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Development of Continuous Nitrato-nitramine Synthesis via Advanced Flow Reactor

NDIA Insensitive Munitions Energetic Materials Technology Symposium

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Naval Surface Warfare Center Indian Head EOD Technology Division
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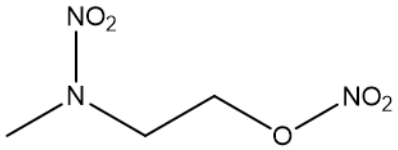
MethylEthyl NitratoEthyl NitrAmine Me/EtNENA

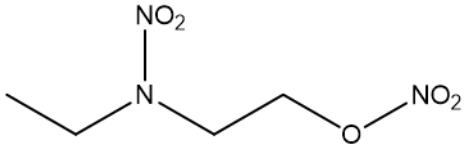
- Methyl Ethyl NENA is a liquid energetic plasticizer used in propellant formulations (GLGP, ERMA, etc.)

- Methyl Ethyl NENA is a mixture of two NENAs



57-59%

Methyl nitratoethyl nitramine (MeNENA)



41-43%

Ethyl nitratoethyl nitramine (EtNENA)

- The starting materials, methyl and ethyl ethanolamine, can be co-nitrated opposed to individually nitrated and blended later
  - Significantly improves synthesis efficiency
  - Remains a liquid mixture throughout synthesis process

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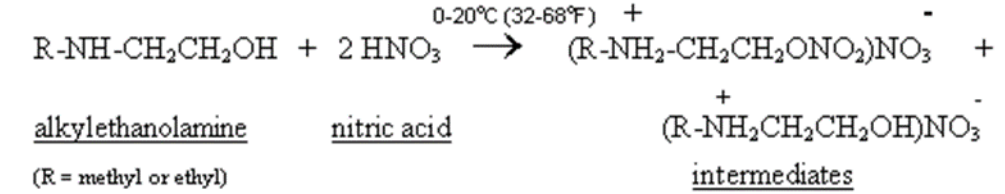
MeEtNENA – Chemistry

Process Overview

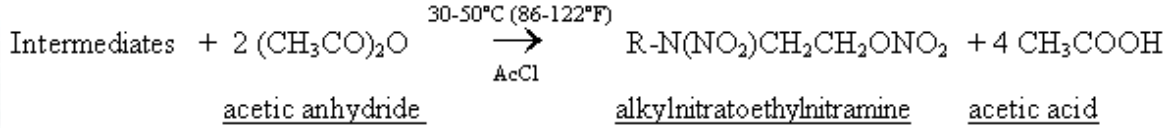
O-Nitration and Nitrate salt formation

Step #1

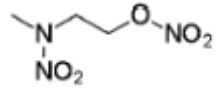


N-Nitration

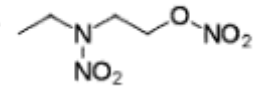
Step #2



- Process is run neat (no solvent)
- Fuming nitric acid
- Potential to form acetyl nitrate (potential concerns on detonability)



Methyl NENA



Ethyl NENA

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CORNING Advanced-Flow© Reactor

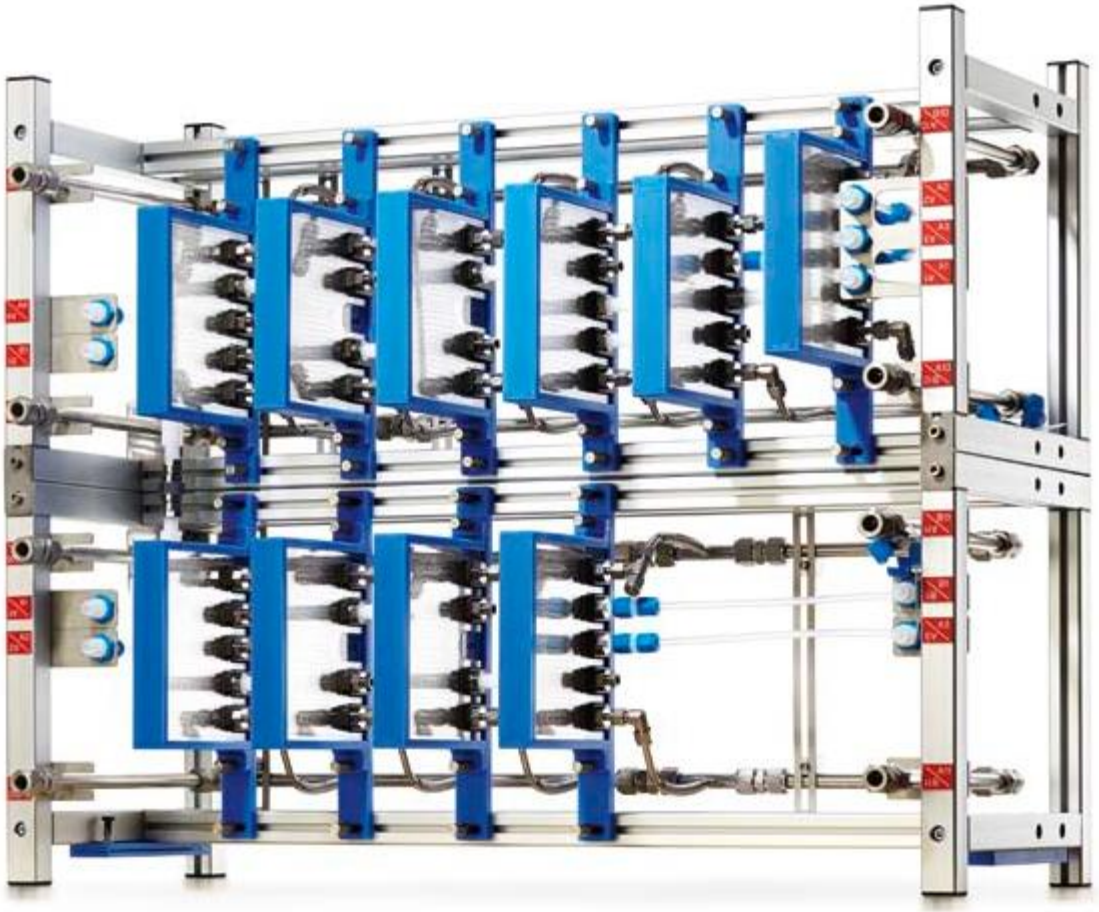
G1 Glass Reactor

Effective continuous-flow process evaluation, development and production with throughputs up to 80 tons annually.

