Calorimetric Techniques to Support your Reactive Hazards Analysis

Presented by:
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Bio

- Gabe Wood – Senior Chemical Engineer
  - B.S.E. in Chemical Engineering from the University of Iowa
  - 14 years at Fauske & Associates
  - Focus on reactive and nonreactive relief device sizing and effluent handling
  - Conduct adiabatic and isothermal calorimetry testing (ARSST, VSP2, DSC, ARC, C80, CPA202)
  - Provide on-site plant support & training
  - AIChE and DIERS member
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Outline

- Reactive Hazards Analysis (RHA)
- Calorimetric Techniques with Acrylic Acid

RHA

- OSHA & EPA require a review of process hazards. When the review is focused on reactive chemical hazards, it is often referred to as an RHA.
- A properly conducted RHA should allow for discovery of all potential reaction hazards so they can be quantified and well understood. Allowing safety systems and controls to be put in place to prevent or mitigate the potential hazards and operate the process safely.
- Potential for thermal runaway
  - 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

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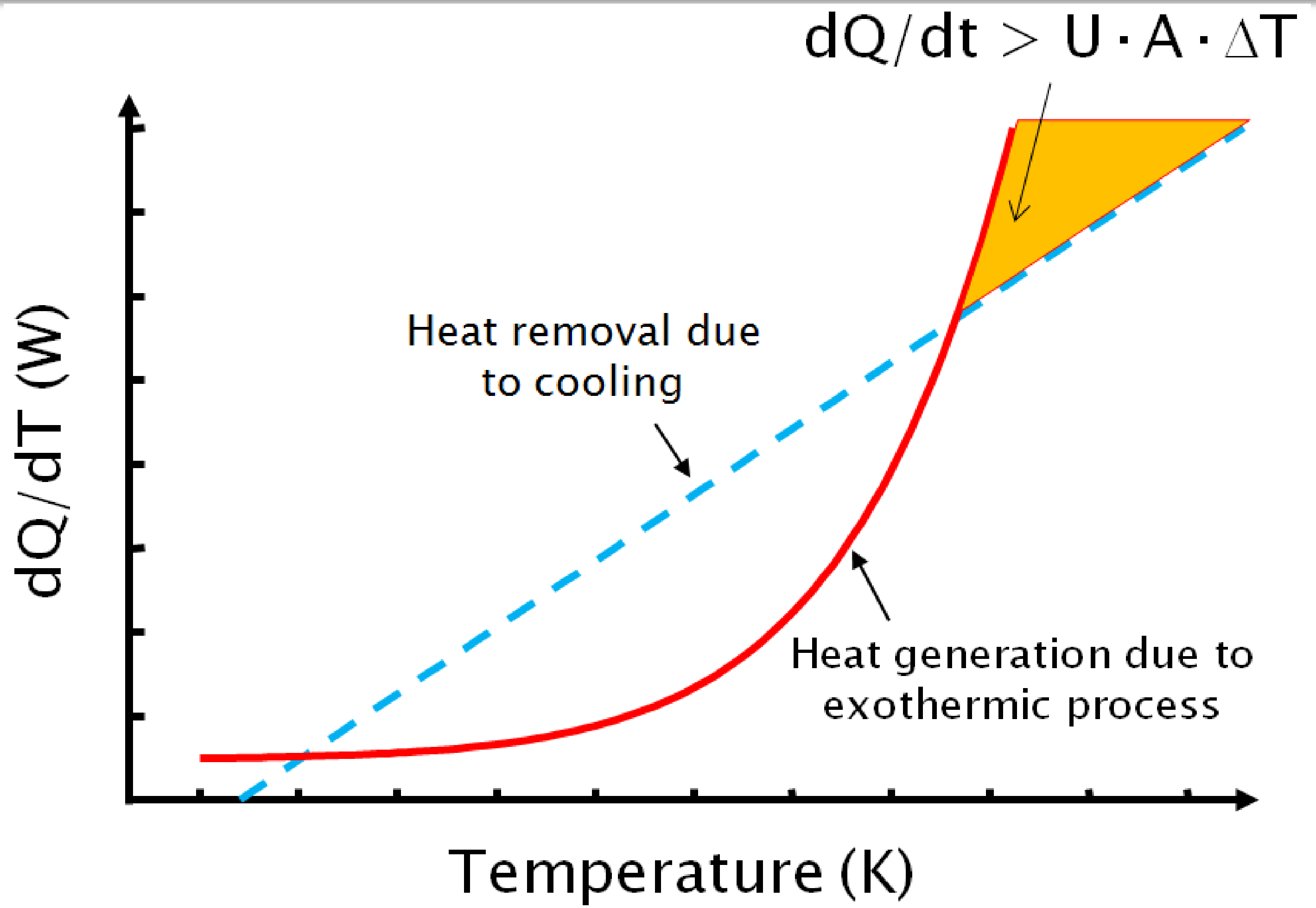
RHA – Thermal Runaway



Heat Generation > Heat Loss = Thermal Runaway

RHA

- Begin with exhaustive search of historical plant documentation and available literature on the chemicals and process.
- Determine whether thermal hazards are present in any reagents, intermediates, or products.
- Consider possible maloperations which could lead to undesired chemistry or the intended chemistry but at an undesired rate of reaction.
- Develop compatibility matrix.
- Where there are gaps in the available data, calorimetry is performed to acquire data to understand the hazard potential and quantify the risk.

