1,2,6,8-Tetranitrocarbazole (TNC): Synthesis and Optimization

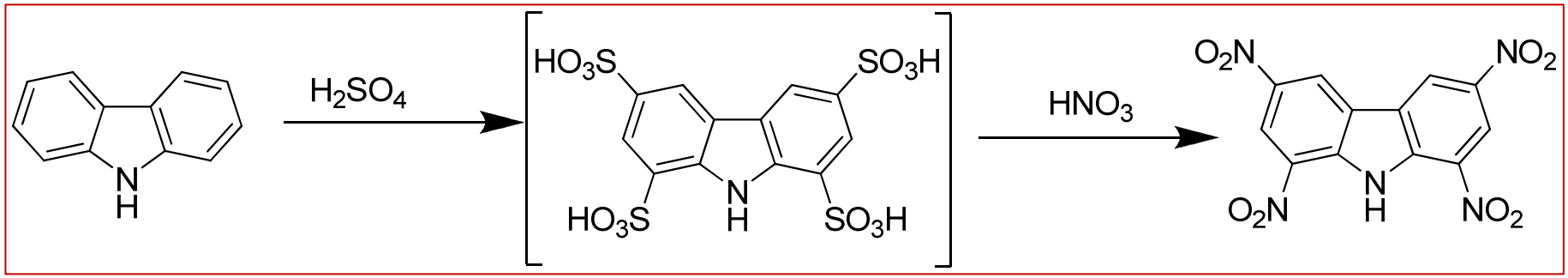
Dr. David Price*, Jim Haynes

BAE Systems, OSI

October 2010

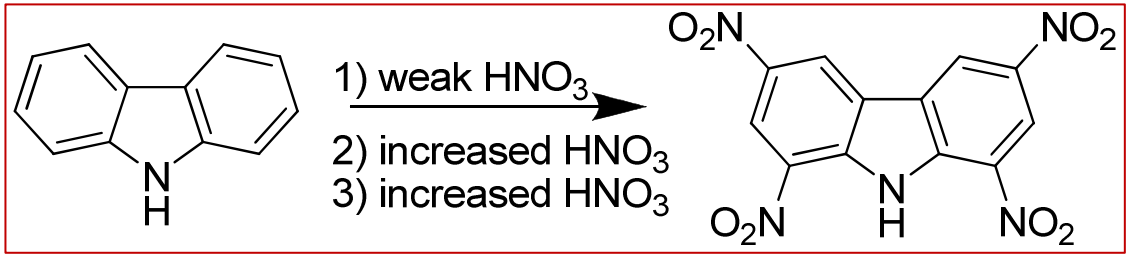
TNC history

- TNC is a minor yet critical ingredient used in 60mm, 81mm, and 120mm illuminating and IR payloads and ignition compositions.
- Current usage is approximately 1000-2000 lbs annually.
- Currently, there is no CONUS source of TNC.
- Standard process for synthesizing TNC utilizes sulfuric acid and nitric acid:



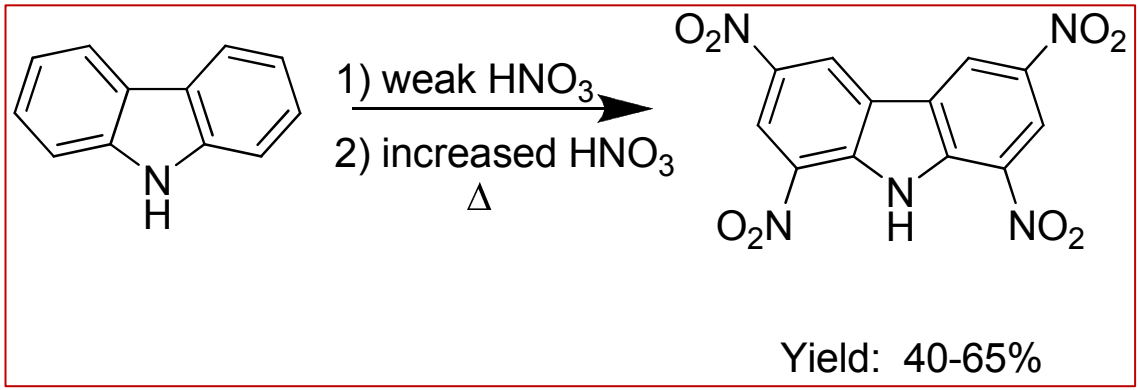
Prior TNC Activities at OSI

- Goal: To capitalize on HSAAP's infrastructure and develop a simple and safe process to synthesize TNC on a production scale in our Agile Facility.
- Initially, a multi-stage, three-pot process was developed using only nitric acid.



