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Dynamic Simulation and Verification Test for Vent Sizing of Runaway Reaction

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Safety valves are installed on process equipment where pressure-rise would occur to prevent rupture of them in chemical plants. However, it is difficult to analyze pressure-rise behavior quantitatively during reaction runaway, especially, in case of occurrence of two-phase flow. It is necessary to apply experimental and analytical technical knowledge for the vent sizing. The vent sizing method for two-phase flow by reaction runaway has been developed by the Design Institute for Emergency Relief Systems (DIERS) established in 1987, and then ISO 4126-10 was published in 2010 and it got the global standard. However, the ISO model is assumed conservative analysis condition to prevent underestimation, and sometimes unrealistic results are obtained. In this study, detailed process dynamic simulation model to estimate accurate vent size was constructed in Aspen Dynamics, process simulation software. In order to construct dynamic simulation model, it is necessary to define reaction rates, mass balance including chemical reactions and flow rate from vent or exhaust gas line, and heat balance between before and after chemical reactions. These parameters regarding the runaway reaction were obtained through Advanced Reactive System Screening Tool (ARSST) experiments. As ISO-omega model is not contained in Aspen Dynamics, ISO-omega model constructed by Aspen Custom Modeler is coupled with Aspen Dynamics as a subroutine program. Process parameters such as temperature, pressure and liquid level in process equipment are calculated comprehensively, and effect of exhaust gas line is also considered in this model. In order to confirm the validation of the results of detailed simulation model, a 40-mL-scale small test apparatus with a safety valve was developed. The maximum pressure with each diameter of safety valve was observed experimentally and they were good corresponding to the results of detailed simulation. Furthermore, this experimental method would be expected to estimate the vent size directly without the complicated analysis such as the ISO method or a detailed simulation model. The combination of case studies of the experiment and simulation also provides various additional knowledge, such as identification of the composition in a reactor in which a less violent runaway reaction occurs or the process condition for which a runaway reaction does not inherently occur. This study would contribute to the design of resilient processes for process upsets and will lead to sustainable and economical design.

1. Introduction

Major accidents due to runaway reactions continue to occur, and it is important to decide and review protection layers such as interlock systems, operation procedures and safety valves in detail. Thermal analysis of hazardous materials was carried out to determine process conditions and set point of interlock systems by using calorimeters such as Differential scanning calorimetry (DSC) or Accelerating Rate Calorimeter (ARC) etc. This is proactive measures, and they are already mature technology. (Francis, 2009; Mohsen et al., 2015; Lamiae and Sébastien, 2015; Alex and Tamás, 2021).

In contrast, it is hard to say that safety measures after occurrence of reaction runaway are sufficient to mitigate consequences. Safety valves represent one of the most important measure for protecting pressurized vessels during an emergency. Safety valves are installed to prevent equipment rupture due to undesired pressure rise from reactions. A vent sizing method for two-phase flow was developed by DIERS under the auspices of AIChE in 1987, and the 9th edition of API standard 520 was published in 2014. In addition, ISO

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4126-10 was published in 2010, and it adopted impossible refined omega-method (Joseph and Hans, 1987; Ralf and Jürgen, 2004; ISO 4126-10, 2010; CCPS, 2017).

However, the required vent sizes by ISO method sometimes are obtained diameters larger than the diameters of the reactors. This is because the assumption of ISO method is that equipment is confined condition, and inventories do not change during runaway reactions. However, many actual equipment are not confined and have gas lines on equipment such as exhaust gas lines or reflux lines. In addition, inventories vary during runaway reaction by vaporization of solvents or generation of non-condensable gases. Decreasing of inventories would contribute to prevent occurrence of two-phase. Therefore, in order to estimate the vent size more realistically, detailed simulation model for dynamic simulation was studied in this study. In addition, a small-scale experiment was carried out to confirm the validity of simulation results.

2. Model process

A Methyl Ethyl Ketone Peroxide (MEKPO) production reactor was used as the model process. The diameter of the reactor was 1.5 m, its height was 3 m, MEKPO was produced by synthesis of Methyl Ethyl Ketone (MEK) and hydrogen peroxide as exothermal reaction and the operation conditions were atmospheric temperature by cooling operation. The components in the reactor were MEKPO which was present at 28 wt.% and solvents which are the mixture of dimethyl phthalate (DMP), and toluene (TOL). To determine the specification of safety valve, hazard identification by HAZOP or what-if analysis should be carried out, and here, the cooling system failure of the reactor was assumed as abnormal scenario. If it occurs, the temperature in the reactor will increase with exothermic reaction, and it evolve into reaction runaway, and pressure rise due to generation of non-condensable gas and vapor of solvents. The safety valve was installed on the top of the reactor, and set pressure was assumed 400 kPag.