Flow rates	30 to 200 mL/min
Temperature	-60 to 200 °C

Features

- Outstanding mixing and heat exchange
- Small internal volume
- High residence time
- High chemical compatibility
- High flexibility due to modular design
- Seamless scale up with other Advanced-Flow® reactors



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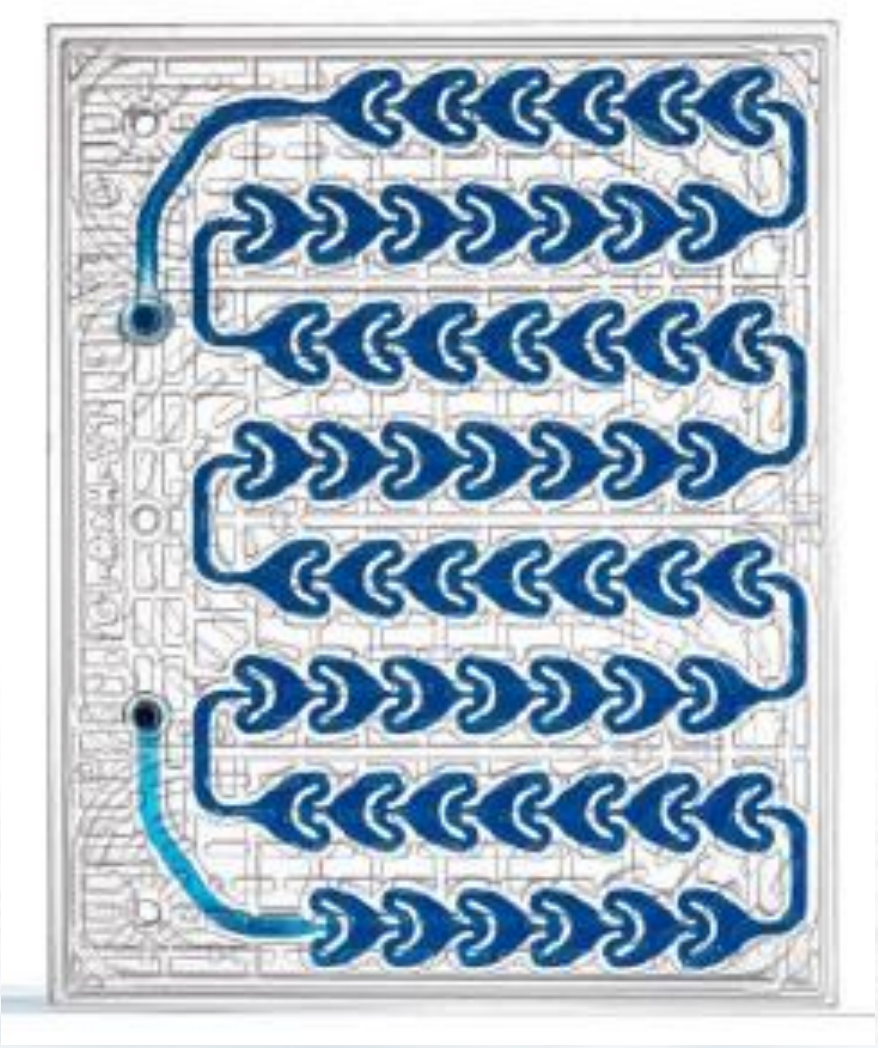

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Analytical Methods

HPLC – Off line analysis

- Peak shapes are broad and quantitation of species aside from the final products is difficult

NMR – Off line analysis

- Rapid sample prep is attainable. Quantitation is limited to ± 5% due to close nature of species resonance.
- "Flow" NMR was limited as an in-situ method in first reaction due to high viscosity of the reaction mixture

In situ Raman – In situ FTIR analysis

- Use of ConcIRT, a Mettler Toledo software that performs curve-resolution via mathematical algorithms, resolved unique peaks for intermediates and product

GC FID – Off line analysis

- Robust method, sharp peak resolution, reliable quantitation

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Process Safety Assessment

Initial and secondary reactions were run using Mettler-Toledo RC1 reaction calorimeter

- Enthalpy (ΔH_{rxn}) of reaction measured during reaction and determined to be very high
- Heat Capacity (C_P) measured via reaction calibration
- Adiabatic temperature (T_{ad}) is automatically calculated
- Maximum temperature of synthetic reaction (MTSR) is automatically calculated

Off line analysis was performed on intermediates

- TSU
- ARC
- DSC

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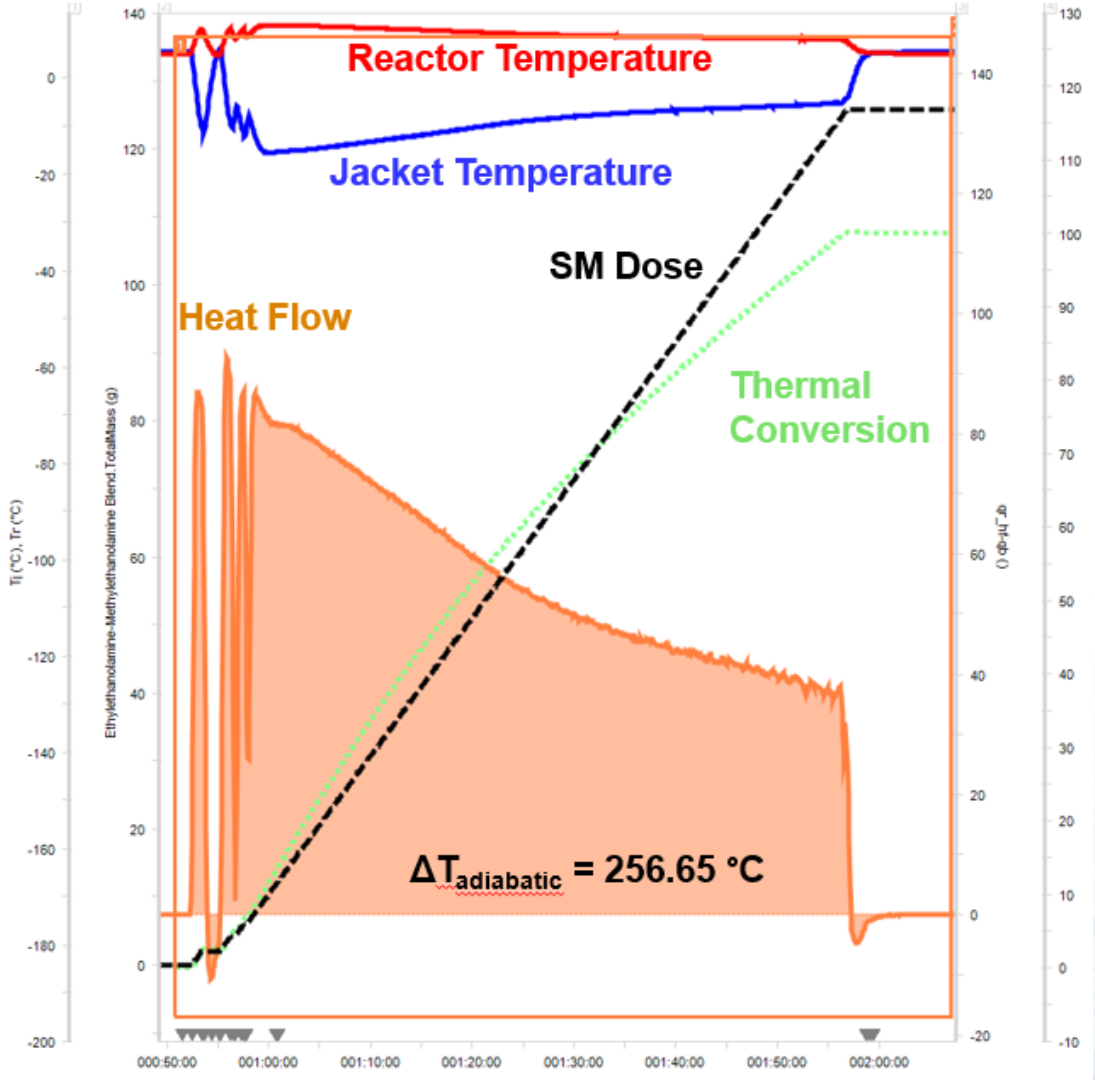
Process Safety Assessment

