Hazards31
IChemE Safety Centre
IChemE ADVANCING CHEMICAL ENGINEERING WORLDWIDE

Detailed Analysis of Temperature and Pressure Behaviour During Reaction Runaway for Vent Sizing

Yuto Mizuta1)2), Motohiko Sumino1), Hiroaki Nakata1)
Yuichiro Izato2), Atsumi Miyake2)

1) Safety Engineering Technology Development Office,
Mitsubishi Chemical, Japan
2) Yokohama National University, Japan

Safety measures in the Chemical Plants

Post active

Proactive

Incidents

RESPONSE

LIMITATION

BARRIER

MITIGATIVE

PREVENTIVE

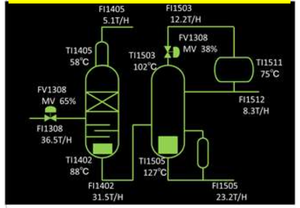
SUPERVISORY

CONTROL

DESIGN

Safety Valve

Interlock System



Alarm System

CCPS Guidelines for
safe automation of chemical processes

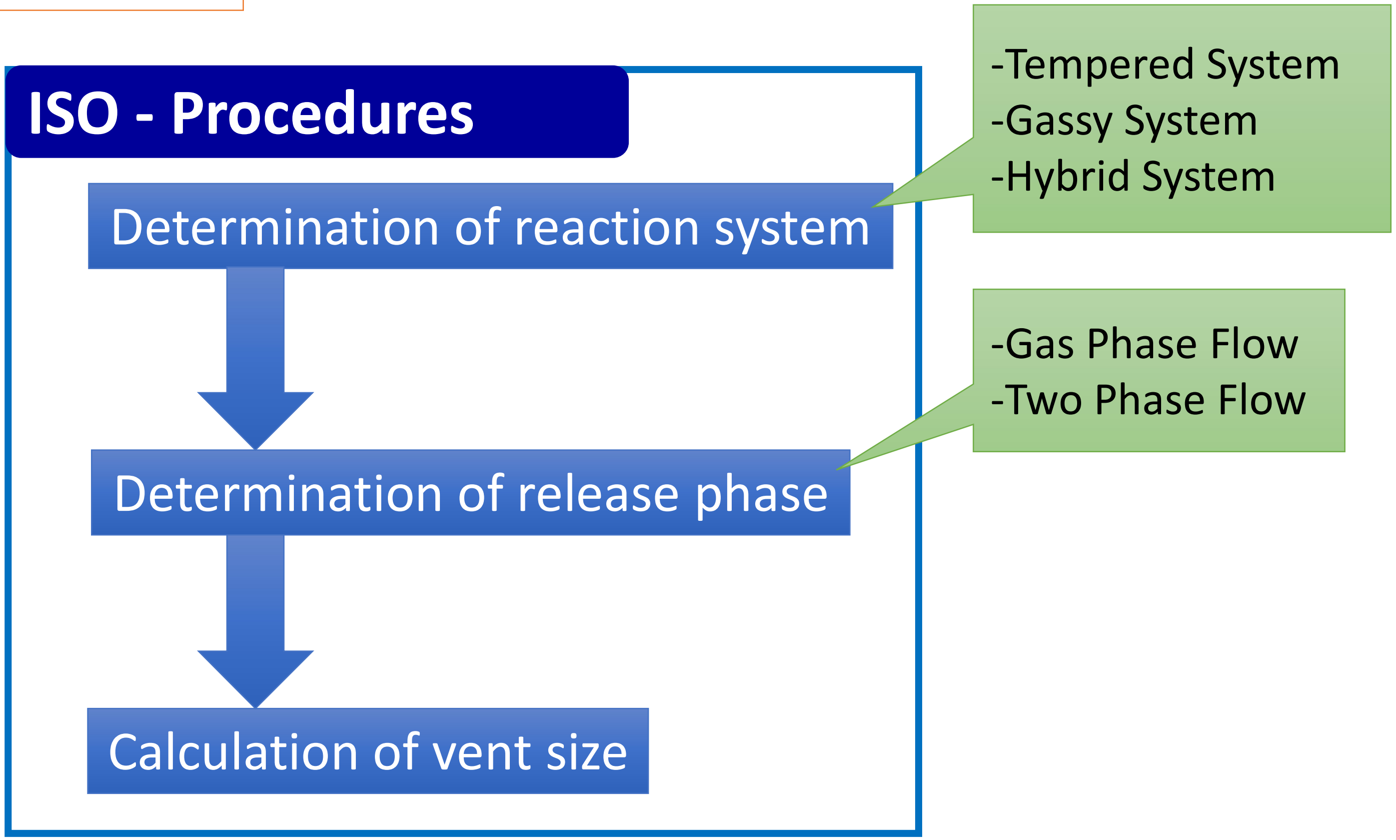
Hazards31

The regulations for vent sizing

Regulation of vent sizing for two-phase flow

- US: API STD 520 (2008)
- EU: ISO 4126-10 (2010)
- Japan: JIS B 8227 (2013)

