



# PRACTICAL APPLICATIONS, EXTENSIONS AND LIMITS OF REACTIVE CHEMICAL TESTING TOOLS

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THE DOW CHEMICAL COMPANY

*May 13, 2021*

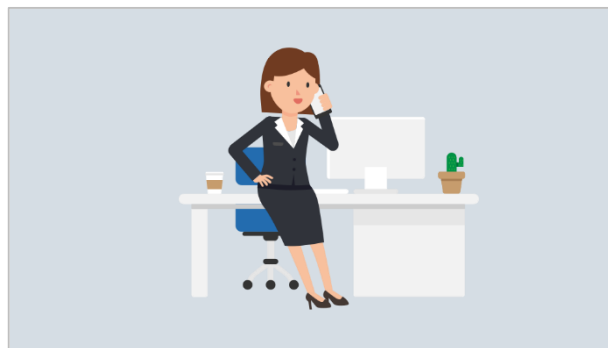
# “TYPICAL DAY”: REACTIVE CHEMICALS SUBJECT MATTER EXPERT

We sampled a railcar of a reactive chemical and it looks discolored- should we be concerned?

Is this chemical product stable up to 400 deg C- our customer needs to know?

Can we increase the pH operating window in a tower reactor?

What will happen if we accidentally unload Chemical “A” into Chemical “B”?



There was an unexpected exotherm when we regenerated a purification bed- what happened?

What is the flammability behavior of this new formulation?

We are planning to perform chemical cleaning of process equipment during turnaround- are there any reactivity risks?

We found a peroxide forming chemical in a lab full of solids-is it safe to handle?



# WHY THE REACTIVE CHEMICALS GROUP EXISTS – PROMOTING SAFETY THROUGH SCIENCE

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- Defining Reactive Chemicals
  - The history, purpose, and key elements of a Reactive Chemicals program
  - What does the Reactive Chemicals group at Dow do?
- Hyphen Techniques
- Answering Reactive Chemicals questions via coupling analytical spectroscopy and calorimetry
- Heat Transfer in ARC spheres: a recent Dow + P2SAC Collaboration



## REACTIVE CHEMICALS PROGRAM: PREVENTING UNCONTROLLED CHEMICAL REACTIONS

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Uncontrolled chemical reactions could result in **injury, property damage, or environmental harm.**

A strong Reactive Chemicals (RC) program:

- Promotes a culture of **safe** processes as the **only way** to do business
- Provides a formal, risk-based process for **hazard identification** and **mitigation**
- Leverages technical **expertise** in experiments and modeling to **solve problems** and **create solutions**
- **Reviews** and revisits processes based on risk
- Maintains a strong corporate **memory**

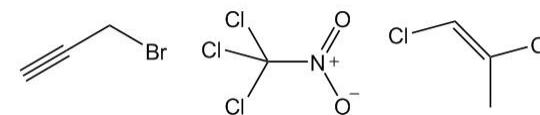


# WHY BE CONCERNED WITH CHEMICAL REACTIVITY?

- Explosions occurred due to mixing of chemicals using two railcars and a tank truck.
- A *shock sensitive* compound was formed.
- Three fatalities.

Dow established the  
**Reactive Chemicals** Program.

Uncontrolled chemical reactions  
could result in **injury, property  
damage, or environmental  
harm.**



Craters in Freeport, TX December 1966



# PROCESS SAFETY & REACTIVE CHEMICALS: ALLIES IN THE FIGHT AGAINST KINETICS & HEAT TRANSFER

Dow's Process Safety Group facilitates

- Process Hazard Analysis Reviews (PHA)
- Layers of Protection Analysis (LOPA)
- Loss Prevention Principles and Audits (LPP)

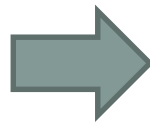
These  
require...

An understanding of thermal stability, flammability, and dust explosion hazards, and expertise in both chemistry and engineering

*Laboratory*



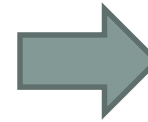
*Scale-up*



*Pilot Plant*



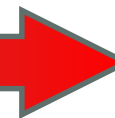
*Scale-up*



*Full-Scale Production Plant*



Increasing risk



# REACTIVE CHEMICALS GROUP: UNITING DIVERSE TECHNICAL EXPERTISE FOR A SAFER DOW

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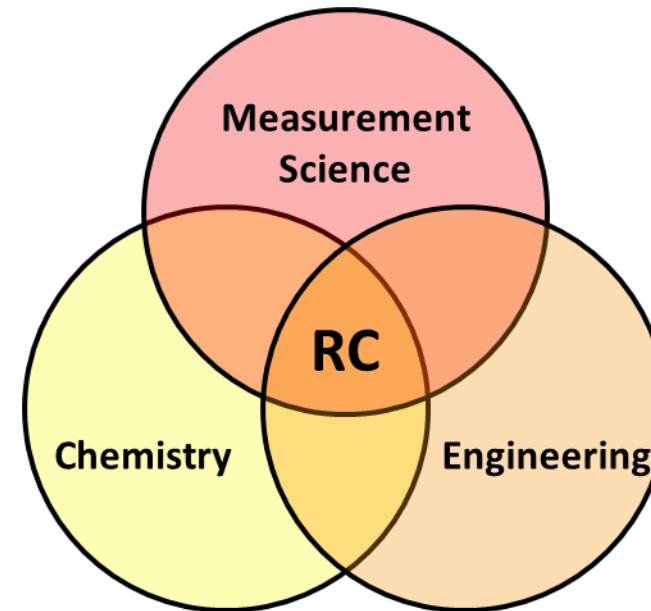
Expertise in analytical **techniques** and experimental **design**

↳ Capability to **modify** and **develop** to meet changing needs and find new solutions

Subject-Matter Experts aligned with and experts in...

The **chemistry**: Physical, analytical, organic, and inorganic **chemists**

The **processes**: **Chemical engineers** with expertise in kinetic modeling, simulation, and energy balances



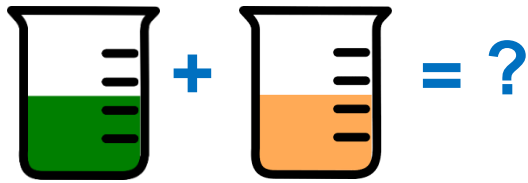
**Continuity** from experimental design through lab, pilot plant, and full scale production

Ensure **safe** operation at **all** scales

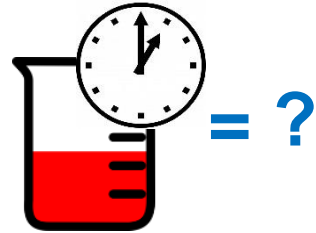


# HOW WE ACCOMPLISH THIS: THE RC TOOLBOX

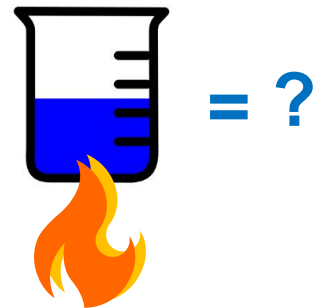
*What if  
I mix these?*



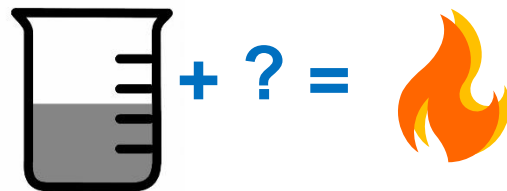
*How stable is this  
over time?*



*What if I  
heat this up?*



*How do I  
set this on fire?*



***How much energy? How fast?***

## Screening techniques

Desktop estimations and calculations  
HOM – Heat of Mixing  
DSC – Differential Scanning Calorimetry  
TSu – Thermal Screening Unit

## Testing thermal stability of materials

ARC – Accelerating Rate Calorimetry  
VSP – Vent Size Package

## Numerous Modeling Capabilities

## Flammability and explosion hazards

FP – Flash Point  
AIT – Auto-ignition temperature  
MIE – Minimum Ignition Energy

MIE testing

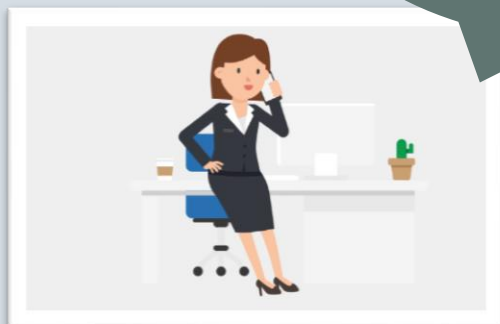




# HOW CAN WE DO MORE OR DO IT BETTER?

- *None of the aforementioned techniques can identify reaction products or intermediates*
  - Looking for endothermic & exothermic reactions, including decomposition
- Often the problems we must solve or incidents we investigate are complex and nuanced

I can tell you under what conditions this system will react to release energy, but I can't tell you what the chemistry is



[This Photo](#) by Unknown Author is licensed under [CC BY-SA](#)

## Gap:

### “Chemistry-blind” Calorimetry

- Based on chemical knowledge and expertise, we can hypothesize and infer what chemical reaction(s) are taking place

## Solution:

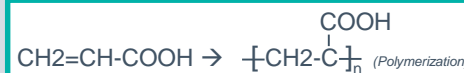
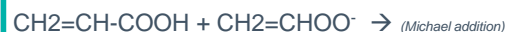
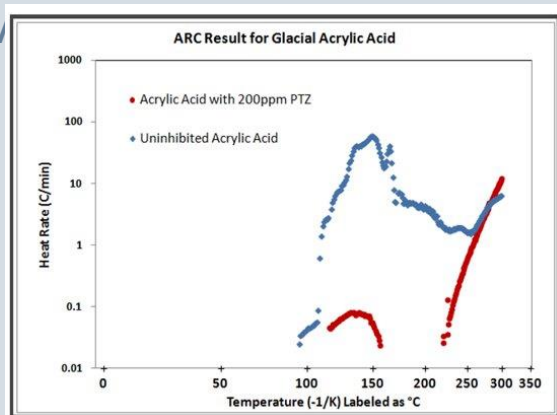
Development and application of hyphen methods @ Dow Reactive Chemicals to go beyond “chemistry-blind”

- *The mechanism(s) or reaction products of many undesired chemistries, such as decomposition are not well characterized*
- *You don't always need to know the chemistry, but when you do, it is almost always important*



# A TALE OF TWO REACTIVE CHEMICALS CONSULTATIONS

## Case 1: The well understood system

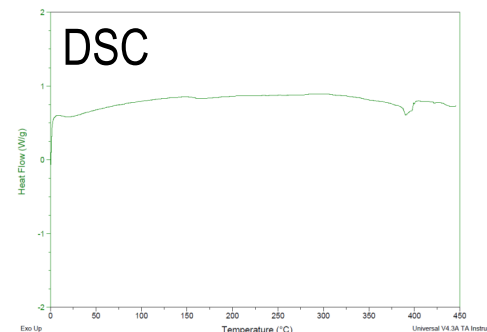


- **Inferred** understanding of these exothermic events (dimerization, polymerization) because there is relevant literature & extensive knowledge
- Pose Reactive Chemicals hazard?
  - Yes; Calorimetry data necessary to quantify heat release rates under specific conditions
- Confusion about chemistry- not so much

[BAMM: Acrylic Acid: A Summary of Safety and Handling](#)

## Case 2: The “not-so-well” understood system

- Chemical “X” – an organic species

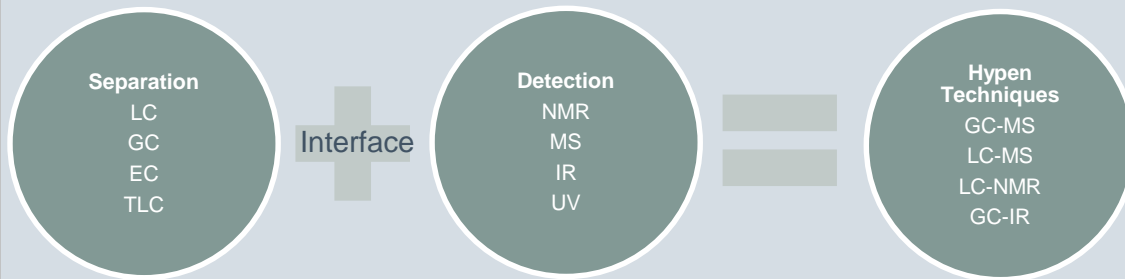


Thermoneutral: Chemistry or stability @ elevated T is unknown...

- Product literature (& DSC) indicates Chemical “X” is stable to T > 500 °C
  - Customer wants to know if a specific species will form under high T application
- Pose Reactive Chemicals hazard?
  - Maybe; Calorimetry data necessary to assess thermal stability
- Confusion about chemistry- YES

# HYPHEN TECHNIQUES

- Refers to the “on-line” combination of two or more analytical techniques
  - Physical interface + computer
  - 70 year history
- GC/MS (est. 1955 @ Dow) ‘best-known’ example
  - Separation followed by spectroscopy
  - Specific, sensitive and quantitative
  - Alphabet soup



Hirschfield, *Anal. Chem.* 1980, 52, 2, 297A–312A, 1980,

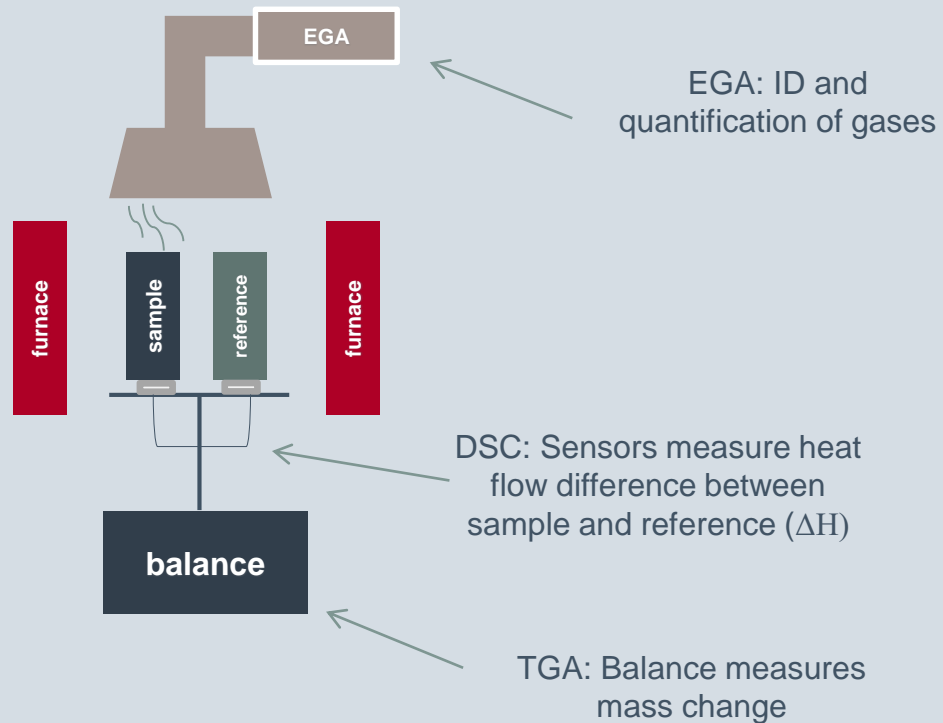
<https://doi.org/10.1021/ac50052a870>

<https://cen.acs.org/acs-news/programs/GCMS-honored-chemical-landmark/97/i29>

- Breakthroughs from the combination of traditional analytical methods
  - Complex problem solving
  - Pharmacy applications
  - Process Analyzer applications
- **Imitation is the sincerest form of flattery**
  - Take inspiration from these successful developments in the world of analytical chemistry? **YES!**
  - Simultaneous Thermal Analysis (STA) & Evolved Gas Analysis (EGA)

# SIMULTANEOUS THERMAL ANALYSIS (STA) & EVOLVED GAS ANALYSIS (EGA)

- STA - combination of Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA/DSC)
- Evolved Gas Analysis- Identifies gases from decomposition or desorption



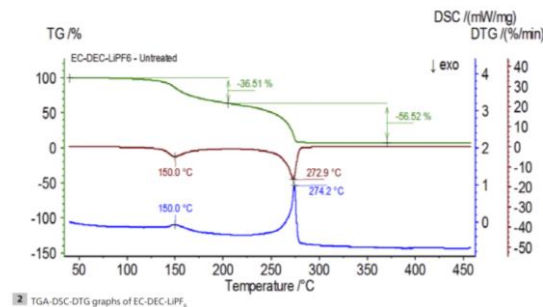
- **One measurement, multiple signals- results not obtainable with either technique alone!**
- 1970, Analytical Calorimetry Conference
  - The Application of Combined Differential Scanning Calorimetry-Mass Spectrometry (DSC-MS) to the Study of Thermal and Oxidative Decompositions
- By mid-1980s, significant literature on EGA
  - Early reports focus on methodology & instrumentation
  - Most recent reports are applications & results
    - ✓ > 20 publications using EGA in 2021 alone
- Today's commercially available units:
  - ✓ DSC-TGA- classic STA
  - ✓ DSC-GC/MS
  - ✓ DSC-MS
  - ✓ TGA-DSC-FTIR-MS
  - ✓ TD-GC-MS

# SIMULTANEOUS THERMAL ANALYSIS IN LI-ION BATTERY SAFETY

- Lithium-ion and lithium-metal batteries bring convenience and joy to consumers
- With the potential to store tremendous amounts of energy also comes risk
- ***While fires involving batteries are not common, they are possible***
  - ***Gas (flammable, toxic), metal shrapnel, fire/explosion***

## STA, EGA for $\text{LiPF}_6$ in alkyl carbonates

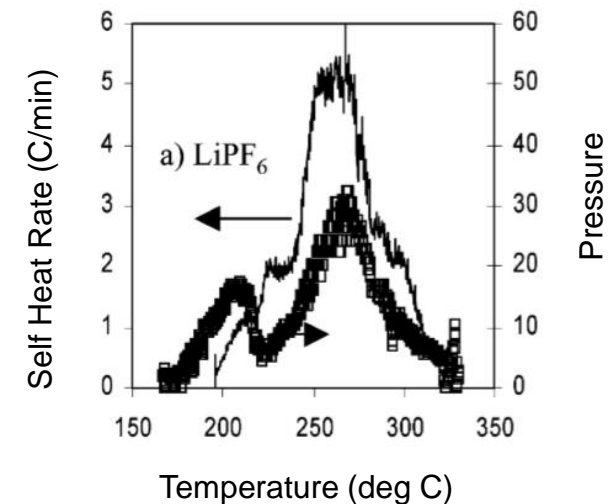
- STA (TGA-DSC) to monitor compositional changes and thermal stability as Temperature is ramped
- EGA to identify gaseous reaction products



Michael Hsu, NETZSCH Instruments North America, Thermal Stability of Lithium Ion Battery Electrolyte, Application Note

## Thermal decomposition of $\text{LiPF}_6$ in alkyl carbonates

- DSC, ARC to characterize thermal events
- GC-MS and NMR to elucidate reaction scheme



J.S. Gnanaraj et al./Journal of Power Sources 119–121 (2003) 794–798

# HYPHEN TECHNIQUES WITH DOW REACTIVE CHEMICALS (RC)

## Considerations for STA/EGA:

- Temperature range
  - Hot enough to get to undesired chemistry of interest?
- Open systems
  - No pressure/gas generation information
- Small sample sizes
  - TGA crucibles, DSC pans (milligram scale)
  - Detection limits if evolved gases are in small qty
- Heating/sample conditions
  - Isothermal, Linear Heat ramp
  - Non-adiabatic

### Screening techniques

Desktop estimations and calculations  
HOM – Heat of Mixing  
DSC – Differential Scanning Calorimetry  
TSu – Thermal Screening Unit

### Testing thermal stability of materials

ARC – Accelerating Rate Calorimetry  
VSP – Vent Size Package



DSC cannot fully  
characterize the  
thermal stability of  
a reactive system.

