Laboratory and Pilot-Scale Synthesis of LLM-105

Insensitive Munitions & Energetic Material Technology Symposium 2015

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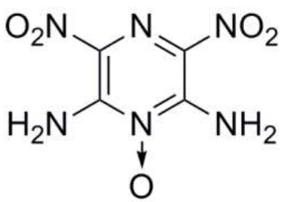
Program Overview



LLM-105

2,6-Diamino-3,5-dinitropyrazine-1-oxide

Property	RDX	LLM-105
Density (g/cm^3)	1.81	1.88
Exotherm Onset (^{o}C)	205	354
VOD (m/s)	8,850	8,667
Detonation Pressure (GPa)	35.2	32.72
Oxygen Balance (%)	-21.6	-37.0
Impact H_{50} (cm)	39	50
Friction (N)	164	>360

- LLM-105 Process Optimization:
  - Improvements in processing conditions to increase yield
- Laboratory Prove-out batches:
  - Synthesis of LLM-105 in laboratory 5-gallon reactor
- Pilot-Plant Scale-up:
  - Synthesis of LLM-105 in pilot-plant 50-gallon reactor

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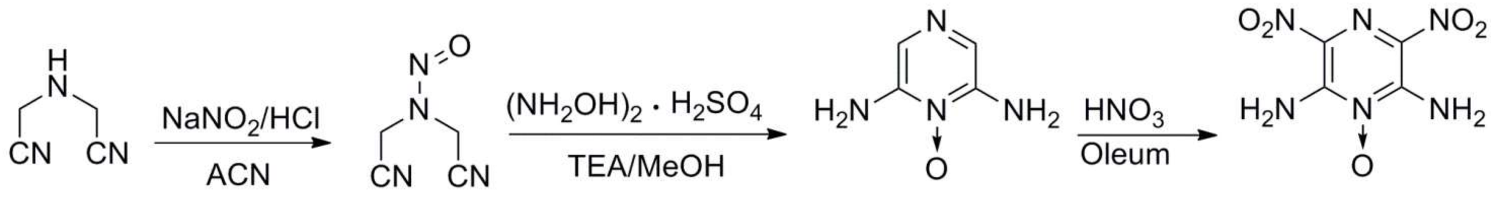
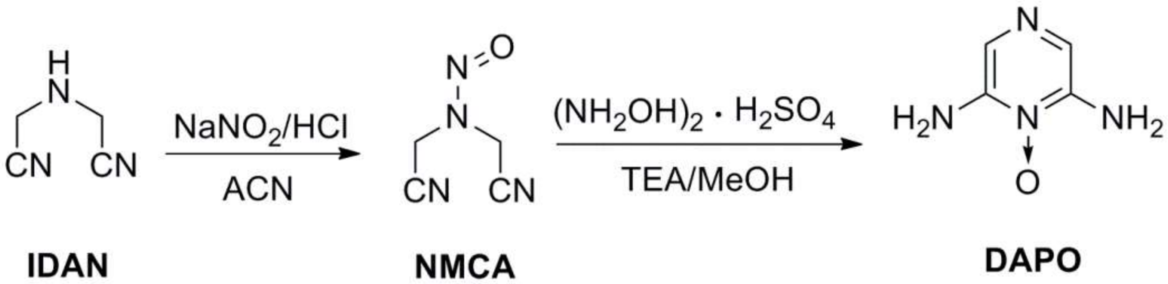
LLM-105 Synthesis Overview



IDAN NMCA DAPO LLM-105

- LLM-105 synthesized in a 3-step reaction from iminodiacetonitrile
  - Process developed at LLNL with refinements at NSWC, Nalas, and BAE Systems
- Route allows the energetic molecule to be synthesized in final step
- Baseline synthetic parameters have been defined: opportunity for additional improvement in yield of final two steps
- LLM-105 is insoluble in most solvents – final quench dictates particle size and purity

DAPO Process Improvement Efforts



- Current NCMA formation from commercially available iminodiacetonitrile is process friendly (yield >90%).
- Current DAPO synthesis process gives a moderate yield:
  - Oligomerization and polymerization likely competing.
  - DAPO easily isolated from reaction mixture
- DAPO process improvements (yield increase of ~15%):
  - Addition rate and order of TEA and NCMA
  - Dryness of solvents and reagents
  - Use of higher molecular weight alcohols (steric hindrance)

