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What do we know already about reactor runaway? – A review

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A R T I C L E I N F O

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A B S T R A C T

Nowadays, reactor runaway is still a crucial phenomen from the safety viewpoint. About 120 scientific journal articles are published every year in the last decade in which thermal runaway is a keyword. The possible cause and consequences of reactor runaway are adressed where the worst case is the explosion of the reactor. Prevention steps to avoid the development of thermal runaway include the appropriate design of the reactor, the operation strategy and an early warning detection system. The available assessment methods for thermal risk analysis are addressed in detail. Reactor runaway criteria can indicate early the thermal runaway, which criteria are addressed in this review in detail under three classes: geometry-, sensitivity-, and stability-based runaway criteria. Operation strategy of semi-batch reactors can be designed by calculating Westerterp-diagram whose evolution is cleary presented. Significant works on the field of the reactor design, operation and reactor safety are collected and evaluated. Finally possible further research areas are suggested to improve our knowledge about thermal safety, such as investigating parameter uncertainty in runaway indication or optimize the safety actions to moderate the consequences of runaway.

Contents

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Nomenclature

A	heat transfer area
C	concentration
c_p	heat capacity
Da	Damköhler number
E	activation energy
Ex	exothermicity number
I	penalty indices
ITHI	inherent thermal runaway hazard index
MF	material factor
MTSR	Maximum Temperature of Synthesis Reaction
q_{gen}	generated heat
q_{rem}	removed heat
P	pressure
Pr	probability
r	reaction rate
R	gas constant
RI	risk index
Ry	reactivity number
S	severity
t_{dos}	dosing time
TMR_{ad}	Time to Maximum Rate under adiabatic conditions
T_c	critical or cooling temperature
T_p; T	process temperature
T_{ta}	target temperature
T_w	wall temperature
U	overall heat transfer coefficient
V	volume
Wt	Westerterp number
X_{ac}	accumulated reagent
ΔT_{ad}	adiabatic temperature rise
ΔH_r	reaction heat
α	$UA/(V\rho c_p)$
β	$\Delta H_r/(\rho c_p)$
γ	inetic parameter
δ	E/R
ψ	Semenov number
ε	relative volume increase
ρ	density
J	Jacobian matrix
I	identity matrix

1. Introduction

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 physic-chemical properties of every component which occurs or can occur in the system (Vernières-Hassimi et al., 2017). 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 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 (Knegtering and Pasman, 2009).

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 operation 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 reactor (Stoessel, 2008).

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 (Pasman et al., 1992). In worst case it leads to a Boiling Liquid Expanding Vapor Explosion (BLEVE). If the pressure increasing rate is higher than the discharge rate, the reactor will explode due to the high pressure (Liu et al., 2018a). In less catastrophic cases prevention of development of thermal runaway should be avoided because so-called hot-spots cause early deactivation of catalyst and/or quality drop. Hence, the determination of stable operating regimes of a reactor is a crucial step in process design and operation (Varga, 2009). From 1995 to 2004 12 % of BLEVE type accidents occurred due to runaway reactions, also from 1926 to 2004 6 BLEVE type accident occurred led to 19 death and 171 injured people (Abbasi and Abbasi, 2007).

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 (Balasubramanian and Louvar, 2002), and reactor runaway was responsible for 25 % of the accidents in French industry (Dakkoune et al., 2018). 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

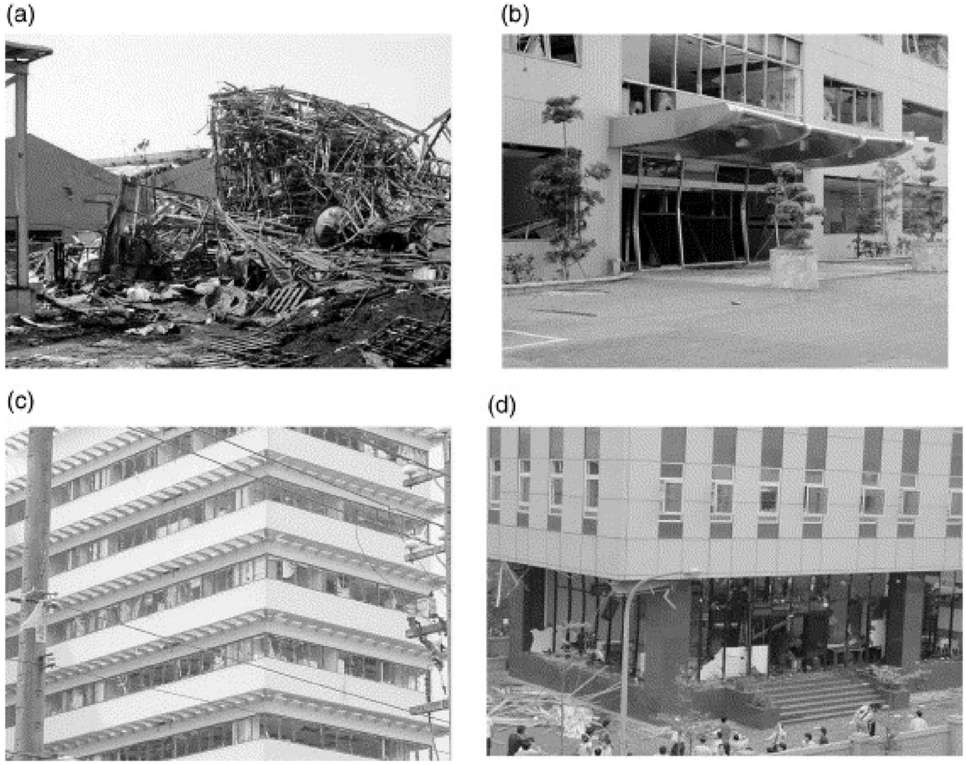

Fig. 1. Explosion of Fu-Kao chemical plant and the damaged nearby buildings. The shock wave destroyed many windows within half-a-kilometer (Kao and Hu, 2002).

