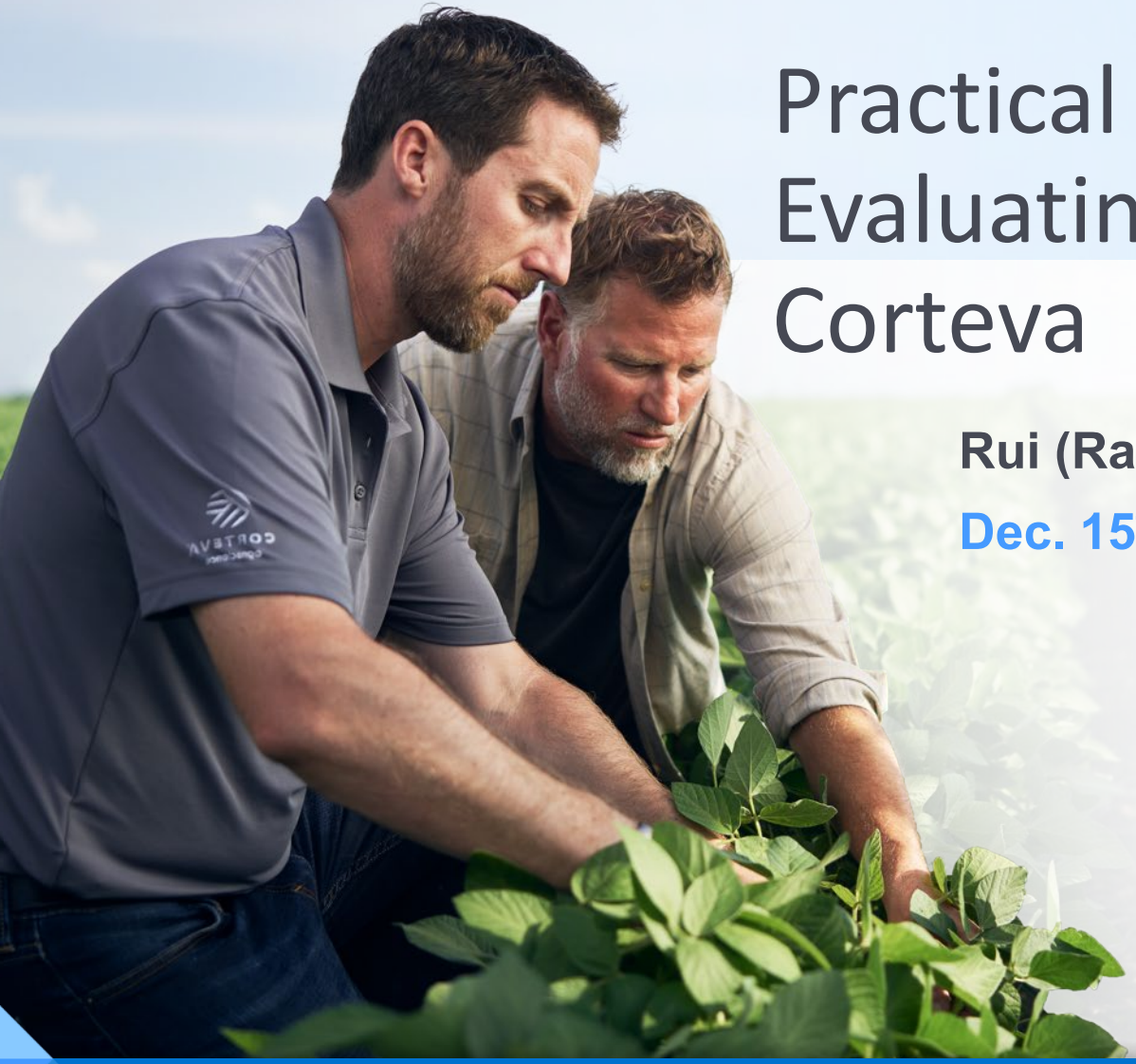

Practical Use of AKTS Modeling in Evaluating Autocatalysis Compounds in Corteva

Rui (Ray) Xu and Daniel Valco

Dec. 15th 2022

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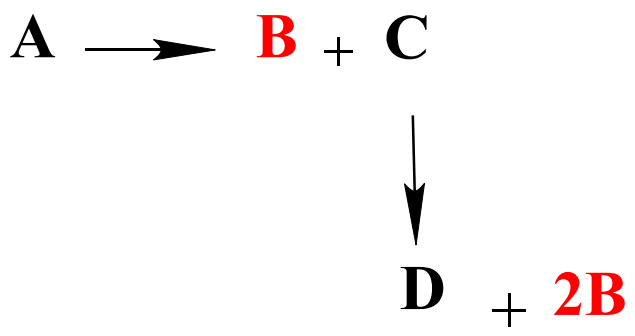
Outline

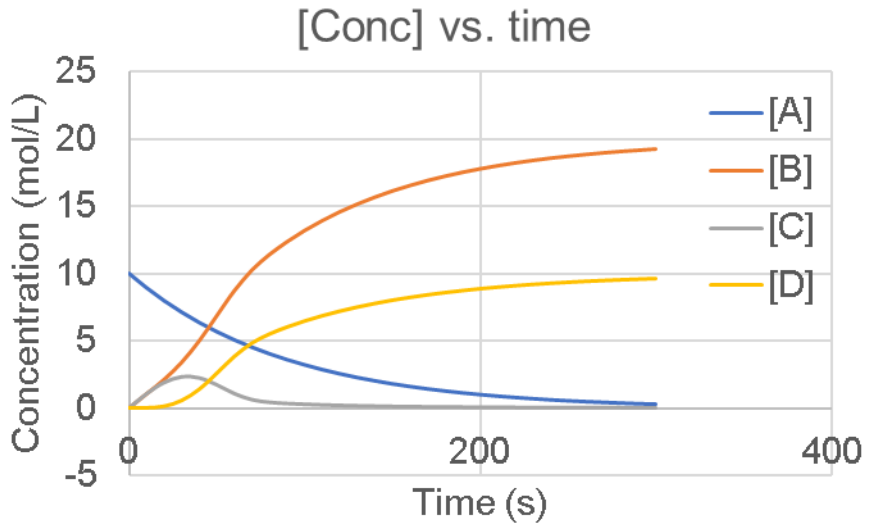
- Identification and confirmation of autocatalytic behavior
  - Characteristics
  - Issues with autocatalytic decomposition reactions
  - Identification using DSC (Differential Scanning Calorimetry)
- Standard Modeling Procedure
- Application to storage, shipping, and reactive relief design.
  - Case study I – isolation and shipping of boronic acid compound
  - Case Study II – weak autocatalytic decomposition of crotonaldehyde

Autocatalytic Reaction

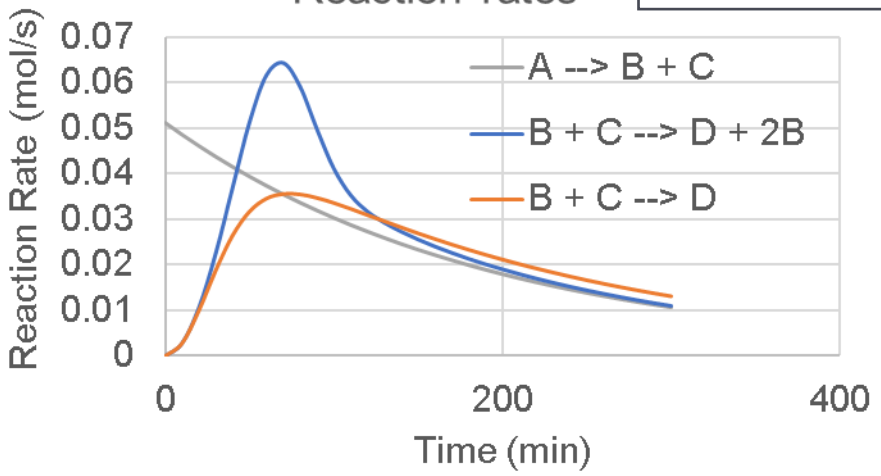
A chemical reaction where at least one of the products also acts as a catalyst for the reaction[1].



Where **A → B + C** is N-order
B + C → D + 2B is Autocatalytic



1st order to B



The reaction rate is proportional to the concentration of a reaction product. Thus, the term of self-accelerating would be more appropriate.

1) L. Bou-Diab, H. Fierz, Journal of Hazardous Materials **93** (2002) 137-146

Reaction Heat from Autocatalytic Decomposition Reactions:

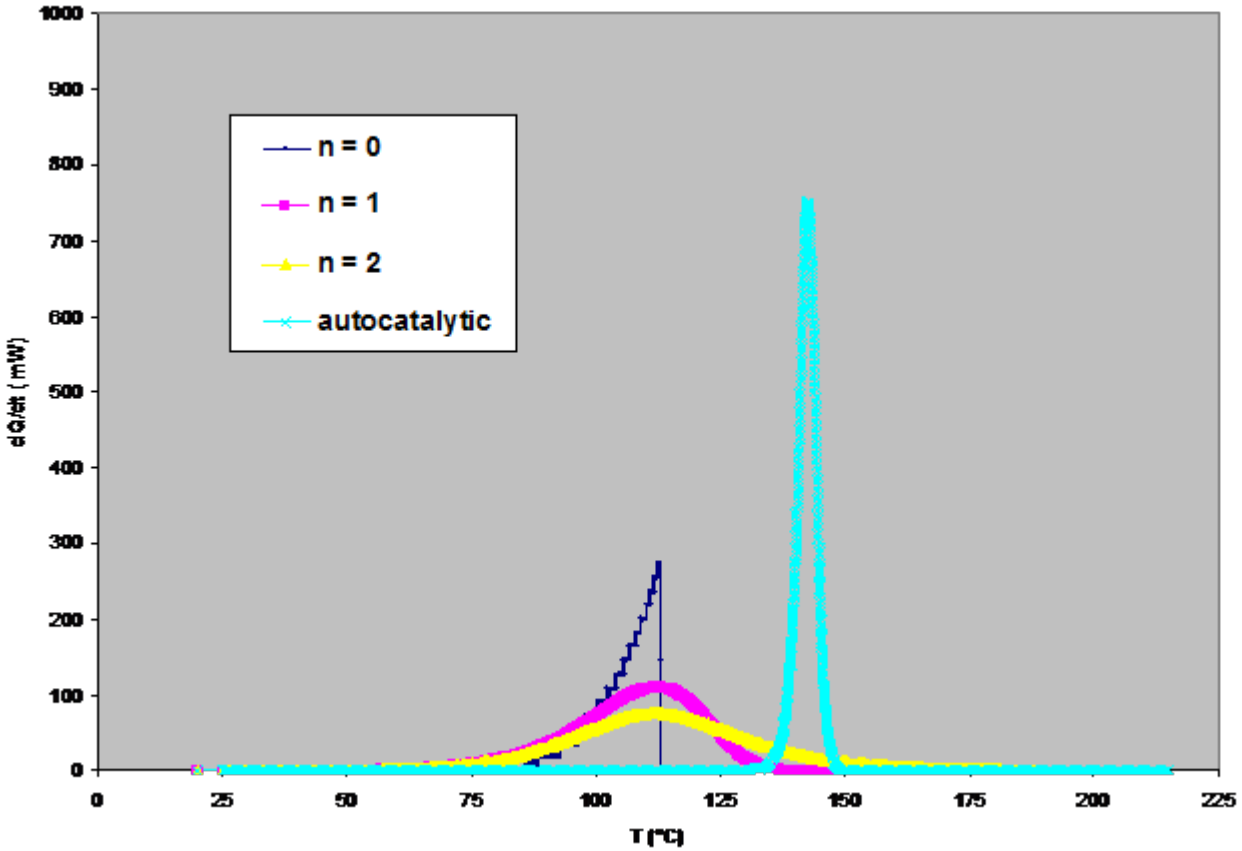
Simple n^{th} Order Reaction

$$\frac{dQ}{dt} = M_s \Delta H_{rxn} A e^{\frac{-E_a}{RT}} (1-\alpha)^n$$

Autocatalytic Reaction

$$\frac{dQ}{dt} = M_s \Delta H_{rxn} A e^{\frac{-E_a}{RT}} \alpha^{n_1} (1-\alpha)^{n_2}$$

M_s = mass of sample
ΔH_{rxn} = heat of reaction
α = fractional conversion
n = reaction order
E_a = apparent activation energy

