

Forget Direct Scale-up Vent Sizing and Master Kinetic Modeling Instead

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**Forget Direct Scale-up Vent Sizing
and
Master Kinetic Modeling Instead**

Process Safety and Risk Management Practices

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1 Direct Scale-up vs. Kinetic Modeling

Direct scale-up methods have been used to develop relief requirements and vent sizing for runaway reactions since the early 1990s. Direct scale-up methods have been popular because one is able to measure in a laboratory test the required relief size in equivalent vent area per unit mass of a reacting mixture, in^2/kg , and then scale it up to plant scale equipment sizes.

The primary advantage of the direct scale-up methods is simplicity. The user does not have to provide thermodynamic, physical, and transport properties or use complex models for relief sizing. However, direct scale-up methods have a lot of disadvantages and are not capable of providing all the information for safe and optimal design that is now required by recognized and generally accepted good engineering practice (RAGAGEP) [1, 2, 3].

Direct scale-up methods are only valid at the conditions of the test. This includes but is not limited to fill level, relief set pressure, chemical composition, heating rate, and vapor/liquid disengagement characteristics of the test cell and associated vent. Additional tests have to be conducted if different conditions need to be considered. This can be costly both in resources and schedules.

Direct scale-up methods can result in overly conservative venting requirements, especially for gassy systems [4]. While this may be considered to be favorable for vessel protection, an oversized vent can cause safety complications for PRV stability, structural supports, effluent handling, and subsequent safe discharge location for flammable or toxic dispersion [3]. A bigger vent is not necessarily better.

Kinetic modeling methods for pressure relief couple detailed chemical reaction models with fluid dynamics to develop the required vent size. These methods have also been in use since the early 1990s when the American Institute of Chemical Engineers (AIChE) first developed the computer program SAFIRE [5] through its Design Institute for Emergency Relief Systems (DIERS). SAFIRE was later replaced with SuperChemsTM for DIERS¹ by Arthur D. Little Inc. under a contract to AIChE DIERS.

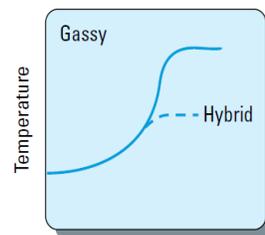
Kinetic modeling methods for pressure relief and effluent handling systems are highly recommended because of their inherent advantages over direct scale-up methods [6]. Once a detailed kinetic model is developed, it can be used over and over again in many process design and modeling applications.

2 Fauske's Direct Scale-up Screening Method

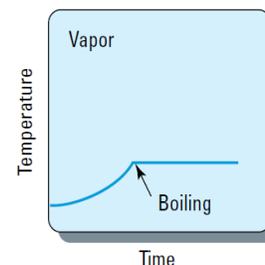
Fauske [7, 8] made notable contributions to twophase flow methods and emergency relief systems design for runaway reactions. Fauske developed semi-empirical vent sizing screening methods based on direct scale-up. These methods gained popularity because of their simplicity. Fauske's vent sizing methods differentiated between three different types of reactions, "vapor", "gassy", and "hybrid".

¹SuperChems is a trademark of ioMosaic Corporation

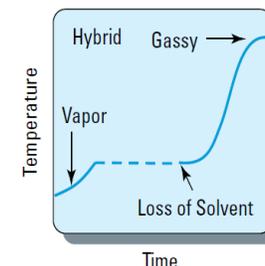
Certain types of liquid reactions use available reaction energy to generate gaseous non-condensable reaction products such as hydrogen, nitrogen, etc. These reactions are referred to as “gassy” reactions. The total pressure reached in the vessel is equal to the gas pressure, i.e. pressure rises in the vessel due to mass addition in the vapor space.



Other types of liquid reactions use their reaction energy to supply boiling energy for the liquid causing the formation of vapor, i.e. the heat of reaction is removed by the internal energy of vaporization. The reaction is therefore referred to as “vapor” or “tempered” by the heat of vaporization of the liquid. The total pressure in the vessel at any time is equal to the vapor pressure of the liquid.



Hybrid reaction systems possess “vapor” and “gassy” features. Non-condensable gaseous products are formed prior to boiling, but the reaction is also “tempered” by vapor generation and depletion. The total pressure in the vessel is the sum of the liquid vapor pressure and the gas partial pressure.



For gassy systems, the rate of pressure rise is most important in finding venting requirements. For vapor systems, the rate of temperature rise at the liquid saturation temperature corresponding to the vent set pressure or peak relief pressure is the most important in determining relief requirements.

For hybrid systems, both the temperature and pressure rise rates at the tempering conditions are required to determine relief requirements.

Fauske's most widely used screening equation for estimating the relief requirement for a runaway reaction is detailed in Equation 1 assuming choked (sonic) all vapor venting:

$$\frac{A_{e,T}}{V_l} = \left(\frac{1}{C_d} \right) \left(\frac{C_o}{P} \right) \underbrace{\left(\frac{1}{\left[1 + \frac{1980}{P^{1.75}} \right]^{0.286}} \right)}_{C_2} \left[a_1 \underbrace{\left(\frac{dT}{dt} \right)}_{q(T)} + a_2 \left(\frac{dP}{dt} \right)_{\max, RSST} (1 - \bar{\alpha}_D) \right] \quad (1)$$

where a_1 and a_2 are defined in Table 1, $A_{e,T}$ is the required vent area in m^2 , V_l is the volume of reactants at commercial scale in m^3 , C_d is the discharge coefficient accounting for overall relief piping flow resistance, C_o is a flow type coefficient normally set to 3.5×10^{-3} , P is the set pressure or peak relief pressure in psig, $q(T) = \frac{dT}{dt}$ is the reaction heating rate at tempering condition or turn around condition in $^{\circ}\text{C}/\text{min}$, $\frac{dP}{dt}$ is the maximum rate of pressure rise in psi/min assuming an RSST containment volume of 350 ml with a 10 g sample, and $\bar{\alpha}_D$ is the complete disengagement average volumetric void fraction. The factor C_2 seems to be an empirical adjustment factor added later on by Fauske [7] to Equation 1 in order to better align the predictions of Equation 1 with test and/or incident data.

Table 1: Equation 1 a_1 and a_2 parameter values for vapor, gassy, and hybrid reactions

System	$\frac{dT}{dt}$ multiplier a_1	$\frac{dP}{dt}$ multiplier a_2
Vapor (non-foamy) - Use with $C_o = 3.5 \times 10^{-3}$	1	0
Vapor (foamy) - Use with $C_o = 7.0 \times 10^{-3}$	1	0
Gassy	0	1
Hybrid	1	1

For vapor systems it is recommended to allow for an overpressure of approximately 40 % on an absolute basis relative to the relief device set pressure.

Fauske [7] recommends the use of Equation 1 where detailed kinetics and physical properties information are not available at emergency relief conditions. We note that physical properties, process information, and chemical reactivity data are required compliance process safety information (PSI) for facilities covered by the OSHA PSM regulation[9] in the US.