Can we do more?

Unique positioning of RC within Dow R&D Analytical Sciences affords easy collaboration with foremost analytical scientists

## Recent internal developments

- Accelerating Rate Calorimetry x GC-MS
- Heat of Mixing Calorimetry x Raman
  - ✓ Drivers
  - ✓ Technical description & approach
  - ✓ Proof of Concept
  - ✓ Applications & Value
  - ✓ Limitations



## Background

- For vessels containing *reactive* chemicals, a *runaway reaction* can occur, generating heat and non-condensable gases
- Calorimetric data is collected to understand rate of heat and gas generation
- To prevent catastrophic vessel failure, a relief device is installed to vent excess pressure
- Data is needed to determine if it is acceptable to vent the effluent directly to atmosphere or route it to a treatment system

## Opportunity

- Coupling adiabatic calorimetric and analytical identification capabilities presents a unique opportunity to simultaneously assess Reactive Chemicals (RC) hazards and identify reaction effluents at a given set of conditions (Temperature, Pressure)

## Value Impact

- Brings value across all Dow businesses with Reactive Relief and/or decomposition scenarios
- Accurate effluent screening is critical when making effluent treatment and routing decisions
- *Risk-reduction savings by getting it right through analytical measurement*
- *Unplanned value*
- *RCAs, mechanistic insight, set SOCs*



# ARCxGC-MS: TECHNICAL DESCRIPTION AND APPROACH

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## 1. Explore what calorimeter/analytical screening method is most suitable for decomposition scenarios

- Evaluated FTIR, MS, GC, GC-MS, QCL
  - **GC/MS**- separation, broad identification, quantification, *instrument availability*
  - Evaluated **ARC (Accelerating Rate Calorimeter)** and VSP (Vent Sizing Package) calorimeters

## 2. Evaluate the existing modules with effluent screening capabilities which are available from external manufacturers

- Evolved Gas Analysis (EGA) coupled to DSC/TGA
  - Small sample sizes → low signals
  - Heated gas transfer (automatic valves, software-controlled)
  - Non-adiabatic conditions
  - Multiple analytical methods (FTIR, GC, MS, GC-MS)
- Open system (loss of mass/solvent, affect the actual reactions and not simulate real world)
- Commercial gas collection system from THT (ARC manufacturer)- available mid-2016.
  - Off the shelf availability
  - Integrated software control
  - Analyzer part not included
  - Not heat-traced or temperature controlled

## 3. Design and build an interface to couple an Accelerating Rate Calorimeter (ARC) to GC-MS.

## 4. Design and perform proof of concept experiments on well-defined systems to evaluate the ARCxGC-MS.

## 5. Characterize effluent from industrially-relevant reactive decomposition scenarios.



# ADIABATIC CALORIMETRY- WHY?

- Need to mimic process situation being studied
  - Many full scale processes are insulated and large
    - ✓ Loss of process cooling results in near adiabatic conditions
  - Reaction trajectory of actual process mimicked when adiabatic is worst case
    - ✓ Adiabatic is not always the worst case (pooling of reactants due to external heat input or loss of agitation)
  - A single experiment provides reaction kinetics and thermodynamic data

## Common Adiabatic Calorimeters in Use



ARC 244



ARC 254



esARC



ARC 2000



Phi-Tec 2



VSP II

# ACCELERATING RATE CALORIMETRY- GOOD & BAD

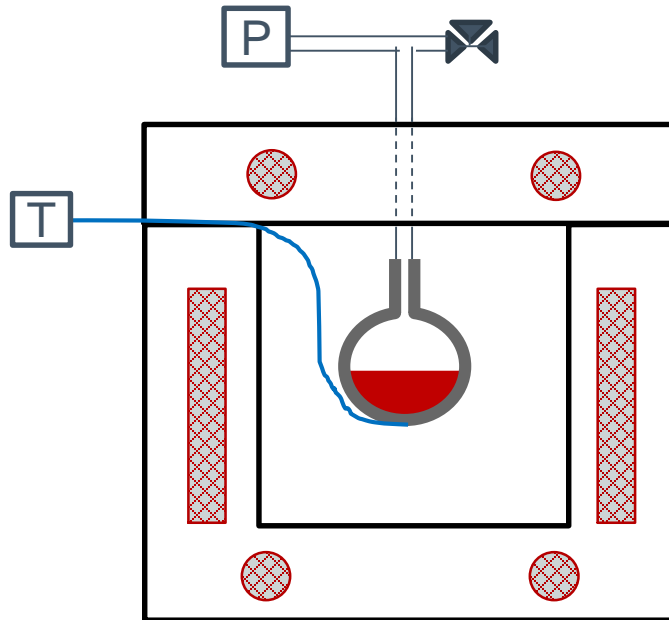
## Pressure and adiabatic\* calorimetry data

- Critical for understanding RC hazards
- Heats of reaction
- Vapor pressure data



Left: Thermal Hazard Technology

### ARC Sphere



**Detects 0.02°C/min  
(vs. 0.4°C/min on DSC)**

- Up to 100°C/min
- 2500 psia max pressure
- Designed to handle 2g TNT
- Use: low viscosity, fully miscible systems, adiabatic worst case, kinetic modeling needed

## Unfortunately...

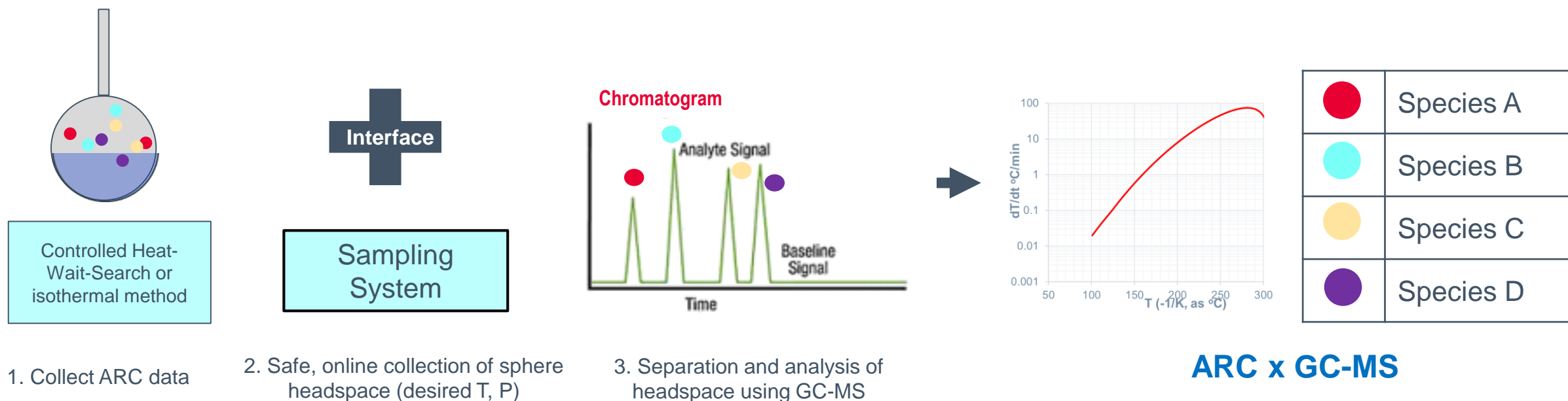
- Poor agitation
- No sub-ambient testing
- \*Adiabatic up to 10-25°C/min
- 14+ hours
- Applying data at scale requires accounting for the PHI factor
- Do not use: systems that require substantial mixing, solids that don't melt during experiment

Dow + P2SAC collab



# ACCELERATING RATE CALORIMETRY (ARC) x GC-MS

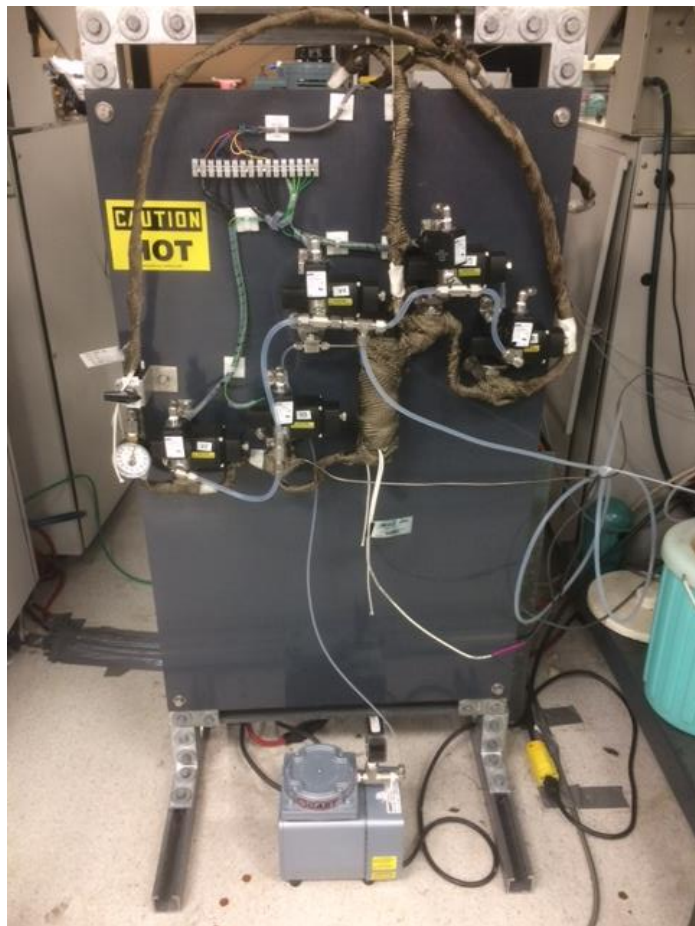
- Prior to ARCxGC-MS, analytical characterization of gas-phase reaction effluent from ARC experiments has often been carried out off-line.
- Cooling the system before sampling allows for possibility of plugged lines, condensation of low-volatile species, gas diffusion outside of gas collection container, and potential for exposure when sampling unknown species.



## ARC x GC-MS

Extend ARC thermal capability to provide **online effluent analysis** of gas-evolving reactive systems  
(not commercially available)

# SAMPLING SYSTEM DESIGN/CONSIDERATION

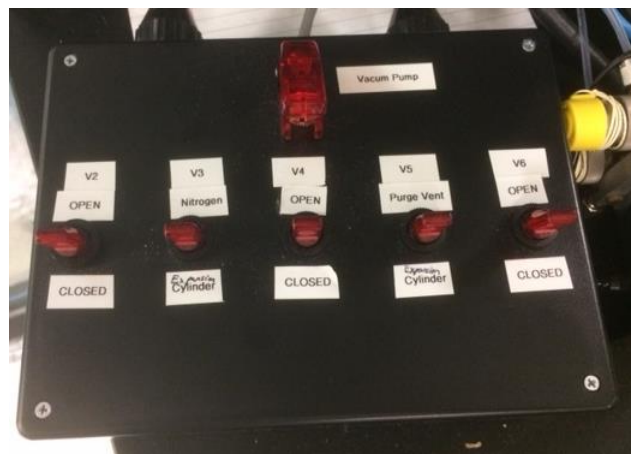


## 3. Design an interface to couple ARC to GC/MS

- Custom-built, mounted on CPVC panel/Unistrut frame
- Insulated & heat traced (reduce effluent condensation)
- Minimize sampling system and transfer line volume
- 316 SS material of construction Automated pneumatic valves allow for safe valve operation & gas sampling
- Electronic control of valve actuation via control box
- Remote (manual) injection onto GC



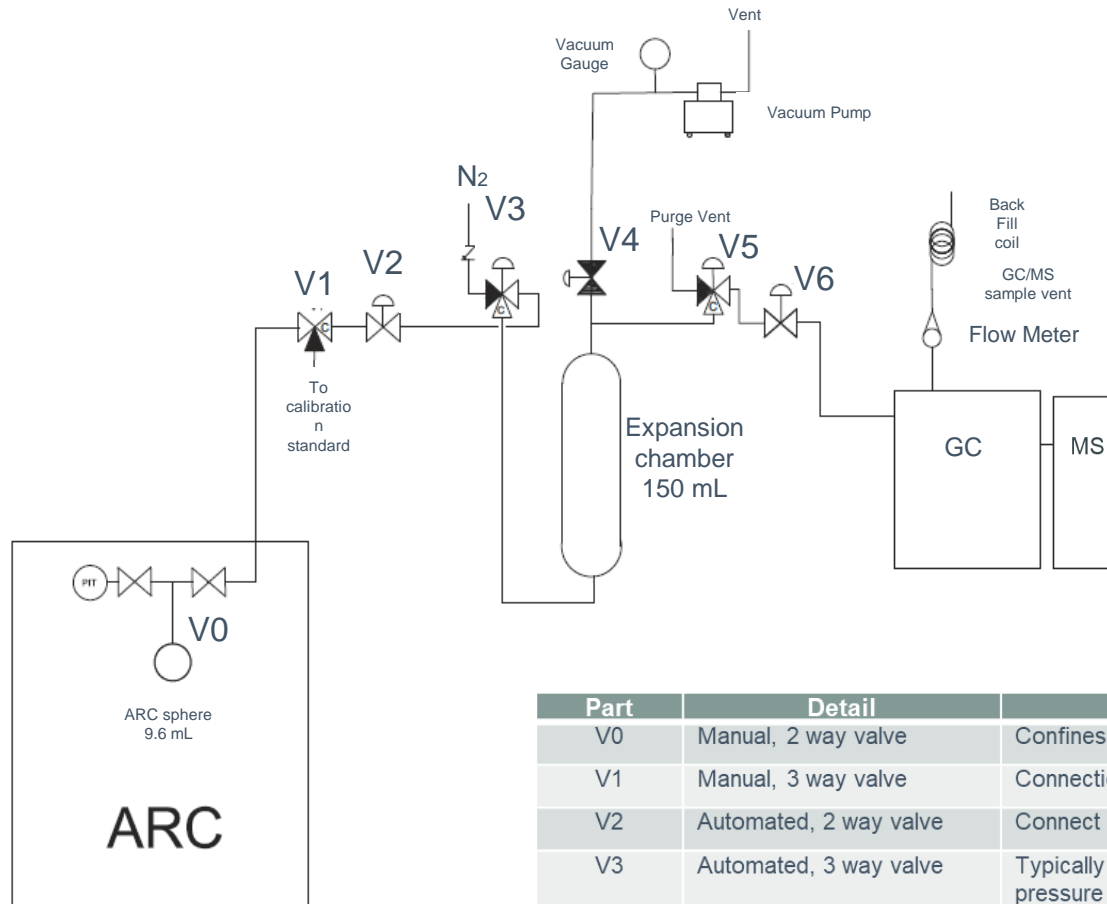
ARC GC/MS



K. Mulligan et al. "Reaction Effluent Analysis Using Adiabatic Calorimetric Experiments." AIChE Spring Meeting & GCPS, 2018.