atmosphere through a rupture disk poisoning almost 37,000 people (Cardillo and Girelli, 1981; Fabiano et al., 2017; Jain et al., 2017). 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 (Cates, 1992), (Mannan, 2014). In 1996 a runaway reaction occurred in a batch reactor creating high pressure that led to rupture of the vessel (Partington and Waldram, 2002). In 1997, Ohio, an explosion occurred in a resins production unit, where one worker died and four employees injured (United States, 1999). In 1998, in New Jersey a violent explosion and fire occurred due to a reactor runaway injuring nine employees (Gyenes and Carson, 2017). 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 destroyed the nearby plants and damaged the nearby buildings, which is shown in Fig. 1 (Kao and Hu, 2002).

In January 2006 an acrylic polymer batch reactor exploded due to this phenomenon (Gyenes and Carson, 2017). In 2007 a reactor exploded and destroyed in T2 Laboratories in Florida because of a thermal runaway reaction lead to the death of four employees (Hall, 2010). In 2008, USA, at Bayer Cropscience pesticide manufacturing unit a thermal runaway caused an explosion which demolished the process unit leading to two lethal damage and eight people inhaled toxic chemicals (Abbasi et al., 2010). Hydrogen peroxide is a widely used chemical, but the exothermic decomposition of this chemical caused some fire and explosion accidents in the recent past (Wu and Qian, 2018). In 2012, an explosion occurred in a chemical plant in Japan injuring 36 person and killing one person due to the runaway polymerization of acrylic acid (Fujita et al., 2019).

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're doomed to repeat it” (the quote is from Jesse Ventura). The first aspect is always the safety, which can be realized through studying the phenomenon of thermal runaway in detail. Our 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. This article provides the main contributions which should be known by every process engineer. 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. Based on the literature review we highlight four future research directions which is about to investigate the impact of parameter uncertainty on runaway indication, handling parameter uncertainty in detection of runaway during operation, presenting in detail the design phases with laboratory and pilot-plant experiments, and performing computational fluid dynamics (CFD) simulations for better understanding of the causes and consequences.

The review was made to give a comprehensive picture about the phenomenon of thermal runaway, what the main causes and consequences of runaway are, and how it can be prevented. The emphasis is clearly on the development and application of thermal runaway criteria including geometry-, stability- and sensitivity based criteria, and we also discuss the topic of safety boundary diagrams from Westerterp.

The roadmap is as follows: Section 2 provides the root causes and consequences of thermal runaway. Section 3 informs the reader about the basic requirements for the prevention of reactor runaway. In Section 4 the reader can get information about how to evaluate the thermal risks of a system. Section 5 presents the stability-, geometric and sensitivity based runaway criteria, and a simple model to investigate runaway criteria is presented. Section 6 gives information about the Safety Boundary Diagrams and some insight about how to apply these. Section 7 provides information about possible safety actions to moderate the consequences of reactor runaway. In Section 8 some application examples is highlighted from the literature with runaway related researches investigating the main problems (reactor and operation design, reactor control, mitigation systems). Section 9 provides insight into the possible future directions of reactor runaway related research.

2. 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 (Barton and Nolan, 1991; Nolan and Barton, 1987).

- 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 (Saada et al., 2015). Different case studies about reactor runaway accidents with causes and consequences is shown in (Gyenes and Carson, 2017; Etchells, 1997; Pasquet, 2017; Ho et al., 1998).

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 Fig. 2 (Liu et al., 2018b).

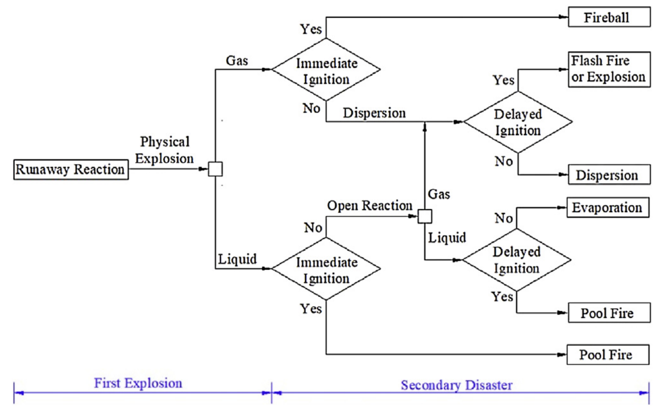

Fig. 2. Flowchart of runaway accident sequences (Liu et al., 2018b).

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 (Liu et al., 2018b). The size of endangered area can be easily estimated based on CFD simulations (Liu et al., 2018a), (Tauseef et al., 2011; Chen et al., 2019).