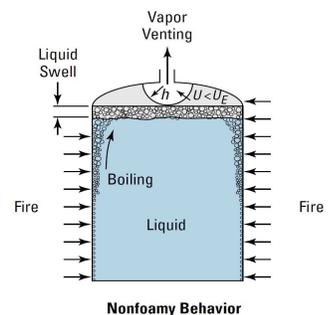
Fauske's screening method (Equation 1) is not meant to be a replacement for accurate methods where kinetics and physical properties are used to calculate emergency relief requirements.

Equation 1 can be used to estimate relief requirements for all three types of reaction systems as shown in Table 1. The recommended value of C_o by Fauske [7] is:

$$C_o = 3.5 \times 10^{-3} \text{ for churn turbulent or non-foamy systems} \quad (2)$$

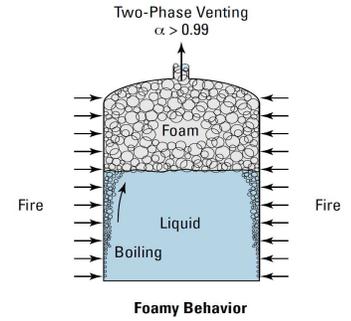
$$C_o = 7.0 \times 10^{-3} \text{ for foamy or homogeneous like systems} \quad (3)$$

It is interesting to note that using a C_o value of 7.0×10^{-3} produces twice the all vapor vent requirement of a churn turbulent or non-foamy system^a. The use of Equation 1 with a $C_o = 3.5 \times 10^{-3}$ requires the absence of vapor generation throughout the bulk of the liquid or volumetric boiling.



^aAssumes an allowance of 40 % overpressure (on an absolute basis) relative to relief device set point. At an allowance of 20 %, C_o should be multiplied by another factor of three (see Section 5 and Figure 3).

Fauske [7] argues that a reaction rate of approximately 20 °C/min or more is required to cause bulk volume boiling and that liquid swell due to wall heating from a fire exposure scenario is not sufficient to cause bulk volume boiling for large vessels without a chemical reaction.



$\bar{\alpha}_D$ is preferably obtained from an actual blowdown test using the VSP or APTAC calorimeters:

$$\bar{\alpha}_D = \frac{V_{TE} - V_l}{V_{TE}} \quad (4)$$

where V_{TE} is the actual (in some cases deformed) empty volume of the test cell at the end of the calorimetry test and V_l is the volume of the sample left over in the test cell at the end of the test. Alternatively, $\bar{\alpha}_D$ can be calculated from the DIERS α vs. ψ chart or the DIERS coupling equation [10, 11]. Setting the value of $\bar{\alpha}_D$ to zero yields the largest relief requirement. For gassy systems, Fauske [7] recommends setting $\bar{\alpha}_D$ to the initial void fraction, α_o .

The pressure rise rate value $\frac{dP}{dt}$ has to be corrected for the type of instrument used. When the VSP or VSP2 is used, the value of $\frac{dP}{dt}$ used in Equation 1 becomes:

$$\left(\frac{dP}{dt}\right)_{\text{RSST}} = \left(\frac{dP}{dt}\right)_{\text{VSP}} \left(\frac{3800}{350}\right) \left(\frac{m_{\text{RSST}}}{m_{\text{VSP}}}\right) \quad (5)$$

where m_{VSP} is the VSP sample mass, normally 60 g, and m_{RSST} is the RSST sample mass, normally 10 g.

3 The Origin of Fauske's Method

If we consider a liquid system where vapor venting is driven by heat addition to the system because of a chemical reaction, or fire exposure, and/or other means of adding heat to the system, we can estimate the volumetric vapor generation, \dot{V}_v , using the following equation:

$$\dot{V}_v = \frac{V_l \rho_l c_{v,l} q(T)}{\lambda \rho_v} \quad (6)$$

where V_l is the total liquid volume in m^3 , ρ_l is the liquid mass density in kg/m^3 , $c_{v,l}$ is the liquid specific heat capacity at constant volume in $\text{J}/\text{kg}/\text{K}$, λ is the internal energy heat of vaporization in J/kg , ρ_v is the vapor mass density in kg/m^3 , and $q(T)$ is the rate of heating in K/s given by the following equation for a chemical reaction:

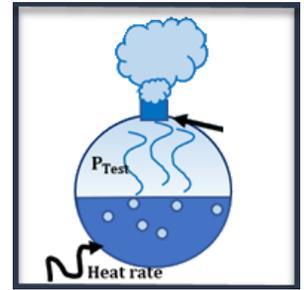
$$q(T) = \Delta T_{ad} \frac{dx}{dt} = -\frac{\Delta_{e,rxn}}{c_{v,l}} \frac{dx}{dt} = \frac{dT}{dt} \quad (7)$$

where $\Delta_{e,rxn}$ is the specific heat of reaction in J/kg, x is the chemical reaction degree of conversion ranging from 0 to 1, and ΔT_{ad} is the overall adiabatic temperature rise in K.

For all vapor venting, Fauske proposes a required vent area proportional to the measured vapor volumetric generation rate using the RSST open test cell calorimeter:

$$A_{e,v} = \frac{\dot{V}_v}{0.61C_d} \left[\frac{\rho_v}{P} \right]^{1/2} \quad (8)$$

where $A_{e,v}$ is the required vent area in m^2 and P is the relief pressure in Pa. Open test cell data may not provide the correct vapor generation rate if the flow through the test cell opening is choked. Where the flow is choked out of the test cell, the rate of pressure rise in the containment vessel can be underestimated.



Assuming ideal gas behavior, $A_{e,v}$ can be expressed as follows:

$$\frac{A_{e,v}}{V_l} = \left(\frac{1}{C_d} \right) \left(\frac{C_{o,v}}{P} \right) q(T) \quad (9)$$

where $C_{o,v}$ is given by:

$$C_{o,v} = \frac{\rho_l c_{v,l}}{0.61\lambda} \left[\frac{R_g T}{M_{w,v}} \right]^{1/2} \quad (10)$$

Using properties for water at 100 °C ($\rho_l = 1000 \text{ kg/m}^3$, $T = 373 \text{ K}$, $c_{v,l} = 4200 \text{ J/kg/K}$, $\lambda = 2.2 \times 10^6 \text{ J/kg}$, and $M_{w,v} = 18 \text{ kg/kmol}$), we calculate a value of $C_{1,v} \simeq 3.14 \times 10^{-3}$ where the scaled vent area requires P to be in psia and $q(T)$ is in °C/min:

$$\frac{A_{e,v}}{V_l} = \left(\frac{1}{C_d} \right) \left(\frac{C_{o,v}}{P} \right) q(T) \text{ where } q(T) \equiv \text{°C/min and } P \equiv \text{psia} \quad (11)$$

Fauske argues that the value of $C_{o,v}$ does not vary significantly for different chemicals (see [12]). However, a value of 3.5×10^{-3} is not representative of a wide range of chemicals as shown in Figures 1 and 2.

