Reactive System ERS Design Basics & ERS Case Studies

Elizabeth Raines

Who is Fauske & Associates (FAI)?

- A World Leader in Chemical and Nuclear Process Safety
- A wholly owned subsidiary of Westinghouse Electric Company, LLC
- ISO 17025 and ISO 9001 Testing Lab and Engineering Firm
- Two Key Programs in the 1980's
  - **DIERS** (Design Institute for Emergency Relief Systems)
    - Principal Research Contractor
  - **IDCOR** (Industry Degraded Core Rulemaking Program)

DiERS

FAUSKE & ASSOCIATES, LLC

Why is ERS Design Important: **ICMESA (Seveso, Italy)**

- Emergency relief systems (ERS) are an important part of process safety
  - Used to protect vessels from overpressurization
  - **Protect people, infrastructure, & the environment**

- At 12:37 pm on July 10, 1976, 6 tons of chemicals including tetrachlorodibenzoparadioxin (TCDD) were released from a reactor
- Hazardous material: TCDD is poisonous and carcinogenic
- Inadvertent heating of reactor led to runaway reaction
- More than 600 people had to be evacuated and as many as 2,000 people were treated for dioxin poisoning
- Led to EU "Seveso Directive" to prevent similar incidents

Risk, Safeguards & Risk Reduction

- **Risk** – The possibility of a process safety incident/time
- The combination of undesired consequences with the likelihood (frequency) that the consequences (adverse event, cost, etc.) will occur
- Risk = Likelihood x Consequence

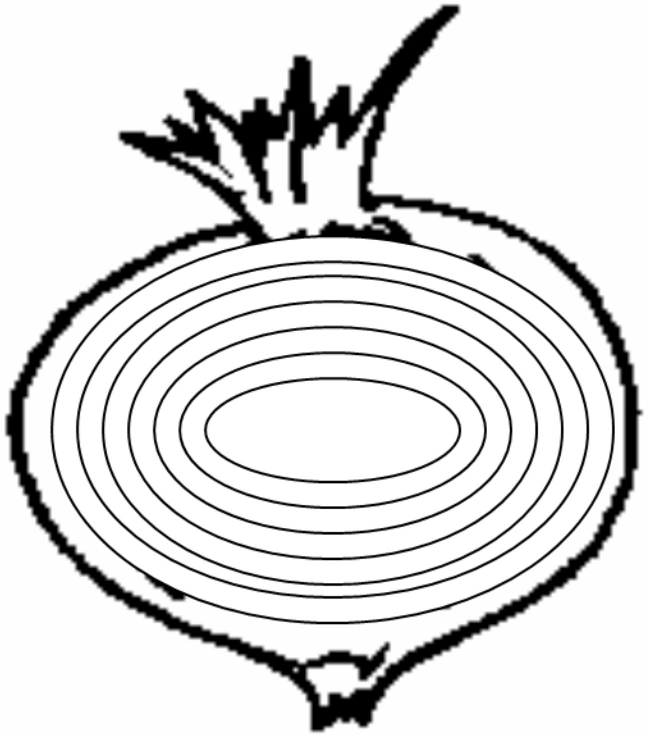
- **Safeguards** can be preventative and mitigating
- **Prevention** reduces the **likelihood** of an incident occurring (control over mischarges to a reactor)
- **Mitigation** reduces the **consequence** of an incident (emergency relief devices)

- **Risk Reduction** ↓:
  - Use Prevention to reduce the Likelihood ↓
  - Use Mitigation to reduce the Consequence ↓

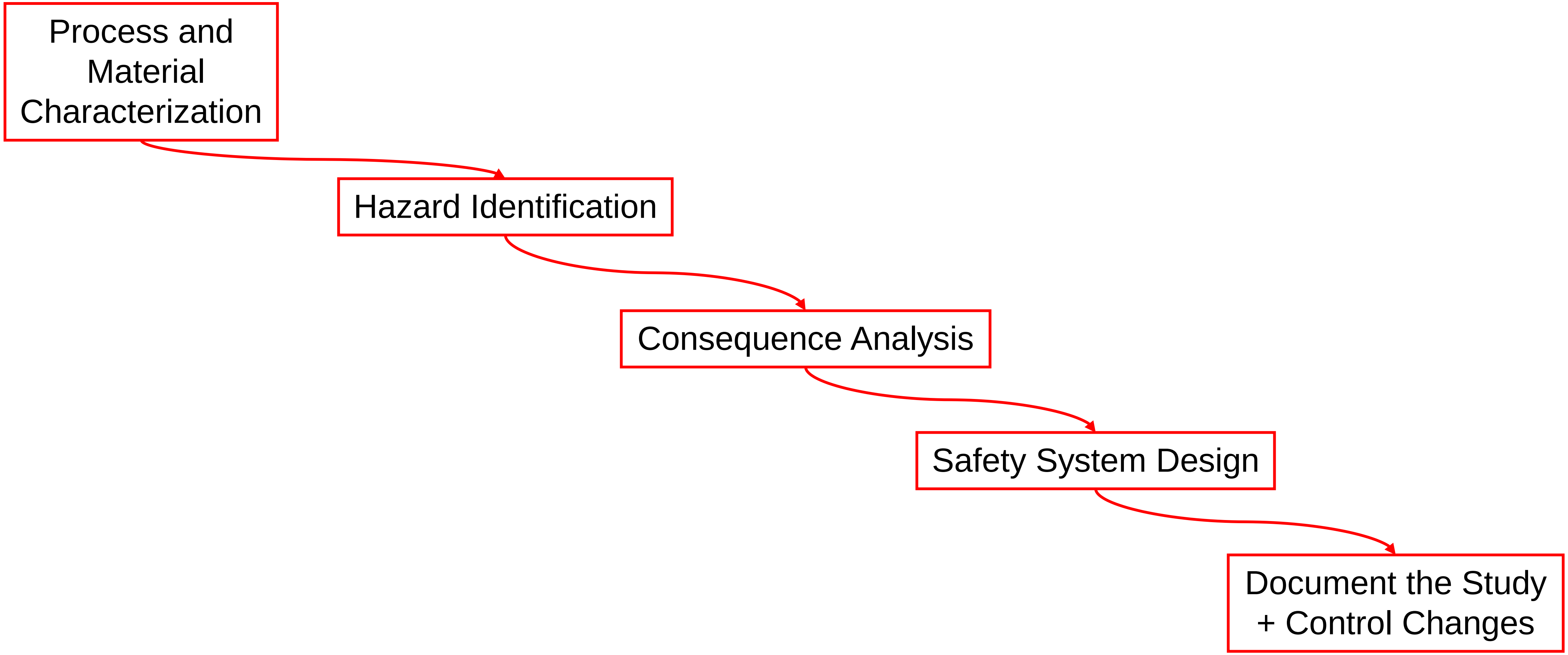
FAUSKE & ASSOCIATES, LLC

Layers of Protection – Multi-Layered Safeguards

- Community Emergency Response
- Site Emergency Response Plan
- Secondary Containment
- **Emergency Relief Systems (ERS)**
- Safety Instrumented Systems (SIS)
- Emergency Shutdown Systems
- Alarms & Operator Action
- Basic Process Control System (BPCS)
- Procedural Checklist and Signoff
- Operating Procedures and Training
- Mechanical Design and Preventative Maintenance
- Process Design

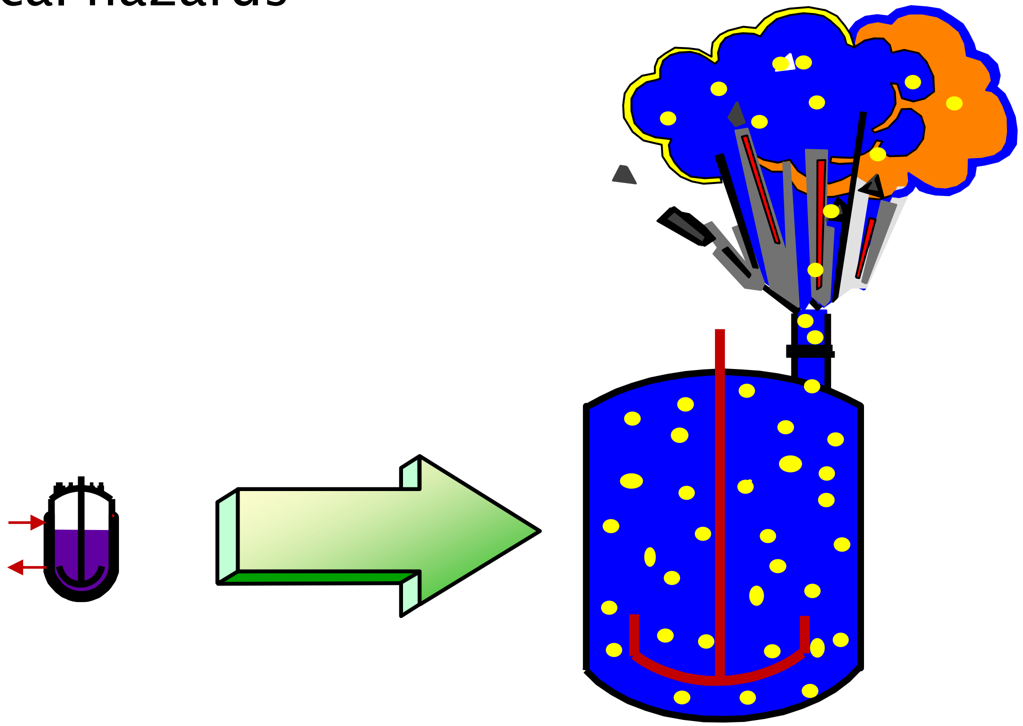


Assessment Strategy



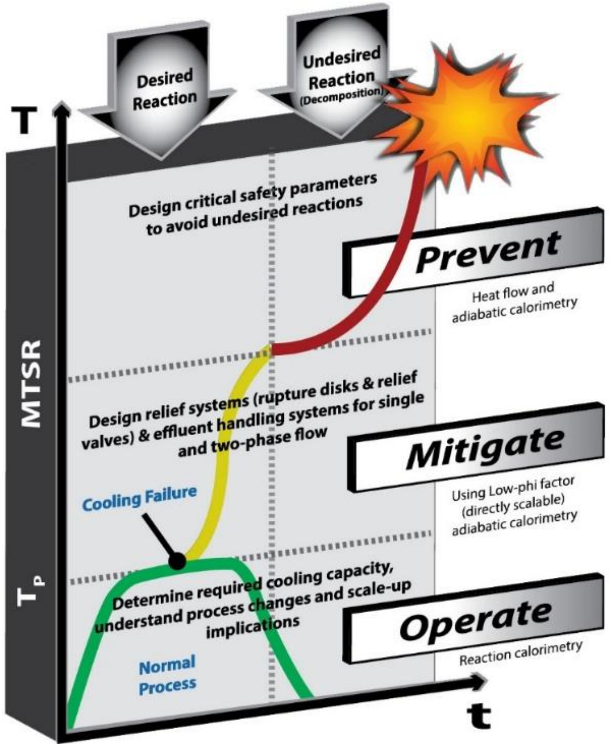
Hazard Identification

- Potential process deviations can only be identified with a detailed knowledge of the chemistry and plant
- Process Hazard Analysis (PHA) = An organized and systematic process to identify and analyze the significance of potential chemical hazards
  - Required by OSHA
- Methods available for PHA include:
  - Hazard and Operability Studies (HAZOP)
  - "What-if" analysis
  - Failure modes and effect analysis (FMEA)
  - Checklist analysis
  - Fault tree analysis



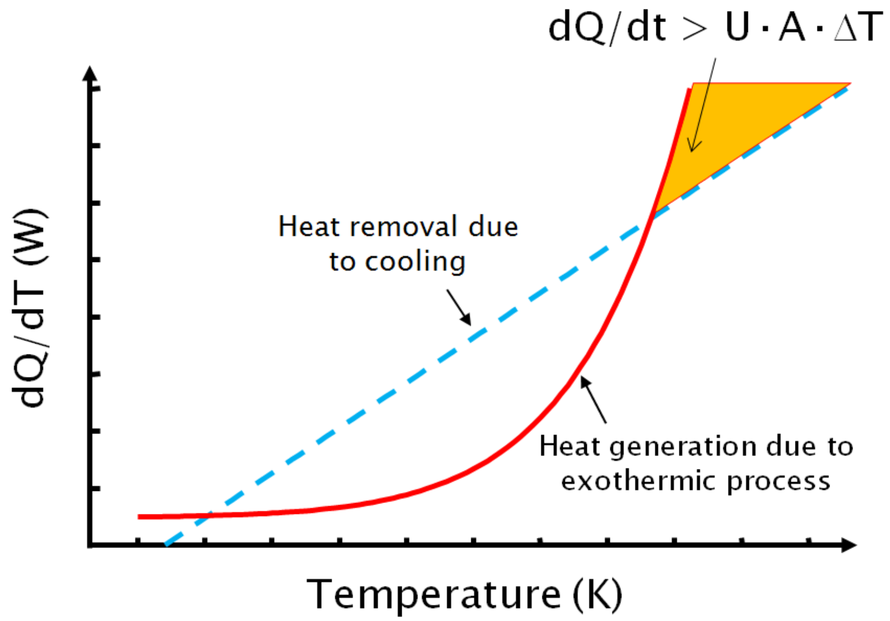
Overpressure – Potential Consequence of Hazards

