CHEMICAL ENGINEERING TRANSACTIONS
VOL. 77, 2019

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Genserik Reniers, Bruno Fabiano

ISBN 978-88-95608-74-7; **ISSN** 2283-9216

DOI: 10.3303/CET1977077

A Study of Vent Sizing for Reaction Runaway and Safety Measures

Tsuyoshi Nagasaka*, Yuto Mizuta, Motohiko Sumino, Youichi Kunito

Safety Engineering Center, Production Technology Dept., Mitsubishi Chemical Corporation
nagasaka.tsuyoshi.ma@m-chemical.co.jp

In this study, prevention of rupture in organic peroxide commercial reactor during runaway reaction has been studied by estimating required vent size and by implementation of effective safety measures. In order to estimate the vent size, it is necessary to obtain the rate of temperature-rise and pressure-rise during runaway reaction, therefore experiments were carried out by ARSST following JIS B 8227 standard. For the case of model substance MEKPO used in this study, required vent size was estimated to be unrealistically large due to formation of two phase flow caused by the fast reaction and gas formation. Regarding safety measures, two methods, inherently safety measures and safety measures by controlling hazard were considered. First, it is the method to moderate runaway reaction by reducing holdup or changing the solvent to reduce the required vent size to realistic value that can be implemented. Second, it is the method to reduce probabilities of runaway occurrence by adding multiple interlock system. It is important to implement safety measures with considering process comprehensively, because available measures are limited by characteristics of processes or substances.

1. Introduction

In chemical plants, safety valves are installed to prevent rupturing of equipment where undesired pressure-rise due to reaction and failure during pressurization or transport operations can be assumed. Typical initiating abnormal events leading to pressure-rise are malfunction of control valves, cooling system failure of reflux or internal coil of reactor, tube failure of heat exchanger and fire case etc. Though there are many considerations for those cases, pressure-rise caused by reaction runaway is difficult to predict. In the case of two-phase flow occurring by reaction runaway, it is especially hard to say that all equipment have been installed sufficient size. Vent sizing method for two-phase flow generated by reaction runaway was developed by DIERS under the auspices of AIChE in 1987, and ISO 4126-10, Safety devices for protection against excessive pressure—Part10: Sizing of safety valves for gas/liquid two-phase flow, was published in 2010. After that JIS B 8227 which has the same content as ISO 4126-10 was published in 2013 in Japan. However, the organization which able to implement vent sizing with JIS method would be few. On the other hand, recently, explosion accidents due to reaction runaway occur successively, and it is considered important to review protection layers. Therefore, it is necessary to review safety protection layers for such equipment, especially the safety valve. In this study, the case study of vent sizing and safety measures were considered with MEKPO (Methyl Ethyl Ketone Peroxide) which production plants had many severe accidents in Japan, Korea and Taiwan.

2. Analysis method

2.1 Model equipment and substances

This study was considered with the model process shown as Figure 1. As the size of the reactor, the diameter is 1.5m, height is 3m, and operation temperature is room temperature and operation pressure is ambient pressure. The reaction is that MEK (Methyl Ethyl Ketone) react with hydrogen peroxide to produce MEKPO. The set pressure of safety valve is assumed 300kPag. The composition in the reactor is assumed as same of

Paper Received: 2 January 2019; Revised: 19 May 2019; Accepted: 20 June 2019

Please cite this article as: Nagasaka T., Mizuta Y., Sumino M., Kunito Y., 2019, A study of vent sizing for reaction runaway and safety measures, Chemical Engineering Transactions, 77, 457-462 DOI:10.3303/CET1977077

past accident, that is, MEKPO is diluted by the solution DMP (Dimethyl Phthalate) and active oxygen concentration is 10%.