Translated guideline of ISO



ISO - Procedures

Determination of reaction system

-Tempered System
-Gassy System
-Hybrid System

Determination of release phase

-Gas Phase Flow
-Two Phase Flow

Calculation of vent size

Hazards31

The features of ISO and actual process

ISO method

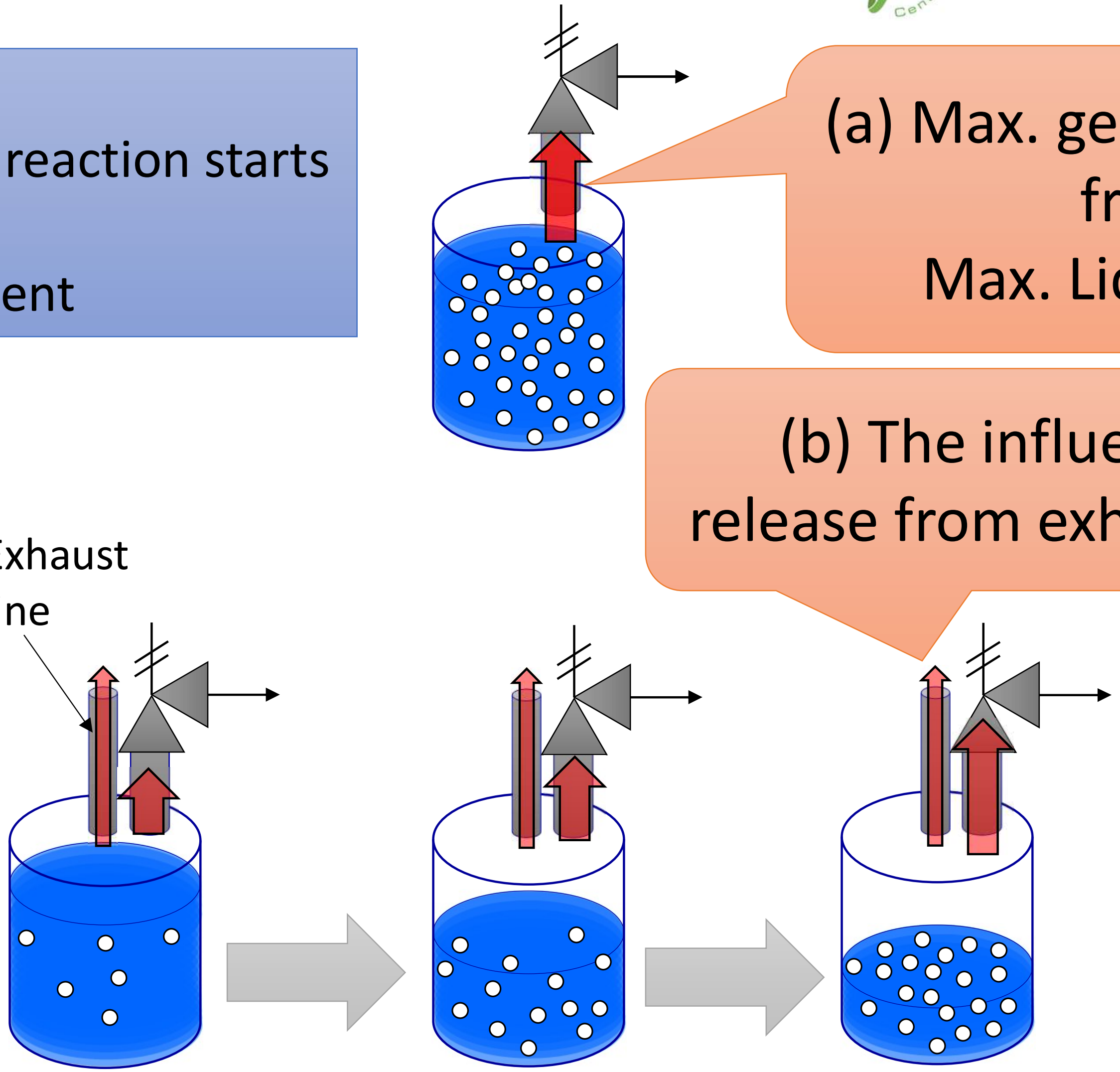
(a) The most violent runaway reaction starts at initial liquid level

(b) Assumed confined equipment

Actual processes

(a) Liquid decrease during runaway reaction

(b) Many equipment are unconfined



(a) Max. generation rate from Max. Liquid level

(b) The influence of release from exhaust line?

Model Process for dynamic simulation

IChemE Safety Centre

IChemE ADVANCING CHEMICAL ENGINEERING WORLDWIDE

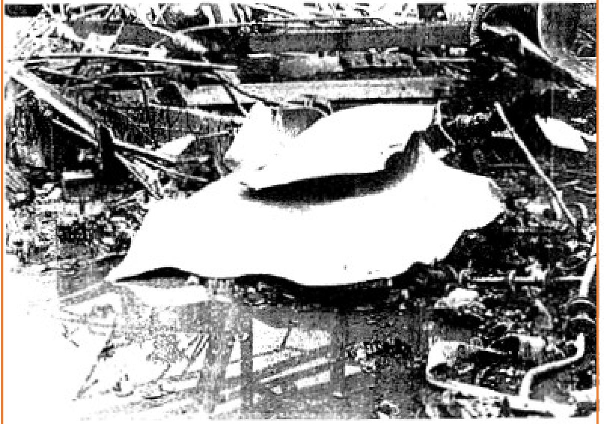
MEKPO thermal explosion incidents in Japan, Taiwan, Korea and China

Date	Country	City	Injuries	Fatalities
1964	Japan	Tokyo	114	19
1978	Japan	Kanagawa	0	0
1979	Taiwan	Taipei	49	33
1996	Taiwan	Taoyuan	47	10
2000	Korea	Yosu	11	3
2001	China	Jiangsu	2	4
2003	China	Zhejiang	3	5

Thermal Hazard Simulations for Methyl Ethyl Ketone Peroxide Induced by Contaminants Jo-Ming Tseng,
Korean J. Chem. Eng., 22(6), 797-802 (2005)