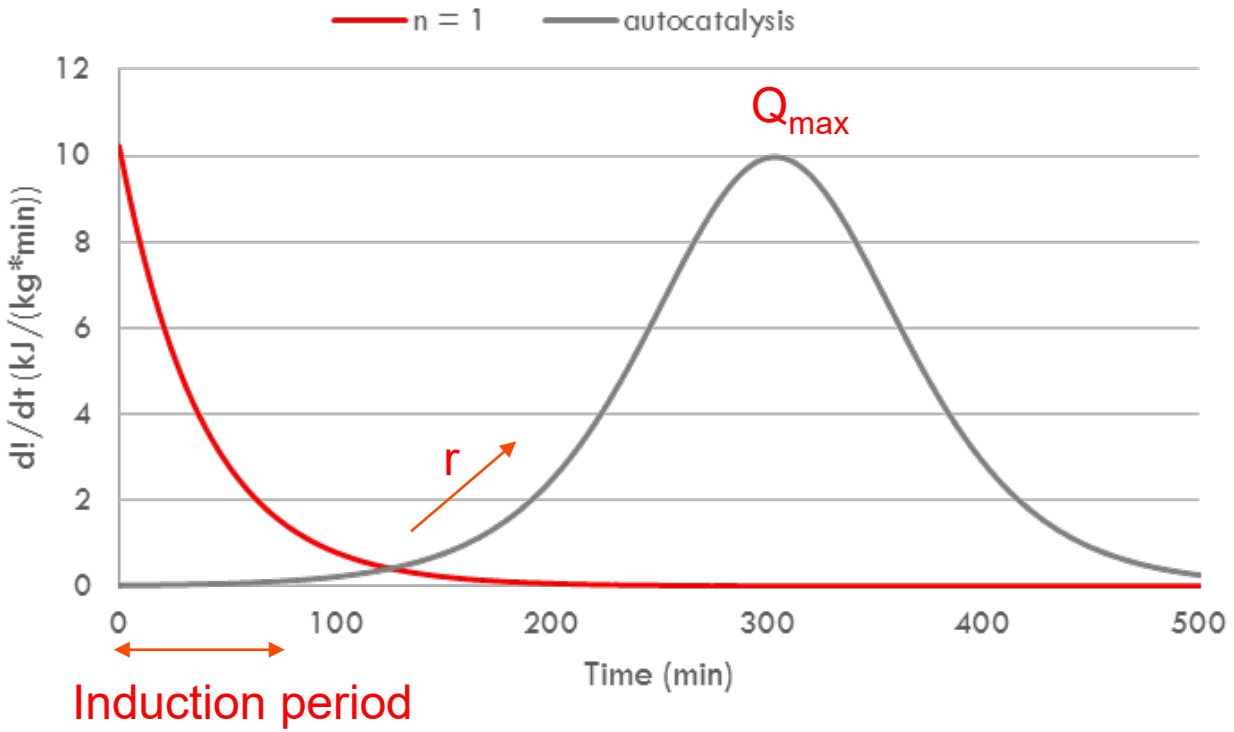


In all cases: Heat of reaction: -335 J/g, Activation Energy: 104.6 kJ/mol, Pre-exponential Factor: 28.4 s^{-1}

* L. Bou-Diab, H. Fierz Journal of Hazardous Materials 93 (2002) 137 - 146

Characteristics of an Autocatalytic Reaction:

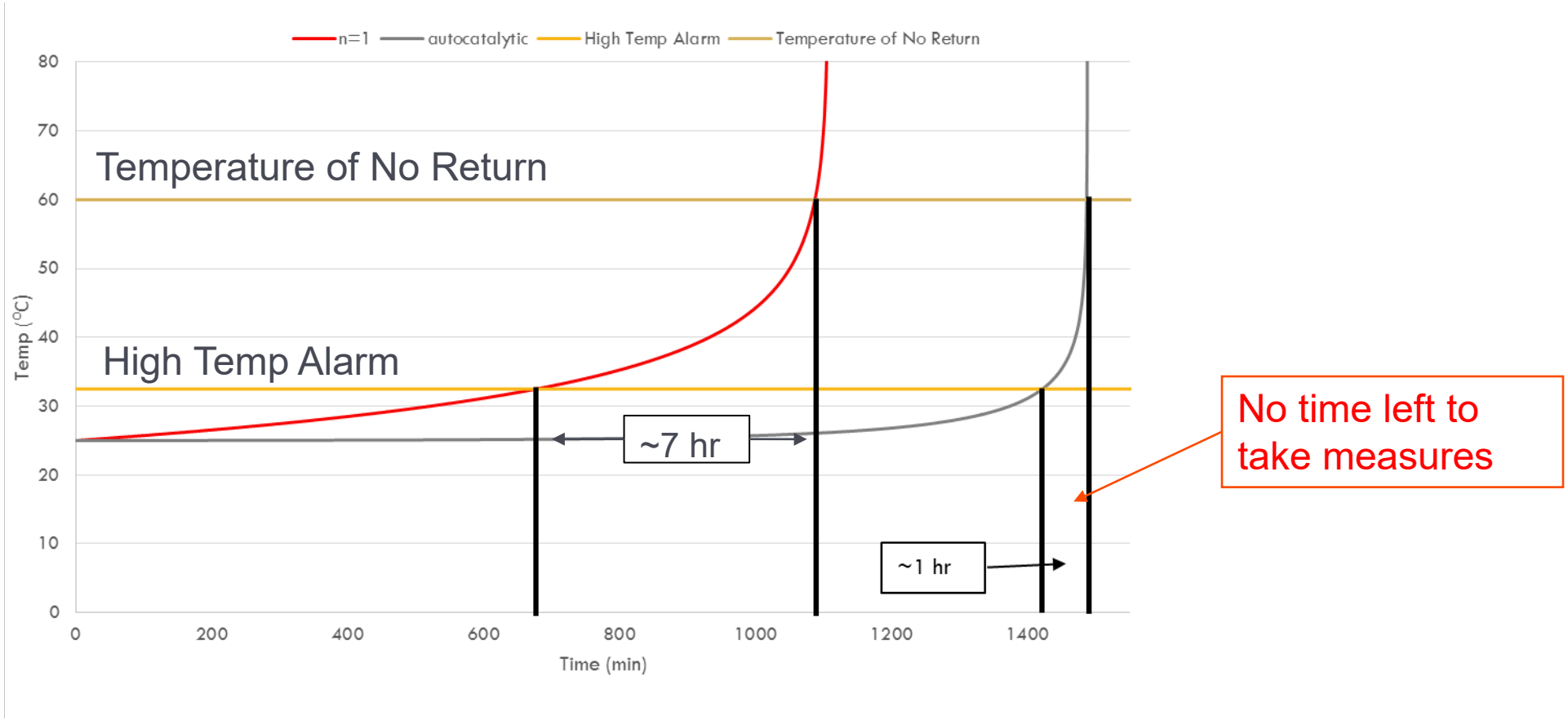
- **Induction period** – the period of time it takes for the critical concentration of intermediate (catalyst) to be produced to kick off the autocatalytic reaction*
- **Typically release only a small amount of heat before self-accelerating***
- **Catalyst created in reaction is often stable so mixing heel with new material may result in substantially reduced induction period***
- **Reaction rate increases with conversion** – in the previous reaction as “A” is consumed more “B” is produced which catalyzes “C” going to “D”*
- **Under isothermal conditions heat release rate passes through a maximum***



* L. Bou-Diab, H. Fierz Journal of Hazardous Materials 93 (2002) 137 - 146

Hazards Associated with Autocatalytic Reactions

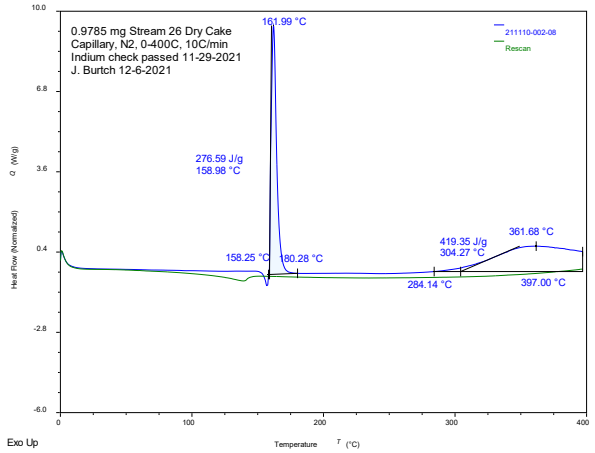
- Can self accelerate under isothermal conditions during storage
- Onset temperature is affected by thermal history



Identification of Autocatalytic Reactions:

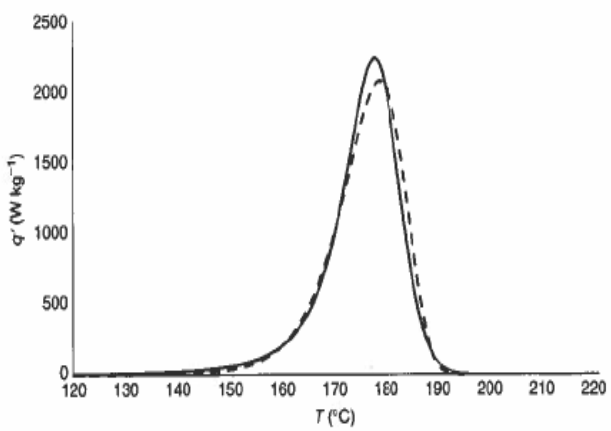
The differential scanning calorimeter (DSC) is an excellent tool that can be effectively used to screen for autocatalytic reactions.

DSC Dynamic Scan



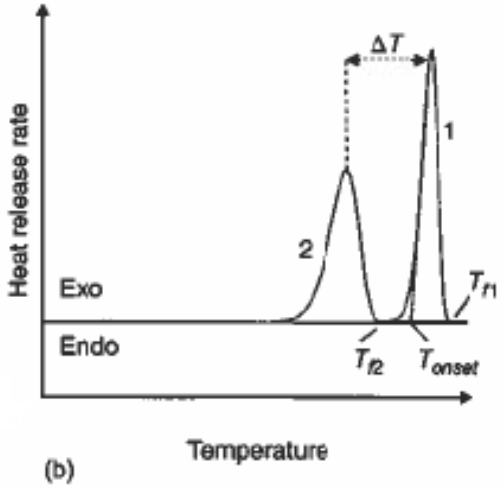
If peak is tall and narrow further investigation is warranted even if onset is well above the temperature the material will be exposed

Quick 1st order model



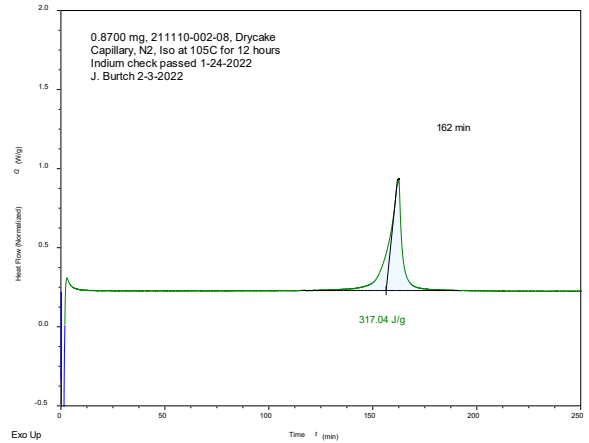
If apparent activation energy is ≥180 kJ/mol an autocatalytic reaction is likely.

Double Scan Test



After aging, the DSC peak may be strongly shifted toward lower temperatures.