For a gassy system, the gas volumetric production rate, \dot{V}_g , is measured using the RSST calorimeter with an open test cell. \dot{V}_g is calculated using direct scale-up by:

$$\dot{V}_g = V_{\text{RSST}} \frac{dP}{dt} \frac{\rho_l V_l}{P m_{\text{RSST}}} \quad (12)$$

where $V_{\text{RSST}} = 3.5 \times 10^{-4} \text{ m}^3$ (350 ml) and $m_{\text{RSST}} \simeq 10 \times 10^{-3} \text{ kg}$ (10 g). As a result, the scaled required vent area, $A_{e,g}$, is given by:

$$\frac{A_{e,g}}{V_l} = \frac{1}{0.61C_d} \frac{\rho_l V_{\text{RSST}}}{m_{\text{RSST}} P} \frac{dP}{dt} \left[\frac{M_{w,g}}{R_g T} \right]^{1/2} \quad (13)$$

We can recast Equation 13 to be expressed like Equation 9:

$$\frac{A_{e,g}}{V_l} = \left(\frac{1}{C_d}\right) \left(\frac{C_{o,g}}{P}\right) \frac{dP}{dt} \text{ where } \frac{dP}{dt} \equiv \text{psi/min and } P \equiv \text{psia} \quad (14)$$

where $C_{o,g}$ is given by:

$$C_{o,g} = \frac{1}{0.61} \frac{\rho_l V_{RSST}}{m_{RSST}} \left[\frac{M_{w,g}}{R_g T}\right]^{1/2} \quad (15)$$

Assuming a gas (CO_2) molecular weight $M_{w,g} = 44$, we calculate a value of $C_{o,g} \simeq 3.5 \times 10^{-3}$. We note that $C_{o,v}$ and $C_{o,g}$ have different units. Fauske adds the vapor vent area requirement to the gas vent area requirement and presents one overall equation for a hybrid system where C_o , a_1 and a_2 values are shown in Table 1:

$$\frac{A_{e,T}}{V_l} = \left(\frac{1}{C_d}\right) \left(\frac{C_o}{P}\right) \left[a_1 q(T) + a_2 \frac{dP}{dt} \right] \quad (16)$$

where $q(T)$ is in $^{\circ}C/\text{min}$, $\frac{dP}{dt}$ is in psi/min , and P is the relief set pressure or peak venting pressure in psia. This is the same equation as shown in Equation 1 without the empirical factor C_2 . Fauske also presented a similar equation for highly subsonic flow:

$$\frac{A_{e,T}}{V_l} = \left(\frac{1}{C_d}\right) \left(\frac{C_o}{\Delta P^{1/2}}\right) \left[a_1 q(T) + a_2 \frac{dP}{dt} \right] \quad (17)$$

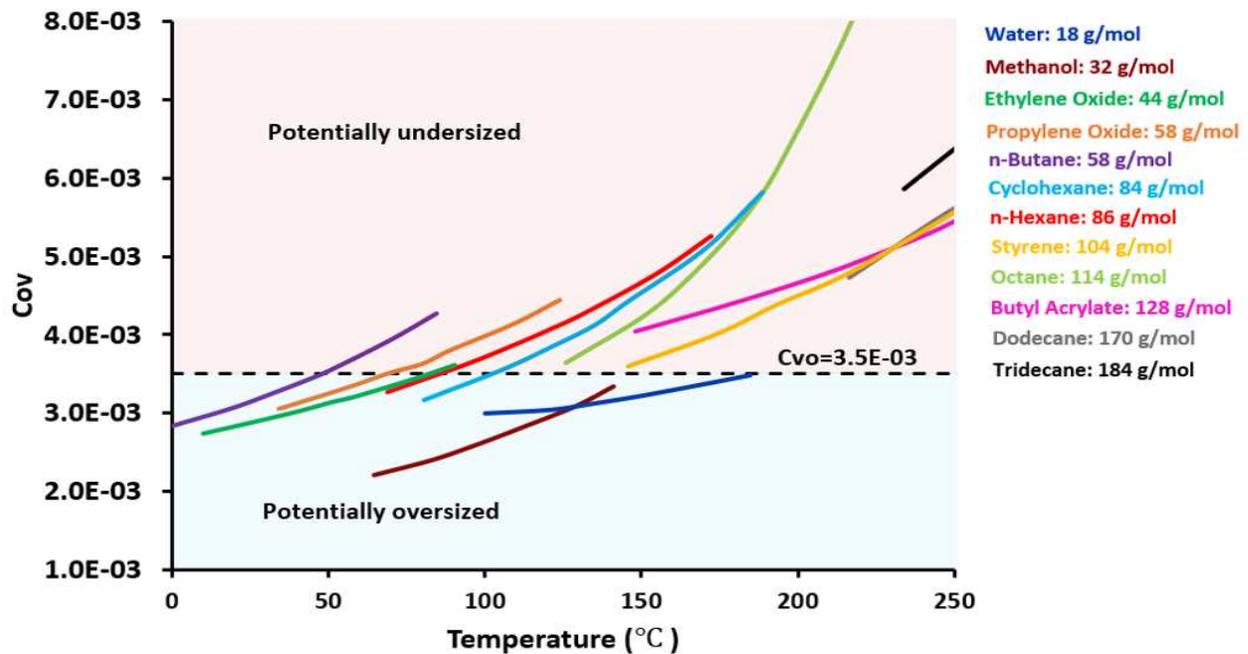
where ΔP is overpressure in psi relative to ambient pressure, $C_o = 4.0 \times 10^{-4}$ for a non-foamy system, and $C_o = 8.0 \times 10^{-4}$ for a foamy system.

The screening method developed by Fauske provides valuable insight into the dependence of required vent flow area on reaction rate.

Because of its inherent uncertainties, Fauske's method is only useful for screening systems with existing relief devices. This method should not be used for the detailed design or evaluation of relief and effluent handling systems.

4 Dependence of C_o on Physical Properties

The value proposed for C_o without knowledge of physical properties is 3.5×10^{-3} . This value is based on water properties at $100^{\circ}C$ for $C_{o,v}$ and a molecular weight of 44 (CO_2) for $C_{o,g}$. The calculated required vent size is directly proportional to C_o . A larger value of C_o will result in a larger required vent size. Typical C_o values are calculated for several chemicals and are shown in Figures 1 and 2. We note that during a chemical reaction, the chemical composition is continuously changing, and as a result the values of C_o will continuously change as well.

Figure 1: Calculated values of $C_{o,v}$ at saturation conditions

5 What is the Basis for the C_o Factor of Two ?

Equations 9 and 10 show the required vent area for all vapor flow based on a measure rate of vapor generation, \dot{V}_v . DIERS published a simple design method for required vent area for homogeneous twophase flow [13]:

$$A_{e,vl} = \frac{1}{2C_d} \frac{\rho_l V_l}{(T/c_{v,l})^{1/2}} \frac{q(T)}{\Delta P} \quad (18)$$