3. A detailed simulation model

3.1 Model description

In this study, the detailed simulation in this study was constructed with Aspen Plus, Aspen Dynamics and Aspen Custom Modeler. Aspen is a specialized simulation software for chemical processes, and it includes various material data such as thermophysical and phase equilibrium properties. Dynamic simulations were carried out with Aspen Dynamics with the reaction model by the results of ARSST tests. The constitution of the simulation model is shown in Figure 1. For the construction of the reaction model, definitions of the reaction formula, reaction rate and heat of formation of reactants and products were necessary. Furthermore, the temperature and pressure rise in the reactor were calculated by the combination among heat of reaction, the amount of generated gas and the vapor pressure of the solvent. Then, the model was validated by checking the simulation results against the original ARSST test. However, a safety valve model is not included in Aspen Dynamics and it is necessary to make such a model in Aspen Custom Modeler.

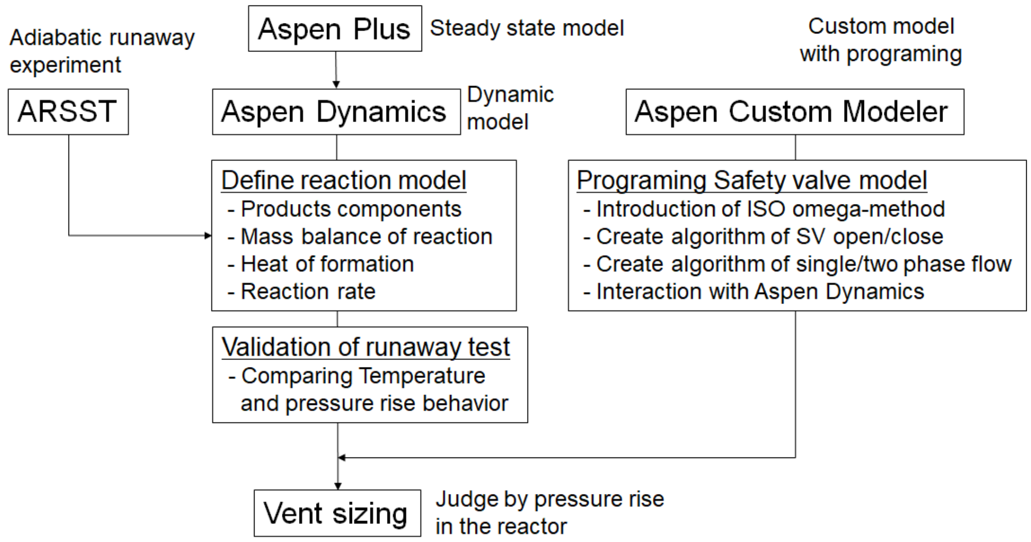


Figure 1. Procedure for construction of model for estimating diameter of a safety valve in Aspen

The equations of two-phase flow from safety valve of the ISO method were used in Aspen Custom Modeler, and the correlation of some parameters were reconstructed. For example, mass flow rate by generated gas/vapor in ISO method is input parameter as experimental result, but it is calculated by reaction rate and phase equilibrium in the detailed simulation model. In the same way, the diameter of safety valve is calculated in the ISO method to prevent pressure rise, but it is input parameter in the detailed simulation model and the pressure of the reactor is calculated.

3.2 Results of detailed simulation and comparison with ISO method

The results of case studies are shown in Table. 1. The components of sample material are MEKPO 28/ dimethyl phthalate 42/ Toluene 30 in weight percentage, wt.%. The ARSST test was carried out, and then reaction formular and reaction rate were constructed in the detailed simulation model. Required vent size preventing pressure rise in the reactor were estimated by calculation repeatedly with various vent sizes. According to comparison of the required vent size, ISO method gave larger size than two detailed simulations, and it was larger than the reactor’s diameter 1.5m.