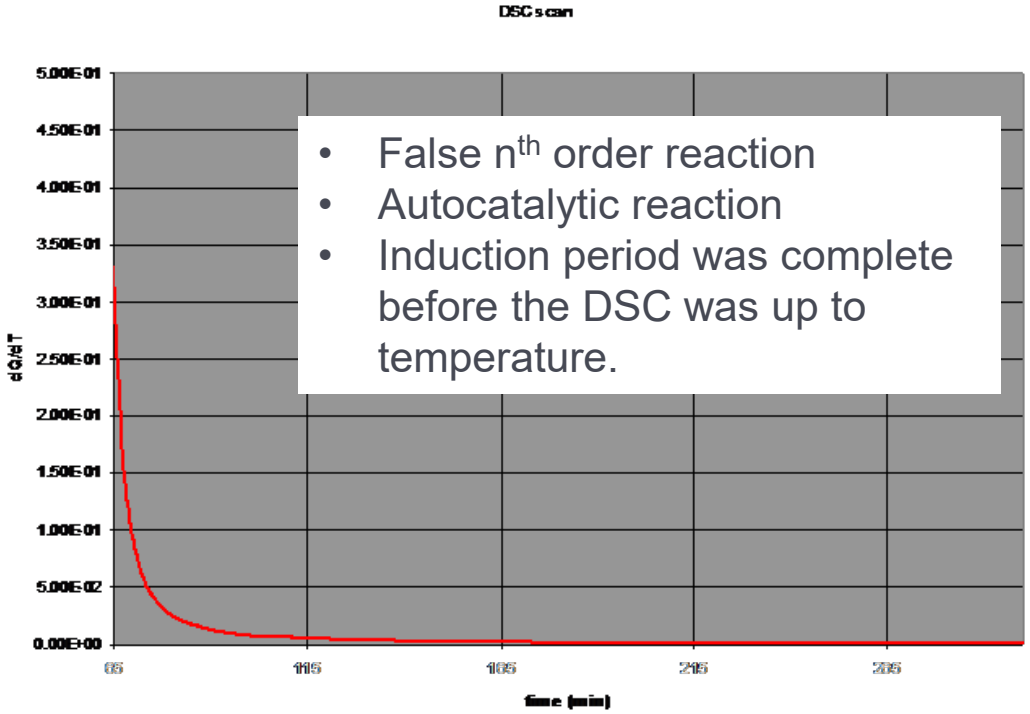
Isothermal DSC



- Heat rate will pass through a maximum under isothermal conditions.
- Most reliable method
- Confirm autocatalytic

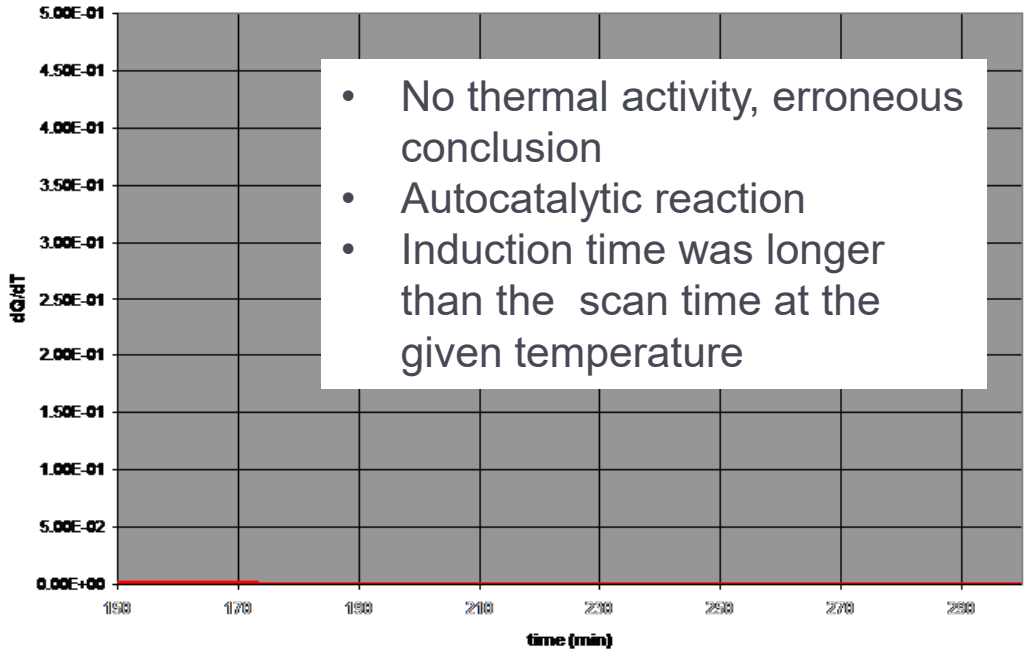
Identification of Autocatalytic Reactions – DSC Isothermal Test

Temperature set too high



- False n^{th} order reaction
- Autocatalytic reaction
- Induction period was complete before the DSC was up to temperature.

Temperature set too Low



- No thermal activity, erroneous conclusion
- Autocatalytic reaction
- Induction time was longer than the scan time at the given temperature

Use modeling approach to develop kinetic model from DSC data to select an appropriate temperature for the isothermal run to produce a peak heat rate in a reasonable time frame (i.e., 2 - 6 hrs.).

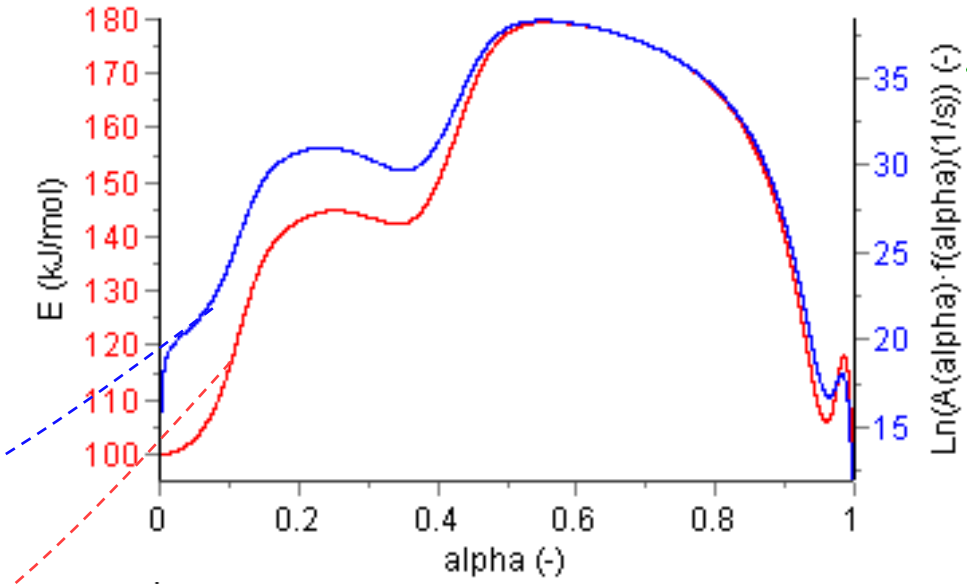
AKTS Modeling

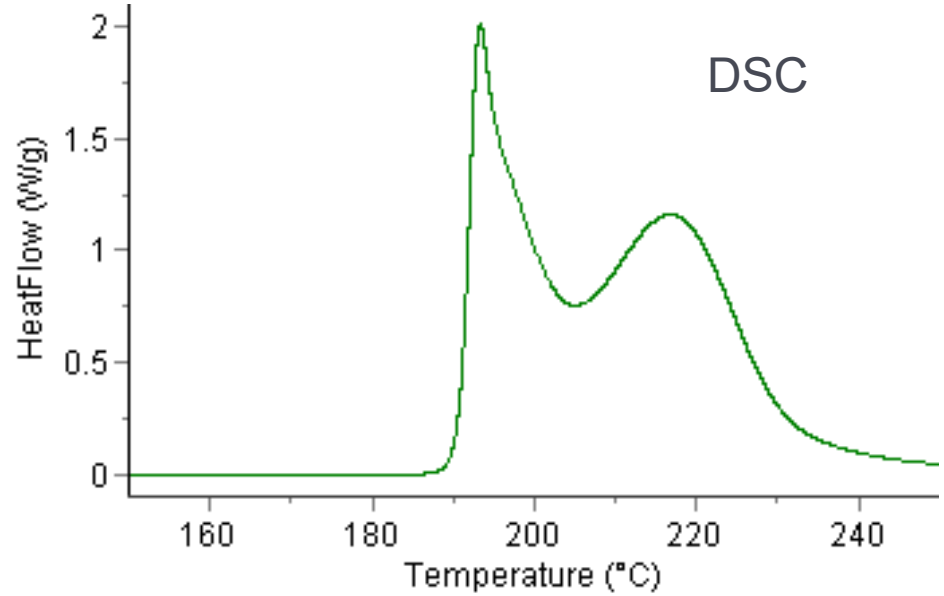
Isoconversional Method

- **Differential (Friedman)**
- Integral (Flynn-Ozawa-Wall)
- Advanced integral based on non-linear procedure (Vyazovkin)

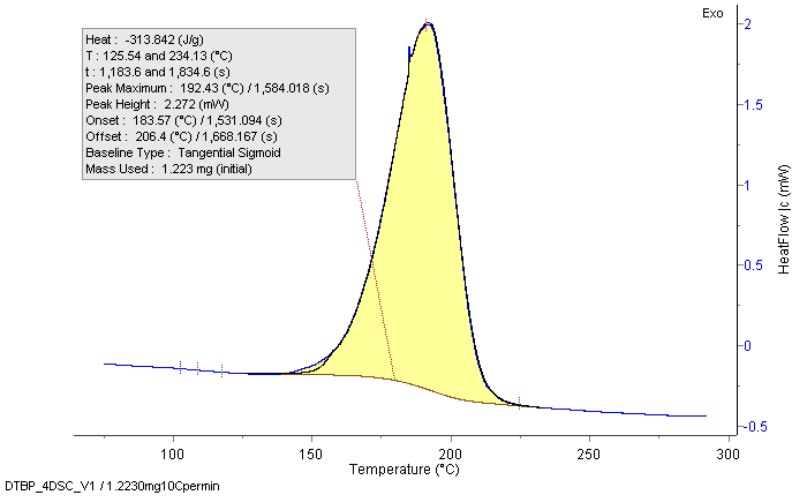
$$\frac{d\alpha}{dt_\alpha} = A'(\alpha) \cdot exp\left(-\frac{E(\alpha)}{R} \cdot \frac{1}{T(t)}\right)$$