3. Prevention of reactor runaway

Prevention of reactor runaway begins in the design phase. As it is shown in Section 2 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 strateges toward ISD (Fei et al., 2018):

- 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 ruanway 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 (Varga, 2009). 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 highle exothermic reactions in (Varga and Abonyi, 2010)
- Time of no Return: after this time it is impossible to cool the reactor (Stoessel, 2008).

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) (Westerterp and Molga, 2006).

4. 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 (Stoessel (2008). The representation of worst-case scenario as a cooling failure were introduced by Gygax (1988), and he made a scenario for thermal assessment, which can be seen in Fig. 3.

In (Nanchen et al., 2009) a good description of Fig. 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.

$$MTSR = T_p + X_{ac}\Delta T_{ad,rx} \quad (1)$$

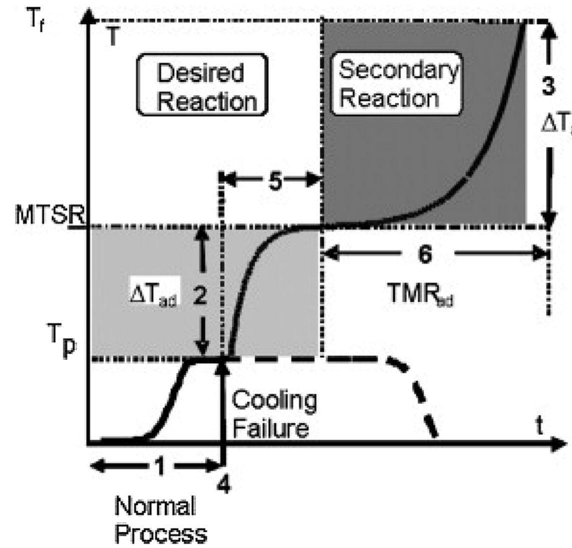

Fig. 3. Runaway scenario, where numbers represent the six key questions (Stoessel, 2009).

Table 1
Assessment criteria for the severity of a runaway reaction (Stoessel, 2009).

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

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

$$TMR_{ad} = \frac{c'_p RT^2}{q_{gen} E} \quad (2)$$

Gygax formulated six key questions which helps for the assessment of thermal risk, which were refined for easier understanding (Nanchen et al., 2009). 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 1 and in Table 2. For defining the probability of runaway an extended Table can be found in (Stoessel, 2009).

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 Fig. 4 (Stoessel et al., 1997). The four specific temperature levels are the following:

- The process temperature (T_p): the initial temperature in the cooling failure;

Table 2
Assessment criteria for the probability of loss of control of a runaway reaction (Stoessel, 2009).

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

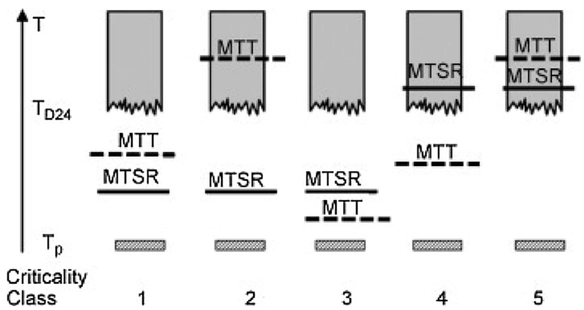

Fig. 4. Criticality classes of scenario (Stoessel, 2009).

- Maximum temperature of synthesis reaction (MTSR): it depends on the defree of accumulation of unconverted reactants;
- Temperature at which TMR_{ad} is 24 h (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.

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 (Stoessel, 2009).

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) (Juncheng et al., 2020).

$$ITHI = MF \cdot RI \tag{3}$$

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

$$RI = S \cdot Pr \tag{4}$$

Material factor (MF) is calculated based on the initial reaction temperature (T_{onset}), and Max power density (MPD), where MF is limited in (Vernières-Hassimi et al., 2017; Knegtering and Pasman, 2009). MPD is the function of heat of decomposition and the maximum reaction rate.

$$MF = 1 + \frac{I_{T_{onset}} \cdot I_{MPD}}{16} \tag{5}$$

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 (Juncheng et al., 2020).

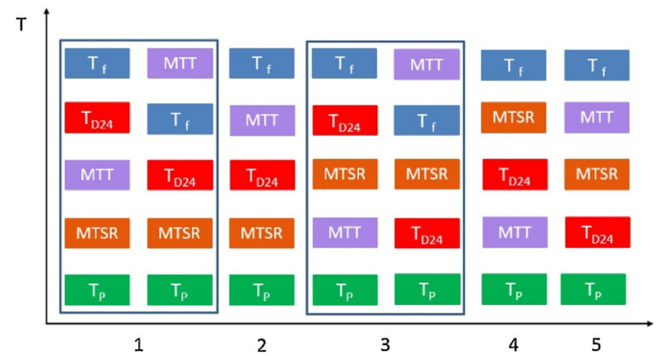

Fig. 5. Modified Stoessel criticality diagram (Jiang et al., 2019).

Jiang et al. developed a modified Stoessel criticality diagram to consider the final temperature (T_f) of the process. Their thought is based on that if the final temperature does not exceed the technical limit (MTT) then the technical safeguard can reduce the accident risk. Based on it they extended the criticality classes 1 and 3, criticality classes 2, 4 and 5 remained the same as Stoessel presented (Jiang et al., 2019). Fig. 5 presents the modified Stoessel criticality diagram.