First reaction thermal profile

- Fuming nitric acid initial contents
- T_p controlled to 5 ºC
- One hour dose of amine
- Calibration before and post amine addition



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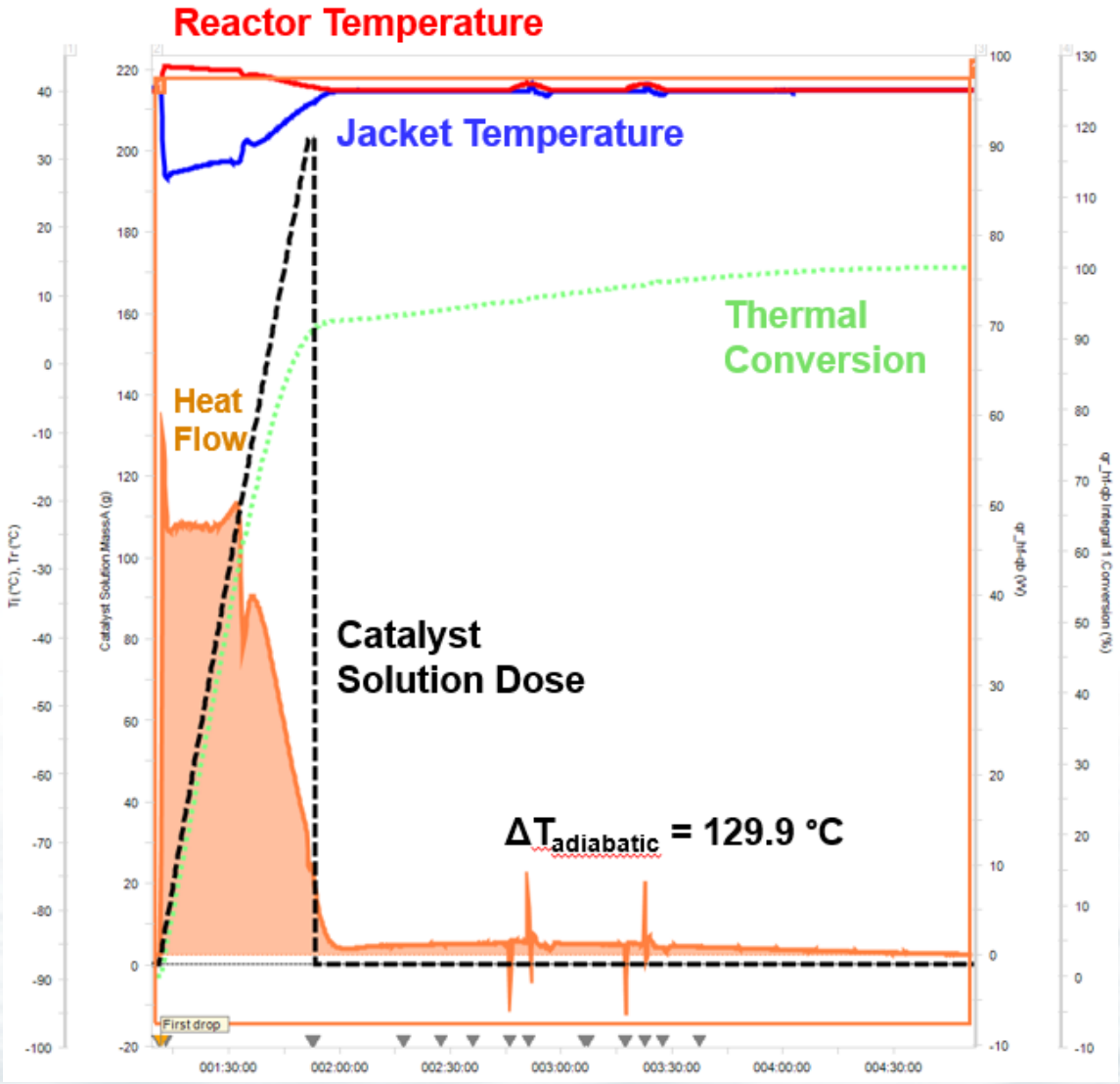
Process Safety Assessment

Second reaction thermal profile

- Results of first reaction, initial contents
- T_p controlled to 40 ºC
- 40 minute dose of catalyst solution
- Calibration before and after catalyst dose



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Nitration Process and Concerns

	NAL-032-05749 Me/Et NENA synthesis		NAL-032-05736 Et NENA synthesis	
	Step 1	**Step 2**	**Step 1**	**Step 2**
Initial material in reactor	Nitric Acid	Me/Et Amine-nitration salt intermediate	Nitric Acid	Et Amine-nitration salt intermediate
Material dosed	Me/Et Amine Blend	AA Catalyst Solution	EEA	AA Catalyst Solution
Cp of final mixture (J/(K· g))	2.03	1.97	2.01	2.07
Total heat measured (kJ)	211.79	104.26	261.14	151.57
Total heat measured (kJ/kg final rxn mix)	520 Critical	256 High	550 Critical	269 High
Adiabatic temperature rise (ΔTad) (°C)	257 Critical	130 High	273 Critical	130 High
Maximum temperature of synthetic reaction (MTSR) (°C)	262	170	278	170
TD24 (°C)	27	44	56	16
Tprocess	5	40	5	40
Criticality Class	**5**	**5**	**5**	**5+**

High heat of reaction (High heat of rxn and resulting T_{ad}) means ideal for a continuous process