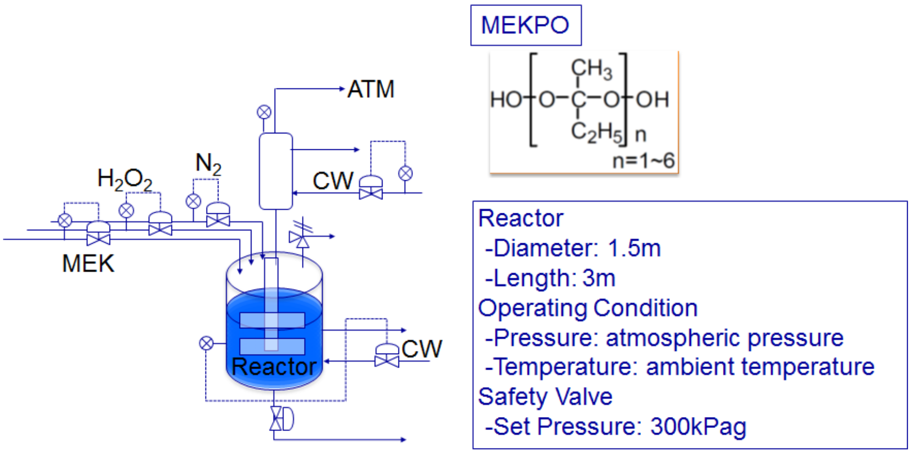

Figure 1: Specification of model equipment of MEKPO reactor

2.2 Analysis method of vent sizing

The vent sizing analysis was carried out by JIS method shown as Figure 2. JIS method had just been issued in 2013 in Japan, but its content does not have concrete description of how to estimate the gas generation rate experimentally, and it is necessary to establish experimental techniques. The vent sizing is carried out with experimental data of the ARSST test of temperature-rise rate and pressure-rise rate. Regarding analysis procedures, each step are described with results of experiments and calculation in chapter 3.

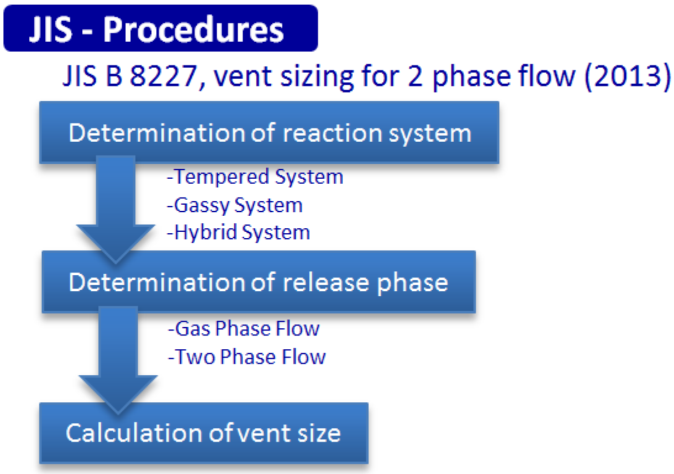

Figure 2: JIS vent sizing method for runaway reaction

2.3 The ARSST test

The set-up of the ARSST test is shown in Figure 3. 5g of the MEKPO/DMP sample is placed in a glass cell, and the sample temperature is measured with the thermocouple. The thermocouple controls the ribbon heater to make adiabatic condition, and temperature-rise and pressure-rise phenomena are recorded. The set pressure of safety valve is 300kPag, and initial pressures in the ARSST were atmospheric pressure, 400kPag, 900kPag because the experimental parameter of 300kPag is interpolated by under and above pressure test. The decomposition mechanism of MEKPO is known in past studies that O-O band cleavage occur first and then radical decomposition of whole molecular of MEKPO. In this study, the slope of graph of temperature–rise and pressure-rise are shown two slopes. In addition, the sharp peak shown in pressure-rise graph would be explosion occurred in the gas phase, because decomposition of MEKPO would produce oxygen and flammable gases. In fact, in addition to safety measures by safety valves, safety measures with a rupture disk would be necessary, but the description of the explosion phenomena is kept to a minimum in order to avoid divergence of the study.