2000 in Korea

MEKPO plant after incident

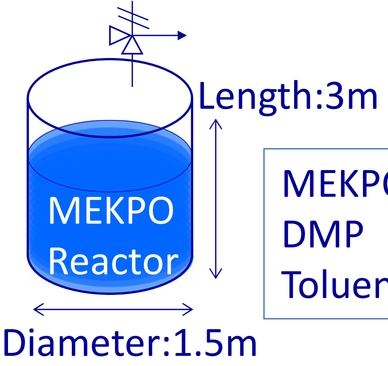


Exploded MEKPO vessel

古積博, 事故・災害事例とその対策, 安全工学会, p.67

Model Equipment

Safety Valve
Set Press: 400 kPag
Diameter: ?? mm

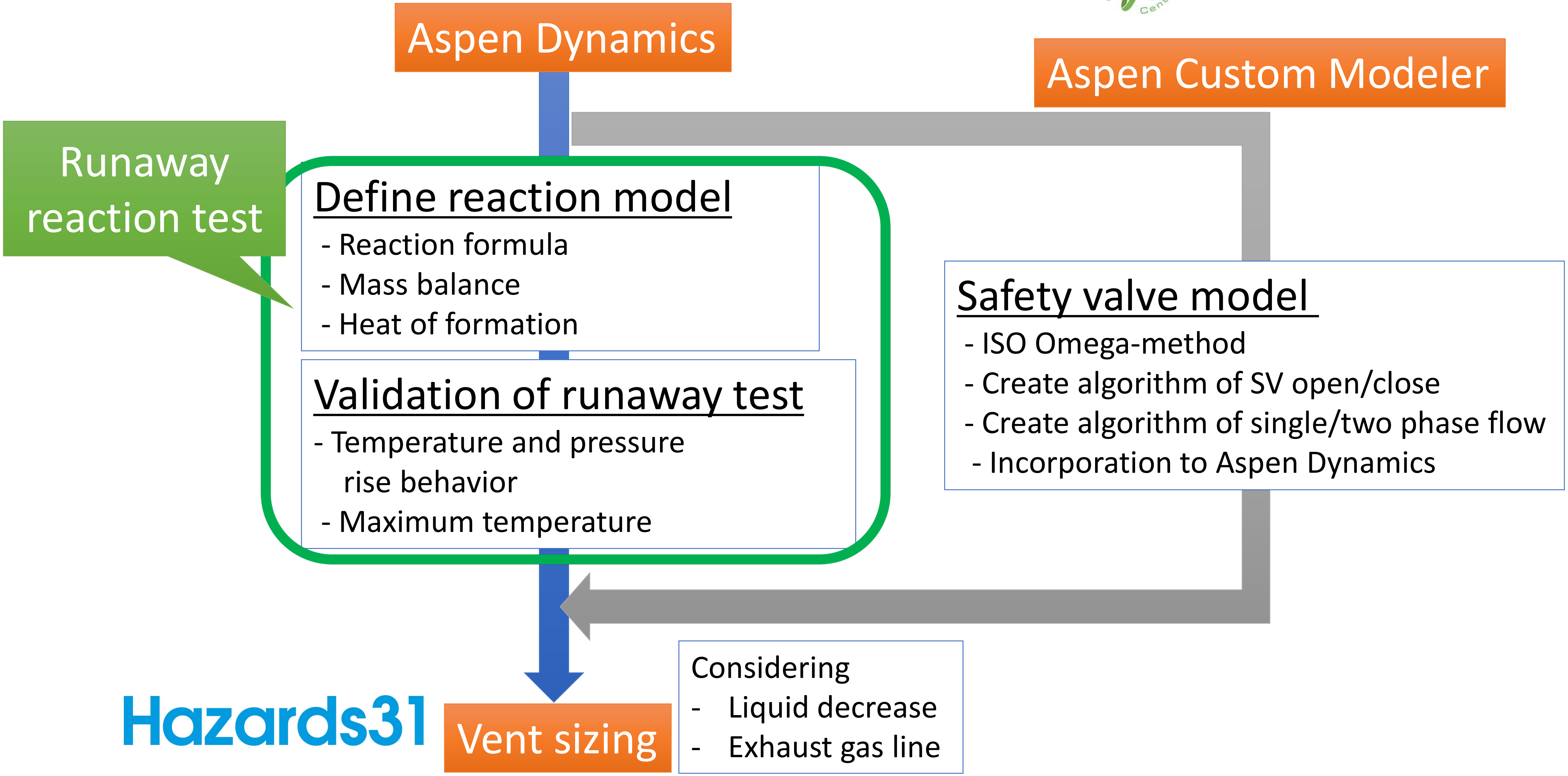


MEKPO	28wt.%
DMP	42wt.%
Toluene	30wt.%

Runaway reaction occur by loss of cooling system

Hazards31

Procedures of dynamic simulation



Aspen Dynamics

Aspen Custom Modeler

Runaway reaction test

Define reaction model

- Reaction formula
- Mass balance
- Heat of formation

Validation of runaway test

- Temperature and pressure rise behavior
- Maximum temperature

Safety valve model

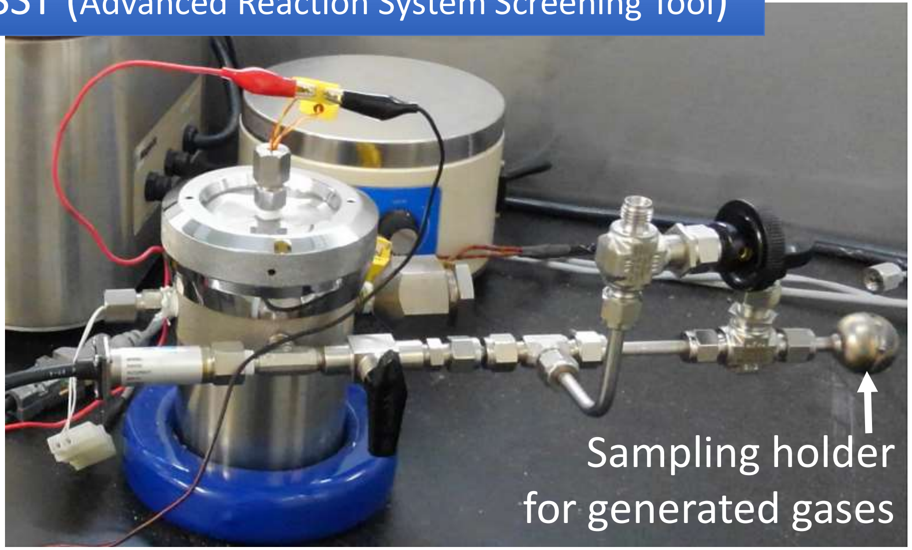
- ISO Omega-method
- Create algorithm of SV open/close
- Create algorithm of single/two phase flow
- Incorporation to Aspen Dynamics

Vent sizing

Considering
- Liquid decrease
- Exhaust gas line

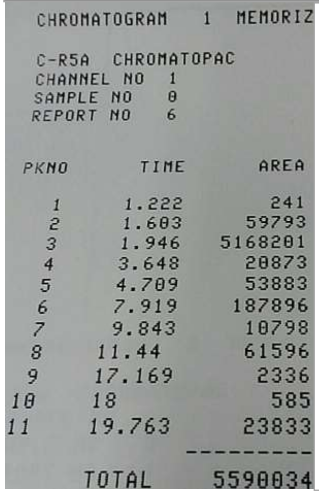
Definition of products and mass balance

ARSST (Advanced Reaction System Screening Tool)