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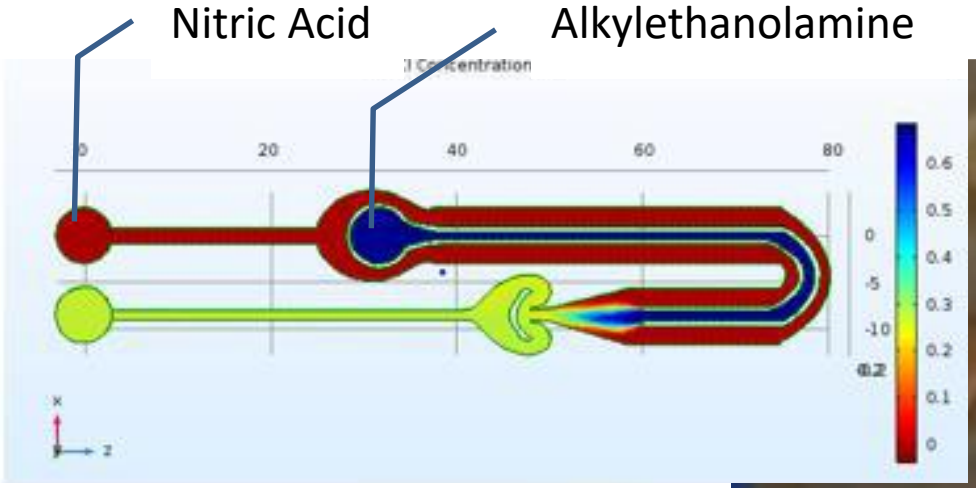
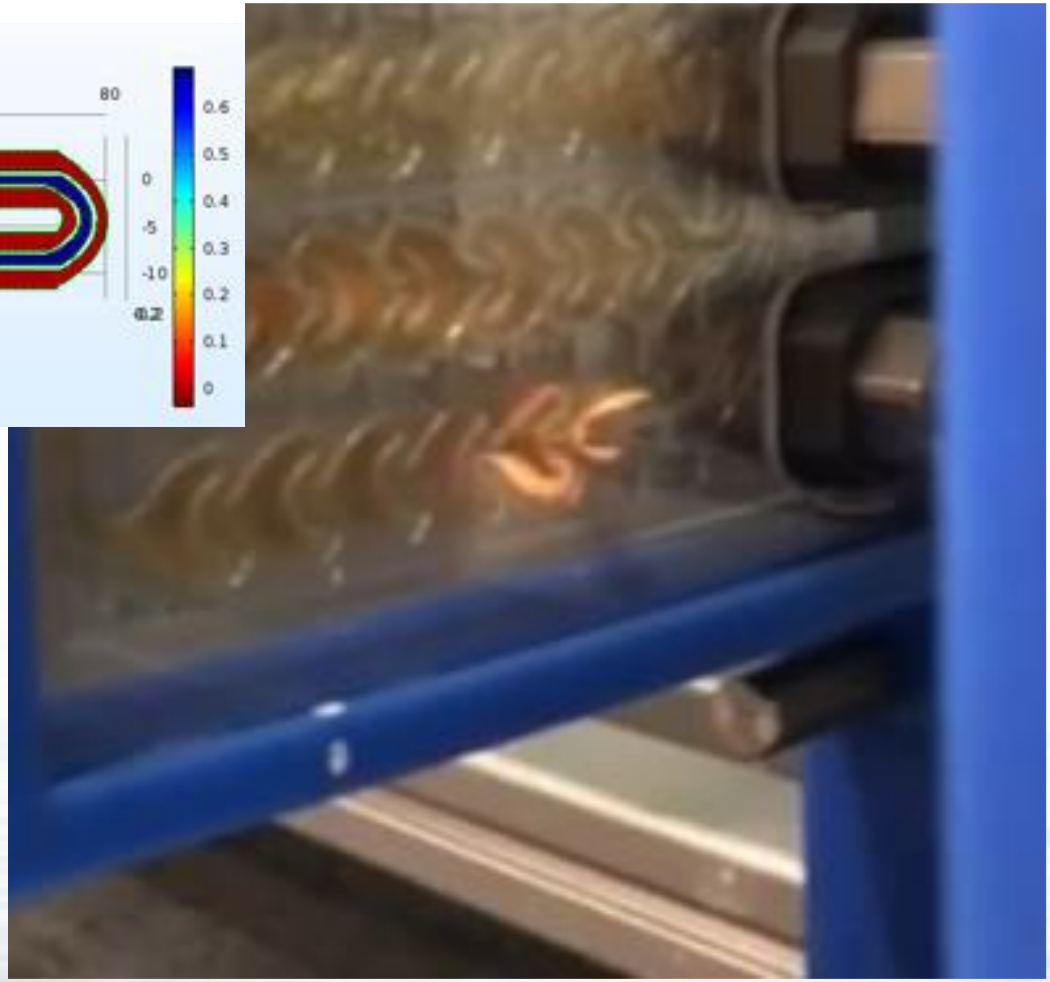
Nitration Process and Concerns





Initial reaction is highly rapid and exothermic

- Resulted in over pressurization and fracture of the reaction plate

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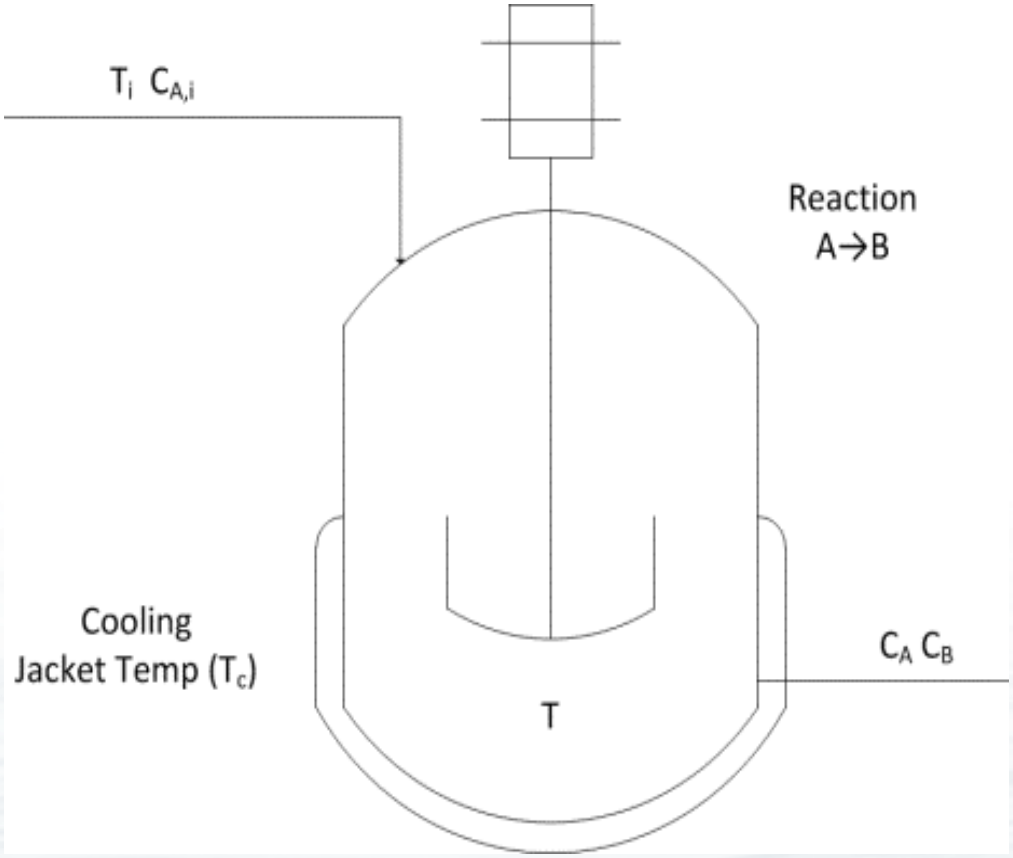
Continuous Stirred Tank Reactor

Why are CSTRs a solution now?

- Initial synthesis step is kinetically instantaneous. *Exciting!*

  - Until 10-15% of dose

- Inherent heat sink of held material
- Laboratory testing indicates a controlled synthesis



