

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

Andrew Pearsall, K. M. Hanson, Shilpa P. Lad, Jerry Salan
Chemical Development Branch/Indian Head Division, Naval Surface Warfare Center
Indian Head, MD, 3019 Strauss Ave, Bldg 855, Indian Head, MD 20640

ABSTRACT

Indian Head Division, Naval Surface Warfare Center (IHD NSWC) developed and scaled-up processes to manufacture 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105). This work was sponsored by the Joint Insensitive Munitions Technology Program (JIMTP) with leveraged funding from the Department of Energy. LLM-105 has performance superior to TATB and TATB like insensitivity. Early synthesis and process development work was completed by Dr. Phillip Pagoria of Lawrence Livermore National Laboratory (LLNL) before transitioning the synthesis to IHD NSWC for scale-up. The process was evaluated utilizing Mettler Toledo's RC1 Reaction Calorimeter and in-situ tools including a particle counter and camera. The heat flow data generated from the reaction calorimeter provided necessary information to identify safe operating temperatures while avoiding decomposition reactions. The particle counter and camera provided critical data to develop process conditions affording the desired particle size distribution and morphology. The effect of processing conditions on purity, conversion, and crystal characteristics were documented. A recrystallization study on LLM-105 included the use of an ionic liquid solvent to aid in dissolution. The successful use of ionic liquids in recrystallizing highly insoluble energetic materials has been previously reported by LLNL and expanded upon by IHD NSWC. The recrystallization study targeted alternative methods to achieve desired particle size, purity, and morphology of LLM-105.

INTRODUCTION

LLM-105 was first synthesized by Lawrence Livermore National Laboratory (LLNL), a Department of Energy (DOE) Laboratory through a modification of a procedure described in a Russian patent referenced by Pagoria, et al¹. LLM-105 is an insensitive energetic material. The overall performance, cold temperature performance, divergence properties, and thermal stability of LLM-105 make it very promising for several applications, including insensitive boosters.²

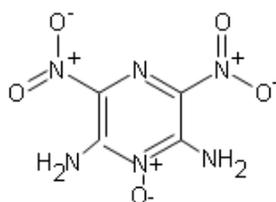


Figure 1: LLM-105 Chemical Structure

Current formulation efforts have targeted the replacement of triaminotrinitrobenzene (TATB) with alternative materials including LLM-105. There is a specific interest in targeting fielded IM compliant booster materials containing TATB that have demonstrated cold temperature performance challenges². The predicted power of LLM-105 is 20-25% above that of TATB (See Table 1). LLNL has demonstrated LLM-105 has superior performance when compared with

suspended in a solution. A Particle Vision and Microscopy (PVM) probe was also used, allowing for in-situ camera images to be taken.

RESULTS AND DISCUSSION

Reducing Quantity of TFA

The oxidation of ANPZ to LLM-105 was successfully completed by adding ANPZ to a quantity of TFA. Hydrogen peroxide was slowly dosed forming the trifluoroperoxy acetic acid. This equilibrium reaction resulted in concentrations of hydrogen peroxide, TFA, and the peroxy acid in solution. In order to maintain a fresh amount of hydrogen peroxide the overall dose was split into two doses. In addition, attempts were made to increase conversion of ANPZ to LLM-105 by increasing the temperature of the reaction mixture after the first dose but prior to the second dose. The hope was to increase the solubility of the ANPZ and overall kinetics to achieve a higher conversion.

Attempts made to reduce the TFA acting as a solvent without compromising yield or purity of the product were completed in the laboratory. IHDIV, NSWC scientists were able to reduce the amount of TFA by 80% utilizing an alternative co-solvent in sulfolane³. The process produced good quality LLM-105 in high yield. However, the explosive formulations requirements were not conducive to the modified particle size and crystal morphology produced with the sulfolane process, so sulfolane was abandoned for future scale-up operations. A comparison of the morphology resulting from the two synthetic routes is presented in Figure 3. The in-situ camera was used and assisted the reaction monitoring. The change in morphology from ANPZ to LLM-105 was obvious using the in-situ camera.

