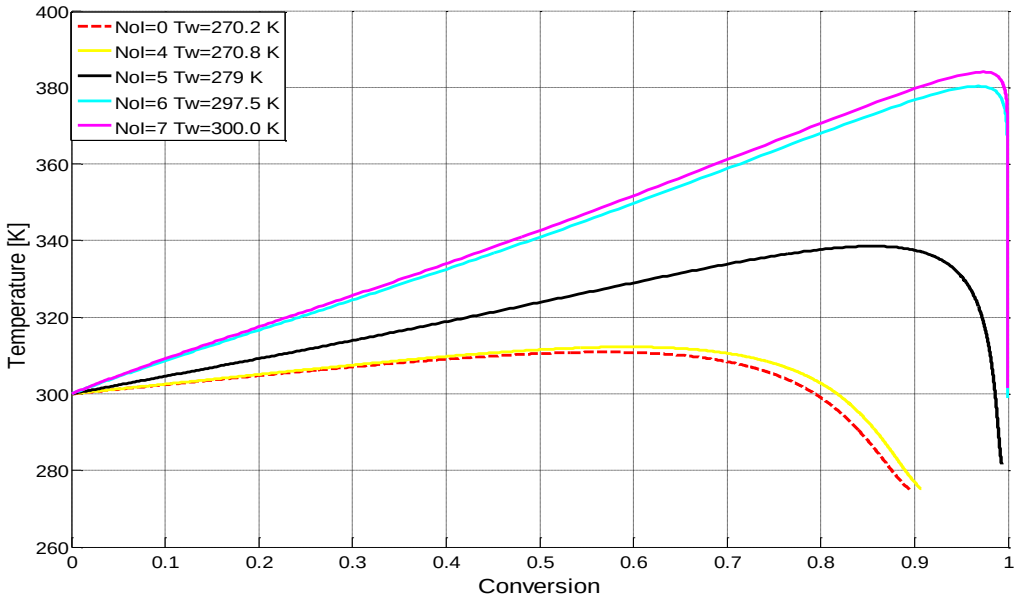

Figure 5.6 Temperature profiles with respect to number of indications (NoI) at CS3

The expectations from runaway criteria are to indicate runaway when a possible hazard situation initiates, and not to when there is no any hazard to avoid false alarms. Confusion matrix can be used to measure the reliability of a runaway criterion, where four classes are defined: true positive (TP), true negative (TN), false positive (FP) and false negative (FN). True positive means that the investigated runaway criterion indicates the development of thermal runaway and it really occurs, and true negative means that runaway does not occur and it is not indicated. Two failure scenarios can be distinguished, which are runaway occurs but there is no runaway indication from criterion (false negative), and the other one is there is no runaway, but there is a runaway indication from criterion (false positive). The first one can have more crucial consequences than the second one, therefore during evaluation the weight of consequences should be considered.

5.4 Performance of the two proposed criteria

For that purpose to investigate the performance of the each runaway criterion thousand simulations were run with different operating parameters. The different operating parameters (feed temperature and wall temperature) were randomly generated in the investigated case studies and runaway indications were collected based on every runaway criteria introduced in Section 4. The interval of randomly generated feed temperature and the parameter to calculate the wall temperature is in *Table 5.2*. The feed and wall temperature have been varied, and the

wall temperature was defined by Eq. (5.11). Applying Eq. (5.11), the wall temperature cannot be higher than feed temperature.

$$T_w = p_1(T_0 - p_2) + p_2 \tag{5.11}$$

where p_1 parameter is a random number between zero and one.

Table 5.2 Interval of generated operating parameters

	CS1	**CS2**	**CS3**
T_0 [K]	300-310	310-340	310-320
p_2	260	300	300

From the thousand operating parameter combinations there was 539 runaway at CS1, 591 runaway at CS2 and 882 runaway at CS3 when most of the criteria indicate runaway. Criteria were analysed by their indication, and the right and false indications were counted. The explanation of cells in *Table 5.4* is shown in *Table 5.3*.

Table 5.3 Explanation of submatrices (confusion matrix) in Table 5.4

	Case study	
Applied criterion	Reactor runaway-indication	Reactor runaway-no indication
	no reactor runaway-indication	no reactor runaway – no indication

The ratios of right and false indications are shown in *Table 5.4*. For example at Case study 1 61% of runaway states were not indicated by 1st group criteria, 39% of runaway states were indicated, and there was no false indication (no reactor runaway-indication). Red cells show that there are cases when runaway occurs and these were not indicated by the specific criterion. Green cells show that there was no any false indication. *Table 5.4* shows that a criterion which performs perfectly does not exist. MDC at CS1 and CS3 indicated every runaway case correctly and there was no false indication. At CS2 there were no any runaway states which were not indicated, but there was 15% false runaway indication, although the rest of the criteria performed poorer.

Table 5.4 Reliability analysis of runaway criteria

	Case study					
Criterion	**CS1**		**CS2**		**CS3**	
1st group	0.39	0.61	0.78	0.22	0.46	0.54
	0.00	1.00	0	1	0.00	1.00
2nd group	0.62	0.38	0.96	0.04	1.00	0.00
	0.00	1.00	0	1	0.00	1.00
3rd group	1.00	0.00	1	0	1.00	0.00
	0.16	0.84	0.25	0.75	1.00	0.00
PD	1.00	0.00	1	0	1.00	0.00
	0.2	0.8	0.5	0.5	0.00	1.00
Maxi	1.00	0.00	0.99	0.01	0.78	0.22
	0.35	0.65	0	1	0.00	1.00
MSC	0.53	0.47	0.95	0.05	1.00	0.00
	0.00	1.00	0	1	0.00	1.00
MDC	1.00	0.00	1	0	1.00	0.00
	0.00	1.00	0.15	0.85	0.00	1.00

The other comparing method for the analysis of runaway criteria is based on the sequence of the runaway indications. I investigated that in which order the investigated runaway criteria indicated the development of thermal runaway. The earliness of indication is crucial feature of a runaway criterion since if the criterion indicates earlier then there is more time to prevent the progress of thermal runaway. *Table 5.5* shows at different case studies the runaway indication order (where at least four criteria indicated). Dark green cell shows at which place the criterion indicated with the highest frequency. Light green cell shows the place where the criterion indicated with significant frequency. Fraction of right indication is the same as shown in *Table 5.4* which gives the fraction of right thermal runaway indication at each criterion. A stricter criterion will indicate runaway earlier than the less strict. However, there is no specific place for each criterion, they have a distribution respect to their indication order. MSC criterion indicated runaway from place 1 to 7, MDC criterion indicated runaway from place 2 to 7 but it can be seen that the proposed two new criteria belong to group of less strict reactor runaway criteria.

Based on the investigations there is no any super runaway criterion which indicates thermal runaway always with the highest reliability and the earliest. Therefore, it is not enough to use only one runaway criterion in the reactor design and operation, we always must check its performances in the given task.

Table 5.5 Indication order analysis of runaway criteria

CS	Place	1st group	2nd group	3rd group	PD	Maxi	MSC	MDC
1.	1	0.00	0.19	0.35	0.03	0.97	0.00	0.00
	2	0.00	0.10	0.65	0.26	0.03	0.00	0.01
	3	0.00	0.33	0.00	0.38	0.00	0.00	0.28
	4	0.18	0.00	0.00	0.33	0.00	0.00	0.38
	5	0.04	0.00	0.00	0.00	0.00	0.22	0.33
	6	0.15	0.00	0.00	0.00	0.00	0.17	0.00
	7	0.01	0.00	0.00	0.00	0.00	0.14	0.00
Fraction of right indication		0.39	0.62	1.00	1.00	1.00	0.53	1.00
2.	1	0.08	0.25	0.86	0.11	0.03	0.07	0.18
	2	0.01	0.00	0.07	0.03	0.90	0.00	0.00
	3	0.01	0.02	0.07	0.81	0.06	0.02	0.02
	4	0.03	0.68	0.00	0.05	0.00	0.06	0.11
	5	0.15	0.00	0.00	0.00	0.00	0.31	0.42
	6	0.36	0.00	0.00	0.00	0.00	0.36	0.06
	7	0.14	0.00	0.00	0.00	0.00	0.13	0.20
Fraction of right indication		0.78	0.96	1.00	1.00	0.99	0.95	1.00
3.	1	0.00	0.40	1.00	1.00	0.68	0.05	0.22
	2	0.00	0.59	0.00	0.00	0.05	0.15	0.16
	3	0.00	0.01	0.00	0.00	0.04	0.64	0.14
	4	0.16	0.00	0.00	0.00	0.00	0.14	0.37
	5	0.30	0.00	0.00	0.00	0.00	0.02	0.11
	6	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	7	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fraction of right indication		0.46	1.00	1.00	1.00	0.78	1.00	1.00

5.5 Conclusion

In this section we have systematized the most applied criteria found in literature, and we have recognized that two theory of thermal runaway was not investigated earlier. Two new criteria (Modified Slope Condition and Modified Dynamic Condition) have been developed, which are promising based on the comparison to other runaway criteria. All runaway criteria indicate thermal runaway at different states. How can we tell if there is a real thermal runaway situation?

Criteria were tested in a new qualification method, where the real runaway states were defined by the number of indications due to different reactor runaway criteria. If more than half of the criteria indicated runaway then the reactor is in runaway state. All the criteria were investigated in three case-studies. The MDC criterion has not missed any thermal runaway occurrence and it indicated runaway correctly. Order of indication of each criterion was compared to each other studying the three case studies. There is no specific place in order of indication for criterion in different case studies and operating regimes. As it was shown all have a distribution respect to their place of indication. Hence, in reactor operation and design that is not enough to apply only one criterion, some kind of combination of existing criteria should be applied instead.

There is no fully general runaway criterion, which is obviously the best method for runaway indication. But, can we identify a critical equation which is tuned for a given and investigated case study which results the best in a warning system? I hope the following section answers this.

6 Genetic programming-based development of thermal runaway criteria

As thermal runaway criteria can separate the non-runaway and runaway states of the reactor system [28], these criteria can be applied to indicate of the development of a reactor runaway [161]. However, as runaway criteria indicate a runaway during different states of the reactor, several different types of criteria must be taken into consideration. Therefore, as no exact definition of runaway development exists, some criteria that already exists are less strict (i.e. these indicate the progress of a runaway later than others), and others are stricter which may prevent the reactor from being operated at high rates of conversion and high profitability due to the cost of the increased safety potential [72].

The identification of suitable criteria is of crucial importance as if the system is appropriately supervised not only are thermal runaways avoidable and the risk of operation is decreasable, but the efficiency of the process can also be improved [139].

Two important requirements of runaway criteria:

- to indicate a runaway then it actually occurs;
- to indicate a runaway as soon as possible.

No criterion in the literature meets both of these requirements, so a perfect criterion does not exist. Furthermore, runaway does not necessarily cause a significant problem in operation as the decreasing concentration of the reagents can prevent the temperature from rising too high.

Therefore, the problem with runaway criteria is that they may indicate runaway states while the maximum temperature during the process does not reach or is far below the Maximum Allowable Temperature (MAT). To handle this problem, the application of the MAT and adiabatic temperature rise to indicate a reactor runaway has already been proposed [153].

The goal of this section is to solve the aforementioned problems by developing a method that can be used for the goal-oriented construction of runaway criteria which takes into account the MAT or any other kind of design specification. The MAT, the earliness and the reliability of the predictions are considered as design specifications. The methodology allows us considering further safety or production-related specifications, for example, maximum allowable pressure, minimal level of conversion, acceptable productivity, or the combinations of any of these.

My key idea is that the task of criterion design can be handled as a classification problem and the critical equation that represents the classifier can be identified by genetic programming. Since the optimized critical equations take into account the MAT and other design specifications, the constructed criteria could become more flexible and problem-oriented. As will be presented in Section 6.1, the proposed method takes into account the intended use of the criteria with regard to the definition of the classification problem and generation of the related training data, it is expected that the optimized criteria perform better than any of the existing criterion found in the literature.

In Section 6.2, the proposed approach is tested in case of a batch reactor (BR) and a continuous stirred-tank reactor (CSTR). For each problem, three criteria were identified: one for early warning, one that is fine-tuned to improving the reliability of the warning, and one for reliable and early indication of a runaway. The results show that with genetic programming, goal-oriented critical equations can be identified that take into account the maximum allowable temperature (MAT) and indicate a runaway with tailored performance.

6.1 Genetic Programming-based design of critical equations

This section provides the methodology of the design of critical equations. Section 6.1.1 presents the formulation of the prediction problem, and Section 6.1.2 provides the steps in the GP design of equations.

6.1.1 Formulation of the runaway prediction problem

The problem of identifying a suitable runaway criterion can be considered as optimisation of the structure and the parameters ***p*** of the critical equation *f(x(k),p)* that indicates the runaway at the *k*-th instance of time as a binary classifier:

$$\hat{y}(k) = f(x(k), p) = 1 \; runaway \tag{6.1}$$

$$\hat{y}(k) = f(x(k), p) = 0 \; normal \; operation \tag{6.2}$$

where the variables of the function are the subsets of the state variables and parameters of the studied process, e.g. $x(k) \subset \{T(k), T_w(k), q_{gen}(k), q_{rem}(k), \dots\}$, where *T(k)* denotes the process temperature, $T_w(k)$ stands for the wall temperature and $q_{gen}(k)$ and $q_{rem}(k)$ are the generated and extracted heat at the *k*-th instant of time, respectively.

Thanks to the utilised genetic programming algorithm the user does not have to put too much effort into the selection of the informative variables, as the most informative subset will be

selected during the optimisation procedure. This method is based on the analysis $i=1,\ldots,N$ operations of the reactor with $k=1,\ldots,t_i$ operating lengths. The proposed voting system integrates *nc* number of different criteria. In this work, seven criteria were analysed; hence, *nc* is seven in the case studies. The investigated criteria are: PD, SZ, Maxi, VH, LPP, MSC and MDC (see Section 2.4). The criteria were chosen because, they are relatively commonly applied and their conservativeness is different from each other.

For each reactor states all the investigated criteria are evaluated, so the criteria are represented by a set of characteristic functions, $I_c(k)$, as $I_c(k)=1$ when the $c=1,\ldots,nc$-th criterion shows runaway at the *k*-th time instant. These criteria indications can be summarized to evaluate the given time instance:

$$I^{(i)}(k) = \sum_{c=1}^{nc} I_c^{(i)}(k) \tag{6.3}$$

As it is crucially important to distinguish between reactor operations with and without a runaway, a z_i characteristic variable has been introduced. To define a robust and reliable sign of the runaway we formed a voting system that indicates the runaway when at least half of the investigated criteria indicate runaway at *i*-th operation and the maximum process temperature exceeded the MAT, that is:

$$z^{(i)} = \begin{cases} 1 \; if \; max_k\left(I^{(i)}(k)\right) \geq \dfrac{nc}{2} \;\&\; T_{max}^{(i)} > MAT \\ 0 \; otherwise \end{cases} \tag{6.4}$$

This equation represents that when the proposed voting system detects at least one time instance a runaway and the maximum process temperature exceeds MAT, then the investigated operation was classified as runaway (z(i) =1). This logical connection reflects that if the maximum process temperature does not exceed MAT, then the time series of reaction states are not dangerous. Also, the reactors are designed for safe operations, which mean that at normal conditions the process temperature should be far away from the MAT, so the process temperature cannot exceed MAT without the development of thermal runaway.

The second important task is to indicate runaway early. As the analysed nc criteria indicate runaway at different states, hence at different time instances, it is crucial to take into consideration each runaway states which are classified as runaway by the criteria. Therefore, the given state at k-th time instance in i-th operation, $y^{(i)}(k)$, is considered as runaway, if the

analysed i-th operation is runaway (z(i) = 1) and at least one criterion indicates runaway ($I^{(i)}(k) \geq 1$).

$$y^{(i)}(k) = \begin{cases} 1 \; if \; I^{(i)}(k) \geq 1 \; \& \; z^{(i)} = 1 \\ 0 \; otherwise \end{cases} \tag{6.5}$$

Runaway criteria can be evaluated and developed concerning the following aims:

1. to indicate the development of a reactor runaway reliably;
2. to indicate early the development of a reactor runaway;
3. to indicate the development of a reactor runaway early and reliably.

In the first task, the aim is to generate a criterion for the reliable indication of runaway development, so the model can be evaluated as a binary classifier. The same method is applied for the reliability analysis as in Section 5. In TP true positive cases the developed runaway was indicated, so $z_i = 1$ and $\hat{z}_i = 1$. We denote TN as the number of true negative cases when a runaway did not develop, and was not indicated, $z_i = 0$ and $\hat{z}_i = 0$. The FP number of false positive cases are the number of operations when a runaway did not develop but was indicated, as $z_i = 0$ and $\hat{z}_i = 1$. In FN false negative cases runaway developed but were not indicated, $z_i = 1$ and $\hat{z}_i = 0$. The objective function for reliable indications is defined as the ratio of correct indications (true positive to true negative cases), which was maximized:

$$f_{correct} = \frac{TP(z, \hat{z}) + TN(z, \hat{z})}{N} \tag{6.6}$$

where N represents the number of studied operations, z and $\hat{z}$ are the real and predicted values respectively.

As the second measure should evaluate how accurately a criterion can provide early warning, the evaluation of the criteria should be based on the actual state of the reactor. For this purpose, the following two variables are introduced to represent the instances of time when indications should occur:

- $t_R^{(i)} = argmin_k\left(y^{(i)}(k) = 1\right)$ to denote the instant of time when runaway occurs;
- $t_S^{(i)} = argmax_k\left(y^{(i)}(k) = 1\right)$ to represent the instant of time when the reactor returns into normal operating regime after runaway.

When a given model is used to estimate the runaway at every k time instant, based on the $\hat{y}^{(i)}(k)$ predictions the start and end of runaways can be estimated similarly, so $\hat{t}_R^{(i)} = argmin_k\left(\hat{y}^{(i)}(k) = 1\right)$ and $\hat{t}_S^{(i)} = argmax_k\left(\hat{y}^{(i)}(k) = 1\right)$ stand for the instances of time when the runaway occurs and the reactor returns into normal operation according to the model, respectively. Based on these variables four types of false indications can be evaluated for every k time instant as it is also illustrated in Figure 6.1:

$$FN_k^{(i)} = \begin{cases} FN_{k,B}^{(i)} & t_R^{(i)} < \hat{t}_R^{(i)} \\ FN_{k,A}^{(i)} & \hat{t}_S^{(i)} < t_S^{(i)} \end{cases} \tag{6.7}$$

$$FP_k^{(i)} = \begin{cases} FP_{k,B}^{(i)} & \hat{t}_R^{(i)} < t_R^{(i)} \\ FP_{k,A}^{(i)} & t_S^{(i)} < \hat{t}_S^{(i)} \end{cases} \tag{6.8}$$

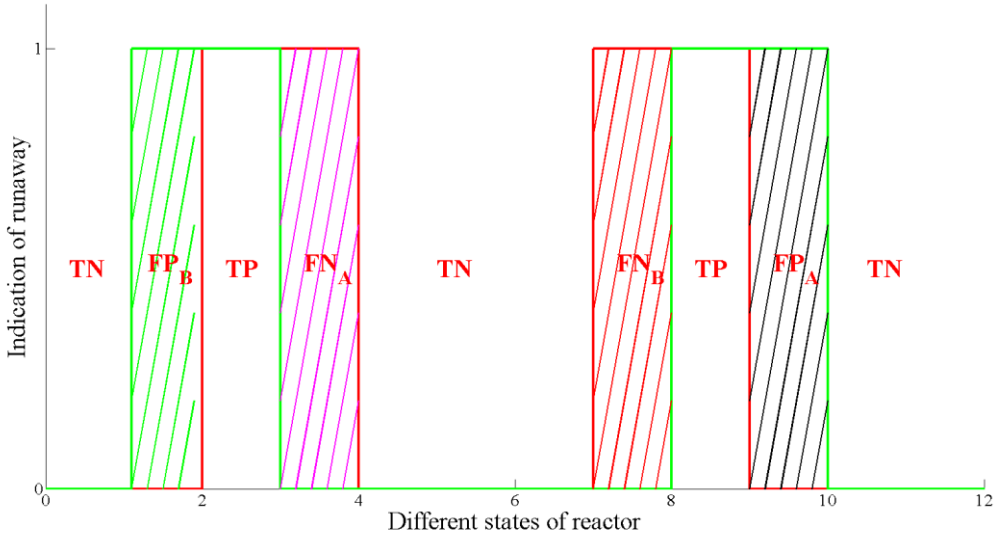

Figure 6.1 The interpretation of different failed indications (green=$y(k)$, red=$\hat{y}(k)$)

These indications of misclassifications can be summed to evaluate a given operation over the t_i time lengths, e.g:

$$FN_A^{(i)} = \sum_{k=1}^{t_i} FN_{k,A}^{(i)} \tag{6.9}$$

and the whole set of i=1,…,N operations:

$$FN_A = \sum_{i=1}^{N} FN_A^{(i)} \tag{6.10}$$

Similarly to the summation of the misclassified states, the number of correct indications is the sum of the $TP = \sum_{i=1}^{N} \sum_{k=1}^{t_i} TP_k^{(i)}$ number of true positive states when the developed runaway was indicated, $y^{(i)}(k) = 1$ and $\hat{y}^{(i)}(k) = 1$, and true negative states $TN = \sum_{i=1}^{N} \sum_{k=1}^{t_i} TN_k^{(i)}$, when a thermal runaway not developed, and was not indicated, $y^{(i)}(k) = 0$ and $\hat{y}^{(i)}(k) = 0$.

The objective function of early indication is considered to be the ratio of correct indications penalized to different types of failed indications, where all terms are weighted by a *w* weighting factor.

$$f_{early} = \frac{w_{TP}TP + w_{TN}TN - \sum_{j=\{A,B\}} w_{FP,j}FP_j - \sum_{j=\{A,B\}} w_{FN,j}FN_j}{\sum_{i=1}^{N} t_i} \tag{6.11}$$

The earliness and the reliability of the indications of thermal runaway development are the two most essential requirements of criterion development. As these goals are competitive we can decide what the importance of the requirements is. As a high-performing runaway criterion should be reliable and able to determine any early indications, we also propose third objective function based on the linear combination of Eqs. (6.10) and (6.11):

$$f_{correct+early} = w_1 f_{correct} + w_2 f_{early} \tag{6.12}$$

6.1.2 Genetic programming-based design of the critical equations

After the definition of a goal-oriented objective function, the next step is the design/selection of an algorithm that is able to find the optimal structure and parameters of the $\hat{y}(k) = f(x(k), p)$ equations.