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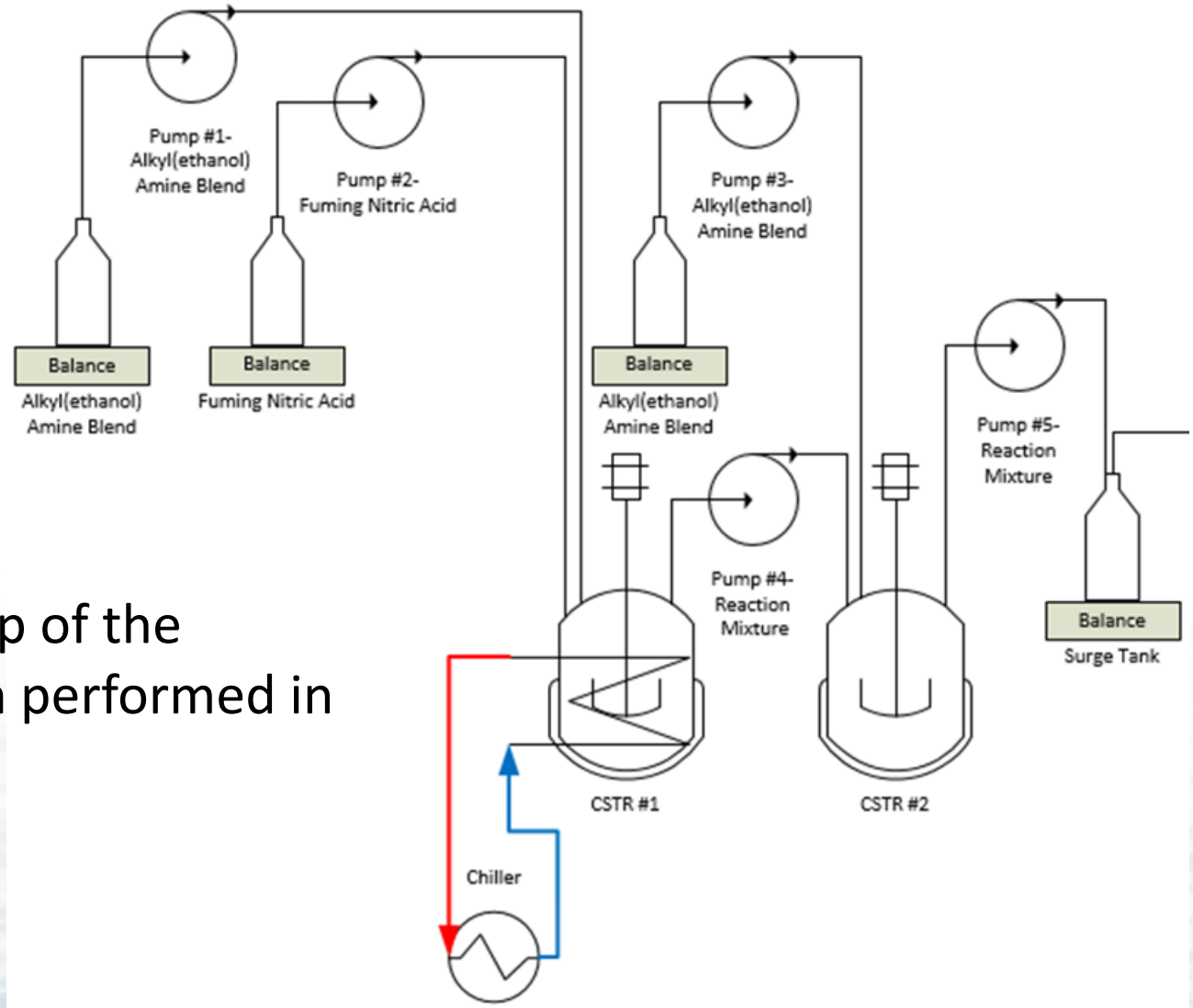
Process Equipment and Throughput



First step of the reaction performed in CSTRs

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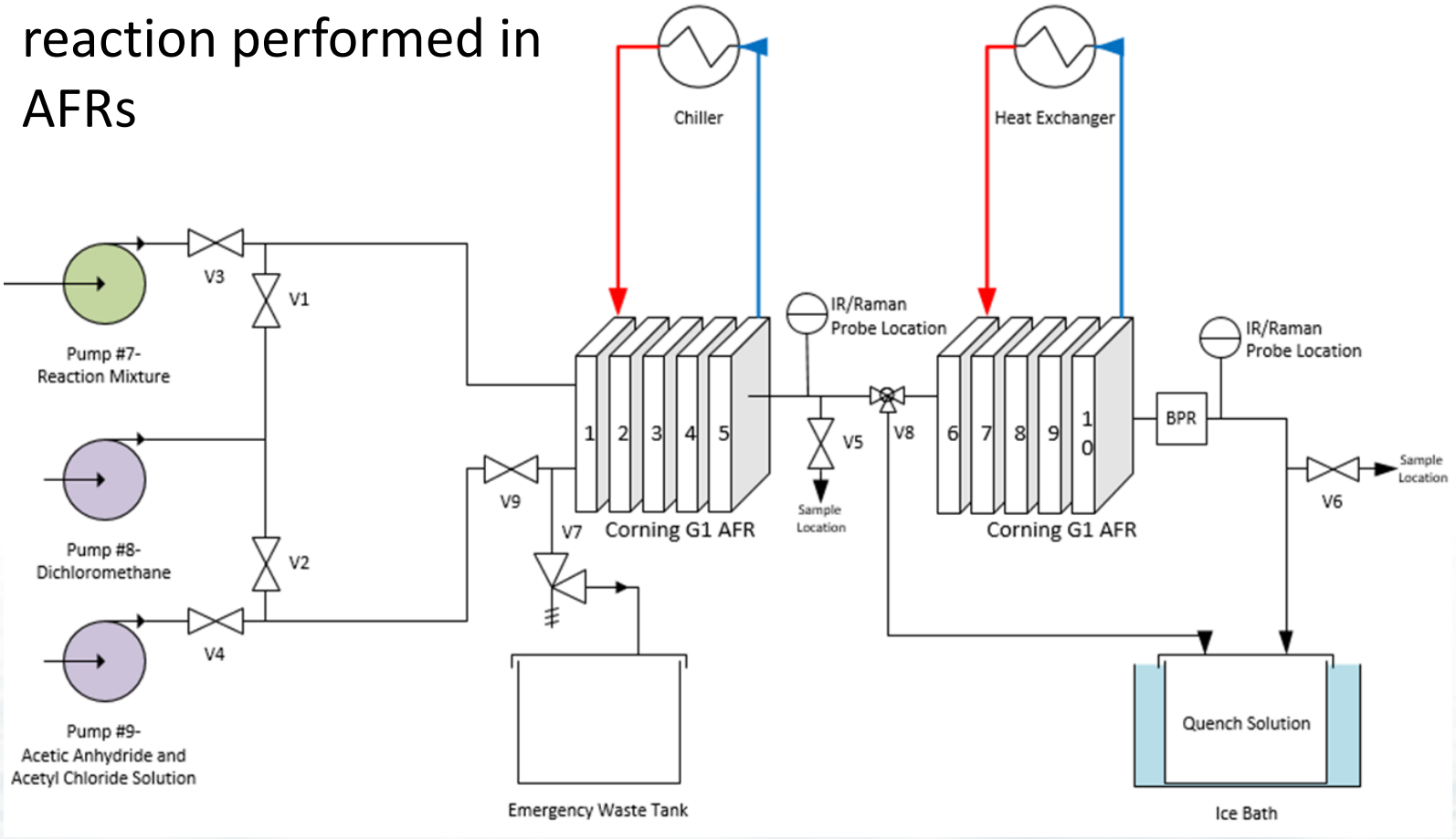
Process Equipment and Throughput

Second step of the reaction performed in AFRs



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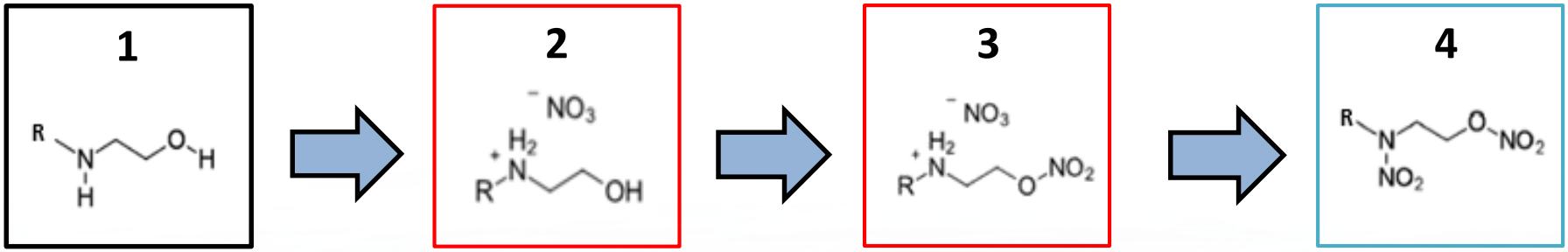
Original Process – 98% Nitric Acid