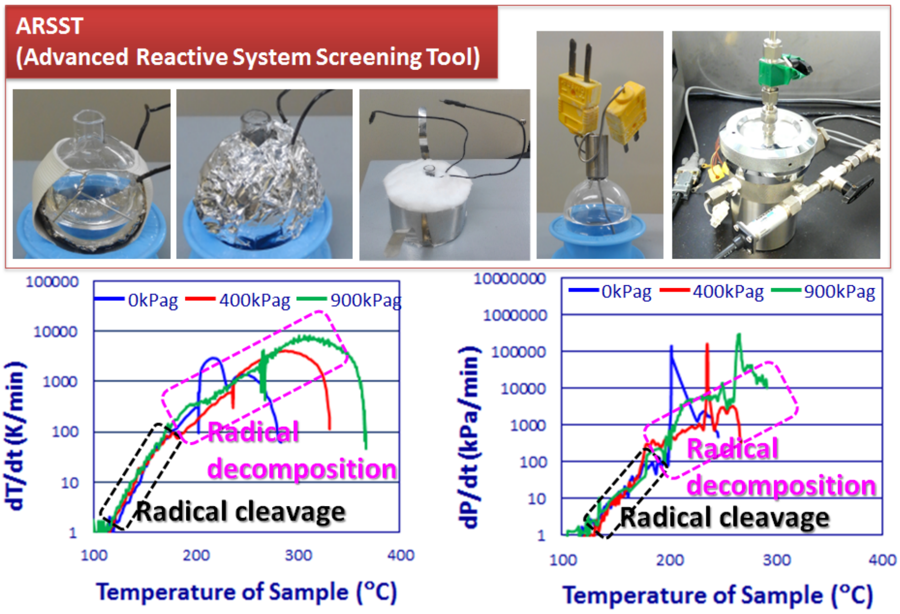

Figure 3: The results of thermal decomposition of MEKPO by ARSST test

3. Vent sizing by JIS

3.1 Determination of reaction system

It is necessary to determine reaction system for the estimation of gas generation rate at the first step of JIS. The experimental result showed that temperature-rise of runaway reaction was tempered at DMP boiling point (B.P. 280 degrees C) and the pressure inside the apparatus remained high after the experiment and therefore the system was determined to be hybrid.

3.2 Determination of release phase

It is necessary to estimate which type of release, gas phase or two-phase flow, would occur from the reactor. The determination of release phase is done by the judgment line as shown in Figure 4. The vertical axis shows the liquid level of the reactor, and the reactor was assumed at 60% as liquid level of the reactor. The horizontal axis is a dimensionless number obtained by taking the ratio of the bubble rising speed to the superficial velocity of the decomposed gas, and the value of the horizontal axis tends to become larger as the gas generation rate is larger. The result of this study was plotted in the part outside the applicable range, and analysis was carried out assuming that two-phase flow is appeared by extrapolating the judgment line.

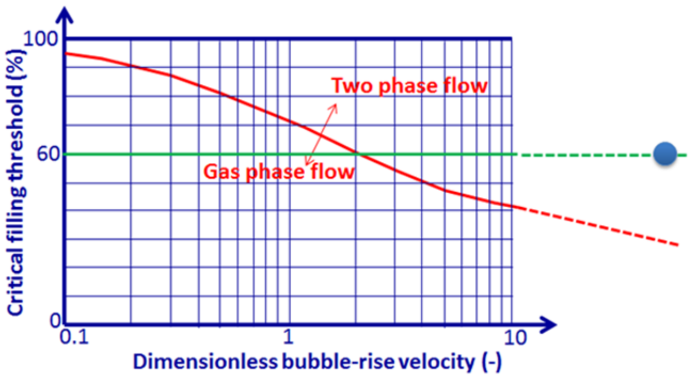

Figure 4: Judgement of release phase from the reactor

3.3 Calculation of vent size

After determining the reaction system and the release phase, each corresponding equation was used for estimation of vent sizing. Required vent size is estimated as the discharge rate is equal to the gas generation rate. The gas generation rate of hybrid type is estimated by pressure-rise rate. The result of estimation of vent size is 4,244mm, which is larger than the diameter of the reactor and is unrealistic.

