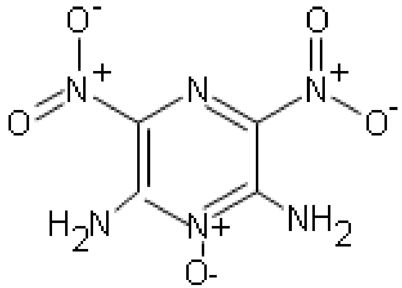
Synthesis, Scale-Up, and Recrystallization Studies of 2,6-Diamino-3,5-Dinitropyrazine-1-Oxide (LLM-105)



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Introduction: Why LLM-105?

- Current Issue
  - TATB: Poor cold temperature performance and initiation properties
    - Demonstrated in cold temperature to have poor divergence properties[1]
      - Poor divergence leads to incomplete initiation resulting in reduced performance

- LLM-105 Performance Comparisons to TATB

	Density (g/cm^3)	D_v (mm/usec)	P_{cj} (kbar)
TATB	1.937*	7.66 @ 1.847 g/cm^3	262 @ 1.847 g/cm^3
LLM-105*	1.913	8.87	335

* Calculated using the CHEETAH chemical equilibrium code

1. T.D. Tran, P.F. Pagoria, D.M. Hoffman, B. Cunningham, R.L. Simpson, R.S. Lee, and J.L. Cutting; "Small Scale Safety and Performance Characterization of New Plastic Bonded Explosives Containing LLM-105": 12th International Detonation Symposium, San Diego, CA; August 11-16, 2002

Introduction: Why LLM-105?

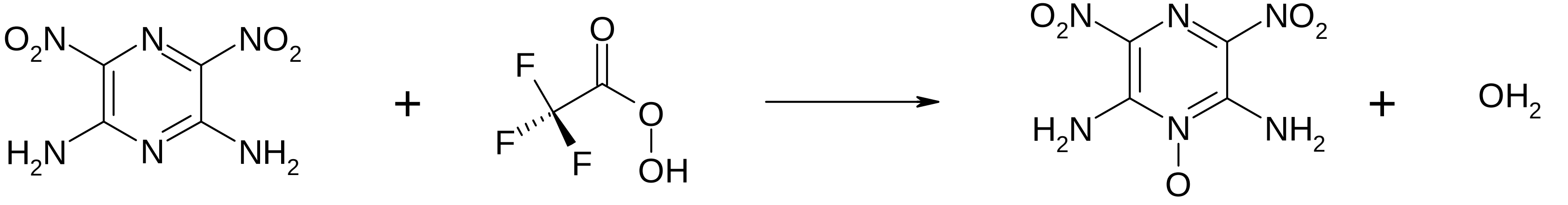
- Lawrence Livermore National Laboratory results
  - LLM-105 → increase in performance, superior divergence
    - LLM-105 with 2.5% Viton shows increased performance over UF-TATB[1]
    - LLM-105 with 2.5% Viton shows complete initiation at 2mm[1]
      - Superior lateral spreading compared to TATB

1. T.D. Tran, P.F. Pagoria, D.M. Hoffman, B. Cunningham, R.L. Simpson, R.S. Lee, and J.L. Cutting; "Small Scale Safety and Performance Characterization of New Plastic Bonded Explosives Containing LLM-105": 12th International Detonation Symposium, San Diego, CA; August 11-16, 2002

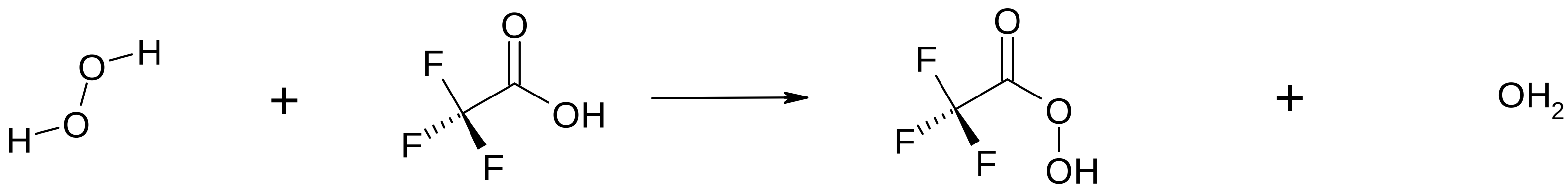
LLM-105: Original synthesis process

1. Add trifluoroacetic acid (TFA) to vessel
2. Add 2,6-Diamino-3,5-Dinitropyrazine (ANPZ) to vessel
3. Add first dose of hydrogen peroxide (H_2O_2) at initally lower temperature
4. Heat reaction to just below decomposition temperature to increase conversion
5. Add second dose of H_2O_2 at this second temperature

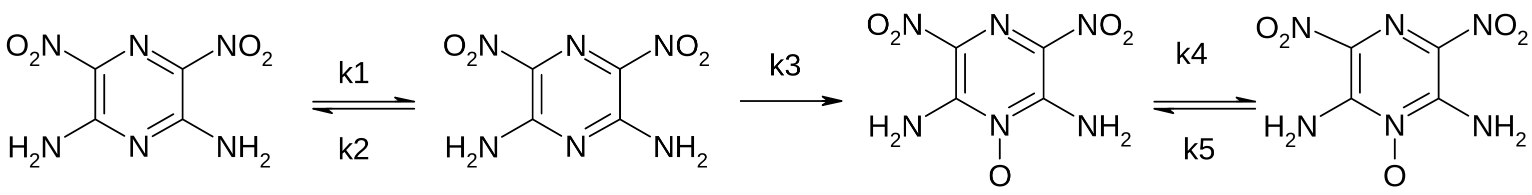
LLM-105: The Chemistry



ANPZ   Trifluoro peroxy aceticacid   LLM-105   Water



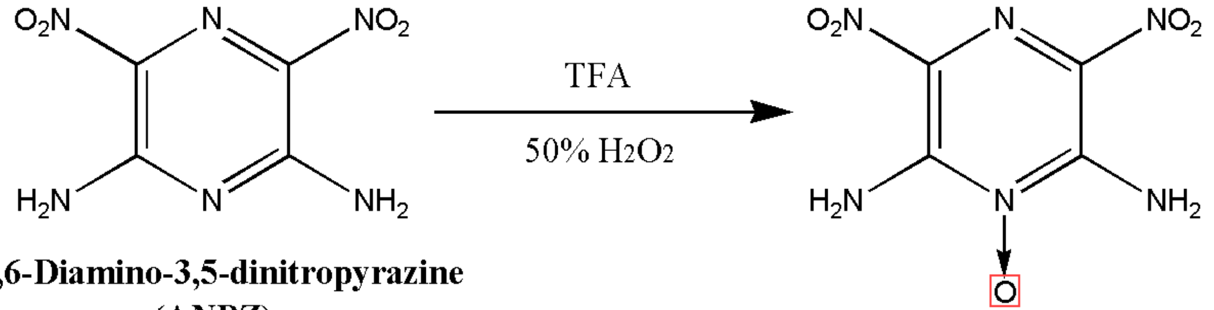
Hydrogen Peroxide   Trifluoroacetic acid   Trifluoro peroxy aceticacid   Water



ANPZ (s)   ANPZ (l)   LLM-105 (l)   LLM-105 (s)

Engineering Challenges: Synthesis

•Challenge: Reduce cost and reduce quantities of hazardous materials



2,6-Diamino-3,5-dinitropyrazine (ANPZ)

2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105)

•Solution: Replace 80 % of more expensive TFA ($30/kg) with sulfolane ($10/kg)