- Determine plausible upset scenarios from Process Hazard Analysis (PHA)
  - Reactive vs. nonreactive
  - API 521 provides a table of "Guidance for Required Relieving Rates Under Selected Conditions"
- Reactive hazards can be present whether the reaction is intended or not
  - $\textbf{Raw Material} \xrightarrow{\textbf{Desired Reaction}} \textbf{Product}\ (Heat/Vapor/Gas)$
  - $\textbf{Raw Material} \xrightarrow{\textbf{Desired Reaction}} \textbf{Product} + \textbf{Heat} \xrightarrow{\textbf{Undesired Reaction}} \textbf{Undesired Product}\ (Heat/Vapor/Gas)$
  - $\textbf{Raw Material} \xrightarrow{\textbf{Upset Scenario}} \textbf{Undesired Product}\ (Heat/Vapor/Gas)$
  - What leads to or triggers runaway reaction?
    - Incorrect reagents or wrong order of addition
    - Reactant accumulation
    - Contamination
    - Corrosion
    - Overcharge / undercharge of reactant, catalyst, solvent
    - Fire exposure leading to reaction or decomposition
    - Loss of power/cooling/mixing/inert environment



Thermal Runaway Definition

- A thermal runaway is the progressive production of heat from a chemical process and occurs when the rate of heat production exceeds the rate of heat removal
- The batch temperature rises because there is insufficient cooling available to remove heat from the system to maintain isothermal conditions



Heat Generation > Heat Loss
= Thermal Runaway

Major Causes of Thermal Runaway Reactions

Analysis indicates that incidents occur due to:

1. Lack of proper understanding of the thermochemistry (heat of reaction) and chemistry (balanced chemical equation)

2. Inadequate engineering design for heat transfer for the scale-up

3. Inadequate control systems and safety back-up systems including emergency relief system(s)

4. Inadequate batch procedures and insufficient operator training

Designing ERS Based on Pressure Sources

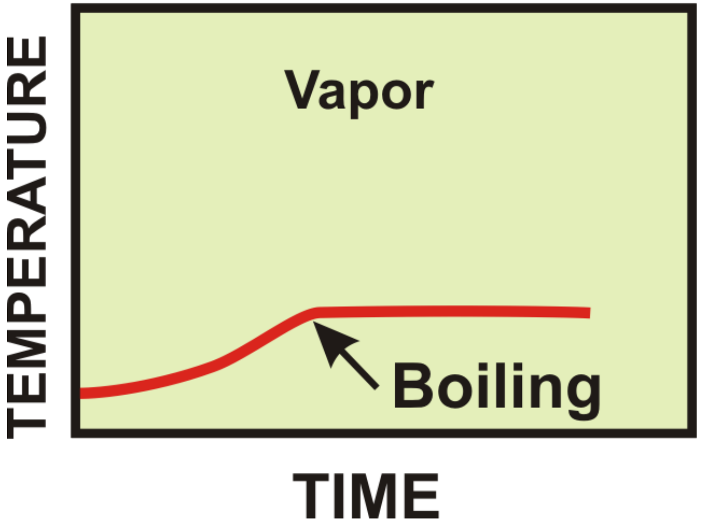
- In reactive ERS design, there are two key sources of pressure:
  - Vapor pressure
    - Common examples: Water, toluene, ethyl acetate
  - Non-condensable gas generation
    - Common examples: Hydrogen, oxygen, nitrogen
- These sources are treated differently, so chemical reactions are classified based on the sources available when the prospective relief device will open

• Vapor: H_2O	Vapor System
• Gas: O_2	Gassy System
• Both: H_2O + O_2	Hybrid System

Vapor Systems

- Source Term = Rate of Vapor Generation
- Pressure generation is due to increase in vapor pressure of liquid
- Latent heat of cooling (vaporization)
- Temperature rise rate is used for vent sizing
- Reaction temperature rise can be controlled by venting

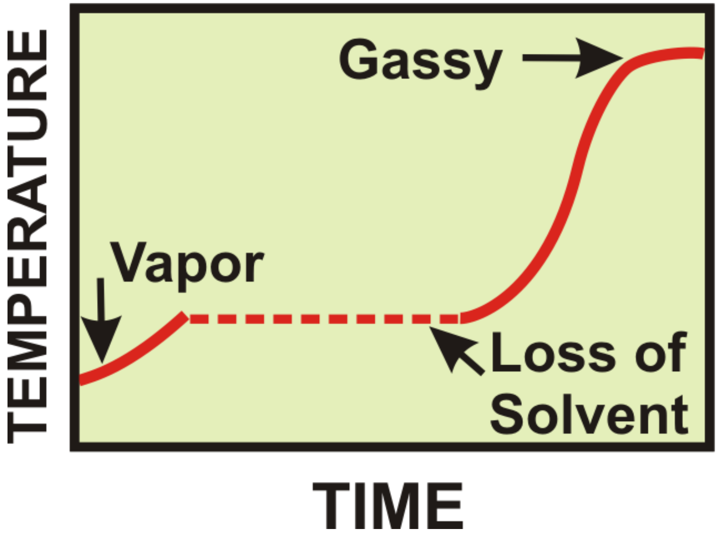
$$\dot{Q}_v = \frac{mc\dot{T}}{\lambda \rho_v}$$



Gassy Systems

- Source Term = Rate of Gas Generation
- Generates non-condensable gas
- Latent heat of cooling not available
- Typical of a decomposition reaction yielding gassy products
- Reaction temperature rise <u>cannot</u> be controlled by venting

$$\dot{Q}_g = \frac{m_o v \dot{P}}{m_t P}$$

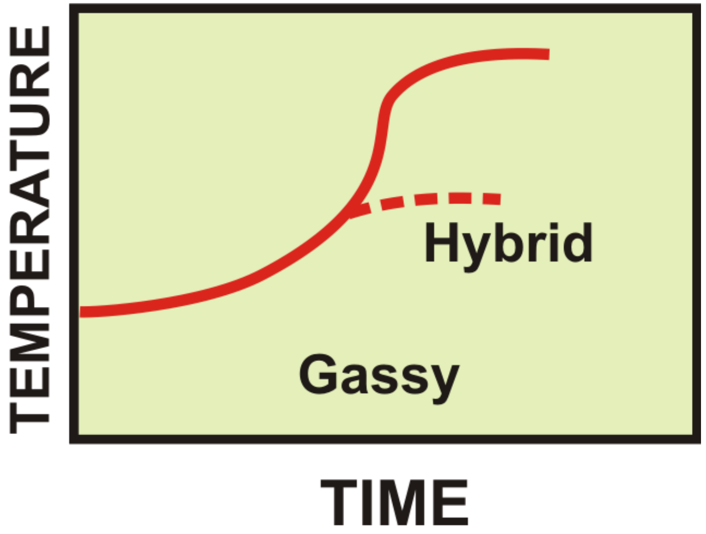


Hybrid Systems

- Sourced Term= Sum of Vapor and Gas Generation
- Latent heat of cooling is available at the relief pressure and temperature (tempered)
- Reaction temperature rise can be controlled by venting
- Generates non-condensable gas

$$\dot{Q}_T = \dot{Q}_v + \dot{Q}_g$$

$$\dot{Q}_T = \frac{mc\dot{T}}{\lambda \rho_v} + \frac{m_o v \dot{P}}{m_t P}$$



Simplified Vent Sizing Equations for Vapor-Gas Venting

- Relief system design is based on a volume balance at the venting conditions
  - Vapor Systems (reactive and nonreactive venting)

$$\dot{Q}_v \left(m^3 s^{-1}\right) = \frac{V \rho c \dot{T}}{\lambda \rho_v}$$

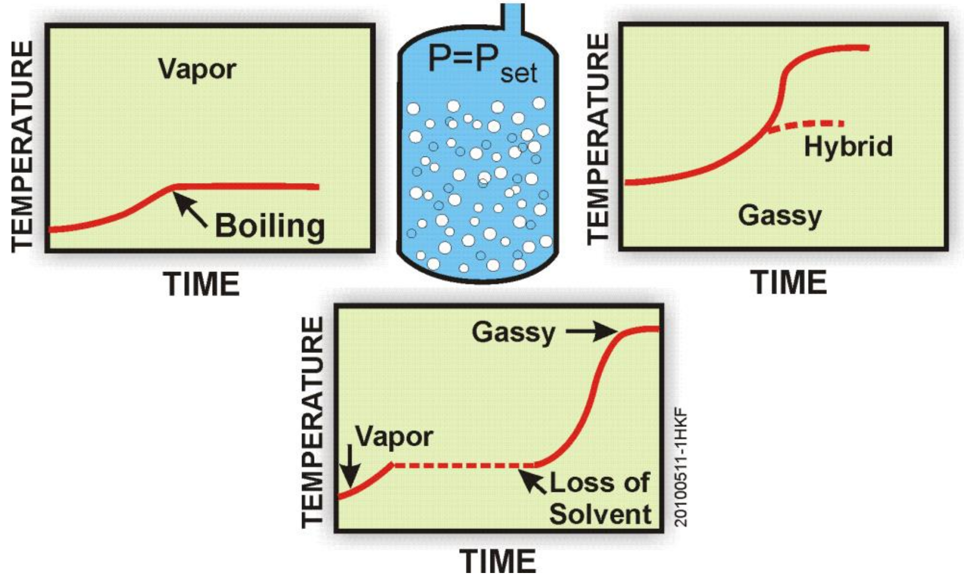
  - Gassy Systems

$$\dot{Q}_g \left(m^3 s^{-1}\right) = \frac{V \rho v}{m_t} \frac{\dot{P}}{P}$$

  - Hybrid Systems

$$\dot{Q}_{v,g} = \frac{V \rho c \dot{T}}{\lambda \rho_v} + \frac{V \rho v}{m_t} \frac{\dot{P}}{P}$$

$$A/V_R \propto \left[\frac{\rho c}{\lambda (M_{w,v})^{1/2}} \frac{\dot{T}}{P} (RT)^{1/2} + \frac{\rho v}{m_t} \frac{\dot{P}}{P} \left(\frac{M_{w,g}}{RT} \right)^{1/2} \right]$$



Key Parameters for ERS Design

- Source of overpressure
- Expected flow regime
- Material properties
  - Flammability and toxicity of materials if release occurs
- Vessel and relief device characteristics

Key Parameters for ERS Design

- Source of overpressure
- Expected flow regime
- Material properties
  - Flammability and toxicity of materials if release occurs
- Vessel and relief device characteristics

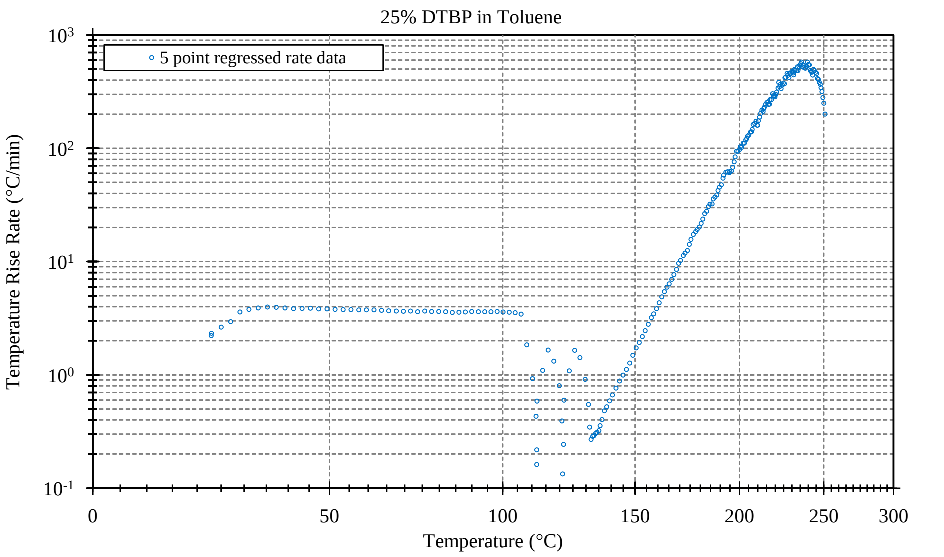
How to Calculate Source Terms?