# SAMPLING SYSTEM DESIGN/CONSIDERATION



## 3. Design an interface to couple ARC to GC/MS.

- Both instruments inside a walk-in ventilated enclosure
- PC control of ARC and GC/MS is outside enclosure
- **ARC experiments routinely generate >2000 psi so headspace concentrations are high**
- An evacuated expansion chamber (150 mL) is filled using pressure differential (dP)
- Gas is sampled from this chamber for analytical analysis by GC-MS
- Expansion chamber allows for multiple injections under well-controlled conditions

Part	Detail	Purpose
V0	Manual, 2 way valve	Confines chemical species to ARC sample sphere. Intrinsic to ARC system.
V1	Manual, 3 way valve	Connection to known gas source. Fill ARC sphere for leak and calibration/validation tests.
V2	Automated, 2 way valve	Connect ARC sphere to sampling system for gas transport.
V3	Automated, 3 way valve	Typically connected to 'house' N <sub>2</sub> line (~ 115 psi). To purge/clean system w/ N <sub>2</sub> and increase pressure in expansion chamber to sweep evolved gas through to GC/MS.
V4	Manual, 2 way valve	Connected to vacuum pump. Evacuate expansion chamber before experiment.
Expansion Chamber	150 mL, 316 SS	Let down high pressure generated from calorimetry experiment for injection into GC.
V5	Automated, 3 way valve	To purge vent. Avoid purging through vacuum pump (contamination) or GC (slow)
V6	Automated, 3 way valve	Sampling expansion chamber for analytical analysis using GC/MS

# ARCxGC/MS: TECHNICAL DESCRIPTION AND APPROACH

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4. Design and perform proof of concept (POC) experiments on well-defined systems to evaluate the applicability of the ARCxGC/MS.

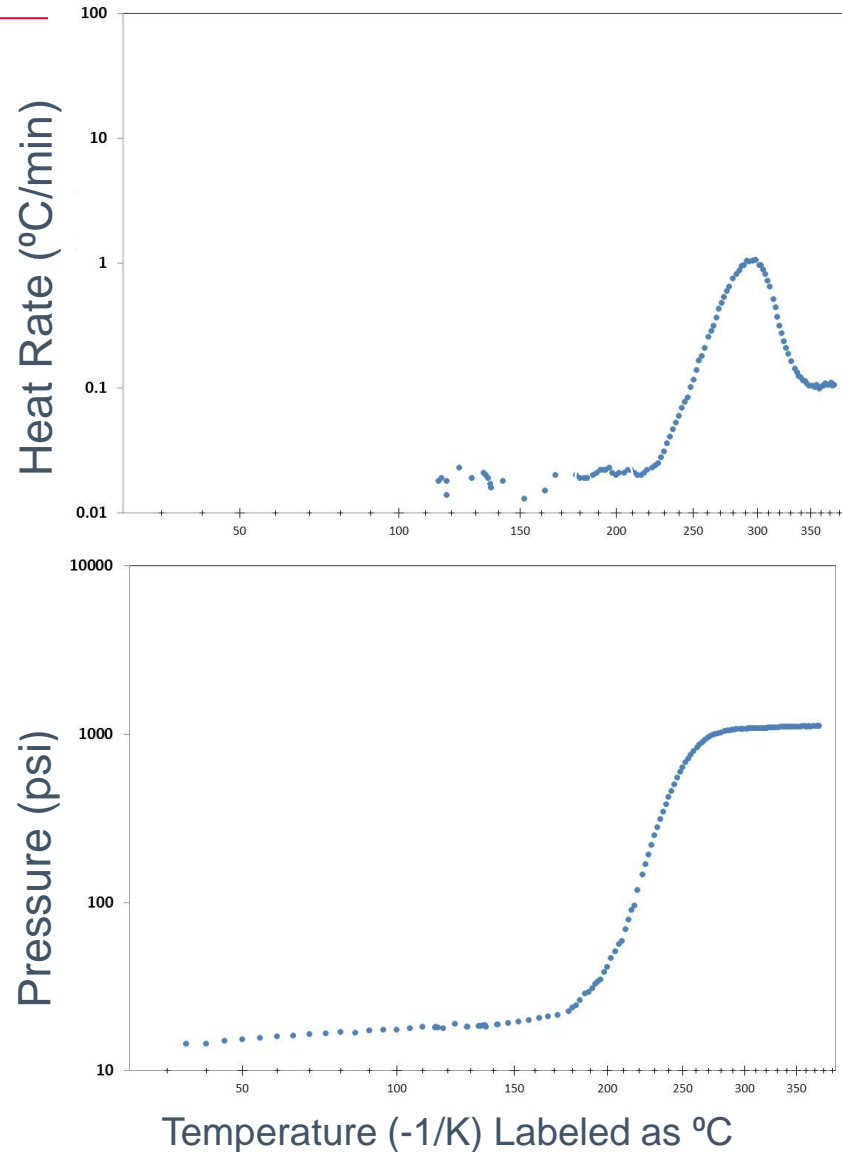
- POC systems chosen on basis:
  - Materials of Construction compatibility
  - Generation of non-condensable gas - avoid vapor pressure only systems
  - Gas generation at  $T < 200\text{ }^{\circ}\text{C}$
  - Easily validated - avoid secondary decompositions and side reactions

5. Characterize effluent from industrially-relevant reactive decomposition scenarios.

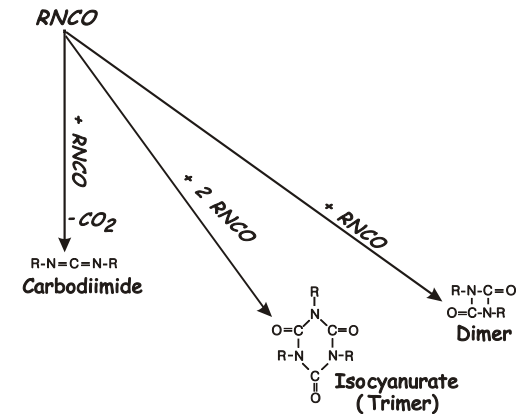
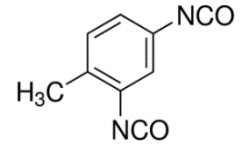




# POC SYSTEM 1 (2,4-TDI): ARC CALORIMETRIC RESULTS

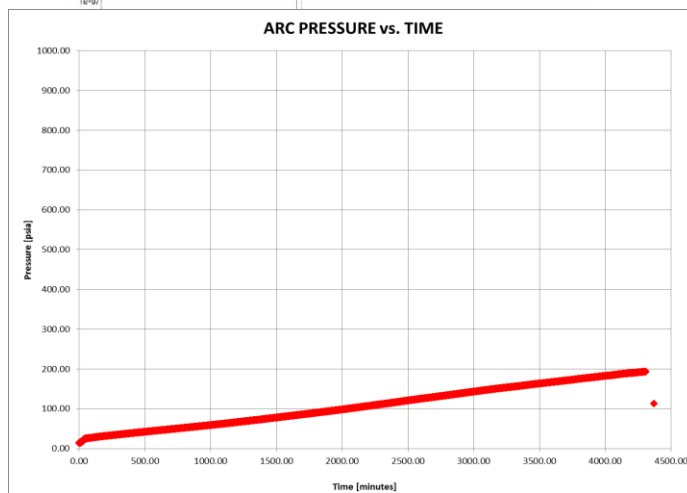
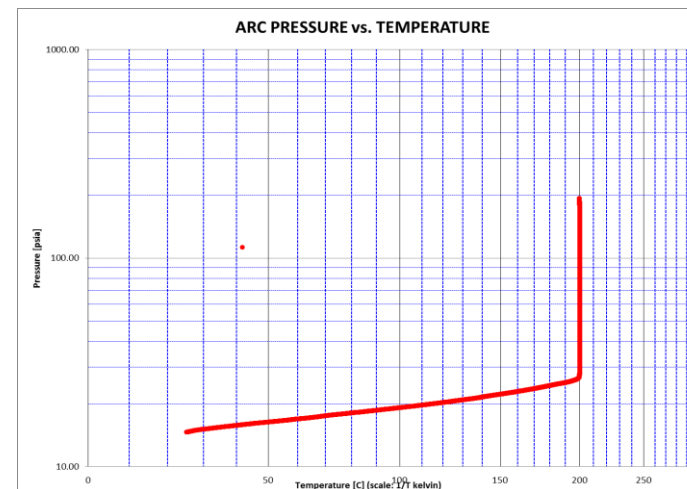
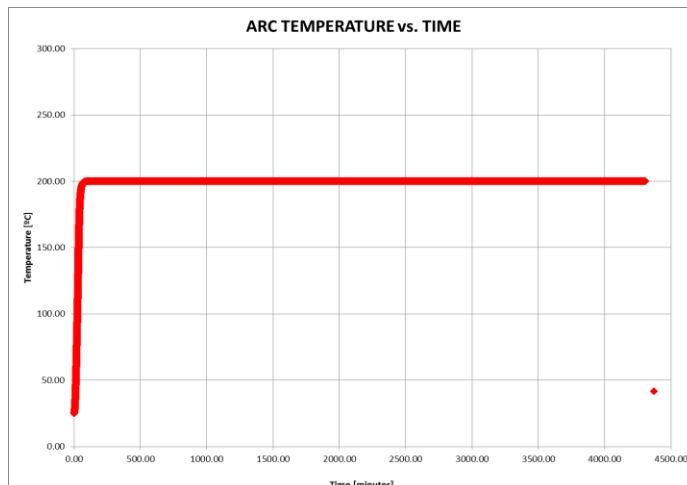


- 2,4-toluene diisocyanate
- Self-reactive molecule with competing, T- dependent mechanisms



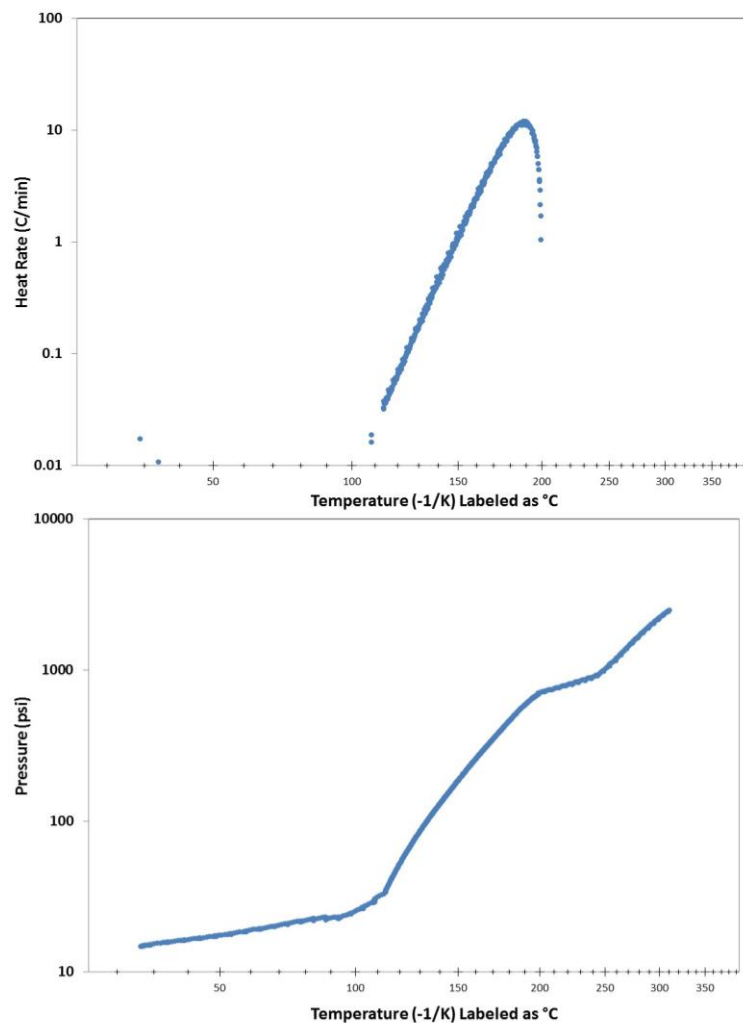
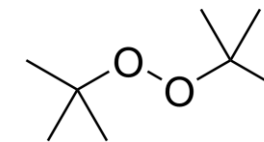
- Exothermic activity and gas generation are well-correlated
- POC test: Isothermal method @ 200 °C (thermoneutral carbodiimide formation & preferential CO<sub>2</sub> evolution)

# POC SYSTEM 1 (2,4-TDI): ARCxGC/MS RESULTS



- 6 g 2,4-TDI loaded into ARC sphere
- Isothermal method @ 200 °C, 72 hours
- $P_{\text{ARCsphere}} = 110 \text{ psia}$  @ 40 °C before releasing headspace into expansion chamber (9 psia after)
- Pressurized expansion chamber to 123 psia ( $\text{N}_2$ )
- No heat trace
- Only  $\text{CO}_2$  and  $\text{N}_2$  detected via GC/MSD
- Indicates desired reaction, carbodiimide +  $\text{CO}_2$

# POC SYSTEM 2 (DTBP): ARC CALORIMETRIC RESULTS

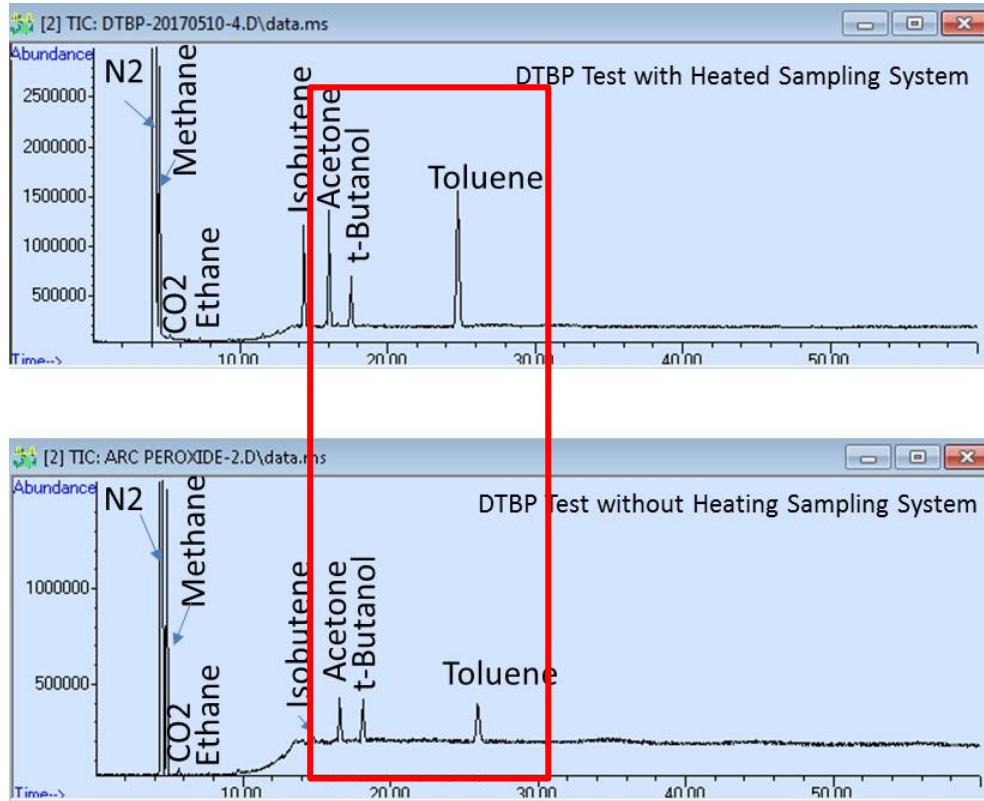


- Adiabatic decomposition of di-tertiary butyl peroxide in toluene
- Standard chemical system for ARC calibration
- Exothermic activity and gas generation are well correlated
- Gassy system with well-known kinetics
- Literature<sup>1</sup> Adiabatic Decomp Products (offline GC/MS):  
DTBP + 2 Toluene → acetone + tert-butyl alcohol + methane + diphenylethane

1. *Ind. Eng. Chem. Res.* **2003**, 42, 2987-2995



# POC SYSTEM 2 (DTBP IN TOLUENE) ARCxGC/MS RESULTS



- Load ~ 5 g 20%wt DTBP (in toluene) in ARC sphere
- Apply same ARC HWS method
- **Sampling system heated to 115 °C vs. no heating, same ARC HWS method**

**Reproducible effluent results and improved signal with heat trace**

K. Mulligan et al. "Reaction Effluent Analysis Using Adiabatic Calorimetric Experiments." AIChE Spring Meeting & GCPS, 2018.

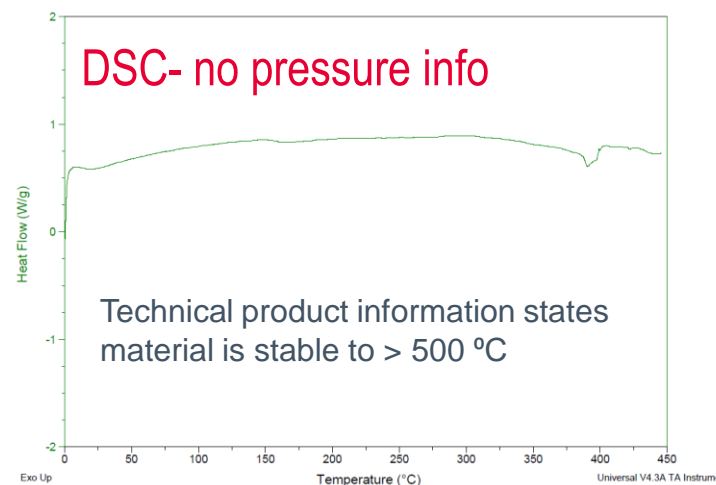


# ARCxGC/MS: TECHNICAL DESCRIPTION AND APPROACH

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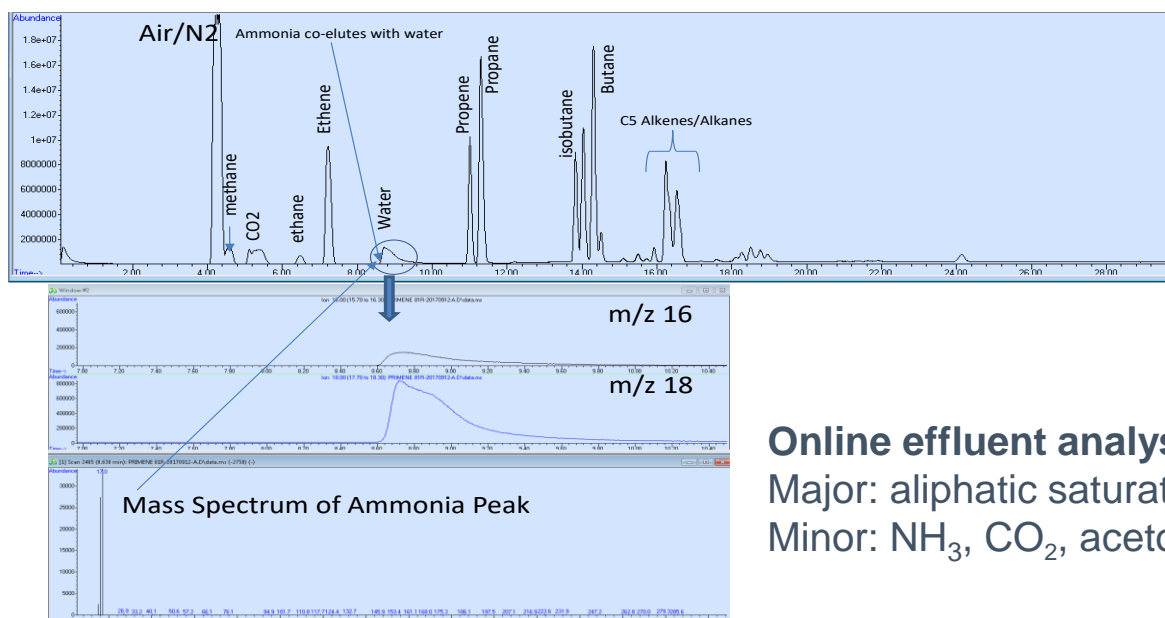
1. Explore what analytical screening method is most suitable for Reactive Relief applications
2. Evaluate the existing modules with effluent screening capabilities which are available from external manufacturers (via literature research and interactions with both manufacturer's representatives and current module users).
3. Design and build an interface to couple an Accelerating Rate Calorimeter (ARC) to GC/MS.
4. Design and perform proof of concept experiments on well-defined systems to evaluate the ARCxGC/MS.
5. Characterize effluent from industrially-relevant reactive decomposition scenarios.