In the first case of criticality class 1 the reaction temperature will not reach the technical limit and it will not cause a secondary reaction. MTT can be reached only if the reaction mixture is left in the heat accumulation for a long time. In the second case if the reaction mixture stays in the heat accumulation for a long time, it may induce a secondary reaction, but the final temperature cannot exceed the technical limit.

In the first case of criticality class 3 the technical limit is reached but a secondary reaction is not triggered. In the second case the secondary reaction is triggered, but the final temperature does not exceed the technical limit.

Nomen et al. developed an opeative tool for the risk assessment (Check cards for runaway (CCR)), which follows a factor-based strategy. Five factors are defined to assess a thermal runaway, which are: mischarging chemicals, autocatalytic reactions, segregation, accumulation, and temperature hazard (Nomen et al., 2004).

5. 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 designing and operation of chemical reactors (Jiang et al., 2011). A brief history about the reactor runaway criteria until 2006 can be found in (Shouman, 2006).

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 5.2–5.4. The runaway criteria and the year of their first publication are presented in Table 3. Section 5.1 presents a simple mathematical model of a tubular reactor (or batch reactor), on which the derivation of runaway criteria can be practiced easily.

5.1. 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

Table 3
Thermal runaway criteria developments over time.

Criterion	Year of publication	Reference
Semenov-criterion	1928	Semenoff (1928), Semenov (1940)
"Practical Design" criterion	1938	Berty (1999)
van Heerden criterion	1953	van Heerden (1953)
Gilless-Hoffmann criterion	1961	Berty (1999), Gilles and Hofmann (1961)
Thomas and Bowes criterion	1961	Thomas (1961), Varma et al. (2005)
Adler and Enig criterion	1964	Adler and Enig (1964)
van Welsenaere and Froment criterion	1970	van Welsenaere and Froment (1970)
Morbidelli-Varma criterion	1987	Morbidelli and Varma (1988)
Adiabatic criterion	1988	Gygax (1988)
Hopf-bifurcation analysis	1989	Colantonio et al. (1989)
Vajda-Rabitz criterion	1992	Vajda and Rabitz (1992)
Strozzi-Zaldivar criterion	2003	Zaldívar et al. (2003)
Lyapunov-stability	2006	Szeifert et al. (2006)
Adiabatic criterion based on Strozzi-Zaldivar criterion	2016	Guo et al. (2016)
Kähm-Vassiliadis criterion	2018	Kähm and Vassiliadis (2018a)
Modified Slope Condition	2019	Kummer and Varga (2019a)
Modified Dynamic Condition	2019	Kummer and Varga (2019a)

the following differential equations can be written to describe the dynamical behaviour:

$$\frac{dc}{d\tau} = -r \tag{6}$$

$$\frac{dT}{d\tau} = q_{gen} - q_{rem} \tag{7}$$

$$q_{gen} = \beta r \tag{8}$$

$$q_{rem} = \alpha (T - T_W) \tag{9}$$

Where

$$r = \exp\left(\gamma - \frac{E}{RT}\right) c \tag{10}$$

$$\alpha = 5\frac{l}{h},\ \beta = 180\frac{m^3 K}{kmol},\ \gamma = 20,\ \frac{E}{R} = 6600K,\ c_0 = 1\frac{kmol}{m^3},\quad T_0 = 300\,K \tag{11}$$

Fig. 5 shows how the presented model (Eqs. 6–11) is sensitive to the wall temperature, and it presents the development of thermal runaway.

5.2. 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.

5.2.1. 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 (Stoessel, 2008; Semenoff, 1928; Semenov, 1940). 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.

Fig. 7 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. Three essential points draw attention in Semenov-diagram, which are marked as A, B and C, and the belonging 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 continuously higher than the removed heat. *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 heat 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 Eqs. 12–15 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.

$$q_{gen} = q_{rem} \tag{12}$$

$$\beta r = \alpha (T_c - T_W) \tag{13}$$

$$\frac{dq_{gen}}{dT} = \frac{dq_{rem}}{dT} \tag{14}$$

$$\beta r_T = \alpha \tag{15}$$

Dividing the 13 and 15. equations the following critical equation is the result:

$$\frac{r}{r_T} = \frac{RT_c^2}{E} = (T_c - T_W) = \Delta T_c \tag{16}$$

Eq. 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.

$$(T - T_W) \leq \frac{RT_c^2}{E} \tag{17}$$

From Eq. 17 the critical temperature can be calculated by solving the quadratic equation.

$$T_c = \frac{1 - \sqrt{1 - \frac{4RT_W}{E}}}{\frac{2R}{E}} \cong \frac{2\left(\frac{RT_W}{E}\right) + 2\left(\frac{RT_W}{E}\right)^2 + 4\left(\frac{RT_W}{E}\right)^3 \ldots}{\frac{2R}{E}} \tag{18}$$

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

$$(T - T_W) \leq \frac{RT_W^2}{E} \tag{19}$$

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

$$\psi = \frac{(-\Delta H_r)\,kc^n}{UA}\frac{E}{RT^2} \tag{20}$$

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

$$\psi < \frac{1}{e} = \psi_c \tag{21}$$

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.