Genetic Programming algorithms can optimize nonlinear equations in tree representations [162]. Because the algorithm of genetic programming is well-known, only the specialties of the proposed method are focused on. The genes represent a hierarchically structured tree consisting of mathematical operators (or elementary functions) and terminal nodes. In our case the set of operators *O* contain basic arithmetic operations: $O = \{+, -, *, /\}$, however Boolean and conditional operators or Automatically Defined Functions (ADFs) can also be used. The set of terminals *T* contains the variables and the parameters, $T = \{x_1, \dots x_D, p_1, \dots p_m\}$. A potential solution may be depicted as a rooted, labelled tree with

ordered branches, using operations (internal nodes of the tree) from the function set and arguments (terminal nodes of the tree) from the terminal set.

In every generation, the algorithm evaluates the individuals, selects the best ones for reproduction according to their fitness value, and generates new individuals by mutation (mutation), crossover (recombination) and direct reproduction. The probability of the selection if proportional to the fitness function that reflects the quality of the mapping simultaneously determined by the genes.

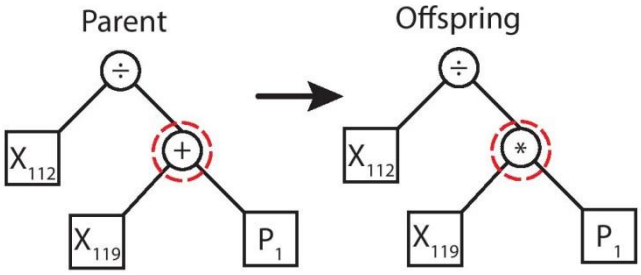

Figure 6.2 The mutation of the equation replaces an arithmetic operator or a terminal node

The parameters of the functions have a significant impact on the performance. Linear-in-parameter models are applied to avoid complex parameter optimization problems of nonlinear model structures in a similar way to [162], and the linear parameters are identified by logistic regression. Since a standard logistic function is used, the model represents the probability of a runaway $P(y(k) = 1|x(k))$.

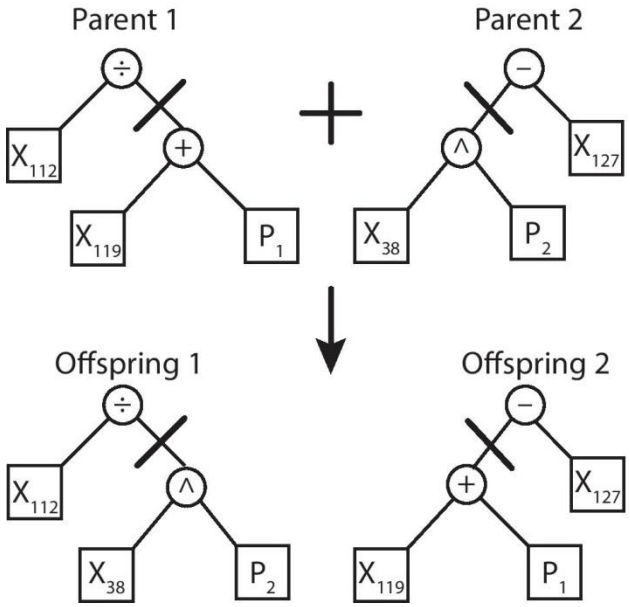

Figure 6.3 The recombination operator changes the branches of the equations

Therefore, the model equation for classifying the runaway and non-runaway states can be written in the following form:

$$\hat{y}(k) = \sigma\big(f(x(k), p)\big) = \sigma\left(\sum_{i=1}^{M} p_i F_i(x(k))\right) \tag{6.13}$$

where $\hat{y}(k)$ denotes the output, $F_1, \dots, F_M$ stand for nonlinear functions and $p_1, \dots, p_M$ represent model parameters, and $\sigma(z) = \frac{1}{1+exp(-z)}$ represents a logistic function. The details of this algorithm are summarized in Algorithm 1.

Table 6.1 Algorithm 1 GP based criterion generation algorithm

Require: random population P[1…Np] with Np individual

Require: ps: probability of selection, pm: probability of mutation

Ensure: $ps + pm < 1$

1: **procedure** GP OPTIMIZATION
2: sel[1…Np] ←0
3: k ←0
4: **while** stop criteria not met do
5: **for** each $i \in P_k$ do
6: sel[i] ←ROULETTWHEEL(Pk[i])
7: **end for**
8: Pc=selectPairs(Pk,ps) #Select pairs for crossover
9: Pm=select(P-Pc,pm) #Select invs for mutation
10: Pu=P-Pc-Pm #Keep invs for direct reproduction
11: **for** each $i \in P_m$ do
12: Pm[i] ←MUTATE(Pm[i])
13: **end for**
14: **for** each $i \in P_c$ do
15: Pc[i]←CROSSOVER(PC[i])
16: **end for**
17: $Pn = Pu \cup Pc \cup Pm$
18: **for** each $i \in P_n$ do
19: fitness[i]←EVALUATE(Pn[i])
20: **end for**
21: **end while**

22:**end procedure**

23:

24: **function** EVALUATE(p)

25: **while** $fit \neq optimal$ do

26: p←OPTIMIZEPARAM / LOGISTIC REGRESSION (Fi)

27: fit←COSTFUNCTION(p)

28: **end while**

29: **return fit**

30: **end function**

The proposed algorithm was implemented in MATLAB as the modification of our MATLAB Genetic Programming Toolbox. The parameters shown in Table 6.2 were used in all optimization tasks since good solutions were found for various problems concerning this parameter set.

Table 6.2 Parameters of GP in the application examples

Population size	200
Maximum number of evaluated individuals	4000
Type of selection	roulette-wheel
Type of mutation	point-mutation
Type of crossover	one-point (2 parents)
Generation gap	0.8
Probability of crossover	0.7
Probability of mutation	0.3

Detailed explanation of the algorithm and its parameters is beyond the scope of this thesis and we refer the interested reader to [162].

6.2 Application examples

To demonstrate the applicability of the previously proposed method two case studies were used, which are presented in Section 3.2.1.1 and in Section 3.2.1.4. The first case study considers a batch reactor (BR) and the second case study considers a continuous stirred-tank reactor (CSTR), both conduct a single reaction. These case studies were selected because of their methodological benefits as the critical equations of runaway criteria can be easily

derived for these case studies, and the different runaway theories can be compared to identify critical equations. The nominal values of the parameters and the initial conditions of the models are listed in Table 6.3, while the critical equations of the studied criteria of thermal runaway are presented in Table 6.4.

Table 6.3 Parameters and initial conditions of the case studies

	BR	**CSTR**	**Unit**
α	5		$\frac{1}{h}$
β	180		$\frac{m^3 K}{kmol}$
γ	20		-
δ	6600		K
cA,0	1		$\frac{kmol}{m^3}$
T0	300	Tin	K
cA,in	-	1	$\frac{kmol}{m^3}$
Tin	-	300	K
τ	-	1	h

Table 6.4 The investigated runaway criteria

Criterion	**BR**	**CSTR**
PD	$r_T \leq \frac{r}{T - T_w}$	$r_T \leq \frac{r}{T - T_w}$
SZ	$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta}$	$r_T \leq \frac{\alpha}{\beta} + \frac{r_c}{\beta} + \frac{2}{\beta\tau}$
Maxi	$r_T \leq \frac{\alpha}{\beta}$	$r_T \leq \frac{\alpha + \tau^{-1}}{\beta}$
VH	$r_T \leq \frac{\alpha}{\beta} + \frac{r r_c}{\beta r - \alpha(T - T_w)}$	Numerical evaluation
LPP	$r_T \leq \frac{r}{T - T_w} + \frac{r r_c}{\beta r - \alpha(T - T_w)}$	Numerical evaluation
MSC	$r_T \leq \frac{\alpha}{\beta} + \frac{r}{T - T_w}$	$r_T \leq \frac{\alpha + \tau^{-1}}{\beta}\left(1 + \frac{q_{gen}}{q_{rem}}\right)$
MDC	$r_T \leq \frac{r}{T - T_w} + \frac{r_c}{\beta}$	$r_T \leq \frac{r_c}{\beta} + \frac{\alpha + \tau^{-1}}{\beta}\frac{q_{gen}}{q_{rem}}$

According to these thermal runaway criteria, different critical wall temperatures can be determined that ensure a runaway is avoided. The resultant temperature profiles as a function of conversion are depicted in Figure 6.4 which reflects the maximum reachable conversion according to the different criteria. If the applied criterion does not indicate a runaway in time, then the built-in safety system may not prevent the development of a runaway. Runaway criteria are compared to each other in Figure 6.4 in terms of early warning. As the Maxi criterion indicates a runaway earliest (after 0.2 hours), and the MSC latest (after 0.64 hours), the Maxi criterion provides the most time to intervene into the process to avoid undesired events. However, it should be highlighted that the Maxi criterion facilitates the operation of the reactor at the lowest level of conversion (see Figure 6.4) resulting in a significant economic loss. As a runaway criterion which indicates a runaway only when the maximum process temperature exceeds the MAT, the reactor operates at a higher degrees of conversion and productivity, so this example demonstrates that an indication system that both ensures early and reliable warnings is required.

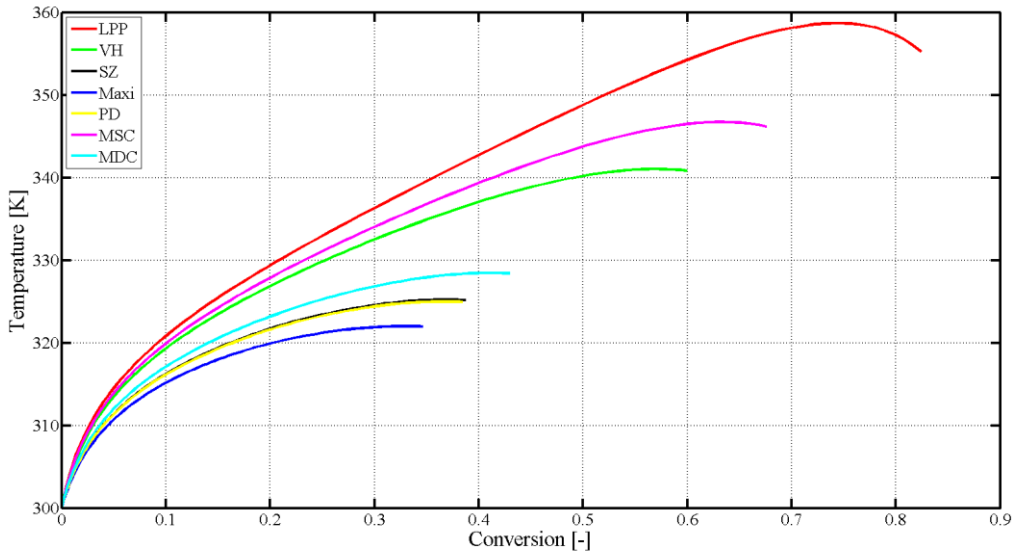

Figure 6.4 The smoothest temperature profiles according to different runaway criteria

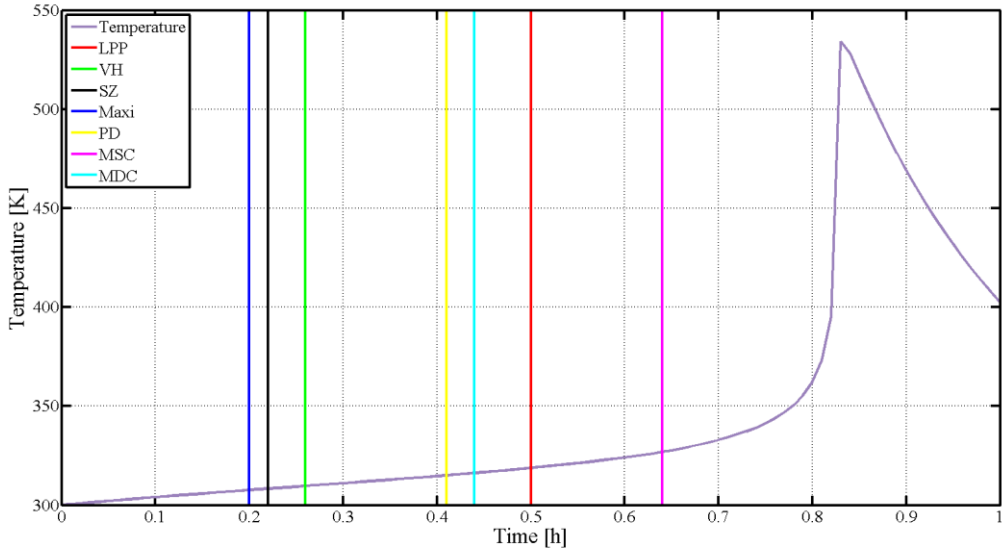

Figure 6.5 Runaway indication of criteria in case of the batch-reactor

The previously presented criteria may unnecessarily indicate a runaway, e.g. when the maximum process temperature is less than the MAT. By introducing the derived critical equations, the set of potential variables at each case studies used to identify the criterion can be defined (Eq. (6.14)). The adiabatic temperature rise was also added to this set because it plays an essential role in defining the severity of a runaway [1]:

$$X = \{T, T_w, q_{gen}, q_{rem}, \alpha, \beta, \tau, r, r_T, r_c, \Delta T_{ad}\} \tag{6.14}$$

where T denotes the process temperature, T_w the wall temperature, q_{gen} and q_{rem} the generated and extracted heat, respectively. α the heat transfer parameter, β the heat of reaction parameter, τ the residence time, r the reaction rate, r_T and r_c the derivations of the reaction rate in terms of the process temperature and concentration of reagents, and T_{ad} the adiabatic temperature rise. Figure 6.4 and Figure 6.5 show the smoothest temperature profiles and the order of runaway indications according to different criteria. Strict criteria (like Maxi) indicate the earliest development of thermal runaway thanks to the lowest allowed temperature. However, if the MAT allows operating the reactor at higher temperatures, the runaway indication by a strict criterion would be false, which decreases the reliability of this criterion. There is a balanced goal (early and reliable indication), where the constructed criterion indicates runaway more reliable than the standard criteria from literature and still indicate the runaway early enough.

6.2.1 Case study I. – Identification of criteria for a batch reactor

The training dataset was generated by 200 independent simulations with uniformly distributed random parameters as described in Table 6.5:

Table 6.5 The investigated interval of parameters (CS1)

Parameter	Minimum	Maximum
$c_{A,0}\left[\frac{kmol}{m^3}\right]$	1	1.2
T_w [K]	305	315
$\alpha\left[\frac{1}{h}\right]$	4	6
$\beta\left[\frac{m^3K}{kmol}\right]$	170	190

Results of simulations can be seen in the phase plane of the temperature and concentration (see Figure 6.6). During the first hour of operation, 100 states were analysed in every simulation to detect a runaway. The proportion of runaway states in the data was 29%, so the generated data was ideal for the GP-based construction of critical equations.

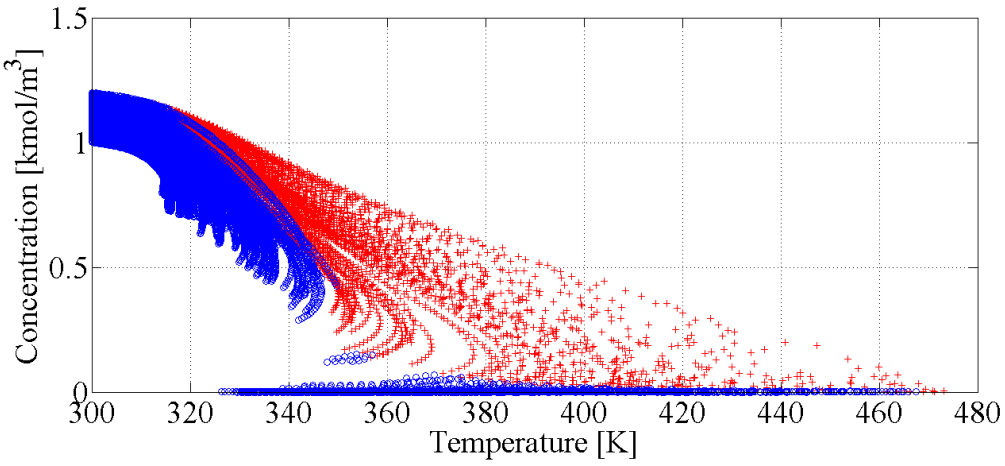

Figure 6.6 States of the reactor following 200 independent simulations with varying parameters. Runaway and non-runaway states are distinguished by colours: red crosses represent states after runaway and blue circles stand for states in normal operating regions (CS1)

6.2.1.1 Proper indication of runaway cases

As genetic programming is a stochastic optimisation algorithm, the repetitive and independent optimisations generate more than one runaway criterion. The performances of the resultant

models were statistically analysed and the best models selected. As this paper focuses on the prediction of runaways and not on the development of the genetic programming algorithm, only the best models are presented along with the method of how the performances of the models were evaluated by cross-validation.

The first optimization problem resulted in the following criterion:

$$0 < -1.156\left(\frac{\Delta T_{ad}(T-\Delta T_{ad})}{\beta T} - r\right) - 1.086 \qquad (6.15)$$

where $\Delta T_{ad} = \beta c_A$.

The models were validated by 1,000 independent simulations. To visualise the performances of the models, safety boundary diagrams (Figure 6.7) were generated (in which the correct and false runaway indications are highlighted) to help understand how the application of appropriate criteria can increase productivity. For this purpose, a thousand simulations were run with uniformly distributed Tw = [305; 315] wall temperatures and $c_{A,0}$ = [1; 1.2] initial concentrations.

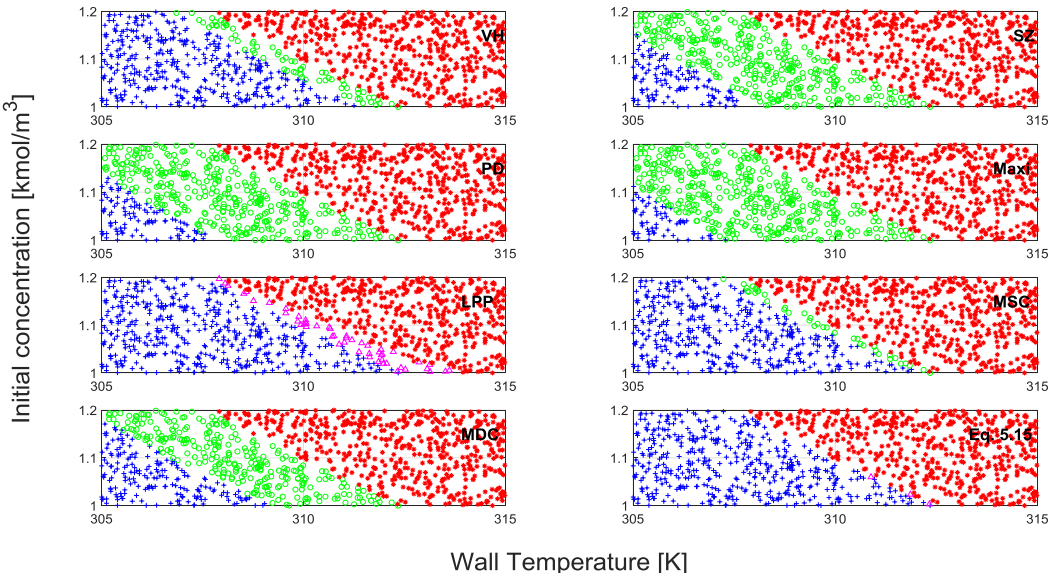

Figure 6.7 The performance of different criteria in case of BR (blue plus - TN, green circle - FP, red star - TP, magenta triangle – FN)

The constructed criterion shows the best performance in terms of indicating a thermal runaway correctly, only two Type I and three Type II false indications were identified from a total of 1,000 simulations. Type II failure is more important in terms of runaway indication (FN), therefore, three operations were further investigated. The temperature profiles of the

reactor operations can be seen in Figure 6.8. The maximum process temperature was 350.7 K, which exceeds MAT, however the constructed criterion did not indicate that safety issue. The temperature difference between the MAT and maximum process temperature was not significant.

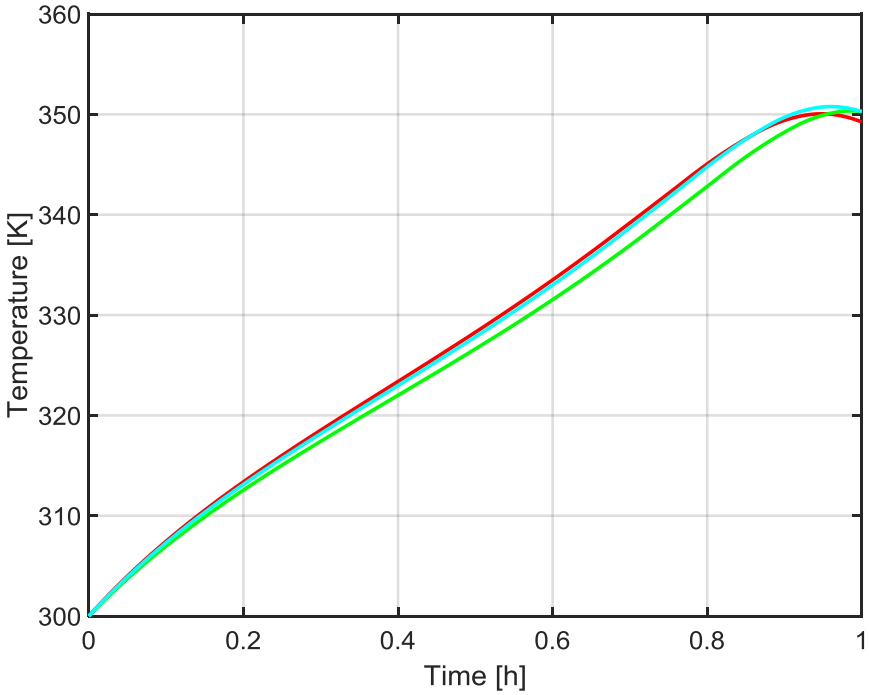

Figure 6.8 Temperature trajectories of the reactor operations in the event of failed runaway indications (CS1)

The Lyapunov-stability in the phase plane failed to detect some runaways (FN) because a runaway was not indicated although the maximum process temperature exceeded the MAT. The remaining criteria were stricter and indicated the occurrence of a runaway even though the maximum process temperature did not exceed the MAT (FP).