Calorimetry – DSC

- Heat flow calorimeter
- Sample size usually 1–10 mg
- Heats samples using a thermal scan (rate typically 0.5–10°C/min)
- Tests can be held isothermally
- Does not measure pressure or have mixing

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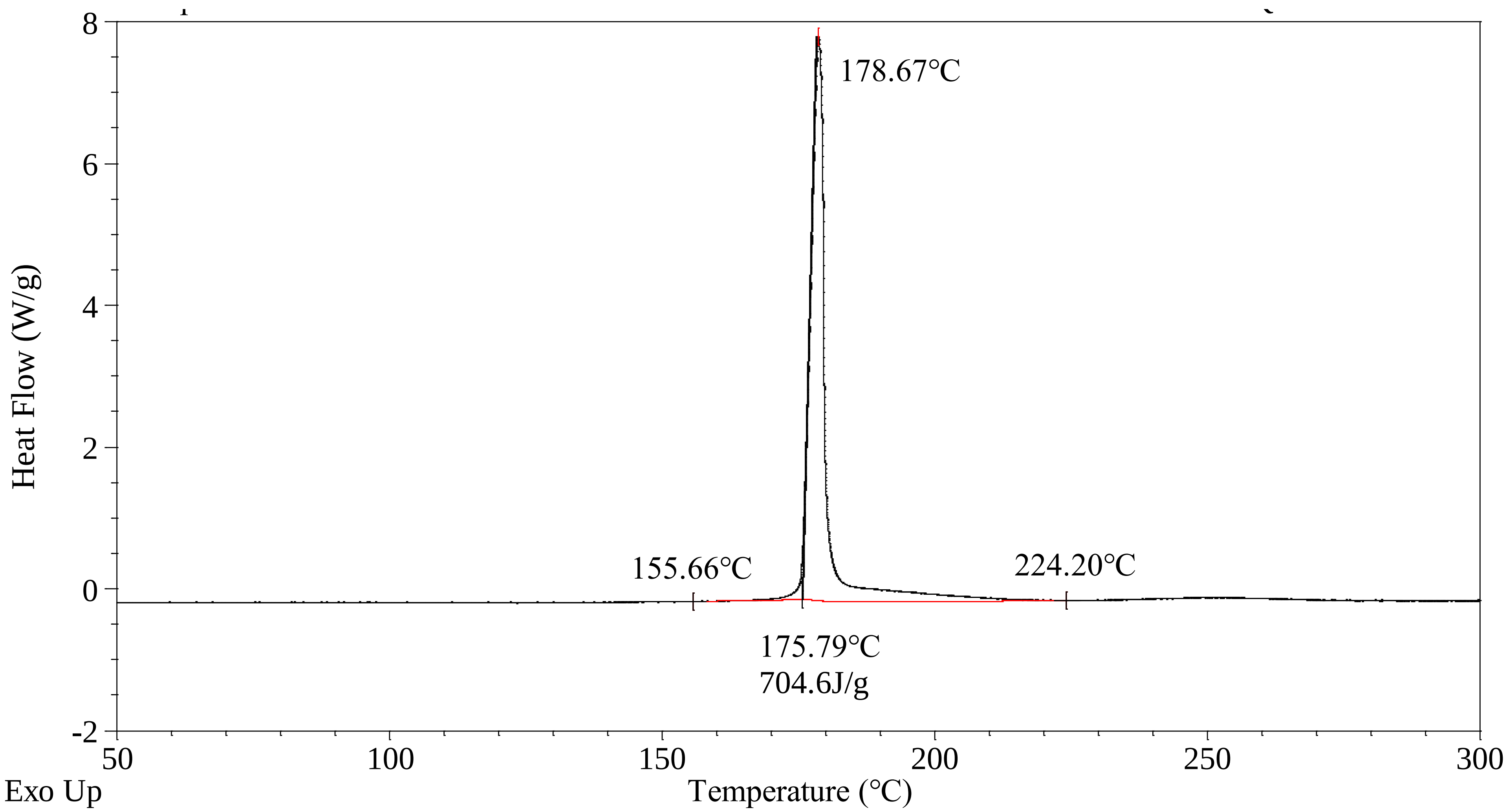
Calorimetry – Screening