# AMINE PRODUCT: UTILIZING ARCxGC/MS TO DETERMINE DECOMPOSITION BEHAVIOR AND REACTION PRODUCTS



Customer desired to understand stability and decomposition products for high temperature applications ( $T > 500\text{ }^{\circ}\text{C}$ ).

**GC-MS**



## Online effluent analysis via ARCxGC/MS

Major: aliphatic saturated and unsaturated C1-C5 hydrocarbon mix

Minor:  $\text{NH}_3$ ,  $\text{CO}_2$ , acetonitrile, water



# ARCxGC-MS TO SUPPORT ROOT CAUSE INVESTIGATION FOR UNEXPECTED EXOTHERM

A Dow process utilizes a molecular sieve bed to remove water and methanol from propylene.

- Propylene is drained from the bottom of the bed before regeneration: stepwise heating of the bed & flow of H<sub>2</sub>/CH<sub>4</sub> gas
- 1<sup>st</sup> time this bed was regenerated after being in propylene service, an **unexpected exotherm** (observed T rise: 50 °C)

Root Cause Investigation was carried out which included representatives from the facility, R&D, technology and Reactive Chemicals experts

Hypothesis: organic(s) on the molecular sieve reacts exothermically with regeneration gas

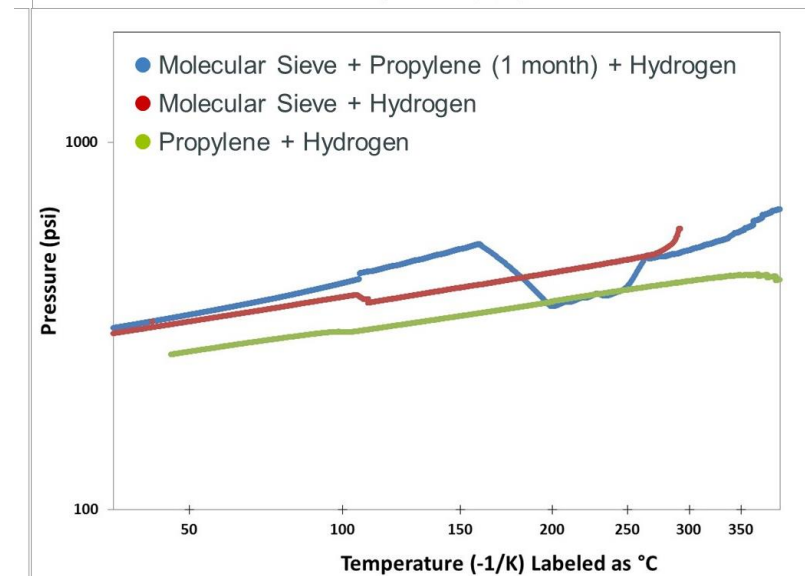
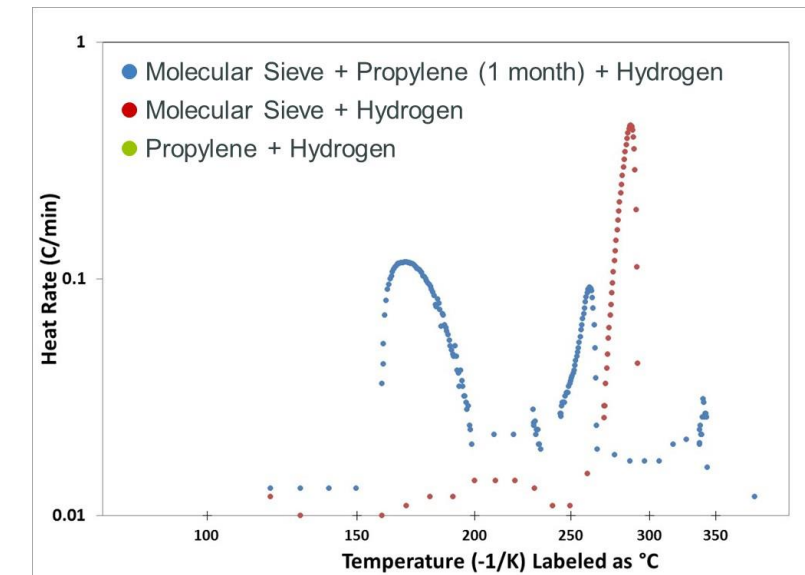
- (1) Can the exotherm be reproduced in the ARC?
- (2) What is the chemistry that is causing the exotherm?

Experiment:  
ARCxGC-MS



In-Line  
Sampling  
System

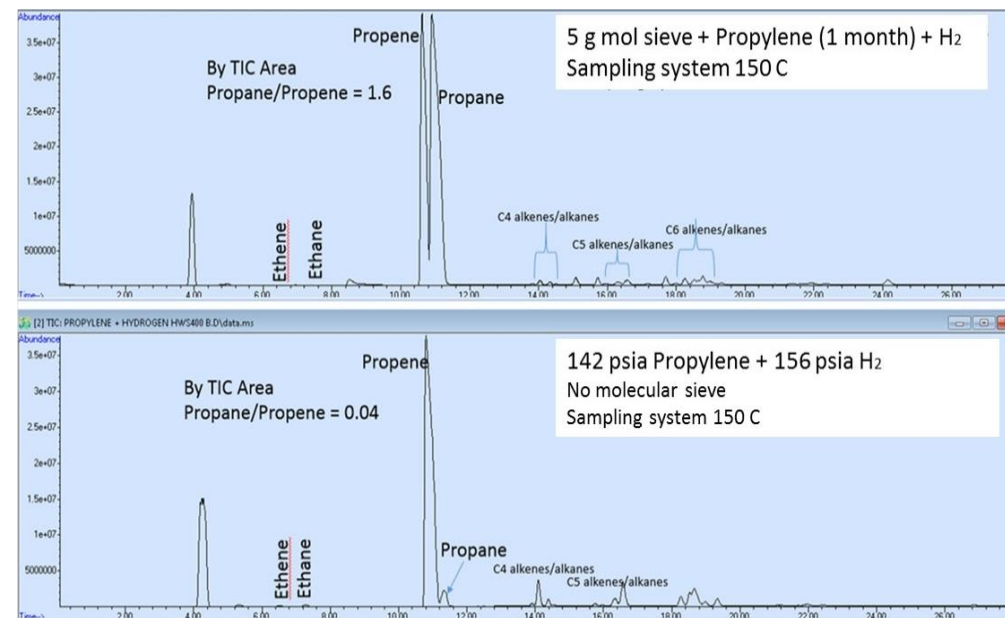
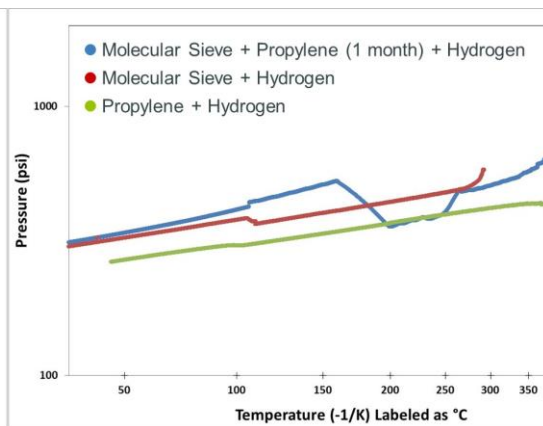
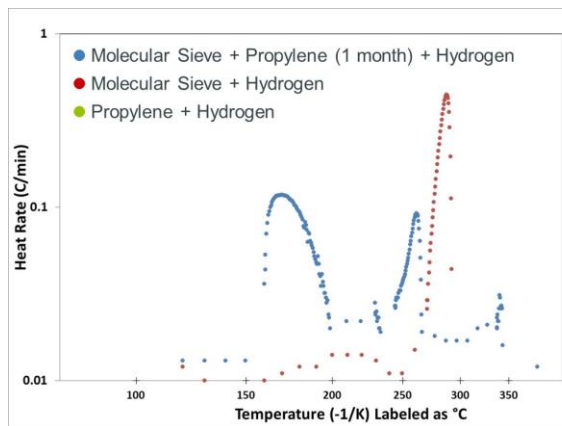
1. Monitor the sample's P and T, during a calorimetric test to observe reaction
2. Sample the headspace, and send to GC/MS, GC-TCD, GC-FID for speciation





# ARCxGC/MS TO SUPPORT ROOT CAUSE INVESTIGATION FOR UNEXPECTED EXOTHERM

Sample Sieve Description	Headspace	Thermal data summary	Composition data from ARCxGC/MS
<b>Test 1:</b> Fresh molecular sieve + 1 month treatment with propylene	hydrogen	Moderate exotherm from 150-200C, peak 1 at 250C, peak 2 at 350C. Gas consumption (pressure drop) at 150 C.	Propane/Propylene ratio = 1.6
<b>Test 2:</b> Fresh molecular sieve: no propylene treatment	hydrogen	Moderate exotherm above 250C. No gas generation.	No organics
<b>Test 3:</b> None	propylene + hydrogen	No exotherm, gas generation or consumption observed.	Propane/Propylene ratio = 0.04



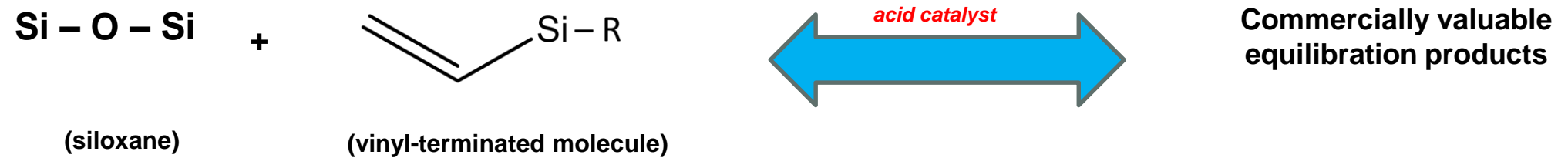
ARCxGC-MS proves the molecular sieve is catalyzing hydrogenation of adsorbed propylene at  $T < 200^\circ \text{C}$ .

Outcome: Update regeneration procedure to mitigate exotherm hazard & prevent runaway in the bed



# VINYL-SILOXANE CLEAVAGE

## Chemical Process of Interest

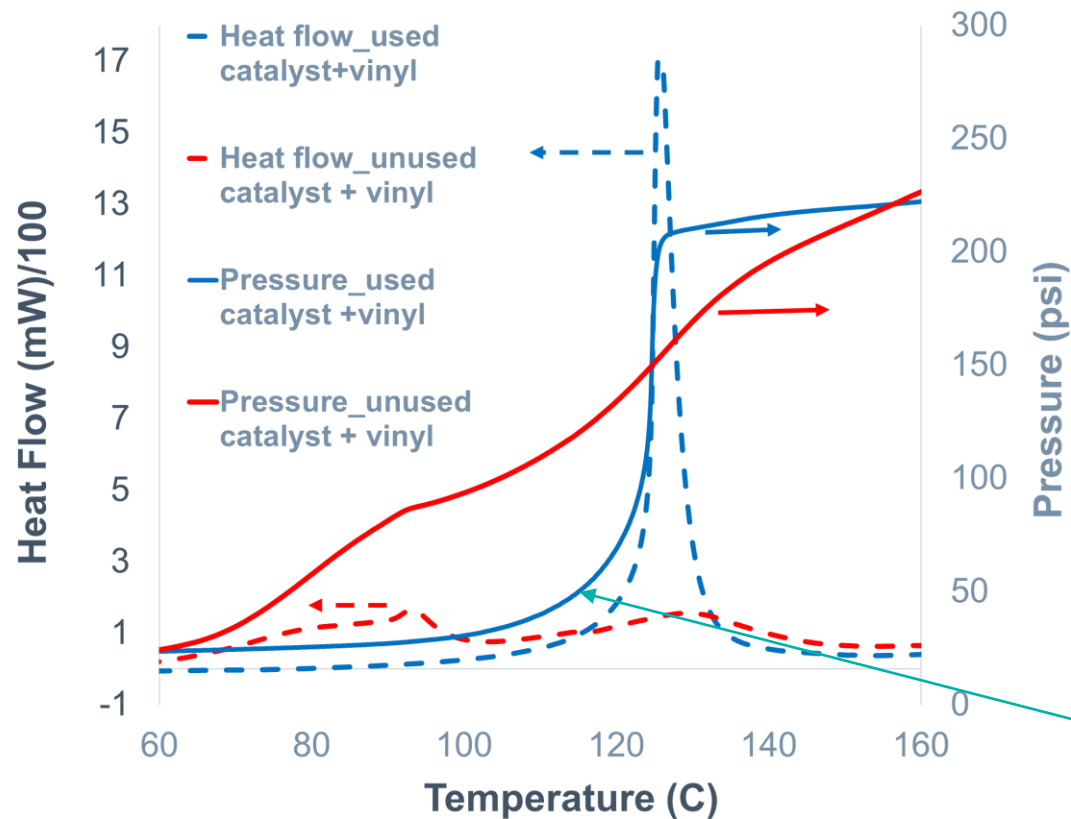


## Goals:

- Investigate the potential exothermic and gas-generation potential due associated with a chemical process to inform reaction engineering and reactor design
- Determine- what chemistry is “in-play”?
  - Wouldn't that be nice?!

S. Dutta, et. Al. "Vinyl-Siloxane Cleavage: Applying Thermo-Analytical and Hybrid Calorimetry Techniques to Inform Process Safety and Design". AIChE Spring Meeting & GCPS, 2020.