4. Safety measures

According to the analysis result of JIS method in this study, the critical diameter of safety valve was 4,244 mm, and installation on the reactor was unrealistic. Therefore, two methods were considered as safety measures, that is, inherently safety measures and safety measures by controlling hazard.

4.1 Inherently safety measures

4.1.1 Reducing inventory

It seems that reducing inventory would be one of efficient safety measure because reduction of gas generation rate and prevention of occurrence of two-phase flow, and it was considered at first. The original liquid level of the reactor is assumed to 60%, but even if it is reduced to 40%, it is not possible to prevent occurrence of the two-phase flow, and the estimation result of the vent size is 2,828 mm, and it still has an unrealistic size that was difficult to install. It is necessary to reduce liquid level to 20% for prevention of two-phase flow, but it lead to reduced production of this batch process, and it is not easy to implement.

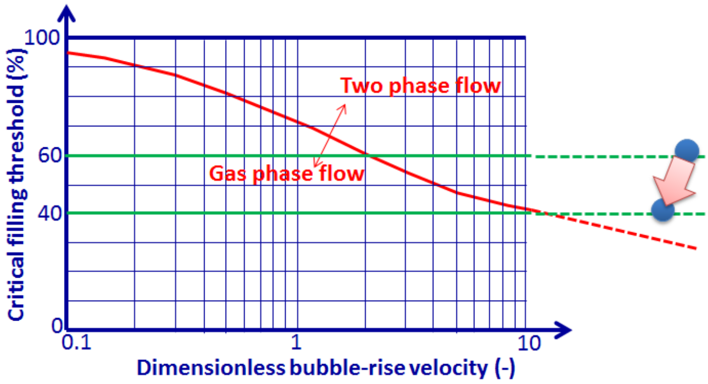

Figure 5: Judgement of release phase from the reactor_ reducing inventory

4.1.2 Substitution of solvent

The decomposition rate of MEKPO is very high, because the boiling point of solvent DMP is high and the heat of decomposition is used for sensible heat and temperature is rose up to the boiling point. It is possible to reduce decomposition rate by changing solvent to the one with low boiling point, because decomposition rate is limited by low boiling point. In this experiment, it was difficult to replace DMF with another solvent completely, but its effect, that reaction rate at runaway condition is tempered by boiling point, was confirmed by adding another solvent. In this study, toluene, which has boiling point as 110 degrees C, is added as a solvent, and the experiment is carried out with the ARSST. Figure 12 shows the experimental results of adding 30% and 50% by weight of toluene. In the case of addition of 30% and 50% of toluene, the temperature-rise rate and the pressure-rise rate had peaks at the temperature estimated as boiling point from the Raoul's law of the mixed solution of DMF and toluene, and it seemed that further violent runaway do not occur. In addition, the explosion did not occur, because it is considered that toluene is at boiling condition, and the composition of the gas phase would be beyond upper limit of explosion. Estimated critical diameter of the safety valve was 2,744 mm when 30% of toluene was added, and 79 mm when 50% was added. The difference between the results of 30% and 50% toluene addition is large, because 30% toluene addition form two-phase flow and 50% toluene addition form gas single flow. The list of results of safety measures are shown as Table 1. The realistic result is considered the case of 50% toluene addition. However, it is necessary to confirm that reduction of reaction yield and increase of byproduct and whether there are problems at customer about the quality of MEKPO as initiator or crosslinking agent.