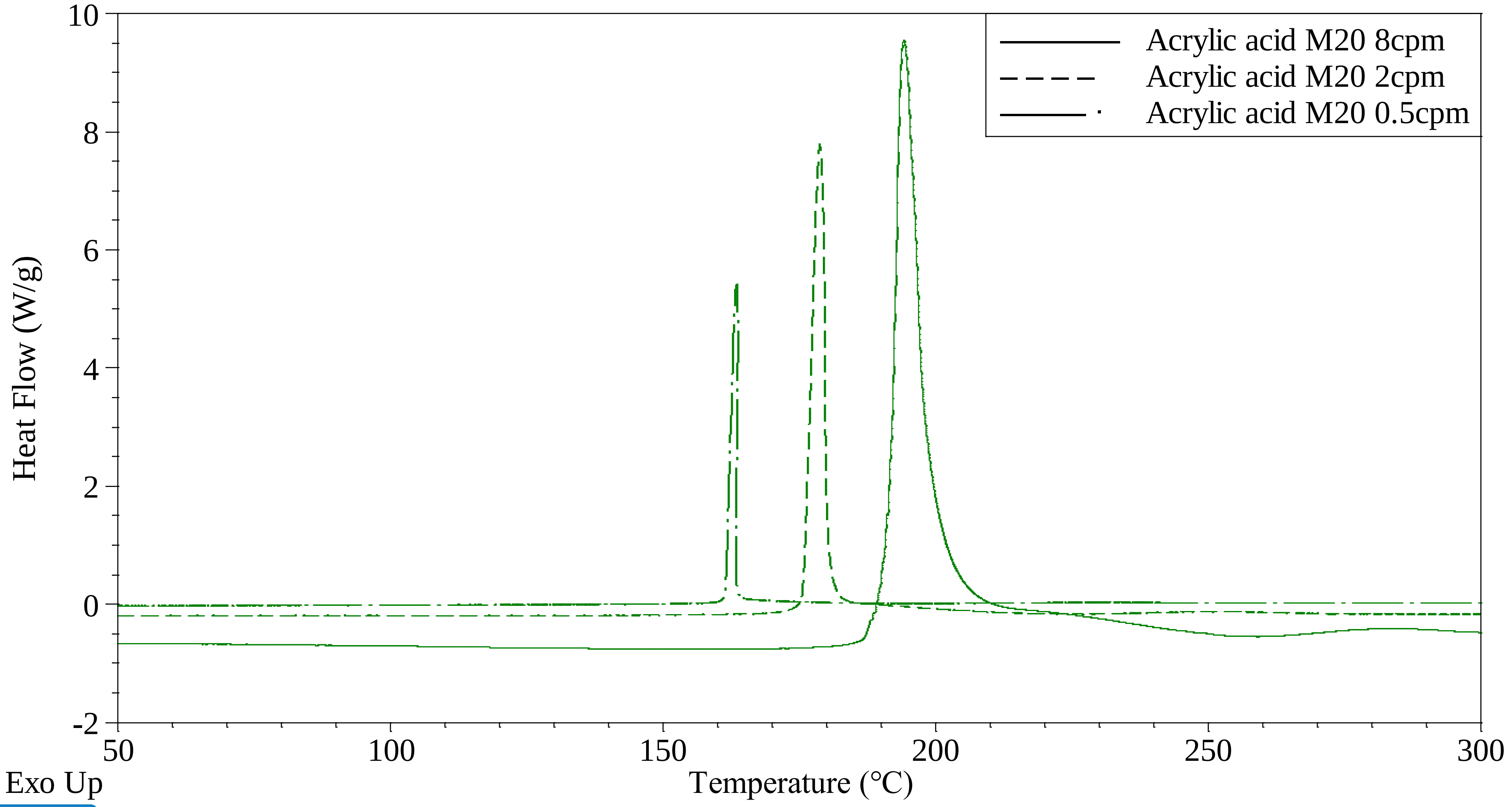
- Perform quick screening using a thermal scan to determine whether a thermal hazard is present.
- DSC scans can determine temperature range of reactivity and quantify heat of reaction (endothermic/exothermic, heat of reaction, kinetic modeling).
- Onset Temperature
  - Temperature at which an instrument, with a given set of conditions, is sensitive enough to detect the reaction. Based on several parameters such as: type of instrument, sensitivity criterion, type of test cell, amount of sample, scan rate, etc.
  - Not an absolute value.
  - Best way to determine risk of a given operating temperature or storage/shipping temperature is to model the kinetics of the reaction and determine if the time to maximum reaction rate is acceptable based on process conditions and your corporation’s risk tolerance.