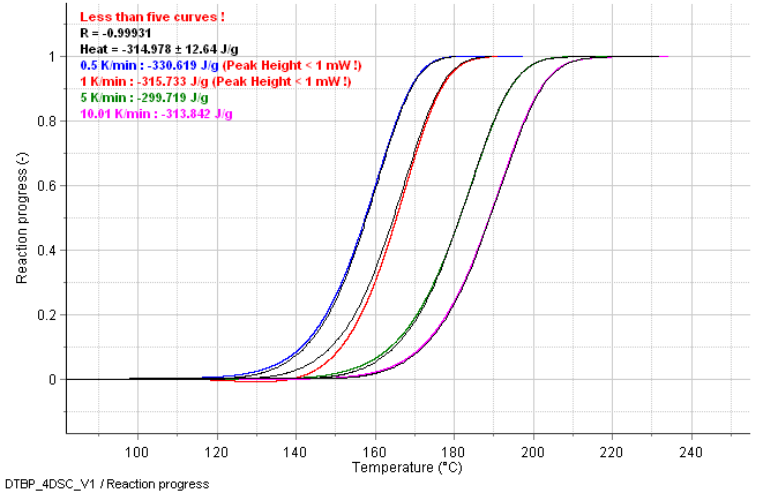
Kinetic Parameters

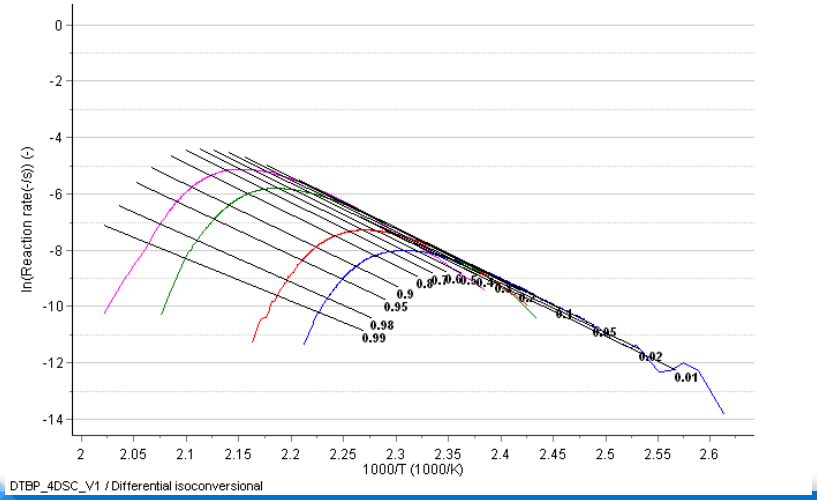


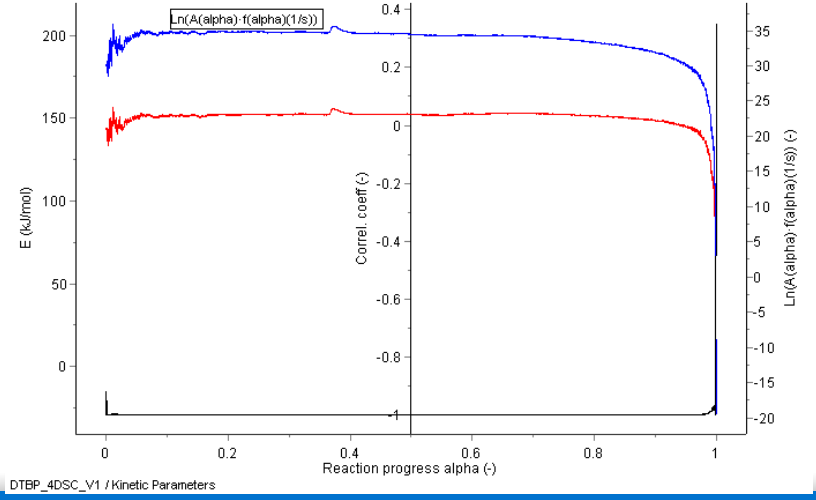


Modeling the Decomposition of DTBP/Toluene in AKTS

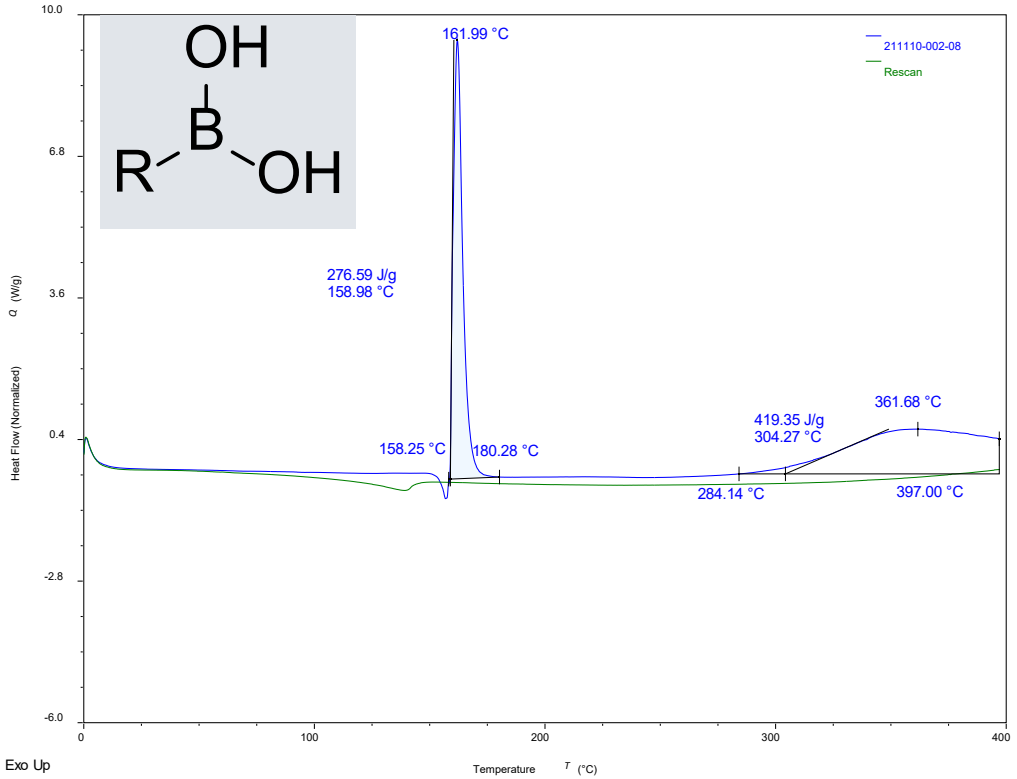


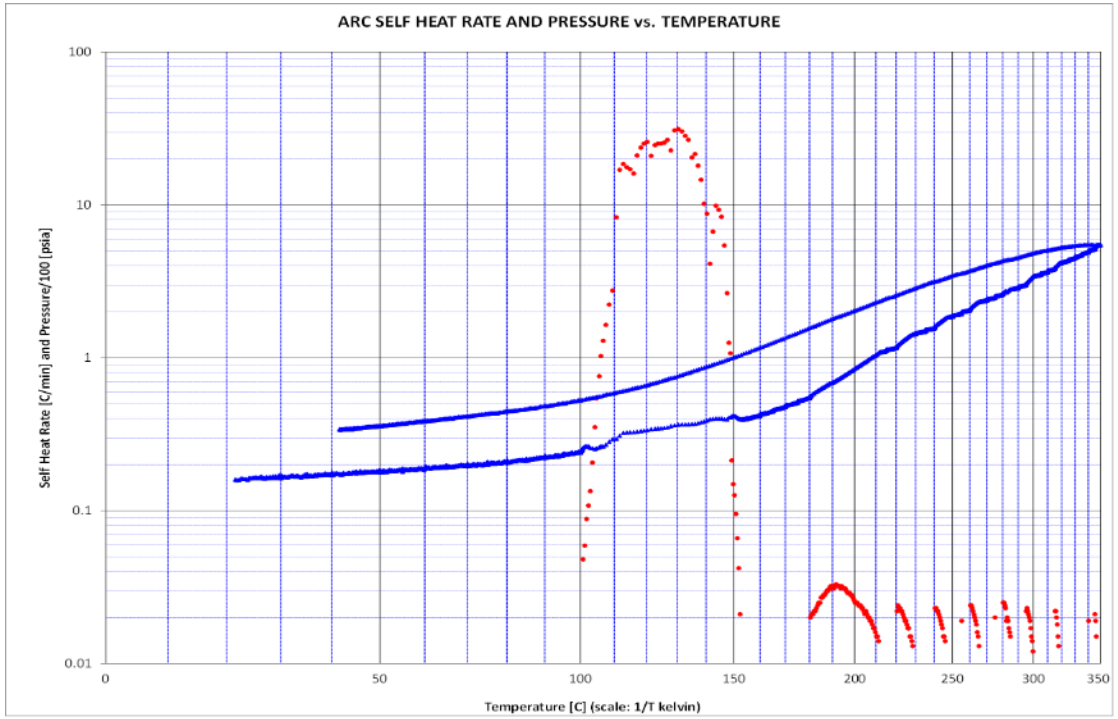






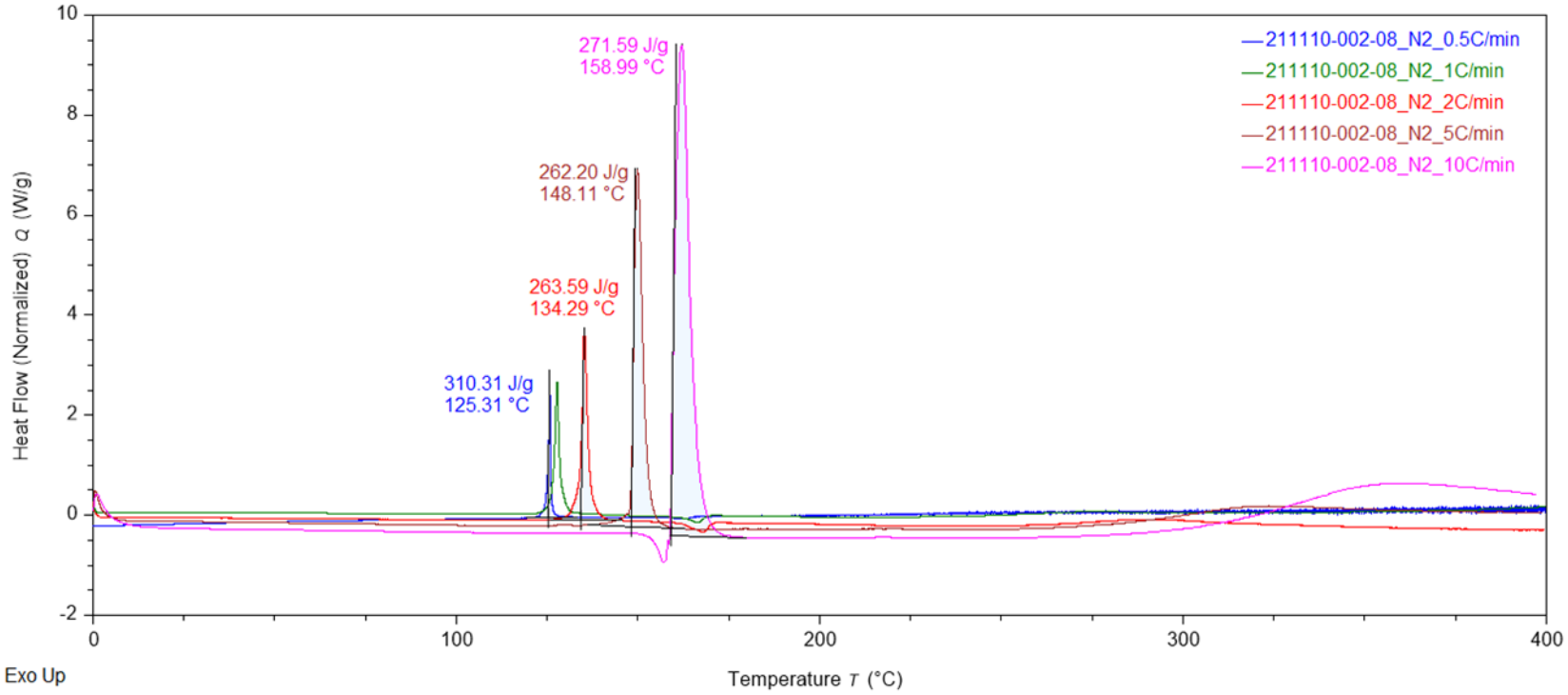
Case Study I – Boronic Acid Isolation





- A tall and narrow peak with a peak height of over 6 W/g
- Onset temperature at 158 °C
- Decomposition Energy, -276 J/g

Kinetic Model for Predicting Isothermal Temperature

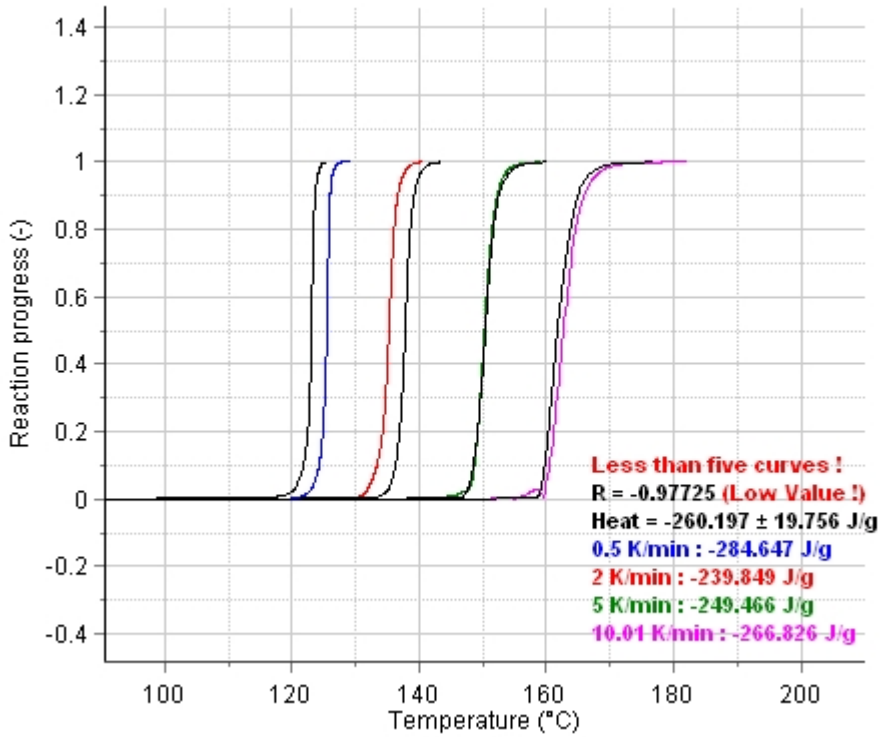


With Slower Heating:

- Longer aging
- More catalysts
- Onset Temp shift lower
- Unchanged peak shape

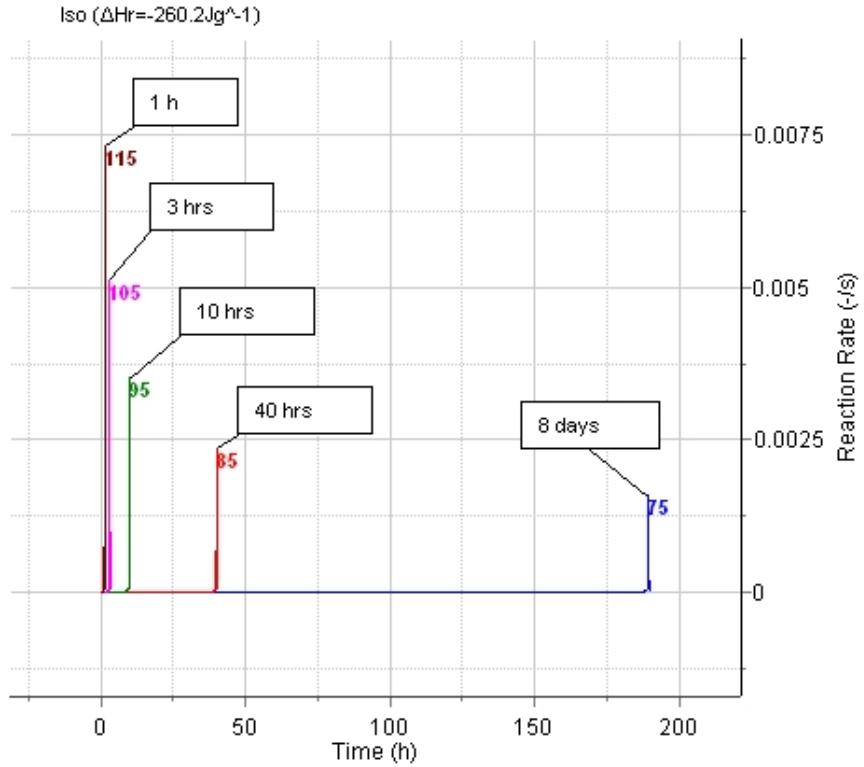
Kinetic Model for Predicting Isothermal Temperatures