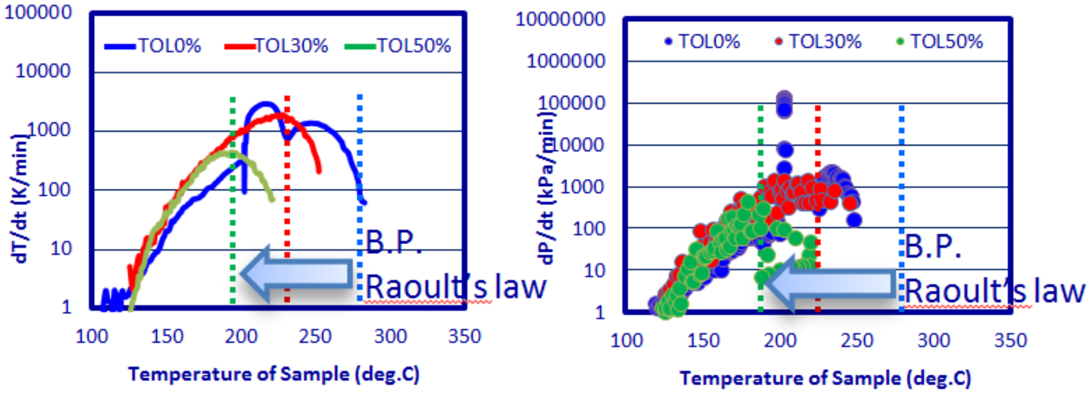

Figure 6: The effectiveness for runaway behaviour by adding toluene

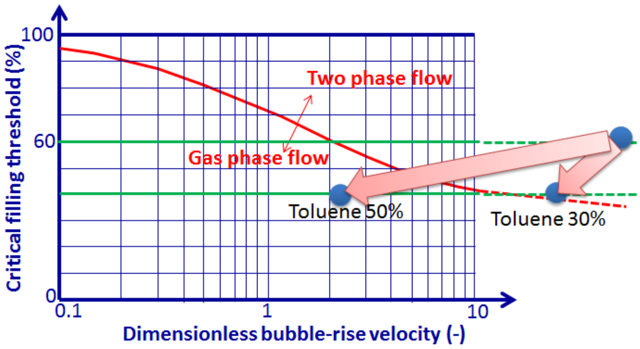

Figure 7: Judgement of release phase from the reactor_ substitution of solvent

Table 1: Results of vent sizing for MEKPO reactor

Case No.	Safety Measure (remarks)	Vent Size (mm)
Original	(*necessary to consider about RD)	4,244
Safety Measure-1	Liquid level 0.6 to 0.4 (*same above)	2,828
Safety Measure-2	Liquid level 0.6 to 0.4 and add toluene (30%) -> Two-phase flow	2,744
Safety Measure-3	Liquid level 0.6 to 0.4 and add toluene (50%) -> Gas phase flow	79

4.2 Safety measures by controlling hazards

The consideration of inherently safety measures such as reduction of inventory and substitute solvent are discussed in chapter 4.1. However, in case that it is difficult to implement those safety measures, it is necessary to reduce probabilities of accident to acceptable region by adding alarm or interlock system in the aspect of multiple protections. The example implemented such safety measures for model process by HAZchart analysis which is developed by Mitsubishi Chemical is shown. At first, the explanation of model process shown Figure 1 is described below. The reactor is a batch reactor, and after MEK (Methyl Ethyl Ketone) is charged in the reactor MEKPO is produced by dosing of hydrogen peroxide. The reaction is exothermic reaction and cooling water is fed to the jacket of the reactor, and temperature of the reactor is control by thermometer controlling valve opening degree of cooling water. The reflux is installed at the top of the reactor and cooling water of reflux flow constant flow rate. Nitrogen is fed into the gas phase of the reactor, at constant flow rate, because oxygen would be generated by decomposition of hydrogen peroxide or MEKPO production. The probabilities of accidents are calculated with assuming that the control valve of cooling water of reactor is closed, as the example of the calculation. If the cooling water is stopped while dosing hydrogen peroxide, the reactor would rupture by pressure-rise of runaway reaction. The alarms for reactor temperature detectors and reflux pressure detector are effective as safety measures at the current model process, and the probability is shown at the star described “original” in Figure 8. As the acceptable region is defined as green area, the current process is necessary to be carried out safety measures, and the considerations are described below from (A) to (C). First, safety measure (A), the flow meter is installed on the line of cooling water, and control of cooling water is changed to cascade control of temperature of the reactor and flow of the cooling water, and the interlock system which the feed valve of hydrogen peroxide is closed by 1 out of 2 of that temperature and flow detectors is added. The probability is not decreased greatly because one of the failure causes of the cooling water valve would be the detector of temperature and flow, and that are also used for the detector of interlock system. In the safety measure (B), the reflux pressure detector was added to interlock system. Though the probability is decrease because of increased detection equipment, it is not enough to reach the acceptable region on the risk matrix. In the safety measure (C), independent reactor temperature detector for interlock system is installed, and the shut valve for interlock system which MEKPO is fed into MEK storage tank also installed. As MEKPO is fed into MEK storage tank, concentration is diluted and temperature is cooled, and it is able to prevent occurrence of runaway reaction. The result of probability is reduced to acceptable region.