Calorimetry – Quantify Hazard

Inhibited Acrylic Acid – Ramp 2°C/min



Calorimetry – Onset Temperature



Calorimetry – Material Compatibility

- Consider material compatibility when designing your test.
  - Potential for undesired reactions
  - Impact on kinetics (catalyze, poison, or inhibit reaction)
  - Speed up or delay onset of reaction
  - Is passivation necessary?
  - Seal under air, nitrogen, or argon?
- Examples of tests on inhibited acrylic acid in both gold-plated (M20) and stainless steel (F20) high pressure crucibles.

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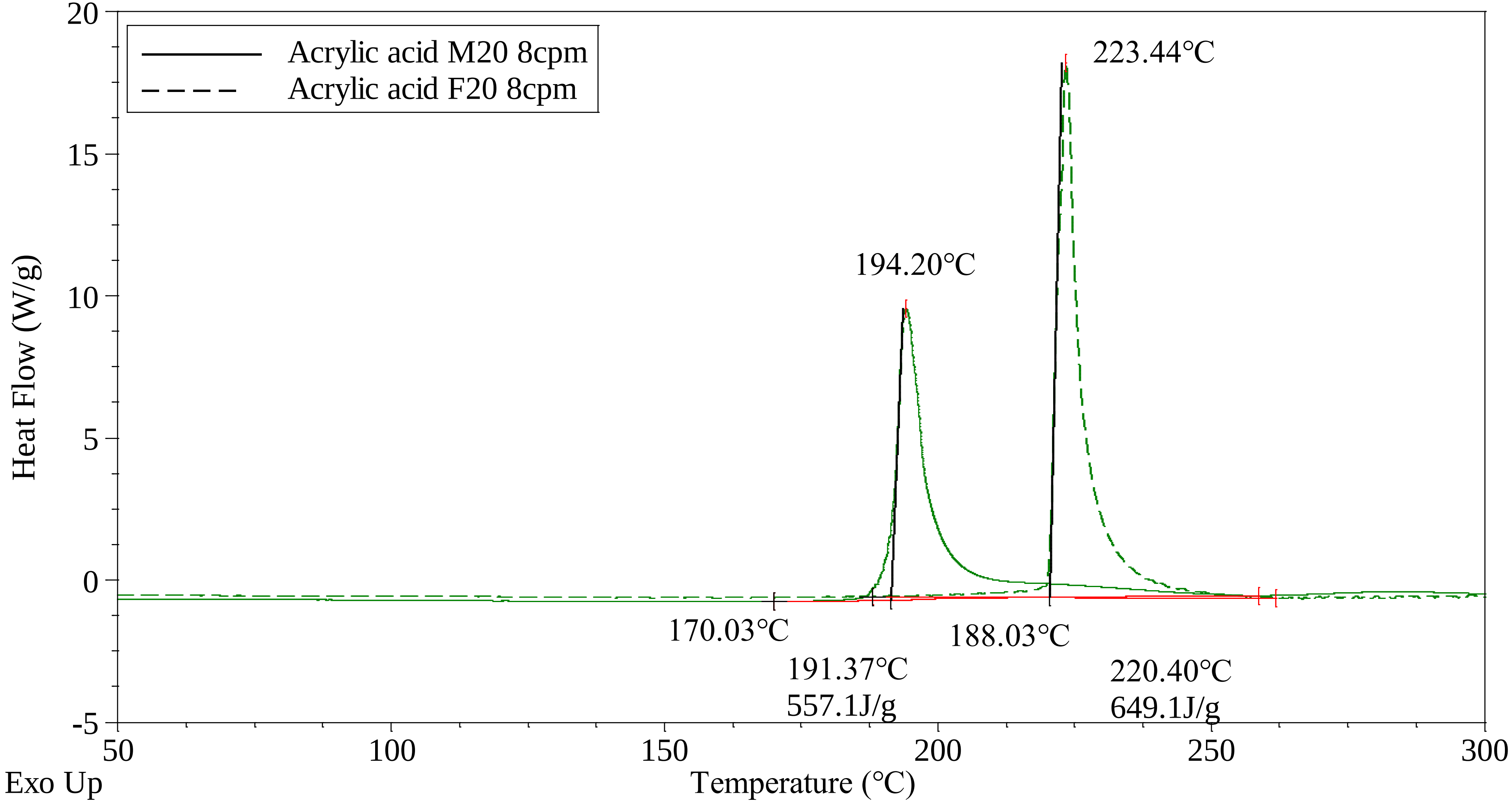
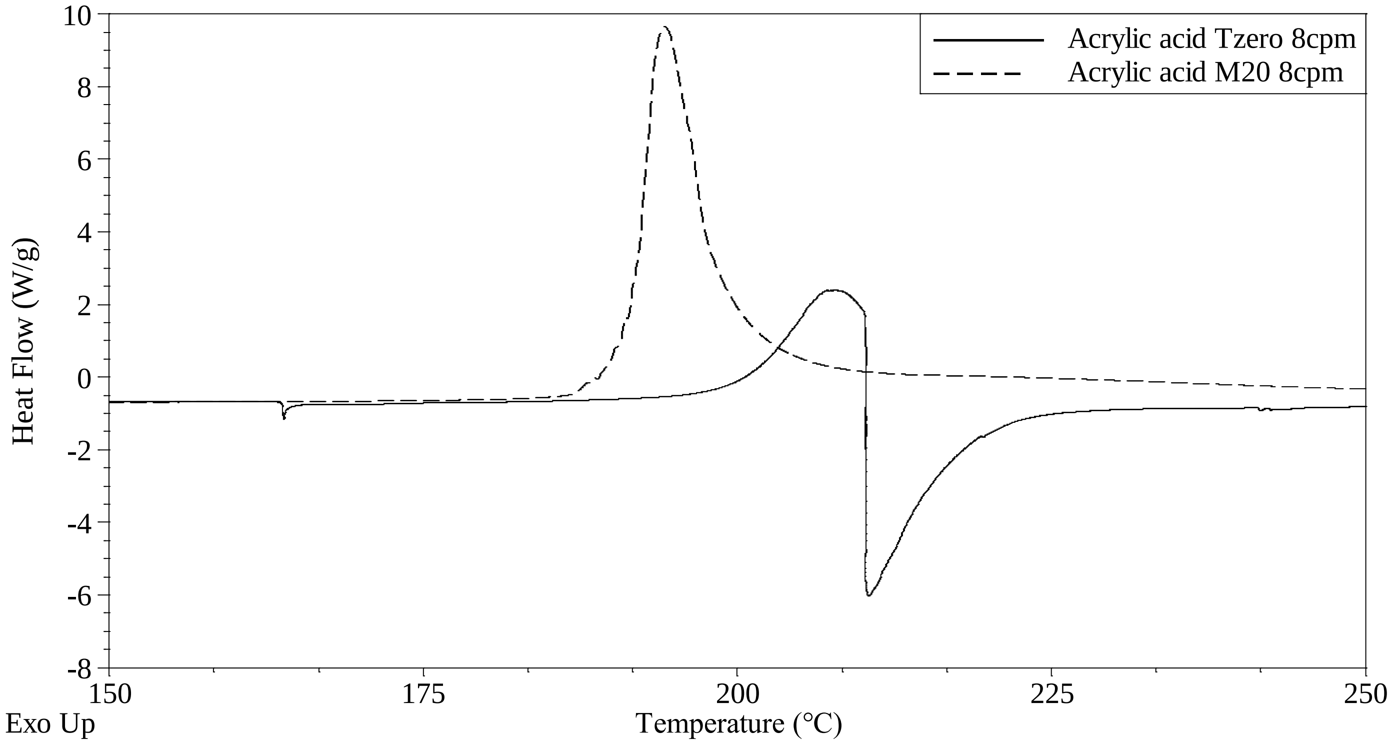
Max. operating pressure: 217 bar
Max. operating temperature: 400°C

