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Laboratory and Pilot-Scale Synthesis of LLM-105

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ABSTRACT

LLM-105 is a developmental explosive that has greater performance than TATB, while still maintaining excellent thermal, shock, spark, friction, and impact sensitivity. Formulations with LLM-105 are of interest for a number of booster applications within the DOD including PBXN-9 and PBXN-5 replacements. Although LLM-105 has been of great interest to the energetics community for some time, it has only been synthesized on the laboratory scale to date. The originally developed synthetic procedures still needed to be optimized for pilot- and full-scale production.

This paper describes the recent LLM-105 developmental effort by BAE Systems on the laboratory and pilot-scale at the Holston Army Ammunition Plant. The initial laboratory effort determined the synthetic robustness and heat of reaction of the LLM-105 synthesis process, which was then proven-out on the 5-gallon laboratory scale. This process was then prepared for scale-up to the Energetics Pilot Plant at Holston.

1. INTRODUCTION

LLM-105 is a developmental explosive that has greater power than TATB, while still maintaining excellent thermal, shock, spark, friction, and impact sensitivity. The LLM-105 synthetic procedures, which were developed at LLNL, still need to be optimized. The current routes produce material with either a large amount of impurities, or the wrong crystal size and morphology. Formulations with LLM-105 are of interest to both the DOD and the DOE.

The scope of this effort is to optimize the synthesis of DAPO and LLM-105 on the lab-scale using the new DAPO process. Currently, the new process produces material with low-levels of impurities while still giving a decent particle size. However, there is still a need for further optimization. Upon optimizing each of the reaction steps, the new process would be available for scale-up

2. LLM-105 Synthesis Program Overview

As shown in the Table below, LLM-105 exhibits excellent thermal, shock, spark, friction, and impact sensitivity while having performance closer to RDX than TATB.

Table 1

Property	RDX	LLM-105
Density (g/cm^3)	1.81	1.88
Exotherm Onset (°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

There are three major areas of focus for this program:

a. LLM-105 Process Optimization:
   - Improvements in processing conditions to increase yield

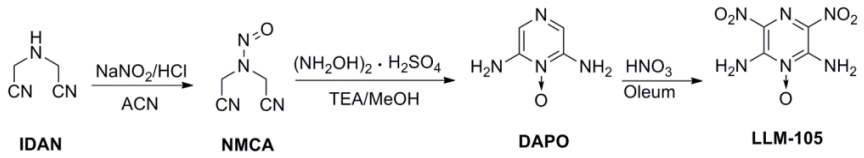
b. Laboratory Prove-out batches:
   - Synthesis of LLM-105 in laboratory 5-gallon reactor

c. Pilot-Plant Scale-up:
   - Synthesis of LLM-105 in pilot-plant 50-gallon reactor

LLM-105 is synthesized in a 3-step reaction from iminodiacetonitrile through a process that was developed at LLNL with refinements at NSWC, Nalas, and BAE Systems. The route allows the energetic molecule to be synthesized in final step as shown in Figure 1 below. Baseline synthetic parameters have been defined for this reaction, however there is an opportunity for

additional improvement in yield of final two steps. Also, the LLM-105 is insoluble in most solvents, therefore, the final quench dictates both particle size and purity.

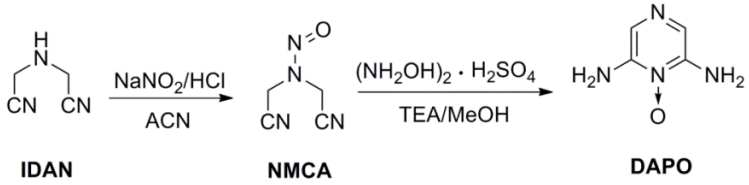
Figure 1



2.1 DAPO Process Improvements

Current NCMA formation from commercially available iminodiacetonitrile is process friendly (yield >90%) , as shown below in Figure . Because of the ease of synthesis and high yields, there was little need to investigate this reaction further.