The performances of criteria can be seen in Table 6.6 in the form of percentages, where the constructed criterion was responsible for the least failed indications, namely 0.5% of a total of 1,000 simulations.

Table 6.6 The performance of criteria based on correct and fail indications (CS1)

	VH	**SZ**	**PD**	**Maxi**	**LPP**	**MSC**	**MDC**	**Eq.(6.15)**
TP [%]	51.4	51.4	51.4	51.4	44.8	51.4	51.4	51.1
FN [%]	0.0	0.0	0.0	0.0	6.6	0.0	0.0	0.3
FP [%]	7.9	35.1	37.3	41.5	0.0	3.8	28.5	0.2
TN [%]	40.7	13.5	11.3	7.1	48.6	44.8	20.1	48.4

6.2.1.2 Early warning of a reactor runaway

A critical equation that indicates a reactor runaway as soon as possible was identified as shown in Eq. (6.16). If the value of right-hand side of Eq. (6.16) is positive, then a possible runaway is indicated.

$$0 < 1.6023\frac{q_{gen} - \alpha - q_{rem}}{2\alpha + q_{rem}} + 0.0042\alpha - 0.5867 \tag{6.16}$$

The weights of the fitness function (Eq. (6.11)) can be seen in Table 6.7:

Table 6.7 Weights of the fitness function (Eq.(6.11), CS1)

w_{TP}	w_{TN}	$w_{FN,B}$	$w_{FN,A}$	$w_{FP,B}$	$w_{FP,N}$
2	0.5	5	0.0	0.0	0.0

The validation dataset was generated by running ten independent simulations as presented in Figure 6.9. The parameters were varied over the same intervals as shown in Table 6.5. A comparison between the identified and existing criteria is shown in Figure 6.10 and as can be seen the identified critical equation possesses a feature that indicates a thermal runaway earliest compared to the analysed criteria. However, this may means the indication of a runaway when the maximum process temperature does not reach the maximum allowable temperature.

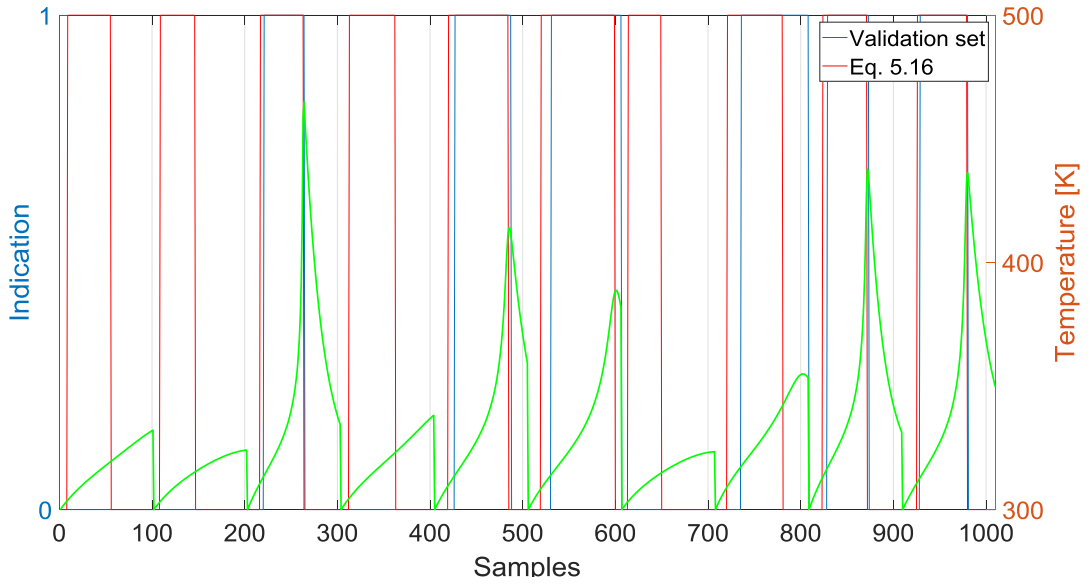

Figure 6.9 The validation of the identified critical equation (CS1)

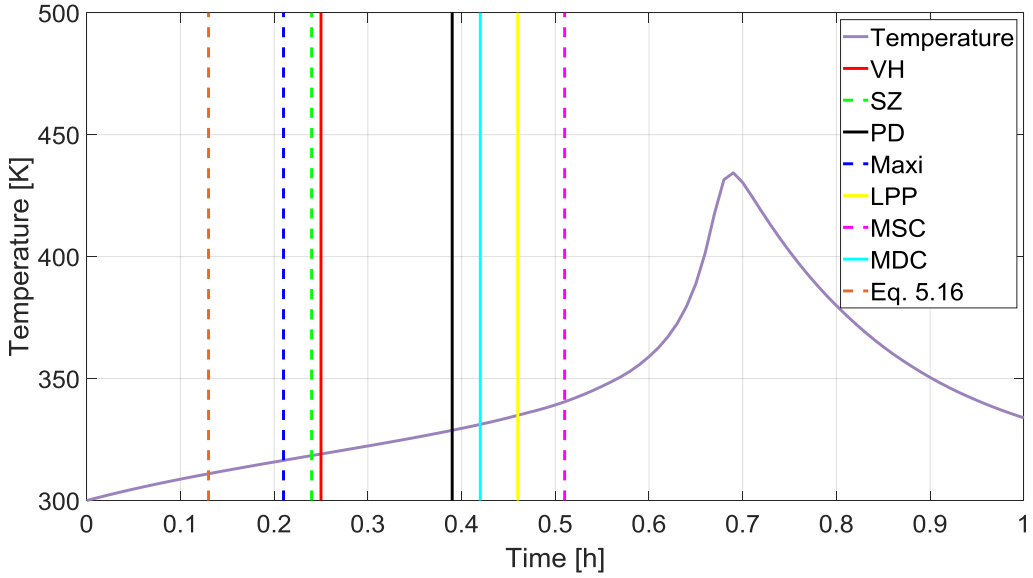

Figure 6.10 Thermal runaway indications according to the criteria investigated (CS1)

100 independent simulations were run during which a thermal runaway developed and the order of indications between the investigated and identified criteria compared in Table 6.8. If two or more criteria indicate a runaway simultaneously, then they are assigned the same order. If a criterion failed to indicate a runaway, then it is not assigned a placement. The constructed equation for the proper indication of runaway cases (Eq. (6.15)) is also presented and, as can be seen, indicates a runaway last, so another critical equation which indicates the development of a runaway earlier is required.

Table 6.8 Order of runaway indications according to different criteria (CS1)

	VH	**SZ**	**PD**	**Maxi**	**LPP**	**MSC**	**MDC**	**Eq.(6.15)**	**Eq.(6.16)**
1.	0	0	0	7	0	0	0	0	97
2.	2	1	0	93	0	0	0	0	2
3.	20	99	0	0	0	0	0	0	1
4.	78	0	0	0	0	0	0	0	0
5.	0	0	100	0	0	0	0	0	0
6.	0	0	0	0	0	0	100	0	0
7.	0	0	0	0	82	16	0	6	0
8.	0	0	0	0	0	52	0	54	0
9.	0	0	0	0	1	32	0	40	0

Figure 6.11 shows the performance of the identified criterion compared to other analysed criteria according to 50 independent simulations. Different types of failures and correct indications are denoted by different colours at each state. Red crosses denote the runaway states which are indicated, blue crosses stands for the non-runaway states which are not indicated and yellow crosses represent the non-runaway states which are indicated by the specific criterion. Black crosses denote that a runaway was not detected by the specific criterion and green crosses show that a runaway was indicated earlier compared to other criteria. The Maxi criterion performs quite well, because all the runaway states were indicated (black crosses). Moreover, the identified criterion recognized several states that they led to a thermal runaway (green crosses) although more operating conditions which are false were indicated (yellow crosses).

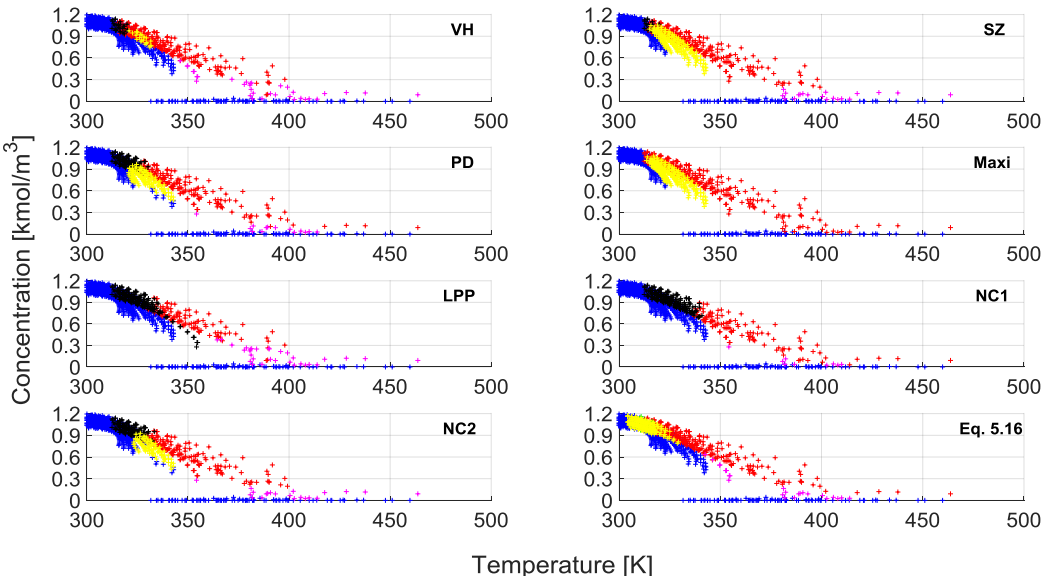

Figure 6.11 The performance of the identified criterion compared to other criteria at CS1 (blue crosses TN, red crosses TP, black crocces FN_B, magenta crosses FN_A, green crosses FP_B, cyan crosses FP_A)

6.2.1.3 Reliable and early warnings of the occurrence of a runaway

A critical equation to indicate the development of a runaway early and reliably was identified in the form of the following equation:

$$0 < -0.035T_w - 0.036\frac{q_{rem}}{T_w + \beta} + 1.463r_T\Delta T_{ad} + 0.67 \tag{6.17}$$

Its reliability and early warning feature is presented in Table 6.9 and Figure 6.12. As can be seen, the earliest indicators are the criteria Maxi-, SZ- and VH although their reliability is insufficient since 10.3%; 35.5% and 41.2% of false indications resulted respectively. The criteria LPP and MSC are the most reliable, although these criteria do not provide early indications. The identified critical equation only produced 6.6% false indications and warnings of a runaway with sufficient notice before reaching the MAT.

Table 6.9 Performance of criteria based on correct and fail indications (CS1)

	VH	SZ	PD	Maxi	LPP	MSC	MDC	Eq.(6.17)
TP [%]	53.1	53.1	53.1	53.1	44.6	53.1	53.1	52.9
FN [%]	0	0	0	0	8.5	0	0	0.2
FP [%]	10.3	35.5	38.7	41.2	0	5	30	6.4
TN [%]	36.6	11.4	8.2	5.7	46.9	41.9	16.9	40.5

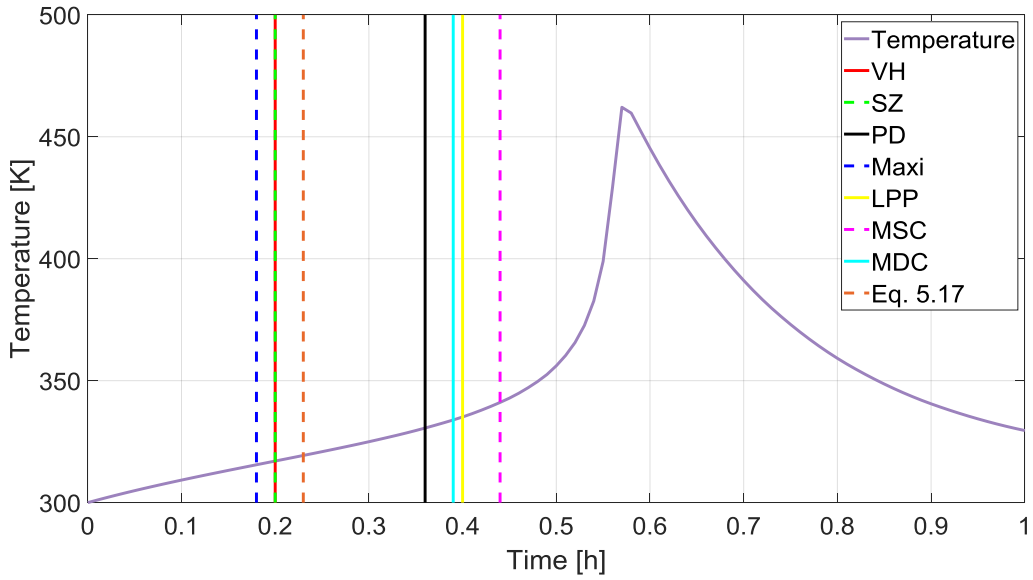

Figure 6.12 Thermal runaway indications according to the criteria investigated (CS1)

6.2.2 Case study II. – Identification of criteria for a CSTR

In the case of continuous stirred-tank reactors, the training dataset was generated by running 200 independent simulations with randomly varying operating and model parameters, namely the initial concentration, feed concentration, wall temperature, heat transfer parameter, heat of reaction parameter and residence time. The intervals of uniformly distributed random parameters can be seen in Table 6.10.

Table 6.10 The variation of parameters to generate a training set (CS2)

Parameter	Minimum	Maximum
$c_{A,0}\left[\frac{kmol}{m^3}\right]$	1	1.2
$c_{A,in}\left[\frac{kmol}{m^3}\right]$	1	1.2
T_w [K]	310	320
$\alpha\left[\frac{1}{h}\right]$	5	7
$\beta\left[\frac{m^3K}{kmol}\right]$	170	190
τ [h]	0	2

The results of simulations can be seen in Figure 6.13, where the temperatures and concentrations are in a phase-plane. During the first hour 100 states were analysed in every simulation to detect runaway states. Runaway and non-runaway states are distinguished, red crosses denote runaway and blue circles non-runaway states. In this case, the proportion of runaway states in the training set was 58%.

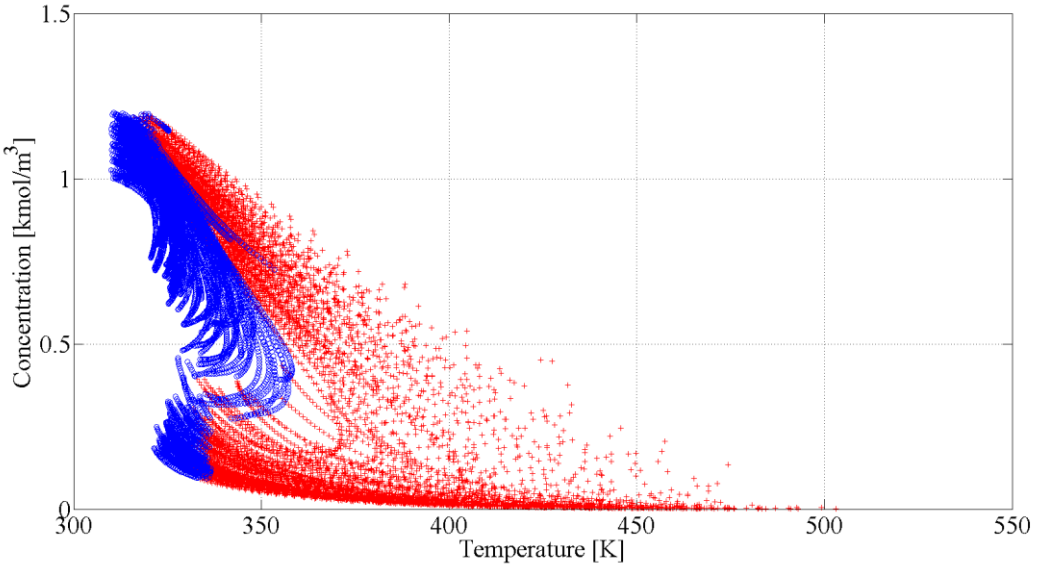

Figure 6.13 States of the reactor following 200 independent simulations with varying parameters (CS2)

6.2.2.1 Proper indication of runaway cases

A critical equation that correctly indicates runaway cases was identified as can be seen in Eq.(6.18). If the value of the identified equation is greater than zero, then a runaway will occur.

$$0 < 0.3128\left(r_c - \left(\frac{r}{r_c} - r_T\right)(2\alpha + r_T - r_c)\right) + 0.0461 \qquad (6.18)$$

The validation dataset was generated by running 1,000 independent simulations, where the parameters varied over the same range as shown in Table 6.10. The results can be seen in Figure 6.14 and Table 11 shows that the identified critical equation possesses the least failed indications although some parameter combinations are present where a runaway did not occur but was indicated.

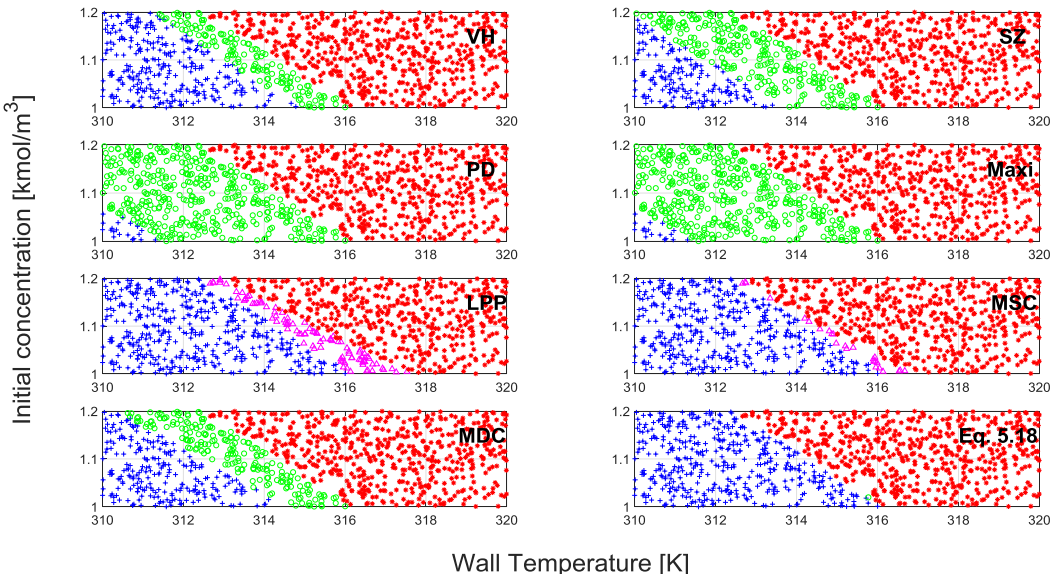

Figure 6.14 The performance of different runaway criteria (blue plus - TN, green circle - FP, red star - TP, magenta triangle - FN)

The performances of criteria are summarized in Table 6.11. The Lyapunov-stability in the phase-plane and the MSC failed to indicate every runaway. As can be seen the identified criterion yielded the least failed runaway indications, namely 0.1 % of total of 1,000 simulations. Moreover, each failed indications were true positive cases.

Table 6.11 The performances of criteria based on correct and failed runaway indications

	VH	**SZ**	**PD**	**Maxi**	**LPP**	**MSC**	**MDC**	**Eq.(6.18)**
TP [%]	58.5	58.5	58.5	58.5	49.6	55.4	58.5	58.5
FN [%]	0	0	0	0	8.9	3.1	0	0
FP [%]	11	22.6	38	38.6	0	0	16.8	0.1
TN [%]	30.5	18.9	3.5	2.9	41.5	41.5	24.7	41.4

6.2.2.2 Early warning of a reactor runaway

A critical equation that indicates a reactor runaway as soon as possible was identified, as can be seen in Eq. (6.19). If the identified value of this equation is positive, then a possible runaway is indicated. The weights of the fitness function (Eq. (6.11)) can be seen in Table 6.12:

Table 6.12 Weights of the fitness function (Eq. (6.11), CS2)

w_{TP}	w_{TN}	$w_{FN,B}$	$w_{FN,A}$	$w_{FP,B}$	$w_{FP,N}$
2	0.5	5	0.0	0.0	0.0

The critical equation is the following:

$$0 < -2.1230(\alpha - q_{rem} - 1) - 0.0189 \tag{6.19}$$

The validation dataset was generated by running ten independent simulations as presented in Figure 6.15, where the parameters varied over the same intervals as shown in Table 6.10. A comparison between the investigated criteria is shown in Figure 6.15 and Figure 6.16 and it can be seen that the constructed critical equation indicates a runaway first.