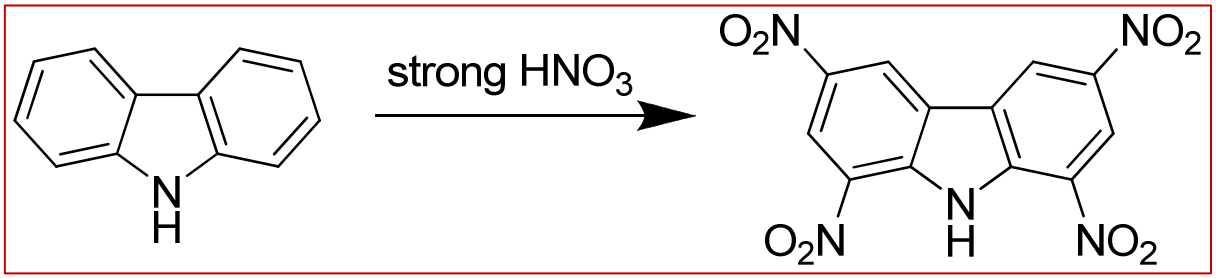
- However, final TNC purity was an issue and difficult to overcome.
- Also, a multi-pot process is not the most desired solution

Subsequent Activities: Nitration of Carbazole



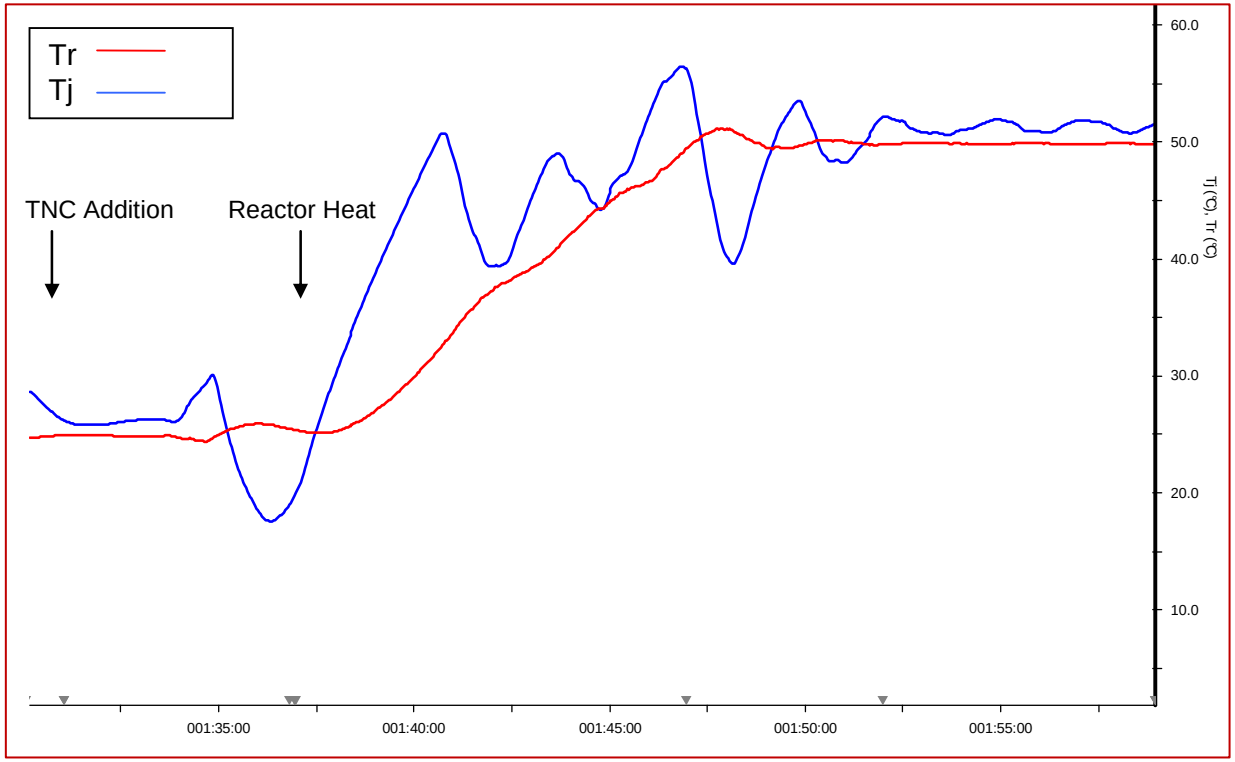
- One-pot, two-stage process developed in an effort to increase yield
- Yield: 40 - 65 % (0.83 - 1.35 lbs. TNC per pound carbazole)
- mp: 293.2 - 296.7°C
- Average Particle Size (PS) Range*: 20 μm (99.8% < 150 μm) to 80 μm (76.4% < 150 μm)
- However, this process still possessed significant safety concerns…