Sampling holder
for generated gases

Gas chromatography



```
CHROMATOGRAM    1  MEMORIZ

 C-R5A  CHROMATOPAC
 CHANNEL NO   1
 SAMPLE NO    0
 REPORT NO    6


PKNO        TIME         AREA

   1       1.222          241
   2       1.603        59793
   3       1.946      5168201
   4       3.648        20873
   5       4.709        53883
   6       7.919       187896
   7       9.843        10798
   8      11.44         61596
   9      17.169         2336
  10      18              585
  11      19.763        23833
                    ---------
        TOTAL         5590034
```

Composition(%)

H2	3
O2	18
CO	15
CO2	44
C1	7
C2	11

$$MEKPO \rightarrow \underbrace{n_1H_2 + n_2O_2 + n_3CO + n_4CO_2 + n_5CH_4 + n_6C_2H_6}_{\text{Gas phase}} + \underbrace{n_7RESIDUE}_{\text{Liquid phase}}$$

$C_xH_yO_z$
x, y, z: decimal number

- Reaction Formula
- Mass Balance
- Heat of Formation of MEKPO and RESIDUE

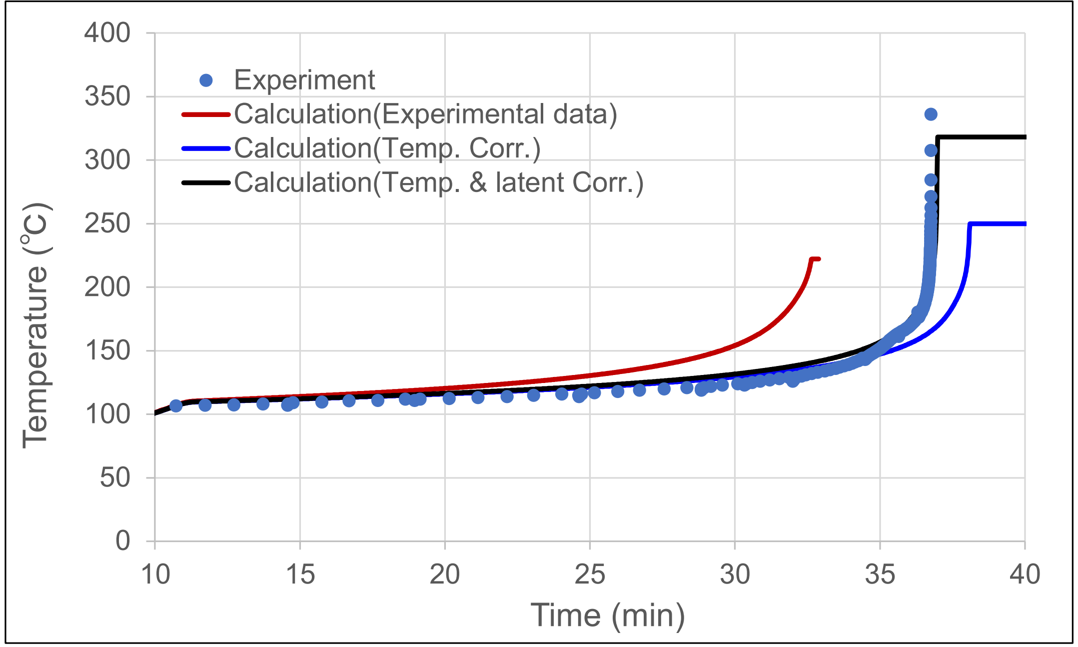
Hazards31

Definition of reaction rate

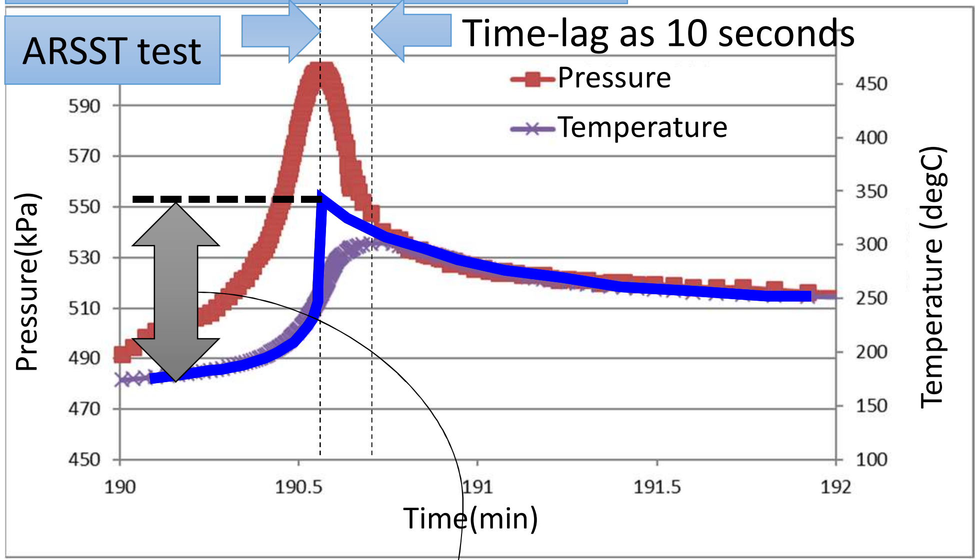
Arrhenius type equation with thermal conversion by ARSST test

$$\frac{dr}{dt} = \frac{d}{dt}\left\{ n_0\Big|_{MEKPO}\left(1-\frac{T-T_0}{\Delta T_{\max}}\right)\right\} = A_{pre}\exp\left(\frac{-Ea}{RT}\right)$$

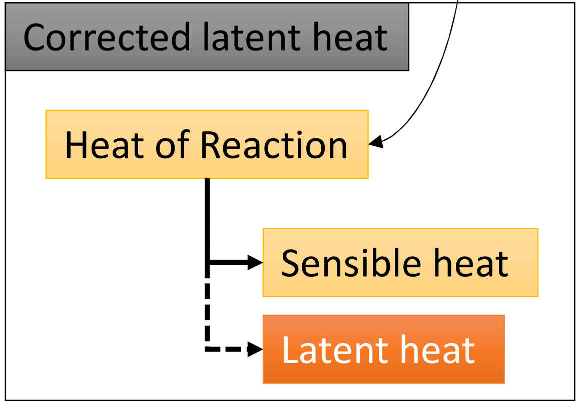
Comparison among experimental data and calculations