Step 1 – Dose of Ethanolamine to Fuming Nitric Acid

98% Nitric Acid at 5 °C → Dose Me-Et Ethanolamine blend

Step 2 – Dose of Catalyst Solution

Bring reaction mixture to 40 °C → Dose Acetic Anhydride / Acetyl Chloride Blend



During Step 1, water is formed as a byproduct. After a period of time, enough water is generated that the formation of species **3** halts. At this point species **2** begins to accumulate because it is not proceeding to **3.**

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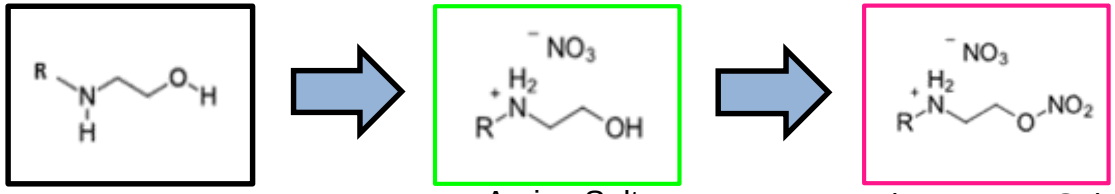
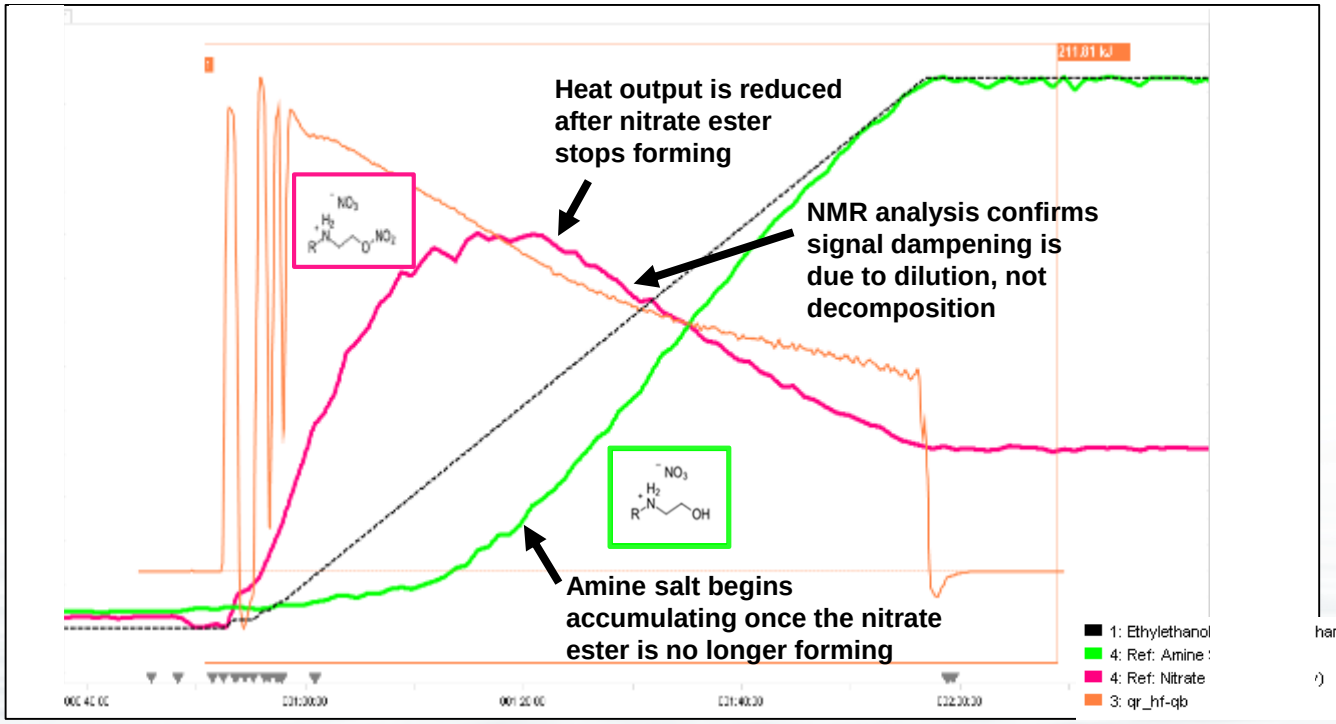
Reaction Step 1
Dose of Me/Et ethanolamine to 98% Nitric Acid
Confirmation of Intermediate Formation via Raman Analysis



Alkylethanolamine | Amine Salt | Nitrate Ester Salt



The change in heat flow profile corresponds with the time point where the Raman signal for the nitrate ester salt begins to disappear.

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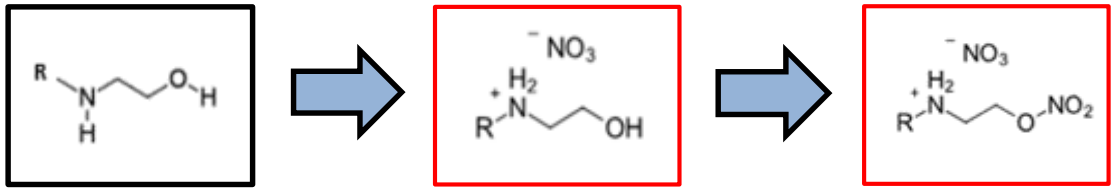
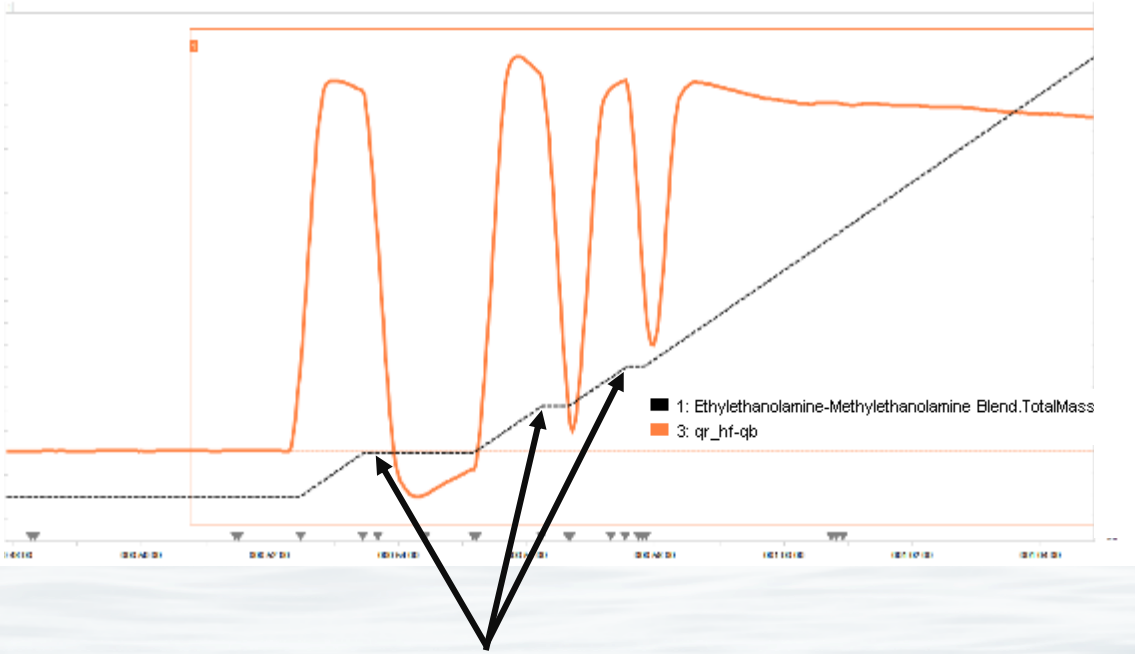
Reaction Step 1 – Dose of Me/Et ethanolamine to 98% Nitric Acid iControl Heat Flow Analysis