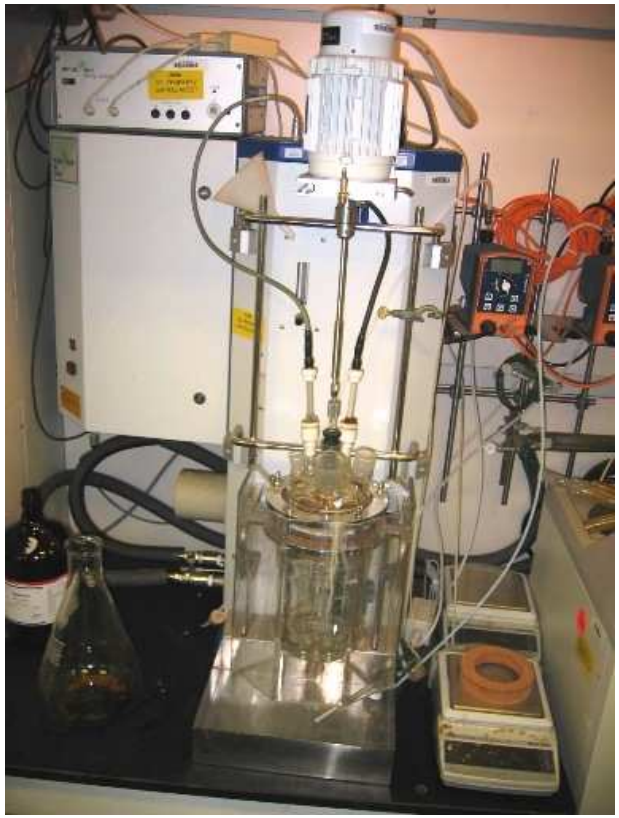
Current Activities: Nitration of Carbazole



- Current process is much simpler and safer.
- **One** pot, **one**-stage process
- Yield: ~50% (~1 lb. of TNC per pound carbazole)
- mp: >296°C

Reaction Calorimetry





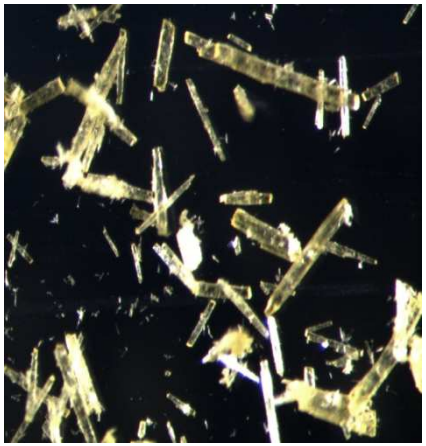
- Performed in Mettler RC1
- Heat-up was programmed incrementally in an effort to better observe exotherms.

Quench Studies: Composition of quench (25 g scale)