•LLM-105 produced in high yields

•Similar in quality to material before replacement

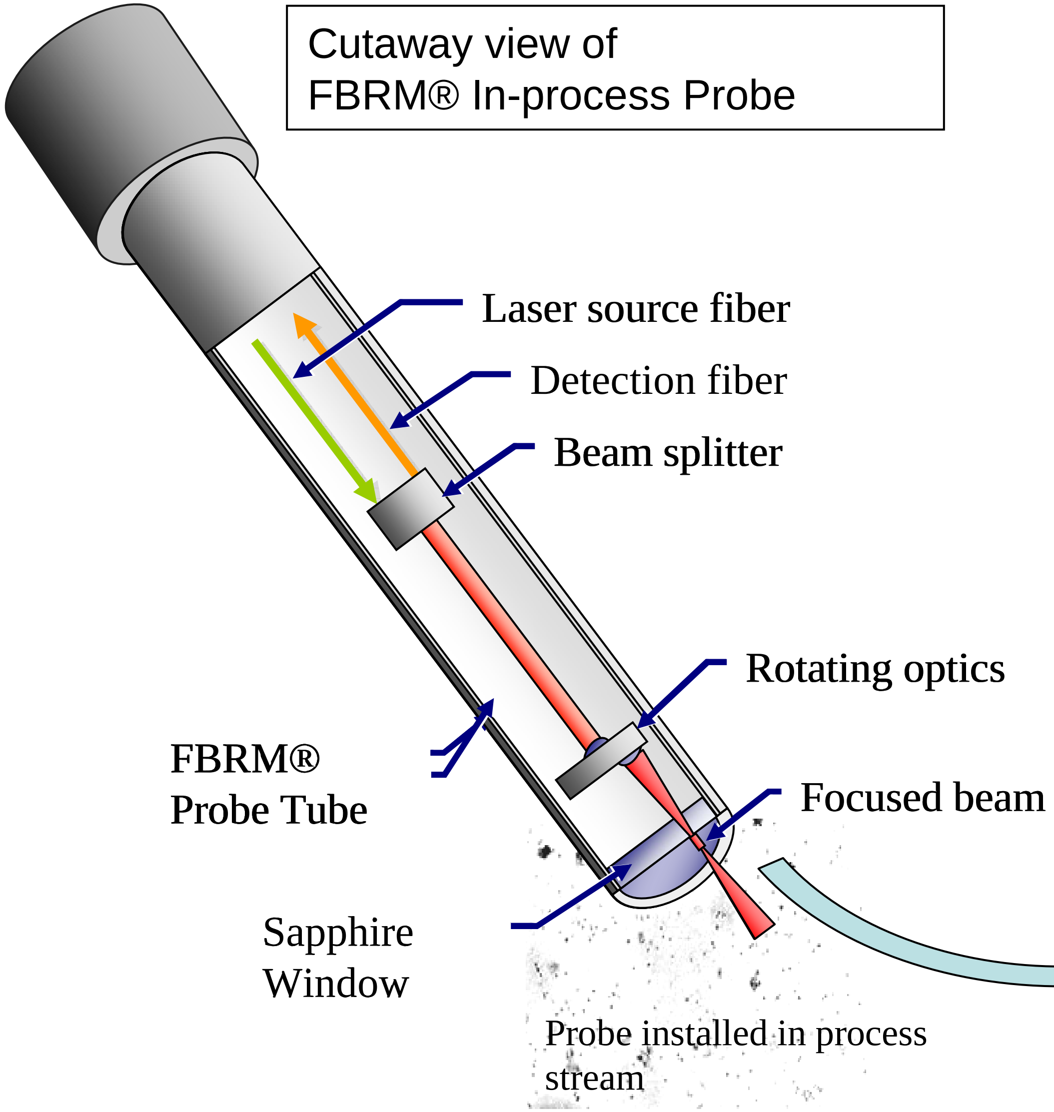
Technical Approach: Scale-Up

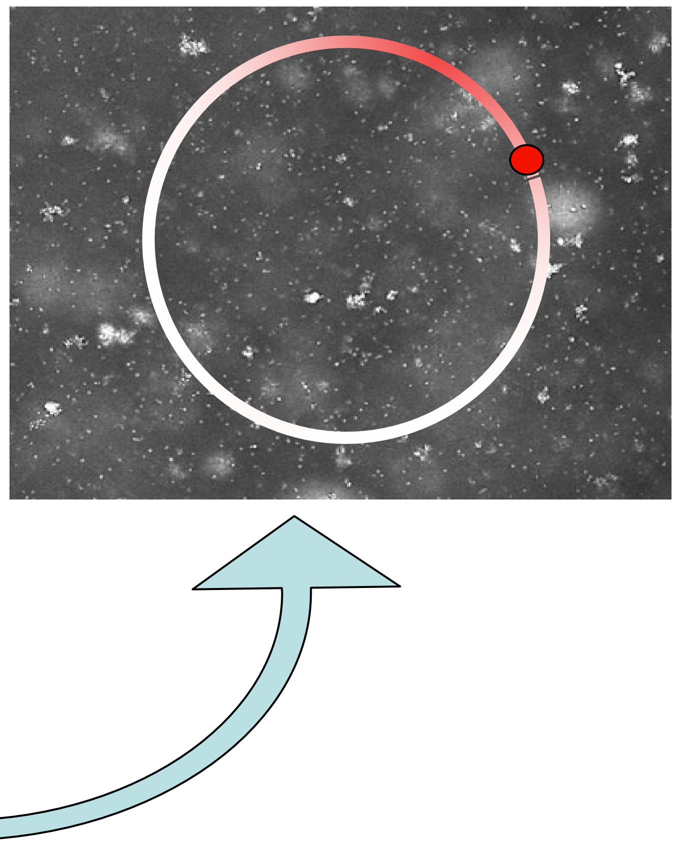
EasyMax- 10-100-ml scale, rapid screening of process parameters through use of multiple reactors, data collection enhanced with FBRM technology

RC1: 0.08-2-L scale, accurate heat flow on reactions, data collection enhanced with ability to use FBRM, PVM, ReactIR

ChemGlass Glass Reactors: 5-100-L scale, unnatended dosing and temperature control capabilities