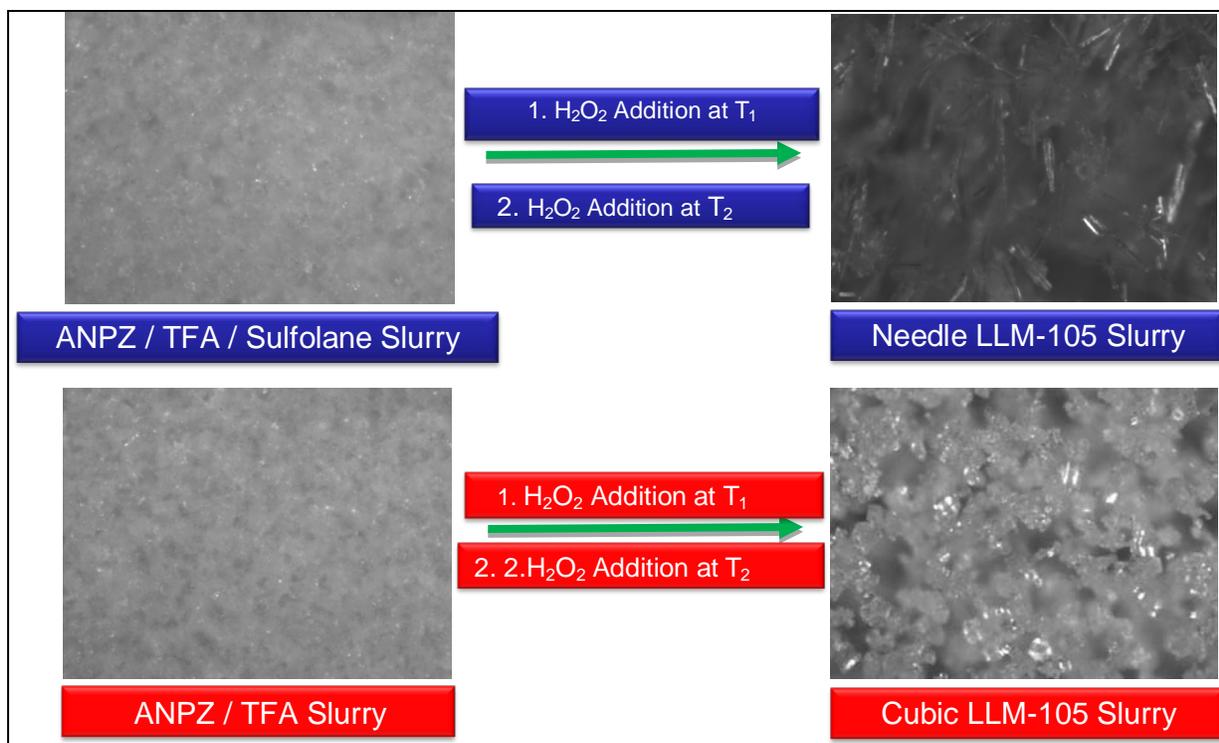


Figure 3: PVM Comparison of a reaction with and without use of Sulfolane as a solvent

The process was also tracked using FBRM. The particle trends show the transformation of the heterogeneous mixture containing small-particle size ANPZ into the larger particle size LLM-105 (Figure 4). The linear trends were the first indication that the reaction was significantly mass transfer limited. As predicted, the increase in temperature resulted in increase solubility of ANPZ. This is confirmed through the FBRM data. Notice the inflection point and disappearance of the finer ANPZ particles (Figure 4) and growth of the more coarse LLM-105 particles during the heating ramp. Although this reaction was not monitored directly using traditional analytical techniques, the reaction was monitored using the particle counter and in-situ camera.