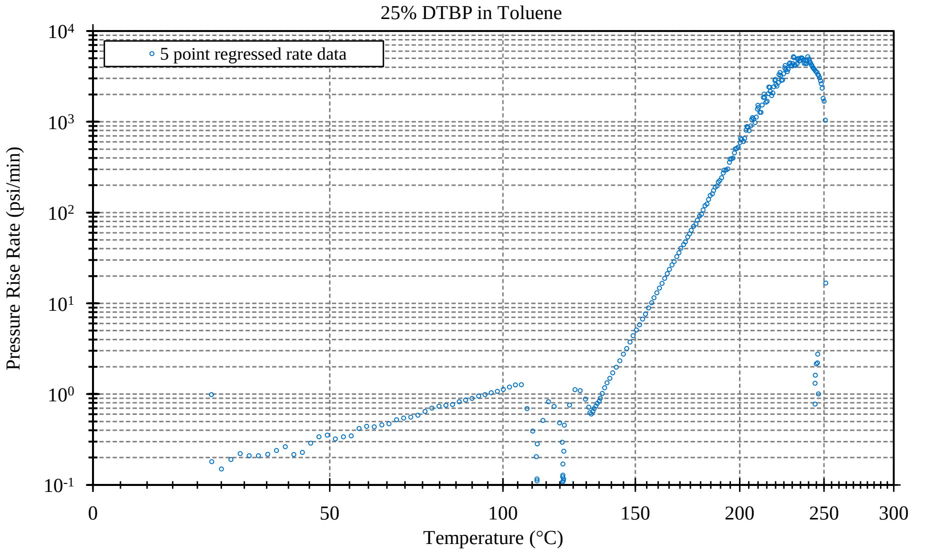
- These source terms are based on the expected material properties of the venting fluids plus a temperature rise rate and/or pressure rise rate
- These parameters (dT/dt and dP/dt) can be difficult to estimate
- Low phi-factor adiabatic calorimetry allows for direct measurement
  - Directly simulate upset scenarios of interest

FAUSKE & ASSOCIATES, LLC

Data from Adiabatic Calorimetry

- Temperature rise rate as a function of temperature
  - Source term for ERS design
- Pressure rise rate as a function of temperature
  - Source term for ERS design
- Adiabatic temperature rise
- Adiabatic heat of reaction
- Quantity of noncondensable gas generated
- Vapor pressure
- Flow regime



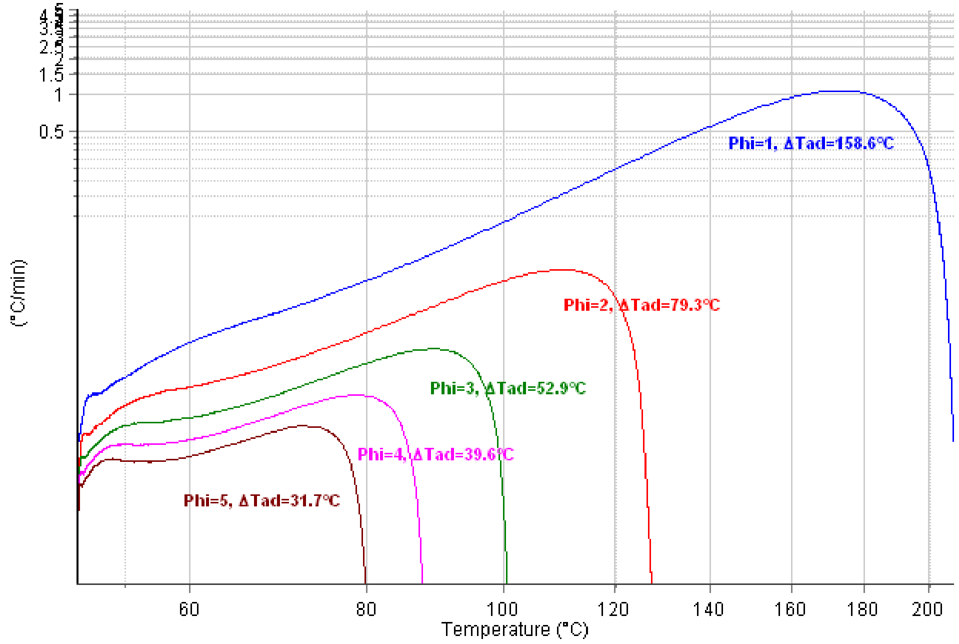


FAUSKE & ASSOCIATES, LLC

Why is Phi-Factor Important?

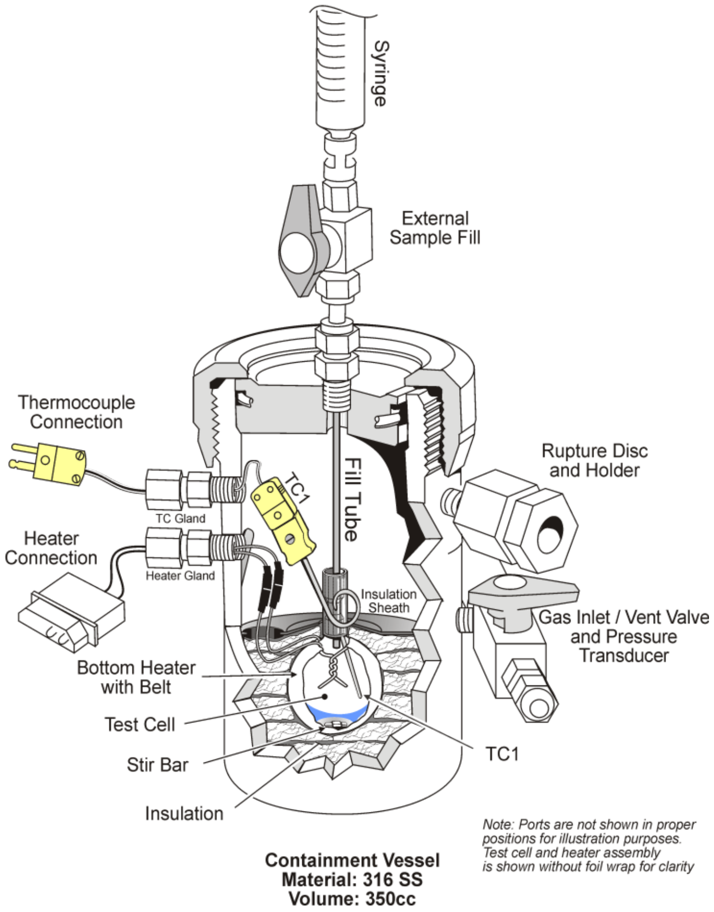
- The phi-factor is the ratio of the total heat capacity of a test system to the heat capacity of a test sample
  - Indication of the relative heat absorbed in a test system by the sample holder
  - Key simplifying assumption is that sample is in thermal equilibrium with sample holder
- Allows for the data to be directly used for pilot or plant sized vessels (where the phi-factor is close to 1)

$$\Phi = \frac{m_s c_s + m_b c_b}{m_s c_s}$$



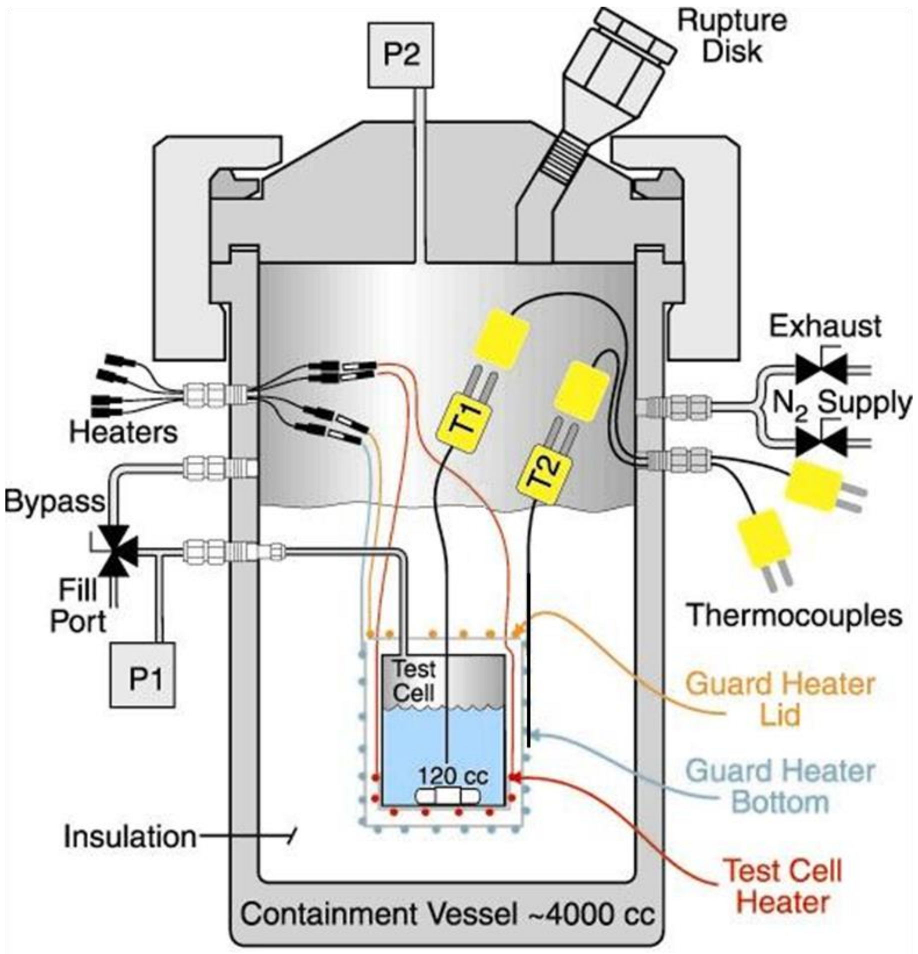
Adiabatic Calorimetry ARSST

- Low thermal inertia ($\phi = 1.05$)
- Thermal scan to identify moderate to high exothermic activity
- Open system
  - Impose backpressure to suppress boiling
  - Initial pressure depends on goal of test
- Direct measurement of sample temperature



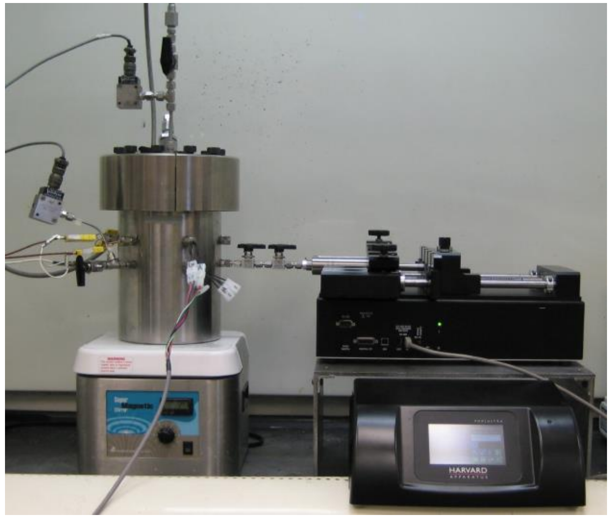
Adiabatic Calorimetry
VSP2

- Low thermal inertia
  (ϕ = 1.05–1.15)
- Simulate normal process or upset conditions
- Identify mild to high exothermic activity
- Open or closed cell
- Uses pressure-balancing technique



FAUSKE & ASSOCIATES, LLC

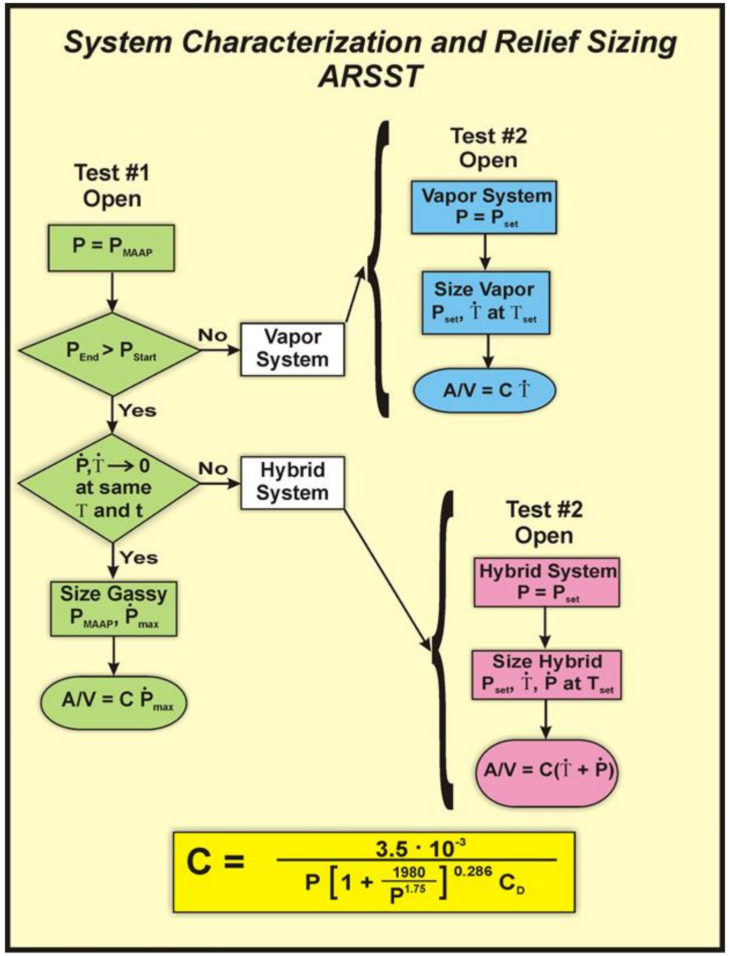
Adiabatic Calorimetry
VSP2 – Test Options to Simulate Upset Scenarios

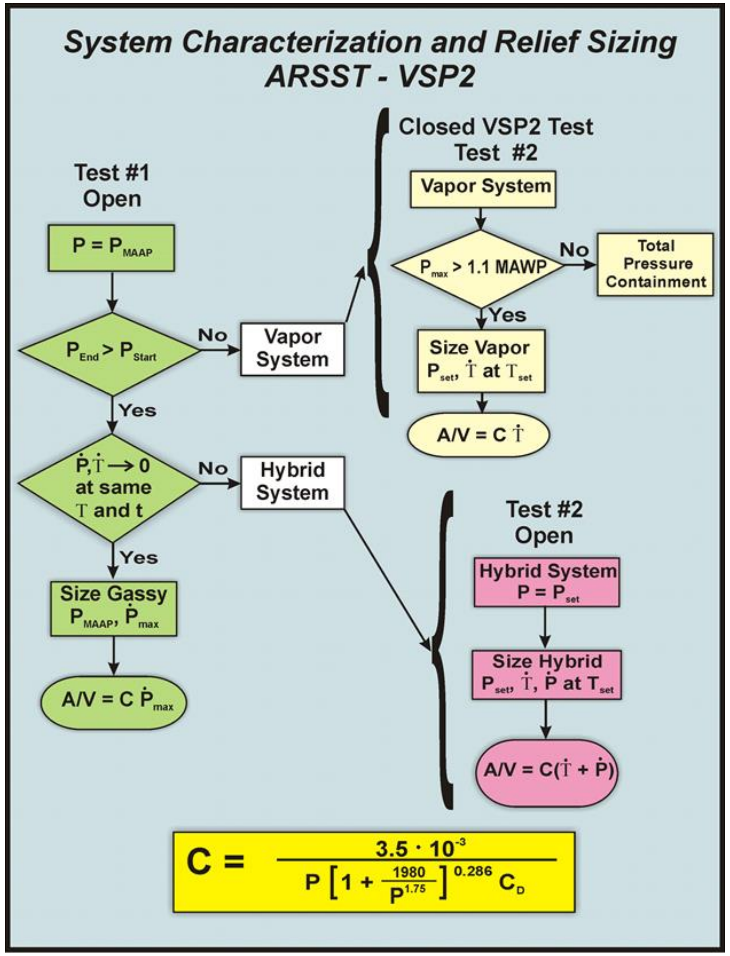


What leads to or triggers runaway reaction?