5.2.2. Van Heerden and "practical design" criterion

Berty clearly presented the theory behind Van Heerden criterion, which is often called as "Slope Condition" (Berty, 1999; van Heerden, 1953). 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:

$$\frac{dq_{gen}}{dT} \le \frac{dq_{rem}}{dT} \tag{22}$$

The area of sensitive domain was defined by Van Heerden in 1953 (van Heerden, 1953). Perkins assumed zero order kinetics to define a safe boundary. Considering Eqs. 22 and 12 the following criterion can be defined:

$$T - T_w \le \frac{RT^2}{E} \tag{23}$$

Bashir et al. derived the same criterion investigating the inflection point in a geometric plane (Bashir et al., 1992), stating that the calculated maximum temperature in Eq. 23 is the limiting value for runaway at the inflection point.

5.2.3. 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 (Berty, 1999; Gilles and Hofmann, 1961).

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_c + \left.\frac{\partial m}{\partial c}\right|_T \le \frac{dq_{rem}}{dT} \tag{24}$$

where m is the material balance function.

5.2.4. Lyapunov-stability in geometric- and phase-plane

Szeifert et al. proposed to use Lyapunov's indirect method to forecast reactor runaway (Szeifert et al., 2006; Sastry, 1999). 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.

$$\boldsymbol{J} = \frac{\partial f}{\partial x} \tag{25}$$

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 (López-García and Schweitzer, 2008). 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 (Vajda and Rabitz, 1992).

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 (Colantonio et al., 1989; Ball and Gray, 2013; Gómez García et al., 2016; McAuley et al., 1995; Kim et al., 1991; Ball and Gray, 1995; Ball, 2011).

5.2.5. 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 (Strozzi et al., 1999). 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 (BR, SBR, CSTR) and for multiple reactions, also with and without of a control system (Zaldívar et al., 2003).

Strozzi and Zaldivar provided the following derivation of their runaway criterion (Strozzi et al., 1999). 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 (Arnol'd, 2006).

$$\frac{dV(t)}{dt} = \int div\,F\,[x(t)]\,dx_1(t)\ldots dx_d(t) \tag{26}$$

where the divergence of the system can be calculated as

$$div\,F\,[x(t)] = \frac{\partial F_1[x(t)]}{\partial x_1(t)} + \frac{\partial F_2[x(t)]}{\partial x_2(t)} + \cdots + \frac{\partial F_d[x(t)]}{\partial x_d(t)} \tag{27}$$

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

$$\frac{dV(t)}{dt} = V(t)\,div\,F\,[x(t)] \tag{28}$$

Integrating Eq. 28 the initial phase-space volume V(0) changes with time as

$$V(t) = V(0)\,exp\left(\int_0^t div\,F\,[x(t)]\,d\tau\right) \tag{29}$$

Hence the rate of change 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 is 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:

$$div\,F\left[x\left(t\right)\right] \leq 0 \tag{30}$$

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 (Copelli et al., 2014), (Kahm, 2019).

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 (Strozzi et al., 1994; Strozzi and Zaldívar, 1994). 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 (Strozzi et al., 1999). 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 (Kähm and Vassiliadis, 2018a; Kähm and Vassiliadis, 2018b; Kähm and Vassiliadis, 2018c).

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) (Bosch et al., 2004a; Bosch et al., 2004b). Although there is several methods of reconstruction, but there is no a priori method to decide which one is the best. In (Zalı́dvar et al., 2005) 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 points in the state space reconstruction (Bosch et al., 2004b).

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 (Guo et al., 2016; Guo et al., 2017a).

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 (Kähm and Vassiliadis, 2018a; Kahm, 2019; Kähm and Vassiliadis, 2018d). The proposed stability criterion is successfully generalized for multiple reactions (Kähm and Vassiliadis, 2019).

5.2.6. Modified dynamic and slope condition

Kummer and Varga investigated the most frequently applied criteria and derived two new criteria as a result (Kummer and Varga, 2019a). Eq. 31 presents the Modified Slope Condition (MSC) and Eq. 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.

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_{c} \leq \frac{dq_{rem}}{dT}\left(1+\frac{q_{gen}}{q_{rem}}\right) \tag{31}$$

$$\left.\frac{\partial q_{gen}}{\partial T}\right|_{c} + \left.\frac{\partial m}{\partial c}\right|_{T} \leq \frac{q_{gen}}{q_{rem}}\frac{dq_{rem}}{dT} \tag{32}$$

5.3. 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.

5.3.1. 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 (Thomas, 1961; Varma et al., 2005).

$$\frac{d^2T}{dt^2} < 0 \, while \, \frac{dT}{dt} > 0 \tag{33}$$

Dente and Collina in 1964 independently proposed the same criterion (Varma et al., 2005).

5.3.2. 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 (Adler and Enig, 1964).

$$\frac{d^2T}{dx^2} < 0 \, while \, \frac{dT}{dx} > 0 \tag{34}$$

5.3.3. 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

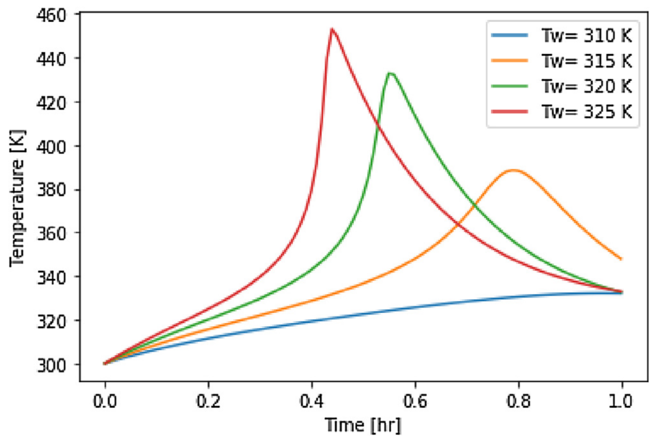

Fig. 6. Sensitivity of the reactor model with respect to wall temperature.