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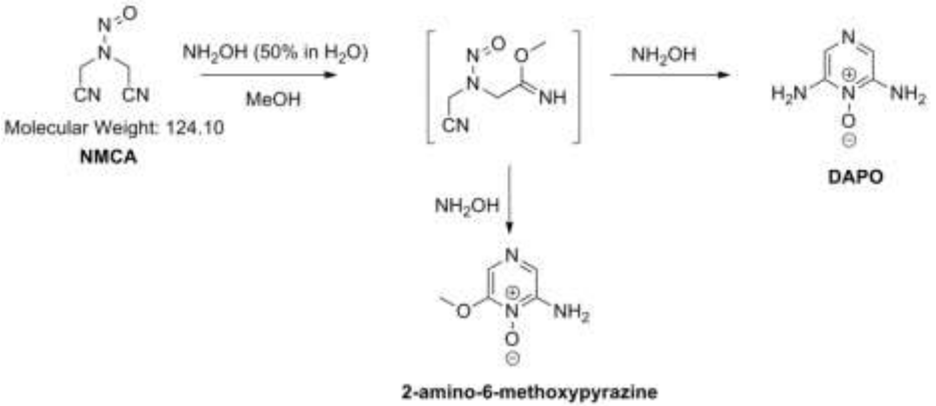
DAPO Process Improvements

Proposed Mechanism:



- 2-Amino-6-methoxypyrazine source of impurity when alcohol is used
- Various reaction conditions excluding the alcohol have been explored
- Reduction or removal of the alcohol prevents the formation of DAPO
  - Suggests both solvents play a role in the mechanism of the reaction, owing to the lack of steric congestion and relatively potent nucleophilicity
- Also evaluated alternate synthesis routes: Chichibabin Amination and DDQ oxidation
  - Neither routes proved effective

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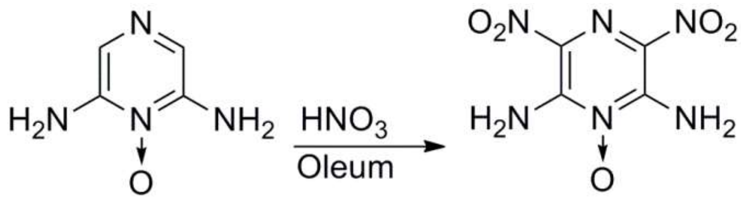
LLM-105 Synthesis Process Improvements



DAPO **LLM-105**

- LLM-105 synthetic baseline parameters:
  - Nitration of DAPO in oleum followed by water quench
  - Significant foaming observed during and after nitric acid addition
  - Off-gassing suggests consumption of the intermediate or final product
- LLM-105 Process Improvements:
  - Reaction Temperature (higher temperatures lead to decreased yield and foaming)
  - Reduction in nitric acid loading (increased yield and reduction in foaming)
  - Reactant concentration (increased throughput)
  - Oleum Concentration (greatly effects yield of LLM-105)
  - Final Reaction Temperature (reduction in foaming)

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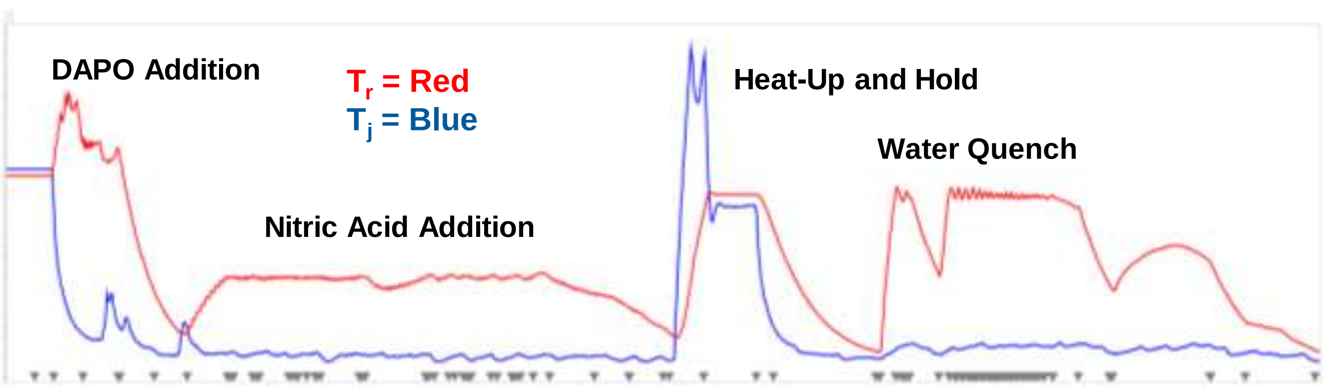
RC-1 Synthesis of LLM-105