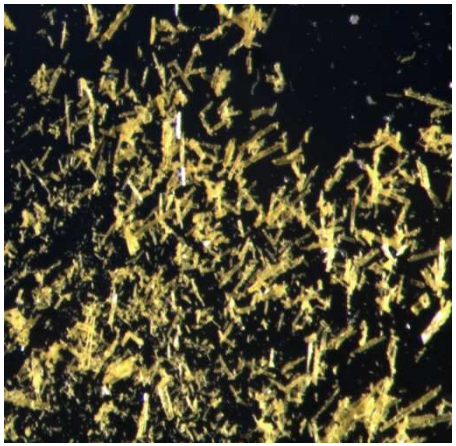
No quench

Dilute acid quench

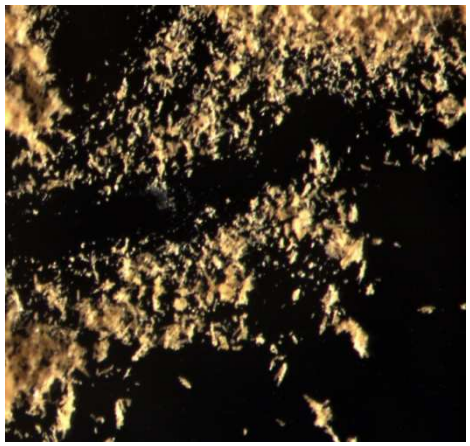
Water quench



PS: 80 μm



PS: 20-40 μm

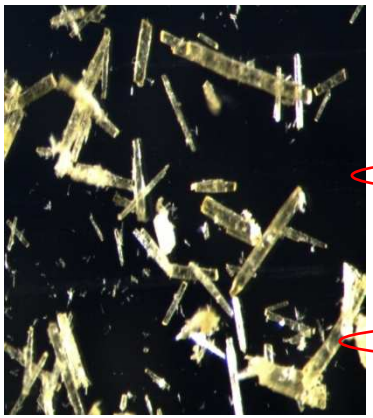


- TNC that crystallizes with no quench has larger particle size although lower yield

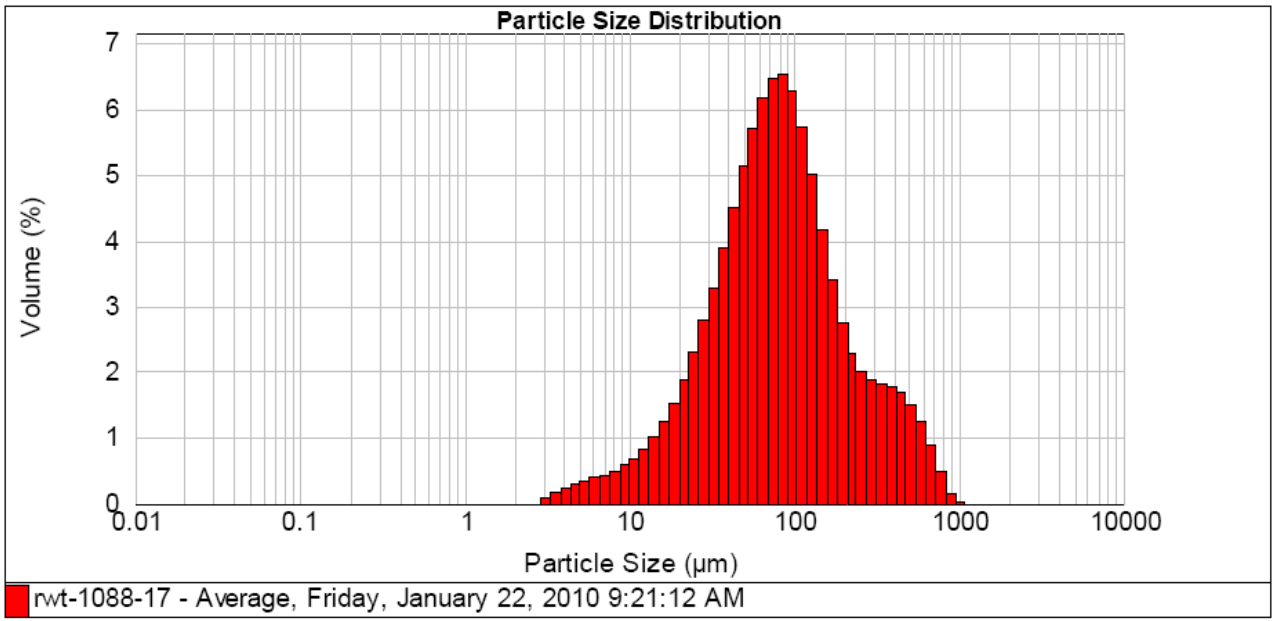
- A dilute acid quench provides a higher yield of TNC, comparable DSC MPs, and a smaller PSD.

(50x magnification)

Particle Size Distribution (No Quench)

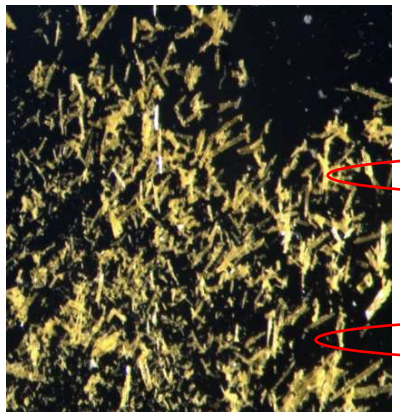


Mesh No	Aperture µm	Volume In %	Vol Below %
35	500	2.09	96.24
40	420	2.19	94.15
45	354	2.31	91.96
50	297	2.41	89.65
60	250	2.82	87.24
70	210	3.46	84.42
80	177	4.54	80.95
100	149	5.93	76.41
120	125		70.48