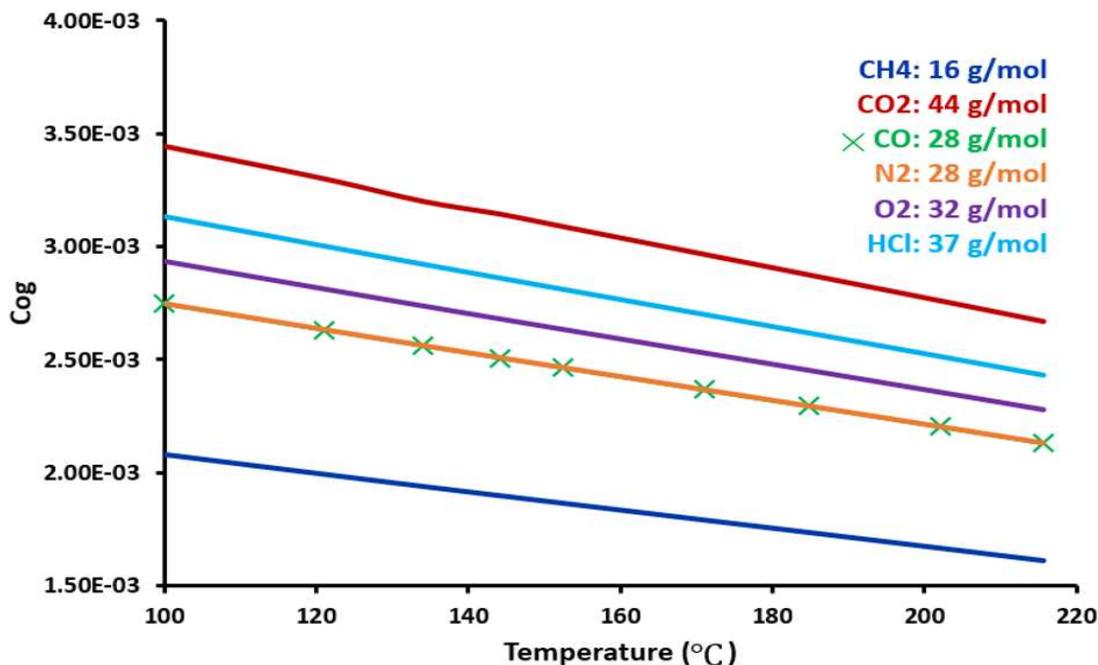
where $A_{e,vl}$ is the required twophase flow area ² in m², ΔP is overpressure in Pa, P is the relief set pressure in Pa, and T is the saturation temperature corresponding to P in K.

Fauske [7, 8] divides Equation 18 by Equation 8 (also see Equations 9 and 10) to obtain the following relationship between $A_{e,v}$ and $A_{e,vl}$:

$$\frac{A_{e,vl}}{A_{e,v}} = 0.3 \frac{\lambda}{T} \frac{P}{\Delta P} \left(\frac{M_w}{c_{v,l} R_g} \right)^{1/2} \quad (19)$$

where λ is the latent heat of vaporization in J/kg. The ratio $\frac{A_{e,vl}}{A_{e,v}}$ is inversely proportional to overpressure. For an overpressure of 22 % based on an absolute basis (28 % gauge basis), Equation 19 yields a ratio of $\frac{A_{e,vl}}{A_{e,v}}$ equal to 2 approximately for a styrene system (see Fauske [7]) where P is

²Equation 18 sometimes appears in the literature without the 1/2 factor because it is multiplied by a safety factor of 2 to account for uncertainties in measurements and thermophysical properties.

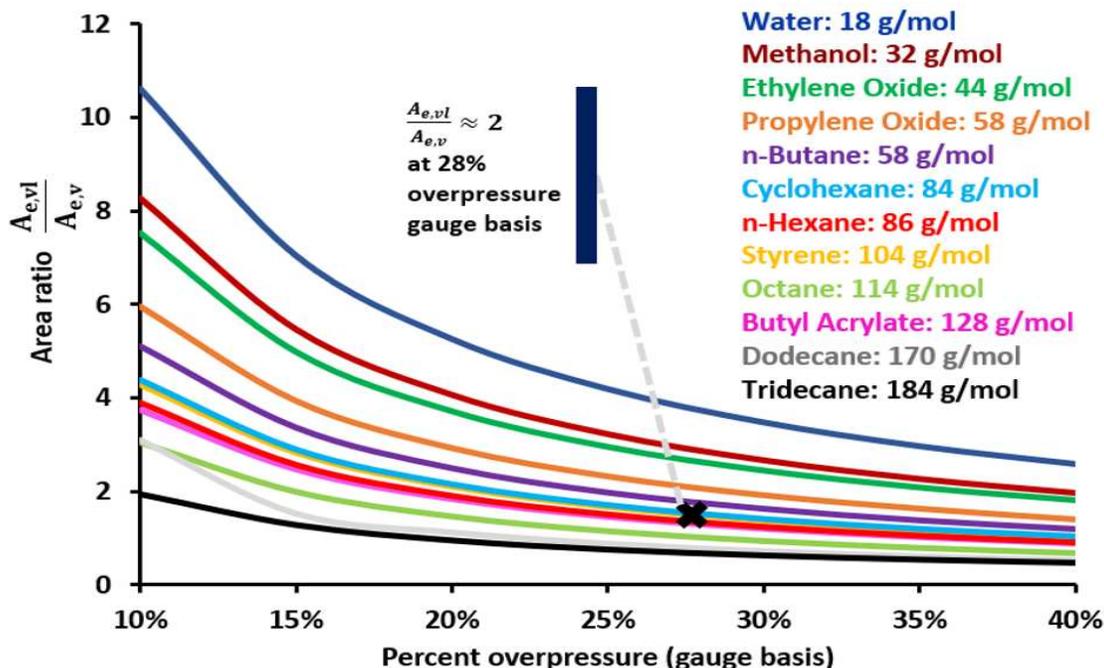
Figure 2: Calculated values of $C_{o,g}$ at saturation conditions. Basis for the liquid portion is water.

set at 4.5 bara. This is the basis for the rule of thumb used by Fauske indicating that the twophase required vent area is approximately twice the vapor required vent area at an overpressure of 40 %. Figure 3 shows how $\frac{A_{e,vl}}{A_{e,v}}$ depends ³ on chemical specific properties and overpressure levels for a relief device set pressure of 4.5 bara. The assumption of an area ratio of two ($\frac{A_{e,vl}}{A_{e,v}} = 2$) is not appropriate for all systems.

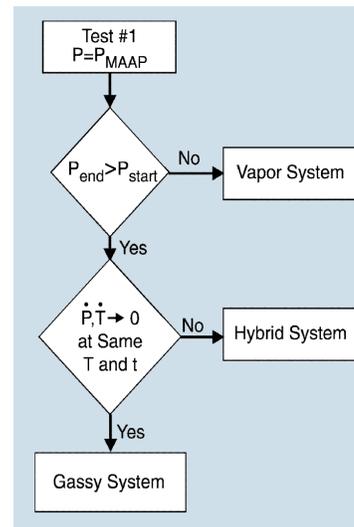
6 Proper Use of Fauske's Method

Use of Equations 1, 16 and 17 requires measured values of $q(T)$ and/or $\frac{dP}{dt}$ from an open calorimetry test using the RSST, ARSST, VSP, VSP2, APTAC, or another suitable calorimeter.

³ Assumes liquid heat capacity at constant pressure is equal to the liquid heat capacity at constant volume.