Table 1. Comparison of results by ISO method and detailed simulation model

	ISO method	Detailed simulation model	
		Confined reactor	Reactor with 0.2m-dia. exhaust gas line
Maximum temperature [°C]	302	315	339
Non-condensable gas generation rate [kg/sec]	79	19	56
Vaporization rate [kg/sec]	-	129	238
Required vent size [m]	1.9	0.5	0.7

The runaway reaction behavior of the ISO method and two detailed simulation model are plotted on the flow regime as shown in Figure 2. The x-axis in Figure 2 represents the reaction progress from left to right. The plot for the ISO method is only one point because it is calculated as the maximum value of the gas generation rate. In contrast, the gas generation rates of the detailed simulation models are calculated with the progress of the runaway reaction and plotted on the flow regime. The vertical axis is the liquid level in the reactor. In case of confined reactor of detailed model, the liquid level rises slightly depending on the liquid expansion. In case of unconfined reactor of detailed model, the liquid level decreases slightly depending on the blow-out from exhaust gas line.

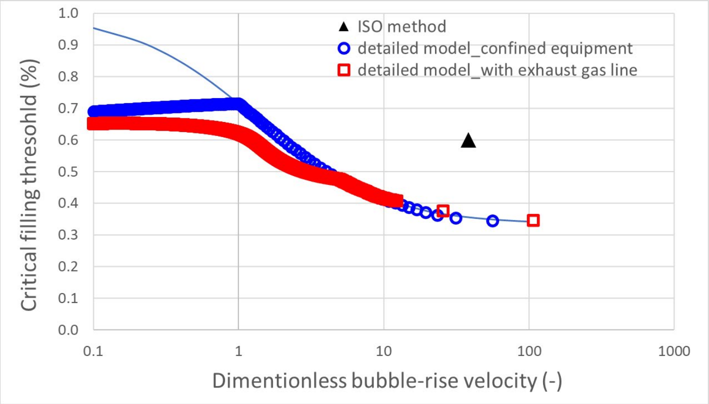


Figure 2. The runaway reaction behavior of ISO method and detailed simulation model

After the reaction passes the borderline into two-phase flow, drawn with a blue curve, the line liquid level decreases, and then they pass the border-line again from up to down to single-phase gas flow. Finally, they pass the borderline again from left to right to return to two-phase flow. In this way, both plots move to the lower right along the borderline of two-phase flow. The results of detailed calculation models show that two-phase flow occurs as the runaway reaction progresses and the values of X-axis are larger than the ISO method, but required vent size are smaller. This is because the liquid level decreased and void fraction of homogeneous two-phase flow are high, and mass flow rate of two-phase flow would be smaller. Regarding the case that the exhaust gas line exists, the required vent size is larger than confined reactor. The solvent as toluene is vaporized and blow-out from the exhaust gas line before runaway reaction finish, and the most violent reaction is not tempered by latent heat of toluene.

4. A small-scale vent sizing test

4.1 Test apparatus

A 40-mL small-scale vent sizing test apparatus was developed in this study. It would be expected that the required vent size is obtained directly without complicated estimation methods such as the ISO method and it could be confirmed the accuracy of the results of the detailed simulation model. An overview of the test apparatus is shown in Figure 3.