Figure 2



On the other hand the current DAPO synthesis process (Figure 2) was identified as needing further refinement. The original process gave a moderate yield with oligomerization and polymerization likely competing, however the DAPO product easily isolated. An effort was undertaken to understand, and improve the chemistry of the DAPO synthesis. This lead to DAPO process improvements with an increase in yield of ~15%). Parameters optimized include:

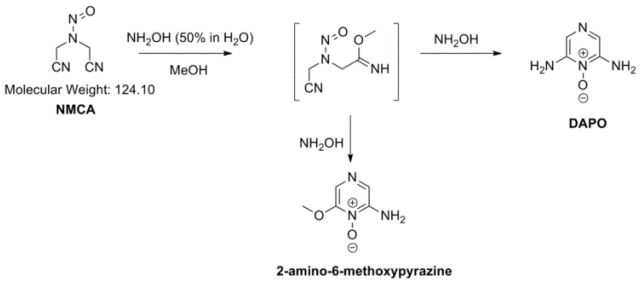
a. Addition rate and order of TEA and NCMA (increase in yield)

b. Dryness of solvents and reagents (increase in yield)

c. Use of higher molecular weight alcohols for steric hindrance (increase in yield)

It was identified that 2-amino-6-methoxypyrazine is a source of impurity when any alcohol is used in the reaction. Various reaction conditions excluding the alcohol have been explored, however, reduction or removal of the alcohol prevents the formation of DAPO. This suggests both solvents play a role in the mechanism of the reaction, owing to the lack of steric congestion and relatively potent nucleophilicity (Figure 3). There was also an effort undertaken to evaluate alternate synthesis routes including using a Chichibabin Amination and DDQ oxidation. However, neither routes proved effective.

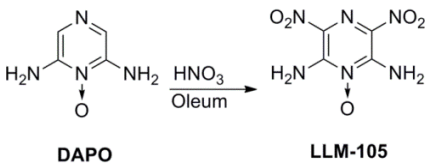
Figure 3



2.2. LLM-105 Synthesis Process Improvements

The LLM-105 synthetic baseline parameters were developed by LLNL with further refinements by NALAS Engineering and the Navy (Figure 4). LLM-105 is synthesized by the nitration of DAPO in oleum followed by quenching into water or ice. Significant foaming observed during and after nitric acid addition. The off-gassing suggests consumption of the intermediates.

Figure 4



A number of process improvements for the LLM-105 synthesis process were developed. These improvements lead to a better understanding of the process including increasing the yield and decreasing the amount of foaming observed. The process improvements include:

a. Reaction Temperature (higher temperatures lead to decreased yield and foaming)

b. Reduction in nitric acid loading (increased yield and reduction in foaming)

c. Concentration of solids (increased throughput)

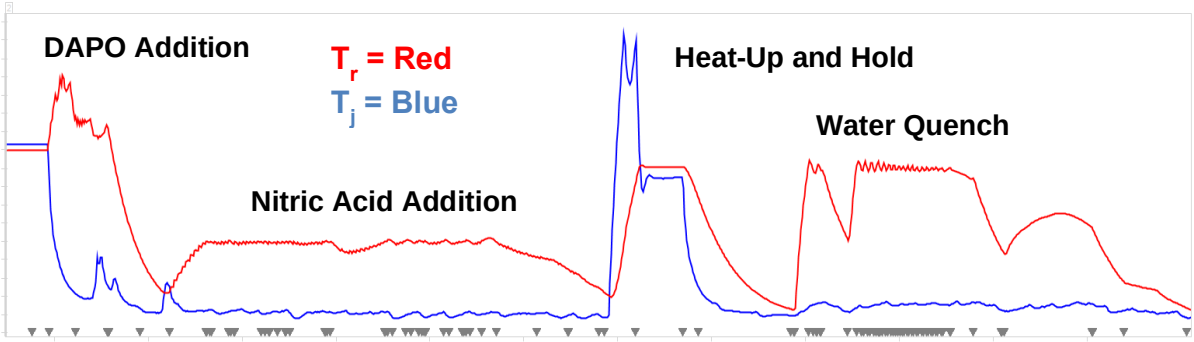
d. Oleum Concentration (greatly effects yield of LLM-105)

e. Final Reaction Temperature (reduction in foaming)