# MICROCALORIMETRY SCREENING – VINYL SPECIES + CATALYST



Exothermic activity observed **only when vinyl species** is present

- Relevant mixtures tested, data not shown

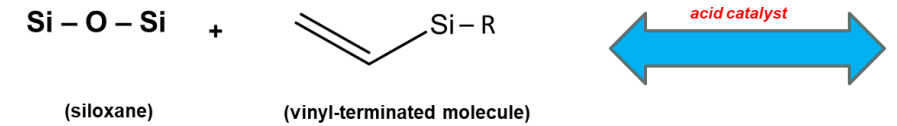
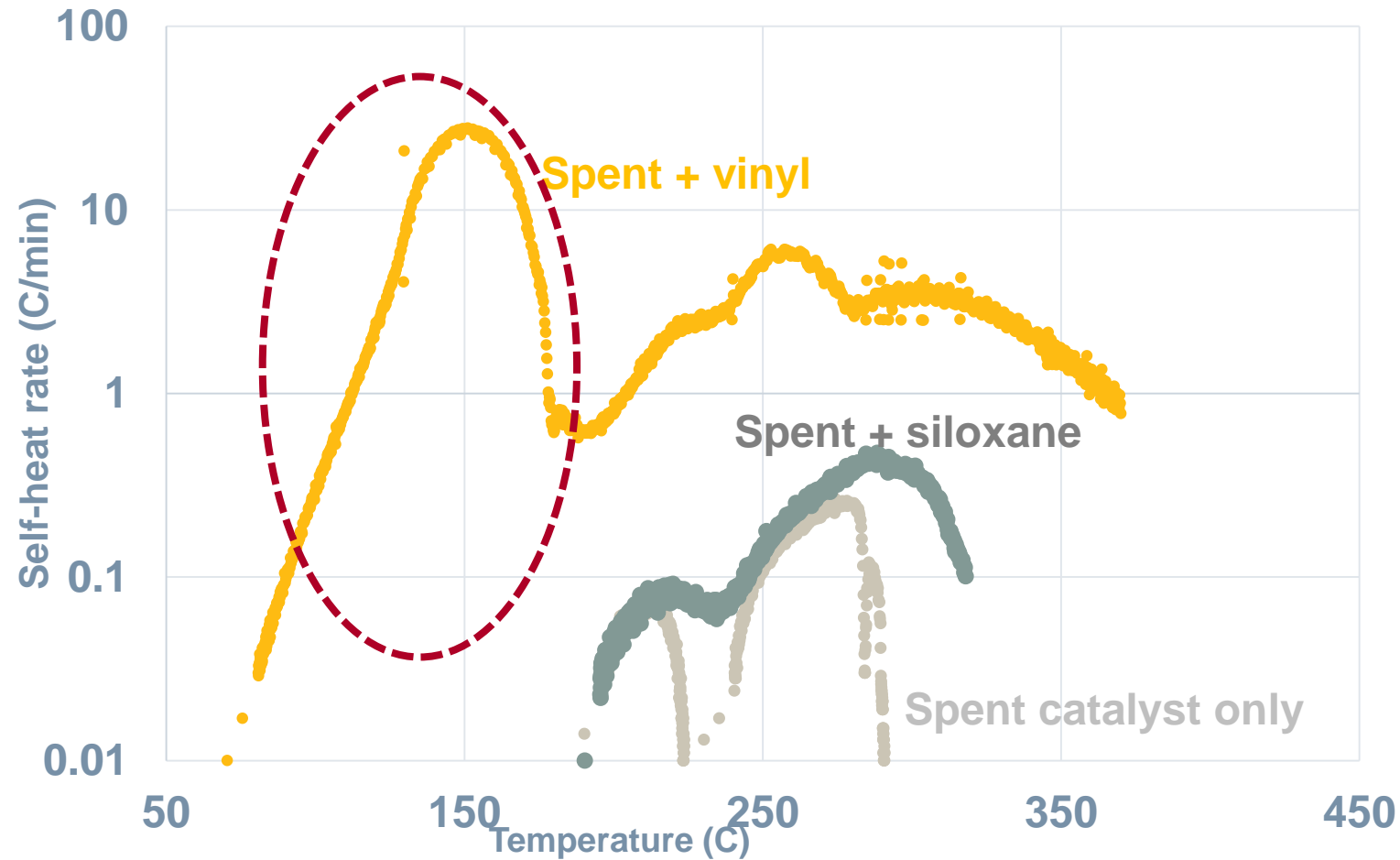
Fresh vs. Spent Catalyst

- Exotherm and gas generation
- Observed significant difference in reaction rate while area under curve (total heat release) remains same

**Sudden pressure rise accompanied by exothermic activity suggests gas-generating reaction**

**Omnical SuperCRC  
Metal Pressure Cells  
Linear T ramp to 180 C**

# ARC RESULT: COMPARISON WITH DIFFERENT TEST MIXTURES




Large initial exotherm **only** observed in presence of vinyl + catalyst

Significant exotherm, onset at 80°C, accompanied by pressure rise

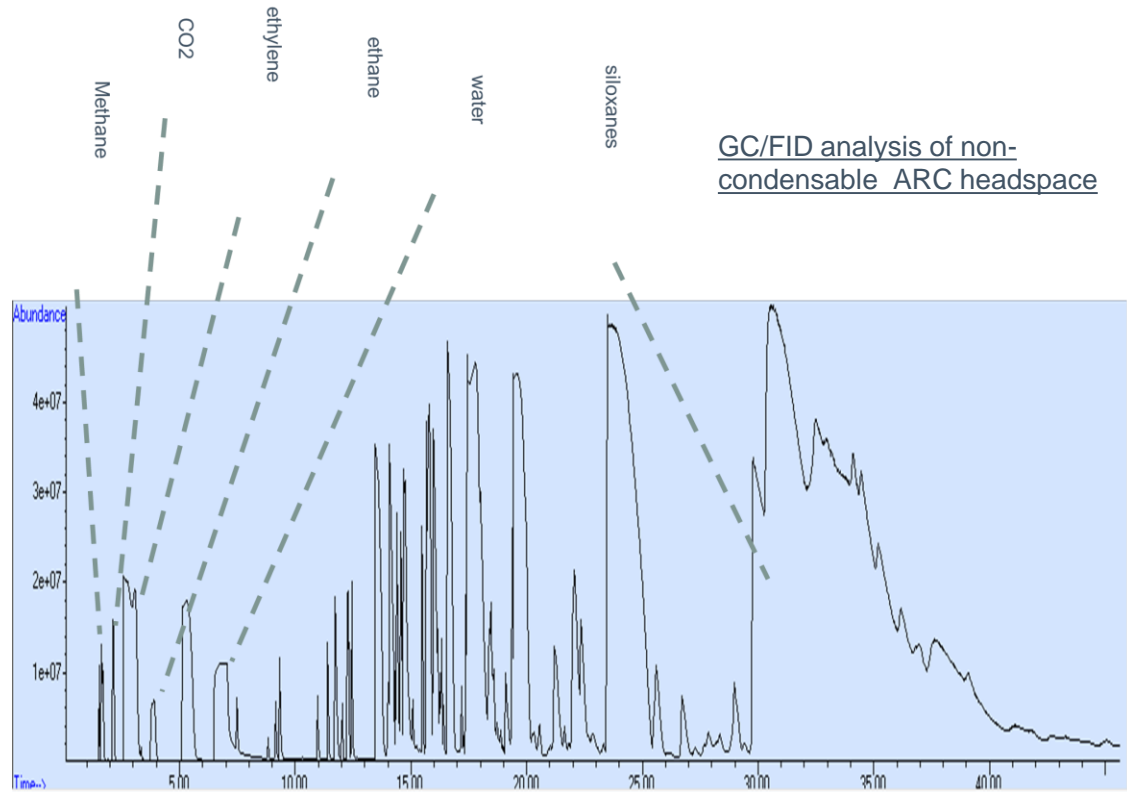
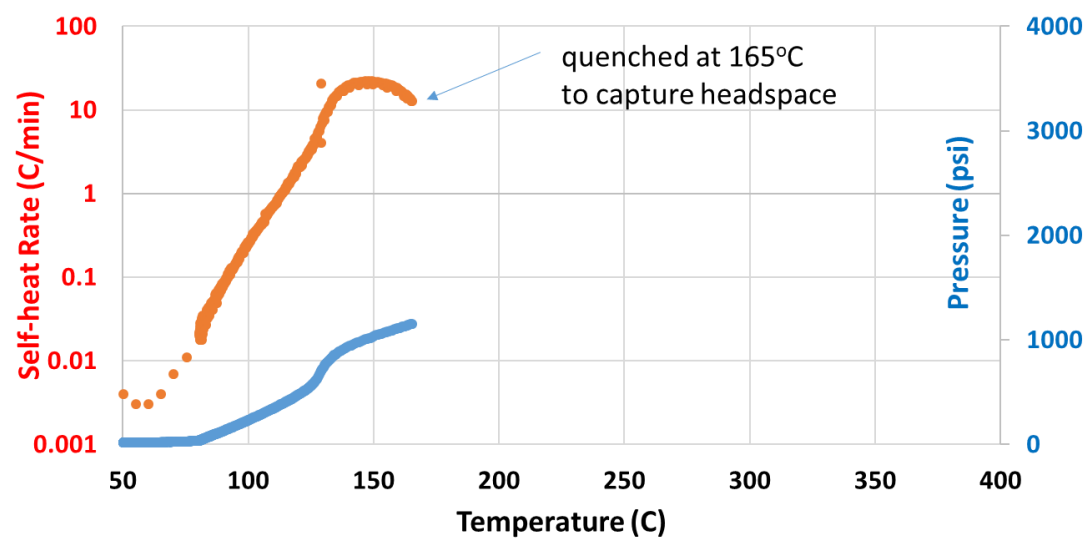
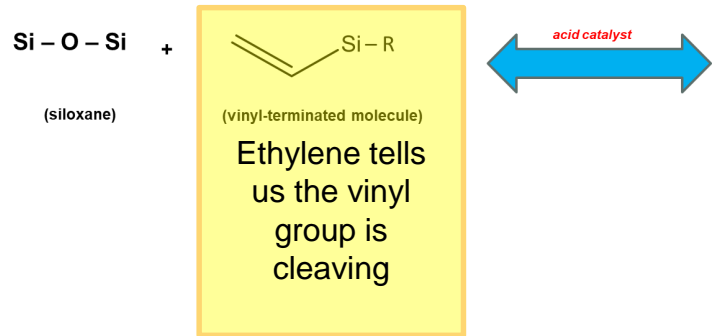
S. Dutta, et. Al. "Vinyl-Siloxane Cleavage: Applying Thermo-Analytical and Hybrid Calorimetry Techniques to Inform Process Safety and Design". AIChE Spring Meeting & GCPS, 2020.

# WHAT IS DRIVING THE “LOW T” EXOTHERM BEHAVIOR?

**Experiment:**  
ARCxGC-MS

 **In-Line Sampling System**

1. Monitor the sample's P and T, during a calorimetric test to observe reaction
2. Sample the headspace, and send to GC/MS, GC-FID for separation & speciation



Complex mixture – analysis focused on non-condensable gases only for further analysis

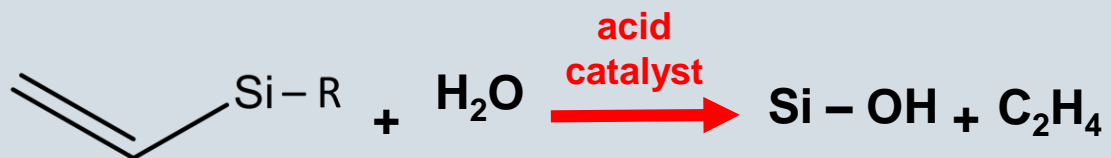
	Spent catalyst (v/v)	Spent catalyst + vinyl (v/v)	Spent catalyst + vinyl (quenched at 165°C) (v/v)
methane	84.5%	67.2%	0.2%
ethylene	0.01%	9.3%	85%
ethane	0.01%	5.2%	0%

S. Dutta, et. Al. "Vinyl-Siloxane Cleavage: Applying Thermo-Analytical and Hybrid Calorimetry Techniques to Inform Process Safety and Design". AIChE Spring Meeting & GCPS, 2020.



# ARCxGC-MS vs. THEORETICAL PREDICTION OF C<sub>2</sub>H<sub>4</sub> FORMATION

## Proposed vinyl cleavage reaction



Theoretical Heat of Reaction = - 982 J/g of vinyl  
(using Molecular modeling/Benson Group Additivity)

Observed exotherm from ARC = - 700 J/g of vinyl

*Note: ARC known to predict ~ 20% lower Heat of Reaction due to pseudo-adiabatic conditions*

S. Dutta, et. Al. "Vinyl-Siloxane Cleavage: Applying Thermo-Analytical and Hybrid Calorimetry Techniques to Inform Process Safety and Design". AIChE Spring Meeting & GCPS, 2020.

## Conclusions

- Vinyl cleavage and consequent ethylene formation is an exothermic reaction
  - validated by ARC data, online GC-MS analysis and thermochemical predictions
- Detected onset temperature from ARC suggests that exothermic reaction may occur close to ambient
  - A key consideration for reactor design/process development
- No significant difference in kinetics of vinyl cleavage on un-used vs. used catalyst under adiabatic conditions
  - Suggests that vinyl cleavage may be an intrinsic side reaction on acid catalysts

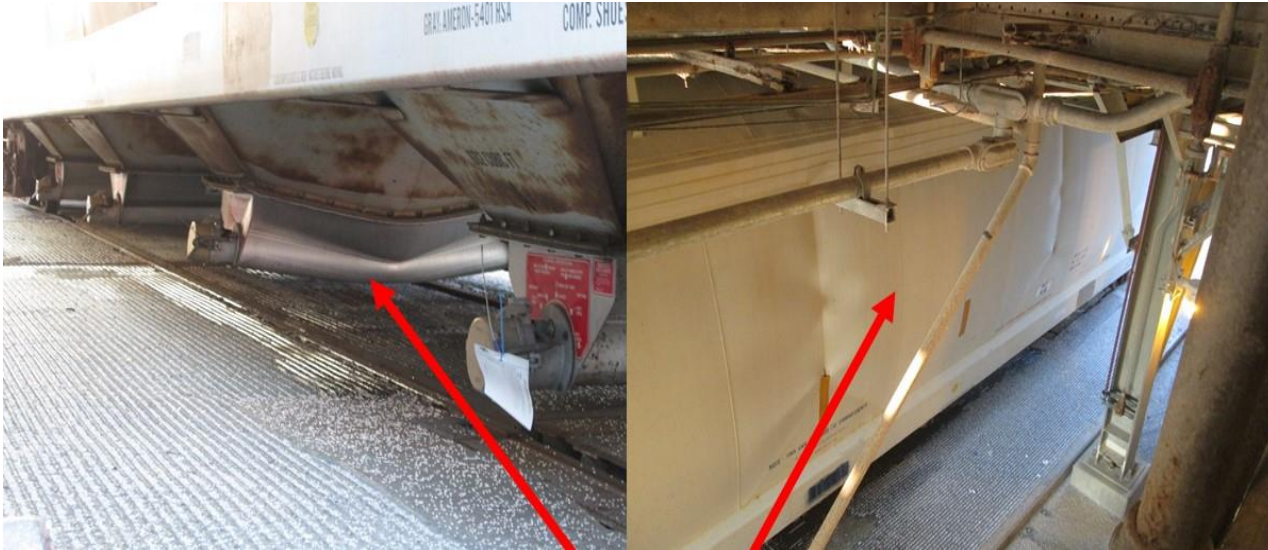


# CASE STUDY: POLYMERIC RESIN DEFLAGRATION

A deflagration occurred at a Dow facility in 2018

- An off-grade polymeric resin (non-flammable) was being loaded into a railcar
- The railcar compartment was partially filled
- The operators observed a “natural gas odor”, and stopped loading to investigate
- When loading resumed, an explosion occurred in the railcar
- The deflagration ejected the loading spout from the railcar compartment
- The railcar and loading spout were damaged
- Fortunately, there were **no injuries**

**Railcar damage** Red arrows indicate damage to the railcar's center compartment



**Loading Spout Damage**

Red: Previous position





# RULING OUT POTENTIAL EXPLANATIONS

## Hypotheses:

1. ~~Residual, unreacted material or other raw materials caused flammable gas in the railcar compartment~~
2. ~~Fine polymer particles caused a dust explosion~~
3. ~~Solid additives caused a dust explosion~~
4. A flammable atmosphere was (somehow) generated in the railcar

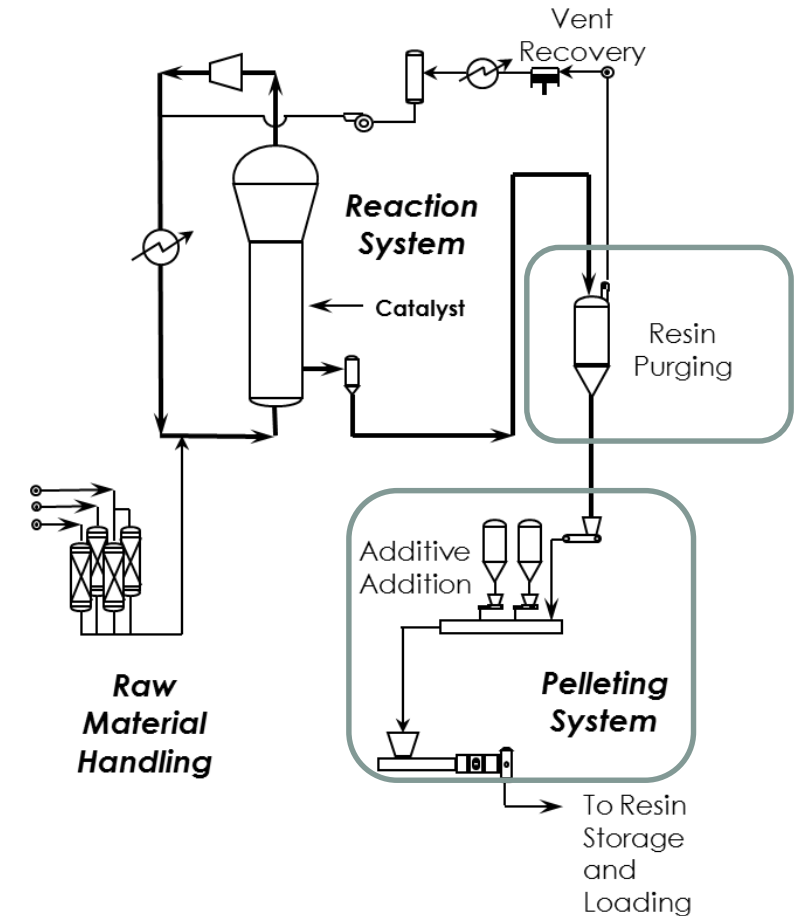
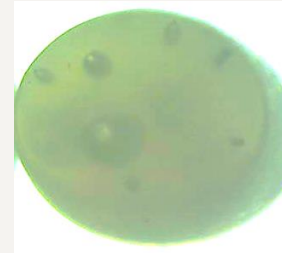
1. A purge step removes flammable volatiles, and was adequate
2. The polymer pellets contained no fines and were not flammable
3. No fines due to additives, also not flammable

These hazards were **known** in the open literature **and accounted for** by existing layers of protection.