- Incorrect reagents or wrong order of addition
- Reactant accumulation
- Contamination
- Corrosion
- Overcharge / undercharge of reactant, catalyst, solvent
- Fire exposure leading to reaction or decomposition
- Loss of power/cooling/mixing/inert environment

Testing Strategy



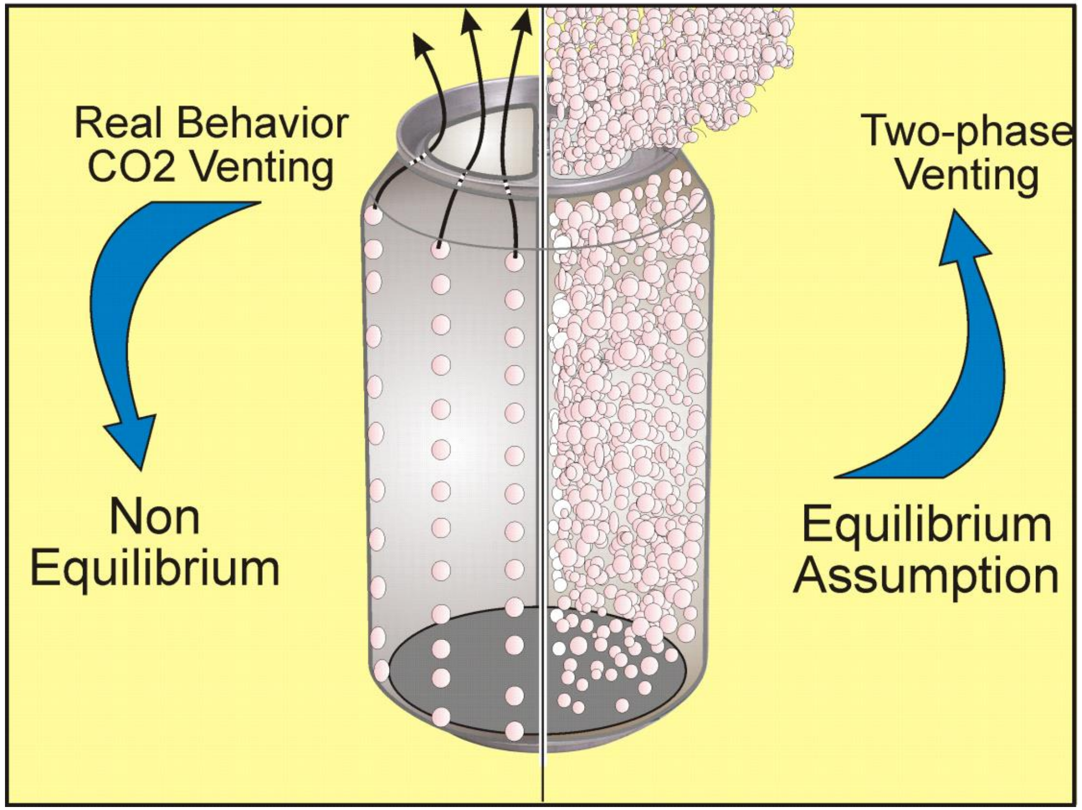


Key Parameters for ERS Design

- Source of overpressure
- **Expected flow regime**
- Material properties
  - Flammability and toxicity of materials if release occurs
- Vessel and relief device characteristics

What is Two-Phase Flow?

- Have you ever accidentally shaken a can of pop?
- Nonequilibrium gives rise to viable beverage industry
  - Localized nucleation sites on the walls minimizes rate at which CO_2 leaves the liquid solution
  - Allows for gas-liquid disengagement resulting in minimal liquid flow out the vent
- Equilibrium conditions following popping of the can would give rise to
  - Homogeneous-like behavior
  - Explosive ejection of the beverage
- This phenomena is an example of two-phase flow

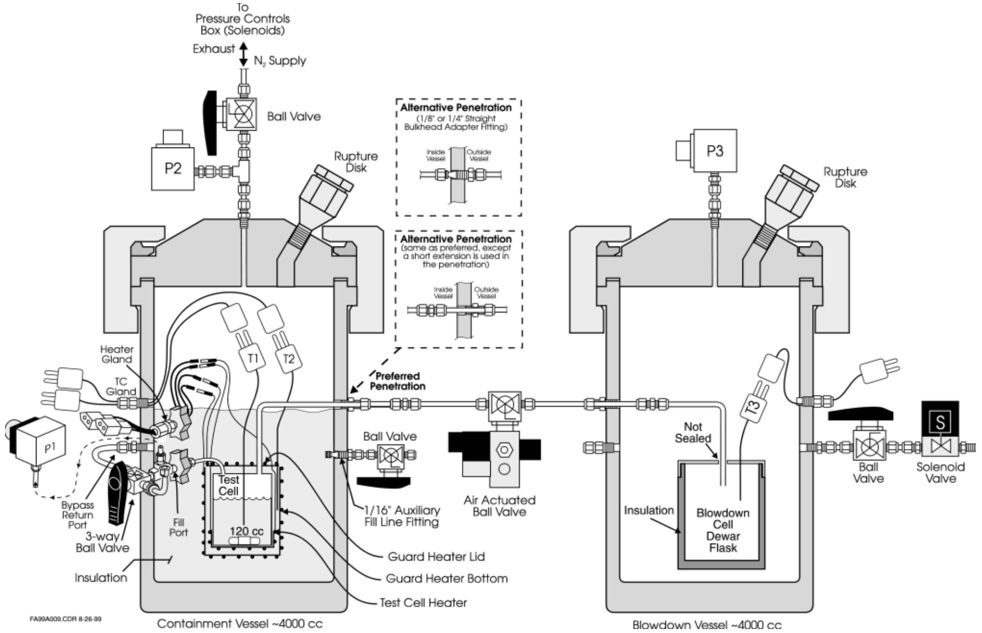


The Impact of Two-Phase Flow on ERS Design

- The presence of two-phase flow increases the required size of relief devices, relief piping, and/or effluent handling systems
- It is common in reactive system venting that at least some quantity of two-phase flow will occur
- This phenomena is caused by a lack of vapor and liquid disengagement which may be caused by liquid swell from the vapor/gas generation, thermal expansion of the vessel contents from an increased temperature, or a high superficial velocity through the vessel and relief device, or it may be some combination of these
- In ERS design there are two main locations where two-phase flow occurs
  - Within the pressure vessel (typically subsonic or unchocked flow)
  - Within the relief line (typically sonic or choked flow)
- If two-phase flow is not considered, you may not be adequately protecting your vessel from overpressurization

Flow Regimes

- Common flow regimes considered:
  - Homogeneous – no disengagement)
  - Bubbly (minimal disengagement)
  - Churn Turbulent (significant disengagement)



Bubbly

Churn

* Video and images courtesy of Dr. B. Doup and Dr. X. Sun (The Ohio State University)

Key Parameters for ERS Design

- Source of overpressure
- Expected flow regime
- **Material properties**
  - **Flammability and toxicity of materials if release occurs**
- Vessel and relief device characteristics

FAUSKE & ASSOCIATES, LLC

Material Properties for ERS Design

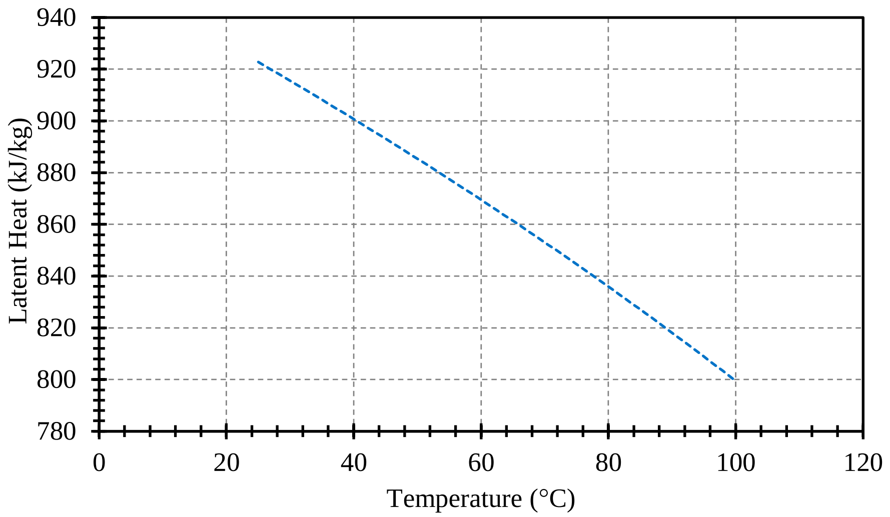
- Properties are composition and temperature dependent
  - Interested in properties at the venting temperatures (pressures)
- Research pure component or mixture properties in the literature
  - NIST Webbook
  - SDS
- Experimentally measure properties

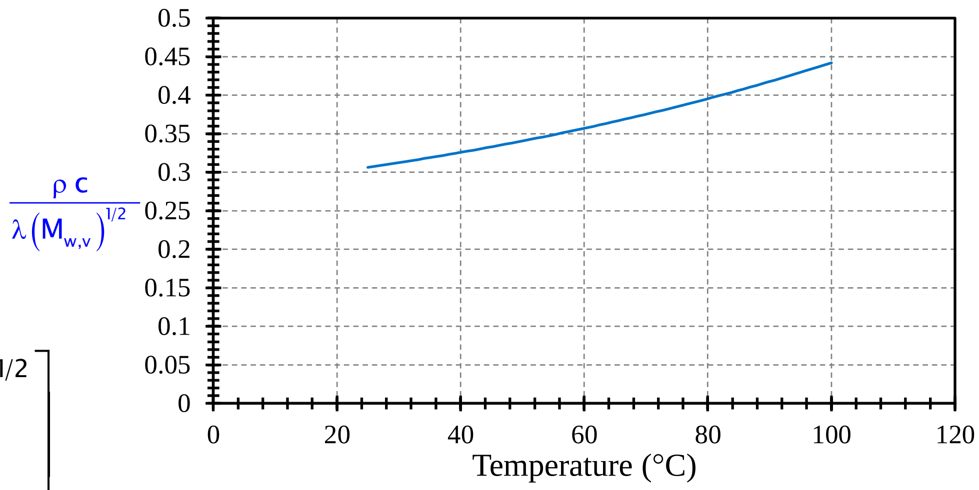
Staged Approach to Material Property Estimation

1. Single component as a representation
2. Ideal Mixing properties
3. Utilize Thermodynamic Mixing Models

$$A / V_R \propto \left[\frac{\rho\, c}{\lambda \left(M_{w,v}\right)^{1/2}} \frac{\dot{T}}{P} (RT)^{1/2} + \frac{\rho\, v\, \dot{P}}{m_t\, P} \left(\frac{M_{w,g}}{RT} \right)^{1/2} \right]$$

Ethanol





Key Parameters for ERS Design

- Source of overpressure
- Expected flow regime
- Material properties
  - Flammability and toxicity of materials if release occurs
- **Vessel and relief device characteristics**

FAUSKE & ASSOCIATES, LLC

Vessel and Relief Device Details

- Vessel Dimensions
  - Vessel diameter can impact two phase flow
  - Void volume
  - Vessel head type and fire heating
  - Design pressure
- Relief Line Characteristics
  - Rupture disk vs. PSV vs. Combination
  - Pressure losses in a relief line
  - Valve stability
  - Set pressure
  - Equivalent Length
- Effluent Handling Systems
  - Location of inlet and outlet lines

FAUSKE & ASSOCIATES, LLC

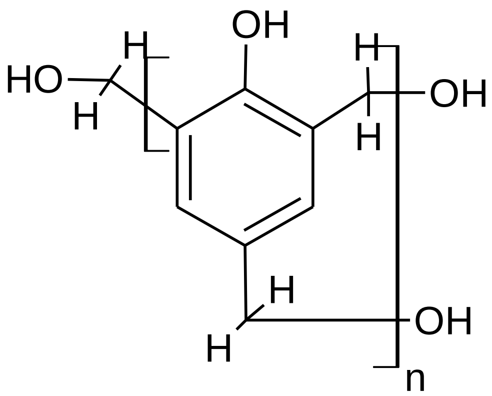
Case Studies & Introduction to FERST Powered by CHEMCAD

33

Case Study 1 – Repurposing a Vessel

- Problem statement: Repurpose an existing vessel and consider two potential uses:
  - Reactor for Phenol-formaldehyde process:
    - In 2001, the worldwide production was > 4 x 10^6 metric tons, ~50% in the US
    - Wood bonding, ablation (heat shields), abrasives, coatings (can lining), composites, felt-bonding, foams, foundry (casting), friction, laminating (PCB), molding, proppants (fracking), refractory, rubber, substrate saturation (paper)
  - Storage vessel for process water
- Vessel parameters:
  - Volume: 12 m^3
  - Internally agitated
  - Spare 4" diameter nozzle that can be repurposed as a relief path
    - Considering a rupture disk with a set pressure of 3.8 bara
  - Maximum allowable working pressure: 7.9 bara

- Need to determine if existing vessel is adequate for intended purpose.