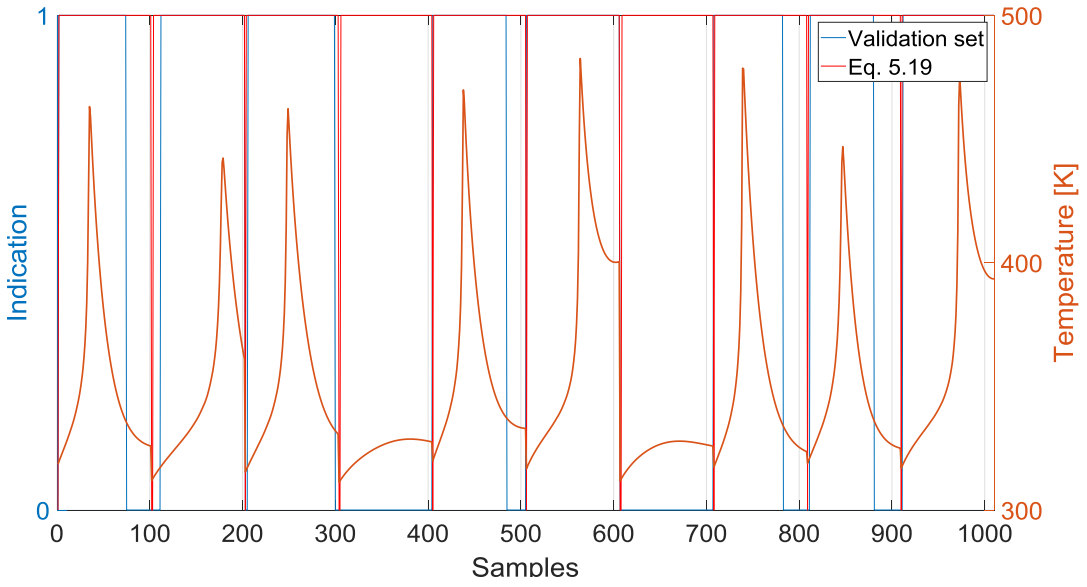

Figure 6.15 Validation of the identified critical equation (CS2)

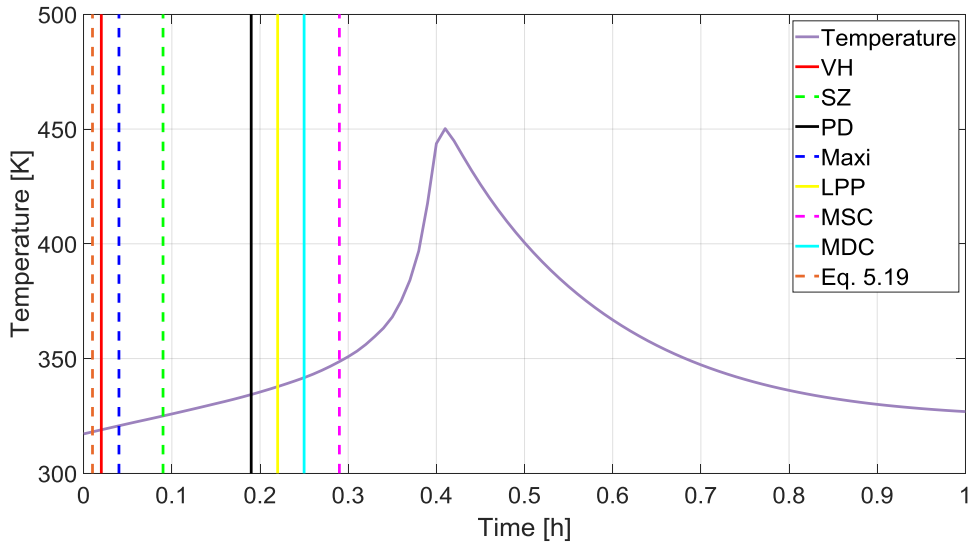

Figure 6.16 Thermal runaway indications according to the criteria investigated (CS2)

100 independent simulations were run where a thermal runaway developed and the order of indications between investigated and identified criteria are compared in Table 6.13. The identified criterion did not indicate in every case the development of a runaway first. The constructed critical equation for the proper indication (Eq. (6.18)) of runaway cases is presented too, which is last to indicate the development of runaway.

Table 6.13 Order of runaway indications according to different criteria (CS2)

	VH	SZ	PD	Maxi	LPP	MSC	MDC	Eq.(6.18)	Eq.(6.19)
1.	40	0	0	14	0	0	0	0	70
2.	49	0	0	30	0	0	0	0	19
3.	11	0	0	56	0	0	0	0	11
4.	0	90	10	0	0	0	0	0	0
5.	0	6	90	0	8	0	0	0	0
6.	0	4	0	0	58	0	52	0	0
7.	0	0	0	0	32	1	47	2	0
8.	0	0	0	0	0	88	1	13	0
9.	0	0	0	0	0	9	0	85	0

In Figure 6.17 the different types of failures are denoted by different colours, and in this case all the criteria investigated except for VH and the constructed criteria indicate a runaway later than is first recognisable (black crosses).

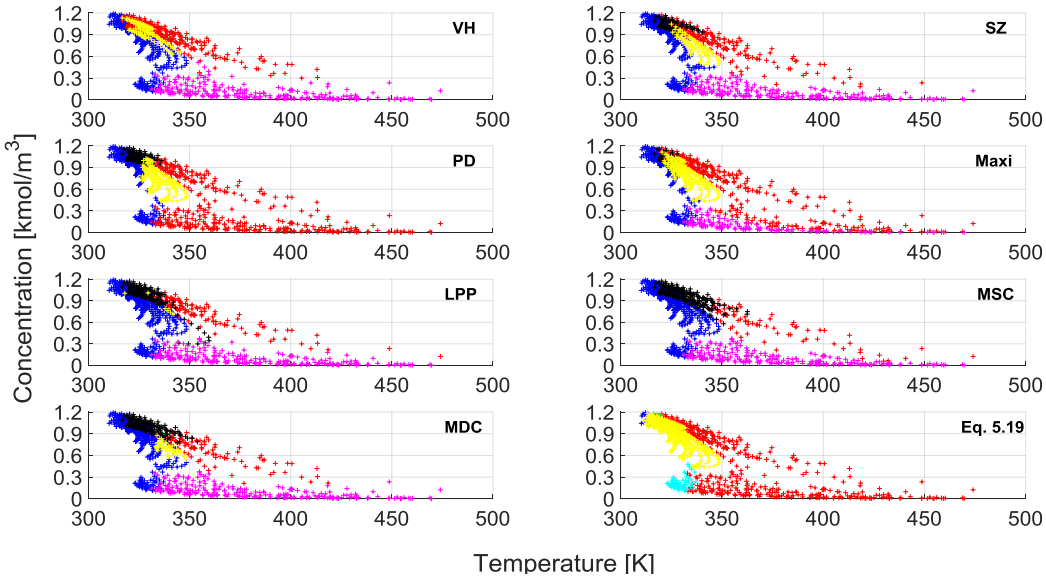

Figure 6.17 The performance of the identified criterion compared to other criteria at CS2 (blue crosses TN, red crosses TP, black crocces FN_B, magenta crosses FN_A, green crosses FP_B, cyan crosses FP_A)

6.2.2.3 Reliable and early warnings of a runaway

A critical equation that indicates the development of a runaway early and reliably was identified in the form of following equation:

$$0 < -0.45\left(r_T - r + \frac{\tau + \alpha}{\Delta T_{ad}}\right) - 0.60 \tag{6.20}$$

Its reliability and early warning feature are presented in Table 6.14 and Figure 6.18. As can be seen, the earliest indicators are the Maxi, SZ and VH criteria although their reliability is insufficient yielding 41:1%; 24:7% and 12:5% false indications, respectively. The criteria LPP and MSC criteria are the most reliable although these criteria do not provide early indications. The identified critical equation yielded only 4.1 % false indications and warned of a runaway with sufficient notice before the MAT was reached.

Table 6.14 The performances of criteria based on correct and failed indications (CS2)

	VH	**SZ**	**PD**	**Maxi**	**LPP**	**MSC**	**MDC**	**Eq.(6.20)**
TP [%]	57.1	57.1	57.1	57.1	47.8	53.9	57.1	57.1
FN [%]	0	0	0	0	9.3	3.2	0	0
FP [%]	12.5	24.7	40.6	41.1	0	0	19.4	4.1
TN [%]	30.4	18.2	2.3	1.8	42.9	42.9	23.5	38.8

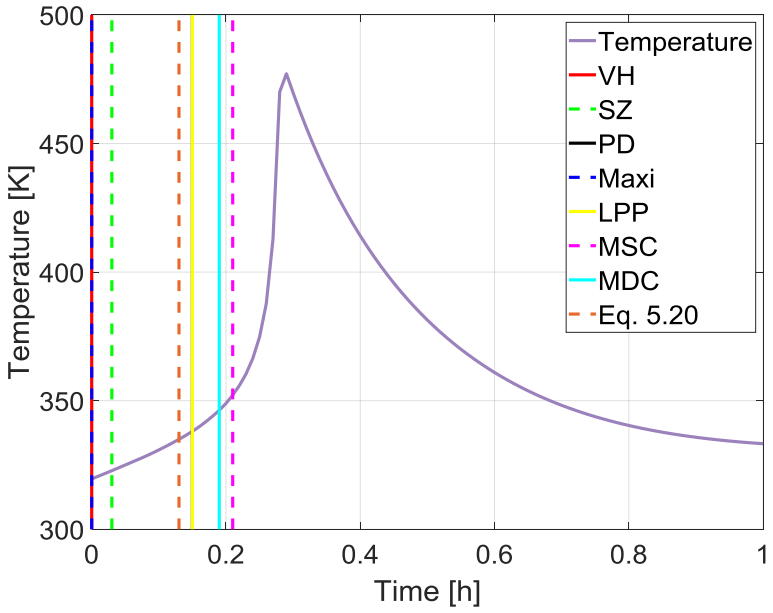

Figure 6.18 Thermal runaway indications according to criteria investigated (CS2)

6.3 Conclusion

Genetic programming was applied to construct critical equations to indicate the development of thermal runaways correctly. Runaway criteria from the literature fail to take into account the MAT because these criteria can only determine if the investigated reactor state is runaway or non-runaway and cannot predict future states. By applying genetic programming, goal-oriented critical equations can be identified which take into account the MAT as a necessary design specification of the system. The applicability of the proposed method was demonstrated in case of a batch reactor and a continuous stirred-tank reactor by constructing critical equations that satisfy reliability and early warning related goals.

Now, that we have a deep knowledge about thermal runaway criteria, and we have a picture about their applicability in different systems (reliability and earliness), we can apply them in different tasks. The following section (Section 7) presents a feeding trajectory optimization problem where runaway criteria were applied as a non-linear constraint. Section 8 presents the solution of an online application, where a temperature control of an SBR is presented.

7 Feeding trajectory optimization in fed-batch reactor with highly exothermic reactions

Semi-batch reactors are applied in case of chemical reactions with a high heat effect, so one of the reagents is slowly fed to the other component(s), which is already in the reactor. The heat evolution can be kept controlled and a suitable cooling system can be designed to remove all reaction heat based on a reliable process model of the system [102]. For instance, oxidation of 2-octanol with nitric acid [154], Williams-Otto process [158] and synthesis of lithium-etinolate are performed in semi-batch reactors. However, generally the feeding strategy is really simple using a constant feeding rate over the entire process which results in a higher batch times than in case the feeding rate are manipulated during the operation. In case of constant feeding rate the earlier presented Westerterp-diagram is an excellent solution for the design of operation (see Section 2.5), but as it was mentioned, it does now allow to vary the feed rate constraining the efficiency of the operation.

An optimization of feeding trajectory with an exothermic reaction carried out in a fed-batch reactor is presented in this section without neglecting the possibility of runaway. The investigated model system is the production of 2-octanone, which was earlier presented in Section 3.2.2. Particle Swarm Optimization (PSO) [163] and Sequenced Quadratic Programming (SQP) [164] method is used to find the optimal feeding trajectory with applying the right criterion as non-linear constraint. Varga et al. showed how evolutionary strategy and Lyapunov-stability analysis in geometric plane can be combined to find the optimal feeding trajectory in case of a fed-batch reactor with exothermic reactions [165]. The goal is to manifest the importance of choosing the right criterion to reach the highest safety and profit. Six criteria (Van Heerden-criterion, Inflection-point in phase plane, divergence criterion and "Practical Design", Modified Slope and Dynamic Condition) are applied to optimize the feeding trajectory. As a result of optimization we can see how these criteria influence directly the temperature trajectory and indirectly the selectivity of the production. Since all the applied runaway criteria are model based, there is a need for an adequate model with correct model parameters. Without that the indication of runaway can be unreliable, no matter what criterion is applied.

7.1 Optimization problem

Linear feeding trajectory was optimized between time intervals, and this optimization problem was solved using PSO and SQP methods, where the searching variables are the width of each time interval (t_i) of feeding and the volume flow rate at the end of each time interval (B_i). Figure 7.1 shows a general linear feeding trajectory.

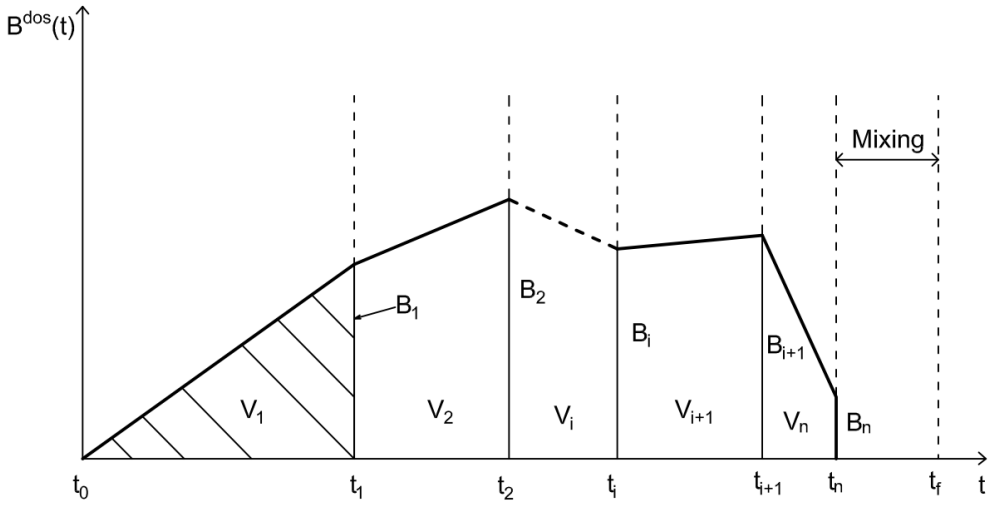

Figure 7.1 General linear feeding trajectory

The following equations describe the feeding trajectory:

$$t_{i-1} < t < t_i \qquad i = 1, \dots, n \tag{7.1}$$

$$B^{dos}(t) = a_i \cdot (t - t_{i-1}) + B_{i-1}^{dos} \tag{7.2}$$

Slope of linear can be calculated by the following equation.

$$a_i = \frac{B_i^{dos} - B_{i-1}^{dos}}{(t_i - t_{i-1})} \tag{7.3}$$

The following constraints need to be satisfied.

$$V_{dos} = \sum_{i=1}^{n} \left(\frac{B_i^{dos} + B_{i-1}^{dos}}{2} \cdot (t_i - t_{i-1}) \right) \tag{7.4}$$

$$t_{dos} = \sum_{i=1}^{n} (t_i - t_{i-1}) \tag{7.5}$$

An objective function is necessary, which contains the mole of products, by-products and raw-material. Productivity has positive, and the sum of molar ration of component A and X has a negative effect on the objective function. The objective function is the following:

$$of = \frac{n_P}{n_{p,max}} - \left(1 - \frac{n_p}{n_p + n_A + n_x}\right) \tag{7.6}$$

I have solved the previously described optimization problem, and the optimal temperature trajectories applying different runaway criteria as a non-linear constraint are shown in *Figure 7.2*. The achieved values of objectives are written in *Table 7.1*. PD and SZ criterion were too strict to be applied in this problem, so there was no possible feeding trajectory in the investigated region where the PD and SZ criteria did not indicate thermal runaway. As it can be seen in *Table 7.1* the value of objective function is highly affected by the applied runaway criterion, however; it is logical, since if we use a stricter and a conservative criterion the result will be more conservative too. The values of objective function can give a picture about the conservativeness order of the applied runaway criteria. As I mentioned earlier a more conservative criterion allows lower temperature gradients and increment. It means that the productivity of a reactor system depends on the applied runaway criterion, and we must consider which criterion we use for design and operation to fulfil the expectation in safety and productivity views.

Table 7.1 Values of objectives applying different criteria

Criterion	**Value of objective function**	**Is constraint violated?**
No constraint	0.3069	No
IPP	0.3059	No
VH	0.3027	No
PD & SZ	0.1878	Yes
MSC	0.3020	No
MDC	0.3016	No

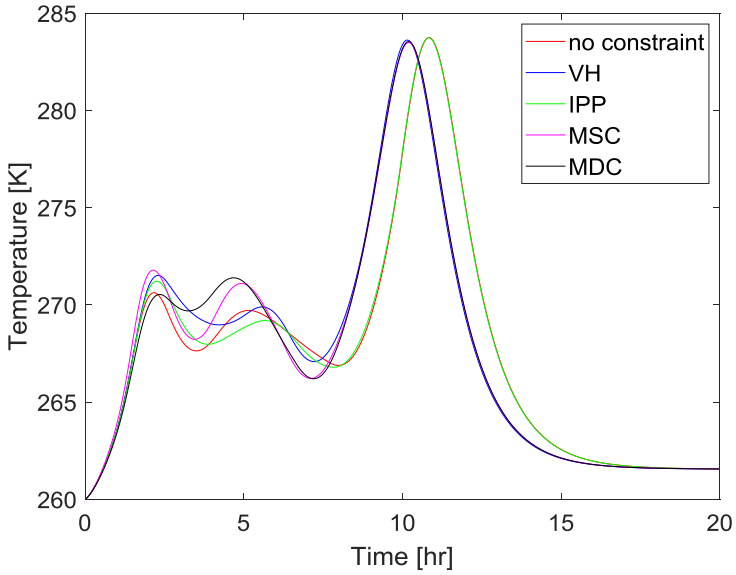

Figure 7.2 Temperature trajectories applying different criteria as a nonlinear constraint

7.2 Conclusion

When we operate a reactor which gives place for exothermic reactions we always must pay much more attention, because in such a case thermal runaway can occur. The results show the importance of choosing the right runaway criterion, because it affects directly the safety and the productivity of the operation. As it was presented some of the runaway criteria are too strict and conservative for the application in some cases (like in the production of 2-octanone), hence they do not give us relevant information about the process since they always indicate the development of runaway. On the other hand, if we use the least conservative criterion then we may operate the reactor too close to the boundary of thermal runaway and we may do not have time to react in case of an emergency situation. Therefore, I can state that the thermal runaway criteria literally help to design the reactor operation, and they can help to maximize the productivity while the reactor can be kept in safe regime, but we always must consider more possibility for the determination of critical boundaries.

8 Semi-batch reactor control with NMPC avoiding thermal runaway

The offline optimization problem is enough if the initial and input parameters are constant during the operation and of course there is no noises in measurements, but it is not quite common. However, we are able to feedback the actual states during the operation in online with Model Predictive Controller (MPC). Detailed and reliable models of batch reactors can be used for a model-based control approach such as nonlinear model predictive control (NMPC) [131]. Moreover, batch and semi-batch reactors carrying out potential runaway reactions have highly nonlinear process dynamics, and the controller has to cope with it. NMPC is a suitable attribute to handle nonlinear processes [132]. Also Model Predictive Control is an advanced control system and it is able to handle system bounds [166]. Since the goal in reactor operation is to maximize productivity while the operation is safe in the entire production time, prevention of thermal runaway is necessary. Optimal feeding trajectories were determined earlier in case of a pilot plant fed-batch reactor, where different thermal runaway criteria were applied as a non-linear constraint in the optimization problem.

8.1 Temperature control of SBR

The main goal of the SBR operation is similar to any other kind of reactor or process unit, such as to maximize the productivity while keeping the reactor safe during the entire operation. The reactor temperature is controlled by manipulating the flow rate of feeding reagents (*TV001*) and cooling agent (*TV002*) into the reactor jacket, which is the often applied scheme. The control structure of the reactor system is shown in Figure 8.1. The mass-flow of reagent feed is integrated, the amount of fed reagent is calculated (V_{dos}), and the liquid level is measured with *LIT001*. When the required reagent is added ($V_{dos,0}$), the reactor temperature control switches the actuator, and the temperature is controlled by manipulating the flow of cooling agent in the mixing phase, which was 80% of the total cooling capacity in the first phase of operation.

$$Actuator = \begin{cases} TV001 & V_{dos} < V_{dos,0} \\ TV002 & V_{dos,0} = V_{dos} \end{cases} \tag{8.1}$$

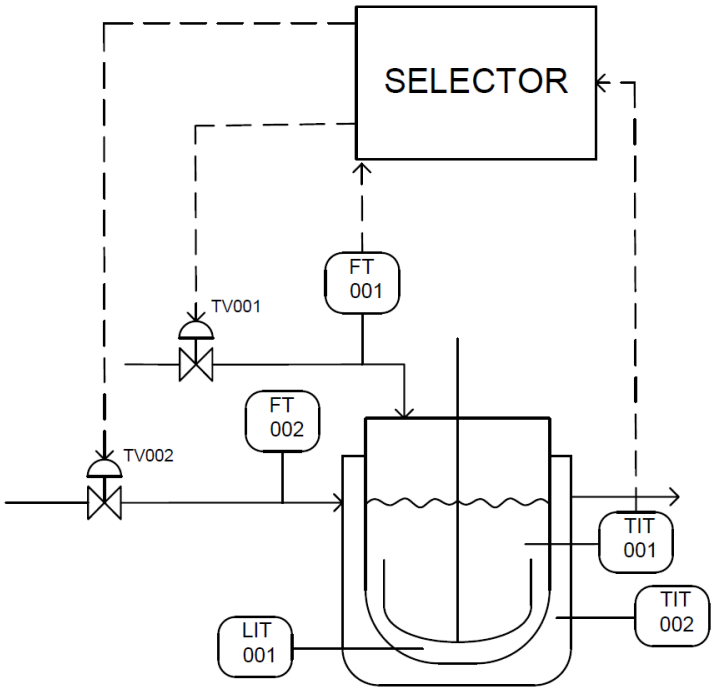

Figure 8.1 Proposed control structure of SBRs

8.2 Safety concepts

A safe operation is characterized by applying two safety regulations. One of them is a predefined MAT, so the reactor temperature (TIT001) cannot exceed MAT. The other safety bound is applying a thermal runaway criterion to avoid dangerous runaway states. Runaway criteria classify runaway and non-runaway states based on the state variables and parameters of the studied process (concentration of reagents, process temperature, heat of reaction, heat transfer parameter, etc.). Therefore, avoiding runaway states increases the safety of the reactor operation.

We applied two runaway criteria to investigate the control schemes, one of them is the Modified Dynamic Condition (MDC) and the other one is the divergence criterion (SZ), which is the most frequently applied and investigated runaway criterion despite its drawbacks presented in Section 2.4.2.5. As a reminder I present again the general formulas of the investigated criteria, MDC is Eq. 8.2 and SZ criterion is Eq. 8.3.

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \leq \frac{dq_{rem}}{dT}\frac{q_{gen}}{q_{rem}} \tag{8.2}$$

$$div[F(x_k)] \geq 0 \;\rightarrow x \; is \; unstable \; state \tag{8.3}$$

Let us introduce variable *I(k)* to evaluate the reactor operation based on runaway and non-runaway states. If Eq. (8.2) or (8.3) is satisfied, then $I(k) = 0$ (normal operation); otherwise, $I(k) = 1$ (runaway), where *k* is the *k*-th time instance.

8.2.1 Length of prediction horizon

In case of MPCs it is crucial to define the proper length of prediction horizon. We defined this length based on the implemented runaway criterion through investigating the process safety time (PST) of the system. In this way we are able to define the minimum length of prediction horizon to capture the development of runaway, which is necessary to keep the reactor states always in the controllable (i.e. non-runaway) zone.