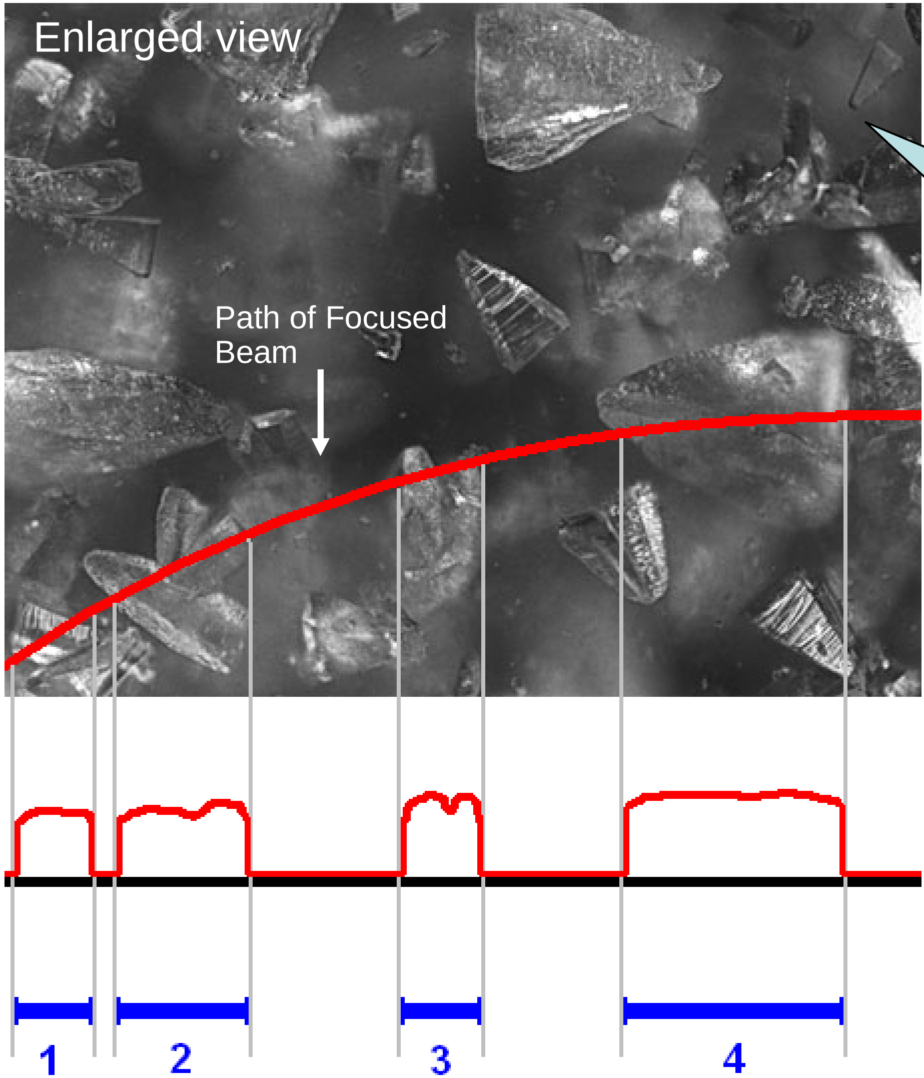
The FBRM®
Method of Measurement



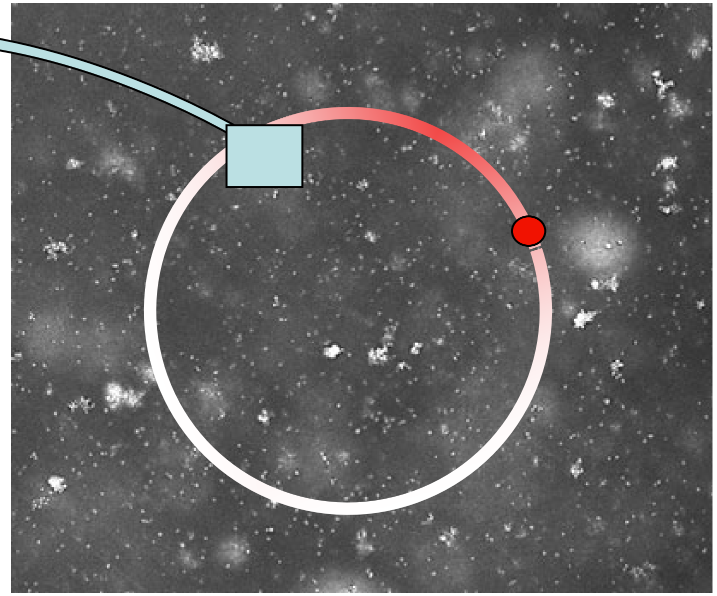


FBRM = Focused Beam Reflectance and Measurement PVM = Particle Vision Microscope

The FBRM®
Method of Measurement



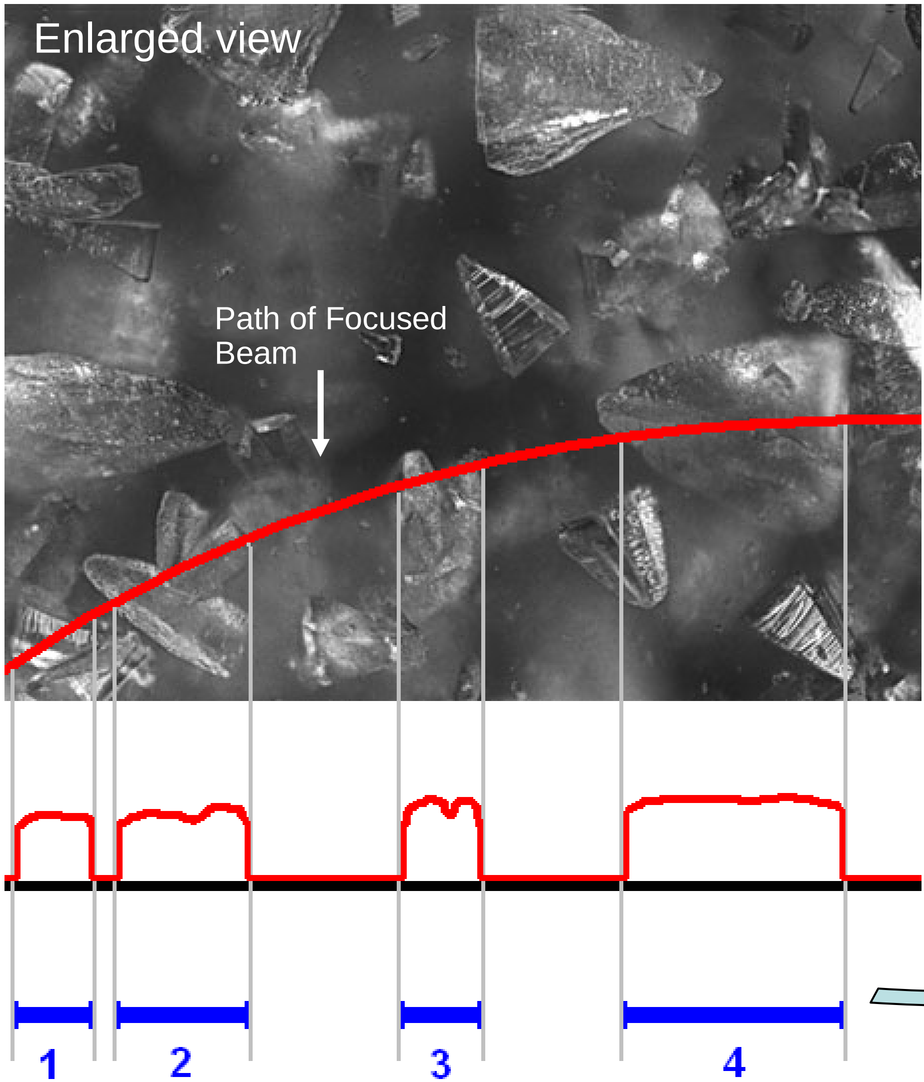
PVM® image illustrating the view from the FBRM® Probe Window

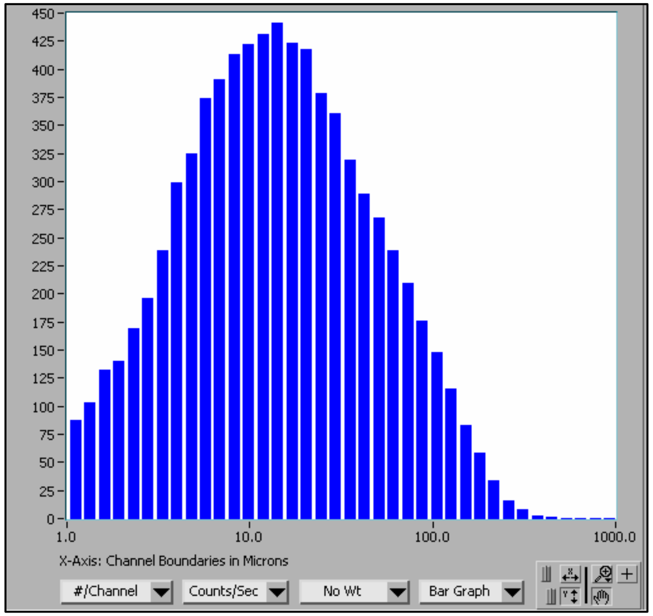


Probe detects pulses of Backscattered light

And records measured Chord Lengths

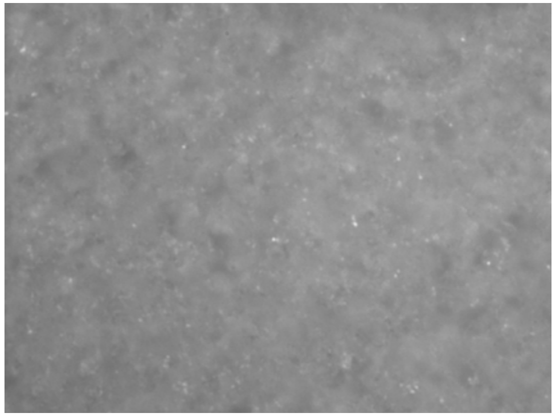
The FBRM®
Method of Measurement





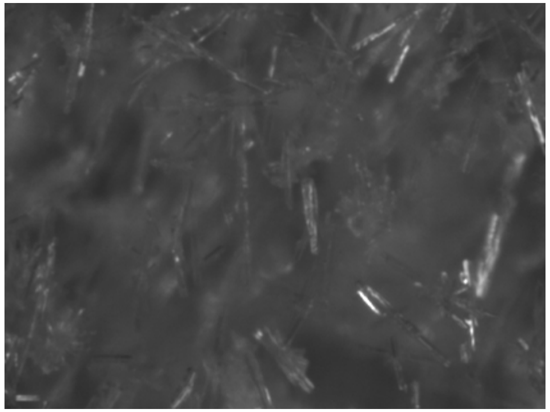
Thousands of Chord Lengths are measured each second to produce the FBRM® Chord Length Distribution :