- Phenol (substituted phenols, resorcinols)
  - Solid (mp 40.5°C)
  - Liquefied (~90% in water)
- Formaldehyde (primarily)
  - 37% or 50% aqueous
  - Paraformaldehyde (solid)
  - Trioxane (solid, mp 62°C)
- Catalysts
  - Aqueous bases (caustics)
  - Organic bases (amines, these get incorporated in the resin)
- Water

FAUSKE & ASSOCIATES, LLC

Case Study 1 – PHA Results – Credible Upset Scenarios

- Potential process deviations can only be identified with a detailed knowledge of the chemistry and plant from multiple different perspectives (chemist, operators, engineers, EHS, etc.)
- Process Hazard Analysis (PHA) = An organized and systematic process to identify and analyze the significance of potential chemical hazards
  - Required by OSHA

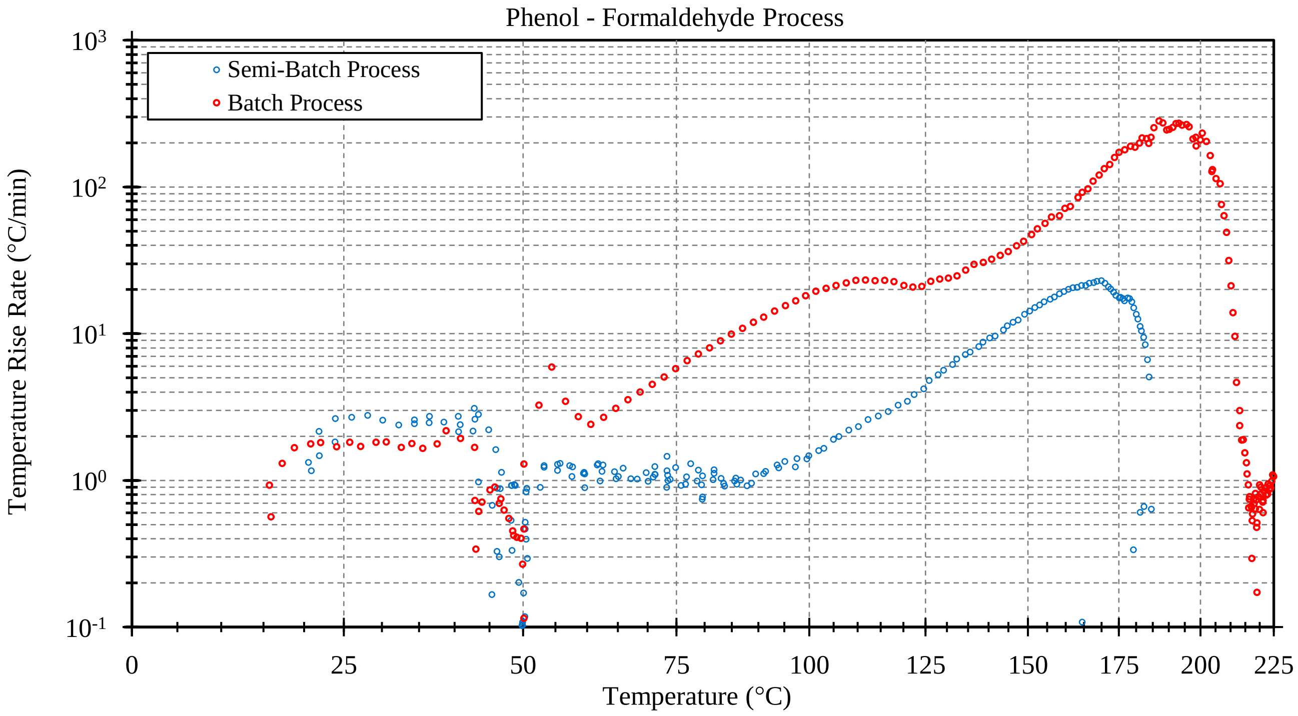
PHA Upset Scenario Findings:

- Phenol-formaldehyde Process
  - Loss of cooling Batch vs. Semi-Batch
- Process Water Storage Tank
  - Fire exposure

Case Study 1 – Source Term Results

Tested Upset Scenarios & Findings:

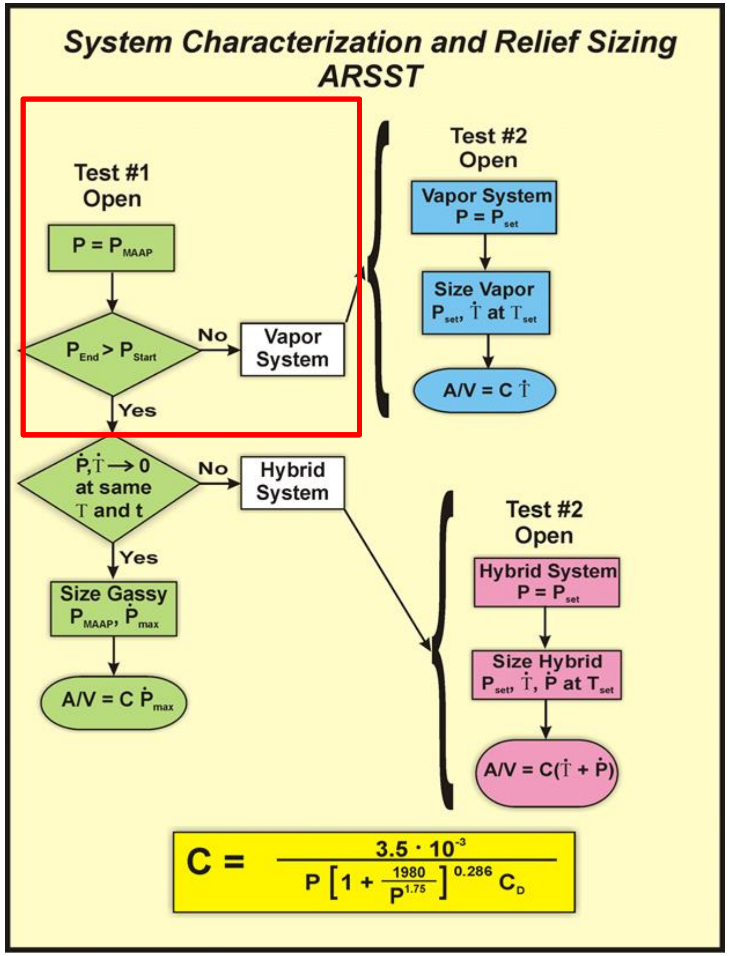
- Storage Tank for Process Water
  - Nonreactive water-like vapor venting
  - Fire heating rate per API 520/521
  - Churn Turbulent or Bubbly Flow Regime
- Phenol Formaldehyde Reactor
  - Reactive vapor venting
  - Loss of cooling at process temperature during a controlled addition of catalyst
  - Loss of cooling at process temperature after batch loading of catalyst
  - Bubbly flow regime

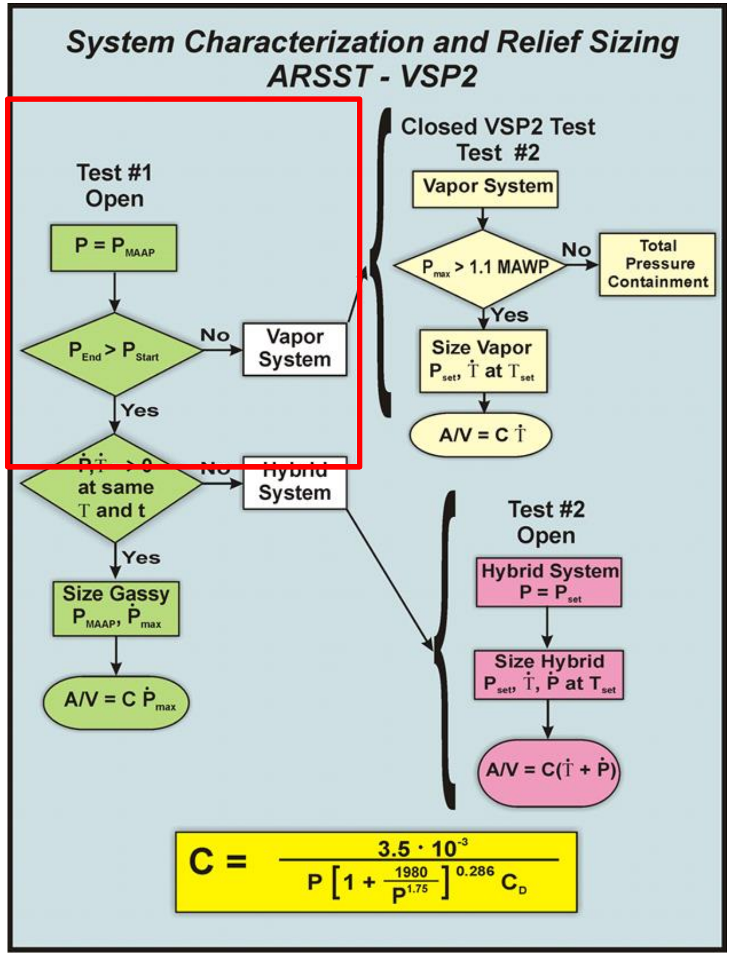


$$\dot{Q}_v \left(m^3\ s^{-1}\right) = \frac{V\ \rho\ c\ \dot{T}}{\lambda\ \rho_v}$$

$$A/V_R \propto \left[\frac{\rho\ c}{\lambda (M_{w,v})^{1/2}}\ \frac{\dot{T}}{P} (RT)^{1/2}\right]$$

Vapor System Testing Strategy





Case Study 1 –Results

Table 1: Ideal Vent Sizing Results from FERST Powered by CHEMCAD

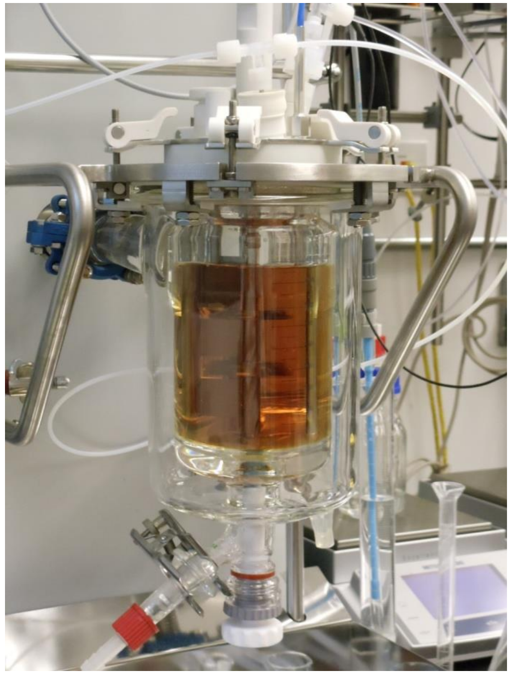
Scenario	Relief Type	Flow Regime	Ideal Vent Area (in^2)	Ideal Vent Diameter (in)	Recommended Nominal Relief Diameter (in)	Allowable 4fL/D
Loss of Cooling during Ph-F Batch Process	Reactive Vapor Venting	Bubbly	226.7	17.0	20.0	1.8
Loss of Cooling during Ph-F Semi-Batch Process	Reactive Vapor Venting	Bubbly	60.3	8.8	10.0	2.6
Fire Exposure to Water-Like Fluid	Non-Reactive Vapor Venting	Churn Turbulent	0.6	0.8	1.0	2.1
Fire Exposure to Water-Like Fluid	Non-Reactive Vapor Venting	Bubbly	4.0	2.3	2.5	0.8

FAUSKE & ASSOCIATES, LLC

Recall, the available nozzle diameter is 4”

Case Study 1 – Conclusion

- This vessel is not currently equipped to handle the phenol-formaldehyde process
  - The ideal vent diameter for both the semi-batch and batch process is > currently installed 4” diameter line
  - Could we lower the set pressure?
- This vessel can serve as a storage vessel
  - Ensure the frictional losses are within allowance
  - If it was not adequate, consider fireproof insulation or other firefighting measures



Ph-F Resin in an RC1

FAUSKE & ASSOCIATES, LLC

Case Study 1 – Conclusions on ERS Basics

- Upset Scenario Selection is Very Important
  - Reactive heat >> fire heat
- Flow Regime Impacts Relief Size
  - Staged approach
  - Experimentally measure
- Vapor Systems
  - Noncondensable gas is not generated in the venting region
  - Temperature rise rate at the set point is driving force for pressurization
  - Latent heat of vaporization is available