Prediction horizon has to be long enough to capture thermal runaway [62], which is especially important in SBRs, since the reagents accumulation can result thermal runaway. PST is the function of state-variables and system parameters and it can be applied to define the length of prediction horizon considering MAT of the system. Another way to determine PST is the application of runaway criteria to calculate how much time we have before the development of runaway. PST basically means the time necessity of process safety manipulations before the detection of unsafe situations to avoid hazard events, presents the time difference between the first unstable and last controllable states [29]. In case of SBRs with NMPC the runaway states are predicted online in prediction horizon, hence the last controllable state and first runaway state should be seen in prediction horizon. Although, with NMPC we can continuously manipulate the input to avoid runaway states, hence we can define PST based on the first time instance exceeding the edge of non-runaway and runaway zone. Therefore, PST can be defined with the following equation:

$$PST = argmin_k(I_k = 1) \tag{8.4}$$

Since the thermal runaway has to be captured in the prediction horizon, we have to design it for the worst-case scenario. For this purpose the SBR system has to be considered as a batch and we have to consider the state variables where the probability of accumulation is the highest (low reactor temperature, initial reagents concentration, etc.). Different scenarios ($i=1...n$) have to be analysed with different initial concentration of reagents (which are fed into the reactor) to define maximum process temperatures ($T^{(i)}_{max}$) and process safety times ($PST^{(i)}$). Let the critical initial states ($x_{0,c}$) be that initial states where the maximum process

temperature equals MAT. In that case the length of prediction horizon will be the PST at critical initial states.

$$t_{pred} = PST|_{i(T_{R,max}=MAT)} \tag{8.5}$$

8.3 Nonlinear Model Predictive Controller

Control of nonlinear system is considered in the discrete-time domain represented by

$$x_{k+1} = f(x_k, u_k) \tag{8.6}$$

where *x(k)* is the state vector at *k*-th time instance, u_k is the vector of control inputs and *f* is a nonlinear state update function. The objective of NMPC is to determine the optimal control inputs over a fixed prediction horizon that drives the system to a desired final state while minimizing a given objective function, and making sure that the system states and control inputs remain bounded [167]. The analysis of stability of SBRs is incorporated into the Model Predictive Control flowsheet proposed by Kähm [62] presented in Figure 8.2.

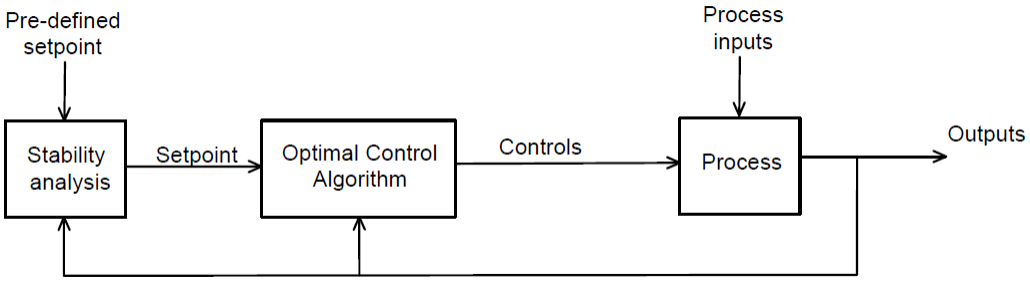

Figure 8.2 MPC with integrated stability analysis [62]

SBR carrying out highly exothermic reactions is difficult to control, because the reagents can accumulate in the reactor follows that the temperature can increase rapidly. Process temperature can be handled by feeding reagents, if the fed reagents consume immediately in the reaction.

Engineers should always plan for plant-model mismatch, since it is difficult to obtain a model that describes the plant with sufficient accuracy. The plant-model mismatch can result in an undesirable event during the operation, and its prevention is necessary. Many methods can be found in the literature to handle this problem, such as considering uncertain parameters or applying state observers. Model Predictive Control (MPC) can provide a robust control approach to handle uncertainties of the system, where the feeding rate can be optimized. MPC

is an advanced control system and can handle system boundaries [166]. An excellent review on the history of industrial MPC applications can be found in [168]. Parameter uncertainty can be considered by applying the well-known min-max formulation [169], multi-stage methods [170], or tube-based methods [171]. Min-max MPC takes into account the worst-case realization of the parameter uncertainty, although it is conservative and may result in an infeasible optimization problem [172]. The conservativeness of min-max MPC was reduced by taking into account the future feedback information [173]. Multi-stage MPC realizes the uncertainty by a tree of discrete scenarios, where each scenario must satisfy the predefined constraints [170]. Puschkle and Misos proposed a robust feasible multi-stage economic nonlinear model-predictive controller (eNMPC) with a heuristic multi-model approach, where the worst-case scenarios are generated based on sensitivities. They neglected the scenarios on the edges of the uncertainty set with low sensitivity [174]. A review of eMPC is found in [175]. Holtorf et al. presented multi-stage NMPC with on-line generated scenario trees that do not directly scale with the number of uncertain parameters [176].

8.4 NMPC control scheme with a general model

This section introduced the NMPC control scheme of the case study presented in Section 3.3.1. Two operation modes will be compared to each other. In the first the reagents are not preheated to the reaction temperature before the feed, and in the other operation mode the reagents are preheated. In industrial practice the latest operation mode is favourable because the safety of the operation can be easier ensured even though the energy consumption of this mode is higher than in the first. However, in case we have some tools which can reliable avoid thermal runaway in the first mode, the energy consumption can be reduced in case of exothermic reactions.

SZ and MDC criteria were implemented in a control algorithm to find the optimal feeding trajectory in case of a fed-batch reactor with highly exothermic reaction. Finally, we proposed to apply NMPC with runaway criterion to decrease the energy usage of fed-batch operation without any significant production drop.

8.4.1 Open-loop optimization problem

The goal is to maximize productivity without the development of thermal runaway. Therefore, the objective function considers that the process temperature follows setpoint temperatures and to avoid runaway zone during operation without significant changes in the manipulated variable.

$$e_k = T_{SP} - T_{R,k} \tag{8.7}$$

where e_k is the error between the setpoint and the current temperature at k-th time instance.

Runaway states can be prevented by considering these (I_k) in the formulation of NMPC.

$$\min_{u} \sum_{k=0}^{t_{pred}} w_e \frac{|e_k|}{T_{R,0} - T_{SP}} + w_u |u_k - u_{k-1}| + w_I I_k \tag{8.8}$$

subject to

$$0 \leq u_k \leq 100\ \% \tag{8.9}$$

$$T_{R,k} \leq MAT \tag{8.10}$$

where w_e, w_u, are weight factors, T_{SP} is setpoint temperature and $T_{R,k}$ is the reactor temperature at k-th time instance.

8.4.2 Process model and analysis

In this section the process model of the investigated semi-batch reactor is presented (see Section 3.3.1), normal and runaway operations and calculation of PST are also presented. In the reactor we carry out a single, highly exothermic reaction.

Process behaviour was analysed without any control system, where the feed rates of both the coolant and the *A* reagent are constant. The same amount of reagent *A* is fed into the reactor with different dosing time. Temperature and concentration profiles can be seen in Figure 8.3, where it can be seen that by increasing the dosing time the maximum process temperature decreases. In Figure 8.3 a) thermal runaway has occurred (which was indicated by *SZ* criterion) and the process temperature exceeded MAT. Figure 8.3 b) presents an operation without thermal runaway. Goal is to maximize productivity, and an optional feeding trajectory can be defined to avoid runaway and a further aim can be the minimization of the reaction time.

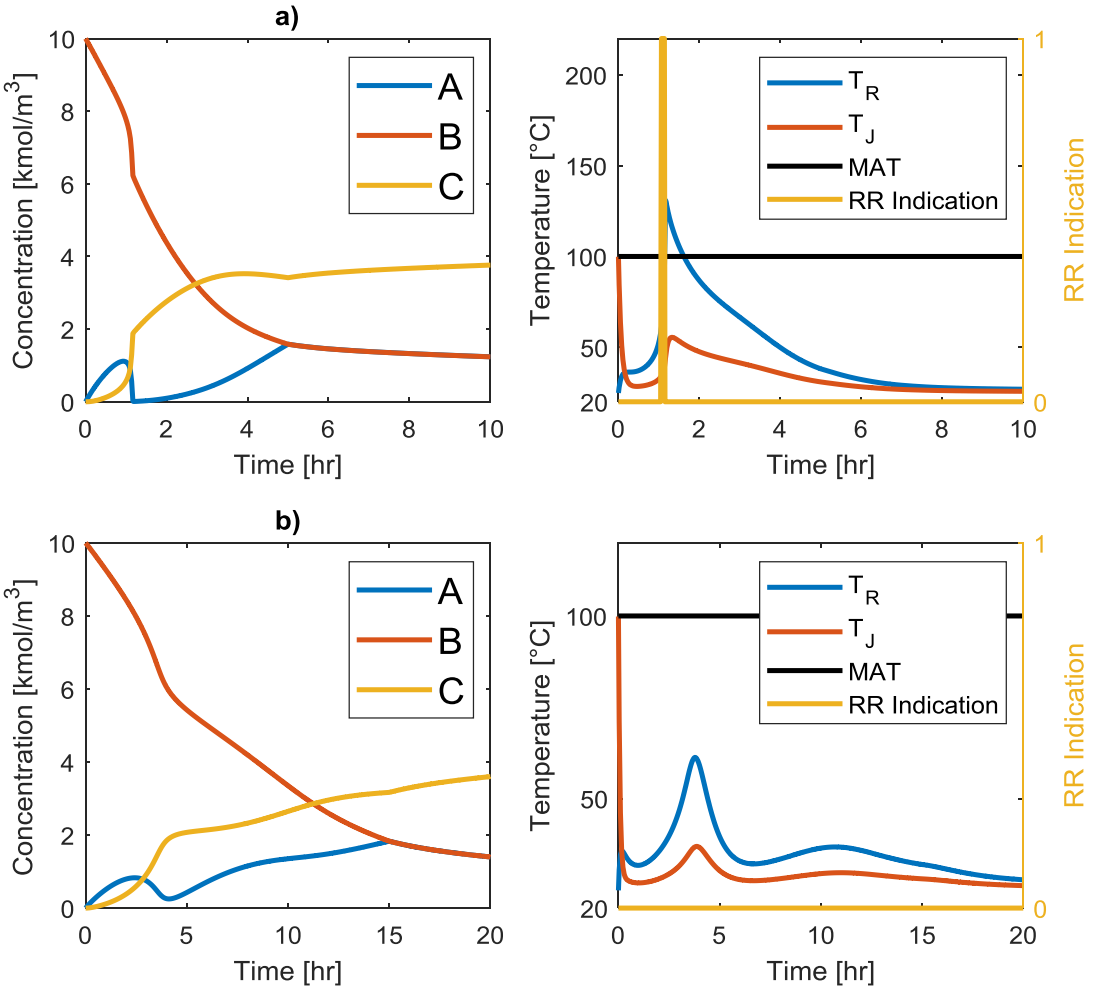

Figure 8.3 Behaviour of reactor in case of different dosing times a) t_{dos} =5 hr, b) t_{dos} =15 hr (RR = reactor runaway)

Runaway and non-runaway states are distinguished by *SZ* and *MDC* criteria. In case of divergence criterion the derived critical equation is the following for the analysed system:

$$-r_{c_A} - r_{c_B} - \frac{F}{V} - \frac{\Delta H_r}{\rho c_p} r_T - \frac{UA}{V\rho c_p} - \frac{UA}{(V\rho c_p)_j} - \frac{F_j}{V_j} \leq 0 \tag{8.11}$$

In case of *MDC* criterion the derived criterion is the following:

$$-r_{c_A} - r_{c_B} - \frac{\Delta H_r}{\rho c_p} r_T - \frac{UA}{V\rho c_p} \frac{\Delta H_r V r}{UA(T_R - T_j)} \leq 0 \tag{8.12}$$

where r_T and r_c are the derivative of reaction rate with respect to temperature and concentration of reagents respectively.

For that purpose to define the length of prediction horizon, process safety times and maximum process temperatures were calculated. In this case SBR was considered as batch (i.e. when runaway indicates usually we have only one possible safety action to moderate its effect, closing the feed valve) and the initial concentration of reagent *A* next to a constant concentration of reagent *B* was increased and maximum process temperatures and PSTs were analysed. In case of *SZ* criterion, as it can be seen in Figure 8.4, maximum temperature exceeds MAT at ~1.58 $\frac{\text{kmol}}{m^3}$ initial concentration with 0.78 hour PST. PST_c defines the minimum time length to notice the development of thermal runaway, hence minimum time length of prediction horizon will be 0.78 hours in this case.

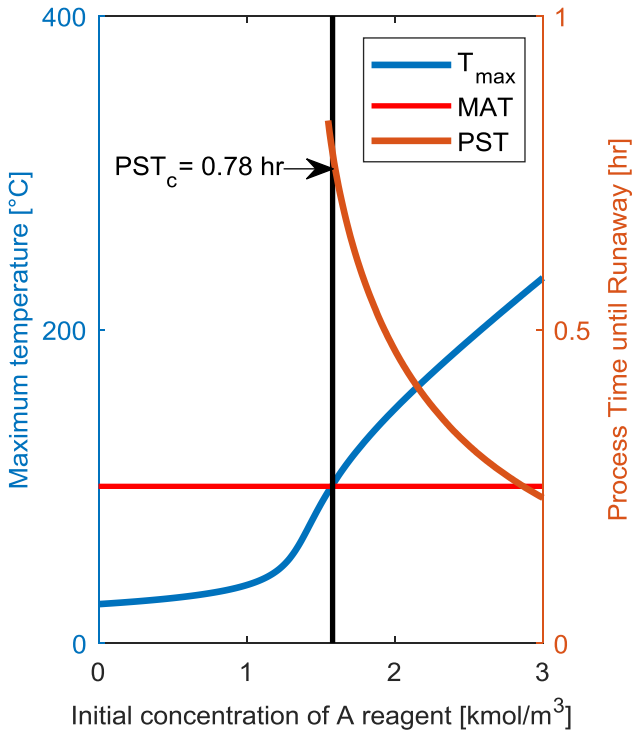

Figure 8.4 Critical PST in case of SZ criterion

In case of *MDC* criterion the results can be seen in Figure 8.5, where PST_c and prediction horizon will be 0.57 hours.

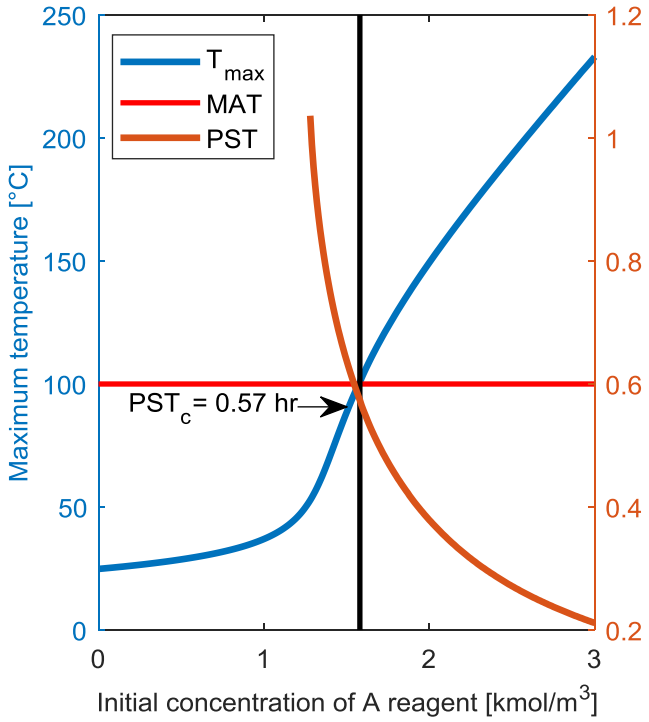

Figure 8.5 Critical PST in case of MDC criterion

At this case *MDC* criterion is stricter than *SZ* criterion, means that *MDC* criterion indicates runaway at ~1.3 kmol/m^3 initial concentration while *SZ* criterion indicates runaway at ~1.5 kmol/m^3. Hence, in that case when the maximum process temperature exceeds MAT *MDC* criterion probably indicates the development of runaway earlier than *SZ*, as it can be seen from critical PSTs. When the length of prediction horizon is chosen based on PST_c and runaway indication occurs before process temperature exceeds MAT, there are some runaway states which cannot be foreseen. However, these runaway states are not relevant from process safety since these runaways do not result that process temperature exceeds MAT and the reactor stays in controllable operating regime. Since there can be runaway states (according to the applied criterion) which not cause that the temperature exceeds MAT, the reaction temperature is higher, it can decrease batch process time because the reaction rate is higher. That is why we do not apply non-linear constraint to avoid all runaway states during the feed, instead of this, the number of runaway states is minimalized (i.e. as a penalty function) as it can be seen in Eq. (8.8). In our case it results that the stricter criterion can result a shorter batch time.

8.4.3 Results and Discussion

This section presents the results of reactor control with NMPC control scheme. Section 8.4.3.1 describes the result of PID control, in Section 8.4.3.2 the configuration of NMPC, in Section 8.4.3.3 the results can be seen with different operation strategies.

8.4.3.1 SBR temperature control with PID

In order to test how a simple control system can be applied to keep the system in safe operating region, a simple PID controller was tested. In case of preheating the reagents the PID controller works reliable, although when the reagents are not preheated the PID controller does not work since it takes time to ignite the reaction. In that case runaway occurs approximately after 30 minutes. Results can be seen in Figure 8.6 when the loaded reagents are preheated and in Figure 8.7 when only the produced heat by the reactions heat up the reactor. Optimal PID parameters were identified by an extremum search algorithm to minimize the difference between PV and SP.

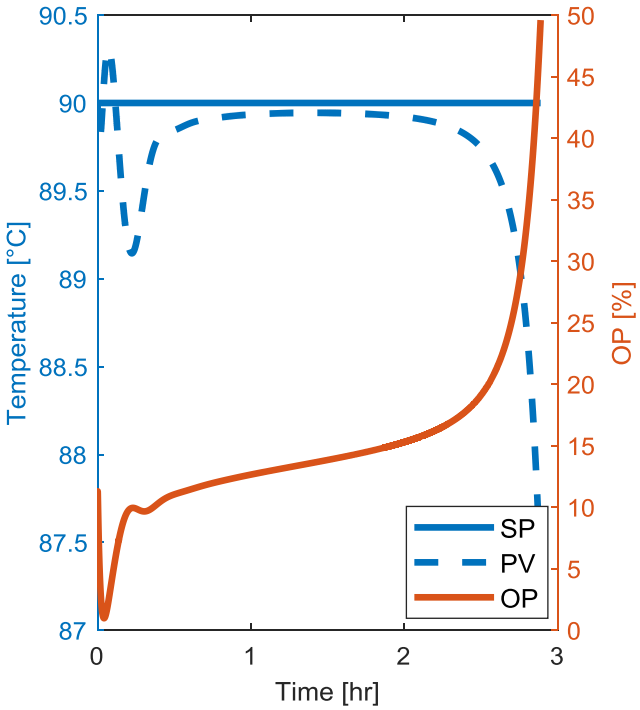

Figure 8.6 SBR temperature control with PID algorithm (Kp=4.65, Ti=401.56, Td=158.3)

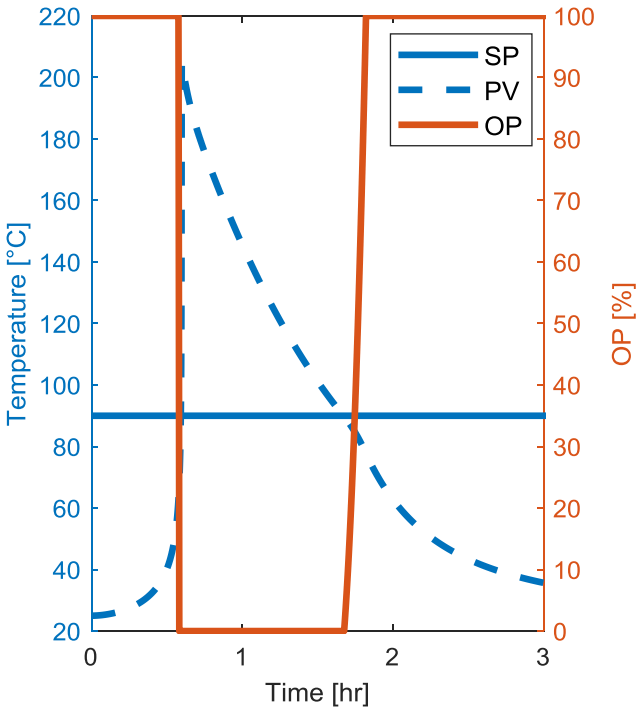

Figure 8.7 PID control without preheating the reagent (Kp=4.65, Ti=401.56, Td=158.3)

If the setpoint changes according to a desired trajectory, then the batch reactor can be operated without preheating the reagent, but it can easily results dangerous situations. A little disturbance can results a runaway behaviour of the reactor. Therefore, when the reagents are not preheated a robust control system should be applied, such as NMPC, which give a more acceptable feeding trajectory and safer process operation.

8.4.3.2 Configuration of NMPC

Open-loop optimization problem has been solved by the classical SQP optimization algorithm. The algorithm proceeds with a moving horizon. The applied parameters of NMPC are summarized in Table 8.1.

Table 8.1 Parameters of NMPC

Sample time	T_0	120 s
Prediction horizon (*SZ*)	t_{pred}	2280 s
Control horizon (*SZ*)	t_{contr}	600 s
Prediction horizon (*MDC*)	t_{pred}	1440 s
Control horizon (*MDC*)	t_{contr}	600 s
Maximum Allowable Temperature	MAT	100 °C
Weight factor in Eq. (8.8)	w_e	1
Weight factor in Eq. (8.8)	w_u	$\frac{T_0}{1000 t_{contr}}$
Weight factor in Eq. (8.8)	w_I	10^5

8.4.3.3 Results of open-loop NMPC

NMPC is tested in case the earlier introduced two operation modes in this section. Figure 8.8 presents the control of the semi-batch reactor without preheating the loaded reagent when *SZ* runaway criterion is applied as non-linear constraint in the optimisation task. As it can be seen the proposed control algorithm is able to keep the operation in the controllable zone and thermal runaway does not occur. This is due to the fact that the algorithm is able to handle the accumulation of reagents, since it does not let to feed too much reagents into the reactor until the concentration of the component "*B*" is high. Concentration of component *"A"* reaches ~1 kmol/m^3 and the applied *SZ* criterion does not allow to accumulate more reagent in the reactor. The operating values are bounded by *SZ* criterion until ~2.2 hours, after there is no danger of thermal runaway since the reaction ignited. As it can be seen the temperature of the reactor is controlled accaptable and the proposed NMPC is able to keep the desired setpoint, although the operating values are a little noisy when divergence criterion does not bound the operation anymore. The manipulator switch works smoothly which occurs at ~4.7 hours. From that point the temperature is controlled by manipulating the cooling flow rate.