Preliminary Model Fitting



211120-002-08_MDL_rx_4DSC / Reaction progress

Model Prediction for Isothermal DSC

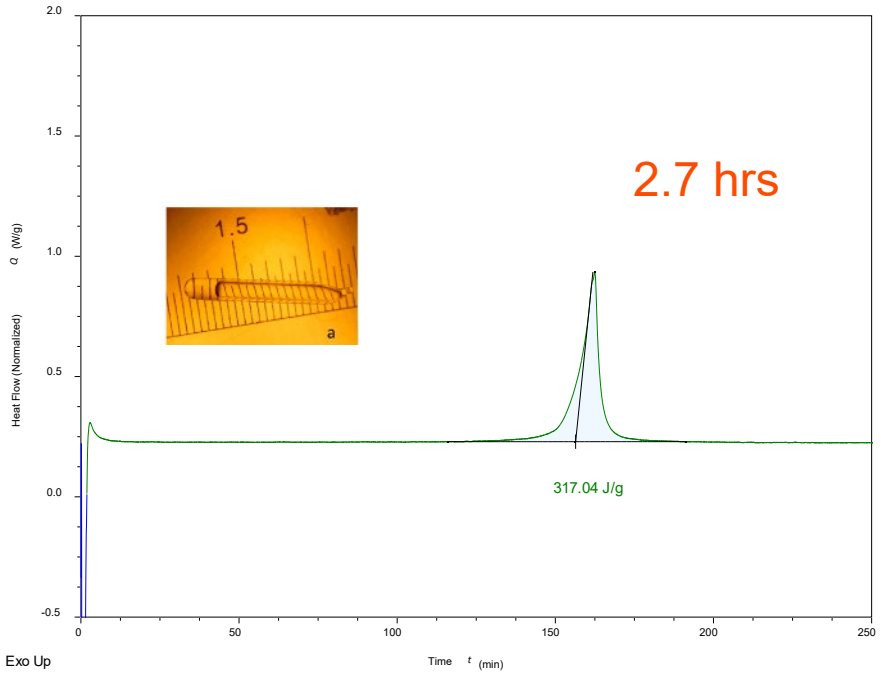


211120-002-08_MDL_rx_4DSC / Iso (DeltaHr=-260.2Jg^-1)

A preliminary model is quite helpful in determining the temperature for isothermal DSC scans. With the addition of an ISO DSC data or ARC testing results, the fitting of the model can be further improved.

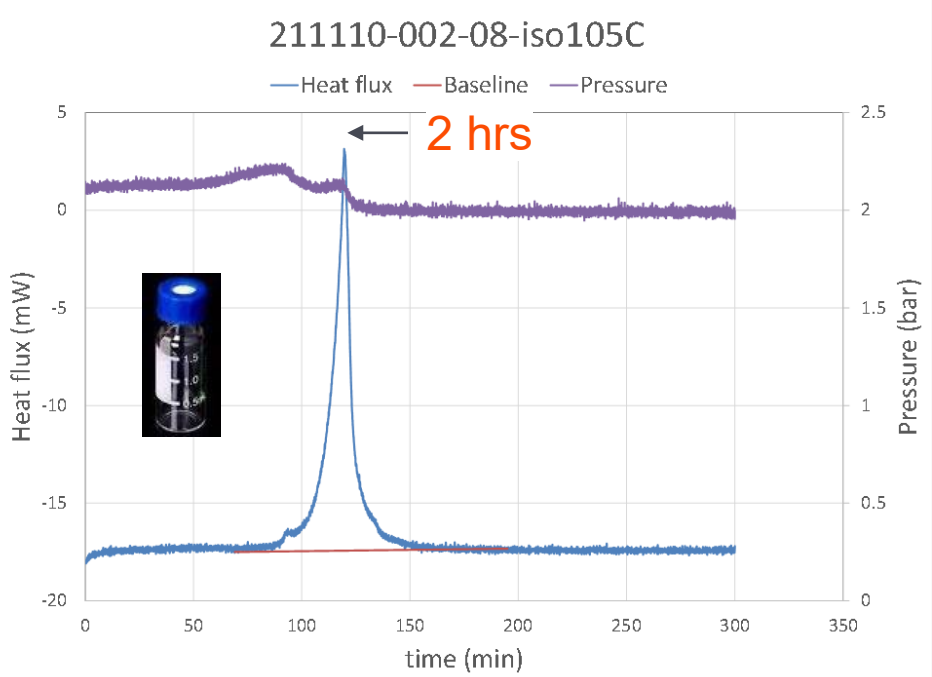
Kinetic Model – Verification

DSC Isothermal Exp at 105 °C



DSC result confirmed the decomposition of this boronic acid compound is autocatalytic.

uRC Isothermal Exp at 105 °C



- With mixing and in a larger scale, earlier peak time was observed in uRC.
- Pressure was monitored during the decomposition, little to none gas generation.

Kinetic Model – Application

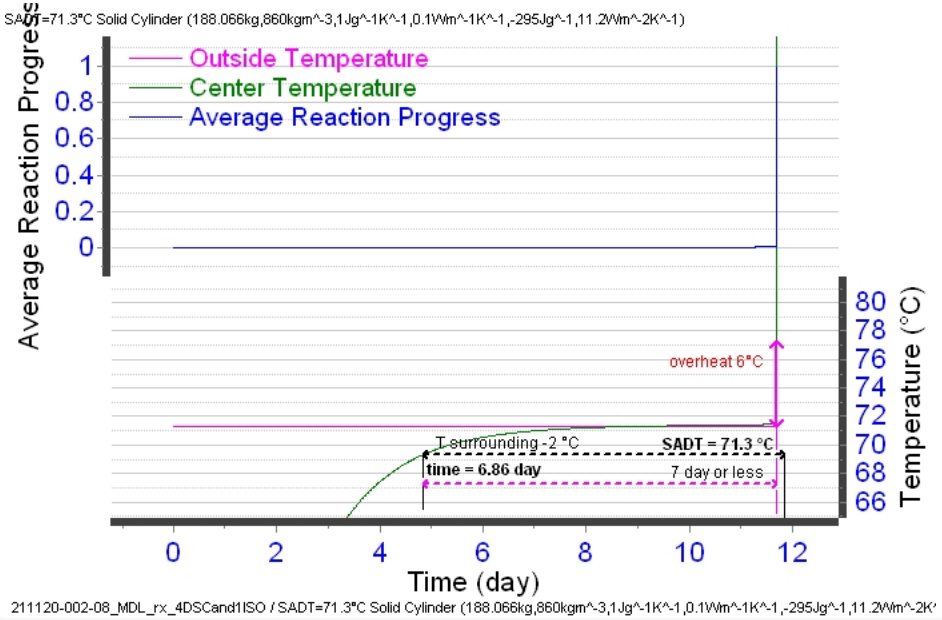
Scenario:

- What temperature should this chemical be stored at?
- How long will it take for 1 kg packages to thermally run away?
- How hot is too hot?
- How many hours before the onset when under heat.

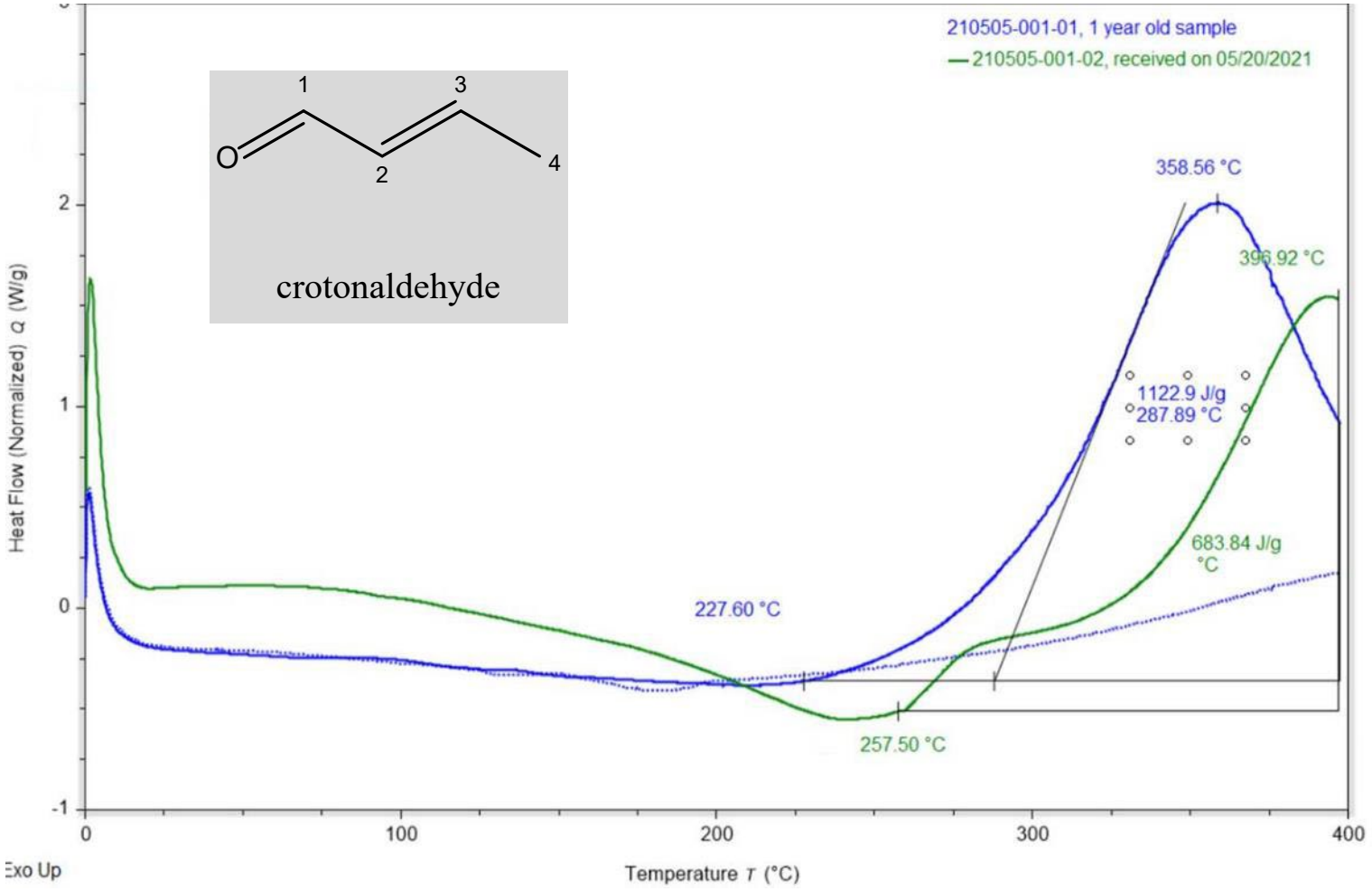
Approach:

- Model predicted TMR (Time to Maximum Rate) under adiabatic conditions (worst-case)
- TNR (Temperature of no return)
- SADT (Self Accelerating Decomposition Temperature)
  - e.g., SADT = 71.3 °C for a 55-gallon drum

Temperature (°C)	TMR_{ad}
60	65 days
70	12 days
80	16 hrs
90	4 hrs



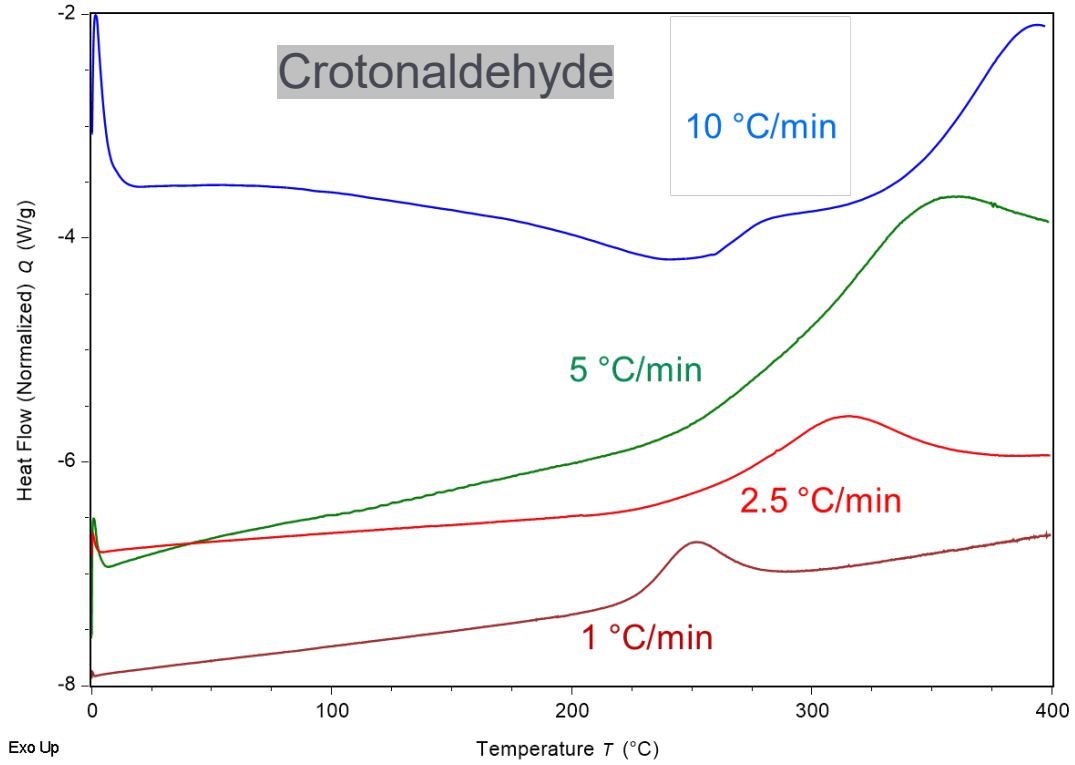
Case Study II – Crotonaldehyde with no BHT Stabilizer



While determining the stability and reactivity of the crotonaldehyde (without BHT stabilizer), it was observed that the decomposition/polymerization might be “autocatalytic”.