Calorimetry – Material Compatibility



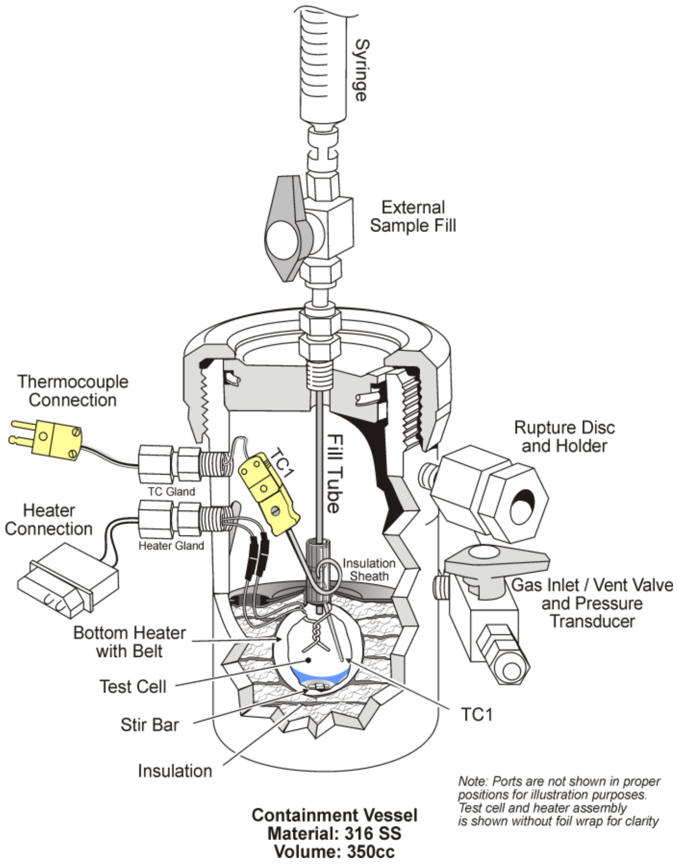
Calorimetry – Low or High Pressure Crucible?