Corrected temperature time-lag



Corrected latent heat

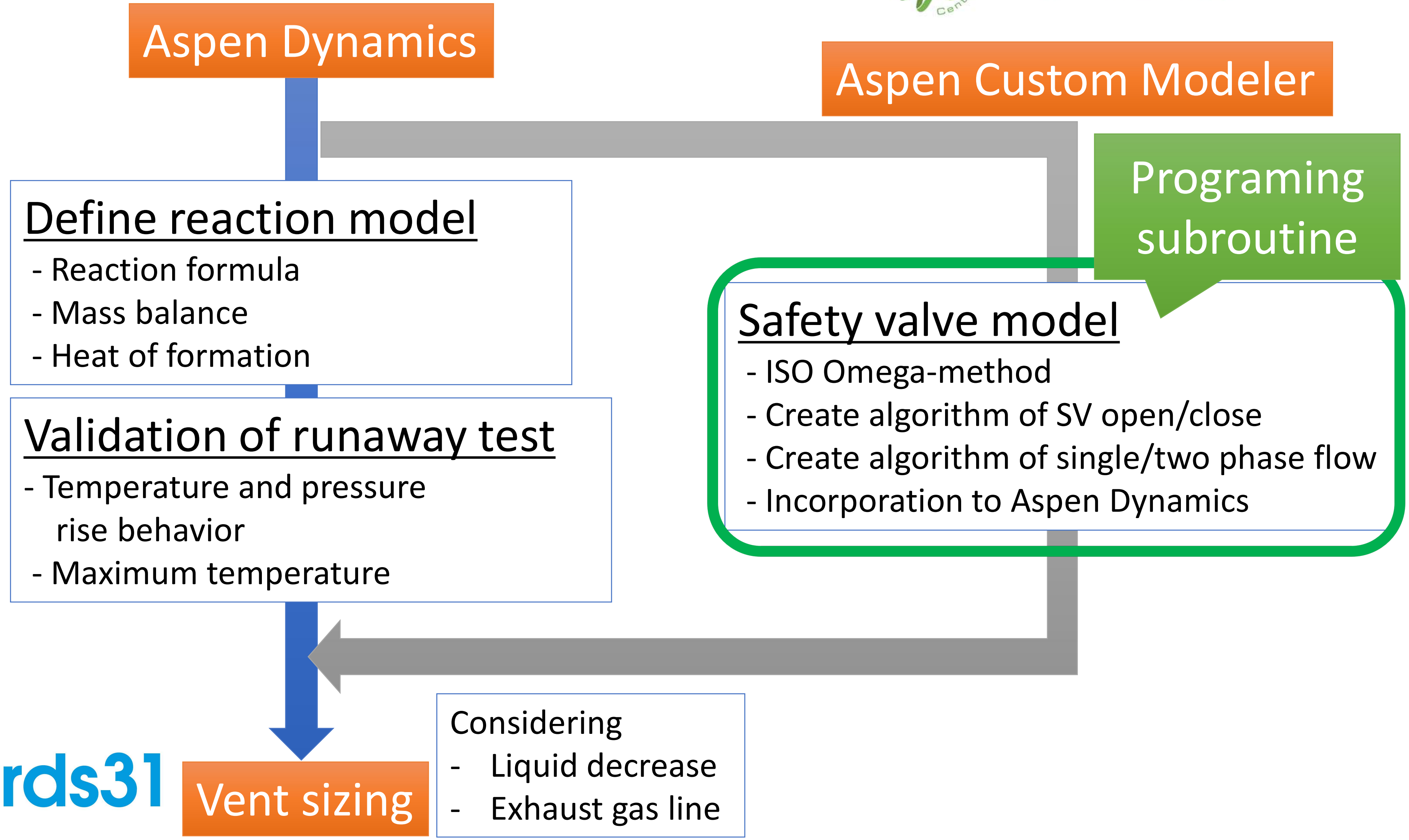


Heat of Reaction

Sensible heat

Latent heat

Procedures of dynamic simulation



Aspen Dynamics

Define reaction model
- Reaction formula
- Mass balance
- Heat of formation

Validation of runaway test
- Temperature and pressure rise behavior
- Maximum temperature