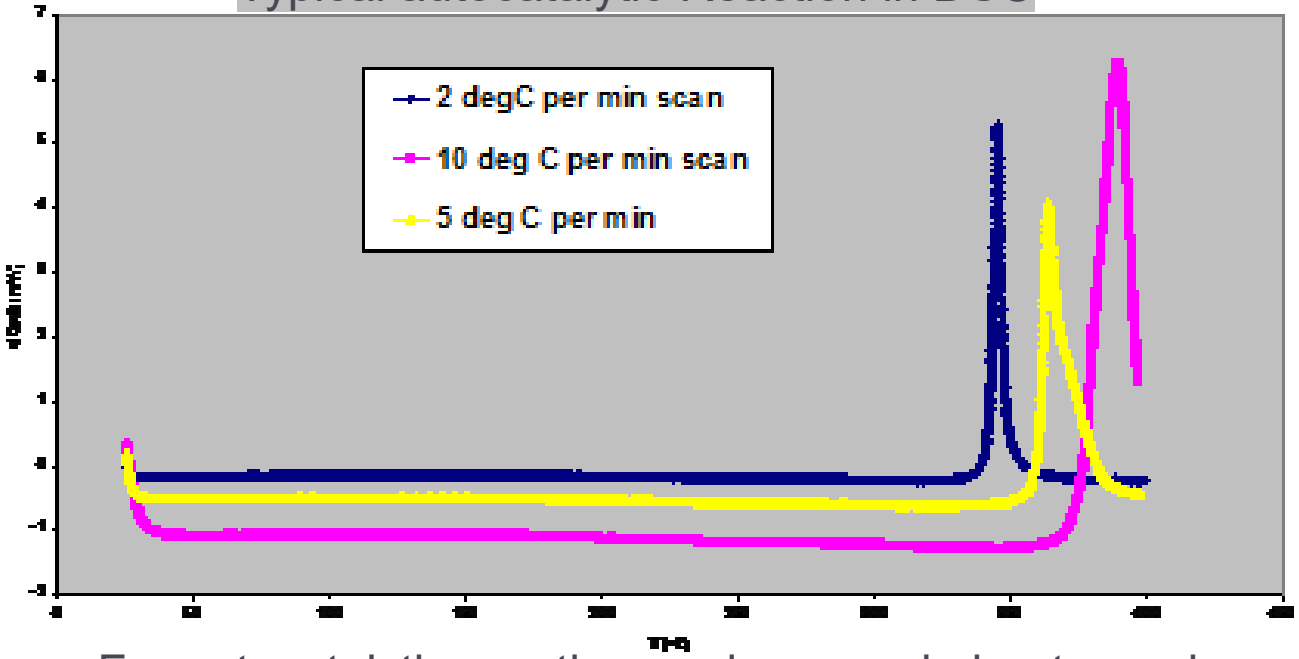
- One-year-old sample has lower T_{onset} and T_{peak}

Dynamic DSC Scans of Crotonaldehyde at Various Rates



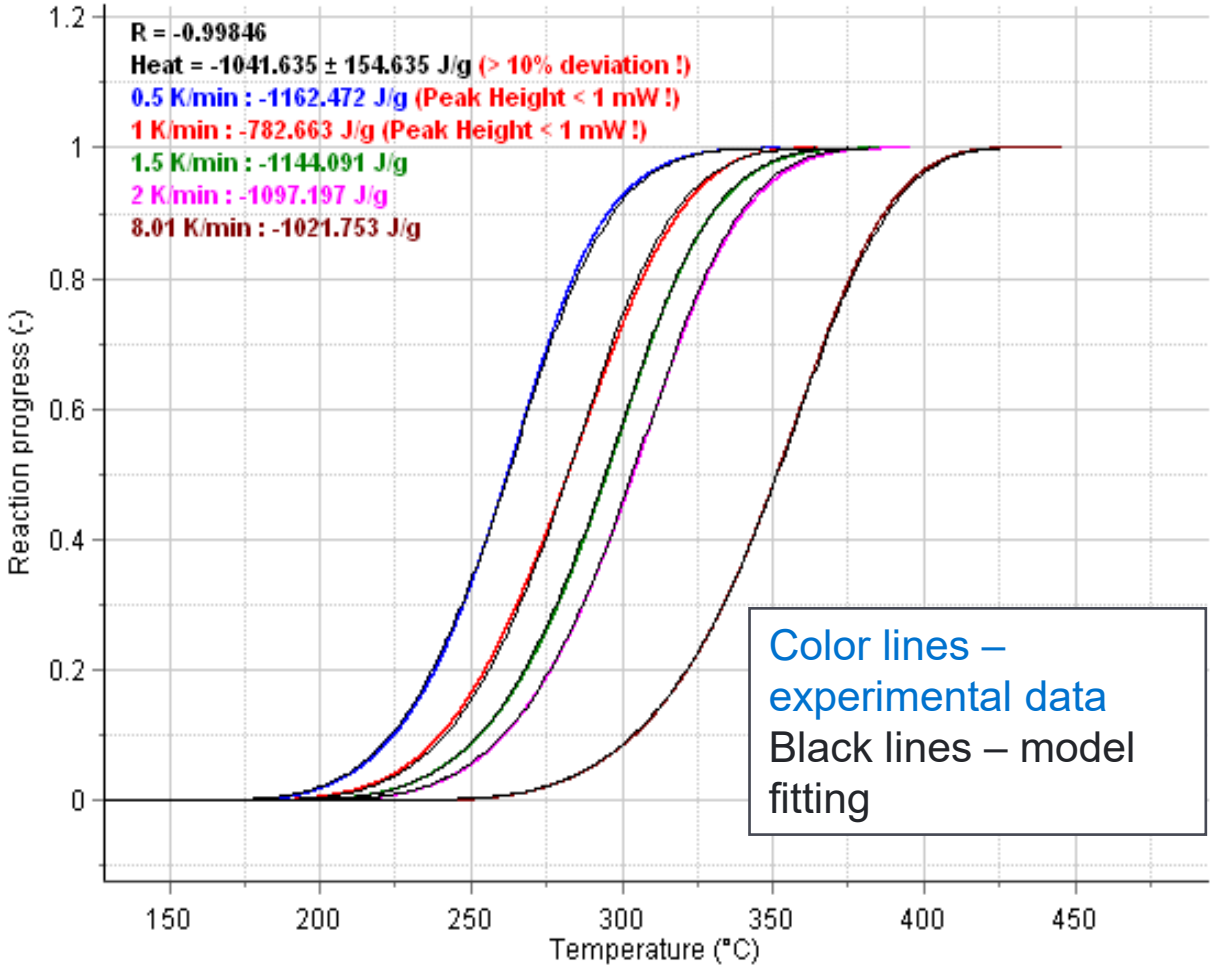
- Onset T shift left at lower heating rates
- Peaks are broad not narrow
- “Weak” autocatalytic
- Impacted by thermal history

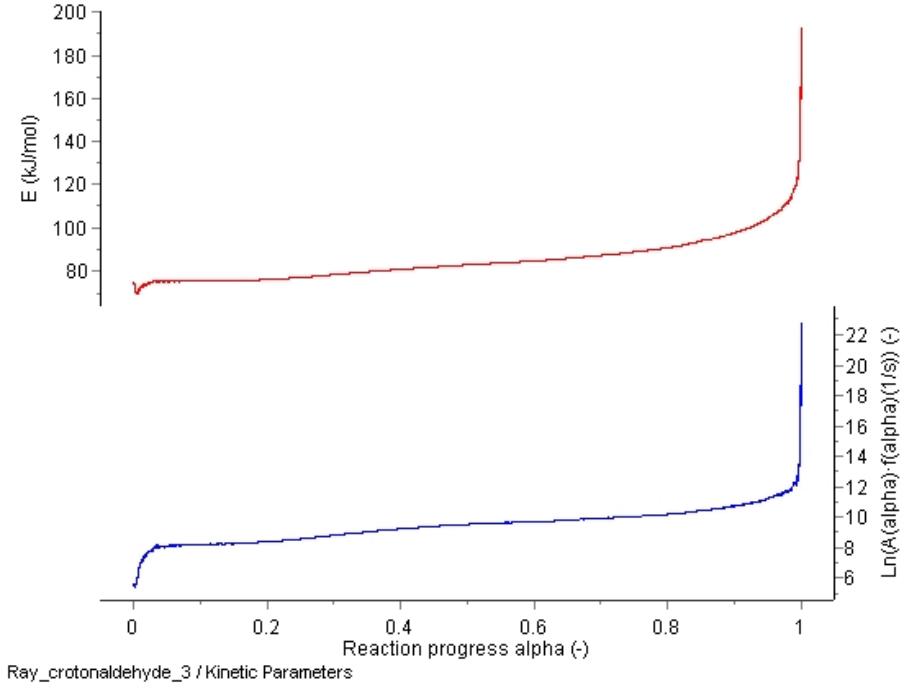
Typical autocatalytic Reaction in DSC



- For autocatalytic reactions a decrease in heat ramping rate will typically shift the detected onset temperature to a lower temperature as well as the peak heat rate position.
- In autocatalytic reactions, the width of the peaks will decrease or remain virtually the same as scan rate is decreased.

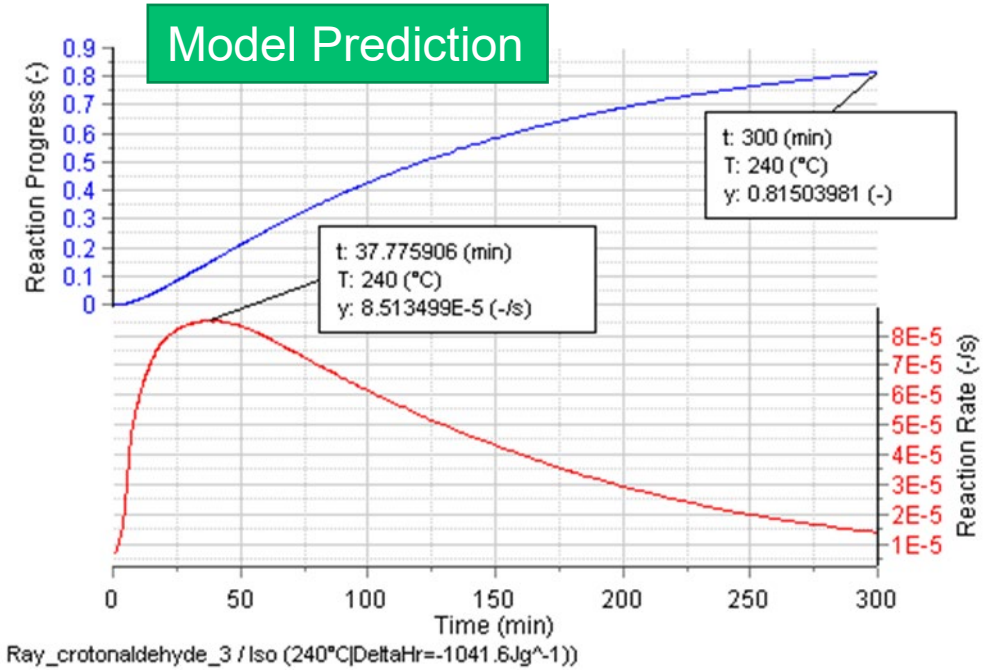
Kinetic Modeling – Isoconversional Method