Synthesis and Morphology

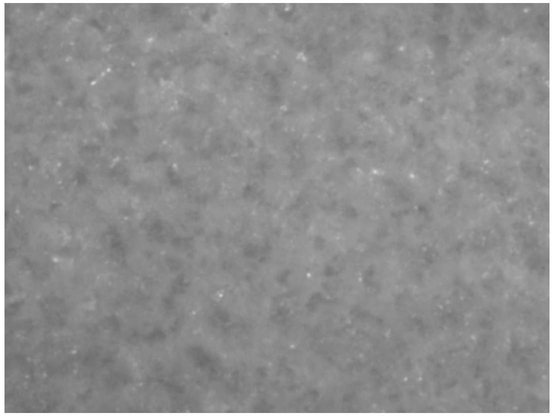


ANPZ / TFA / Sulfolane Slurry

1. H_2O_2 Addition at T_1
2. H_2O_2 Addition at T_2

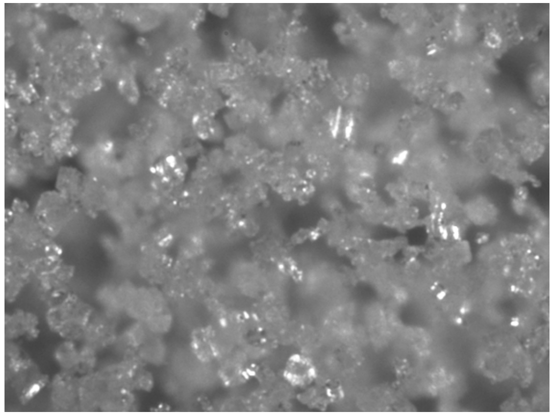


Needle LLM-105 Slurry



ANPZ / TFA Slurry

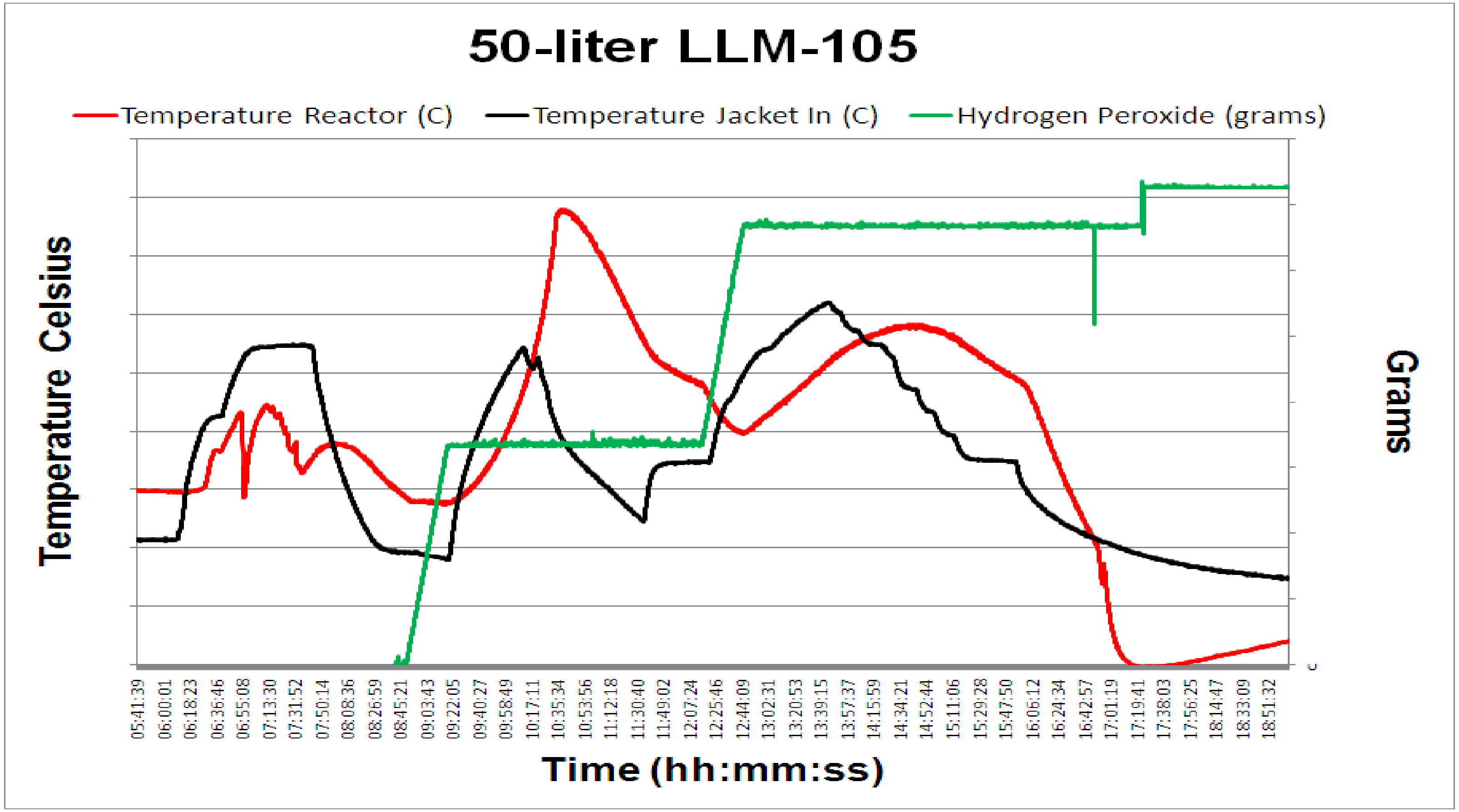
1. H_2O_2 Addition at T_1
2. H_2O_2 Addition at T_2