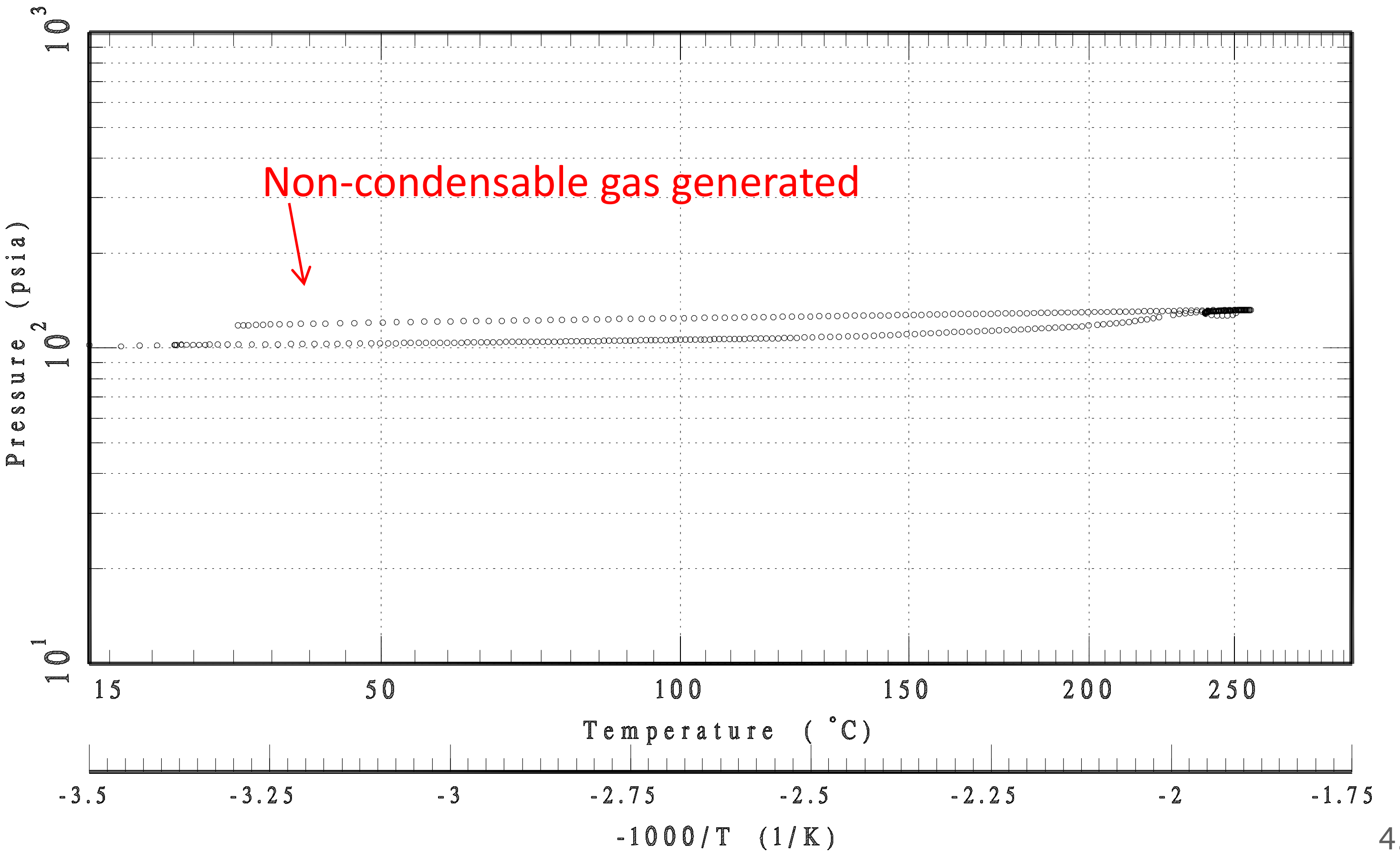
Case Study 2 – Evaluate the Adequacy of a RD on 2 Vessels

- Problem statement: We are moving a new product into identical storage vessels, and want to ensure our rupture disk is adequately sized
  - 40% dicumyl peroxide in 2,2,4-trimethyl-1,3-pentanediol diisobutyrate
  - Upset scenario = Fire Exposure with 0.5 °C/min
- Vessel parameters:
  - Volume: 12 m^3
  - Filled with 150 kg
  - Storage tank MAWP is 80 psig
  - Rupture disk set pressure is 50 psig
  - Nominal RD Diameter is 8”, and
  - The total piping frictional losses (4fL/D) = 3.5 for Vessel 1 and 6.5 for Vessel 2

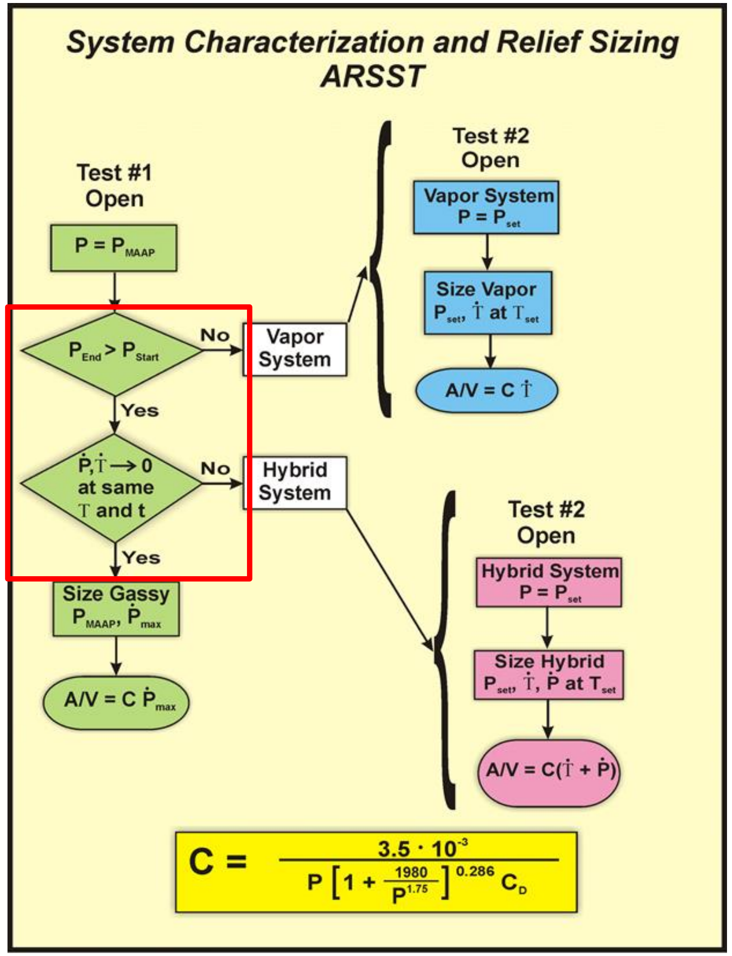
Case Study 2 – Source Term Results

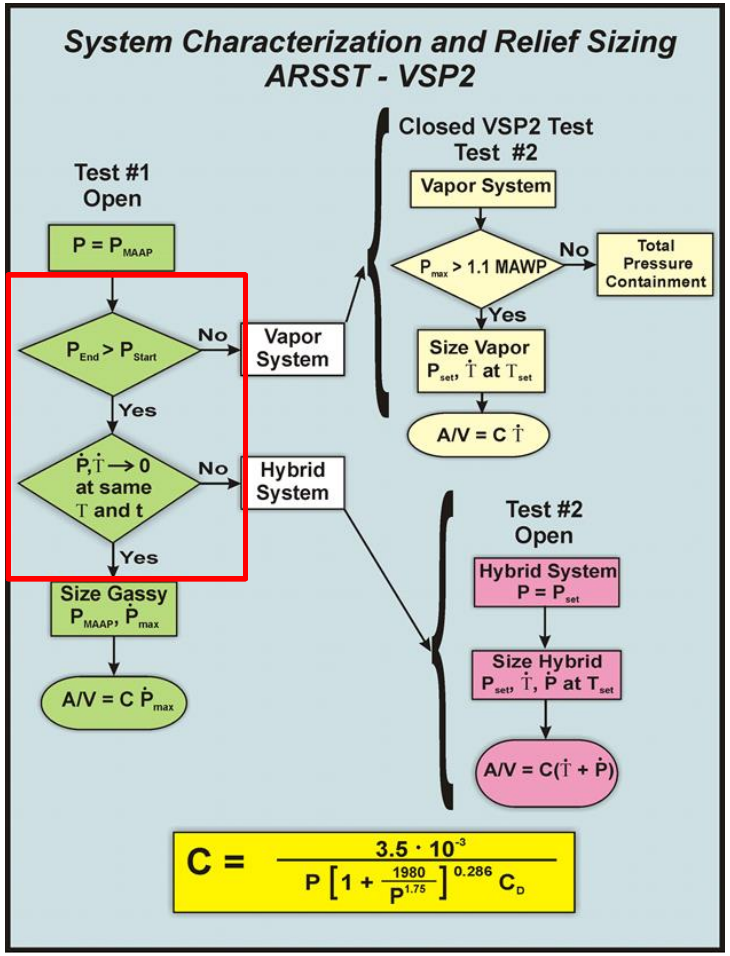
Calorimetry Testing:

- Open cell ARSST test, using a nitrogen backpressure of 88 psig
  - Containment Volume: 350 ml
  - Sample Mass: 8 grams



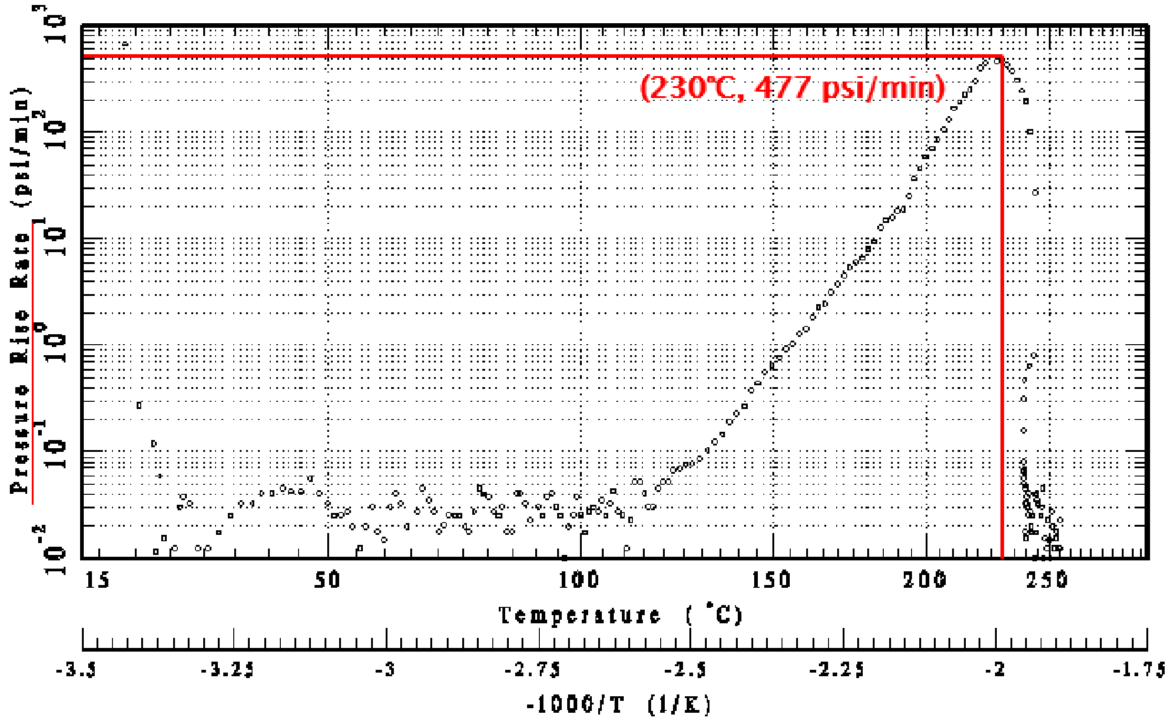
Gassy System/Hybrid System Testing Strategy