- Tzero mass loss (initial sample 5.39 mg, final sample 0.58 mg, 89% loss)
- Potential to underestimate total energy



Calorimetry – ARSST

- Low thermal inertia adiabatic calorimeter
- Sample size ~ 10 mL
- Typically uses a thermal scan mode
- Measures temperature and pressure
- Has magnetic stirring



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Evaluate Pressure

- ARSST measures pressure in addition to temperature.
- Data can be used to determine moles of noncondensable gas generated.
- Example: ARSST test performed on neat, inhibited acrylic acid. Change in initial and final pressure was 28.6 psi which corresponds to 2.73×10^{-2} moles of noncondensable gas. *Note: pure component acrylic acid vapor pressure from DIPPR.*

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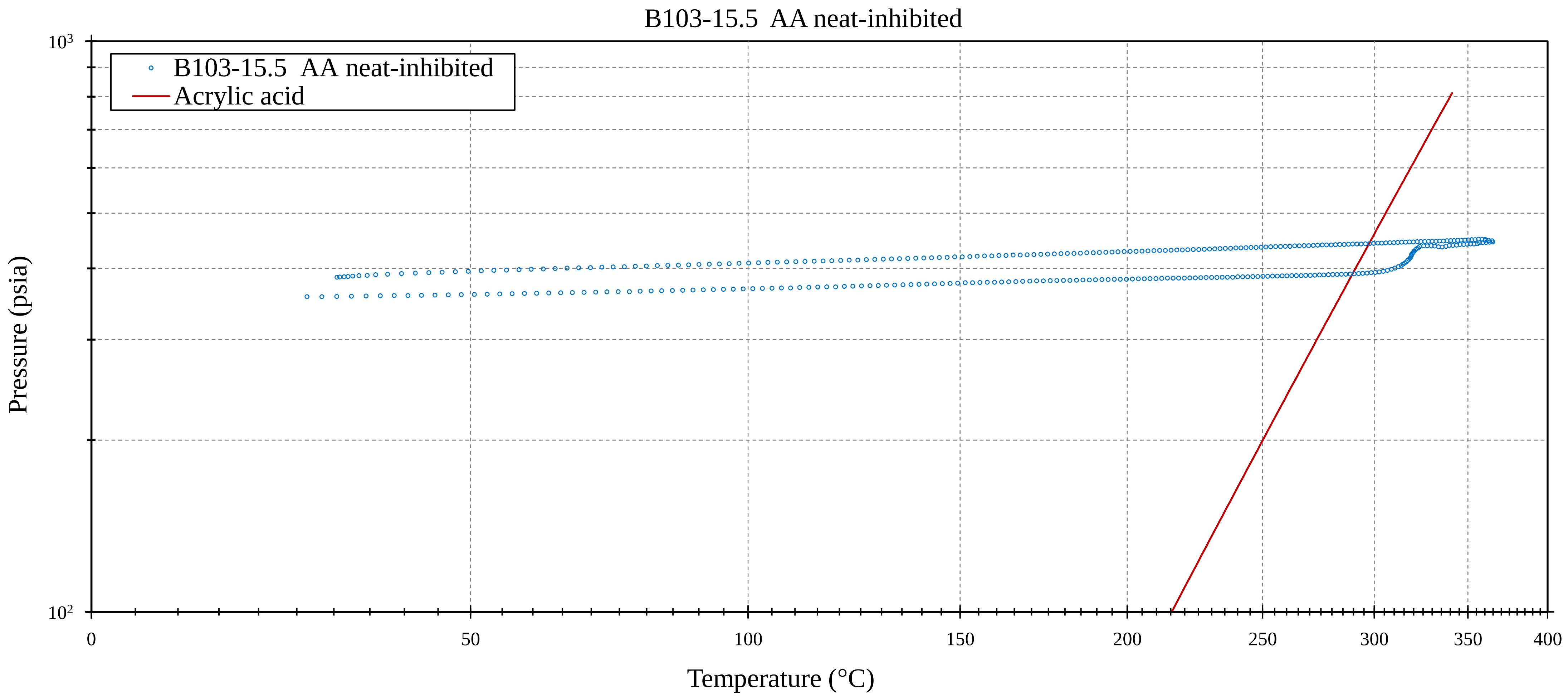
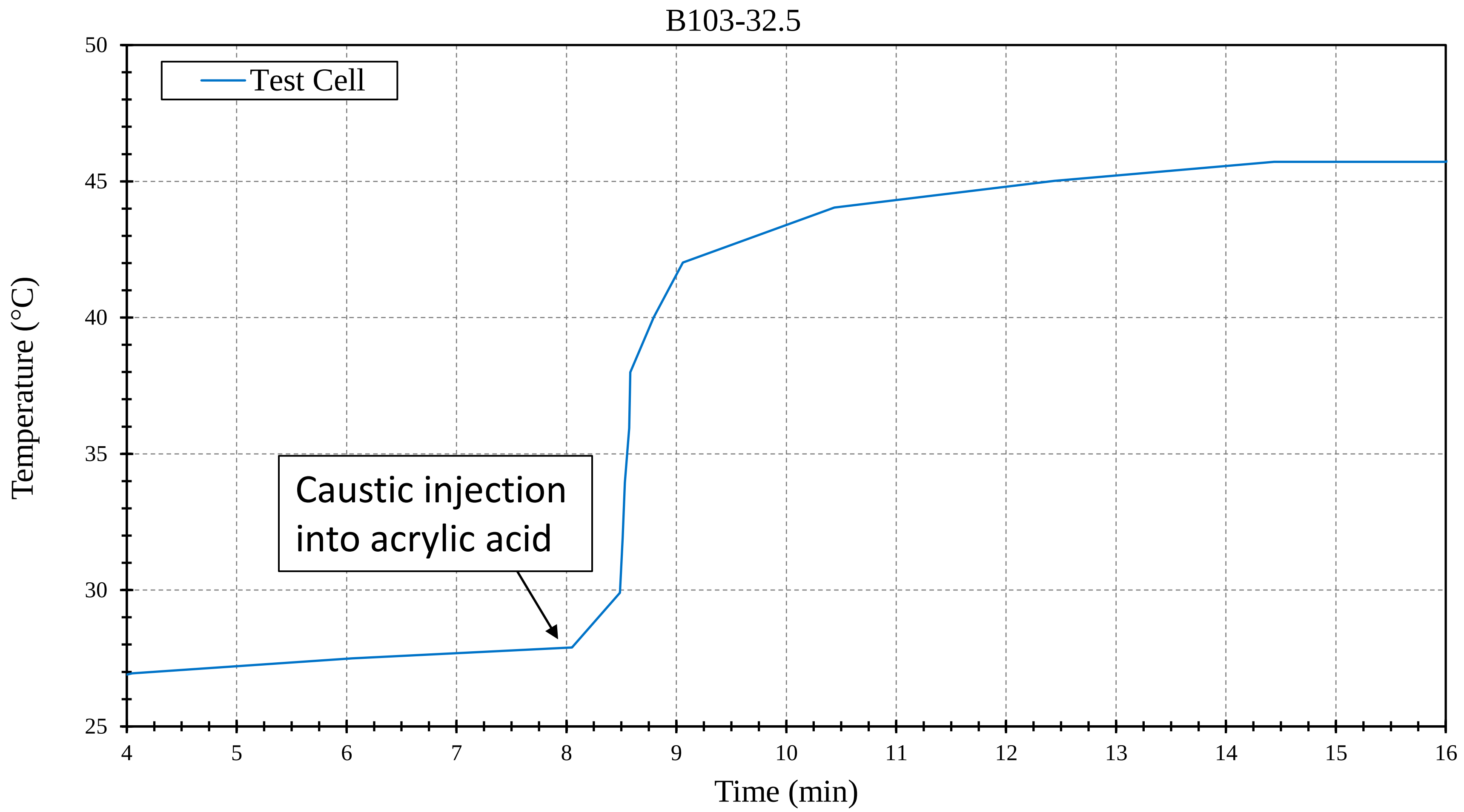
Pressure Data for Acrylic Acid



Compatibility Matrix

- Quick tests to determine whether materials are compatible.
- Load one sample in the ARSST and then inject the second sample.
- Monitor temperature and pressure to determine whether materials are compatible and complete the matrix.
- Example: ARSST test performed where caustic was injected into acrylic acid. Instant exotherm detected indicating chemicals are not compatible.