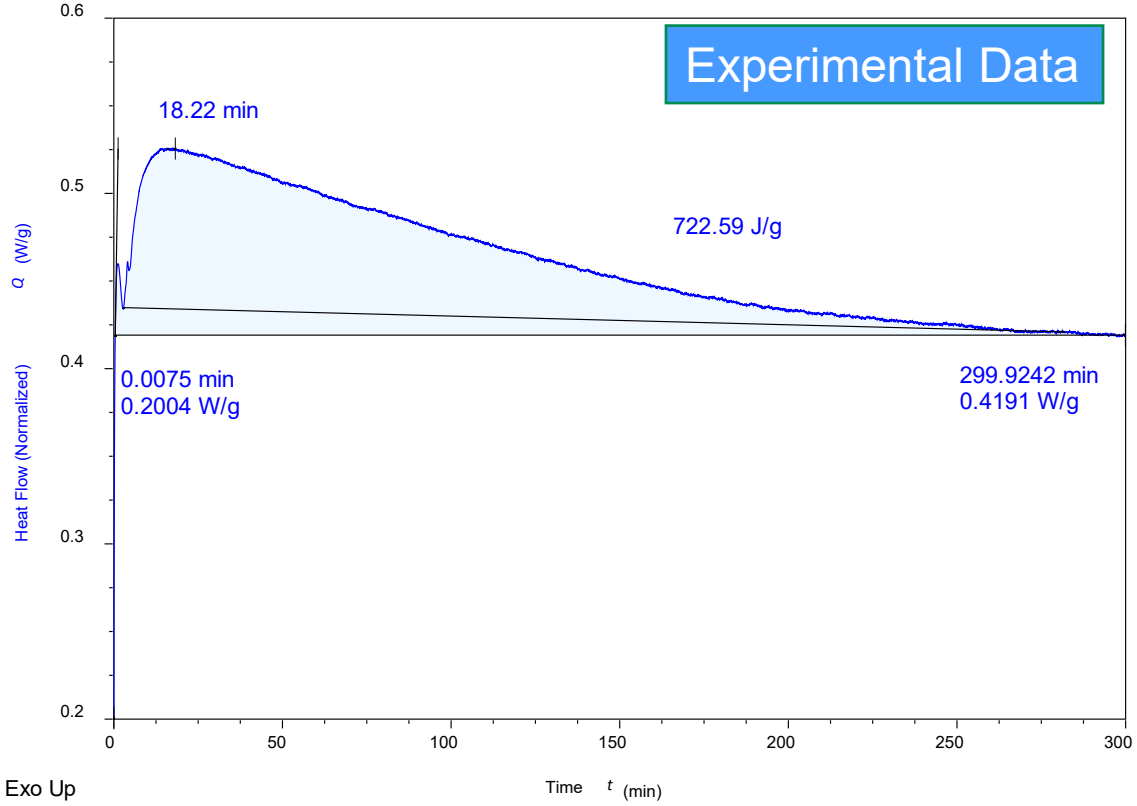




- Model fittings agree with data well

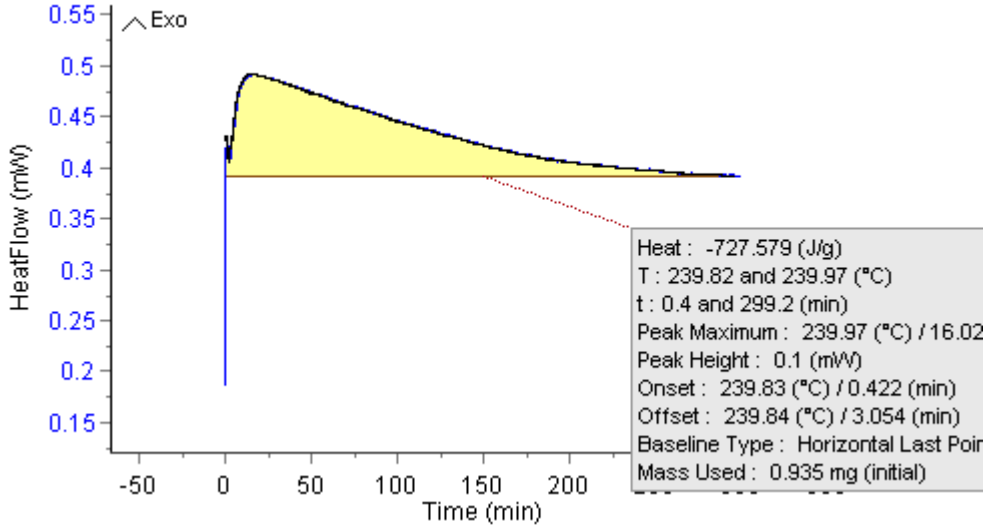
Verifying Model with an Isothermal DSC Scan

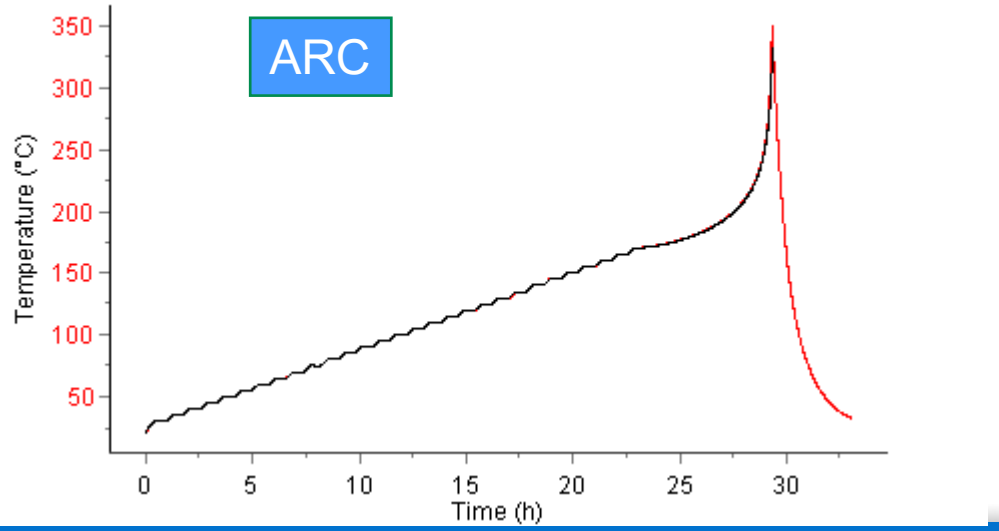


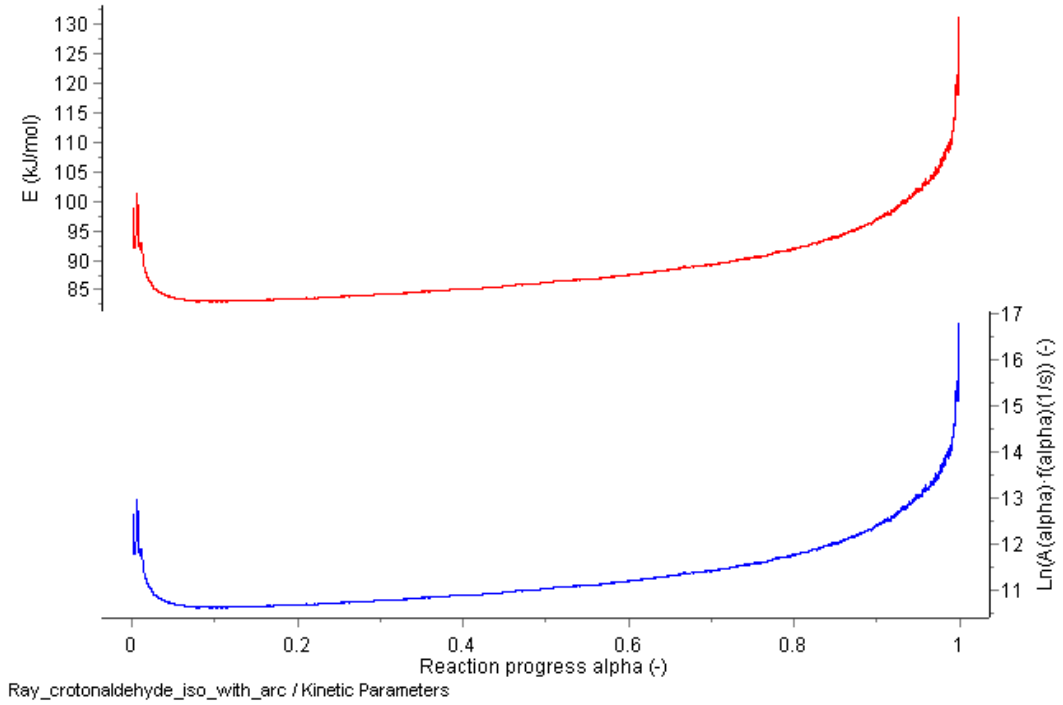


- experimental data: max heat flow at 18.22 min.
- Model underpredicted the time to maximum rate at 240 °C.
- Combined this iso with an ARC data, a new model was built with improved fitting.