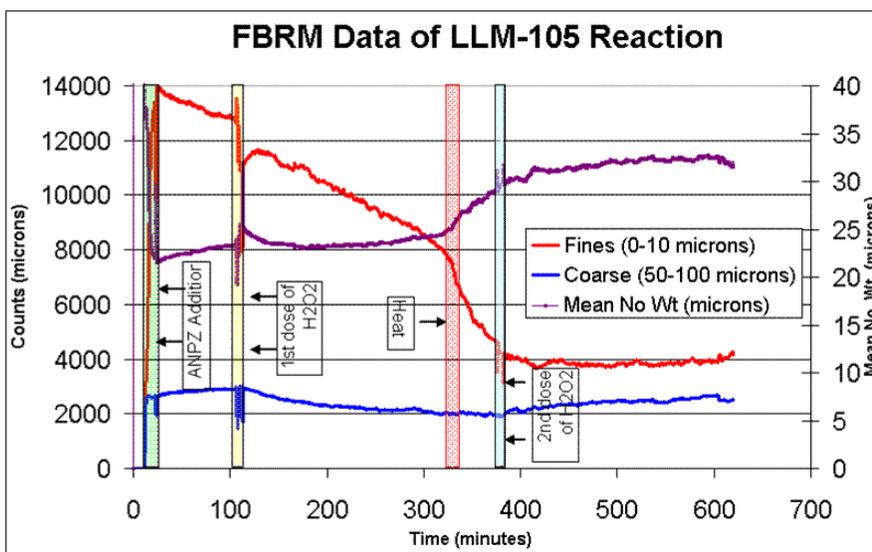


Figure 4: FBRM Data of LLM-105 Reaction with a Temperature Ramp

Scale-up to 50-liter Reactor

A typical energy balance is completed for each reaction prior to scale-up. The oxidation was evaluated for rate of heat output and total heat output. However, it should be noted that the heat of reaction during a temperature ramp is not easily obtained. This was evident during scale-up to the 50-liter reactor. At the 50-liter scale an exotherm resulted in the reaction temperature reaching the boiling point of the solvent (Figure 5). This event was not expected but examined in detail following this event using the RC1. Initial observations indicated that the dose of hydrogen peroxide exceeded the limits of mass transfer for the system to convert ANPZ to LLM-105. This results in an accumulation of the peroxy acid ready to react once ANPZ is in solution. Sufficient time for the mass transfer limited reaction to take place was not provided at the 50-liter scale. As the reaction mixture was warmed, the mass transfer improved making more ANPZ available to react. This resulted in a higher rate of conversion of starting material to product. The higher rate of conversion resulted in a higher heating rate (Joules/second). The accumulated heat warmed the reaction mixture to the boiling point of the solvent.

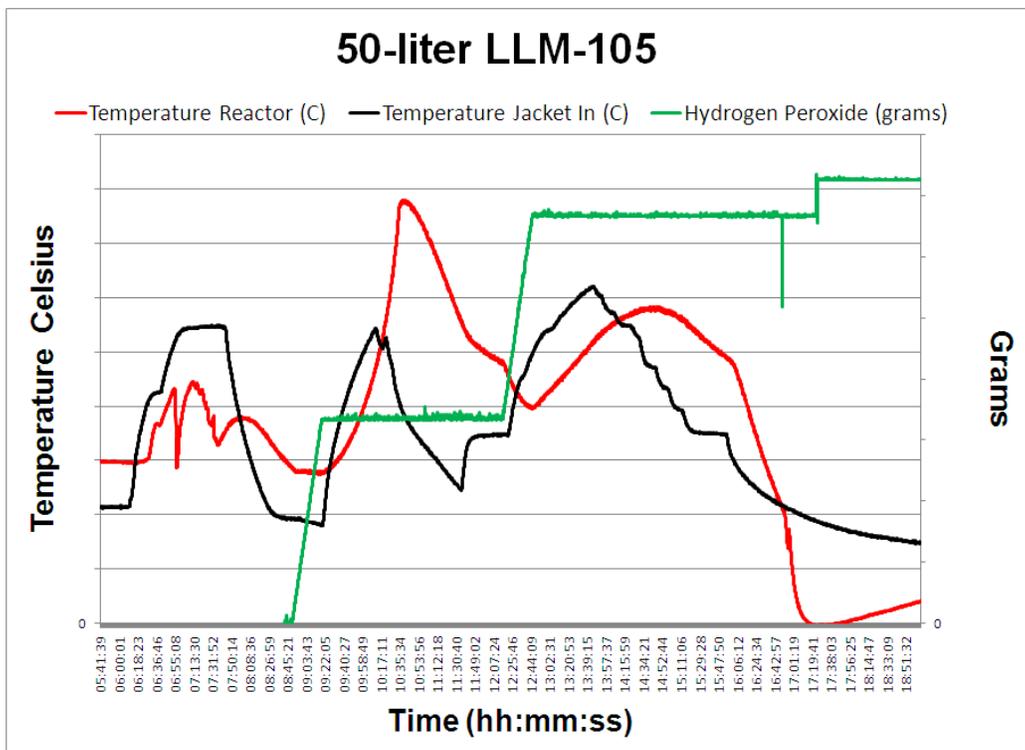


Figure 5: 50-liter temperature and dosing trend data

It became evident that changes were required to safely produce material at this scale and any larger scale.