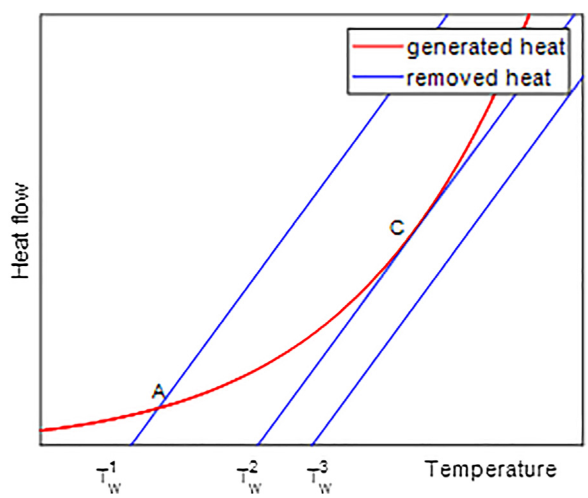

Fig. 7. Semenov-diagram.

evolving at different cooling agent temperatures (van Welsenaere and Froment, 1970).

$$\frac{dT}{dx} > 0 \, \frac{dc_m}{dT_m} > 0 \tag{35}$$

5.3.4. 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 (Abel et al., 2000).

$$T_p + \Delta T_{ad} = MTSR \leq MAT \tag{36}$$

5.4. Sensitivity analysis of chemical reactors (Morbidelli-Varma criterion)

A.Varma et al. wrote an excellent book about the parametric sensitivities in chemical systems (Varma et al., 2005). The analysis of how a system responds to changes in the parameters is called parametric sensitivity (Varma et al., 2005). 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 (Bilous and Amundson, 1955; Bilous and Amundson, 1956; Gray et al., 1981; Emig et al., 1980; Gray et al., 1981). The result of a similar analysis can be seen in Fig. 6. 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 (Emig et al., 1980; Lewis and Von Elbe, 2014), 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 ($\mathbf{y}$) with respect to the input parameters ($\boldsymbol{\phi}$) can be calculated based on the following form:

$$s_{\boldsymbol{\phi}}^{\mathbf{y}} = \frac{\partial \mathbf{y}}{\partial \boldsymbol{\phi}} \tag{37}$$

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

$$S_{\phi}^{y} = \frac{\boldsymbol{\phi}}{\boldsymbol{y}} \frac{\partial \mathbf{y}}{\partial \boldsymbol{\phi}} = \frac{\partial \ln \mathbf{y}}{\partial \ln \boldsymbol{\phi}} = \frac{\boldsymbol{\phi}}{\boldsymbol{y}} s_{\boldsymbol{\phi}}^{\mathbf{y}} \tag{38}$$

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 (Morbidelli and Varma, 1988), (Morbidelli and Varma, 1989; Chemburkar et al., 1986). Lacey (1983) and Boddington et al. (1983) 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:

$$\max\left(s_{\boldsymbol{\phi}}^{\mathbf{y}}\right) = 1\,(except\, t = 0) \tag{39}$$

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 (Jiang et al., 2011).

5.5. Data-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 (Varga et al., 2009) 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 (Dakkoune et al., 2020), 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 (Amine et al., 2018). The major drawback of these criteria, that a huge amount of process simulations should be performed to obtain the necessary amount of data. 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. Kummer et al. developed a genetic programming-based method for constructing tailored runaway criteria to reach a more specific critical equation, this technique can be used for any kind of combination of reactor and reaction systems, and the resulted criterion is much more suitable for that system than any general criteria from the literature (Kummer et al., 2019).

6. Safety boundary diagrams

In case of operation of batch and semi-batch reactors 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*, (Pohorecki and Molga, 2010)) 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 (Hugo and Steinbach, 1986; Hugo et al., 1988). Westerterp et al. generalized the concept of avoiding reagent accumulation through safety boundary diagrams. They investigated heterogeneous liquid-liquid and homogeneous reactions too (Steensma and Westerterp, 1988; Steensma and Westerterp, 1991; Steensma and Westerterp, 1990). 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 (Molga and Lewak, 2009). 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 (van Woezik, 2000; van Woezik and Westerterp, 2002),

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 (Westerterp et al., 2014).

$$T_{ta} = T_c + \frac{1.05\,\Delta T_{ad,0}}{\varepsilon\left[Wt\left(1+\varepsilon\theta\right)+R_H\right]} \tag{40}$$

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. 40. can be used to define the target temperature beside $\theta = 1$. 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 Fig. 8. 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

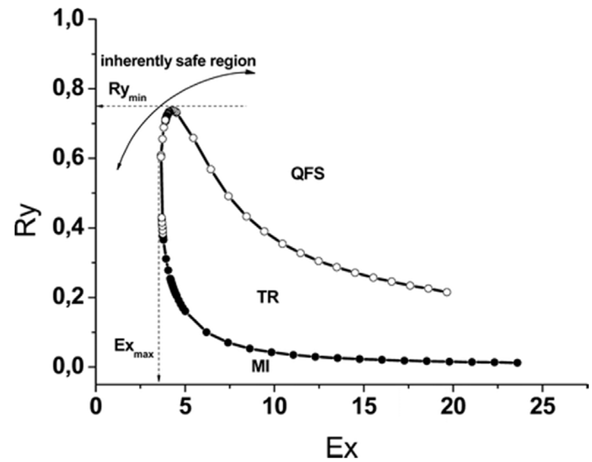

Fig. 8. Safety boundary diagram (Westerterp et al., 2014).