Model with a DSC and an ARC Data

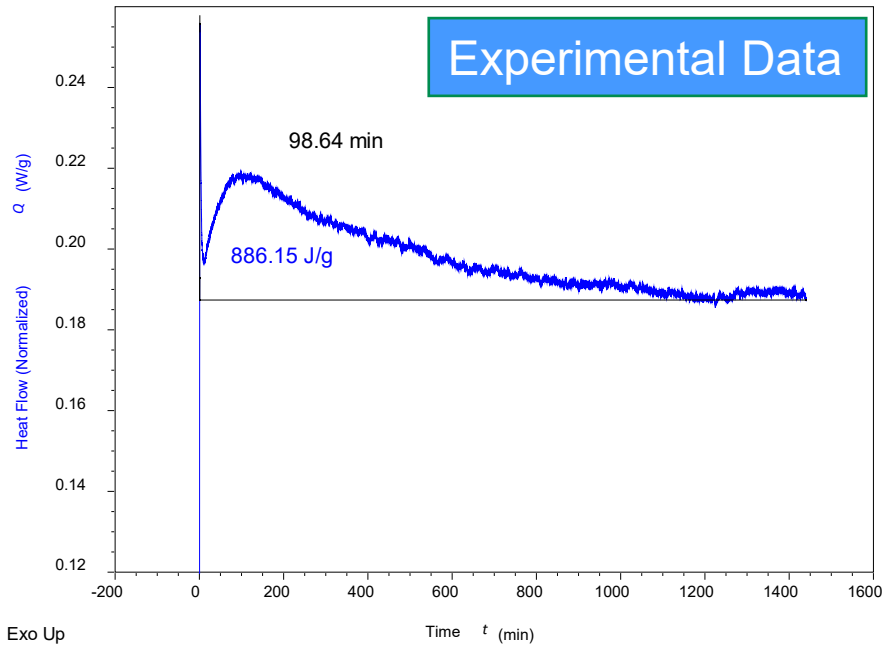


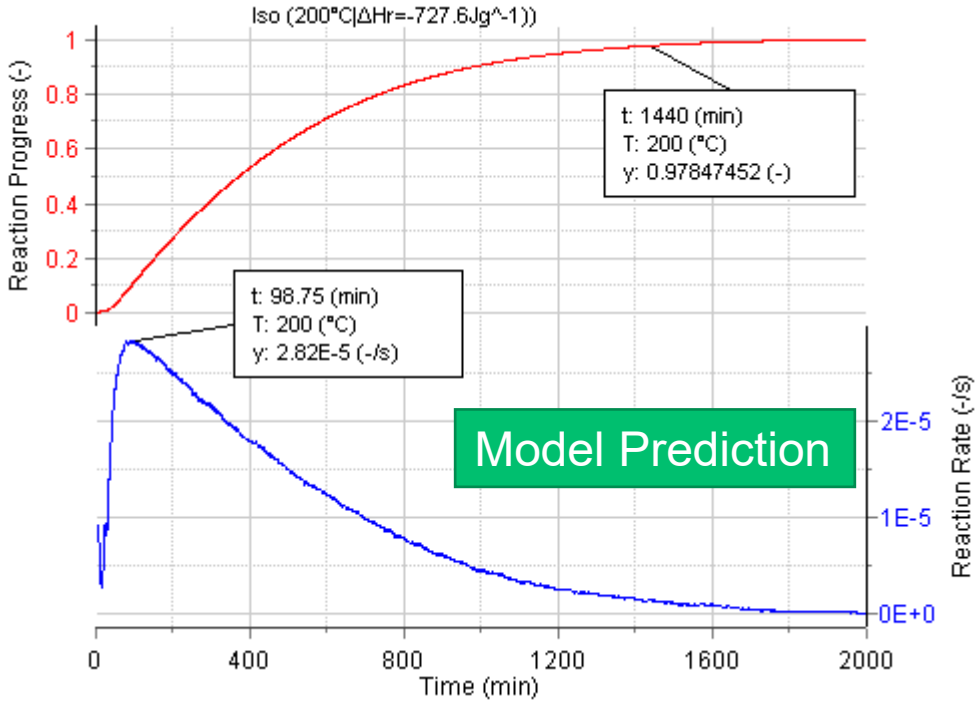




Verifying New Model with an Isothermal DSC Scan

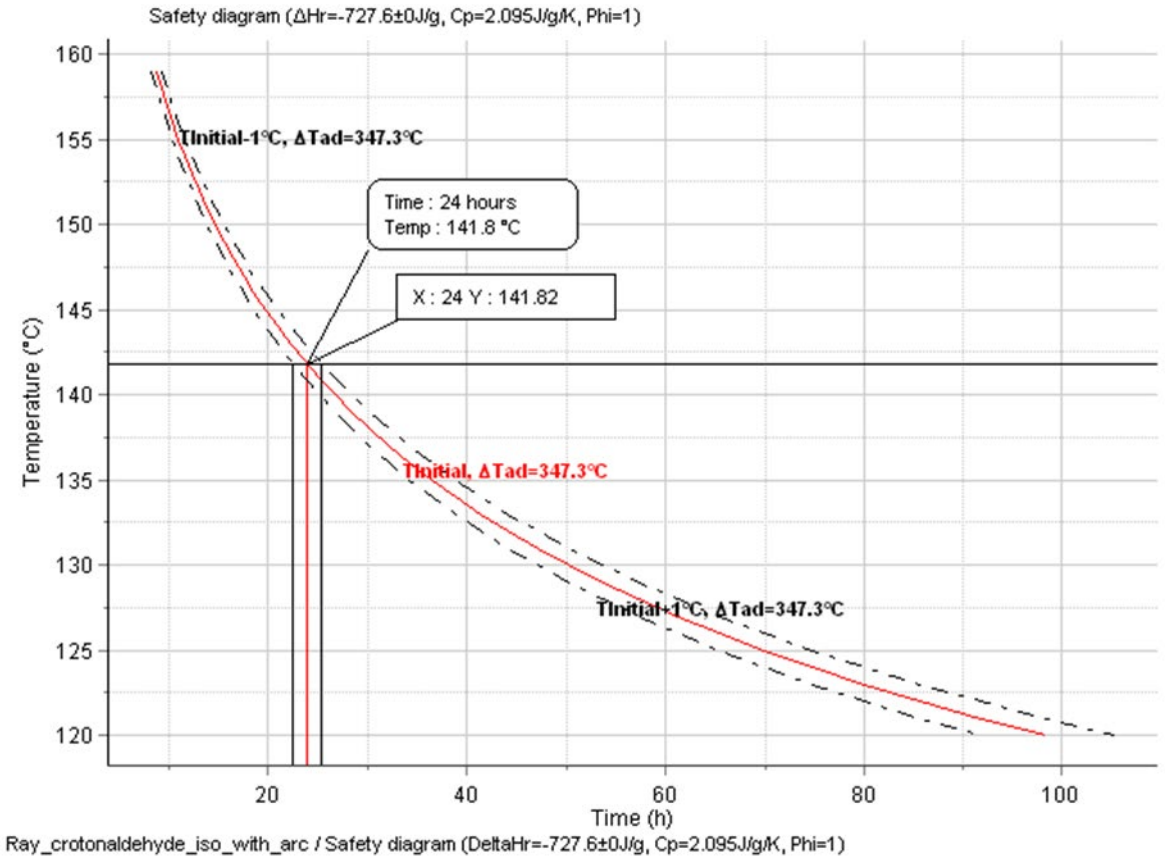
200 °C DSC ISO Scan





Now, the model prediction matched the experimental data a lot better, as the peak in reaction rate both occurred around 98 mins.

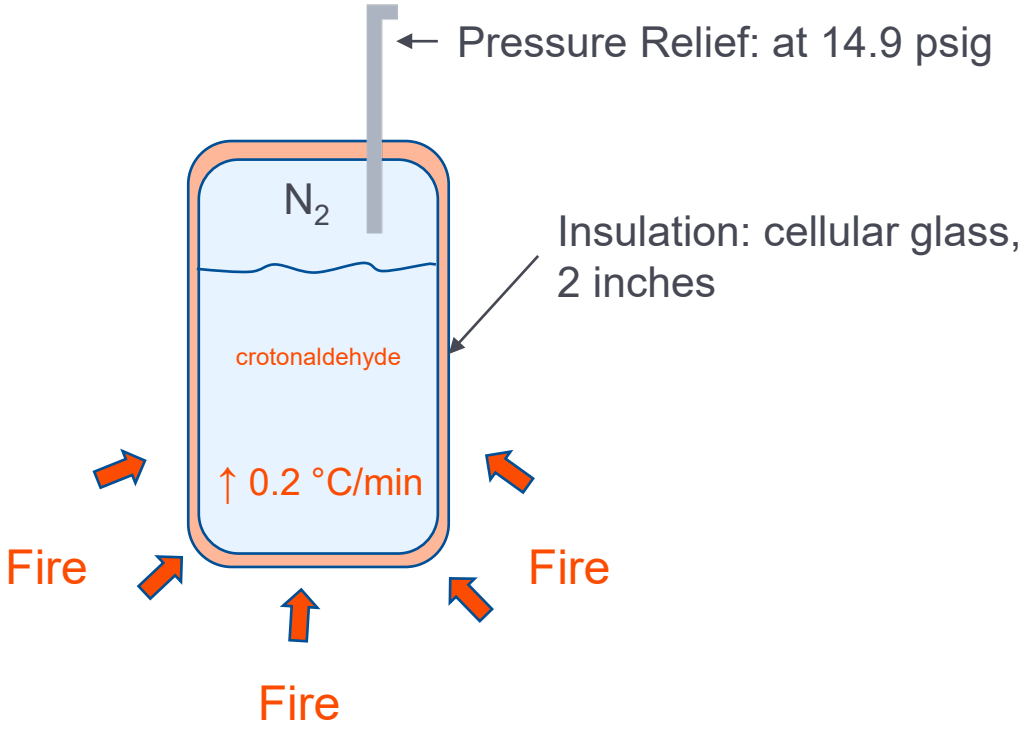
Model Prediction of TMR(Time to Maximum Rate)$_{ad}$



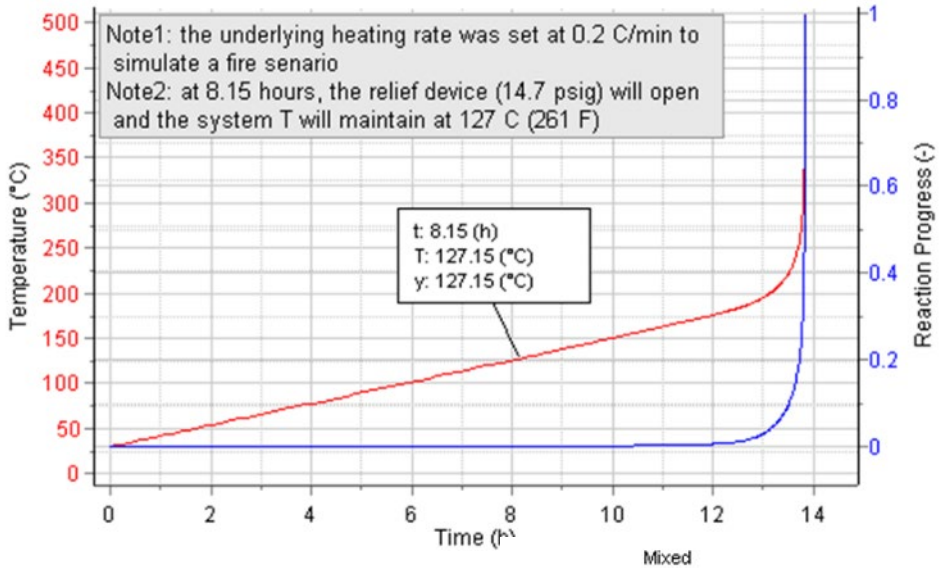
Temperature (°C)	TMR$_{ad}$ (hours)
141.8	24
160.9	8
174.0	4
188.2	2

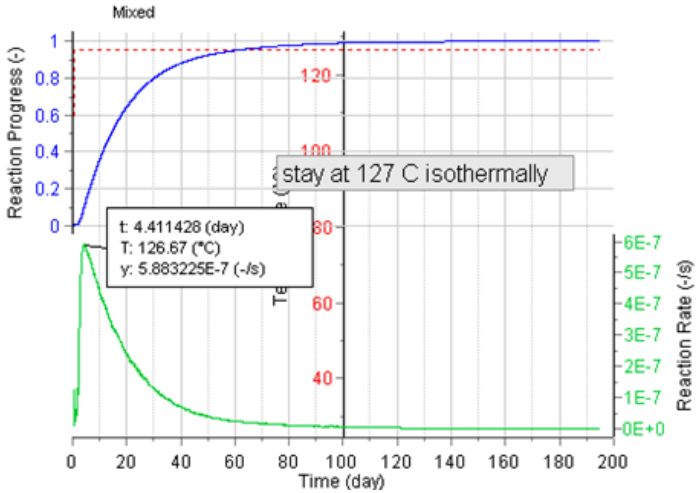
The critical value TMR$_{ad}$ = 24 hours, commonly accepted as the safety limit in the industrial scale, was obtained at 141.8 °C.

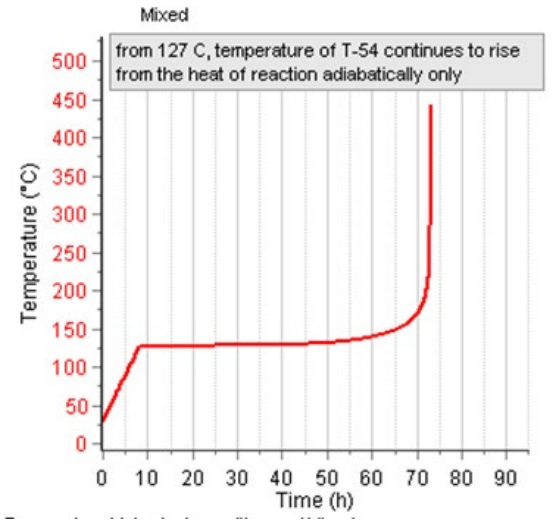
Case Simulation: Fire near the Storage Tank of Crotonaldehyde



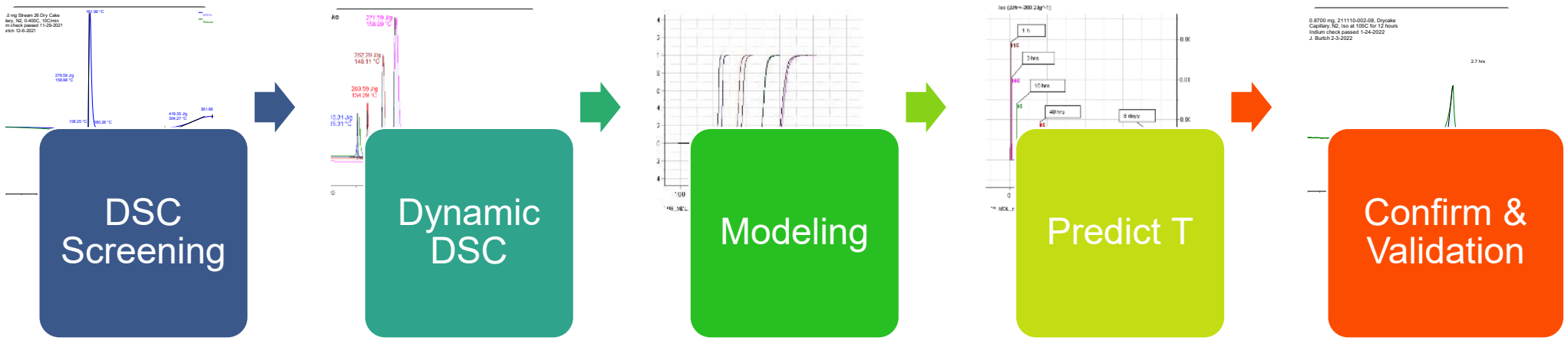
Scenario A: fire
Scenario B: fire was out, tank stays at 127 °C
Scenario C: fire was out, reaction heat was not removed by boiling







Conclusion



- Tall narrow peaks seen in curves of dynamic DSC experiments may indicate autocatalytic reaction
- Fitting dynamic DSC data to a first order kinetic modeling using heat of reaction, heat production rate, and activation energy as fitting parameters can indicate an autocatalytic reaction if the activation energy is 180 kJ/mol or higher
- Decreasing the scan rate will typically lead to a lower detected onset temperature and narrowing of the peak for a dynamic DSC scan of an autocatalytic reaction
- Kinetic software can be used to develop a model to predict the time to peak heat rate for isothermal DSC scans
- An isothermal DSC scan which has a peak heat rate increasing to a maximum and then decreasing is proof of an autocatalytic reaction

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