Figure 3: Calculated area ratio $\frac{A_{e,vi}}{A_{e,v}}$ at saturation conditions, P = 4.5 bara

Two tests are usually required. The first test is conducted by setting the containment vessel pressure to the maximum allowable accumulation pressure (MAAP), typically 110 % of the maximum allowable working pressure (MAWP) in gauge pressure. After the test is completed, the final vent containment pressure at ambient temperature is compared to the starting test pressure. If the pressure are essentially equal, this indicates the formation of condensible vapors only. As a result, the system is a vapor or tempered system. If the ending pressure at ambient conditions is larger than the starting pressure, this indicates the formation of non-condensable gas components. The system can be either a gassy or a hybrid system. If the temperature and pressure rise rates at turnaround conditions ($q(T) = 0$ and $dP/dt = 0$) occur at the same temperature and time, then the system is gassy. If not, the system is hybrid.



An additional test is typically required, as shown in Figure 4, to determine the final relief requirement. We note that for energetic reactions, it is possible to choke the flow out of an open test cell depending on the fill level, the size of the test cell nozzle size, and the length of the nozzle. Where the flow is choked out of the test cell, the rate of pressure rise in the containment vessel can be underestimated. We also note for some systems, the preferential depletion of a solvent or light ends during heating can cause the concentrating of an active ingredient. Spontaneous decomposition or deflagration of the concentrated ingredient can cause extremely rapid pressure rise rates. The proper and safe relief requirement for such systems may not be adequately represented by the

direct scale-up methods outlined by Fauske.

7 Advantages and Disadvantages of Fauske's Direct Scale-up Method

Establishing the required relief rate and relief device size is just but one aspect of pressure relief systems design. Depending on whether or not the relief system will be discharging to atmosphere, to an effluent handling system, or to a vent containment system, additional information is required.

Once a vent size is established, there is a need to determine the mass and volumetric flow rate, the exit pressure, the exist temperature, the exit composition, and the vapor to liquid ratio of the discharge.

The requirement for this additional information nullifies the most important features of direct scale-up and shortcut methods like the one discussed in this document by Fauske, i.e. minimal or no thermodynamic, physical, and transport properties.

First and foremost, this information is required for purchasing specification of a new relief device. It is also needed to determine the reaction forces that will be applied to the relief systems inlet and discharge piping as well as to the vessel and its structural supports. In many situations, supporting reaction forces and thrusts in excess of 25,000 lbf will be difficult and impractical for most relief systems installations. It is also well known that direct scale-up and shortcut methods can result in significantly oversized relief devices which exacerbates the challenges of structural supports.

Pressure drops, sound power levels, pressure relief device stability, excessive temperatures, and the potential for slug formation in the relief system piping, represent additional information that cannot be reasonably and practically established without clarity on what is being vented and the associated thermodynamic, physical, and transport properties.

If the relief system is being discharged to the atmosphere, numerous safe discharge locations calculations will be required, such as the extent of dispersion to specific threshold values for flammability and/or toxicity, thermal radiation and/or overpressure from potential discharge immediate or delayed ignition, and the potential for condensed phase droplet formation and rain out. We note that an oversized vent, while certainly can help protect the vessel from overpressure, can cause a substantial challenge and negative impact on safe discharge location considerations due to the increase in mass flow rates associated with the larger relief device. Oversized pressure relief valves can exhibit instability (chatter) and can also induce twophase flow because of increased superficial vapor velocity.

If the relief system is being discharged to an effluent handling and/or vent containment system where vapor and liquid separation or quenching may be required, clarity on what is being vented and the associated thermodynamic, physical, and transport properties become increasingly more important.

In addition, direct scale-up methods should only be used at the same test conditions, i.e. set point of the relief device, initial void fraction, the maximum allowable accumulated pressure or relief pressure, and most importantly chemical composition. Often, pressure relief systems calculations involve multiple iterations with normal conditions and also with either startup or shutdown or abnormal conditions. If the vent sizing design results in a proposed change in the field, multiple iterations might also be required in order to develop an optimal and risk effective solution.

For all the reasons mentioned above, the most effective and singular use of direct scale-up or shortcut methods like Fauske's method is to obtain an indication of whether an existing relief device (not relief system) is likely to have been sized adequately. Furthermore, additional expense and effort will be required to specify a new relief device if the direct scale-up method determines that the existing relief device does not have adequate relief capacity.

8 Detailed Kinetic Modeling Methods using SuperChems Expert

A disadvantage of the kinetic modeling methods is the availability of suitable detailed chemical reaction models, stoichiometry, thermodynamic, physical, and transport properties to couple with fluid dynamics models. Fortunately, the development of detailed chemical reaction models has become much more practical over the years as discussed below. Detailed chemical reaction models can be developed quickly and cost effectively using a combination of adiabatic calorimetry testing and advanced computational tools such as SuperChems Expert .

The development of reaction models suitable for pressure relief systems design or evaluation requires experience and the availability of software tools such as SuperChems Expert to dynamically simulate the reaction calorimetry test. The development of reaction kinetic models [14, 15, 6, 16, 17, 18, 19, 20, 21, 22, 23] for pressure relief and effluent handling systems design and evaluation has evolved over the last two decades and is now mainstream.

Software like SuperChems Expert [24] can be used to process calorimetry data, develop reactions stoichiometry, simulate the calorimetry testing, and provide scale-up of calorimetry data. The kinetic models are coupled with fluid dynamics to develop venting requirements [25], vent containment design [26], safe discharge location [3], and to satisfy additional RAGAGEP requirements [1].

The simulation should start at the beginning of the test, well before any reaction takes place. Small amounts of non-condensable gas generation and/or small temperature deviations can have a significant impact on pressure-temperature behavior of the system. First, simulate the calorimetry test without a reaction to confirm the reactants thermodynamic properties, physical properties, and vapor-liquid equilibrium behavior. Then a kinetic expression is developed using simple methods and used as a starting point for the dynamic simulation.

In order to develop a valid kinetic model, five indicators must be demonstrated to have good fits as shown in Figures 5 and 6:

1. Temperature vs. time: This should include the heat-wait-search portion of the calorimetry

test or the constant heat ramp portion of the test.

2. Pressure vs. time: This should include the heat-wait-search portion of the calorimetry test or the constant heat ramp portion of the test.
3. Pressure vs. temperature: This is a critical system curve because it establishes the reaction rate at the opening pressure of a relief device. This relationship is sometimes intentionally biased to be slightly conservative to account for uncertainties in testing methods and thermophysical properties.
4. $\frac{dT}{dt}$ vs. time: This is used to also show the goodness of fit for the cool down portion of the test. Often, a logarithmic plot of $\frac{dT}{dt}$ vs. Temperature is used.
5. $\frac{dP}{dt}$ vs. time: This is used to also show the goodness of fit for the cool down portion of the test. A logarithmic plot of $\frac{dP}{dt}$ vs. Temperature or $\frac{dP}{dt}$ vs. $\frac{dT}{dt}$ is also used.

The simulation should also include the calorimetry test cool down portion to confirm that the right amounts of non-condensable gas are reflected by the kinetic model. The drift portions of the test should also be replicated by the dynamic simulations as shown in Figure 5. In general, it is preferred to demonstrate the performance of the kinetic model against additional test data.

For complex reaction systems, the reactions have to be decoupled and fit in sequence. This can be tedious and can require a lot of effort for very complex chemistries where multiple reactions are taking place. Kinetic models are used to extend the use of the measured data over wide temperature, pressure, and composition ranges and conditions. Less effort is typically required for single molecule decompositions or polymerization reactions.