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.

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

$$Ex = \frac{\Delta T_{ad,0}(E/R)}{T_c^2\varepsilon\left(R_H+Wt\right)} = \frac{\Delta\gamma_{ad,0}\gamma}{\beta_c^2\varepsilon\left(R_H+Wt\right)} \tag{41}$$

$$Ry = \frac{Da\left(T_R\right)exp\left(\gamma\left(1-\frac{1}{\beta_c}\right)\right)}{\varepsilon\left(R_H+Wt\right)} \tag{42}$$

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 (Molga et al., 2007). 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:

$$Wt = \frac{(UA)_0 t_{dos}}{\varepsilon\left(V\rho c_p\right)_0} \tag{43}$$

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 (Westerterp and Molga, 2004). There is an inherently safe region, as it can be seen in Fig. 8. They determine the maximum of the exothermicity values below which the heat evolution is always too low, hence reactor runaway does not

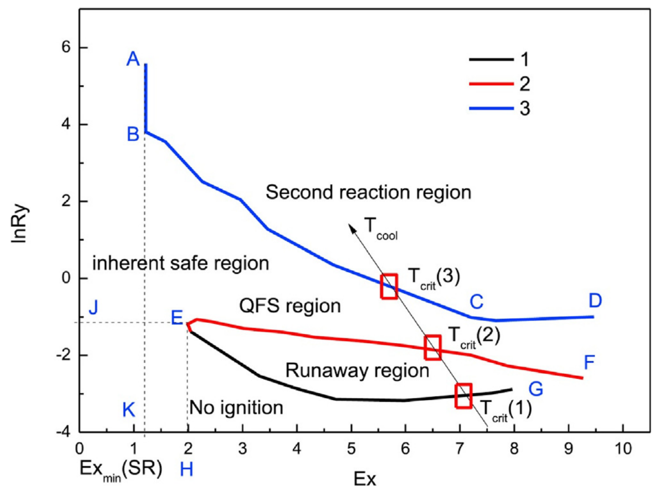

Fig. 9. Safety boundary diagram considering MAT (Ni et al., 2016).

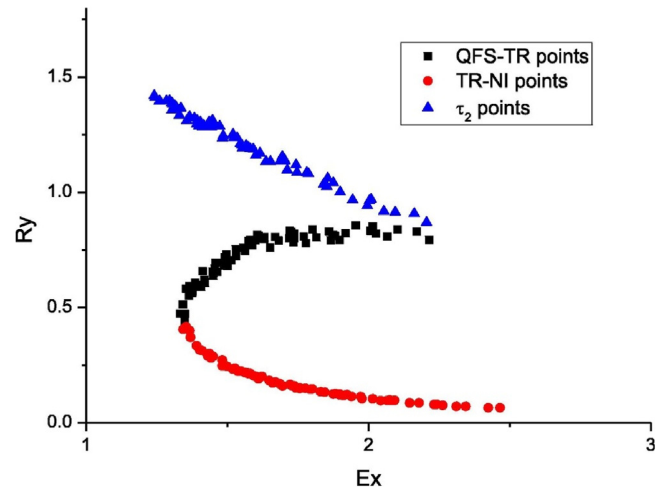

Fig. 10. Extended Boundary Diagram (Guo et al., 2018).

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 (Westerterp and Molga, 2006). 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 (Westerterp et al., 2014). 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 scaling up reactors (Maestri and Rota, 2005a; Maestri and Rota, 2005b), and also a kinetics-free approach can be found in (Guo et al., 2019). Flowchart for designing thermally safe operating conditions based on safety boundary diagrams can be found in (Molga et al., 2007; Guo et al., 2017b).

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 (Maestri and Rota, 2006a; Maestri and Rota, 2006b; Copelli et al., 2010).

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 Fig. 9. 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 (Ni et al., 2016). 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 (Ni et al., 2017).

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 this phenomenon in detail (Guo et al., 2015). 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) (Bai et al., 2017a). Flowcharts for designing thermally safe operations considering MTSR values can be found in (Bai et al., 2017a; Bai et al., 2017b; Zhang et al., 2019). A more generalized method for including and investigating the maximum process temperatures developing at given operating parameters are proposed in (Guo et al., 2018). Guo et al. proposed an artificially defined constant temperature, which can be calculated as follows:

$$T_n = T_c + \frac{n\,\Delta T_{ad,0}}{\varepsilon\,[Wt + R_H]}\; n \geq 1.05 \tag{44}$$

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 Fig. 10, where MTSR values equals T_2 (Guo et al., 2018).

Recently a multi-feature recognition (MFR) criterion based on pattern recognition was proposed to develop safety boundary diagrams (Zhang et al., 2020).