## Evidence and Key Facts:

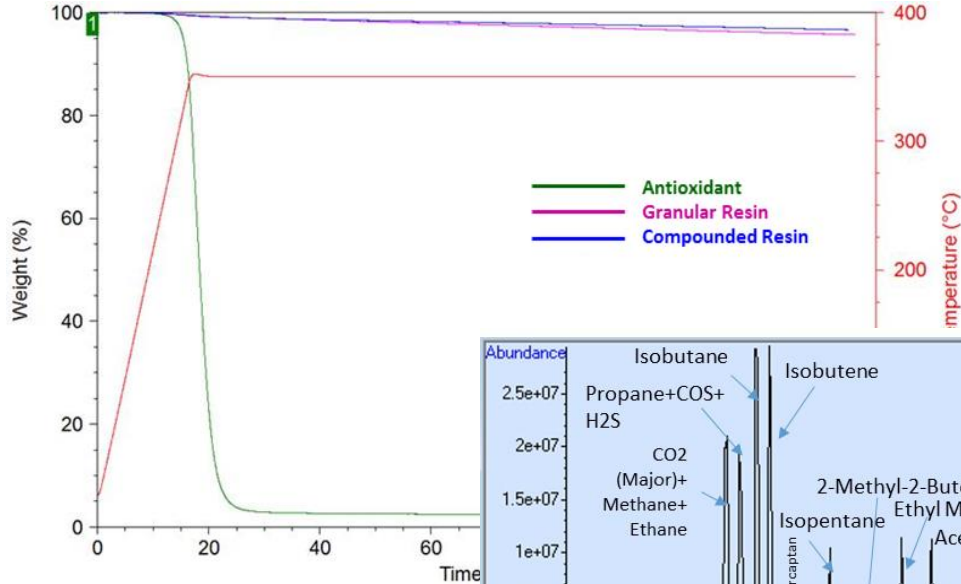
- The extruder barrel reached a high temperature,  $\geq 380\text{ }^{\circ}\text{C}$
- An antioxidant additive was being fed to the extruder
- Gas bubbles were observed in **samples of the resin** →
- Resin was not stored for very long before loading

**Improved hypothesis:** The antioxidant additive decomposed, evolving gases that generated a flammable atmosphere in the railcar



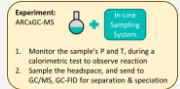
**Simplified Process Flow Diagram**

# VALIDATING THE HYPOTHESIS WITH THERMO-ANALYTICAL TECHNIQUES



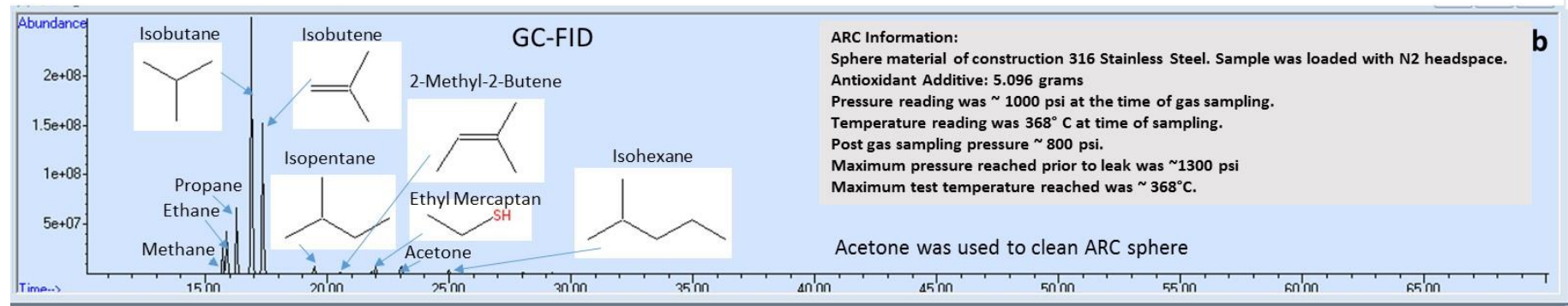
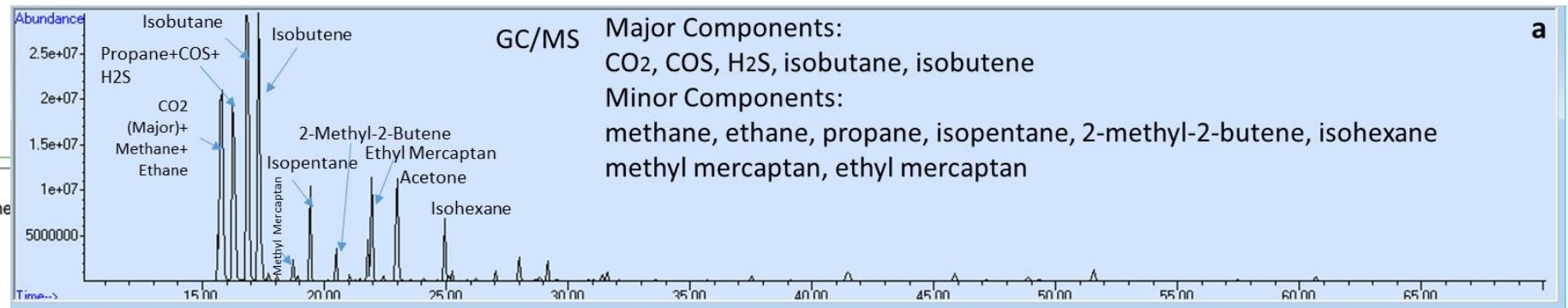
**Test 1:** Thermogravimetric analysis confirms the antioxidant decomposes to release gas, while the polymer resin is relatively stable.

**Test 2:** Antioxidant samples were much less stable at high temperatures. ARCxGC/MS testing determined which gases were formed by decomposition.

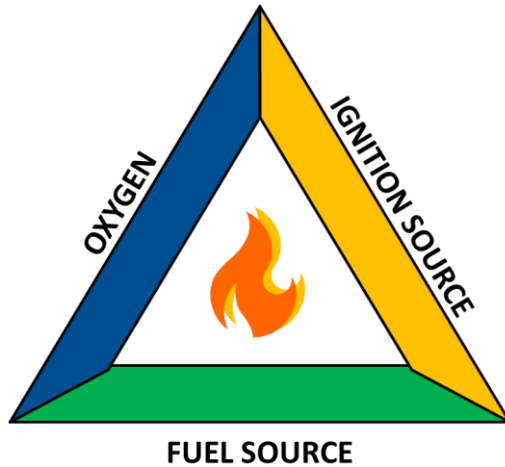


Most evolved gases were flammable.

**Mercaptans** are added to natural gas as a warning property, explaining the odor observed.



# LESSONS LEARNED: SEARCH THOROUGHLY FOR FLAMMABILITY HAZARDS



**Oxidizer?** Air

**Fuel Source?** Flammable gases evolved from antioxidant decomposition, not the polymer resin, confirmed by further testing.

**Ignition Source?** "Ignition sources are free!"

- Resistive pellets are difficult to ground/bond
- Electrostatic discharges are likely

**Goals:** Understand the causes of the incident and prevent future incidents

Root Causes

Corrective Actions

- ❑ Think creatively about what may cause a fire
- ❑ Flammability hazards depend on the conditions
- ❑ Flash point, AIT, and MIE are method-dependent, and should be applied with care
- ❑ Context, environment, and many factors affect the level and type of hazard

Extruder  $\geq 380^\circ\text{C}$ ,  
leading to previously  
unknown flammables

Short residence time  
in storage after  
extrusion

High temperature  
alarms to prevent  
decomposition

Flammable gas  
detectors in post-  
extrusion area

Allow residence time  
in silos for off-grade  
resin

K. Mulligan et al. "Investigation of a Polymeric Resin Deflagration Using Advanced Calorimetric Techniques." AIChE Spring Meeting & GCPS, 2019.

## Background

- Mixing Calorimetry is one of the primary tools used in Reactive Chemicals to assess the hazards associated when different chemicals are mixed.
- Currently the device is capable of providing accurate thermodynamic and kinetic data.
- However, the extent of reaction and the reaction mechanisms are not easily determined from calorimetry alone.

## Opportunity

- Extent of reaction and the reaction mechanisms are not easily determined from calorimetry alone.
- Online, in-situ reaction monitoring is practiced within Dow
- **Combine two orthogonal technologies (spectroscopy and calorimetry)**

## Value Impact

- ***In-situ* analytical methods such as time resolved calorimetry and spectroscopy supply significantly more information.**
- Hints to the existence and structure of metastable intermediates and mechanistic steps that ultimately lead to a detailed kinetic and mechanistic model.
- Prediction of optimal reaction conditions that can even be outside the investigated operating range.

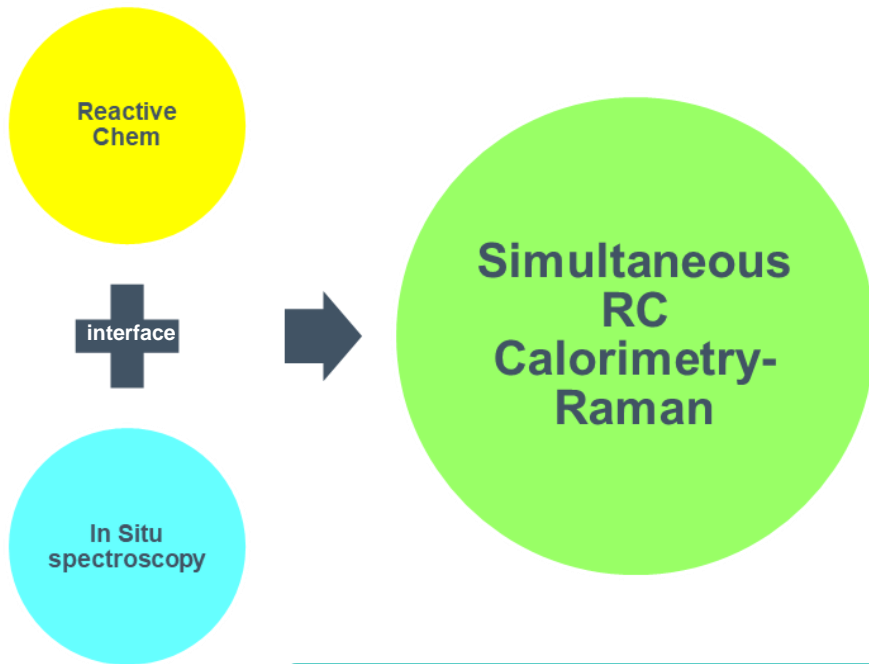
# HOM CALORIMETRY X RAMAN SPECTROSCOPY

Reaction calorimetry can measure heat released/absorbed by chemical reaction

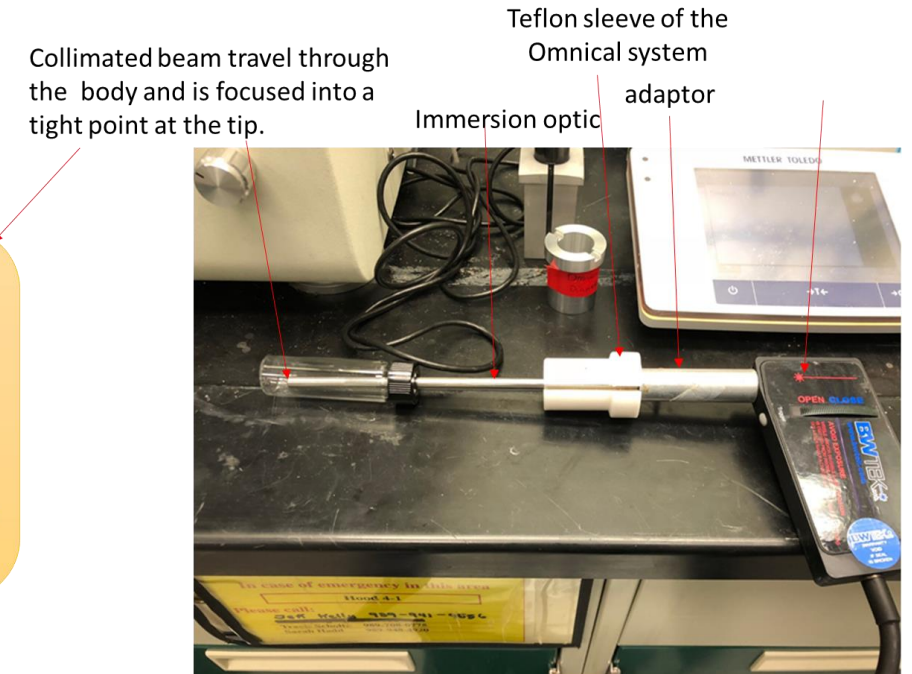
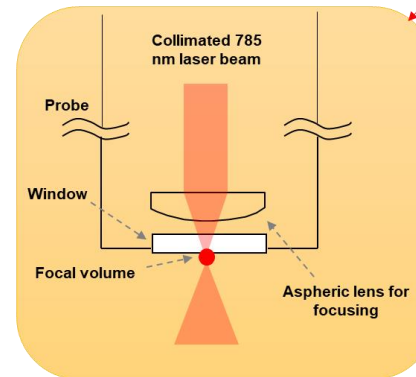
- Useful for scale-up and hazard analysis (heat flow,  $\Delta H_{\text{rxn}}$ ,  $\Delta T_{\text{adiabatic}}$ )

Spectroscopy- a variety of Laboratory and commercial scale instrumentation available

- FTn-IR, Mettler-Toledo React IR45m and REACTRaman, BWTek I-Raman Pro
- *In situ* IR mostly based on ATR (attenuated total reflectance) probes



**Benefits: Small volume reactor (~ 20 mL), portable fiber optic technology, quick set up and data collection (vs. coupling to RC-1)**





# IN-SITU SPECTROSCOPY FOR REACTIVE CHEMICAL MONITORING

## Hypotheses tested:

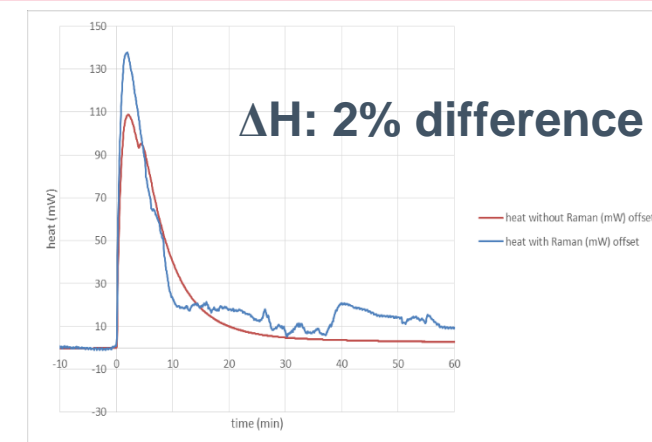
- 1. In-Situ Raman probes can be interfaced with the mixing calorimeter and accurately identify the chemical species formed.
- 2. Energy from the Raman laser will not interfere meaningfully with the reaction path or impact the calorimetric results
  - Run twice, with and without, as many chemistries are photo-sensitive

## Technical Project Description:

- Determine appropriate way to interface the currently available in situ probes to RC instruments without compromising the thermal analysis.
- Evaluate synergy of interfacing the two techniques: When it is value-added to apply such in-situ spectroscopy?

## Project Outcomes:

- Successful simultaneous in-situ spectroscopic analysis for condensed-phase mixing calorimetry
- Established protocol for routinely leveraging in situ Raman analysis +calorimetry for insight into the processes under study



## Milestones

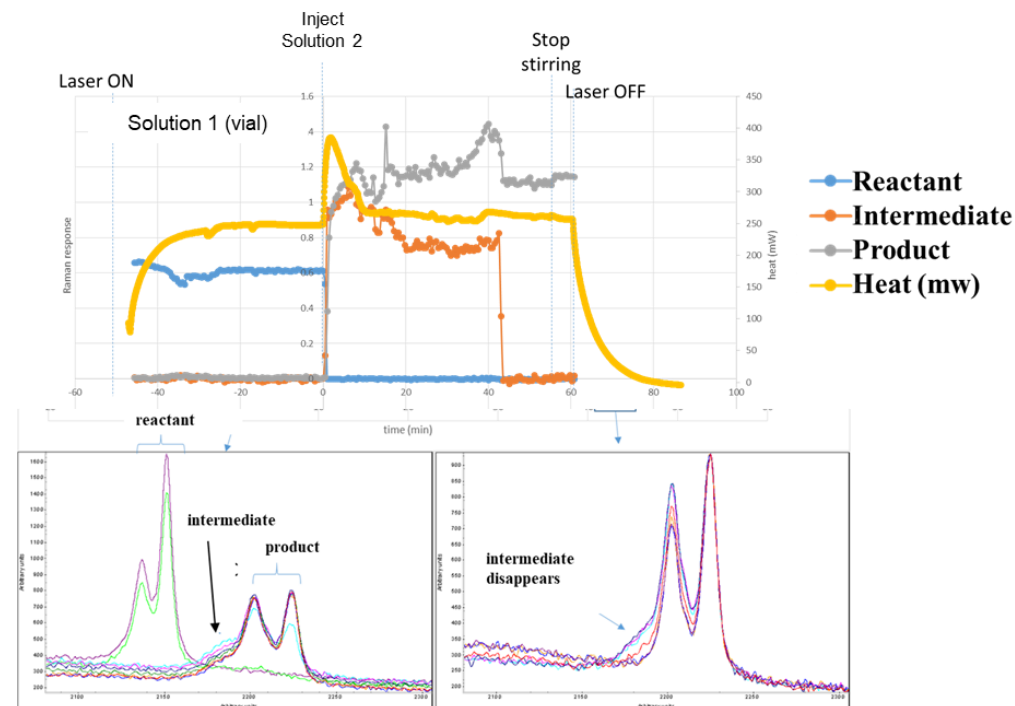
### (1) Control experiments of endothermic reaction of KCl dissolution in water.

- Raman laser does introduce a baseline level heat ~200 mW, with 0.3 mW noise.
- For highly exothermic reactions, which are the most relevant cases for RC evaluations, this has a negligible impact on results.