9 Using Detailed Kinetic Models in Pressure Relief Systems Design

The kinetic model developed for butyl acrylate polymerization and polymer decomposition [20, 27, 18, 19] (see Figure 6) was used to evaluate the relief requirements for a large butyl acrylate storage tank under fire exposure without fire proof insulation or fixed water sprays. The tank has a total volume of 29,000 gal and is normally 92 % full (200,000 lbs). The tank has a design pressure of 150 psig and a design temperature of 150 F. Initially the contents are at 74 F and 0 psig. The tank vents to the atmosphere via an 18 inch rupture disk set at 15 psig.

The contents are typically inhibited with MEHQ. Extended storage durations can deplete the inhibitor. Two simulations were conducted using SuperChems Expert to study the impact of fire exposure on relief requirements. The results are shown in Figure 7 for starting conditions of 1 PPM of MEHQ at initial fill levels of 50 % and 92 %.

As shown by Figure 7 the tank becomes liquid full due to thermal expansion of the liquid at 92 % initial fill level. The rupture disk opens as a result and venting continues at near atmospheric conditions until the reaction rates become high enough to raise the pressure to approximately 80 psig.

This illustration is but a simple example of what can be accomplished when good kinetic models are coupled with detailed fluid dynamics. The simulations enable the user to evaluate many what-if scenarios, to determine the dynamic reaction force loads caused by the rupture disk opening, and to determine the vapor quality and mass flow rate during venting, etc. More detailed dynamics can also be performed [28, 1, 2] to study available pre- or post- release mitigation measures including but not limited to the use of quench fluid, more inhibitor injection, fire proof insulation, fixed water sprays, estimated time to failure, estimated time to yield, safe discharge location, etc.

When planning modifications to existing equipment or developing new designs, kinetic modeling for pressure relief design is almost always more cost effective and yields optimal risk reduction.

10 Cost vs. Benefit Analysis

A simple cost vs. benefit analysis clearly indicates that it is time to move away from direct scale-up methods and to adopt detailed kinetic modeling methods, especially when developing sizing estimates for more than one vessel or system.

The expected cost for a direct scale-up vent sizing for one vessel, assuming a cost of M /calorimetry test, would be $2 \times M$. This cost does not include expected costs for addressing additional information requirements associated with RAGAGEP requirements and safe discharge location estimates. In general we would expect that level of effort to be approximately equivalent to the cost of one calorimetry test. The total cost for performing one sizing calculation for one vessel or system is therefore $3 \times M$. The cost of performing sizing calculations for additional vessels (**assuming the same test conditions apply**), would be M per additional vessel or system. At conditions different than the test conditions, sizing calculations would require additional testing and the cost would be $3 \times M$ per additional vessel or system.

Performing the sizing calculations using a detailed kinetic model requires at least one calorimetry test at a cost of M and the development of a kinetic model suitable for performing the pressure relief systems calculation at an expected cost of $2 \times M$. The cost of performing the actual sizing calculation including additional RAGAGEP requirements and safe discharge location is expected to be $M/2$. As a result the total cost for performing the first sizing calculation would be $3.5 \times M$. The cost of additional sizing calculations for vessels or systems using the same chemistry regardless of conditions would be $M/2$.

Let's explore the costs of pressure relief systems design for five systems, as outlined in Table 2. Assuming that all five systems have the same conditions as the calorimetry testing, the direct scale-up approach cost will be 27 % higher than the kinetic modeling approach cost. If the conditions of the additional four systems are different but still with the same chemistry, the direct scale-up approach costs will be approximately three times the kinetic modeling approach costs or 172 % higher.

It is clear from this analysis (see Table 2) that the detailed kinetic modeling approach is more flexible and cost effective when the sizing requirements involve more than one vessel or systems using the same chemistry. The costs are comparable when dealing with a single system with the detailed kinetic modeling method providing substantial calculation and modeling advantages.

Table 2: Cost vs. Benefit Analysis of Direct Scale-up vs. Detailed Kinetic Modeling

Typical Sizing Cost [†]	Direct Scale-up	Kinetic Modeling
First Vessel or System	$3 \times M$	$3.5 \times M$
Additional Vessels or Systems (same conditions)	M	$M/2$
Additional Vessels or Systems (different conditions)	$3 \times M$	$M/2$

[†] Cost estimates assume the same chemistry applies but different conditions of fill level, composition, relief device set point, and vessel maximum allowable accumulated pressure are required for additional vessels or systems. M is the cost of one *VSP* or *APTAC* or equivalent calorimetry test.

11 Conclusions

Compliant pressure relief systems design and design basis documentation, especially where chemical reactions are involved, must address the safe discharge location requirements as well as a multitude of additional RAGAGEP requirements.

Direct scale-up methods are only useful in providing a rough estimate of required vent size and can be overly pessimistic at times. These methods are not meant to be a replacement for detailed kinetic methods that can provide all the information that is required for a safe and compliant design.

Because of the inherent limitations of direct scale-up methods, they are only recommended for screening existing relief systems installations. They are not recommended for the detailed design and/or evaluation of pressure relief and effluent handling systems.

Detailed methods based on kinetic modeling are highly recommended. We have demonstrated that these methods provide all the necessary information for safe and compliant designs and are more versatile and cost effective than direct scale-up methods for studies involving multiple systems.

12 Additional Resources

The following additional white papers available from ioMosaic (www.iomosaic.com) may be useful when considering the chemical reactivity and hazard potential of chemical substances or chemical mixtures [29, 30, 31, 32, 33, 34].

Figure 4: Methodology for system characterization from open test data [12]