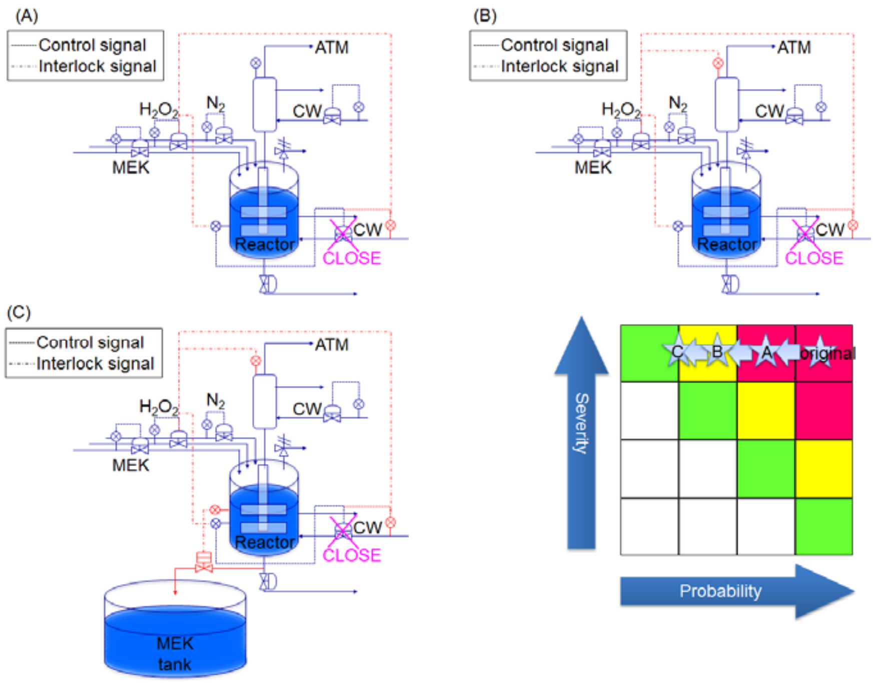

Figure 8: Implementation of safety measures and calculation results on risk matrix

5. Conclusions

The estimation of vent sizing and safety measures for MEKPO production reactor was considered in this study. The result of estimated vent size of the model reactor was unrealistically large in diameter. Two methods as safety measures are considered, inherently safety measures and safety measures by controlling hazard. Regarding inherently safety measures, reasonable vent size is obtained by changing solvent to low boiling point solvent, but the confirmation of productivity and quality is necessary. Regarding safety measures by controlling hazard, safety level of the model reactor was improved by adding detectors and interlock systems until reaching tolerant area. It is important to implement safety measures with considering process comprehensively, because available measures are limited by characteristics of processes or substances.

References

Hans K. Fauske, 2000, properly size vents for nonreactive and reactive chemicals, Chemical engineering progress

Jen-Hao Chi, Sheng-Hung Wu, 2009, Thermal explosion analysis of methyl ethyl ketone peroxide by non-iso thermal and isothermal calorimetric applications, Journal of hazardous materials, 171, 1145-1149

Jiann-Rong Chen, Jo-Ming Tseng, 2008, Adiabatic runaway studies for methyl ethyl ketone peroxide with inorganic acids by ven sizing package 2, Korean J. Chem. Eng., 25(3), 419-422

Po-Yin Yeh, Chi-Min Shu, 2003, Thermal hazard analysis of methyl ethyl ketone peroxide, Ind. Eng. Chem. Res., 42, 1-5