- Optimized process initially scaled to 2-L RC1 Reactor
  - Quantitative measurement of reaction heat flow
  - Insures heat removal capacity in 5-gallon and pilot equipment
  - Controllable exotherms seen throughout reaction

Process Step	Comment
DAPO/Oleum Solution Formation	Mild exotherm observed
Nitric Acid Addition	Exotherm controlled through addition rate
Aqueous Quench	Heat controlled by quench rate



LLM-105 Scale-up (5-gallon)

- Largest lab-scale synthesis of LLM-105 in a 5-gallon glass-lined reactor (7 batches)
- Process readily scaled from RC-1 reactor
  - No unusual exotherms observed
- Further process improvements were performed on this scale:
  - Reaction temperatures
  - Addition times
  - Pre-quench reaction temperature
- LLM-105 was easily isolated and washed to remove residual acid

LLM-105 5-Gallon Analytical Results

- Process gives LLM-105 in high yields and purity with low residual acidity:

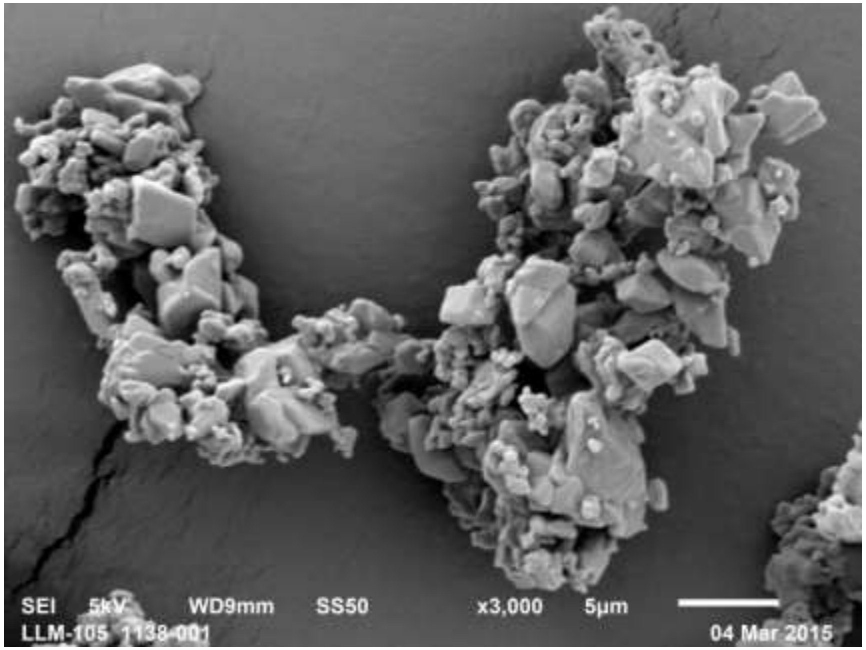
Batch	Yield (%)	HPLC Purity (%)	Particle Size (µm)	DSC Onset (°C)	Nitrate (wt%)	Sulfate (wt%)
Batch 1	62.3	100	4.8	315	0.21	0.33
Batch 2	63.6	100	6.3	306	0.25	1.00
Batch 3	64.6	100	5.5	342	0.23	1.70
Batch 4	63.4	100	5.0	330	0.16	1.68