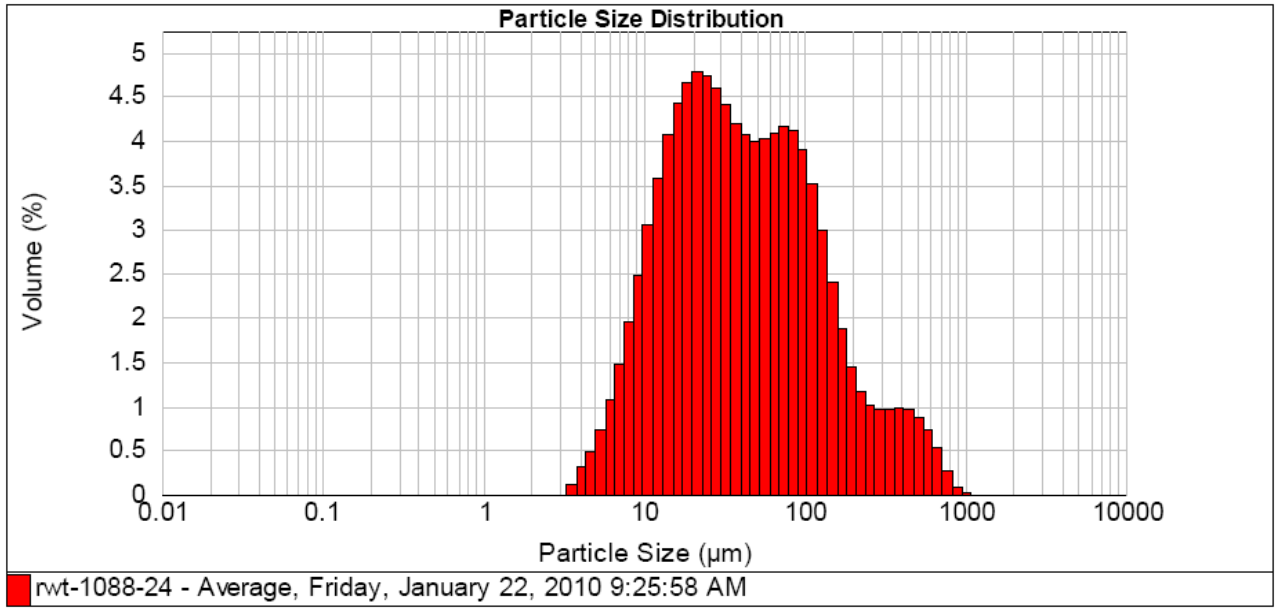


- Non-quenched TNC:
  - Meets spec for particle size
  - Has good color
- Nice crystal quality

Particle-Size Distribution (Dilute Acid Quench)