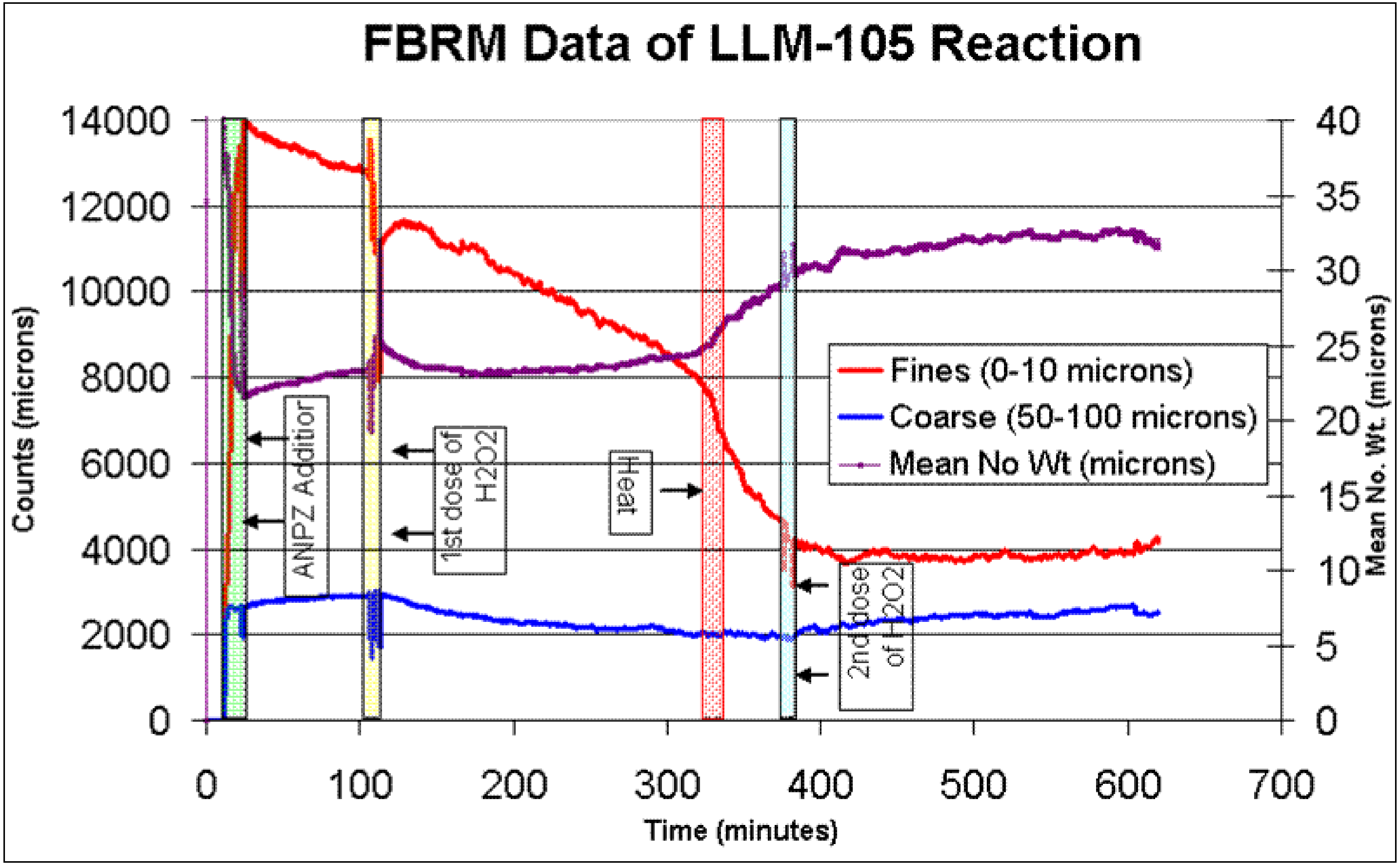
Cubic LLM-105 Slurry

Engineering Challenge: Scale-up

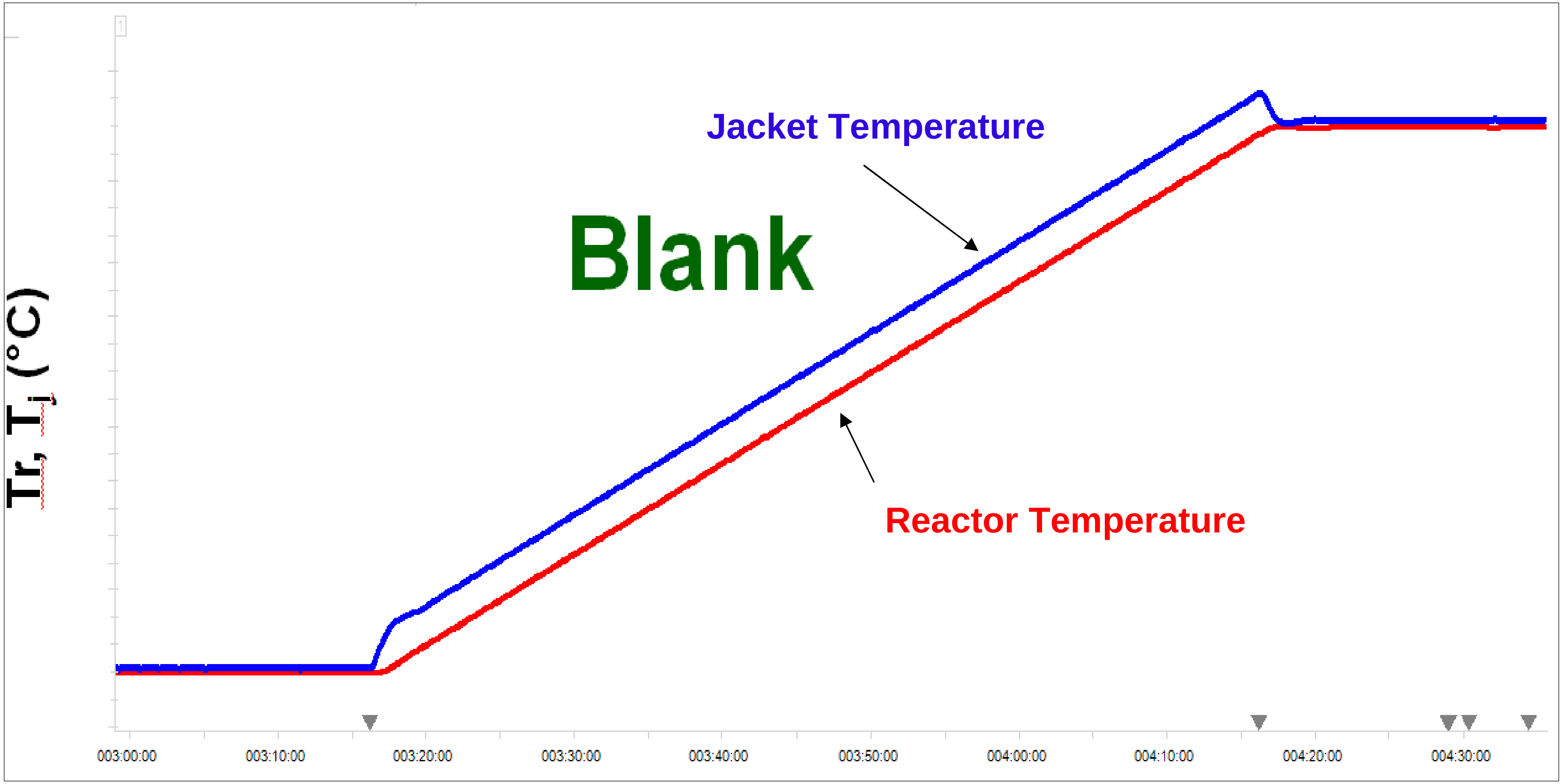
- 50-L scale: exotherm not observed using heat flow calorimetery
  - After 1st peroxide dose, temperature of reaction rose to 78℃. (b.p. of TFA = 72.4℃)