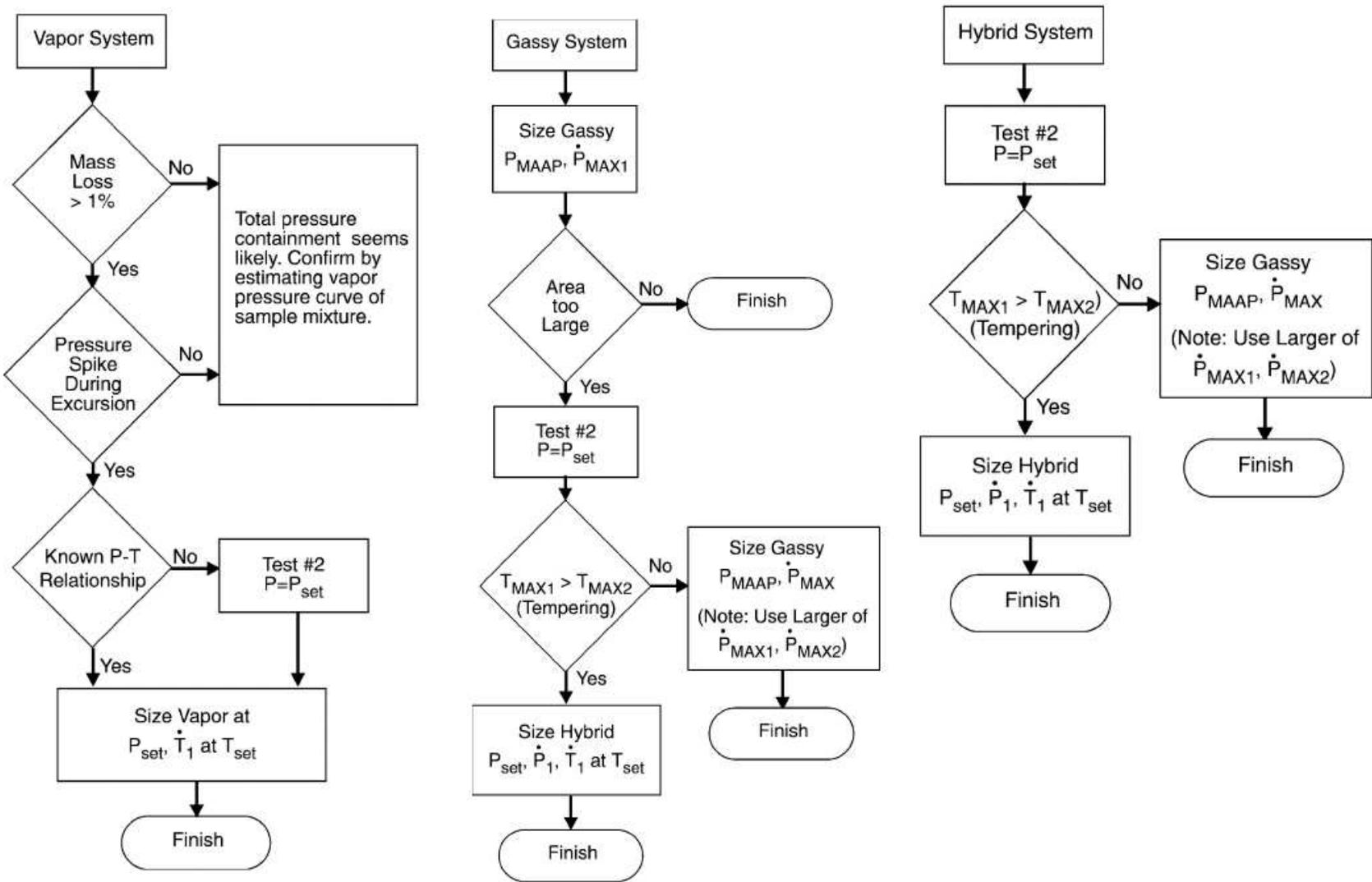


Figure 5: Best fit kinetic model developed using SuperChems Expert for the decomposition of 50 % dicumyl peroxide in toluene

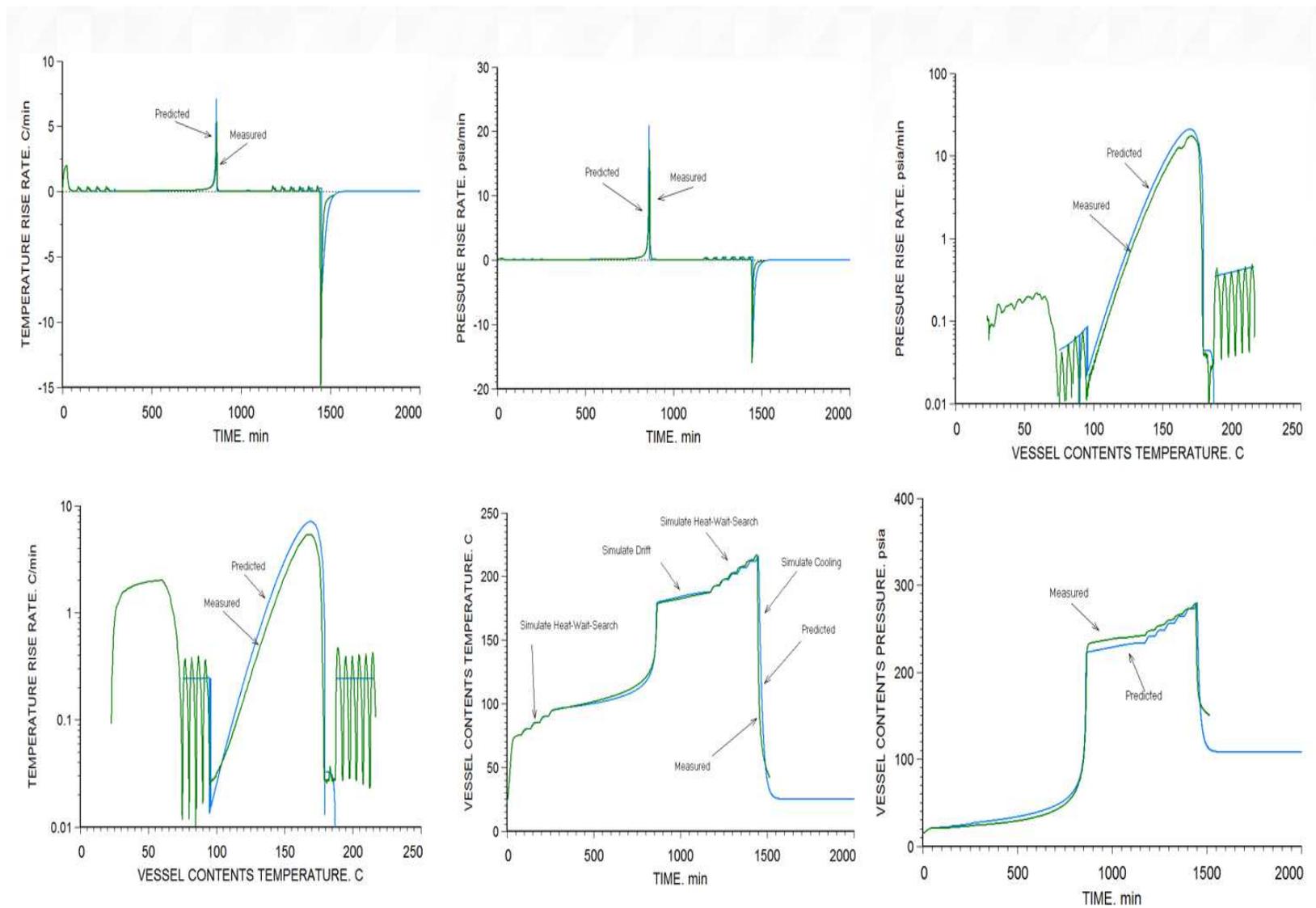


Figure 6: Best fit kinetic model developed for the polymerization (and polymer decomposition) of butyl acrylate inhibited with MEHQ