Scale down study: Synthesis

A scale down study was completed to further evaluate the process based on mass transfer, kinetics, decomposition reactions and heat of accumulation. This information would be used to scale the reaction to a 100-gallon reactor.

The first series of reactions included the evaluation of the heat generated during the temperature ramp. An initial reaction was completed to identify heat profiles of the temperature ramp without the presence of the starting material ANPZ. This was compared to an experiment following the same temperature ramp with the starting material ANPZ in the reactor. Figure 6 shows a constant difference between the jacket temperature (T_j) and reactor temperature (T_r). When the experiment is completed with the ANPZ present T_r approaches and eventually exceeds T_j ; this is an indication that a chemical reaction is taking place during the ramp (Figure 7).

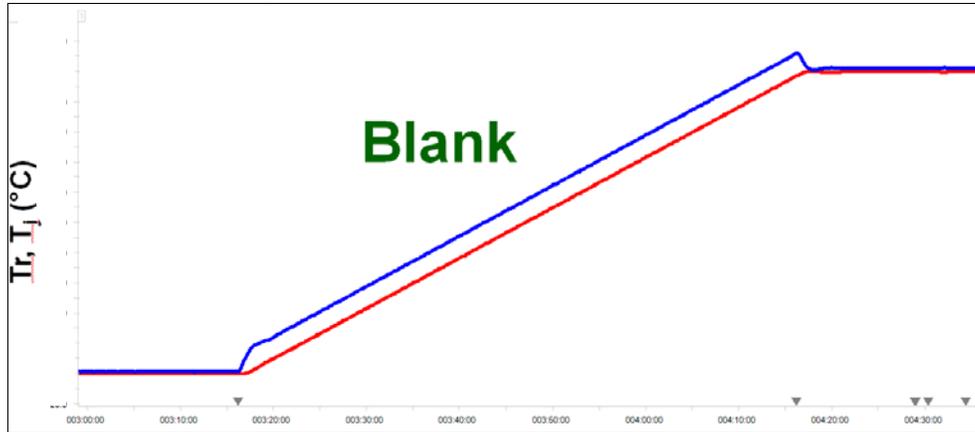


Figure 6: Reactor and jacket temperature plotted during temperature ramp (Blank)

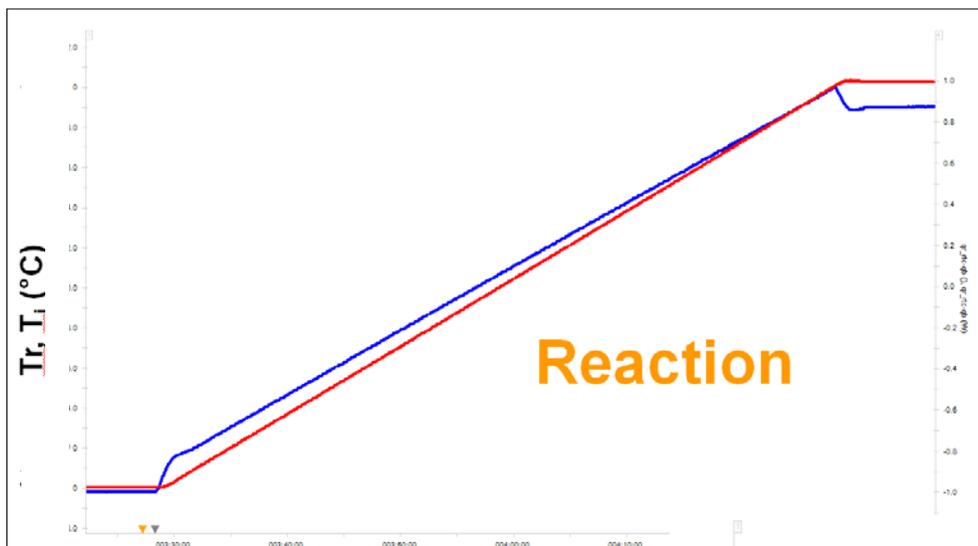


Figure 7: Reactor and jacket temperature plotted during temperature ramp (Reaction)