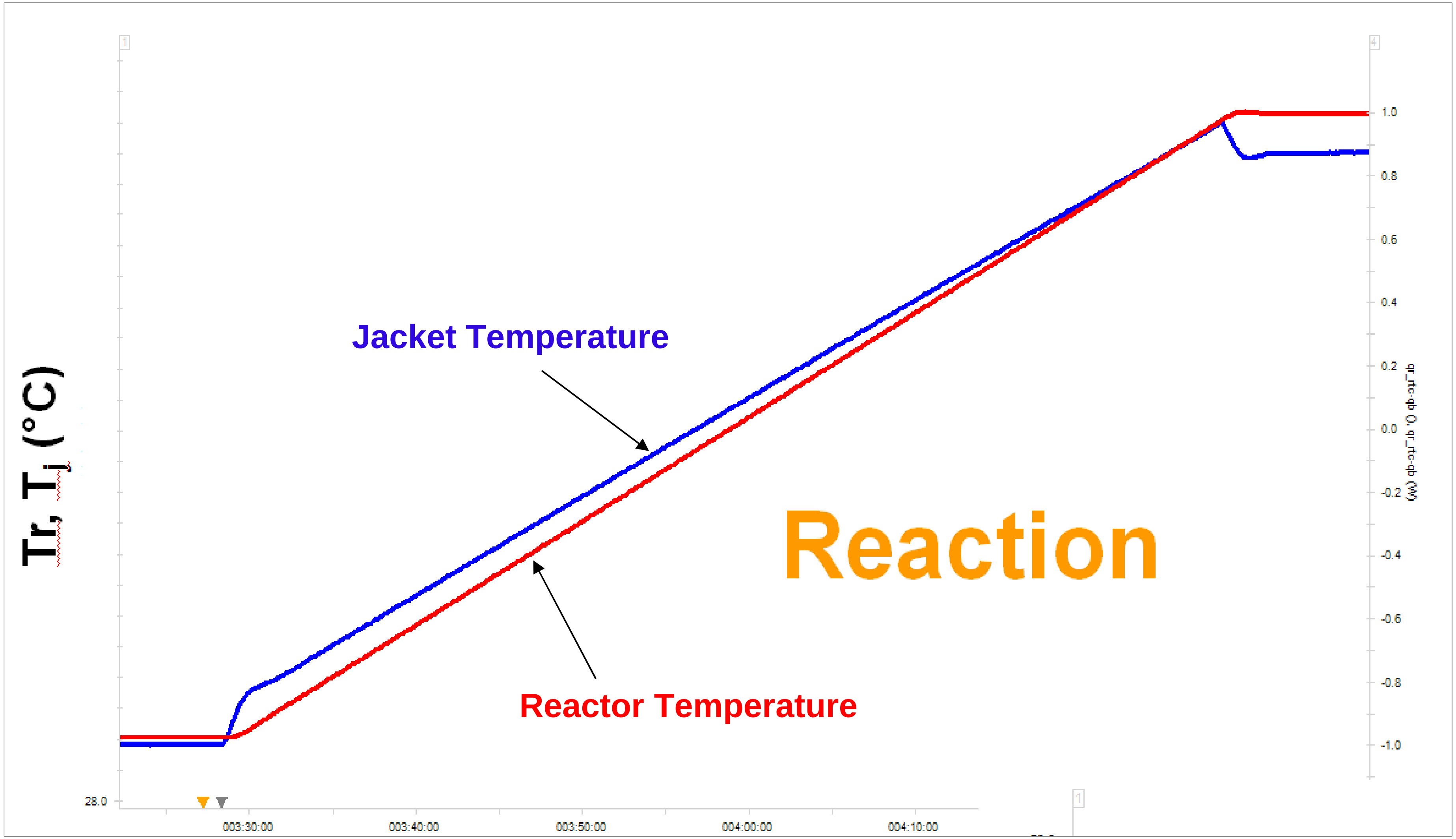
Examining the Temperature Ramp



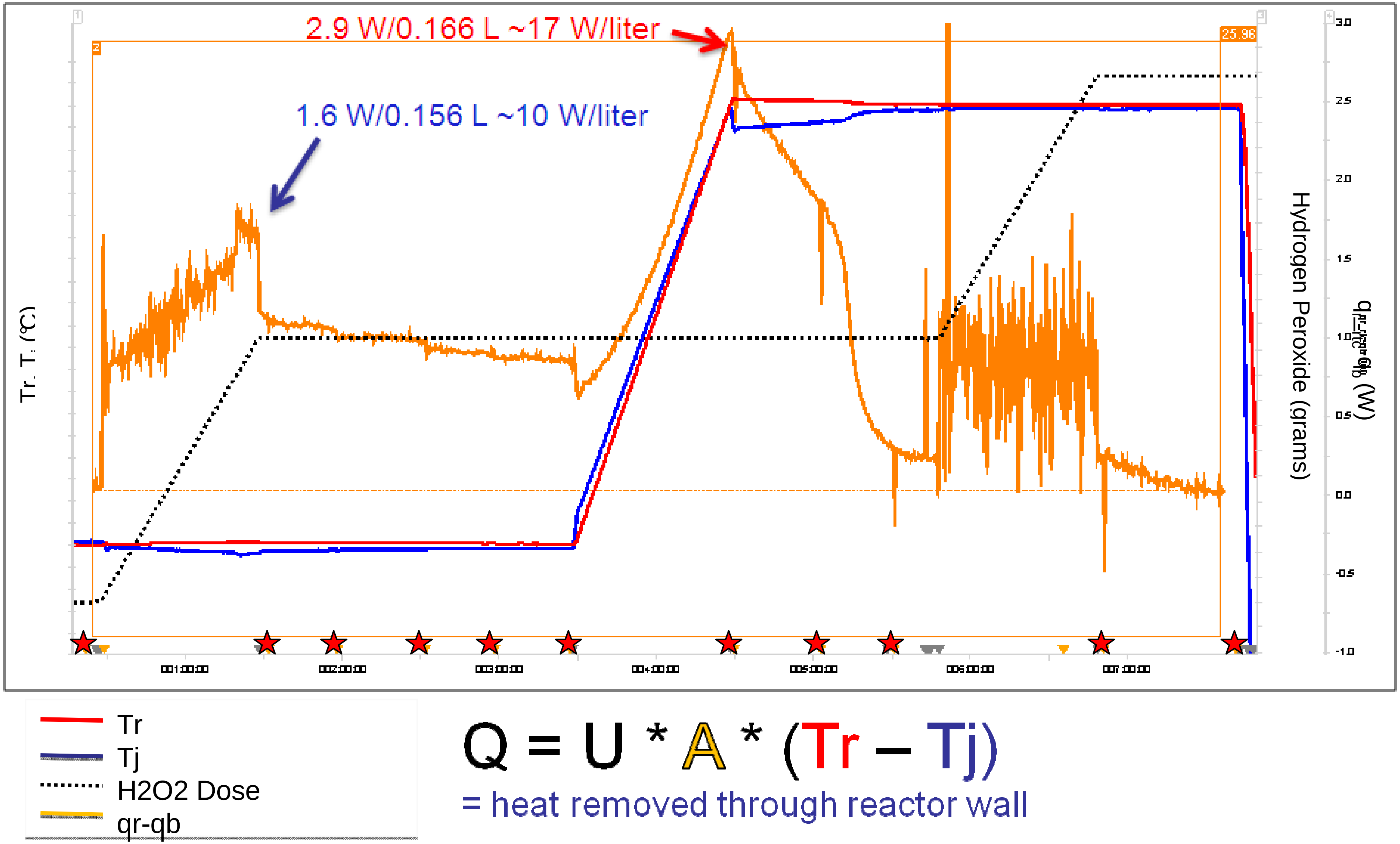
Heat Flow: Without Reaction



Heat Flow: With Reaction



Heat Flow vs. Time



$$Q = U * A * (Tr - Tj)$$

= heat removed through reactor wall

LLM-105 Technical Issues: Addressing the Exotherm

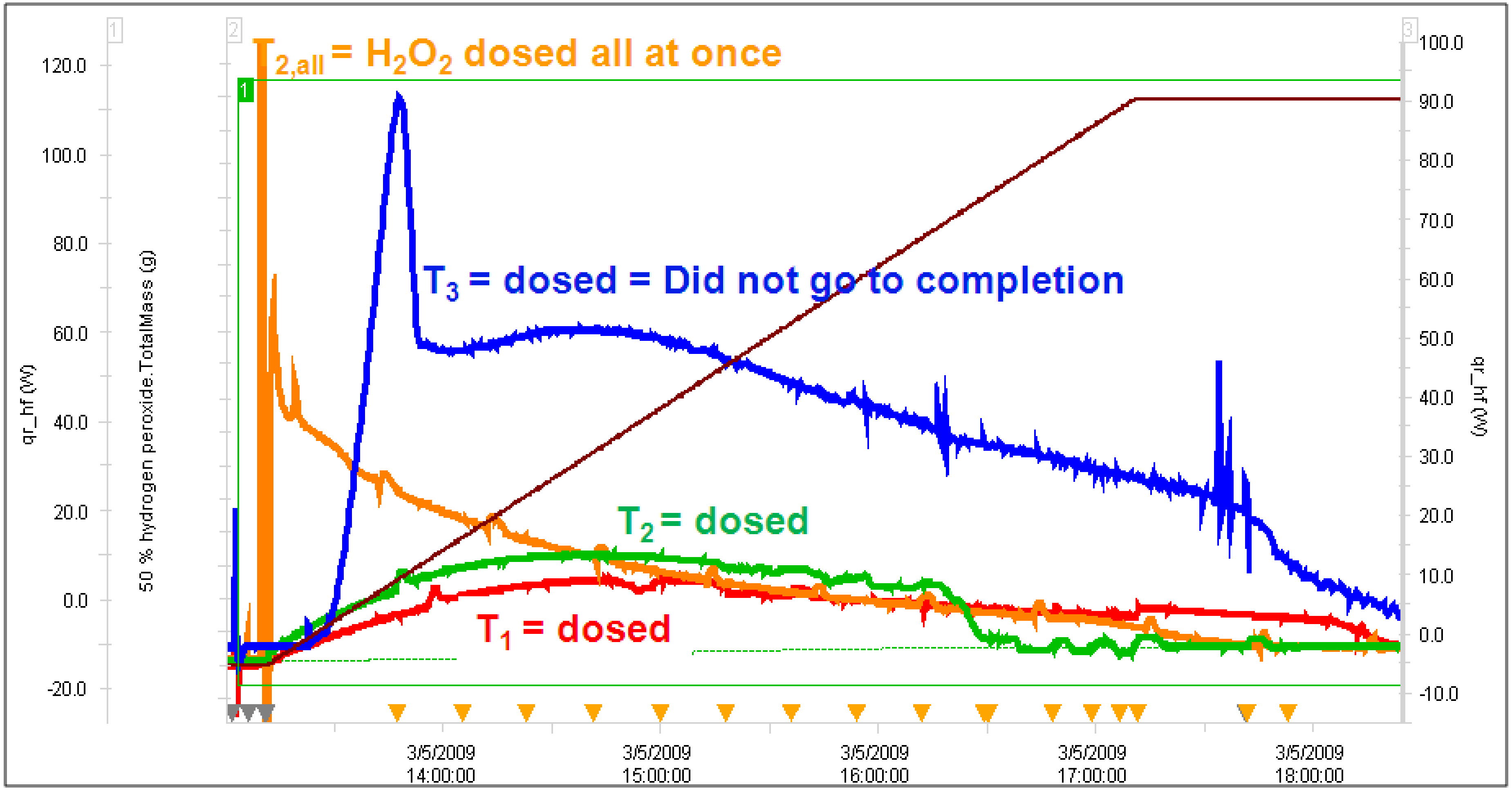
- *Cannot use heat generated from reaction to aid in heating without full understanding of effect!*
  - Important to maintain control of reaction temperature at all times. Decided to do one dose at constant temperature.
- What is causing exotherm?
  - Breaking down of hydrogen peroxide at high temperatures?
- Does operating at higher temperature improve solubility of ANPZ which thus increases conversion?
  - Can reaction be controlled through slow dosing of H_2O_2?
  - Run reaction in calorimeter at 60℃ and measure he at flow and conversion