Compatibility Matrix



Determine Ideal Formulation

- Perform tests with varying concentrations to determine the formulation that has an acceptable reaction rate.
- Add solvent or reduce limiting reagent to decrease reaction rate, total heat of reaction, and adiabatic temperature rise to make process safer.
- Test how solvents can impact the vent sizing requirement or venting conditions.
- Example: ARSST tests performed where different amounts of isobutanol have been added to inhibited acrylic acid.
  - Test B103-15.5 neat inhibited acrylic acid
  - Test B103-16.5 acrylic acid & isobutanol (3.8:1 molar ratio)
  - Test B103-18.5 acrylic acid & isobutanol (1.0:1 molar ratio)

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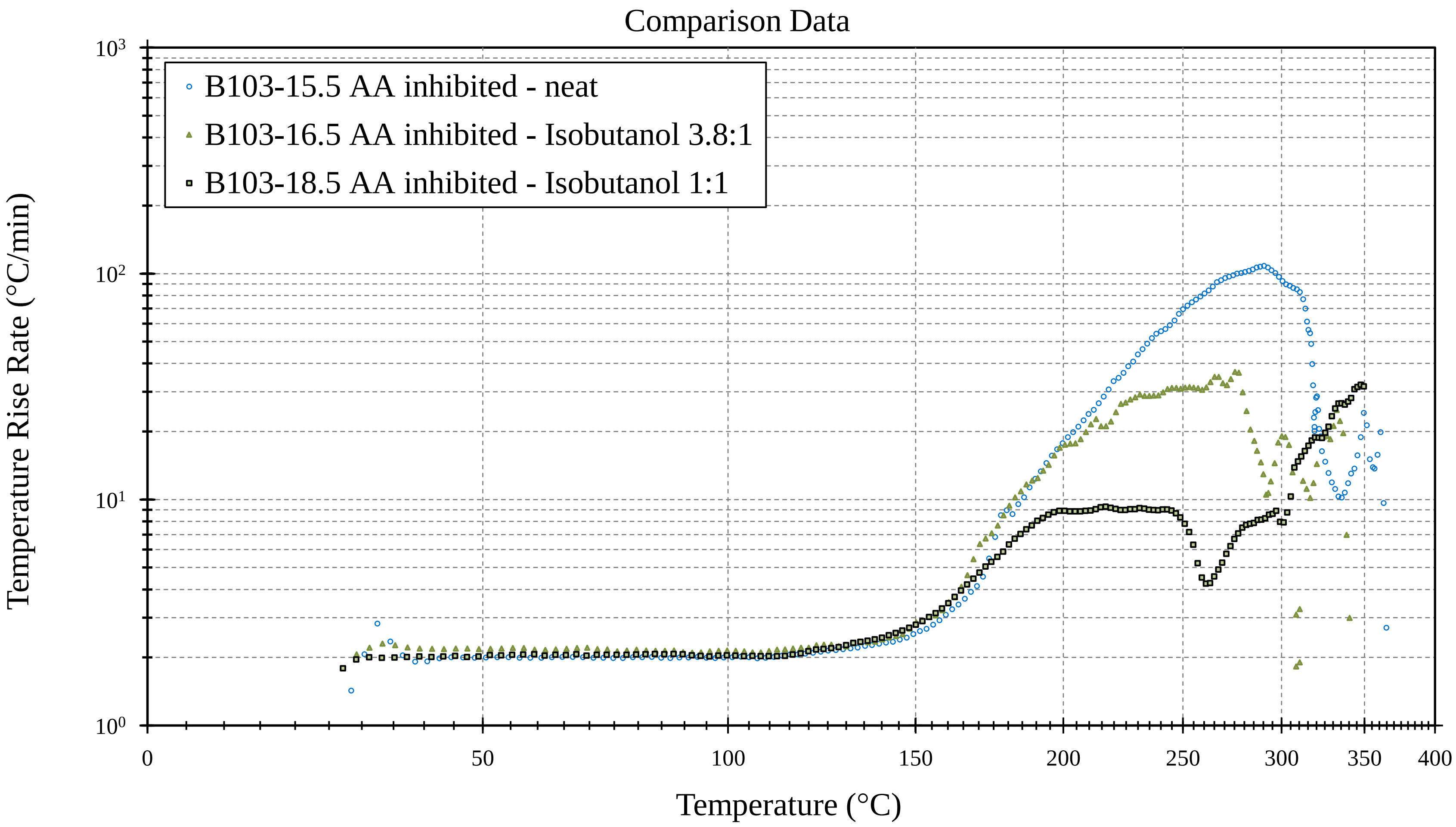
Comparison of Formulation



Conclusions

- A Reactive Hazards Analysis (RHA) is used to identify and better understand potential reactive hazards of reagents, intermediates, and products.
- Where plant documentation and literature data are not available, calorimetry should be used to fill gaps.
- Identify which calorimeter is appropriate to obtain the desired information.
- Understand strengths and weaknesses of the instrument and design the test accordingly.
- Decisions will be based on available data. Important to obtain quality data in order to accurately quantify risk and make appropriate decisions to operate safely.

Questions?

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