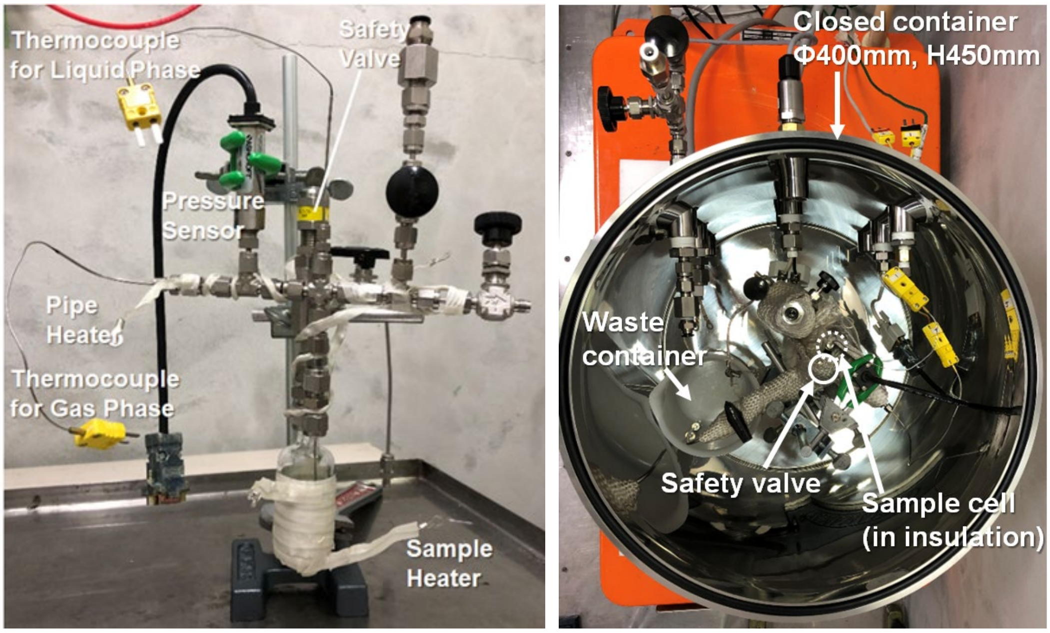
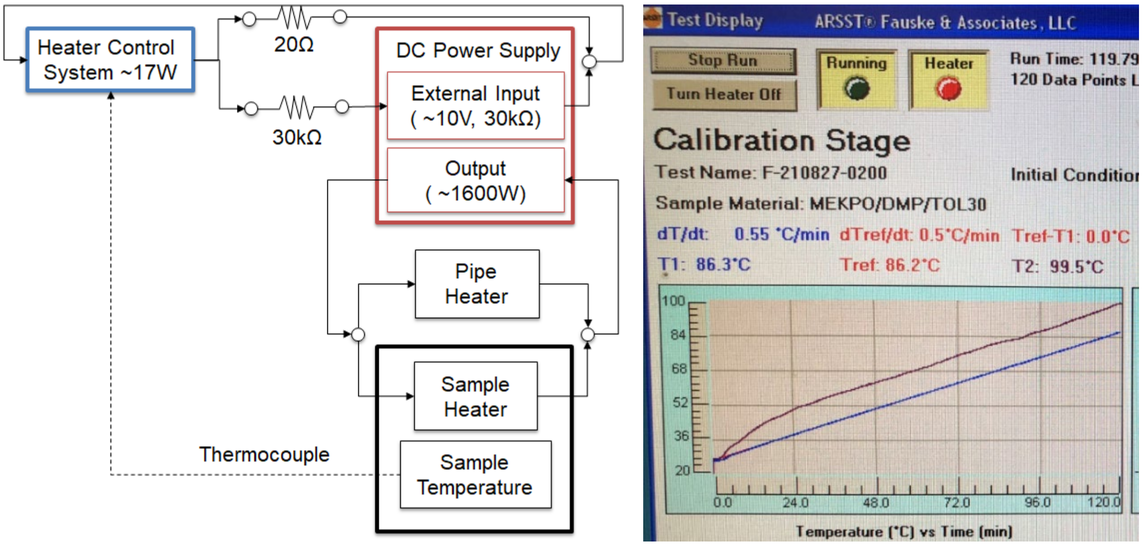


Figure 3. Experimental layout of the small-scale runaway reaction test (left) and a photograph taken from above (right)

The specification of sample cell is that the diameter is 35 mm, length is 70mm, the thickness is 2.4 mm, the internal volume is 40-mL, and it is made of pressure-resistant glass certified over 1 MPa. The sample cell is connected to two ports with metal piping, one is to a safety valve and another is to the line of the pressure sensor and thermocouples. For the case in which the diameter of the safety valve is smaller than required, the pressure in the sample cell is increased and the sample cell may rupture or catastrophically depart the system. Therefore, the apparatus is installed in a 40-L closed container made of stainless steel. In addition, a large amount of generated flammable gas may be dispersed if the sample cell is ruptured during runaway reaction, so the inside of the closed container is filled with nitrogen to prevent explosion and fire. The end of the outlet pipe from safety valve is set under the water in the waste container, and vaporized solvents such as toluene are trapped on the water. The heaters are installed around sample cell and upper pipelines such as safety valve and the lien for pressure and temperature measurement to prevent condensation and reflux in the upper pipelines. An adiabatic control of the sample cell is a key factor in creating an adequate runaway reaction in a small-scale test and is used as the ARSST control system as shown in Figure 4. However, the maximum electrical power for the ARSST to the sample heater is 17 W for 10-mL scale sample cell, which is not adequate for this study 40-mL scale. Therefore, the electricity is amplified by a power supply unit, and a circuit for external input from the ARSST to the power supply unit was developed. The right figure in Figure 4 shows the control panel of the control system which was used the ARSST interface which is a credible and good operable system. The temperature of pipeline is a little higher temperature than sample cell to prevent condense vapor. Regarding the pipe heater, it is not controlled directly, and the power supply for pipe heater is distributed by the relationship among the resistances of sample heater and pipeline heater and each heat capacities. The diameter of safety valve cannot be changed easily for small scale such as millimetre order, and the orifice is installed just upstream of the safety valve. The selection of the material of O-ring of safety valve is important. The default material of FKM was not adequate and broken during runaway reaction, as a result, Kalrez were used.