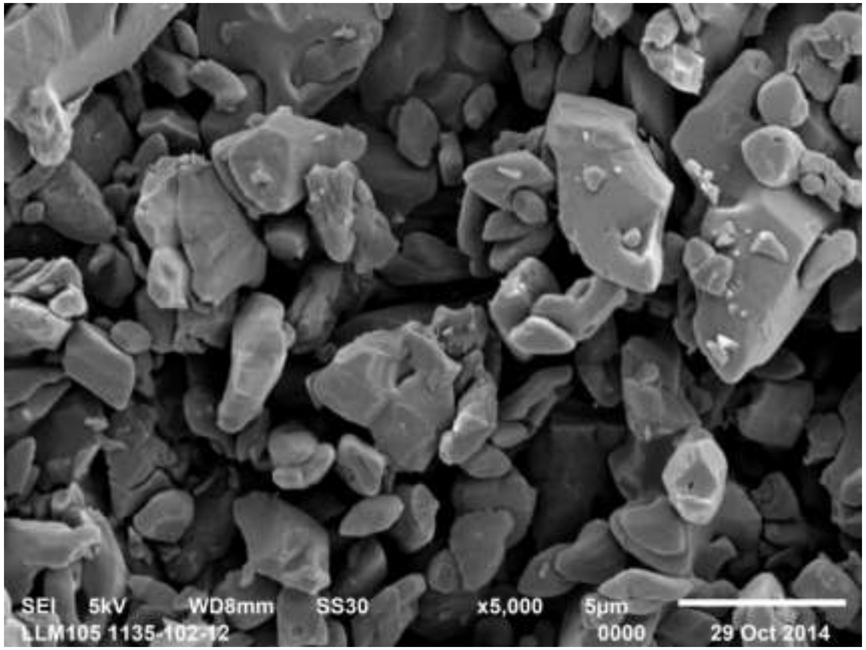
LLM-105 easily purified to reduce acid levels further:

Batch	Nitrate (wt%)	Sulfate (wt%)
Batch 3	0.23	1.70
Batch 3 (Purified)	0.09	0.08

LLM-105 SEM

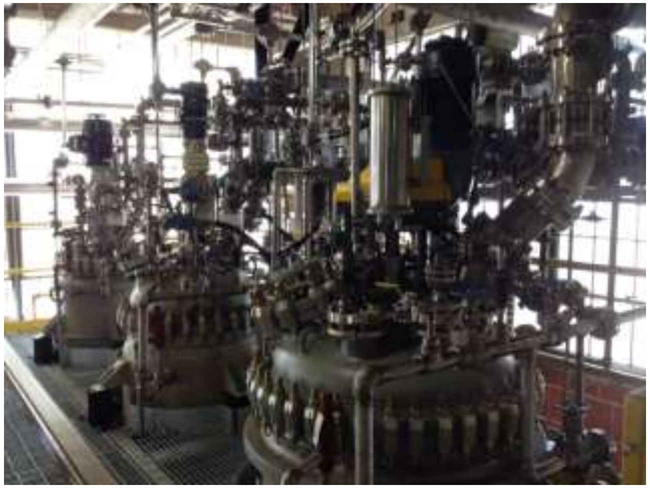
- LLM-105 crystals match shape and size seen on smaller scale
- SEM results match Malvern results of small, uniformly distributed particles
- Larger particles may be obtained in pilot plant using slower quench