Scale Down Synthesis: Technical Approach

- Find a temperature where the decomposition reaction is minimized and desired reaction still takes place
  - *Laws of kinetics*:
    - Lower temperature, lower reaction rate
    - Higher concentration, faster reaction rate
    - Need to find a temperature range that still allows conversion
  - Slowly dose hydrogen peroxide to mixture at 40 ℃ and 45 ℃, minimizing decomposition of reagent
  - At 45 ℃, “dump” all H_2O_2 in to simulate effect of having all ingredients in vessel at once
- Monitor conversion of starting material to desired product
  - How much peroxide is needed for reaction? Because it decomposes, excess amounts are required.
- Test effect of operating above decomposition temperatures, 60 ℃

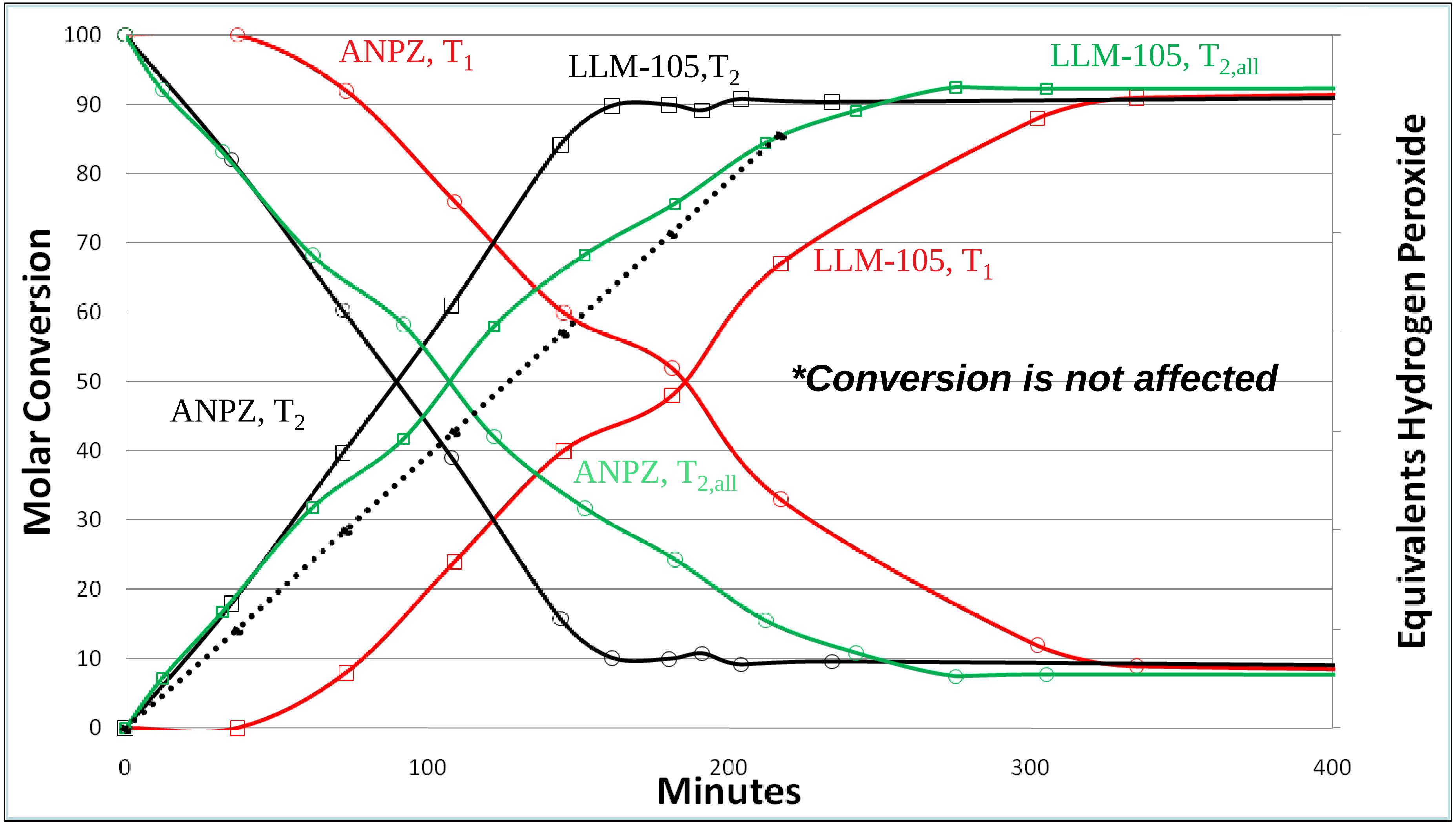
Total Heat Generation (area under curve)