### (2) Performed two tests (exothermic reactions) based on synthesis chemistry

- One was run with Raman, and one without Raman
- Very similar results (2% difference in energy release)

### (3) Calorimetric test coupled with the Raman monitoring yielded real time conversion results that matched expectation

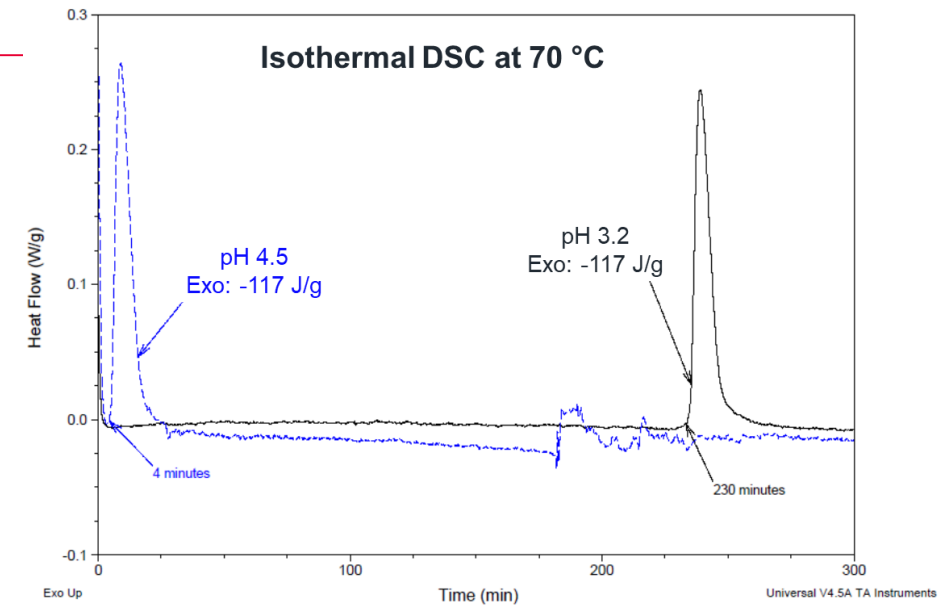


# A TALE OF pH AND AUTOCATALYSIS

- R&D Project: Understand chemistry of “Chemical X” using spectroscopy
- MOC: Conduct thermal stability of Chemical X as a function of pH
  - Varying pH crucial to gain desired process knowledge
  - Reactive chemicals testing uncovers a ‘bump’ in the road

## DSC

- Induction time and shape of exotherm suggest an **autocatalytic reaction**
- Isothermal DSC: induction time decreases at higher pH

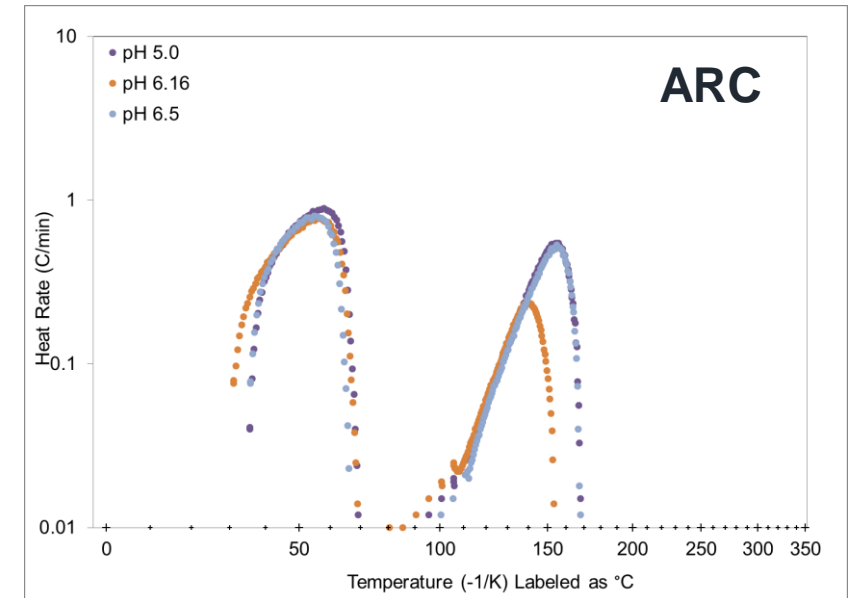


## ARC

- At higher pH, large exotherm w/ unusual curvature @ low T
  - This exotherm is not detected at lower pH
- Exo 1: Does not appear to follow Arrhenius kinetics, high  $E_a$ 
  - non-linear SHR (log plot)

**Autocatalysis- reactant self-reacts to generate product(s) that catalyze subsequent reaction**

- Large apparent  $E_a$
- Reaction rate increases under isothermal conditions → “induction time” observed
- Lack of understanding/detection of autocatalytic behavior can lead to non-conservative safety assessments





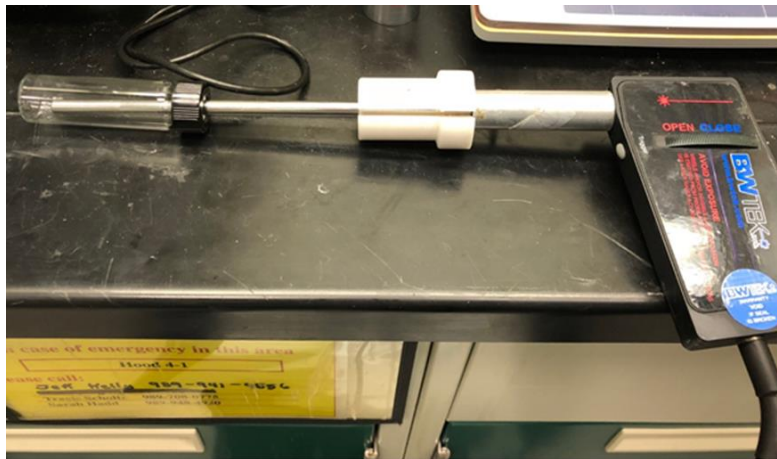
# HOW DO WE MOVE FORWARD? UTILIZE HOMxRAMAN



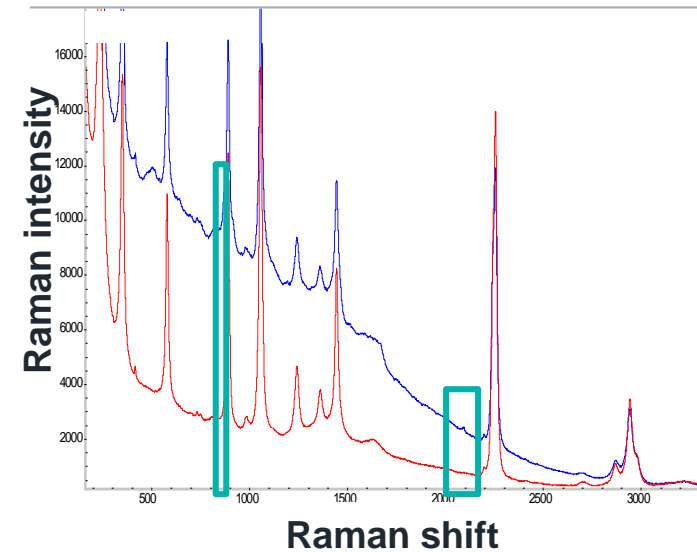
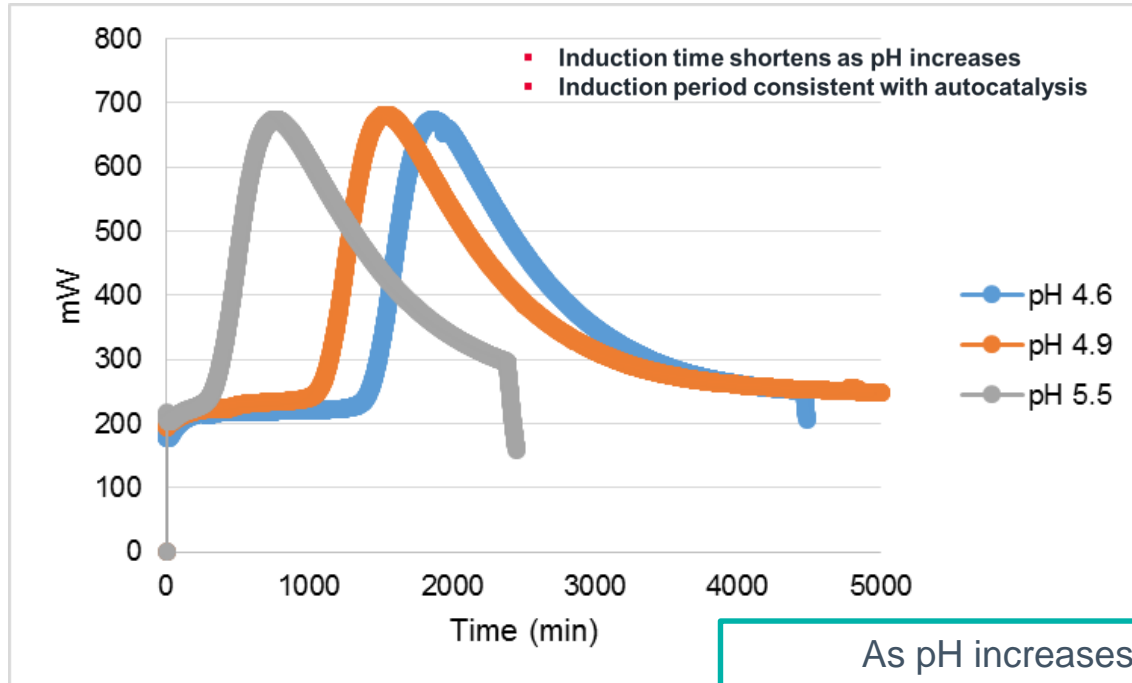
Quantification of heat gained when chemicals are mixed

Gain mechanistic insights

Obtain real-time information about reaction kinetics and reaction heat



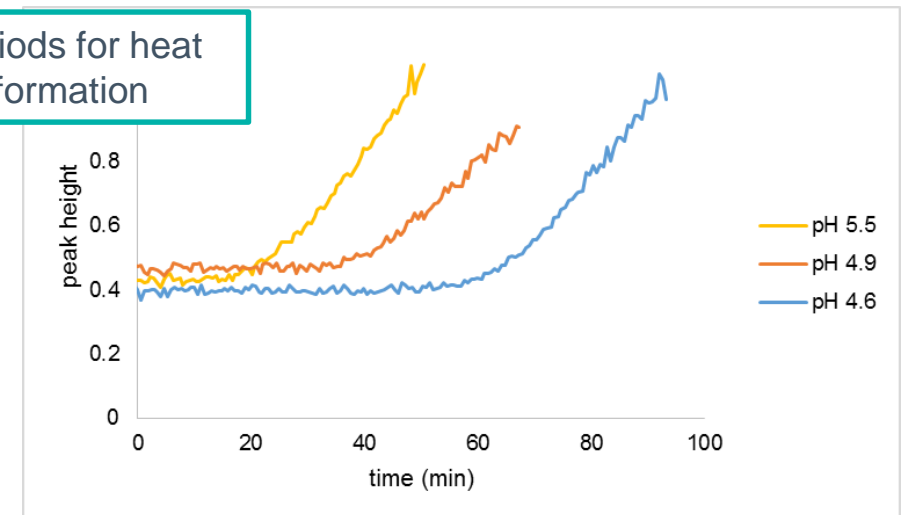
# CALORIMETRY AND SPECTROSCOPY OVER pH RANGE- LOTS OF DATA IN ONLY 2 DAYS!



**Peaks “grow in”**  
As chemistry progresses during isothermal hold, new Raman-active species are observed

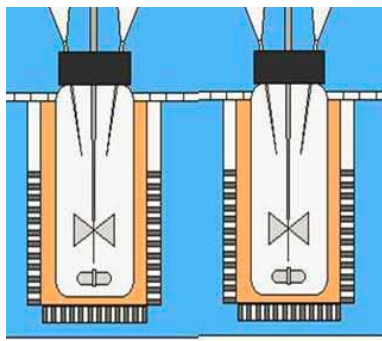
As pH increases, shorter induction periods for heat evolution and degradation product formation

Raman data tell us how long these species are around (“labile”) and allows for application of other analytical methods for speciation.



# IN-SITU SPECTROSCOPY FOR REACTIVE CHEMICAL MONITORING

## Simultaneous Heat of Mixing Calorimetry Coupled with In-situ Raman Spectroscopy



Small scale - low cost reaction screening

Scalability - from grams to manufacturing

Kinetics - heatflows that match GC/LC



Reaction heat data  
Process design & safety  
Large Scale Processes in Small Scale Calorimeters

In situ Raman spectroscopy  
Tracking concentration in real-time  
Understand speciation and reaction pathway

**Advertise your capabilities**

They aren't worth as much if those that would benefit are unaware!

Combining these two orthogonal technologies to provide more comprehensive and conclusive reactive chemicals solutions.

Are you willing to give this a try?  
Do you have any system that may benefit from either one, or this combined technology?



# ARC: HIGHLIGHTING & ADDRESSING A LIMIT

Accelerating Rate Calorimetry: Can low sample thermal conductivity ( $k$ ) lead to temperature gradients?

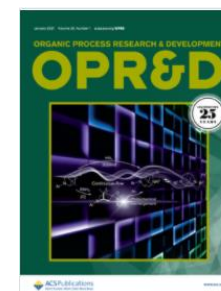
- Could this suspected phenomenon contribute to non-conservative reaction kinetics or application of ARC results?

## Recent Dow + P2SAC Collaboration

- 2020 PMP Summer Project
  - Led by Soham Dutta, Dow Reactive Chem
  - Sanjit Sounderrajan and **Brittany Roopnarine**
- 2020 Fall UG Project (continuation)
  - Madison Draper

Related thermal lag phenomena in ARC measurements have been explored in literature:

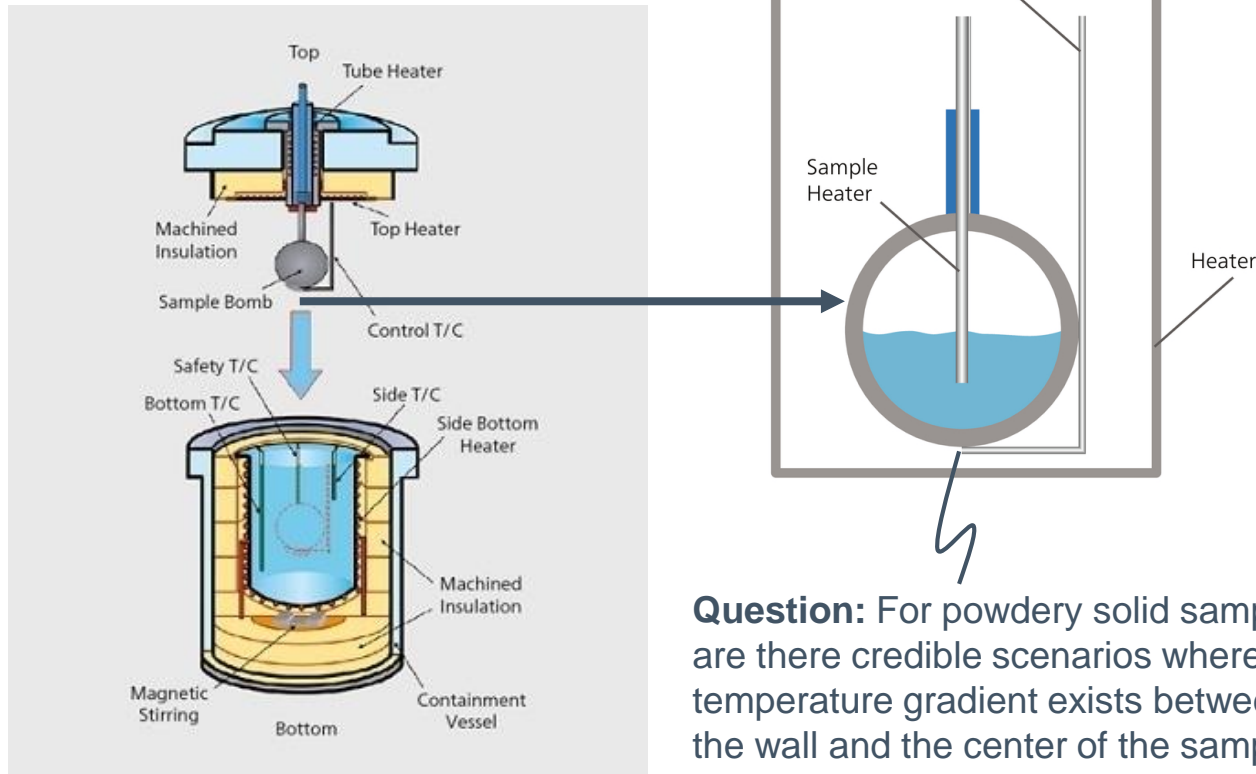
- Kossoy A, Sheinman I. Effect of temperature gradient in sample cells of adiabatic calorimeters on data interpretation. *Thermochim Acta*. **2010**;500:93–9.
- Min Sheng, Daniel Valco, and Craig Tucker; *Organic Process Research & Development* **2021** 25 (1), 108-119; DOI: 10.1021/acs.oprd.0c00459
- Qiyue Xu, Jiong Ding, Suijun Yang, Shuliang Ye; Modeling of a power compensated adiabatic reaction system for temperature control design and simulation analyses; *Thermochimica Acta*, Volume 657, **2017**, Pages 104-109.
- Zhang, J., Ma, Y., Dong, Z. *et al.* Numerical simulation to study and optimize the significant hidden temperature gradients in adiabatic tests. *J Therm Anal Calorim*, **2020**. <https://doi.org/10.1007/s10973-020-09972-6>



# DOW x P2SAC: 2020 PMP CAPSTONE PROJECT (SUMMER 2020)

“The effect of spatial temperature variation of sample inside ARC sphere on industrial hazard assessment”

Accelerating Rate Calorimeter (ARC)  
Used to evaluate thermal hazards of chemicals



**Question:** For powdery solid samples, are there credible scenarios wherein a temperature gradient exists between the wall and the center of the sample?