BAE Systems Energetics Pilot Plant

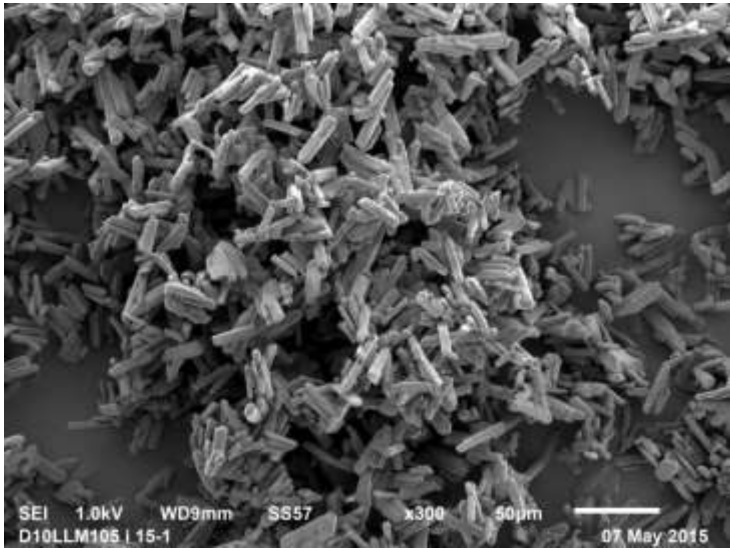
- 50-, 100-, 200-Gallon glass-lined reactors
- Better transition from lab scale to Production Facilities
- Commissioning completed Fall 2013
- Several ingredients successfully produced (military and commercial):
  - Class 1 NTO, PrNQ, NONA, TATB, DNMT, Granular IMX-104
- Ongoing upgrades to capabilities:
  - Sub-ambient chiller system (2014)
  - Stainless-steel filter press (2014)
  - Vacuum system (2015)
  - 100- and 400-gallon formulation stills (2015)

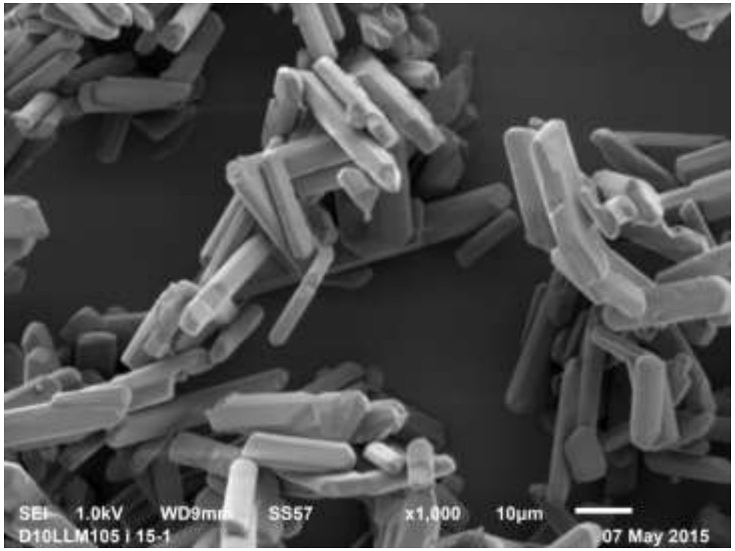


LLM-105 Pilot Plant

- LLM-105 successfully produced in Pilot Plant **(>100-lbs)** – May 2015

Batch	HPLC Purity (%)	Particle Size (µm)	DSC Onset (°C)	Nitrate (wt%)	Sulfate (wt%)
Batch 1	100	14.0	311	0.15	0.22
Batch 2 (Purified)	100	11.5	347	0.02	0.08





Conclusions

- LLM-105 shows potential as an insensitive high-temperature stable crystalline explosive ingredient
- Baseline LLM-105 reaction conditions exhibited a number of issues
- Optimized process conditions allowed for safe production of LLM-105 on the laboratory and 5-gallon scale
  - Increase in yield, throughput, and decrease in problematic foaming
- Initial LLM-105 pilot-scale run in May 2015
- Formulation efforts using LLM-105 are currently ongoing

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Acknowledgements

SERDP DOD • EPA • DOE	**Strategic Environmental Research and Development Program** Robin Nissan -Program Funding
USAPHC ARMY INSTITUTE OF PUBLIC HEALTH	**US ARMY Public Health Command** Dr. Mark Johnson and Dr. William Eck USA Public Health Command (USAPHC) -Providing expertise in toxicology
NALAS Engineering Services, Inc.	**NALAS Engineering** Jerry Salan, Dr. David J. am Ende -Starting material, process optimization
BAE SYSTEMS INSPIRED WORK	**BAE SYSTEMS** Dr. Neil Tucker, Brian Alexander, Matt Hathaway, Dr. Jeremy Headrick, Robyn Wilmoth, Kelly Guntrum, Chris Long, -Synthesis, Formulation and Testing