Theses of the doctoral (PhD) dissertation

Development and application of thermal runaway criteria

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1 Introduction and the aim of the work

The worst consequence of a thermal runaway (which is thermal explosion) shows that process engineers must have a detailed knowledge about this phenomenon. 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, where a runaway of a polymerization reaction occurred. 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.

I studied thermal runaway in detail and I present a review about the topic including: the possible cause and consequences of reactor runaway, the prevention steps and 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. Different mitigation methods to moderate the consequences of reactor runaway are also discussed.

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. Runaway criteria investigate the different states of the reactor and they classify these as runaway or non-runaway, but there are differences in the decisions. Consequently, there are correct and false indications, but there is no an explicit definition to characterize runaway. The two main expectations from thermal runaway criteria are to indicate runaway reliably and as early as possible. I evaluated and compared the two new runaway criteria to the widely applied criteria from the literature. In the investigated case studies MDC criterion was the most reliable and its earliness was average.

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. In this problem I built critical equations based on two aspects, which are maximizing the reliability and minimizing the indication time. The tailored critical equations outperformed the criteria from literature in the investigated system.

For further investigation of the applicability of runaway criteria I used some criteria from the literature (Inflection point criterion, Van Heerden criterion, Strozzi-Zaldivar criterion, etc.) 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, in which parameter uncertainty is considered too. In the application of MPCs in case of exothermic reactions for appropriate operation it is a key to define the length of prediction horizon carefully, since we must see the development of thermal runaway. For this purpose, I worked out a methodology to define the minimal length of prediction horizon which is the critical process safety time. I compared Multi-Stage NMPC and worst-case scenario NMPC to handle parameter uncertainty. Based on my studies the worst-case scenario NMPC is feasible since the computational times per iterations are lower than the usually applied sample time in process control.

2 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

3 Utilization of the results and future aims

The detailed investigation of thermal runaway criteria result in the fact that there is no a best or a worst runaway criterion, and each criterion has its own right. The developed new runaway criteria (Modified Slope and Dynamic Condition) can be implemented and applied for the indication of reactor runaway and based on this different prevention and safety actions can be performed. With the proposed genetic programming-based identification method system-specific runaway criteria can be developed which may indicate runaway with higher reliability and with sufficiently low indication time compared to criteria from the literature.

As I presented runaway criteria can be implemented to increase the safeness of reactor operation, thermal runaway criteria can be applied for reactor and operation design. I presented that the online application of runaway criteria is feasible and it helps to avoid dangerous events.

The results show that criteria could be implemented in an industrial environment beside the working safety protocols, and its applicability could be tested further for the prediction of non-desired events. In the future maybe we will be able to widen the safe operation regime to make a better use of the opportunities, but for that we need to perform a lot of laboratory and pilot tests.

4 Publications related to theses

Articles in international journals

1. 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. 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. 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. 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. 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. Kummer and T. Varga, "What do we know about thermal runaway? – A review", Submitted to the *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 proceedings

7. 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. 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. 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

1. 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

2. 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 proceedings

3. Kummer and T. Varga, “Dynamic process simulation based process malfunction analysis” in *Computer Aided Chemical Engineering*, vol. 43, Elsevier, 2018, pp. 1147–1152.

4. 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