Aspen Custom Modeler

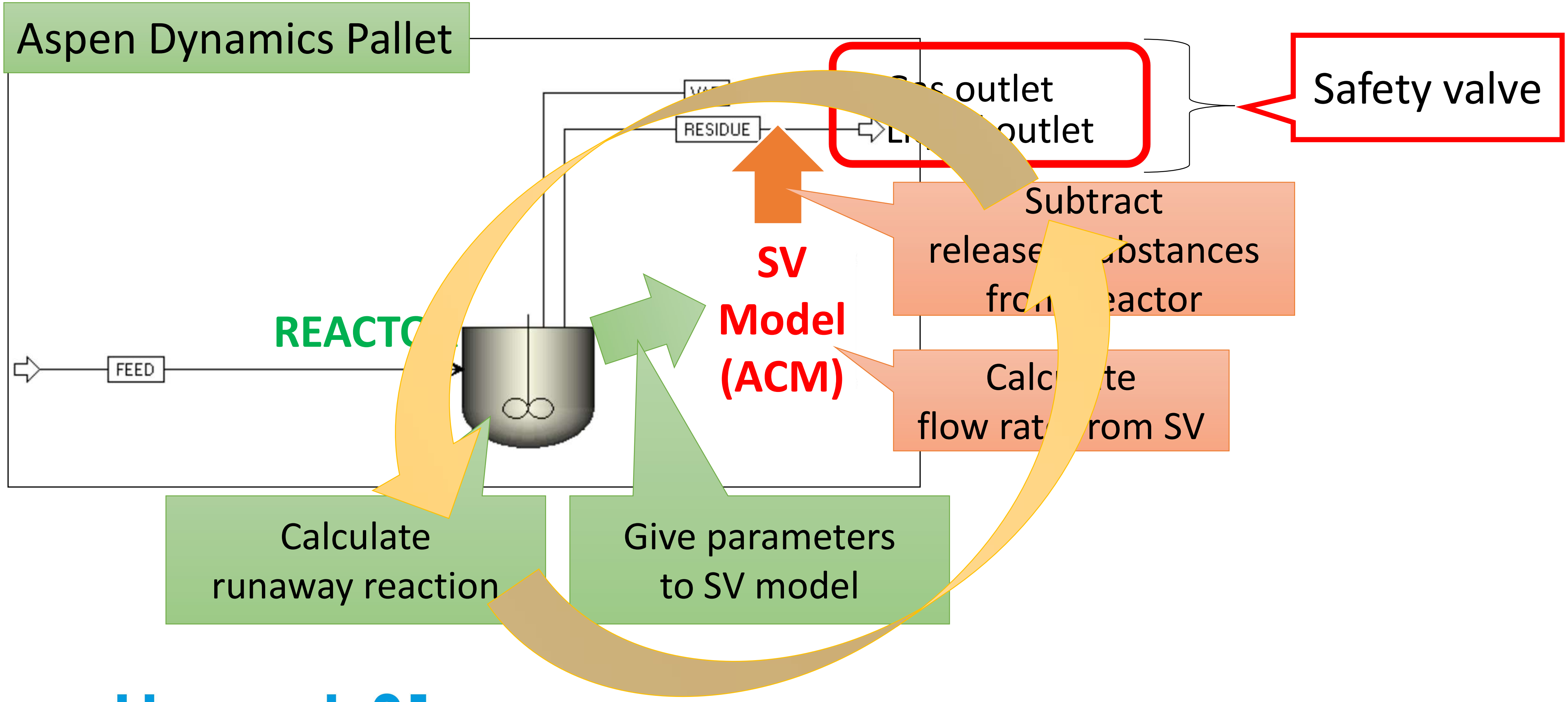
Programing subroutine

Safety valve model
- ISO Omega-method
- Create algorithm of SV open/close
- Create algorithm of single/two phase flow
- Incorporation to Aspen Dynamics

Vent sizing

Considering
- Liquid decrease
- Exhaust gas line

Interaction of Aspen Dynamics and ACM



Aspen Dynamics Pallet

REACTOR

Gas outlet
Liquid outlet

Safety valve

SV Model (ACM)