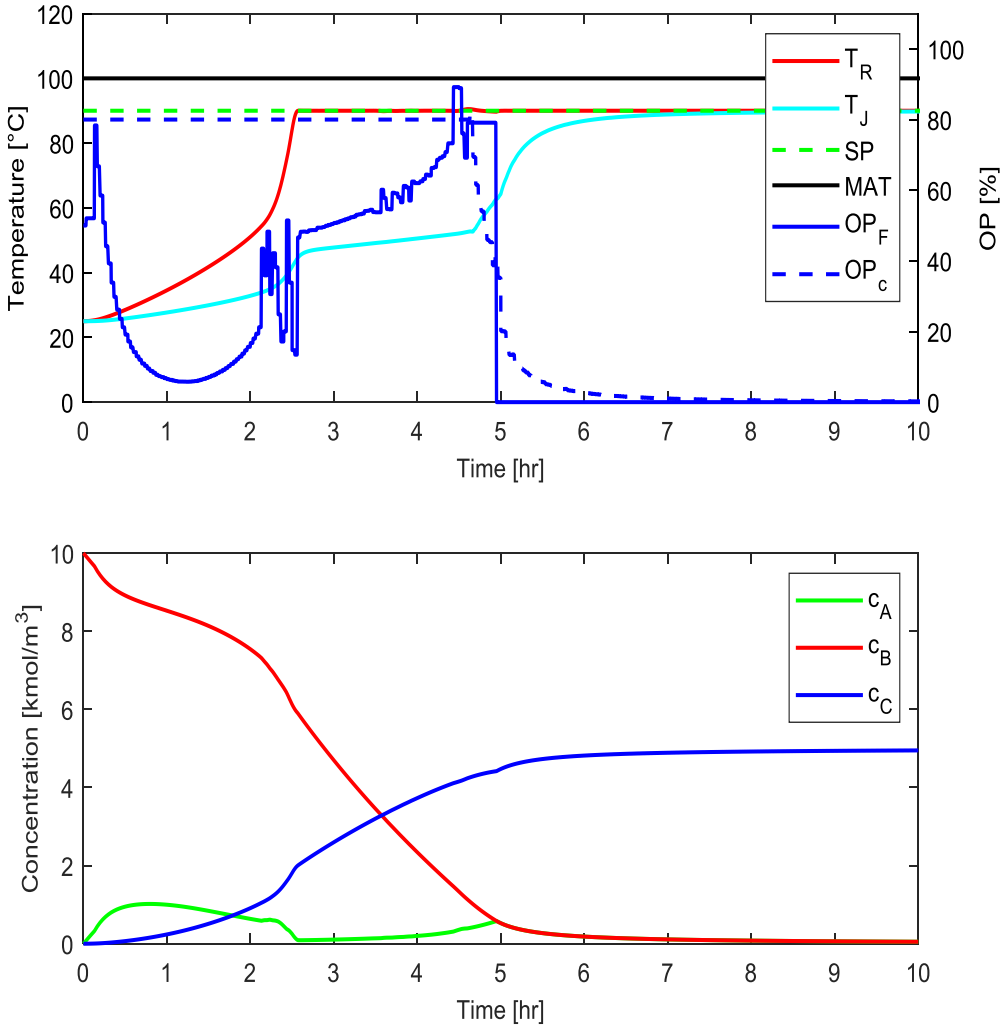

Figure 8.8 SBR temperature control without preheating the loaded reagent (SZ criterion)

Figure 8.9 shows the SBR control result in case of applying the *MDC* criterion without preheating the loaded reagent.

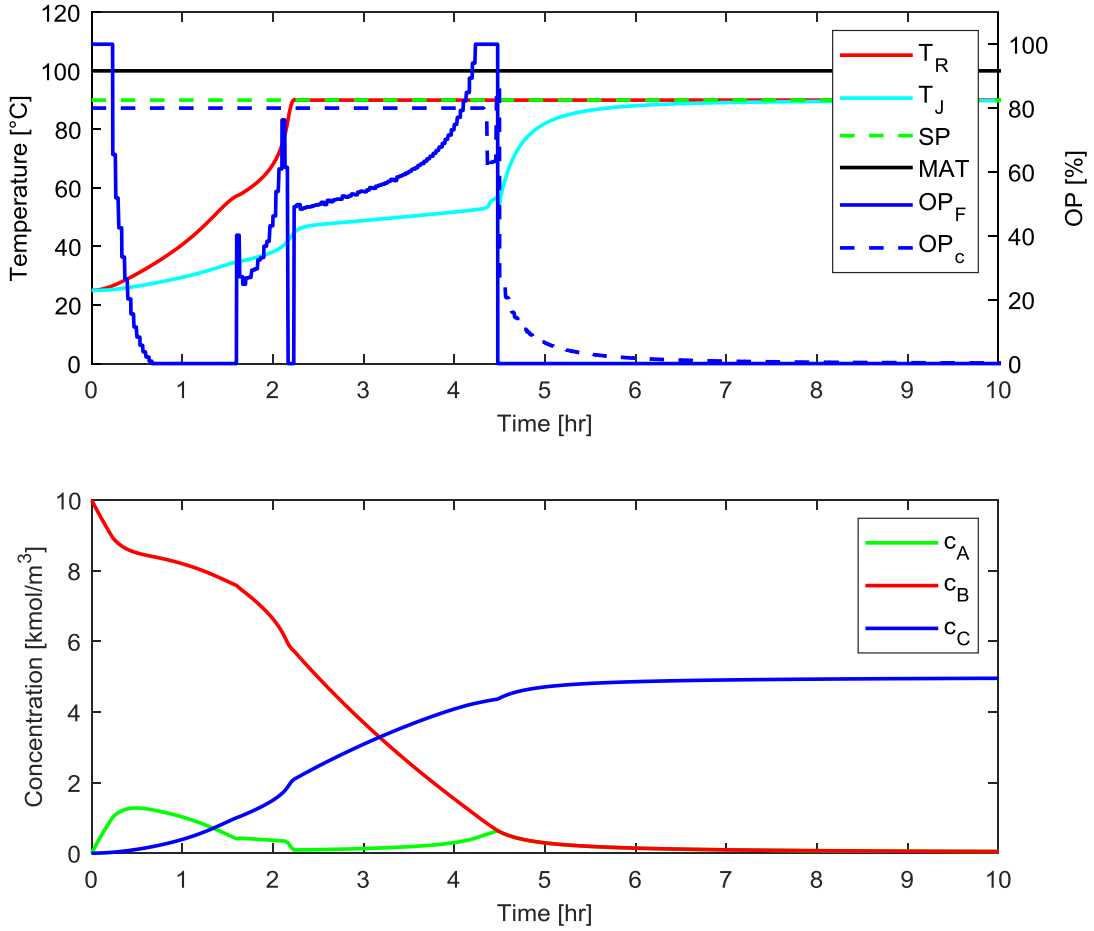

Figure 8.9 SBR temperature control without preheating the loaded reagent (MDC criterion)

MDC criterion performs similarly to *SZ* criterion, although in case of *MDC* criterion the reagents are fed in shorter period of time (*SZ*: 4.7 hours against *MDC*: 4.3 hours). The concentration of component *"A"* reaches 1.3 kmol/m^3 with *MDC* criterion, then the feeding rate of component *"A"* is stopped to avoid the accumulation of reagents. The operating values are bounded by *MDC* criterion until ~1.6 hours. The temperature control performs well. Operating values are less noisy with this criterion and the switch of manipulators works smoothly too which occurs at ~4.3 hours.

If the loaded reagent is preheated to the reaction temperature, there is a lower risk for the accumulation of fed reagents. Figure 8.10 presents the temperature control in this case.

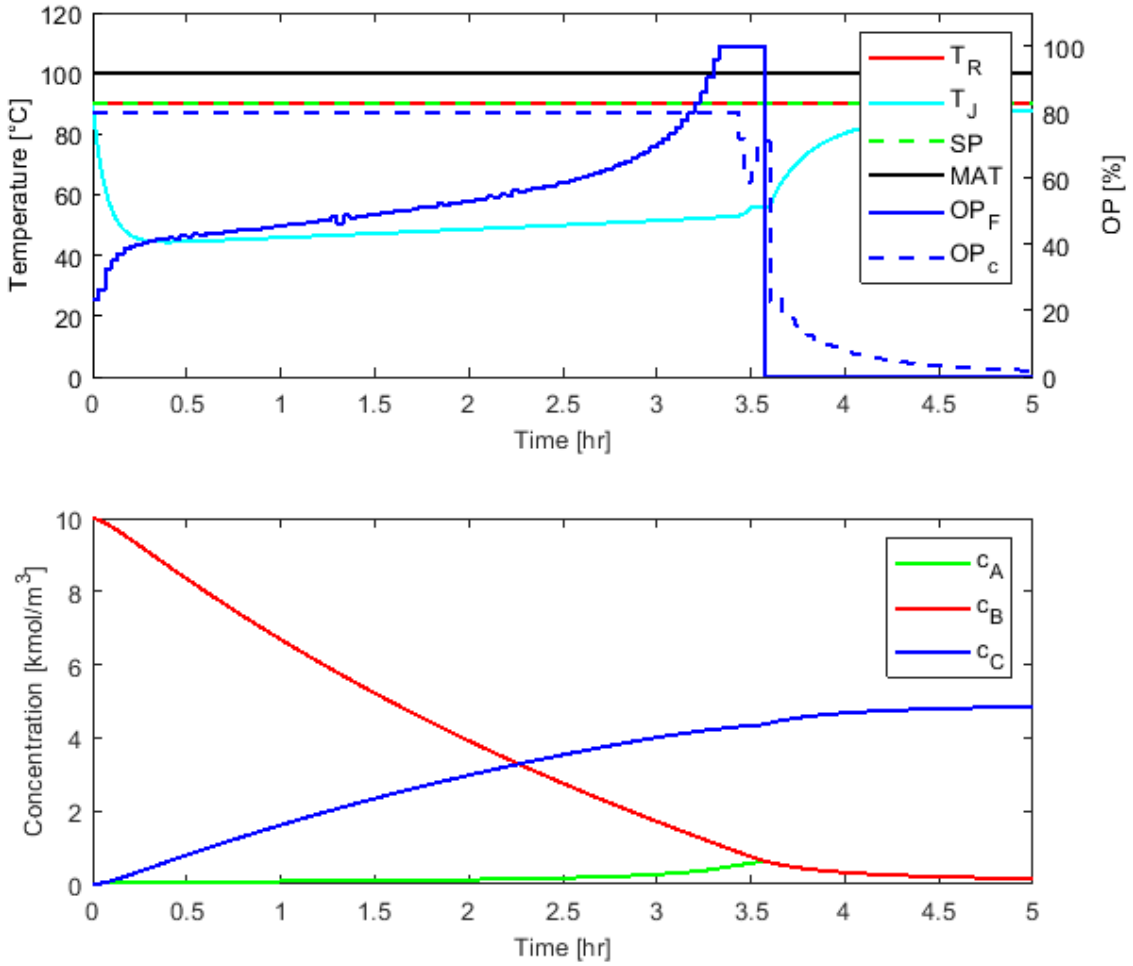

Figure 8.10 SBR temperature control with preheating the loaded reagent

As it can be seen in Figure 8.10, the fed reagents react almost immediately, hence there is no risk of thermal runaway, means that the operating values are not bounded by thermal runaway criteria. Flow rate of component *"A"* increases continuously to keep the reactor temperature at the setpoint. Switch of manipulators occurs at ~3.6 hours which occurs smoothly too.

When SBR is operated, thermal hazard risk can be decreased by preheating the reagents. Although, implemented thermal runaway criteria are an additional safety factor in reactor operation which can help to prevent reactor runaway in case of wrongly chosen operating parameters.

Average computational time is 37.6 second and the sampling time is 120 second, hence the proposed method can be implemented in a real time problem too, although in that case we will have to take into consideration parameter uncertainty.

8.4.4 Performance analysis

The different operation modes are compared to each other based on energy consumption and batch time. Batch time consists of preheating and reaction times next to other operation steps, with much lower time requirements. Hence, only these two are considered to calculate the batch time in each case. Preheating time is calculated based on the following equations, where the heating medium is 100 °C saturated steam:

$$Q_{preheat} = V_0 \rho c_p \Delta T = 156000\ kJ \tag{8.13}$$

$$t_{preheat} = \frac{Q_{preheat}}{UA_0 LMTD} = 0.73\ hr \tag{8.14}$$

Table 8.2 Performance analysis of the proposed NMPC in case of the considered operation modes

	SZ criterion without preheating	**MDC criterion without preheating**	**Operation with preheating**
Heating energy requirement [kJ]	-	-	$1.56 \cdot 10^6$
Cooling energy requirement [kJ]	$1.43 \cdot 10^6$	$1.43 \cdot 10^6$	$1.54 \cdot 10^6$
Preheating time [hr]	-	-	0.73
Feeding time [hr]	4.95	4.48	3.57
Batch time [hr]	4.95	4.48	4.3

Table 8.2 shows that the case when the loaded reagent is not preheated and runaway criteria are applied as a constraint in reactor operation, the energy consumption is less by ~7% compared to operation in which preheating is applied. In case of applying *MDC* criterion the batch time is higher by ~4%, and in case of applying *SZ* criterion the batch time is higher by ~15%. Therefore, with implemented runaway criterion energy consumption can be decreased in operating of semi-batch reactors carrying out exothermic reactions.

8.4.5 Conclusion

A nonlinear model predictive control approach has been analysed in case of a semi-batch reactor carrying out potentially runaway reaction. Divergence runaway criterion and modified dynamic condition was applied as an additional safety constraint in the formulation of NMPC beside that the process temperature cannot exceed the maximum allowable temperature. To

avoid thermal runaway, runaway states have to be seen in prediction horizon. For this purpose process safety time (PST) of the system was investigated. PSTs were calculated for the worst cases, hence the SBR system was considered as a batch with low reactor temperature and initial reagents concentrations. PSTs were defined by the first time instance exceeding the edge of non-runaway and runaway zone. Different scenarios were analysed with different initial concentration of reagents (which are fed into the reactor) to define maximum process temperatures and PSTs, and the critical scenario is when the maximum process temperature equals MAT. PST of critical scenario is selected as the length of prediction horizon, because in this case we are able to see the development of runaway leading to dangerous situation, hence we are able to avoid it. Although, when there are thermal runaway indications before maximum process temperature exceeds MAT, then these runaway states (according to the applied criterion) cannot be foreseen. However, these runaway states do not lead the reactor out of controllable regime, since these do not cause the process temperature become higher than MAT. Moreover, these runaway states can be favourable since these states causes higher temperature and through higher reaction rate the batch time decreases.

Two operation modes were analysed, in the first case the reagents are not preheated to the reaction temperature, and in the other case the reagents are preheated. On the first operation mode the effect of criterion constraint is well-seen. Until the concentration of charged reagents is higher the feeding rate and process temperature is constrained since the fed reagent cannot be consumed at the lower process temperature. It follows that thermal runaway criteria can be applied in NMPC as an additional constraint to increase the safeness of the system. However, if the charged reagent is preheated then the fed reagent cannot accumulate leads to that the reaction is inherently safe. If the reactor is heated up by the reaction less energy is consumed, while the batch time is not significantly higher. Therefore, runaway criteria can be applied as a non-linear constraint in NMPC to operate SBRs to avoid the development of thermal runaway, while the energy consumption can be decreased too.

8.5 Semi-batch reactor control with NMPC avoiding thermal runaway under parameter uncertainty

As we have seen in the previous Section, the combination of MPC and a runaway criterion is a promising and general tool to provide the optimal control of SBRs. However, plant-model mismatch is not negligible in the application of NMPC which has not been analysed. Since thermal runaway can have lethal consequence, the parameter uncertainty must be handled so that the probability of runaway is close to zero. Therefore in the following, I extend the previously presented control frame to handle parameter uncertainties too. I consider the multiplicative uncertainty, so the model matrices are uncertain. The most crucial uncertainty sources from the reactor runaway viewpoint can be the kinetic parameters, heat transfer parameters and mixing efficiency for SBRs. The uncertainty in kinetic parameters is considered the source of model-plant mismatch in this section. I investigated worst-case scenario and Multi-Stage NMPC to handle parameter uncertainty, although the computation cost of MS-NMPC is much higher. The goal is to develop a control framework for SBRs with exothermic reactions, which can be applied online in real reactor systems, so the computation time is critical. Therefore, I investigated the worst-case scenario with iteratively updating uncertain parameters by the least-squares method. NMPC naturally includes the model of the process, although the real process in this case is also a model. Our future work will be about implementing the proposed control scheme into a real laboratory reactor system. Currently, I can generate a plant-model mismatch to investigate the proposed control framework, which is a more safe solution during the development phase.

8.5.1 Proposed control structure of SBRs

This section will introduce the proposed general control methodology for SBRs that perform potential runaway reactions. The practical application of this control structure will be presented in Sections 8.5.3.

The proposed control scheme for SBRs is shown in Figure 8.11. When exothermic reactions are carried out in the reactor, the not perfectly identified kinetic parameters (or other model parameters) can easily lead to the development of thermal runaway. In the proposed control scheme, the parameter uncertainty is handled by the combination of state estimation and a model identification algorithm. Although I investigated multi-stage NMPC, its high computational cost is not encouraging (see Section 8.5.3.2); hence, I suggest applying the worst-case scenario with updating uncertain parameters (see Section 8.5.3.2).

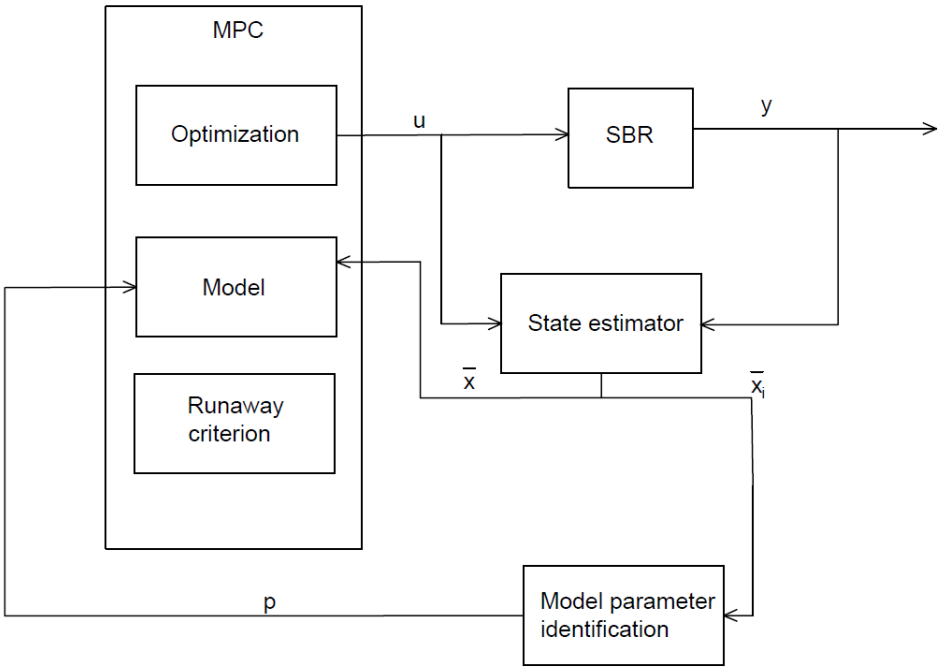

Figure 8.11 Proposed control scheme for SBRs

In Figure 8.11, u is the control inputs, y is the reactor measurement outputs, $\bar{x}$ is the estimated states of the reactor, and $\bar{x}_i$ is the required estimated states for model parameter identification. This scheme is a general representation of the proposed control structure. In our case, u consists of OP_F *and* OP_C (valve positions in the feed line and cooling agent line, respectively). y includes T_R, T_J, and V_L (reactor temperature, jacket temperature and liquid volume in the reactor). $\bar{x}$ consists of $\bar{c}, \bar{T}_R, and\ \bar{T}_J$ (estimated concentration, reactor and jacket temperature, and reaction rate constants). $\bar{x}_i$ in our case includes $\bar{k}$ (reaction rate constants), and p consists of $\bar{k}_0\ and\ \bar{E}$, which are identified parameters. In the following sections, I introduce parts of the proposed control structure in more detail.

8.5.1.1 Open-loop optimization problem

The goal is to maximize the productivity while thermal runaway does not develop, so the conversion of the key component (x_{KC}) and selectivity for the product (S_P) are considered in the objective function next to the runaway states (I_k), and higher reactor temperatures than MAT (e^+) should be avoided. The objective function (or stage cost if I refer to Multi-Stage NMPC) is denoted by L, which represent a general cost function. The terms of the cost function are weighted (w_x, w_s, w_u, w_I, w_T), so a well performing control can be reached in different applications. In the third term in Eq. (8.16) the significant changes in the manipulated variables are penalized.

$$e^+ = max\left(T_{R,k} - MAT; 0\right) \tag{8.15}$$

$$L = -w_x x_{KC} - w_s S_p + w_u|u_k - u_{k-1}| + w_I I_k + w_T e^+ \tag{8.16}$$

$$\min_{u_k} \sum_{0}^{t_{pred}} L(x_k, u_k) \tag{8.17}$$

which is subject to

$$x_{k+1} = f(x_k, u_k, d_k) \tag{8.18}$$

$$0 \leq u_k \leq 100\% \tag{8.19}$$

where $u_k \in R^{n_u} u_k$ is the control input (control valve), n_u is the number of control inputs, each state ($x_{k+1} \in R^{n_x}$) is a function of the previous state (x_k), and n_x is the number of states. The realization of uncertainty is denoted as $d_k \in R^{n_d}$, where n_d is the dimension of the uncertainty vector.

8.5.1.2 NMPC to handle parameter uncertainty

I always must count on plant-model mismatch, so I must address the parameter uncertainty. This section introduces the formulation of Multi-Stage NMPC and Worst-case Scenario to handle this problem.