2.3 Synthesis of LLM-105 on the RC-1

The optimized process was initially scaled to Mettler Toledo 2-L RC1 Reactor, in order to give a quantitative measurement of the reaction heat flow. This insures heat removal capacity in 5-gallon and pilot equipment. As expected, only controllable exotherms were seen throughout reaction by controlling the addition rates throughout the synthesis. The RC-1 reaction is shown below in Figure 5.

Figure 5



2.4 LLM-105 Scale-Up (5-gallon)

The largest lab-scale synthesis of LLM-105 was performed in 5-gallon glass-lined reactor (3 batches completed). The process readily scaled from RC-1 reactor with no unusual exotherms observed. Although not originally planned, some further process improvements were performed on this scale including modifications to the reaction temperatures, addition times, and pre-quench reaction temperature. These improvements lead to additional increase in yield and some reduction of the foaming. LLM-105 was easily isolated and washed to remove most of the residual acid. The process gives LLM-105 in high yields and purity with low levels of residual acidity as shown below in the Table 2. LLM-105 from the three batches are shown below in Figure 6.

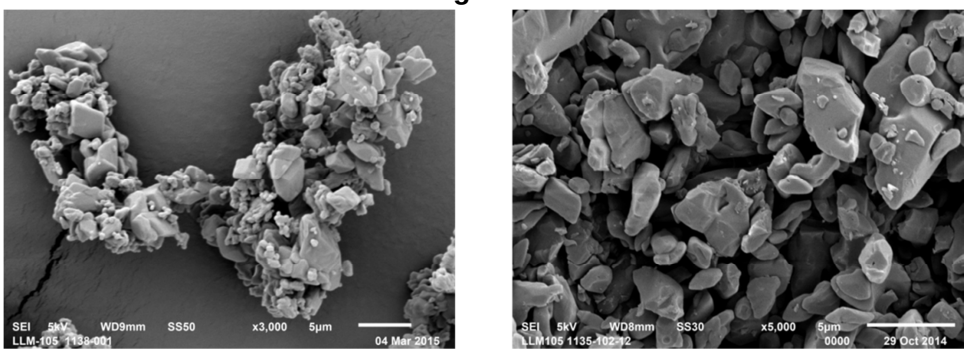
Figure 6

Table 2

Batch	HPLC Purity (%)	Particle Size (μm)	Residual Acid (%)	DSC Onset (°C)
Batch #1	99.6	5.5	0.59	347.4
Batch #2	99.7	7.2	0.39	353.7
Batch #3	99.2	7.9	0.42	358.5

The particle size by SEM matches shape and size seen on smaller scale. It also confirms the Malvern results of small, uniformly distributed particles as shown in Figure 7. Larger particles may be obtained during pilot-plant effort using slower quench.

Figure 7



3. CONCLUDING REMARKS

LLM-105 shows potential as an insensitive high-temperature stable crystalline explosive ingredient. Baseline LLM-105 reaction conditions exhibited a number of issues including moderate yields and excessive foaming during and after the nitration. Optimized process conditions allowed for safe production of LLM-105 on the laboratory and 5-gallon scale, which included an increase in yield, throughput, and a decrease in the problematic foaming. The process is now ready for scale-up to the Energetics Pilot Plant at Holston, with the initial LLM-105 pilot-scale run scheduled for May 2015. In addition, on this program, formulation efforts using LLM-105 are currently ongoing.

4. ACKNOWLEDGEMENTS

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