ARC: thermocouples are external to sample spheres

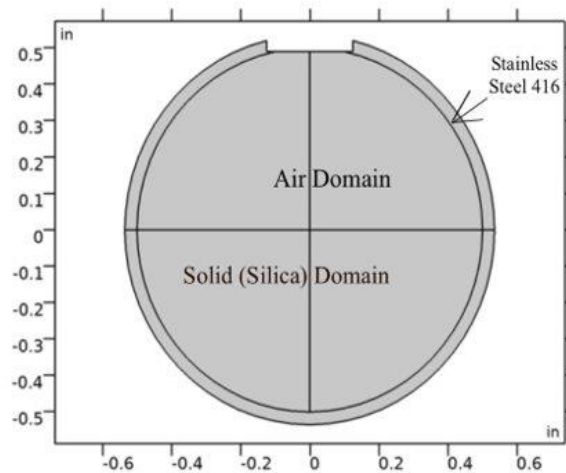
- Clipped to side or bottom
- Can we quantify temperature difference between sample center to the wall of the sphere?

**FEM (Finite Element Method)** software COMSOL to model the sphere and determine if the hypothesized temperature difference exists

# Dow x P2SAC: 2020 PMP CAPSTONE PROJECT (SUMMER 2020)

## Effect of spatial temperature variation of sample inside ARC sphere on industrial hazard assessment

### Geometry for the simulation



### Step 1: Simulate the heating of the entire ARC sphere before any exothermic reaction occurs

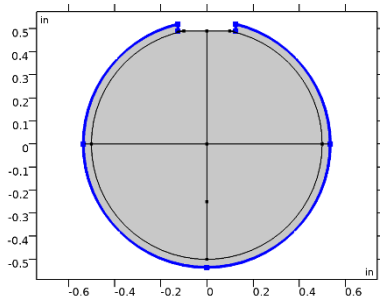
- Heat flows from external heaters into sphere
- Non-reactive, inert sample
- Assume no convection

COMSOL Heat Transfer in Solids and Fluids module solves the time-dependent Equation of Energy

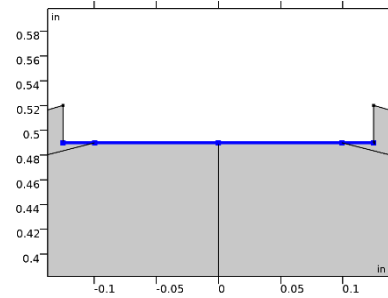
$$d_z \rho C_p \frac{\partial T}{\partial t} + d_z \rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = d_z Q + q_0$$

$$\mathbf{q} = -d_z k \nabla T$$

### Boundary conditions for the simulation



Thermal Insulation & Boundary Heat Source



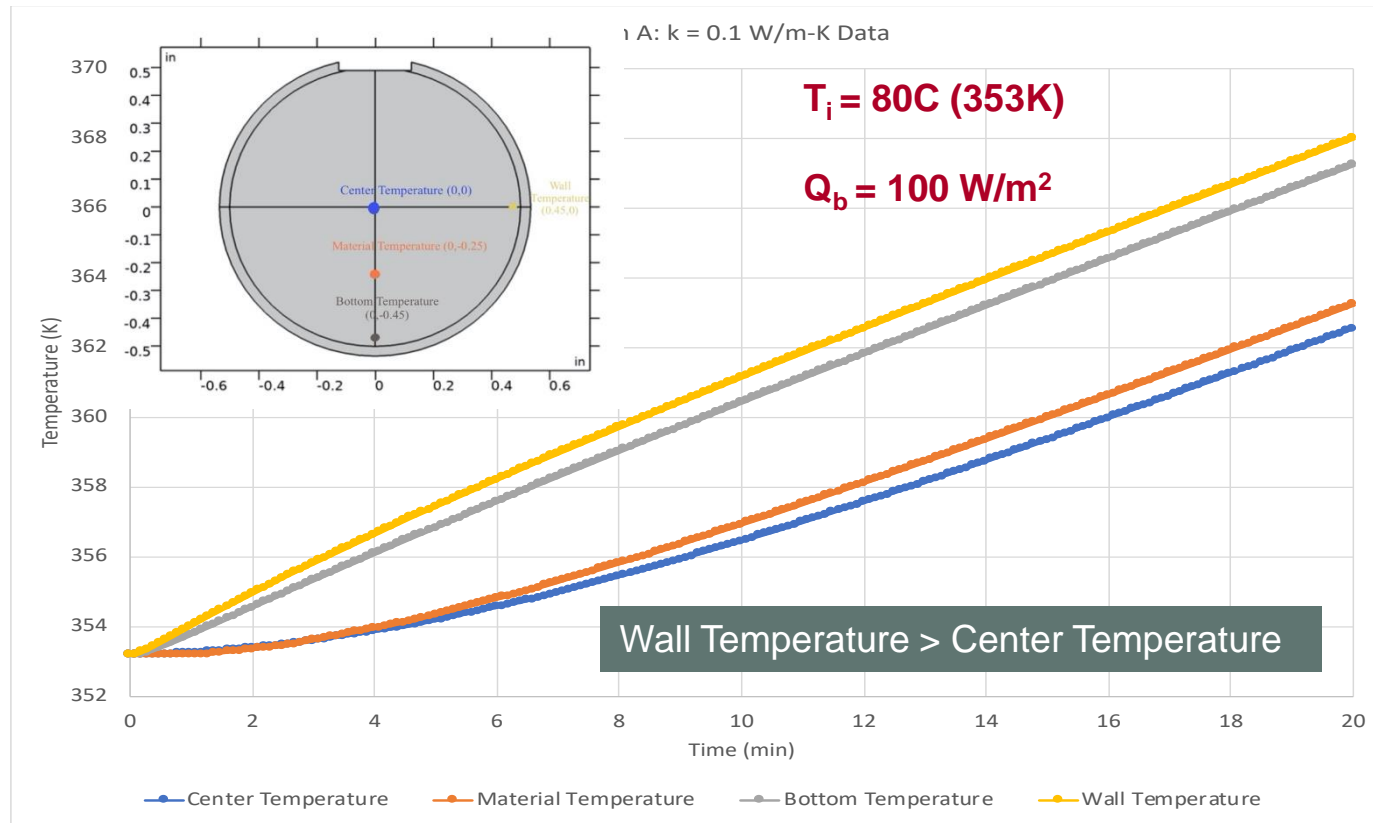
Neck of ARC sphere loses heat , ~2%

### Boundary conditions:

- No heat is generated on the outside of sphere
  - all generated heat contained in sphere
- A heat source boundary,  $Q_b$  was also applied to the outer boundary of the sphere to simulate the heating of the sphere



# Dow x P2SAC: 2020 PMP CAPSTONE PROJECT (SUMMER 2020)

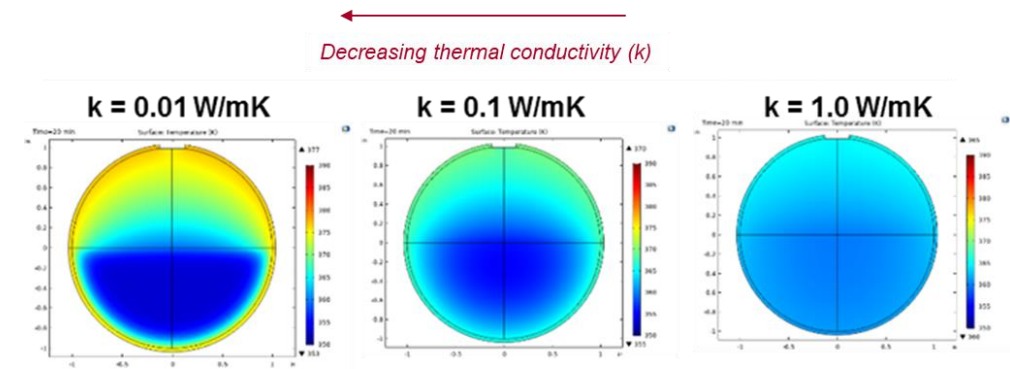


As Thermal Conductivity decreases, the T gradient within the ARC Sphere is more severe

Simulation: heating inert sample from outside

Four Temperature points were recorded for Simulation

- Center Temperature (0,0) is at the Air-Silica Interface
- Material Temperature (0,-0.25) is the Bulk temperature of silica
- Bottom Temperature (0,-0.45)
- Inner Wall Temperature (0.45,0)





# BUILD IN EXOTHERMIC REACTION

## Reaction Kinetics

$$Q = -\rho L \frac{\partial \alpha}{\partial t}$$
$$\frac{\partial \alpha}{\partial t} = (1 - \alpha)^n A e^{-E/RT}$$

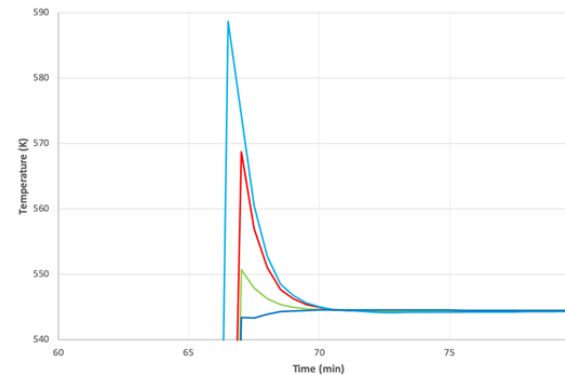
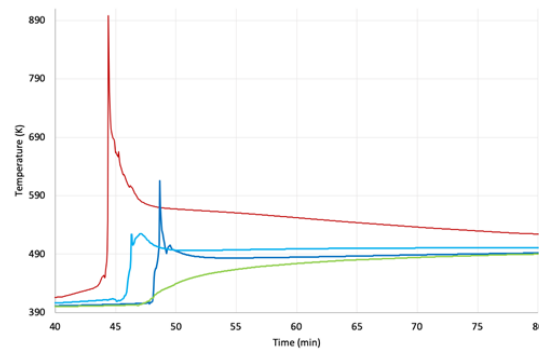
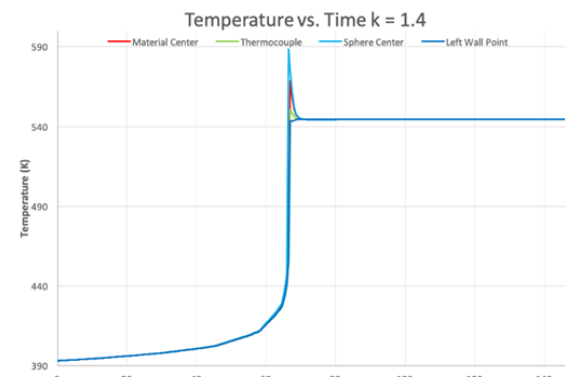
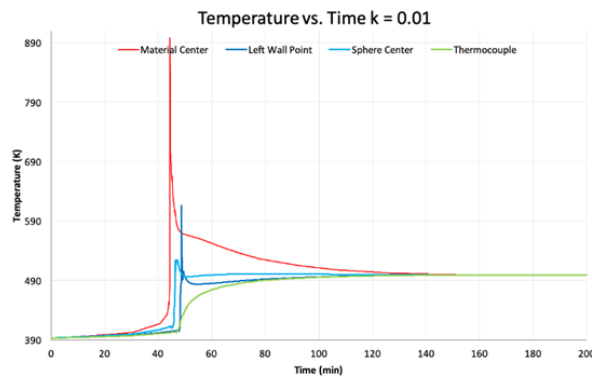
$\alpha$  = fraction of transformation  
 $n$  = reaction order = 1  
 $A$  = Preexponential Factor [=] 1/s  
 $E$  = Activation Energy [=] J/mol  
 $L$  = Enthalpy Change [=] J/kg

## Simulation:

- fast, exothermic reaction to validate the hypothesis of spatial temperature differences inside ARC sphere
- COMSOL Irreversible Transformation domain was used to insert the kinetic values.
  - silica (SiO<sub>2</sub>), but with forced peroxide kinetics
- With exothermic reaction present, the heat source is coming from within the ARC sphere and the gradient is reversed

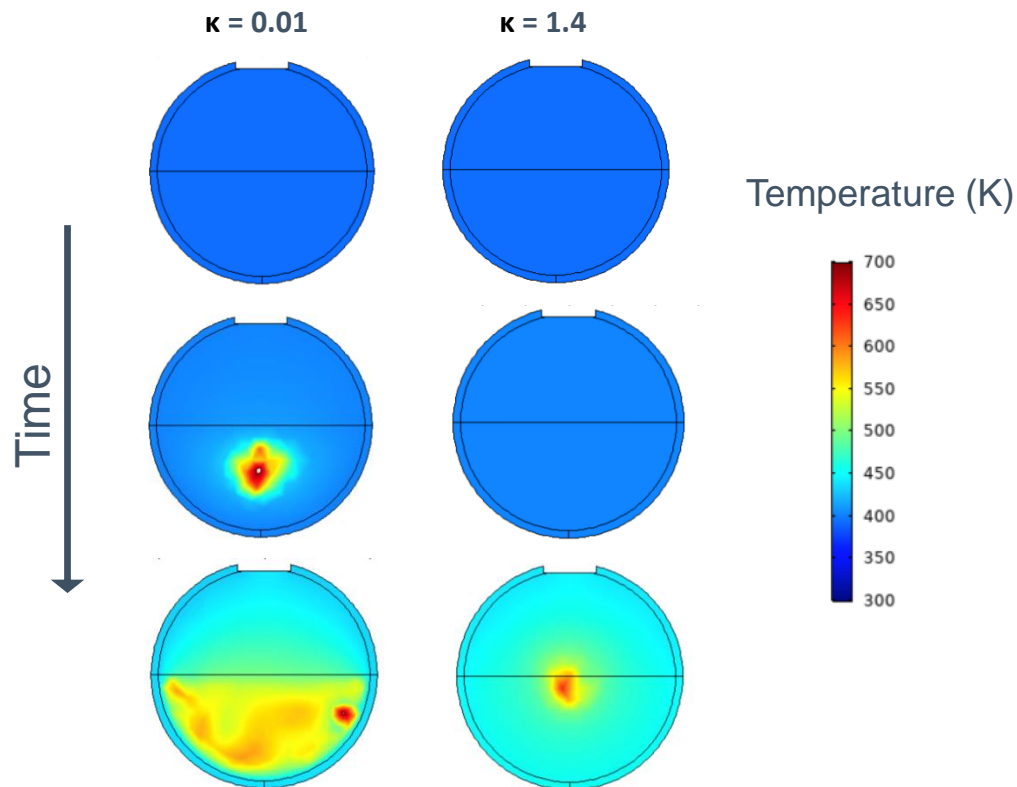
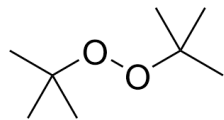
## Results:

- Greater difference in temperature (at wall vs. internal locations) in low  $k$  systems
- High  $k$  system reaches a final, equilibrium temperature in less than half of the time that it takes a low  $k$  system to equilibrate.



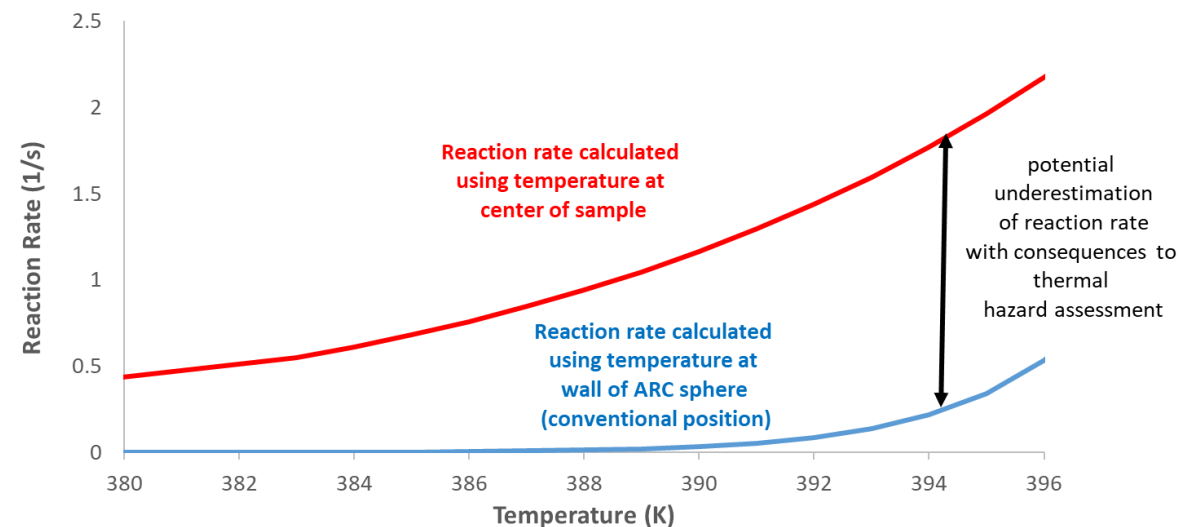
# SUMMARY & FUTURE WORK

The kinetics of di-tert-butyl peroxide (DTBP) thermal decomposition is used to model an exothermic reaction.



Model was developed, shows that for low  $k$  reactive samples the external thermocouple can measure temperatures lower than that at the center of the sample. **This effect must be accounted for during thermo-kinetic modeling of ARC data.**

Rate of Reaction vs. Temperature,  $\kappa=0.01$



## Impact Statement:

- In low thermal conductivity ( $\kappa$ ) samples (ex: powdery solids, solid catalysts, solid peroxides), ARC data as currently measured will underestimate reaction rates and thermal reactivity hazards.

## Future Work:

- Extend simulations into liquid domains, particularly for liquid systems that are highly viscous that are also suspected to be internal heat-dissipation limiting.
- Incorporate internal natural convection into the reactive simulations.
- **This work will help us apply learnings to non-powdery systems**



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# THANK YOU

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Together™