Subtract release substances from reactor

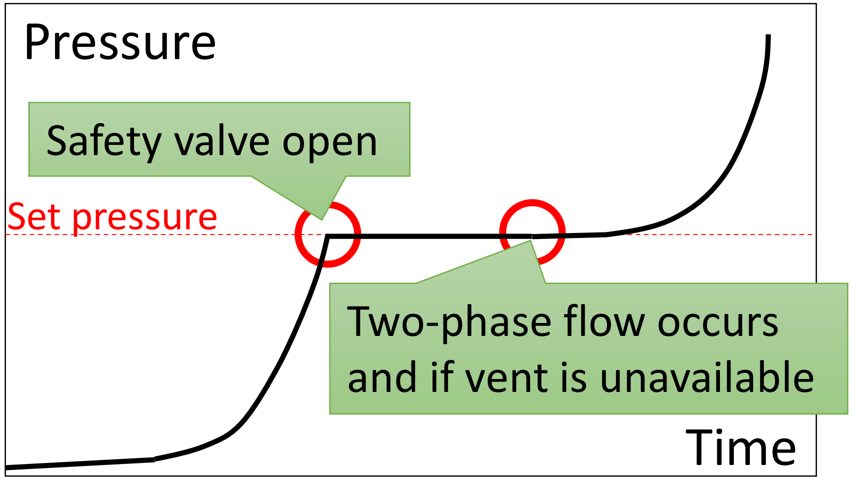
Calculate flow rate from SV

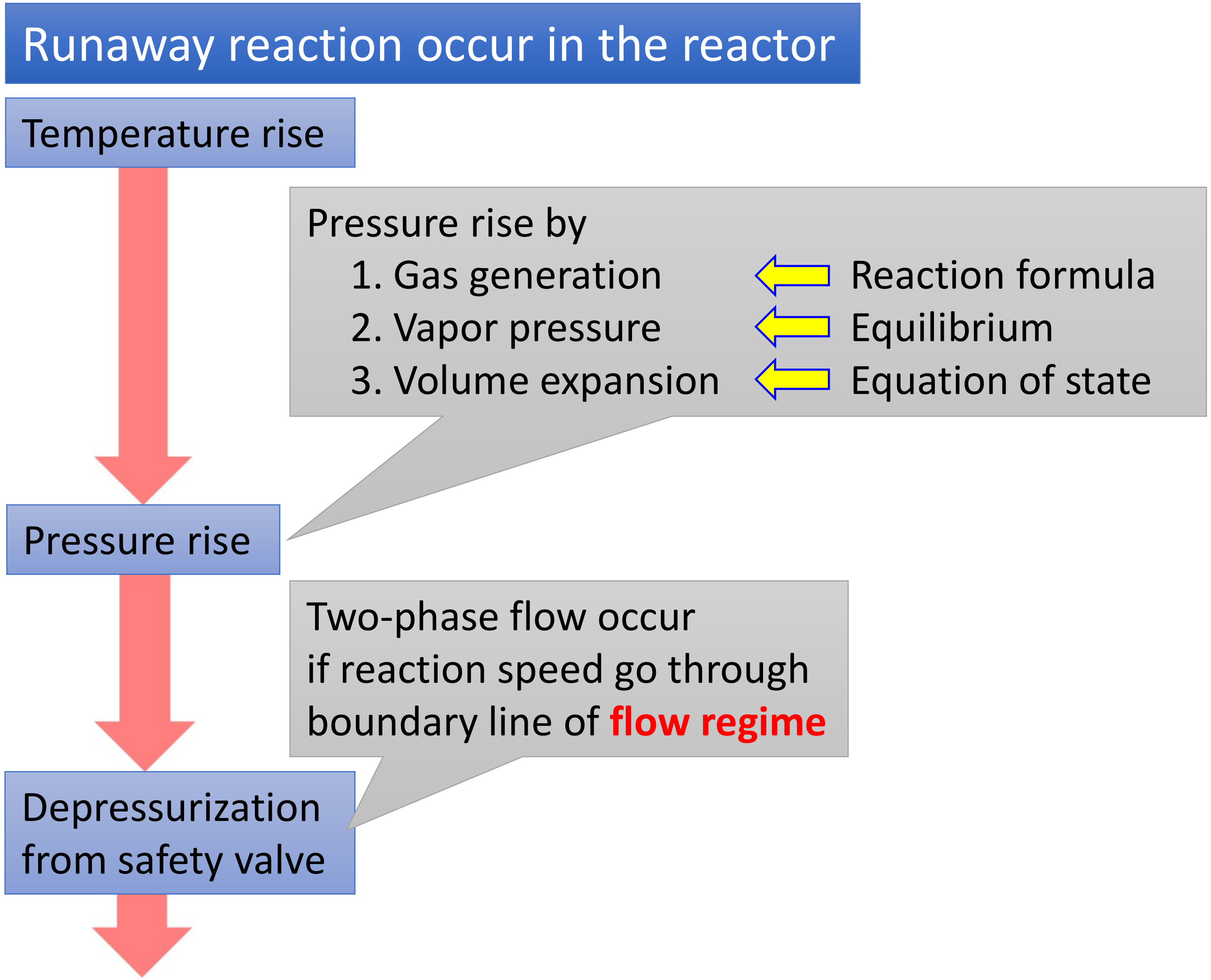
Calculate runaway reaction

Give parameters to SV model

Runaway reaction in the reactor

Pressure in the reactor





Runaway reaction occur in the reactor

Temperature rise

Pressure rise by
1. Gas generation ⇦ Reaction formula
2. Vapor pressure ⇦ Equilibrium
3. Volume expansion ⇦ Equation of state

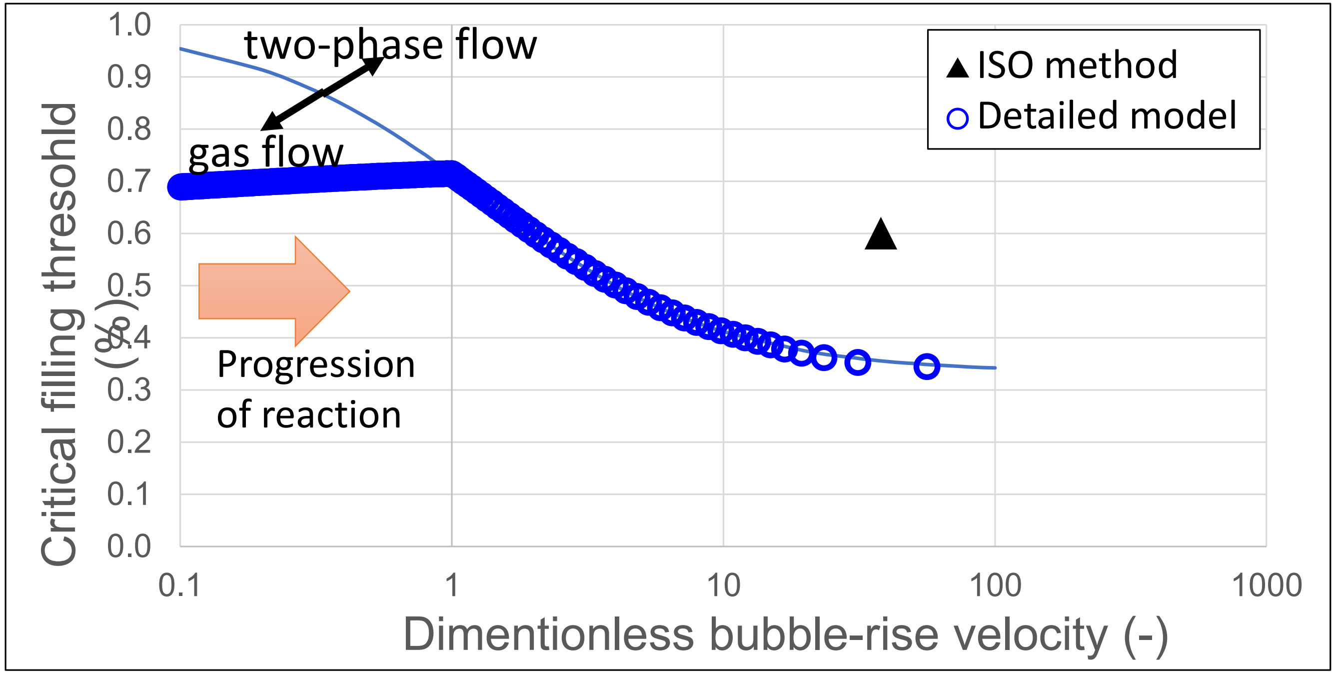
Pressure rise

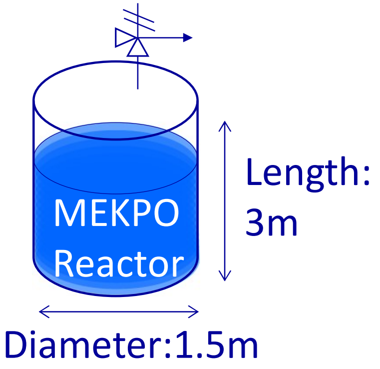
Two-phase flow occur
if reaction speed go through
boundary line of **flow regime**