It was decided at this point that the reaction heat could not be controlled during the temperature ramp and that the ramp would be eliminated for safety reasons. Alternatively, the optimal dosing rate at each temperature could have been identified that would minimize the amount of accumulated peroxy acid present at any given time. It was decided to proceed with a single temperature dose to ease labor requirements in the plant environment. Subsequent experiments would be completed at a single temperature (no ramp). Reactions were completed at two different increasing temperatures (T_1 , T_2) approaching the decomposition temperature of the hydrogen peroxide and one reaction was completed above the decomposition temperature (T_3). Selected heat flow profiles are shown in Figure 8. As the temperature is increased, a competing decomposition reaction is encountered with the hydrogen peroxide and possibly the peroxy acid.

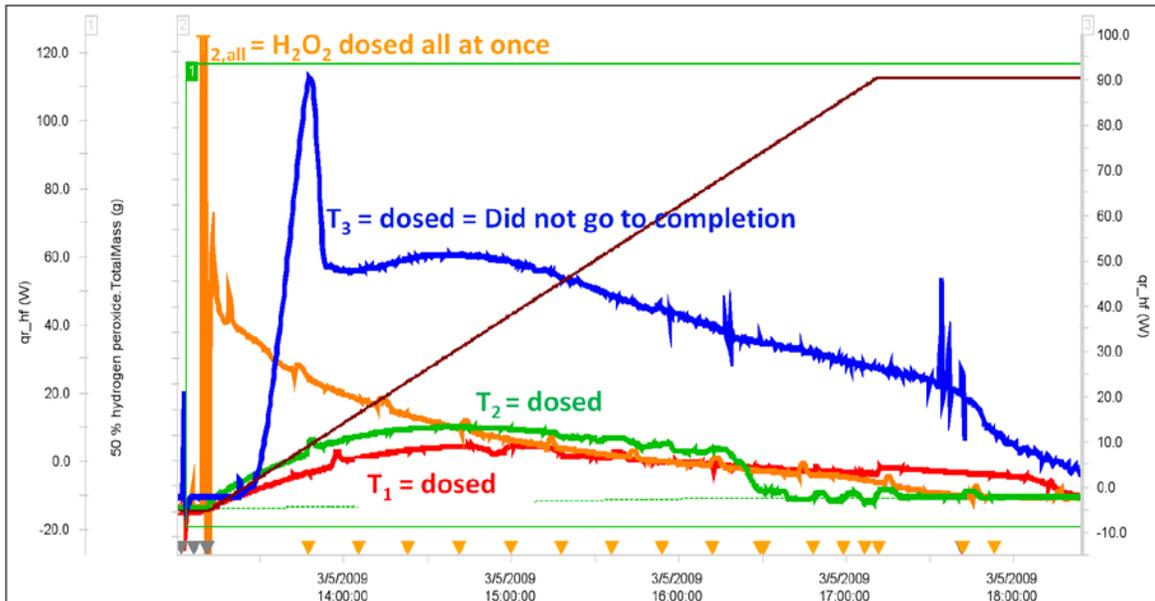


Figure 8: Total heat generation for several experiments in the RC1

Samples were pulled from the reaction mixture as a function of time to further understand the mass transfer limitations of the system during the dose. The samples were analyzed using $^1\text{H-NMR}$. The conversion data of selected experiments are shown in Figure 9. These linear trends show the mass transfer limitations at the respective temperatures. The slow dose in the laboratory also provided insight to dosing temperatures at scale to avoid accumulation. An additional experiment was completed where all the hydrogen peroxide was charged to the reactor quickly. This is represented in Figure 8 and Figure 9 by $T_{2,\text{all}}$. The reaction is slower to progress. This is most likely attributed to water from the hydrogen peroxide diluting the system immediately compared with the slower dose that dilutes over time.