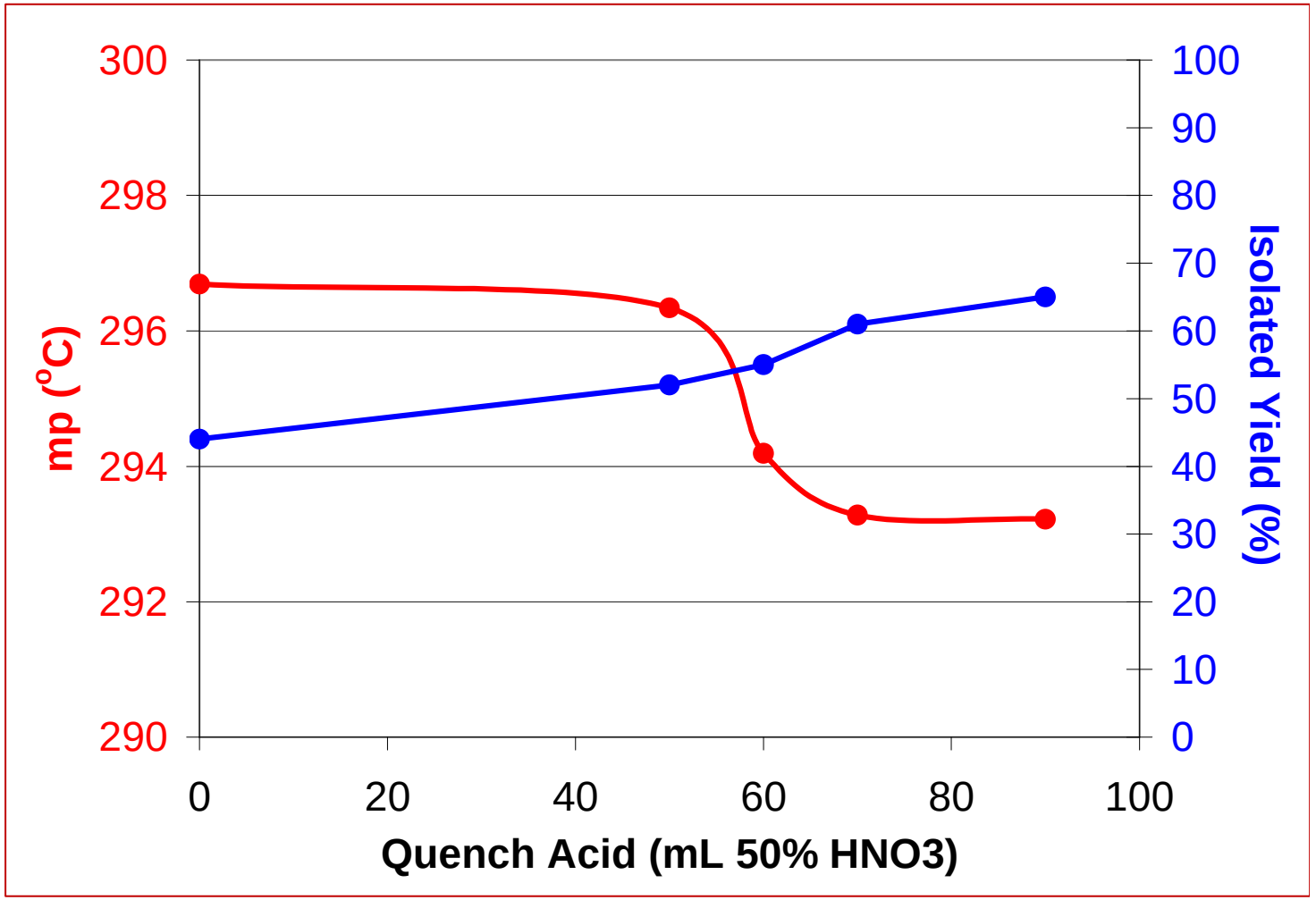
Mesh No	Aperture µm	Volume In %	Vol Below %
35	500	1.19	97.84
40	420	1.21	96.65
45	354	1.22	95.44
50	297	1.23	94.22
60	250	1.43	93.00
70	210	1.82	91.57
80	177	2.53	89.74
100	149	3.49	87.21
120	125		83.72



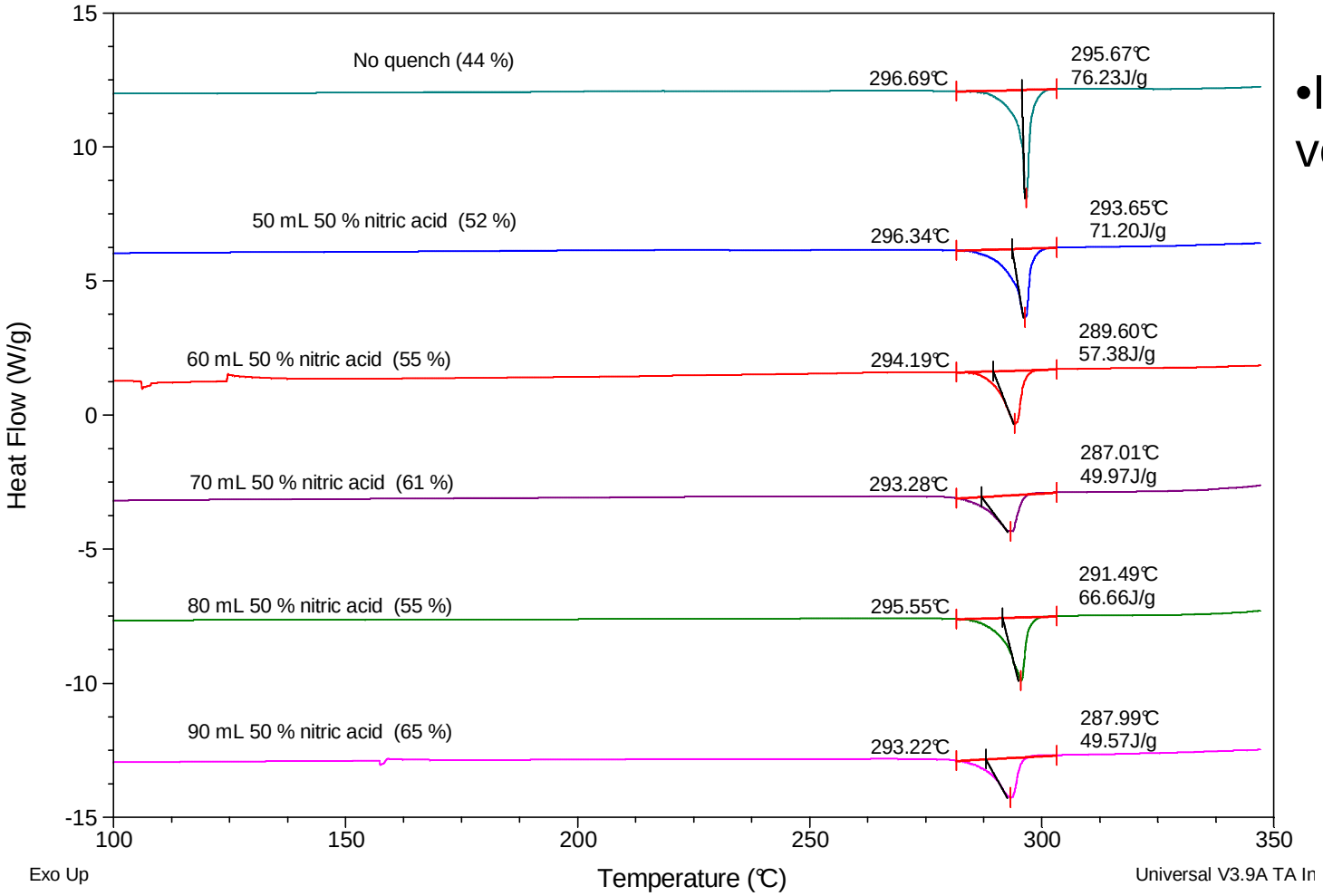
- Dilute Acid Quenched TNC:
  - Meets spec for particle size
  - Has good color
  - Bimodal PSD (slightly trimodal) due to smaller particles crystallizing upon quench