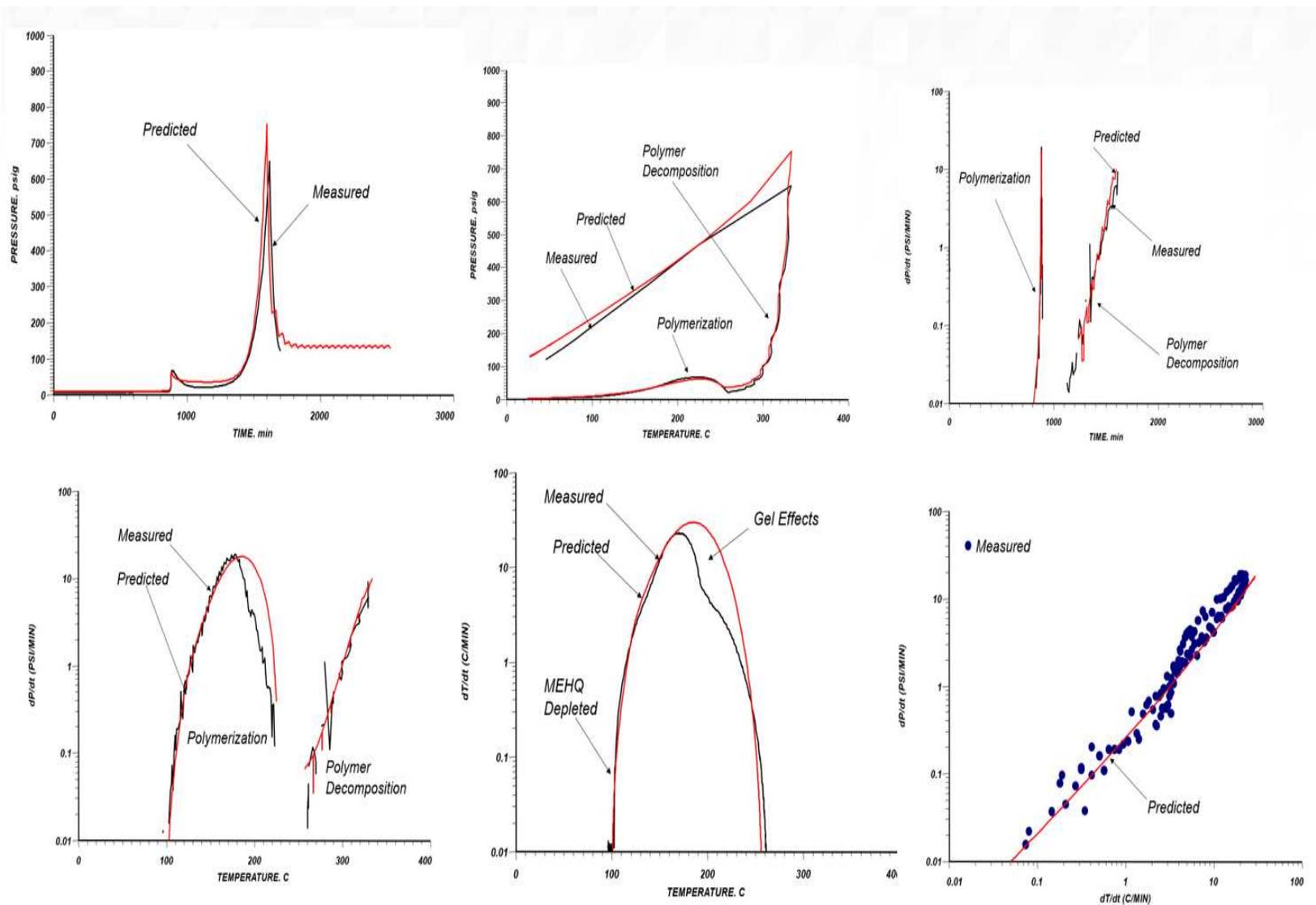
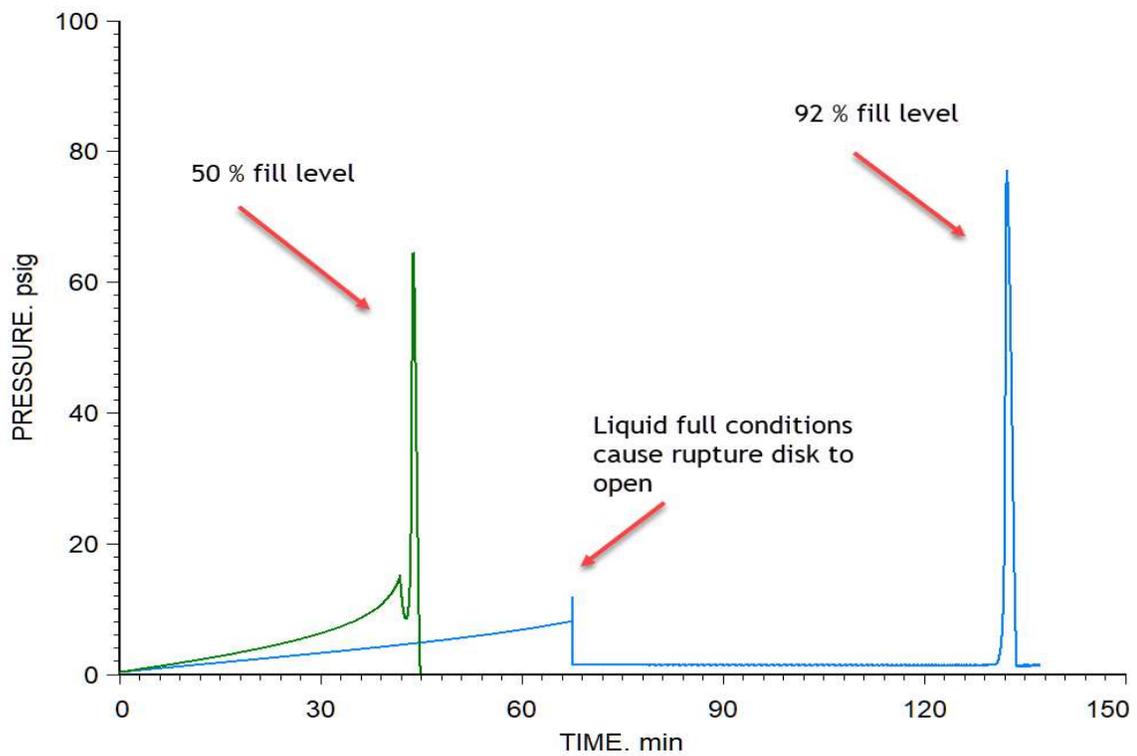


Figure 7: Calculated pressure-time histories for fire induced butyl acrylate runaway polymerization using SuperChems Expert



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Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

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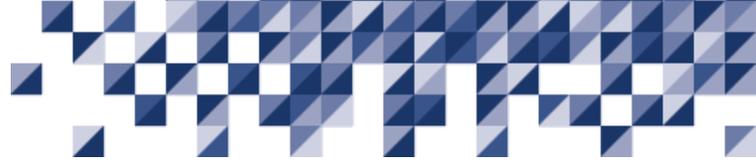
How can we help?

Please visit www.iomosaic.com and www.iokinetic.com to preview numerous publications on process safety management, chemical reactivity and dust hazards characterization, safety moments, video papers, software solutions, and online training.

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.



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About ioMosaic Corporation

Through innovation and dedication to continual improvement, ioMosaic has become a leading provider of integrated process safety and risk management solutions. ioMosaic has expertise in a wide variety of areas, including pressure relief systems design, process safety management, expert litigation support, laboratory services, training and software development.

As a certified ISO 9001:2015 Quality Management System (QMS) company, ioMosaic offers integrated process safety and risk management services to help you manage and reduce episodic risk. Because when safety, efficiency, and compliance are improved, you can sleep better at night. Our extensive expertise allows us the flexibility, resources, and capabilities to determine what you need to reduce and manage episodic risk, maintain compliance, and prevent injuries and catastrophic incidents.

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