Run Time: 119.79
120 Data Points L

Calibration Stage

Test Name: F-210827-0200

Initial Conditior

Sample Material: MEKPO/DMP/TOL30

dT/dt: 0.55 °C/min dTref/dt: 0.5°C/min Tref-T1: 0.0°C

T1: 86.3°C Tref: 86.2°C T2: 99.5°C

Figure 4. Controls system for the sample heater (left) and an output monitor of the temperature of sample cell and pipeline in the ARSST interface (right)

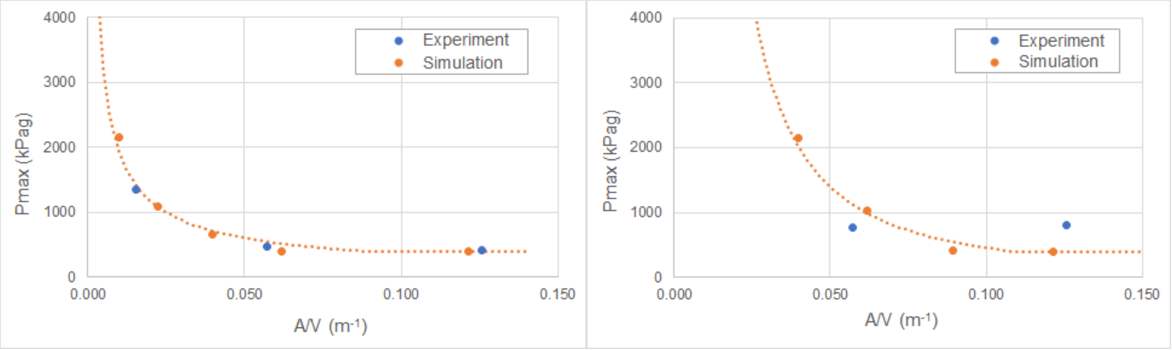
4.2 Results of vent sizing and comparison with detailed simulation

Experimental results for maximum pressure and final liquid level in the sample cell show in Table. 2. The safety valve diameters of the small-scale experiments were estimated by the results of the detailed simulation model based on the assumption that A/V, the ratio of the area of safety valve to the liquid volume in the actual reactor and the small-scale cell, is constant.

Table 2. Experimental results for maximum pressure and final liquid level in the sample cell

No.	Sample	SV diameter [mm]	SV Set pressure [kPag]	Exhaust gas line [Yes/No]	Maximum pressure [kPag]	Final liquid level [%]
(a)-1	MEKPO/DMF/TOL30	2.00	400	No	421	23.6
(a)-2	MEKPO/DMF/TOL30	1.35	400	No	470	23.1
(a)-3	MEKPO/DMF/TOL30	0.70	400	No	1358	19.7
(b)-1	MEKPO/DMF/TOL30	2.00	400	Yes(0.5mm)	797	17.2
(b)-2	MEKPO/DMF/TOL30	1.35	400	Yes(0.5mm)	761	N/A