Effect of Quench Volume on Yield and Purity

- As quench volume increases:
- Yield increases
- Melting point decreases.

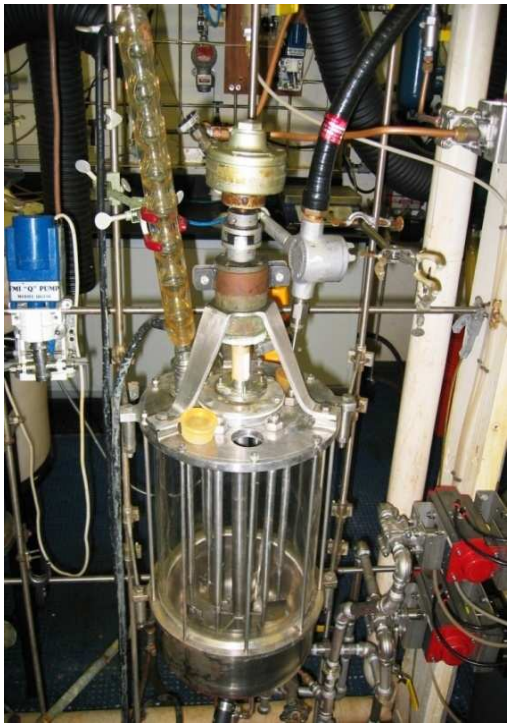


Effect of Quench on Purity (DSC)



- Increased quench volume leads to:
  - Lower melting points
  - Broader melting points (i.e. lower purity)

Scale-up Batches of TNC (DSC)