Multi-Stage NMPC

Figure 8.12 illustrates how the multi-stage NMPC works with the given horizon lengths. For Multi-Stage NMPC, combinations of maximal, minimal and nominal values of uncertain parameters are considered, which usually results in a robust behaviour of the controller [173].

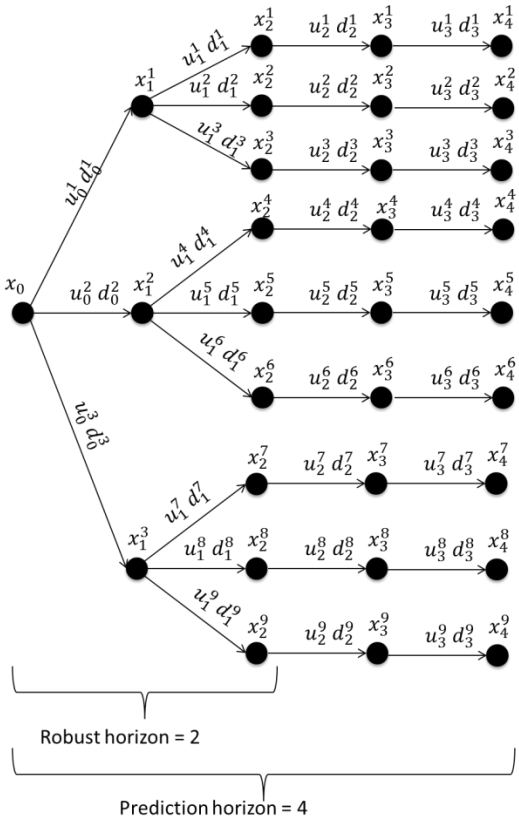

Figure 8.12 Tree representation of the uncertainty evolution for a Multi-Stage NMPC [173]

Each path of the scenario tree is called a scenario and indicated as *i*, and it contains all states x_k^j and control inputs u_k^j of scenario *i*. The set of all occurring indices (*j*,*k*) is denoted by *T* [177]. The number of scenarios is introduced by *N*. The cost of each scenario is considered with the same weight, so the mean value of the costs will give the objective value. The formulation of Multi-Stage NMPC is shown in Eqs. (8.20)-(8.23).

$$\min_{u_k^j} \sum_{i=1}^{N} \frac{1}{N} \sum_{0}^{t_{pred}} L_i(x_k^i, u_k^i, d_k^i) \tag{8.20}$$

which is subject to

$$x_{k+1}^j = f\left(x_k^{p(j)}, u_k^j, d_k^j\right) \qquad \forall (j, k+1) \in T \tag{8.21}$$

$$0 \leq u_k^j \leq 100\ \% \qquad \forall (j,k) \in T \tag{8.22}$$

$$u_k^j = u_k^l \; if \; x_k^{p(j)} = x_k^{p(l)} \quad \forall (j,k), (l,k) \in T \tag{8.23}$$

where $x_k^{p(i)}$ is the parent node. To correctly represent the real-time decision problem, the control inputs cannot anticipate the values of the uncertainty that are realized after the corresponding decision point. It is important because it is not possible to give multiple input variations to the process at the current state [174]. This condition is enforced by Eq. (8.23), which represents the non-anticipativity constraints that require all control inputs at the same node to be equal. In Figure 8.12, this condition implies that $u_0^1 = u_0^2 = u_0^3$; $u_1^1 = u_1^2 = u_1^3$; ... [177].

The optimization problem was solved by the modified progressive hedging algorithm, which is a decomposition algorithm, where non-anticipativity constraints are relaxed by penalizing the difference between the control inputs that should satisfy the non-anticipativity constraints. Its advantage is that the scenarios can be independently solved, so the following (Eqs. (8.24)-(8.27)) optimization problem must be solved. As shown by S. Lucia applying a longer robust horizon of one does not significantly improve the result, but it requires more computational effort, because the size of the optimization problem increases exponentially with it [177]. Since the length of robust horizon is one in this case, only the first control inputs (u_0^i) of different scenarios must satisfy the non-anticipativity constraint.

$$\min_{u_k^j} L_i\left(x_k^i, u_k^i, d_k^i\right) + \lambda^i\left(u_0^i - \hat{u}_0^i\right) + \rho^i\left(u_0^i - \hat{u}_0^i\right)^2 \tag{8.24}$$

which is subject to

$$x_{k+1}^j = f\left(x_k^{p(j)}, u_k^j, d_k^j\right) \qquad \forall (j, k+1) \in T \tag{8.25}$$

$$0 \leq u_k^j \leq 100\ \% \quad \forall (j,k) \in T \tag{8.26}$$

$$\hat{u}_0^i = \sum_{i=1}^{N} \frac{1}{N} u_0^i \tag{8.27}$$

where $\hat{u}_0^i$ is the fictious value towards which the control inputs converge to satisfy the anticipativity constraints. Parameters λ^i and ρ^i are updated at each iteration to improve the convergence, where the update rule is:

$$\lambda^i = \lambda^i + \rho^i\left(u_0^i - \hat{u}_0^i\right) \tag{8.28}$$

$$\rho^i = min\left(\beta\rho^i, \rho_{max}\right) \tag{8.29}$$

where β determines the increase of ρ^i. Eqs. (8.24)-(8.27) are iteratively solved until $max\left(u_1^i - \hat{u}_1^i\right) < \varepsilon$. After several iterations the non-anticipativity constraints are satisfied with desired tolerance ε.

Worst-case scenario

Two non-desired scenarios can be distinguished. In the first scenario, the reaction rate is much higher than expected; then, the generated heat will be much higher in the process than the model, which may cause thermal runaway. In the second scenario, the fed reagent accumulates because the reaction rate is lower than expected. When the concentration increases to a critical point, the reaction ignites, and thermal runaway may occur. To select the worst case scenario. I must choose between these two possible scenarios. There is a huge difference in ignition time between these two scenarios. The first scenario results in a more conservative solution, since the ignition time is lower; hence, if I can handle the first scenario, I can also avoid the second scenario. Therefore, I suggest kinetic parameters for worst cases that result in higher reaction rates, and I will apply the first scenario as the worst case by increasing the pre-exponential factor (k_0) and decreasing the activation energy (E) to the edge of the confidence interval.

8.5.1.3 Parameter identification

The logarithm of the reaction rate constant (k) linearly varies with the reciprocal of temperature (Eq. (8.30)), so the least squares method can be applied to estimate the pre-exponential factor and activation energy of the reaction.

$$ln\left(\bar{k}\right) = ln\left(\bar{k}_0\right) - \frac{\bar{E}}{RT} \tag{8.30}$$

Estimated reaction rate constants are required to calculate Eq. (8.30), so the state observer is necessary in the control structure. Since the reliability of the estimated kinetic parameters depends on the reliability of the state observer, I implement a condition that must be satisfied to overwrite the actual kinetic parameters.

$$RD = 100\frac{\sigma_p}{\mu_p} < 1\% \tag{8.31}$$

where μ_p and σ_p are the mean and standard deviation of uncertain parameters. Due to this condition, the estimated kinetic parameters do not significantly vary, so our reliability in these

parameters is higher. If the estimated parameters are far away from the worst case scenario the uncertain parameters are not updated. Therefore, I update these parameters if Eq. (8.31) is satisfied and if the estimated values are within the confidence interval.

8.5.1.4 State Estimation based on the Extended Kalman filter

In real systems only some measurements are available online, and usually each or none of the concentrations cannot be measured online. Therefore, state estimation of the system is necessary to use an effective NMPC in real systems. I must estimate the concentration of reagents and products and use it as a feedback in NMPC. The state estimation is necessary to identify uncertain kinetic parameters. The extended Kalman filter is a suitable algorithm to estimate states of non-linear systems [178], [179], so I implemented this algorithm. If there is a closed-form expression for the predicted state as a function of the previous state ($\hat{x}_k$), controls (u_k) and noise (w_k), the predicted state is calculated by Eq. (8.32).

$$\hat{x}_{k+1} = f(\hat{x}_k, u_k, w_k) \tag{8.32}$$

The measurement is the function of the state (x_k) and measurement noise (v_k).

$$z_k = h(x_k, v_k) \tag{8.33}$$

Typically for SBRs, the measurement vector (z_k) consists of temperature and level measurements, and the state estimation vector $\hat{x}_k$ consists of concentrations and temperatures.

To improve the state estimation accuracy, additional variables were implemented into the model of EKF, which are the reaction rate constants of the reactions (k_l). Estimating new state variables in EKF is not time consuming, and it does not increase the computational time. To solve this issue, I must know how the reaction rate parameters vary with time; since the reaction rate parameter varies with temperature ($k=k(T)$), the following equation is defined:

$$\frac{dk_l}{dt} = \frac{dk_l}{dT}\frac{dT}{dt} = k_{0,l} exp\left(-\frac{E_l}{RT}\right)\frac{E_l}{RT^2}\frac{dT}{dt} \tag{8.34}$$

8.5.2 Process model and analysis

This section presents the process model of the investigated fed-batch reactor from Williams-Otto process (see Section 3.3.2), where normal and abnormal operations that cause thermal runaway are presented. The process safety time of the system is also calculated to define the length of the prediction horizon.

8.5.2.1 Analysis of WOP in SBR

The behaviour of the investigated reactor system was analysed with no control system (i.e., the B reagent feed is constant), where the maximum process temperatures are analysed in functions of the dosing time and flow rate of cooling agent. The remaining applied parameters are shown in Section 3.3.2. As shown in Figure 8.13, poorly chosen operating parameters can develop thermal runaway. According to the model, the process temperature can exceed 900 K. The maximum temperature rapidly increases, and there is no interior point between normal process temperatures (under MAT) and runaway temperatures (>900 K). Although the optimal feeding trajectory can increase the productivity, increasing the flow rate of cooling agent enables an operation with less dosing time, as shown in Figure 8.13.

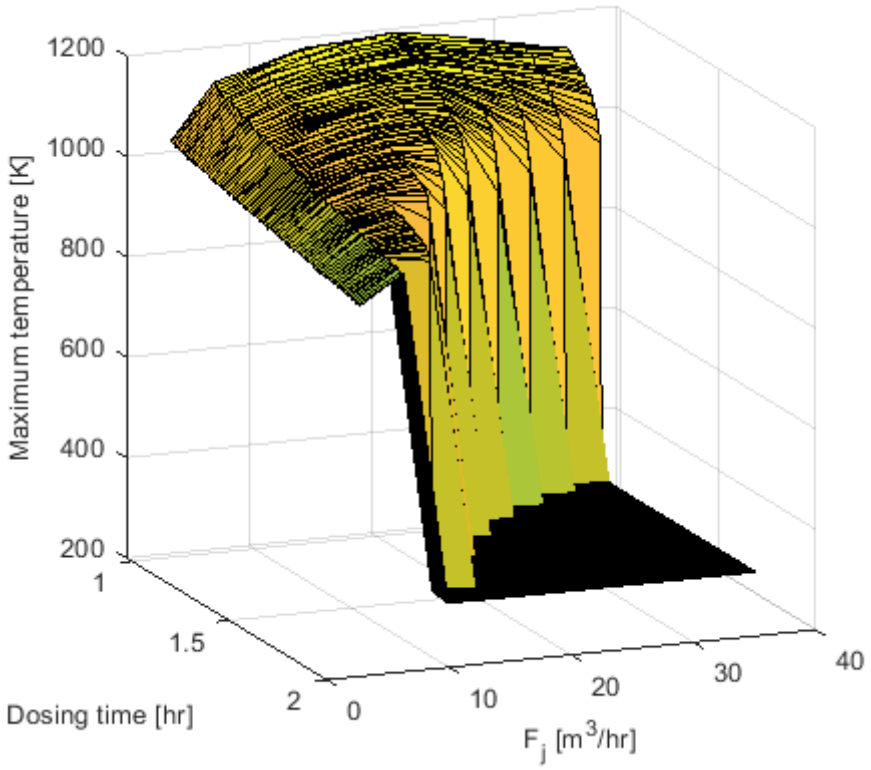

Figure 8.13 Reactor behaviour at different dosing times and cooling agent flow rates

Runaway states are distinguished by the MDC criterion, and the derived critical equation for the process is introduced in Eq. (8.35).

$$\sum_{l=1}^{nr} -\Delta H_{r,j} r_{j,T} V - \sum_{l=1}^{nr} \sum_{i=1}^{nc} r_{l,c_{li}} \leq \frac{\sum_{l=1}^{nr} -\Delta H_{r,l} r_l V}{T_R - T_j} \tag{8.35}$$

where *nr* is the number of reactions, *nc* is the number of reagents in the *l*-th reaction, r_T and r_c are the derivatives of the reaction rate with respect to temperature and concentration of reagents respectively.

To avoid thermal runaway uncertain kinetic parameters are quite significant, so I investigate how the parallel reactions dominate during the reactor operation. Figure 8.14 shows the reaction rates; the first reaction (R1) has the highest rate during the whole operation. To investigate the proposed control scheme, I only choose the kinetic parameters of the first reaction as uncertain. Because the first reaction is dominant, the uncertainty of this reaction has the highest effect on the behaviour of the reactor.

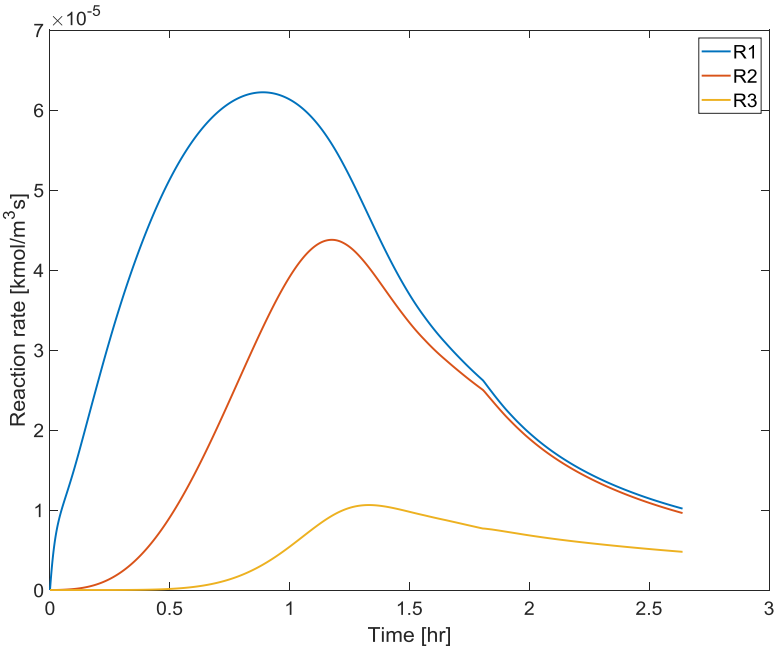

Figure 8.14 Reaction rates during an operation (Dosing time: 1.8 hr, Feed rate: 0.55 m^3/hr, Cooling flow rate: 36 m^3/hr)

8.5.2.2 Process safety time of the system

As presented in Section 8.2.1, the length of the prediction horizon can be defined based on the process safety time of the system. Maximum reactor temperatures and PSTs are investigated, as shown in Figure 8.15. MAT is reached at ~1.36 $\frac{\text{kmol}}{m^3}$ initial concentration, where the PST is 0.59 hours. In this case, the minimum length of the prediction horizon is 0.59 hours.

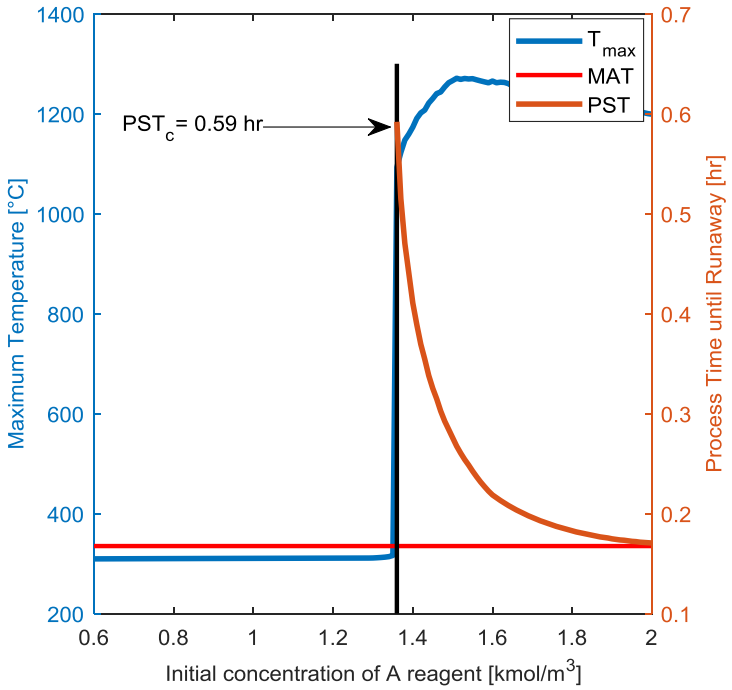

Figure 8.15 PST of the system according to the MDC criterion

8.5.2.3 State estimation of the investigated system

This section presents the efficiency of EKF on the investigated model system. First Eqs. (3.43)-(3.46) were applied to estimate the states of the system, and the measured variables are the reactor temperature, jacket temperature and reaction volume (the inflow rate is measured, which is the only parameter that increases the reaction volume). The results are generated next to 5% parameter deviation in pre-exponential factor and activation energy of the first reaction.

As shown in Figure 8.16a, the estimations of reagent concentration are quite poor, which can result in false runaway indication and thermal runaway of the system. If the first reaction rate parameter (k_1) is estimated with Eq. (8.34) the accuracy can be increased, as presented in Figure 8.16b. The state estimations are acceptable with this modification.

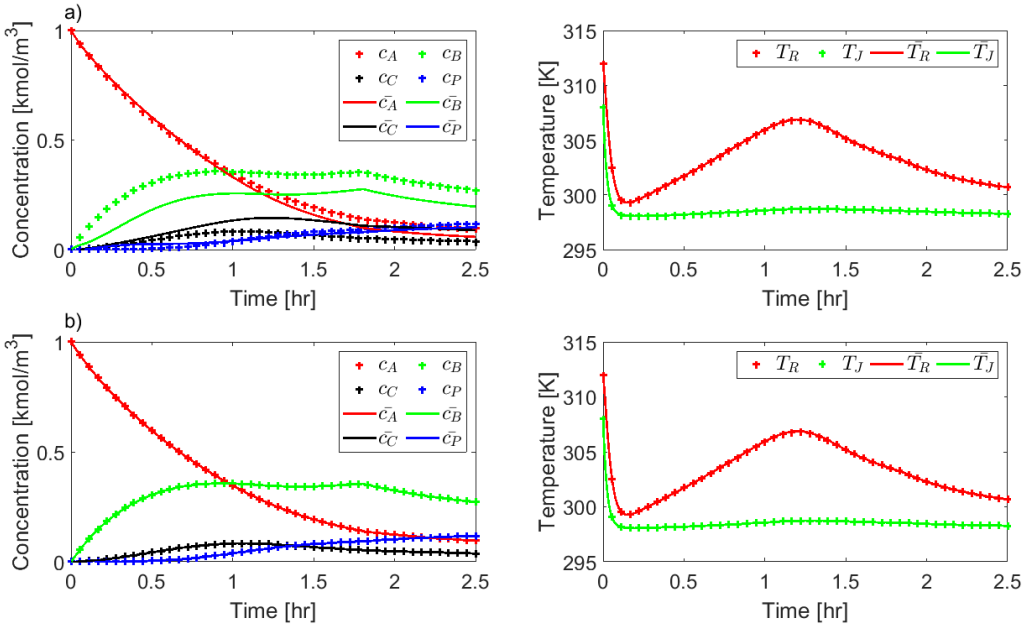

Figure 8.16 State estimation based on EKF

8.5.3 Results using the proposed NMPC based control structure

This section provides the results of NMPC with and without parameter uncertainty. The performance improvement due to parameter identification is presented. The optimization problem was solved by the interior-point algorithm, where the algorithm proceeds a moving horizon [180]. The applied parameters, which were heuristically selected, are summarized in Table 8.3.

Table 8.3 Parameters of NMPC

Sample time	T_0	100 s
Prediction horizon	t_{pred}	2200 s
Control horizon	t_{contr}	500 s
Weight factor in Eq. (8.16)	w_e	500
Weight factor in Eq. (8.16)	w_u	0.01
Weight factor in Eq. (8.16)	w_I	100

8.5.3.1 Results of the open-loop control without parameter uncertainty

NMPC is tested without any uncertain parameter and the results are shown in Figure 8.17. The reactor temperature stays far below MAT since the applied *MDC* criterion constraints the reactor operation that increases the process safety. At 2.5 hours the conversion of component

A is 76%, and the yield of P is 37%. The average computational time is 11.5 seconds per iterations in this case.

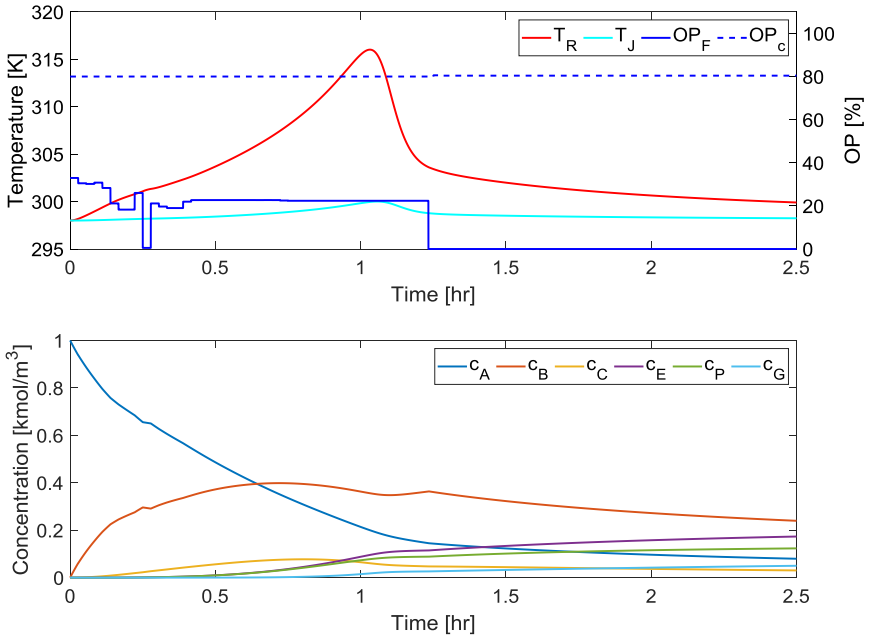

Figure 8.17 Reactor operation with nominal NMPC

8.5.3.2 Results of the open-loop control under parameter uncertainty

The effect of the parameter uncertainty was analysed using two different algorithms in Sections 4.2.1 and 4.2.2. In the first case, multi-stage NMPC was applied, in second case, the worst-case scenario was used to solve the optimization problem under parameter uncertainty. Kinetic parameters of the first reaction ($k_{0,1}$, E_1) were chosen as uncertain, where the confidence interval is ±5%. Section 4.2.3 provides the results of the optimization problem when the uncertain parameters are updated iteratively.