Alkylethanolamine | Amine Salt | Nitrate Ester Salt

Zoom of initial portion of dose



Dose paused because Tr exceeded safety limit of 10 °C

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New Process- 85% Nitric Acid Three Reaction Steps

Step 1 – Ethanolamine Dose to Dilute Nitric Acid

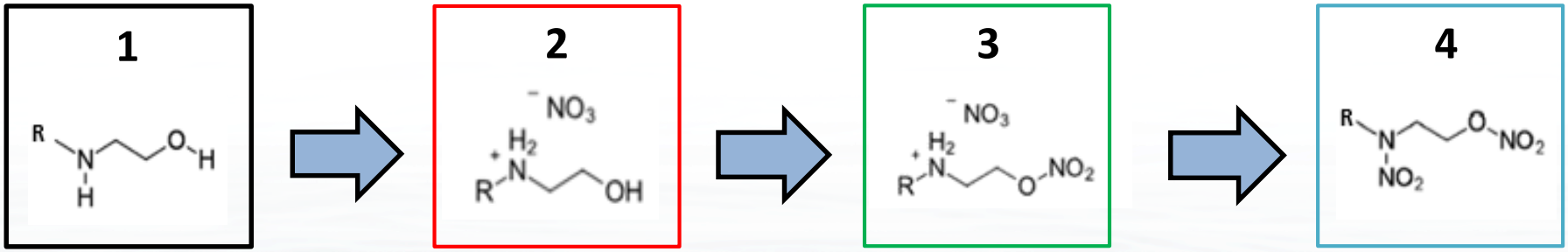
85% Nitric Acid at 5 °C → Dose Me-Et Ethanolamine blend

Step 2 – Dehydration of Reaction Mixture

Reaction Mixture at 5 °C → Dose Acetic Anhydride

Step 3 – Dose of Catalyst Solution

Bring Reaction Mixture to 40 °C → Dose Acetic Anhydride /Acetyl Chloride Blend



Alkylethanolamine

Amine Salt

Nitrate Ester Salt

NENA

Starting material

Formed during amine dose (Step 1)

Formed during anhydride dose (Step 2)

Formed during catalyst dose (Step 3)

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Comparison of amine doses – 98% vs. 85% Nitric Acid

98% Nitric Acid

85% Nitric Acid

- Loud snaps
- Vapors fill headspace immediately
- Dose pauses due to extreme heat evolution

- No snaps
- Vapor forms less violently – does not fill headspace instantly
- Dose never pauses

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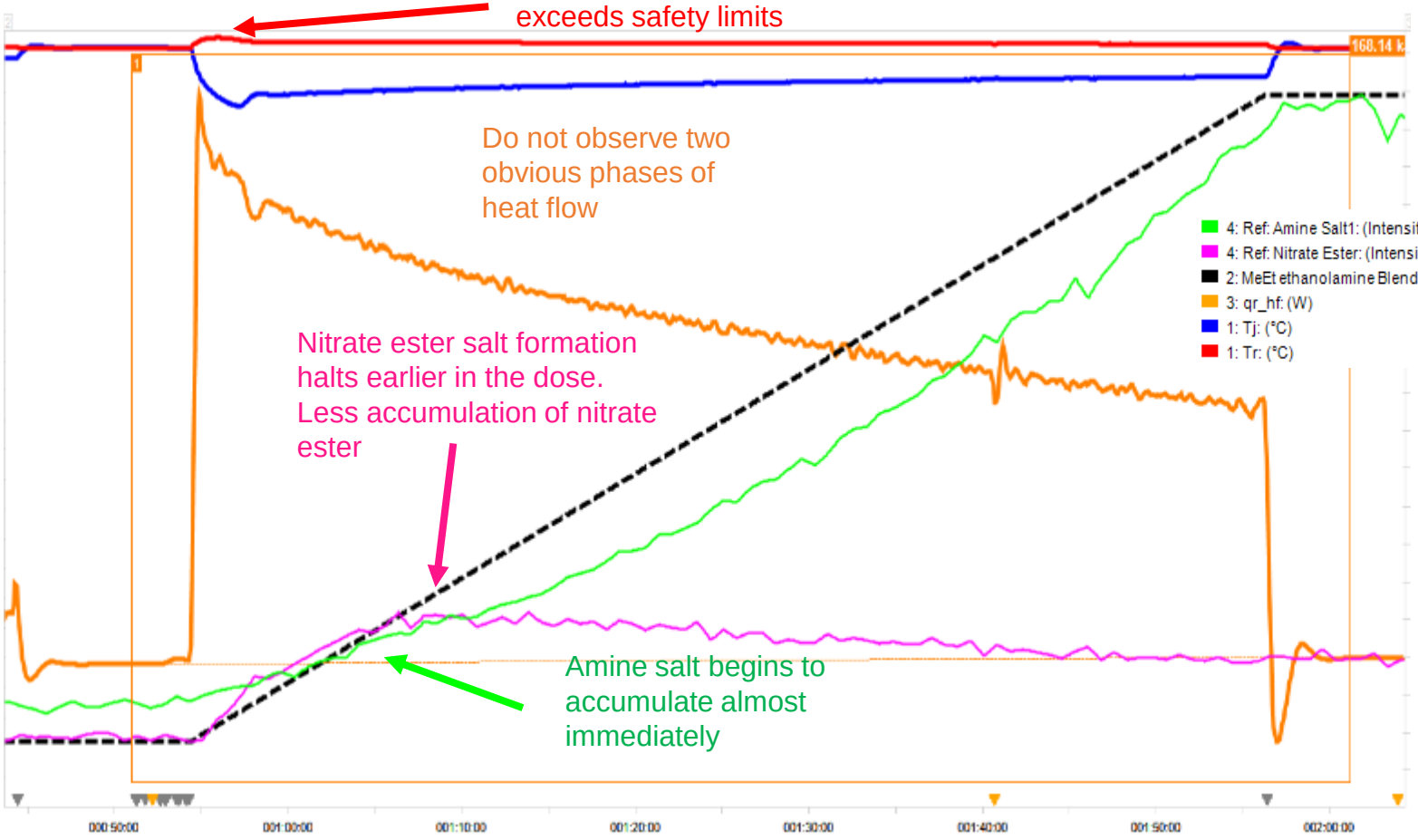
Reaction Step 1 – Dose of Me/Et ethanolamine to 85% Nitric Acid iControl Heat Flow and iC Raman Analysis



Suppressed nitrate ester salt formation and eliminated the violence of the amine dose

NMR analysis ca. 4:1 mass ratio of amine salt:nitrate ester salt upon dose completion. Previously 1:1 mass ratio when dosing into 98% nitric acid.