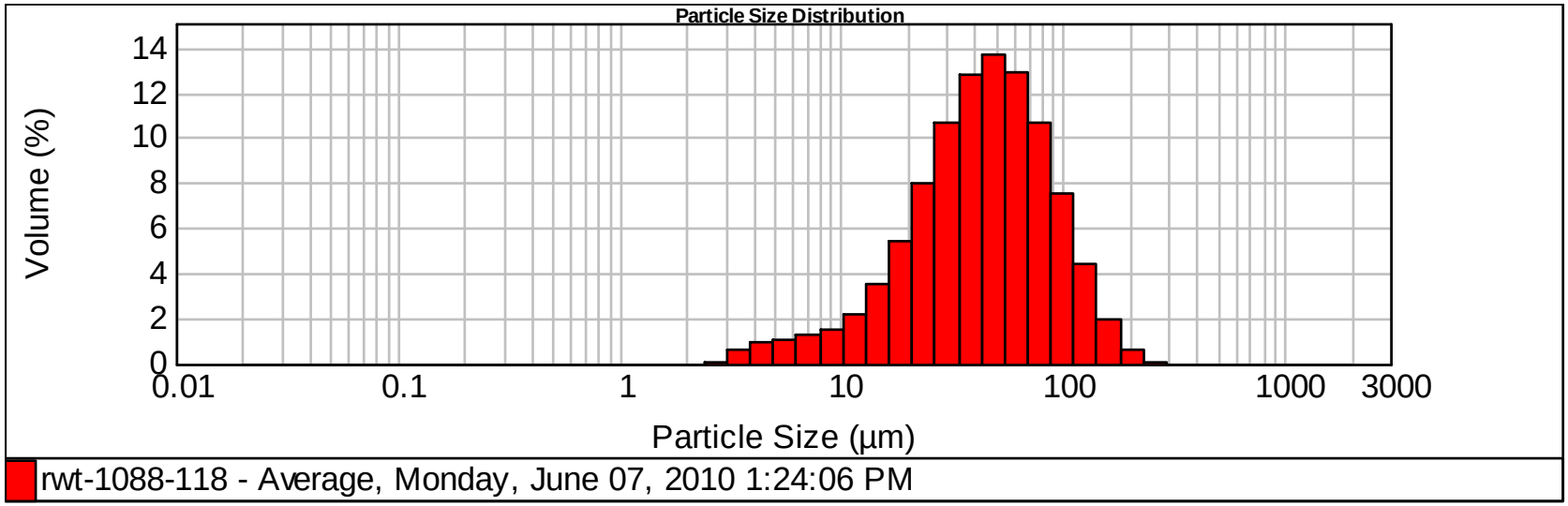
- TNC synthesis has been scaled to multi-pound batch sizes in:
  - 13 Liter reactors
  - 5-gallon glass-lined reactor

1 lb. Batches of TNC (PSD)

Mesh No	Aperture µm	Volume In %	Vol Below %
10	2000		100.00
12	1700	0.00	100.00
14	1400	0.00	100.00
16	1180	0.00	100.00
18	1000	0.00	100.00
20	850	0.00	100.00
25	710	0.00	100.00
30	600	0.00	100.00
35	500		100.00

Mesh No	Aperture µm	Volume In %	Vol Below %
35	500		100.00
40	425	0.00	100.00
45	355	0.00	100.00
50	300	0.00	100.00
60	250	0.03	99.97
70	212	0.16	99.81
80	180	0.52	99.29
100	150	1.37	97.93
120	125	2.66	95.27

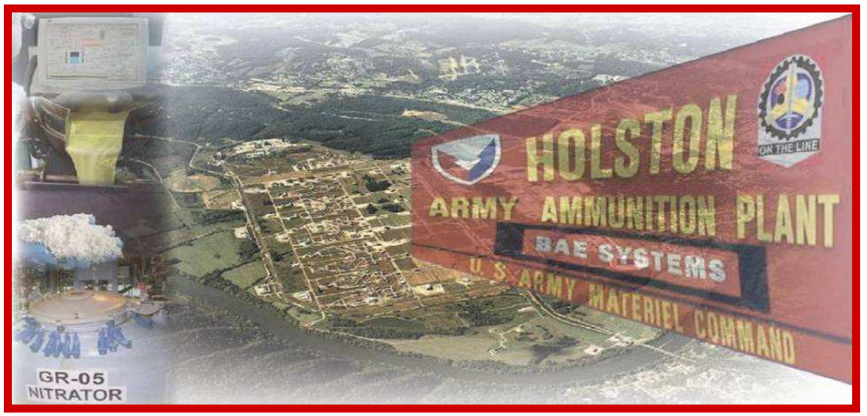
Mesh No	Aperture µm	Volume In %	Vol Below %
120	125		95.27
140	106	3.85	91.42
170	90	5.34	86.07
200	75	7.71	78.36
230	63	8.81	69.55
270	53	9.63	59.92
325	45	9.38	50.54
400	38	9.39	41.16



Summary

- Current process for TNC developed at HSAAP produces high purity TNC meeting all specs tested thus far.
- Nitration of carbazole is straightforward using minimal volume of nitric acid (no mixed acid systems required)
  - One-pot, One-stage process
  - Limited purification required
    - No additional steps needed

- Ready Scalable at HSAAP!



Acknowledgements

- RDECOM-ARDEC
  - Mr. Paul Vinh (funding)
  - Mr. Sanjeev Singh
- BAE Systems
  - Ms. Kelly Guntrum
  - Ms. Lisa Hale
  - Mr. Matt Hathaway