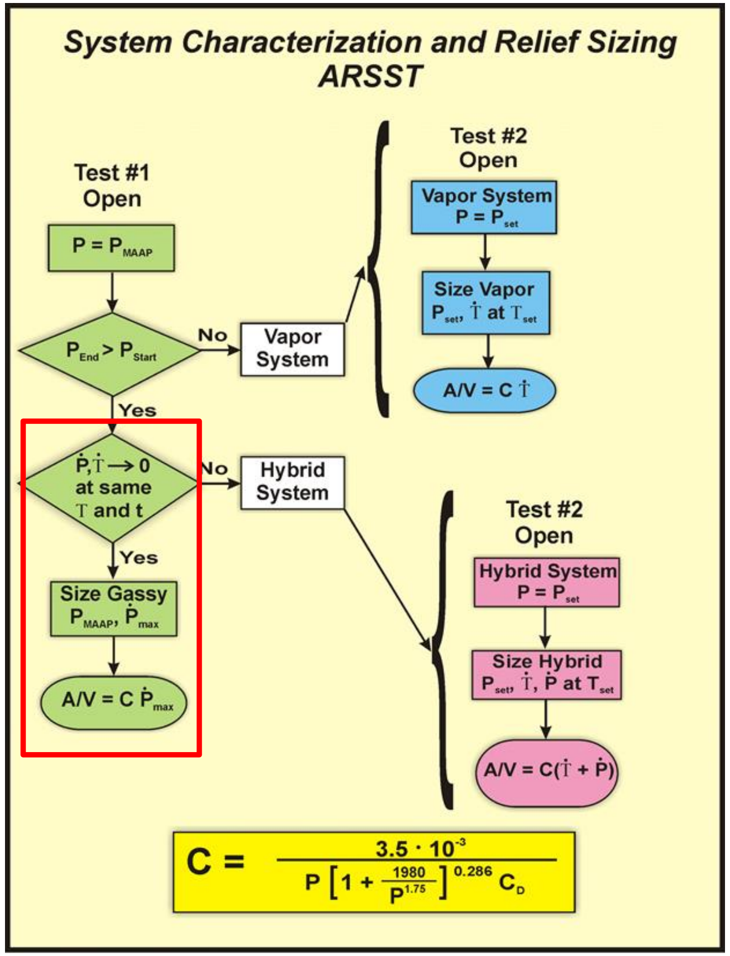


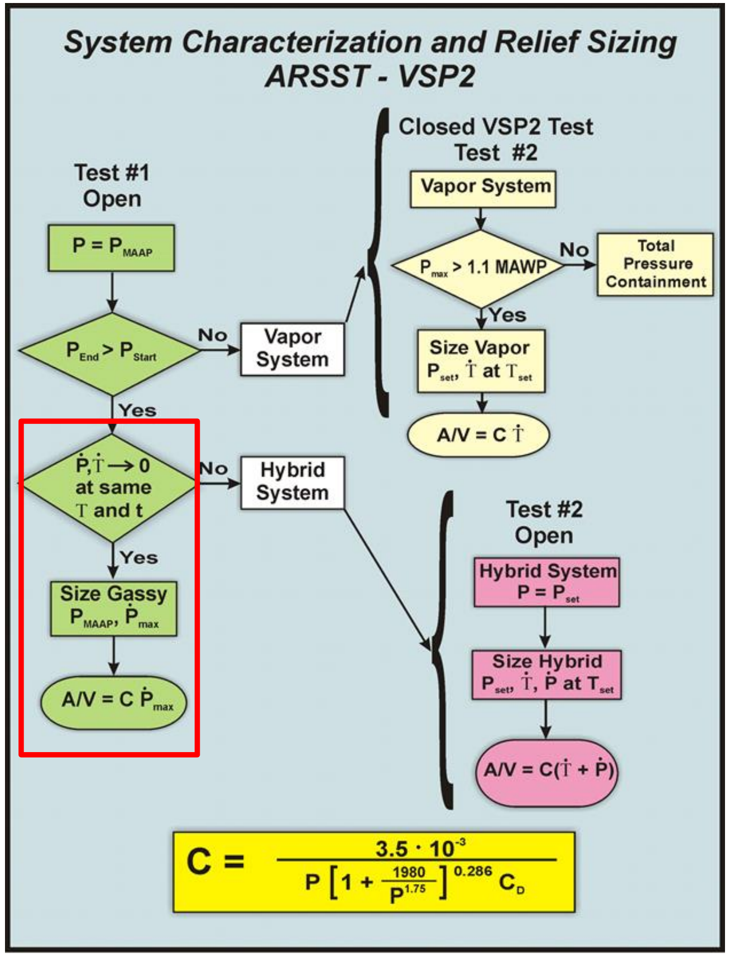
Case Study 2 – Gassy vs. Hybrid

- Predict system vapor pressure
  - Normal Boiling point for dicumyl peroxide = 395°C
  - Normal Boiling point for TXIB = 280°C
  - Peak reaction temperature = 260°C
  - Expect very low or minimal vapor pressure in the venting region
- OR experimentally test for tempering/vaporization



Gassy System Testing Strategy





Case Study 2 –Results

Table 2: Rating Vent Sizing Results from FERST Powered by CHEMCAD

Scenario	Relief Type	Total 4fL/D	Thermodynamic Model	Peak Pressure (psig)
Fire Exposure to 40% dicumyl peroxide in TXIB	Gassy System Venting	3.5	Ideal Mixing	84.8
		6.5	Ideal Mixing	96.6
		3.5	Ideal Mixing, Density taken to be 1.1x	87.0
		3.5	Peng Robinson	85.5
		6.5	Peng Robinson	97.3

Recall, vessels MAAP = 88 psig

Case Study 2 – Conclusion & ERS Basics Conclusions

- The vessel with a total 4fL/D = 3.5 is adequate
- The vessel with a total 4fL/D = 6.5 is inadequate
  - Adjust relief piping?
  - Change the fill fraction?
  - Refine analysis?

- Relief piping impacts effective relief area
- Material properties impact result
  - Staged approach
- Gassy systems
  - Noncondensable gas is generated
  - Peak pressure rise rate is driving force for pressurization
  - Latent heat of vaporization is NOT available

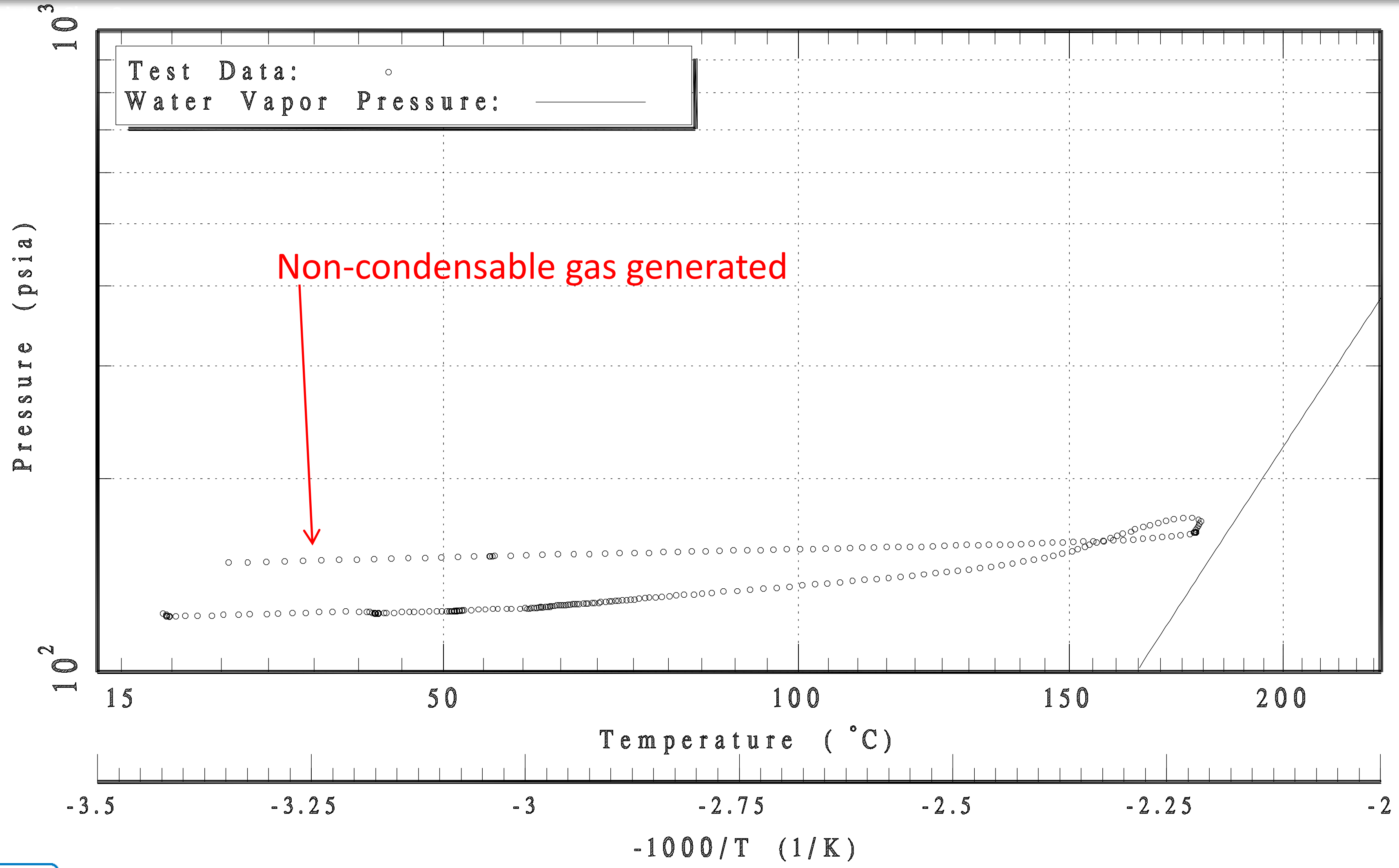
$$\dot{Q}_g \left(m^3\ s^{-1}\right) = \frac{V\ \rho\ v}{m_t}\frac{\dot{P}}{P}$$

$$A/V_R \propto \left[\frac{\rho\ v\ \dot{P}}{m_t\ P}\left(\frac{M_{w,g}}{RT}\right)^{1/2}\right]$$

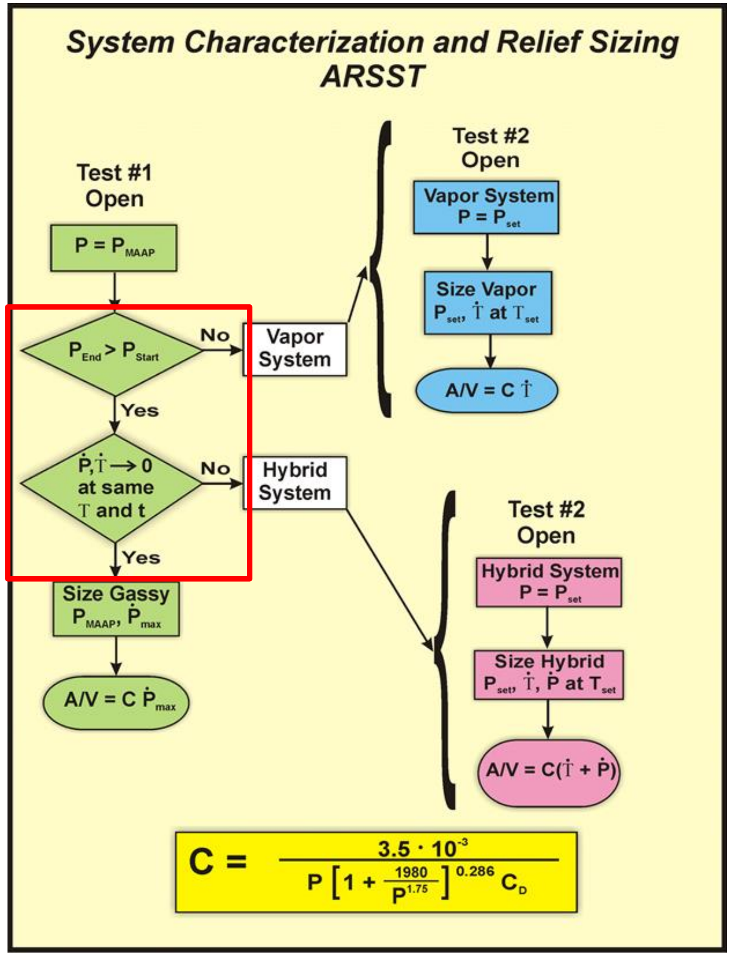
Case Study 3 – Replacing a PSV

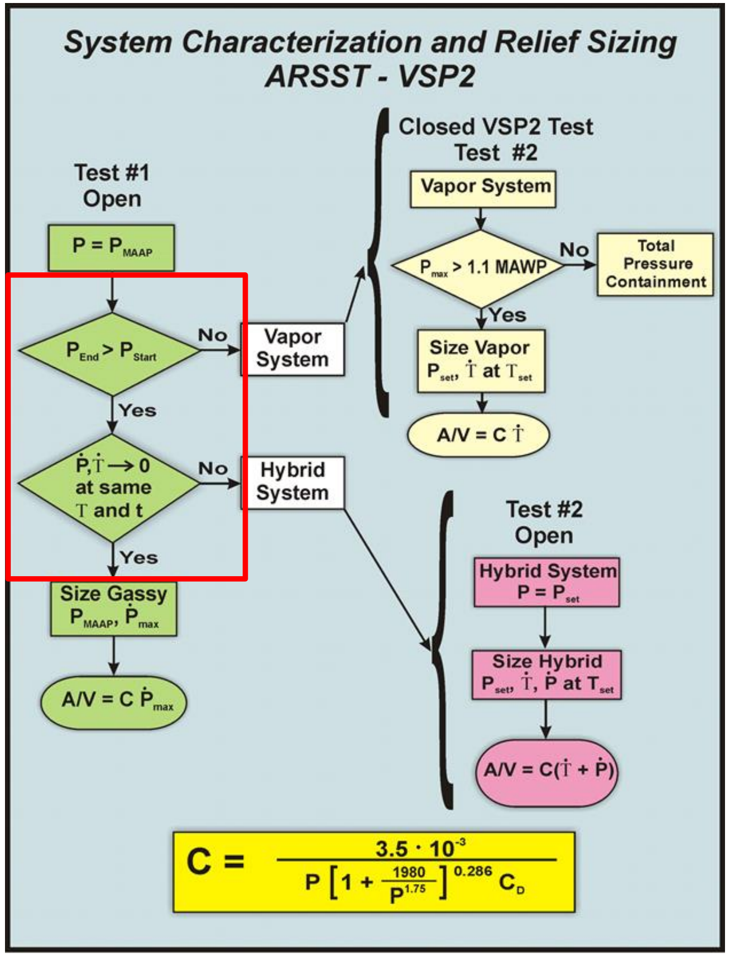
- 25% hydrogen peroxide is stored in a 1.2 cubic meter tank
- Results of PHA indicate iron contamination could cause a runaway reaction due to accelerated decomposition of hydrogen peroxide
  - Tank MAWP is 100 psig
  - Desired set pressure of new safety relief valve is 20 psig
- Common Testing Protocol:
  - High backpressure experiment (MAAP)
    - Is there noncondensable gas generation?
  - Low backpressure experiment (Set Pressure)
    - Is there vaporization of the sample?
- Open test cell VSP2 tests run at 110 psig and 20 psig
- Assume homogeneous-like vessel venting