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Reaction Step 2 – Dehydration via Addition of Acetic Anhydride

Step 1 – Ethanolamine Dose to Dilute Nitric Acid

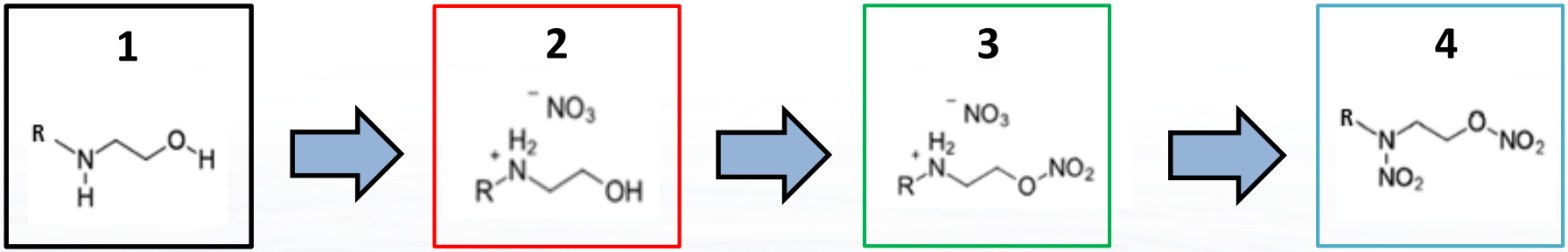
85% Nitric Acid at 5 °C → Dose Me-Et Ethanolamine blend

Step 2 – Dehydration of Reaction Mixture

Reaction Mixture at 5 °C → Dose Acetic Anhydride

Step 3 – Dose of Catalyst Solution

Bring Reaction Mixture to 40 °C → Dose Acetic Anhydride /Acetyl Chloride Blend



Starting material

Formed during amine dose (Step 1)

Formed during anhydride dose (Step 2)

Formed during catalyst dose (Step 3)

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Reaction Step 3 – Dose of Catalyst Solution

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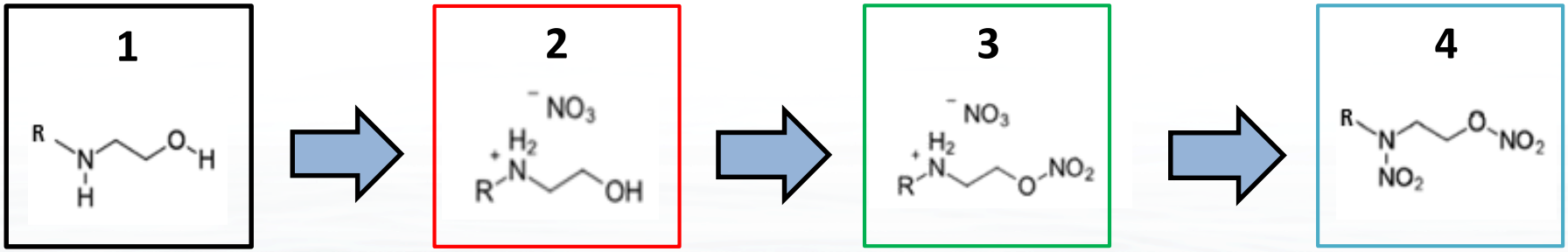

Alkylethanolamine

Amine Salt

Nitrate Ester Salt

NENA

Starting material

Formed during amine dose (Step 1)

Formed during anhydride dose (Step 2)

Formed during catalyst dose (Step 3)

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Continuous Process

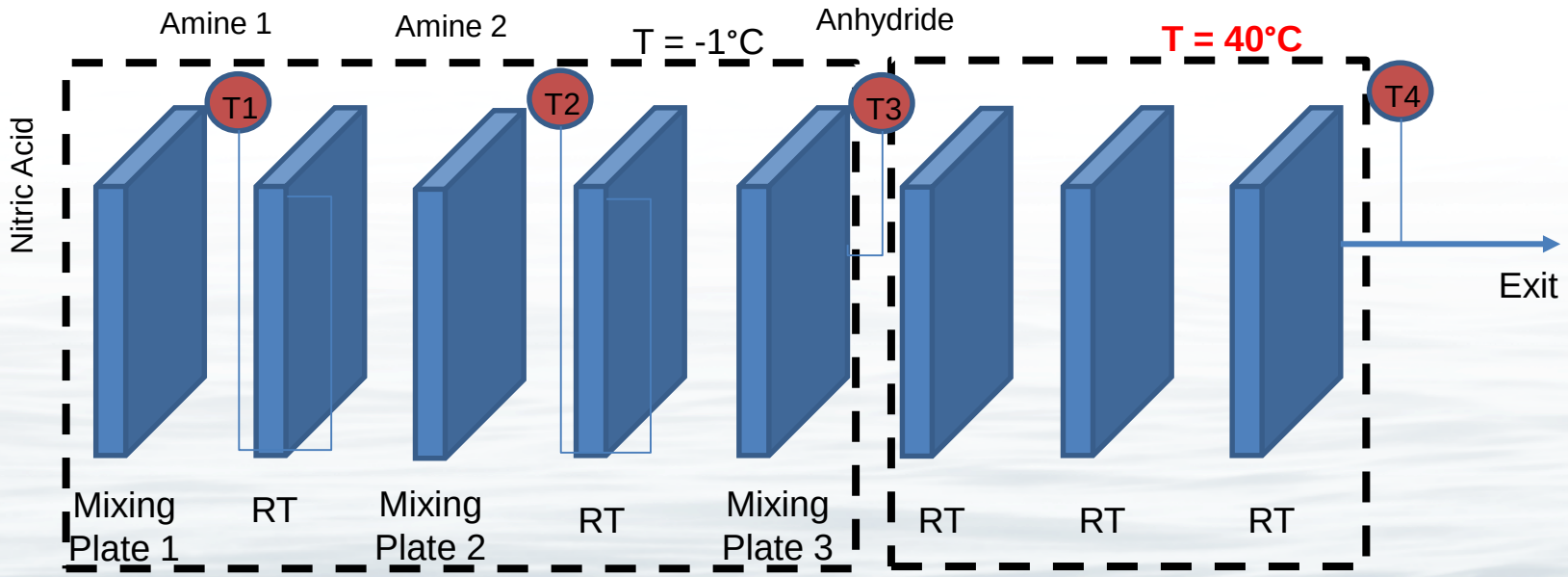
All of the alkyl ethanolamine is added in two doses in the low temperature section

Acetic anhydride is introduced to the last plate in the first section

- dehydrating the reaction mixture
- raising the temperature for increased reaction rate

Acetyl chloride catalyst is dosed into the last plate

Exit to two CSTRs for remaining residence time



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Conclusions

- Initial process was highly exothermic and difficult to “tame” for a continuous process
- Spectroscopic/NMR data led to more fundamental understanding of the chemistry and the effect of water
- Modified process developed allowing for separation of the individual reactions and their corresponding heats
- Reaction engineering and kinetics used to design a continuous process
- Demo validates the approach and shows the ability to run fully continuous process
- Next step is the continuous workup!

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Questions?