Depressurization
from safety valve

Runaway behavior on flow regime and estimated vent size

Flow regime for occurrence of two-phase flow





Analysis method	Vent size [m]
ISO method	1.9
Detailed model	0.5

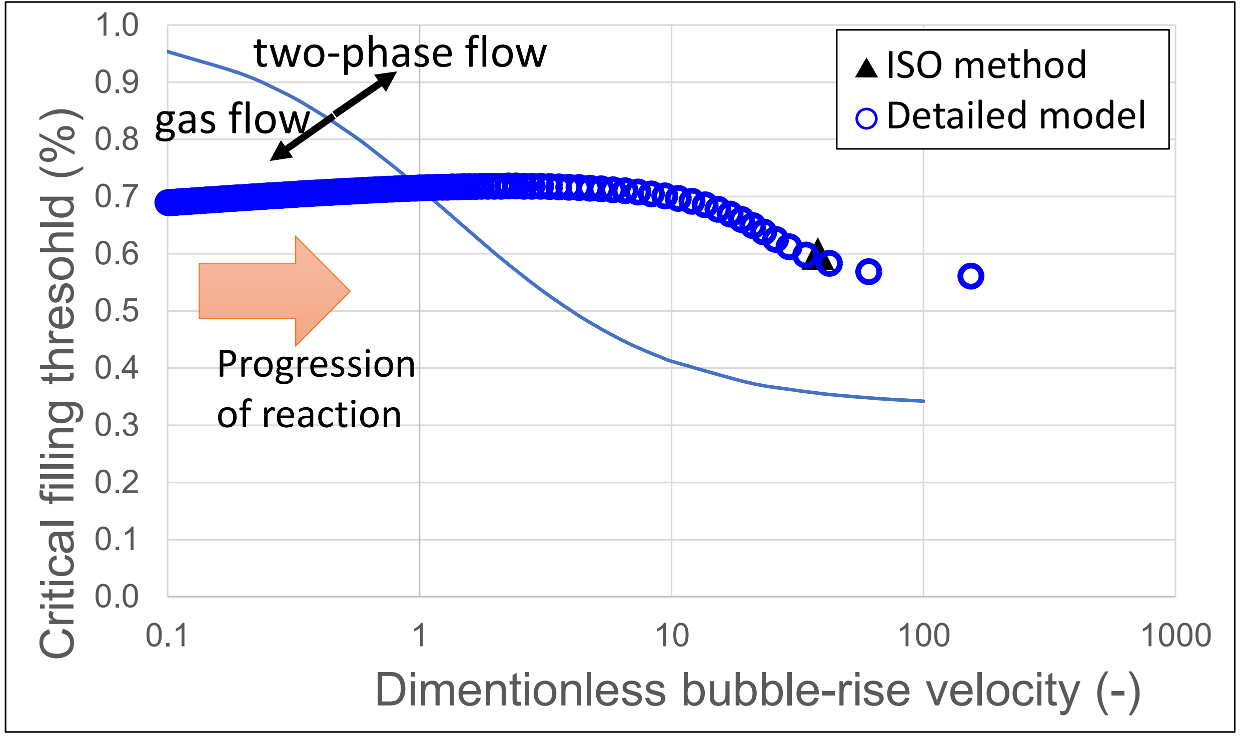
Hazards31

Considering liquid decrease gives reasonable vent size

Comparison of gas and vapor generation rate

In detailed model, liquid did not release for comparison to ISO

Flow regime for occurrence of two-phase flow



No liquid release

	ISO method	Detailed model
Gas generation rate [kg/sec]	79	64
Vaporization rate [kg/sec]	-	320
Vent size [m]	1.9	3.1

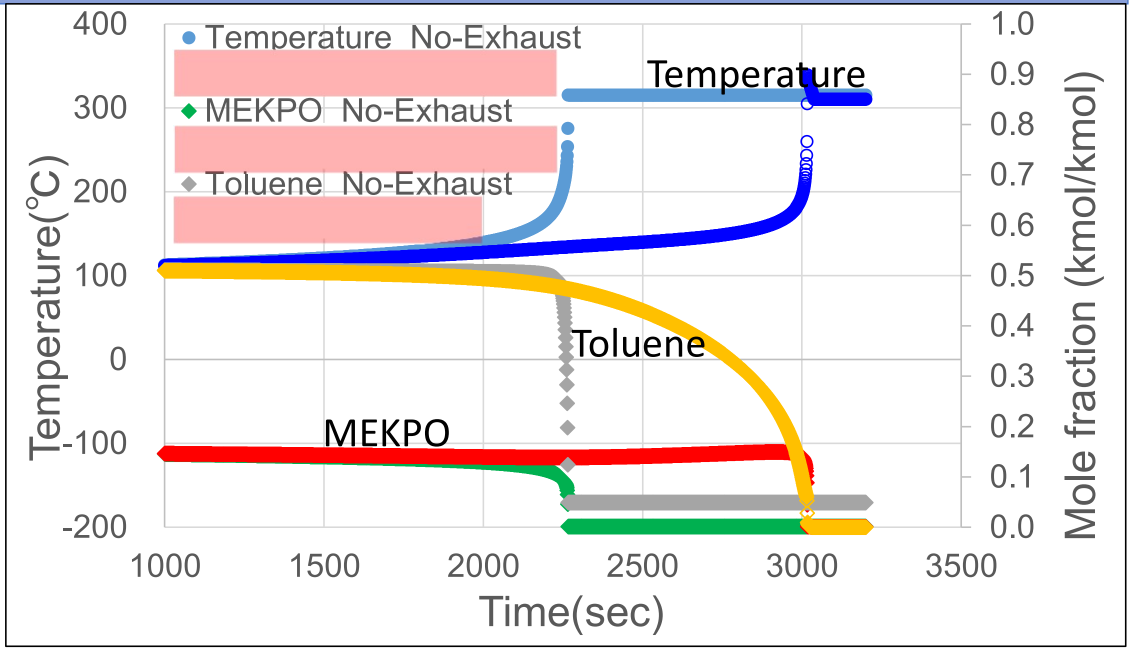
Hazards31

ISO-ARSST not considering vaporization rate could underestimate vent size

Vent sizing considering exhaust gas line

	Confined reactor	with exhaust gas line
Max. temperature [℃]	315	339
Gas generation rate [kg/sec]	19	56
Vaporization rate [kg/sec]	129	238
Vent size [m]	0.5	0.7

Temperature and concentration in runaway reaction



All vaporization of solvents leads to concentrate reactive chemicals and required vent size was larger

Hazards31

Summary and future work

Summary

- Detailed model considering liquid decrease and exhaust gas line is developed
- Considering liquid decrease gives reasonable vent size
- ISO-ARSST not considering vaporization rate could underestimate vent size
- All vaporization of solvents leads to concentrate reactive chemicals and required vent size was larger

Future work

- Small-scale runaway reaction experiment
- Enhance for monomer and foamy substances

Thank you for your attention!

Yuto Mizuta
mizuta.yuto.ma@m-chemical.co.jp
Safety Engineering Technology Development Office,
Mitsubishi Chemical, Japan

Hazards31