Figures 5(a) and 5(b) show the experimental results and comparison with the detailed simulation model. Figure 5(a) showed cases in which a safety valve was installed, but an exhaust gas line was not installed. The results of these experiments and the calculation results were in good agreement. Figure 5(b) showed a case in which an exhaust gas line was installed in addition to a safety valve. The experimental results were different from the calculation results. For example, the plot of approximately A/V = 0.12 was estimated to be sufficient for depressurization by the calculation, but the experimental result shows that the pressure increases to approximately 1,000 kPag. It is considered that this is because the pressure-increase rate due to the reaction runaway was very fast, whereas it took 120 ms for the safety valve to open fully, so that the pressure increased before the depressurization. The pressure-increase rate in this experiment was 8,336 kPa/s, and the pressure increase was estimated to be 1,000 kPag for 120 ms. In addition, the ISO regulation states that the applicable limit of pressure increase that can be depressurized by the safety valve is 20 kPa/s, and depressurization by means of the safety valve is difficult if the pressure limit has been exceeded. Furthermore, the reason why the extremely violent reaction runaway occurred was that the total amount of toluene was vaporized by the decomposition reaction of MEKPO, and MEKPO was concentrated in the liquid phase.



(a) Confined reactor *(b) With the exhaust gas line*

Figure 5. Experimental and calculation results; correlation between pressure increase in the sample cell and vent area divided by sample volume

5. Conclusions

A detailed simulation model to analyze runaway reactions and venting from a safety valve was constructed with Aspen simulation software and ARSST test. The detailed simulation model was considered with liquid decrease during runaway reaction and the existence of the exhaust gas line. The result of the detailed simulation model was compared to those for the ISO model as the confined reactor, and smaller vent size was obtained. This is because liquid decrease contributed to the rest of MEKPO at the end of the violent runaway reaction and the void fraction of two-phase flow. Furthermore, the effect of the existence of the exhaust gas line was confirmed, and the required vent size was larger than the vent size of confined reactor. This is because toluene was vaporized completely before the end of the violent runaway reaction, and it is important to consider the behavior as a whole reaction system.

To confirm the accuracy of the detailed simulation model, a small-scale experimental apparatus was developed. At the same time, this test would experimentally obtain the required diameter of the safety valve without complicated analysis such as by an ISO method, but more detail study is necessary to confirm the scale law in future work. The comparison between the results of experiment and the detailed simulation model were carried out, and good correspondence was obtained in case of the confined reactor. Regarding the case of the existence of the exhaust gas line, the results were not corresponded. This is because the pressure-increase rate was faster than the applicable limit of depressurization of the safety valve, and the pressure of the reactor was increased more than expected pressure. It is indicated that it is important to consider not only the blow-out capacity of safety valve but also the pressure-increase rate.

More realistic vent sizes which could be installed on the actual equipment were estimated in this paper, but it would not include safety allowance. Therefore, it is important to confirm carefully the effects of gas lines or pressure-increase rates against safety valve opening speed. Ensuring the assumption and accurate estimation for vent sizing would lead to effective installation for not only safety but also economically.

References

CCPS, 2017. Guidelines for Pressure Relief and Effluent Handling Systems

Diener R., J. Schmidt, 2004. Sizing of Throttling Device for Gas/Liquid Two-Phase Flow part1: Safety valves. Process Saf. Prog., 23-4, 335-344. https://doi.org/10.1002/prs.10034

Hassimi. L. V., S. Leveneur, 2015. Alternative method to prevent thermal runaway in case of error on operating conditions continuous reactor. Process Saf. Environ. Prot., 98, 365-373. http://dx.doi.org/10.1016/j.psep.2015.09.012

ISO 4126-10, 2010. Safety devices for protection against excessive pressure e sizing of safety valves for gas/liquid two-phase flow.

Kummer A., T. Varga, 2021. What do we know already about reactor runaway? -A review. Process Saf. Environ. Prot., 147, 460-476. https://doi.org/10.1016/j.psep.2020.09.059

Leung J. C., H. K. Fauske., 1987. Runaway system characterization and vent sizing based on DIERS methodology. Plant/Oper. Prog., 6-2, 77-83. https://doi.org/10.1002/prsb.720060208

Naderpour M., S. Nazir, J. Lu, 2015. The role of situation awareness in accidents of large-scale technological systems. Process Saf. Environ. Prot., 97, 13-24. http://dx.doi.org/10.1016/j.psep.2015.06.002

Stoessel F., 2009. Planning protection measures against runaway reactions using criticality classes. Process Saf. Environ. Prot., 87, 105-112. https://doi.org/10.1016/j.psep.2008.08.003