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.

7. 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 (McIntosh and Nolan, 2001).

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 (Balasubramanian et al., 2003). 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 (Dusija, 2004), 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 (Kummer and Varga, 2019b; Kummer and Varga, 2018; Janošovský et al., 2017; Eizenberg et al., 2006; Isimite and Rubini, 2016; Tian et al., 2015)

8. 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.

8.1. 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 (Szeifert et al., 2006), (Kummer and Varga, 2019a; Casson et al., 2012; Broccanello, 2016; Vianello et al., 2018a). Szeifert et al. derived that for the Mathematical model introduced in Section 5.1 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 (2nd group) (Szeifert et al., 2006). 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. The critical curves distinguishing the runaway and non-runaway regimes are shown in Fig. 11 presenting how these criteria indicate runaway in order.

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 (Kummer et al., 2019).

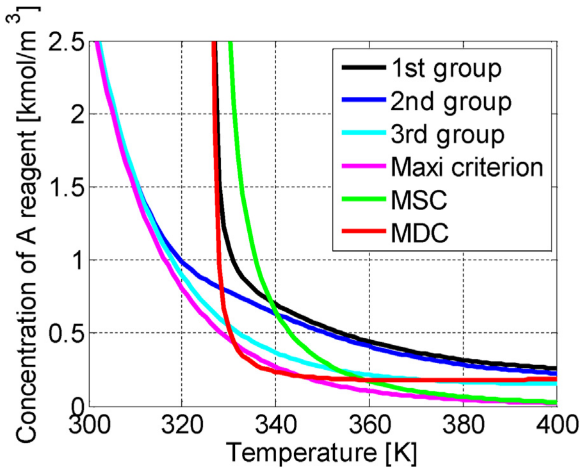

Fig. 11. Critical curves of runaway at Case study presented in Section 5.1 (T_w = 310 K) (Kummer and Varga, 2019a).

8.2. 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 (Szeifert et al., 2006) 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, (Casson et al., 2012; Lu et al., 2004). Vianello et al. calculated the onset temperature based on the variation of the derivative of the temperature (Vianello et al., 2018b). Kummer and Varga used thermal runaway criteria as a nonlinear constraint to define the optimal feeding trajectory in the operation of semi-batch reactors (Kummer and Varga, 2017). Serra et al. investigated the consequences of thermal runaway based on the MTSR values in a jacket-cooled semi-batch reactor through three different scenarios: batch-, stop -, non stop scenario (Serra et al., 1997).

8.3. Process control

Adequate models of reactors can be used for a nonlinear model predictive control (NMPC) (Findeisen et al., 2007). 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 (Seki et al., 2001; Yu and Biegler, 2019). 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 (Kummer et al., 2020a). Kummer et al. proposed a control framework for the operation of SBRs considering parameter uncertainty (Kummer et al., 2020b).

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 (Rossi et al., 2015). Specific classes of deterministic NMPC/DRTO frameworks can identify reactor runaways under parameter uncertainty too (Rossi et al., 2017). Strozzi-Zaldivar criterion can be too strict; hence, it is not suitable to analyse the stability of semi-batch reactors in some cases (Kummer and Varga, 2017). 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 (Kähm and Vassiliadis, 2018a). Their stability criterion was applied to an industrial case study and they considered the parameter uncertainty during the process control (Kanavalau et al., 2019). Lyapunov exponents as an indicator of stability were successfully realized in NMPC to control batch reactors (Kähm and Vassiliadis, 2018e). The operation of an industrial semi-batch polymerization reactor was optimized by considering a cooling system failure (Abel et al., 2000). 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 (Zhang et al., 2018). 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 (Arellano-Garcia et al., 2020).

8.4. Runaway prediction and inhibition

There are several studies about the investigation of short-stopping 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 (Jiang et al., 2016; Zhang et al., 2017; Ni et al., 2020; Dakshinamoorthy et al., 2004; Dakshinamoorthy and Louvar, 2008; Dakshinamoorthy et al., 2006; Chen et al., 2020; Milewska and Molga, 2010; Ampelli et al., 2006). 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 (Jiang et al., 2018). Russo et al. connected the EWDS system (runaway criterion) with the action of protection (Russo et al., 2007).

9. 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 the productivity is increased. In order to fulfil this goal we must extend our knowledge on some fields. As we have seen it, the runaway develops if somehow the balance between the generated and removed heat is upset, and most of the runaway criteria are based on it. Both of the removed and generated heat are the functions of state variables and system properties, such as concentrations, kinetic and heat transfer parameters, etc. which can vary in time. Moreover, these values may not be correctly identified (uncertainty can be especially high at the kinetic parameters). 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 dynamic process simulators can be applied to quantitatively evaluate the mitigation systems.

To further support the spreading of these methods in industrial applications we should investigate industrial case studies to present how production systems can be designed in detail from the basic information we have. In this design process we should focus on the equipment-, process-, control- and mitigation subsystems. Dynamic process simulators can also support this effort; however, the numerical solution methods in these simulators should be developed to reliably calculate the sudden changes in state variables at the start of runaway events.

For the purpose of gaining more information about thermal runaway CFD simulations and experimental studies should be continuoued. In most studies the hydrodynamic conditions, system specific 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 (e.g. catalyst deactivation).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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