The multi-stage NMPC algorithm was tested where the uncertain kinetic parameters were changed by 5%. Two uncertain parameters lead to nine scenarios. As shown in Figure 8.18, the feed rates are maintained at low values due to the uncertain kinetic parameters. The reason is that the constraints must be satisfied in each scenario, so the development of thermal runaway is avoided in each scenario. Therefore, the results with Multi-Stage NMPC are conservative compared to the nominal solution (Figure 8.17). At 2.5 hours the conversion of component A is 15.3%, and the yield of P is 2.4%. The average computation time is 660 seconds per iterations, so real-time optimization is not feasible with the Multi-Stage NMPC algorithm.

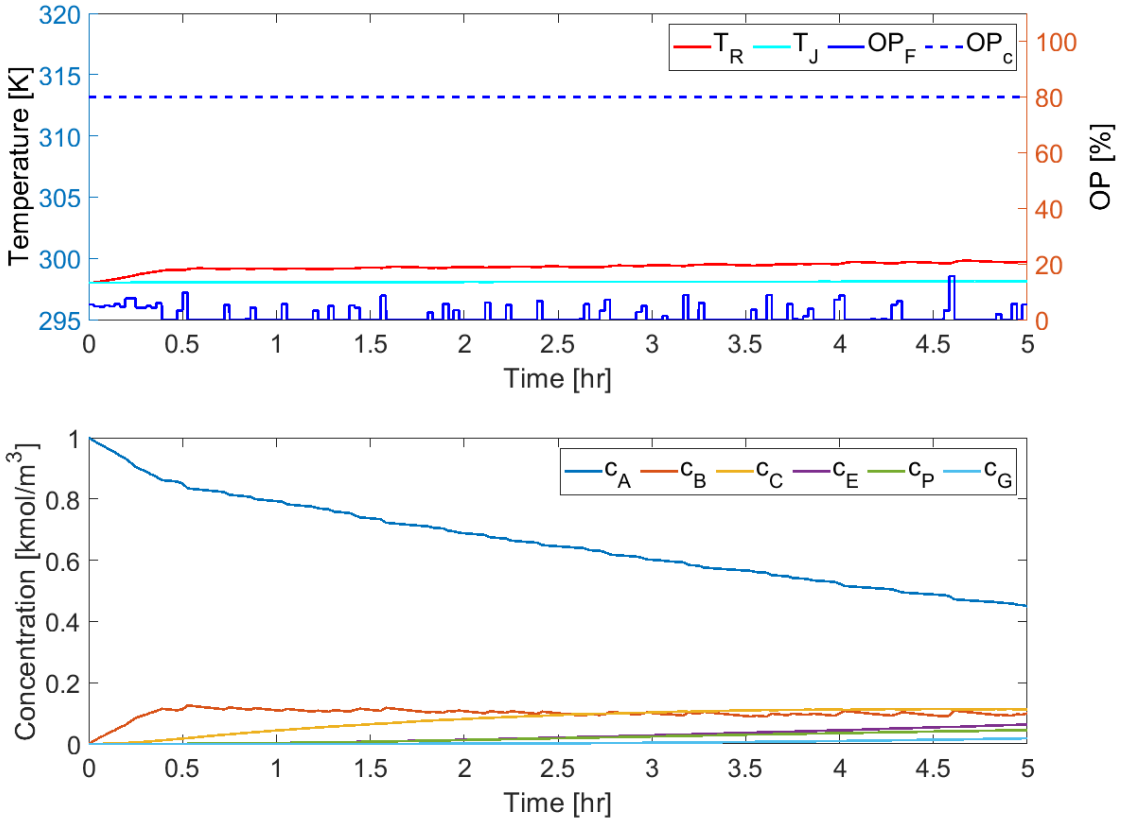

Figure 8.18 Result of MS-NMPC with nominal kinetic parameters

The worst case is that the real reaction rate is higher than expected, so in the worst-case scenario, the uncertain pre-exponential factor increases by 5% ($k_{0,1}$+5%), and the uncertain activation energy decreases by 5% (E_1-5%). The NMPC results are shown in Figure 8.19, which naturally is a conservative result. The conversion at 2.5 hours is 45%, and the yield of product *P* is 16%. In the worst-case scenario, the average computation time is 17.2 seconds per iterations, so real-time optimization is feasible with this algorithm.

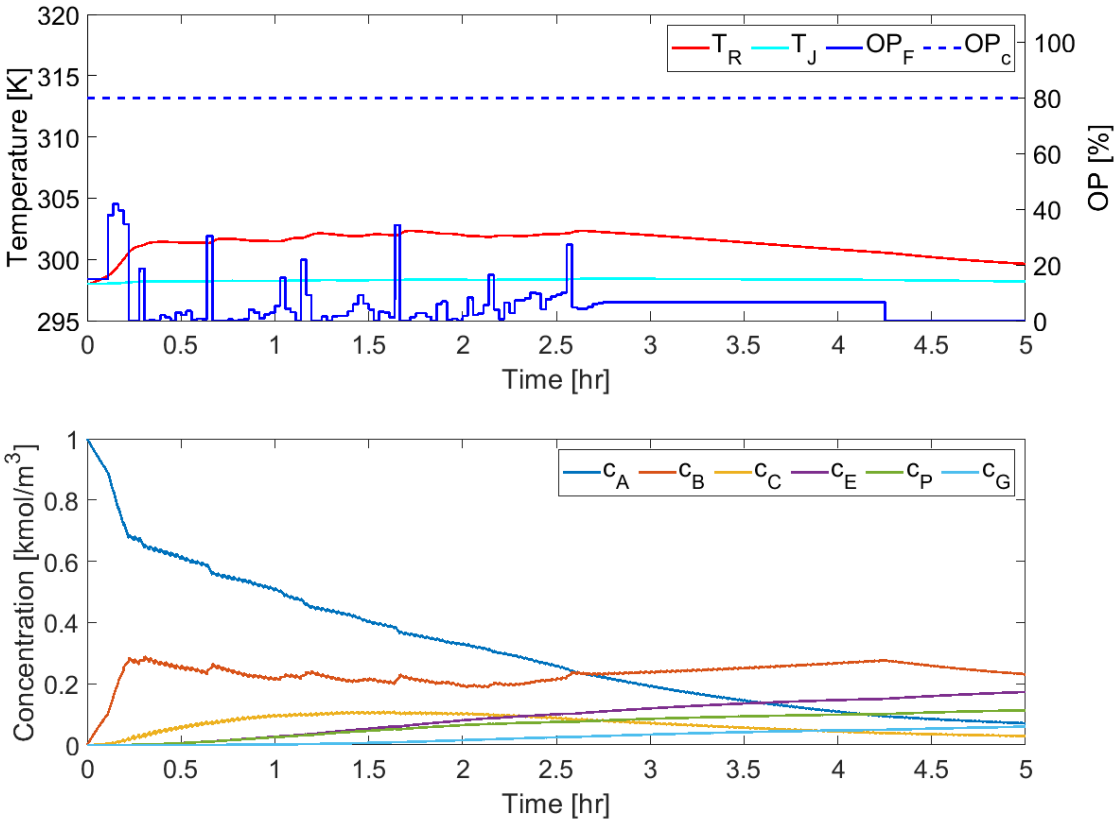

Figure 8.19 Results of NMPC with respect to the worst case

The results of the proposed control structure, which was initialized from the worst case, is presented in Figure 8.20. With updating uncertain kinetic parameters, the reactor temperature control becomes less conservative and improves the productivity of the operation compared to the worst-case scenario.

At 2.5 hours the conversion of component A is 74%, and the yield of P is 36%. Figure 8.21 shows the estimated uncertain kinetic parameters; based on the update criterion (Eq. 19 and estimated values are within the worst case interval) kinetic parameters are first overwritten at 0.61 hours. The average computation time is 12.6 seconds per iterations, hence the real-time optimization is feasible with this algorithm.

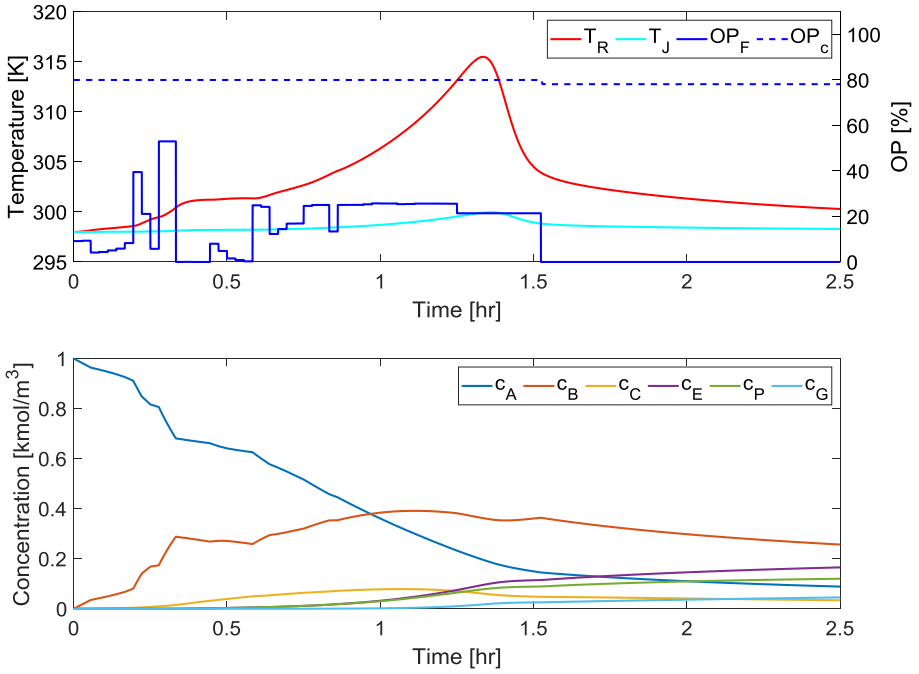

Figure 8.20 Results of NMPC initialized from the worst-case scenario with updating kinetic parameters

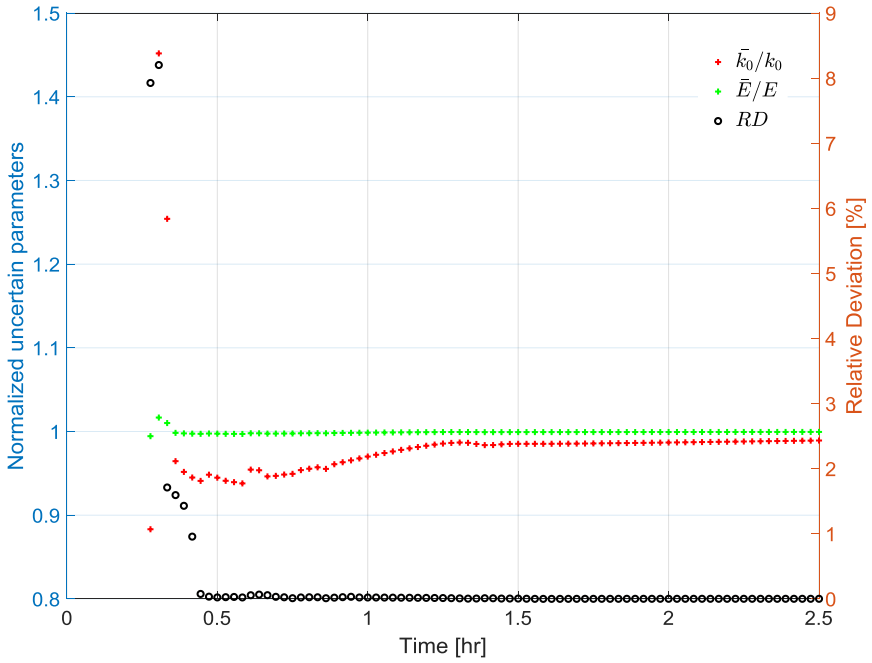

Figure 8.21 Result of the parameter fitness

Figure 8.21 shows how the values of identified kinetic parameters go to the real parameters as more information and measurement is available about the system. Low relative deviations (<1%) indicate that the identified kinetic parameters only slightly change, so I can say that the identified kinetic parameters are near the real system, and I can update the uncertain parameters.

8.5.4 Conclusion

A framework to keep SBRs with exothermic reactions under control in the whole operation using a nonlinear model predictive control approach is proposed. The framework was tested on the semi-batch version of the Williams-Otto process including three reactions. The proposed control approach can also handle the uncertain kinetic parameters of reactions. The parameters of the first dominant reaction are considered the source of uncertainty in the model. The proposed framework consists of NMPC, EKF and an identification step. The Modified Dynamic Condition was implemented into NMPC as an additional safety constraint, and the reactor temperature cannot exceed MAT. EKF is necessary to estimate the state variables of the reactor system and reaction rate constants. Kinetic parameters can be identified with least squares methods based on the estimated reaction constants after some formal transformation.

I have compared the multi-stage NMPC solved by the progressive hedging algorithm and worst-case scenario. Each resulted in a conservative solution, but the worst-case scenario NMPC has lower computation time. In the case of MS-NMPC, the size of the optimization problem increases exponentially with the length of the robust horizon and with the uncertain parameters. Therefore, I have decided to extend the worst-case scenario NMPC with the state estimation and identification algorithms. The results show that the proposed approach can handle uncertain kinetic parameters, and can be applied in real reactor systems in which reactor runaway can develop to ensure the optimal production.

9 Summary and future work

As we have seen the topic of reactor runaway never should be off the table. Despite of the vast knowledge about the phenomenon of thermal runaway the last accident happened in the recent past, in 2012, which was caused by a runaway reaction. In this accident more than 30 people injured and a worker died… This gives me the motivation for studying the thermal runaway. I just hope I left a footprint on the field of thermal runaway with my work.

I summarized the knowledge until this day about this phenomenon, which is presented in Section 2. I think if anyone in the future would like to work on this field, this review is a great introduction for further research. The most important results (at least for me) are the two new thermal runaway criteria, called Modified Slope and Dynamic Condition (MSC, MDC). The presented runaway criteria, mainly MDC performs very well, and it can be easily applied in different tasks (e.g. reactor operation design or early warning). I used MDC criterion in the feeding trajectory optimization of a fed-batch reactor (2-octanone production), and I also tried its performance in an online task, which in I used it as a constraint in a control scheme for safe operation of semi-batch reactors.

These general runaway criteria do not consider the system specifications, like Maximum Allowable Temperature; hence they may indicate runaway when there is no real hazard situation, and they may do not indicate runaway when they really should. I used genetic programming for critical equation construction which considers the system specifications.

Finally, I proposed a control scheme for the optimal operation of semi-batch reactors. This control scheme consists of a NMPC, a state estimation and an identification module. The method was tested only in simulation environment, and it definitely should be tried out as a next step in laboratory-sized equipment.

Our future investigation will be the steps to reach the possibility of industrial application. As a first step I would like to implement the proposed control approach into a lab-scale reactor system. For this purpose we must investigate that how the uncertainty of a kinetic model of the reaction system can be determined and reduced. Lower width of uncertain parameter intervals can result in more efficient and robust controller. Another interesting topic is the scale up of the reactor system, on this field I would like to do further researches. Later I would like to investigate and compare more types of control structure to handle potentially

runaway reactions. For this it is necessary to investigate how we can forecast and avoid thermal runaway in case of different level of uncertainty.

Another research topic is about how to moderate the consequences of a runaway reaction if it cannot be handled with the reactor control system anymore. It includes the investigation of relation between the indication time and the process safety time, and it also includes the investigation of dynamics of different intervention systems.

Theses

Thesis #1. I developed two new thermal runaway criteria whose performances are comparable with the other runaway criteria from literature. The reliability of Modified Dynamic Condition is the highest in the investigated case studies; moreover, its indication time is in midfield.

- I developed the Modified Slope and Dynamic Condition criteria, which were derived from the systematic investigation of earlier presented runaway criteria.
- I suggested using the confusion matrix for the reliability analysis of runaway criteria, where a reactor operation is considered as runaway if more than the half of the investigated runaway criteria indicates its development.
- All the thermal runaway criteria were analysed on general case studies with practical parameter values.

Related publications: 1

Thesis #2. I applied genetic programming-based algorithm to develop system-specific critical equations for the proper indication of reactor runaway.

- Since thermal runaway criteria do not consider the system specific properties, I suggested to identify critical equations which meets the expected requirements. It means that the runaway criteria do not indicate thermal runaway if the maximum process temperature does not exceed the MAT value.
- I suggested to identify critical equations which includes the consideration of Maximum Allowable Temperature in the investigated system.
- I identified new critical equations for batch and continuous-stirred tank reactors to indicate runaway with the highest reliability and as early as it is possible.
- I evaluated the performance of all the investigated criteria and showed that the newly identified criteria gave the best performance.

Related publications: 2, 8, 9

Thesis #3. I determined the conservativeness order of the most common runaway criteria.

- I applied runaway criteria as a non-linear constraint in feeding trajectory optimization task of a fed-batch reactor.
- I evaluated the conservativeness of runaway criteria based on the conversion and selectivity of the reaction system.

Related publications: 1, 3

Thesis #4. I suggested a control scheme for the operation of semi-batch reactors carrying out highly exothermic reactions by Model Predictive Controller with implemented runaway criterion.

- I substantiated that a semi-batch reactor can be started with lower process temperature with the proposed control scheme, and it results in lower energy consumption.
- I developed a method based on the worst-case scenario and process safety time analysis to define the minimum length of prediction horizon.

Related publications: 4

Thesis #5. I extended the proposed control scheme proposed in Thesis #4, to handle model parameter uncertainty.

- I proved that the worst-case scenario with iteratively updating uncertain parameters is an appropriate way to handle model uncertainty in runaway operation with exothermic reactions.
- I verified that the extended Kalman-filter with the proposed further extension of uncertain parameters increase the reliability of state estimation.
- I confirmed that the proposed control scheme is applicable for the control of semi-batch reactors.

Related publications: 5, 7

Publications related to theses

Articles in international journals

1. A. Kummer and T. Varga, “Completion of thermal runaway criteria: Two new criteria to define runaway limits” *Chemical Engineering Science*, vol. 196, pp. 277–290, Mar. 2019, doi: 10.1016/j.ces.2018.11.008.
   Scimago Journal Ranking: Q1, Impact factor: 3.871

2. A. Kummer, T. Varga, and J. Abonyi, “Genetic programming-based development of thermal runaway criteria” *Computers & Chemical Engineering*, p. 106582, Sep. 2019, doi: 10.1016/j.compchemeng.2019.106582.
   Scimago Journal Ranking: Q1, Impact factor: 4.000
3. A. Kummer and T. Varga, “Feeding trajectory optimization in fed-batch reactor with highly exothermic reactions” *Computers & Chemical Engineering*, vol. 98, pp. 1–11, Mar. 2017, doi: 10.1016/j.compchemeng.2016.12.008.
   Scimago Journal Ranking: Q1, Impact factor: 3.334

4. A. Kummer, T. Varga, and L. Nagy, “Semi-batch reactor control with NMPC avoiding thermal runaway” *Computers & Chemical Engineering*, vol. 134, p. 106694, Mar. 2020, doi: 10.1016/j.compchemeng.2019.106694.
   Scimago Journal Ranking: Q1, Impact factor: 4.000

5. A. Kummer, L. Nagy, and T. Varga, “NMPC-based control scheme for a semi-batch reactor under parameter uncertainty” *Computers & Chemical Engineering*, p. 106998, Jun. 2020, doi: 10.1016/j.compchemeng.2020.106998.
   Scimago Journal Ranking: Q1, Impact factor: 4.000
6. A. Kummer and T. Varga, “What do we know about thermal runaway? – A review”, *Journal of Process Safety and Environmental Protection*, vol. 147, pp. 460-476, Mar. 2021, doi: 10.1016/j.psep.2020.09.059.
   Scimago Journal Ranking: Q1, Impact factor: 4.966

Articles in conference publications

7. A. Kummer, L. Nagy, T. Varga, „NMPC based temperature control in fed-batch reactor to avoid thermal runaway“, *Computer Aided Chemical Engineering*, 2020, doi: 10.1016/B978-0-12-823377-1.50182-8

Conference abstracts

8. A. Kummer, T. Varga, J. Abonyi, “Genetic Programming based identification of reactor runaway criteria”, Műszaki Kémiai Napok 2019: Chemical Engineering Conference 2019, Veszprém, Hungary, A. Balogh, M. Klein, Eds.; University of Pannonia, pp. 58
9. A. Kummer, T. Varga, J. Abonyi, “Reaktorelfutási kritérium identifikálása genetikus programozással”, Pannon Tudományos Nap, 2019.10.16, Nagykanizsa

Publications not related to theses

Articles in international journals

10. A. Kummer and T. Varga, “Process simulator assisted framework to support process safety analysis” *Journal of Loss Prevention in the Process Industries*, vol. 58, pp. 22–29, Mar. 2019, doi: 10.1016/j.jlp.2019.01.007.
    Scimago Journal Ranking: Q1, Impact factor: 2.473

11. A. Kummer and T. Varga, “Dynamic process simulator assisted optimization of operating point transition” *Chemical Engineering Transactions*, pp. 565–570, 2018008, doi: 10.3303/CET1870095.
    Scimago Journal Ranking: Q3

Articles in conference publications

12. A. Kummer and T. Varga, “Dynamic process simulation based process malfunction analysis” in *Computer Aided Chemical Engineering*, vol. 43, Elsevier, 2018, pp. 1147–1152.
13. A. Kummer, T. Varga, , “Development of dynamic process simulator: Phenol production from cumene”, Műszaki Kémiai Napok 2017, Chemical Engineering Conference 2017, Veszprém, Hungary, J. Abonyi, A. Balogh, M. Klein, Eds.; University of Pannonia, pp. 17-22

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Never forget: “Time is the most valuable thing a man can spend”

Theophrasztosz