1. Dose slowly
2. Maintain temp well below decomp temp of H_2O_2

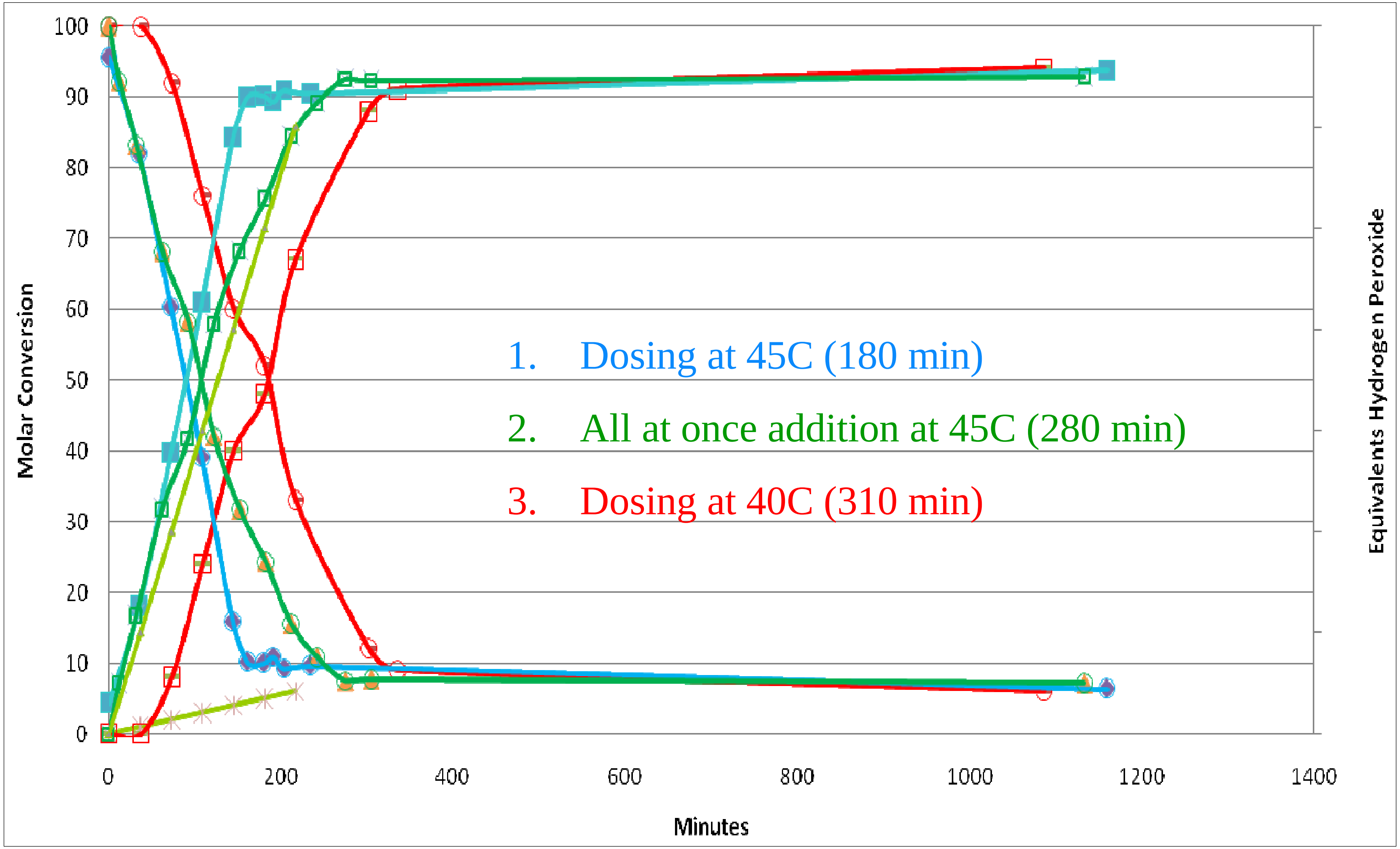


Molar Conversion as a function of temperature

***93% Conversion compared to only 30% above decomposition temperature of H_2O_2**



Reaction Completion Times as a function of temperature



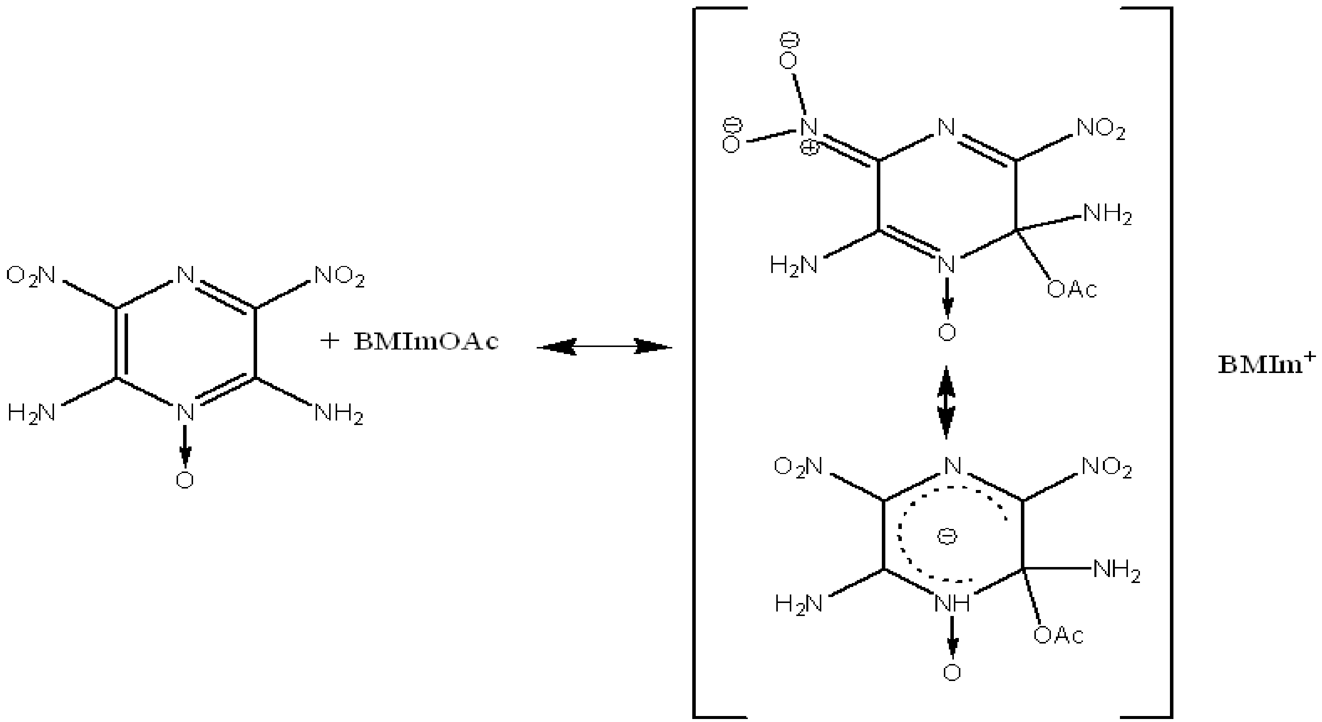
Technical Results: Particle Size

- **Particle Size**
  - **Determine effect of H_2O_2 conditions and scale**
- **Results**
  - FBRM probe shows particle size shift during reaction from smaller ANPZ to LLM-105
  - Mean particle size is typically about 40 microns with distribution from 10-100 microns
  - Mass transfer limited
    - No significant effect from dose rate or temperature
    - No significant changes in particle size upon scaling process

	Mean Value
RC1 Experiments	**(microns)**
Two Doses (30℃, 50℃)	39.3
40℃ Slow Dose	46.2
45℃ Slow Dose	52.7
45℃ Rapid Dose	38.6
50℃ Slow Dose	32.3
50℃ Rapid Dose	36.2
10-Liter (Two dose 30℃, 50℃)	46
100-gallon (40℃)	45

Engineering Challenge: Recrystallization

- LLM-105 found to offer low solubility in typical organic solvents
- Solution: Examine ionic liquid solvents: 1-butyl-3-methylimidazolium acetate



Acknowledgements

- Joint Insensitive Munitions Technology Program
- Chemical Development Brach, IHDIV, NSWC – Support
- NALAS Engineering Services – Project support
- Lawrence Livermore National Laboratory – Dr. Phil Pagoria, Dr. Thomas Lorenz
- Eric Bukovsky, U.S. Army Research Laboratory - Collaboration on project
- Navy Mantech – Chuck Painter
- RDT&E Directorate, IHDIV, NSWC -
  - Dr. Brandon Choi – IHDIV, NSWC – SEM
  - Kim Proctor – IHDIV, NSWC – Microtrac