Case Study 3 – Source Term Results



Gassy System/Hybrid System Testing Strategy

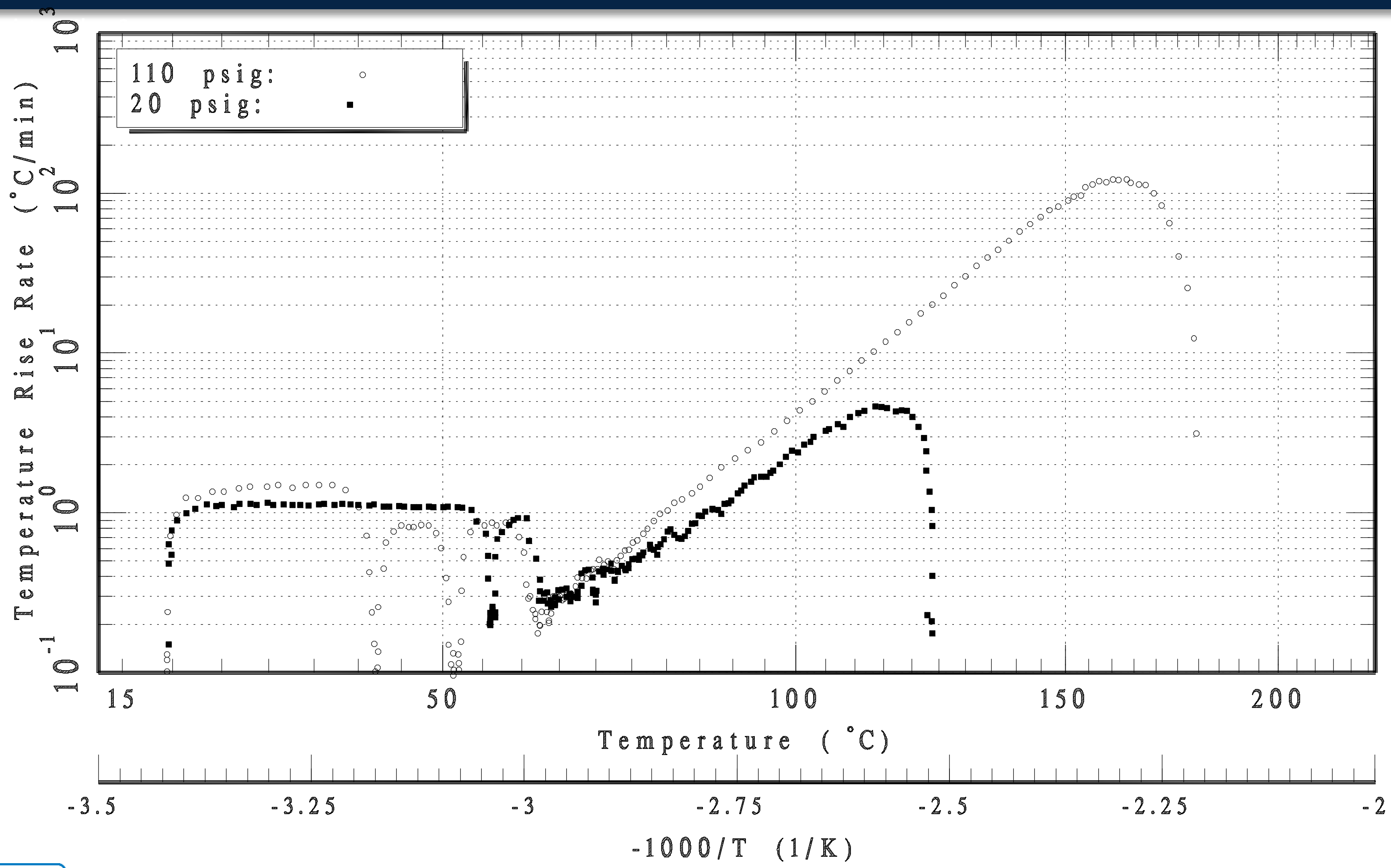




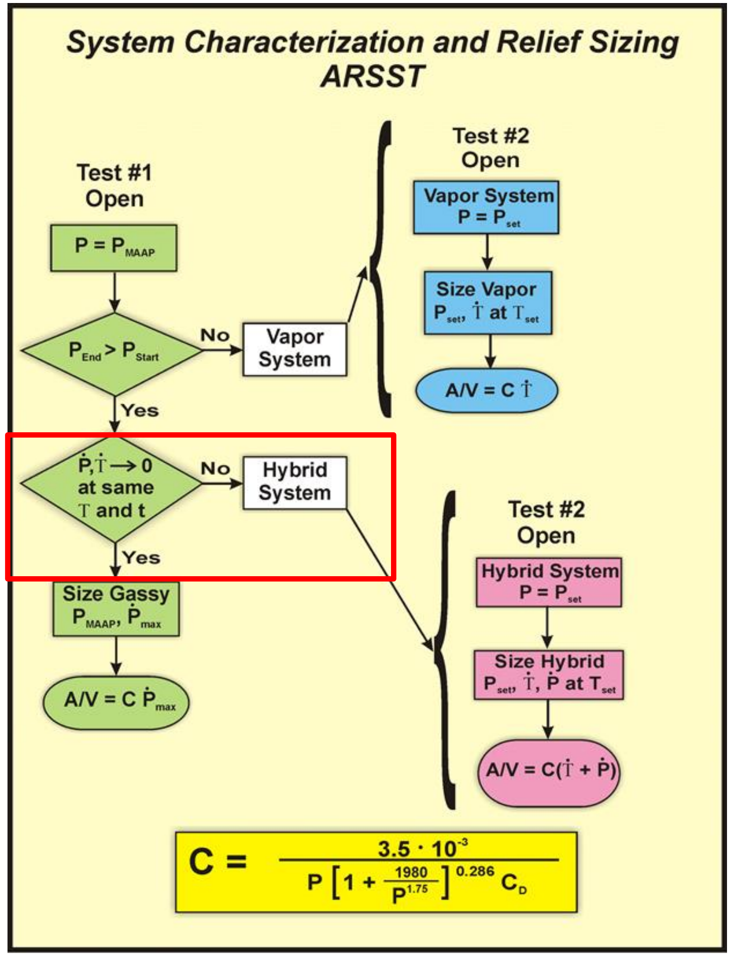
Case Study 3 – Gassy vs. Hybrid

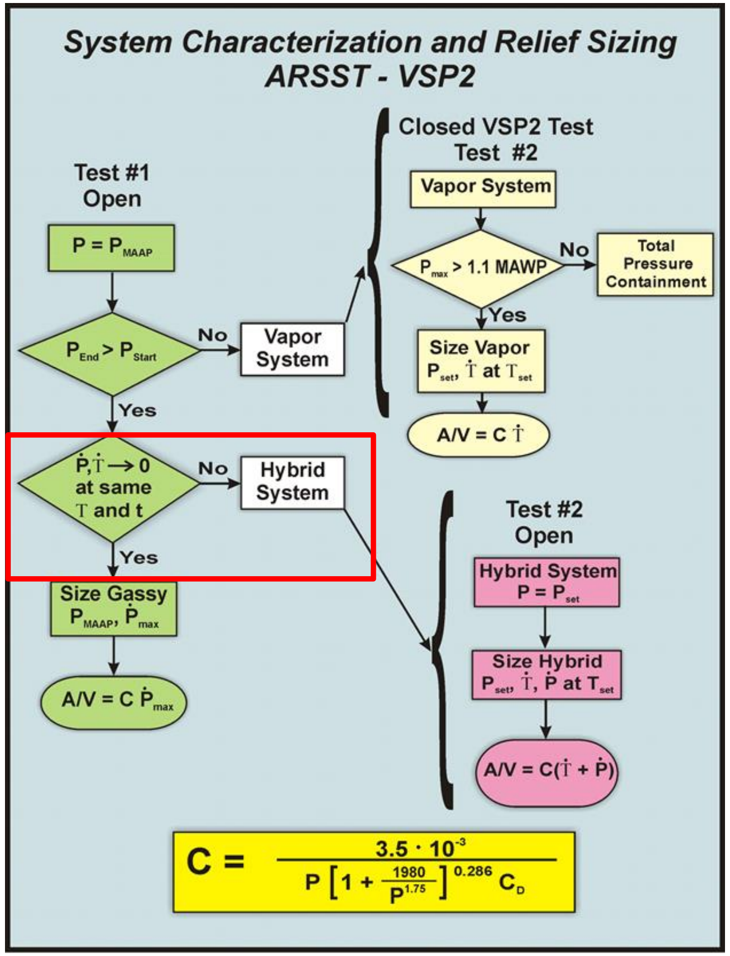
- Predict system vapor pressure
  - Water temperature corresponding to 20 psig (set pressure) = ~125°C
  - Water temperature corresponding to 110 psig (vessel MAAP) = ~173°C
- OR experimentally test for tempering/vaporization

Case Study 3 – Source Term Results



Testing Strategy





FERST Powered by CHEMCAD – ERS Design Results

Table 3: Valve Design Vent Sizing Results from FERST Powered by CHEMCAD

Parameter	20 psig Set Pressure 0.4 Initial Void Frac.	55 psig Set Pressure 0.4 Initial Void Frac.	55 psig Set Pressure 0 Initial Void Frac.
Estimated Relief Set Temperature, °C	123	143	141
Discharge Mass Flow Rate, kg/min	845	4,618	21,756
Ideal Vent Area, cm^2	16.6	86.0	155
Recommended Valve	4 x 6 L	6 x 8 R	8 x 10 T
Allowable Inlet 4fL/D	2.0	0.5	0.2
Allowable Outlet 4fL/D	2.5	2.0	7.0

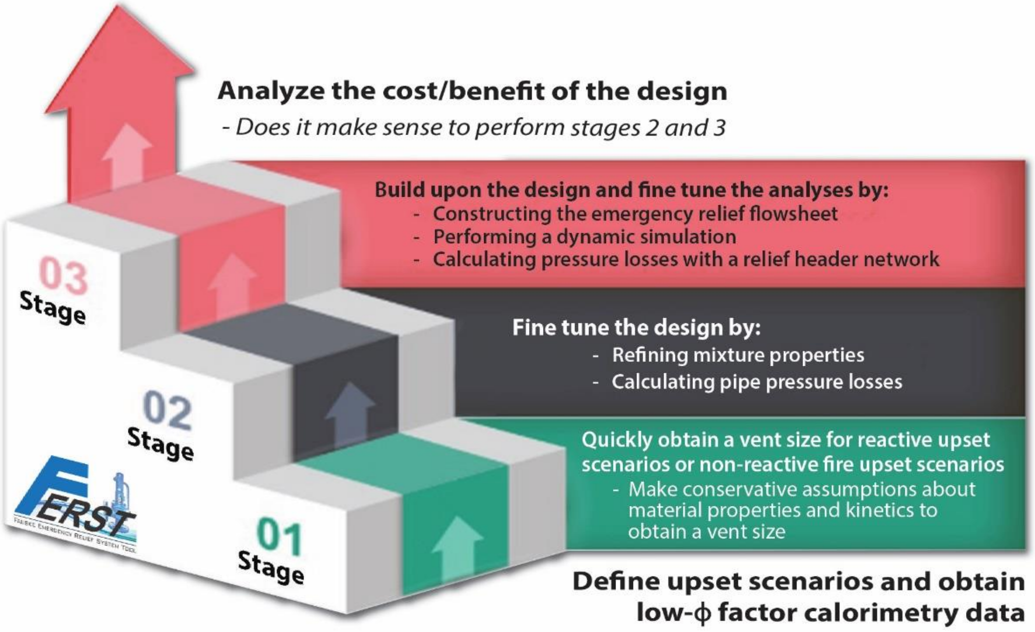
FAUSKE & ASSOCIATES, LLC

FERST powered by CHEMCAD – A Staged Approach to ERS Design

- Fauske Emergency Relief System Tool powered by CHEMCAD allows users to:
  - Quickly and easily obtain a conservative vent size
  - Refine the ERS design if there is a cost benefit for improving the analysis.
- Designed to allow users to quickly obtain a vent size for
  - Reactive upset scenarios
  - Non-reactive fire upset scenario
- Provide the platform to build upon the simple design methods and fine tune the analysis
  - Refine mixture properties
  - Adjust flow regime
  - Perform a dynamic simulation
  - Read in low-ϕ factor calorimetry data
- Provide the platform to perform additional analyses
  - Pipe pressure losses
  - Relief header pressure losses
- Approach is intended to allow the user to perform cost/benefit analysis of fine tuning the analysis

Key Takeaways

- Runaway reactions can lead to catastrophic vessel failure and the source terms should be quantified to ensure the ERS design is adequate
- Upset scenario selection is very important for ERS designs
  - Reactive heat >> non-reactive
- Two-phase flow is expected for venting of most chemical reaction upset scenarios and should be considered in the ERS design
  - Presence of two-phase flow increases ideal vent area
- Material properties of the venting fluid directly impact the results
- Vessel and relief device characteristics play an important role in the result
  - Lower set pressure = smaller area



Contact Me:
Elizabeth Raines eraines@fauske.com

FAUSKE & ASSOCIATES, LLC