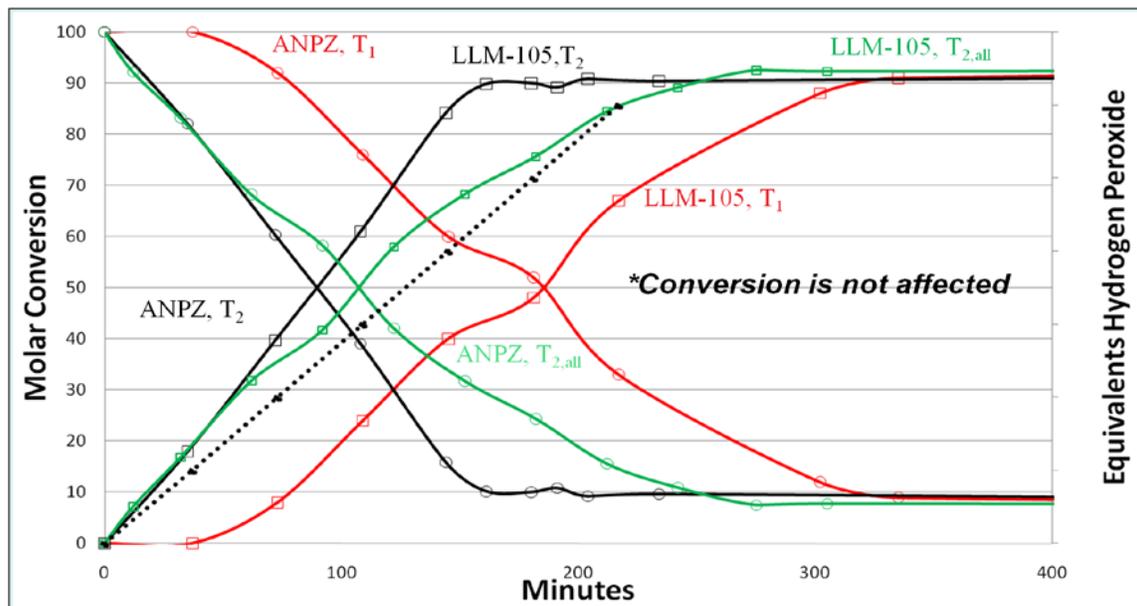


Figure 9: Conversion of ANPZ to LLM-105 over time as compared to the H_2O_2 dose

Figure 9 also demonstrates the fact that conversion reached approximately 93 wt% by $^1\text{H-NMR}$ in all experiments.

Using this information a slow dose of hydrogen peroxide at a lower temperature was completed at the 100-gallon scale safely, avoiding accumulation.

An analysis on particle size changes in the scale down study was also performed. The particle size distribution of LLM-105 remained relatively constant as a function of temperature and H_2O_2 dosing rates. As such, these process condition changes did not dramatically affect the particle size distribution of the end product. The mean particle size distribution consistently fell in the 10-100 micron range with a mean average particle size of about 45 microns. This was seen at all scales for the reaction.

Recrystallization

ANPZ is consistently present in the final isolated LLM-105 product. It is believed that the impurity is included inside the crystal lattice of LLM-105. Once the impurity becomes encapsulated in the solid LLM-105 crystals, it can no longer interact with the oxidizing media to form LLM-105³. ANPZ is typically found in the product in a 5-12 mol% range when analyzed by $^1\text{H-NMR}$. It was desired to evaluate pure LLM-105 in formulations. This could be accomplished through recrystallizations or possibly an alternative synthesis avoiding ANPZ.

In addition to the impurity, it was also desired to evaluate LLM-105 of varying particle size distributions, particle size, chemical impurities and crystal defects. Previous investigators have confirmed these properties influence the sensitivity of energetic ingredients and their formulations. Higher density energetic crystals have been shown to correlate with higher shock initiation pressure⁴⁻⁹. A correlation between particle size and shock sensitivity has also been documented¹⁰⁻¹¹. The explanation for this effect is believed to lie in the fact that smaller particles are less likely to have defects that will lead to unwanted initiation. To study these effects a crystallization effort was completed.

Traditional organic solvents were not suitable for use as recrystallizing media; LLM-105 has limited solubility in organic solvents. In addition, the use of organic solvents has continuously resulted in the formation of LLM-105 with larger than desired aspect ratios.

The use of ionic liquids to dissolve strong inter- and intramolecular hydrogen bonded solids, including the energetic TATB, has been reported by Lawrence Livermore National Laboratory¹²⁻¹⁴. The anions in ionic liquids are believed to disrupt the hydrogen bonding, so that the material can dissolve. This science has been successfully transitioned at NSWC, IHDI in creating concentrated solutions of LLM-105 beyond what was achieved with organic solvents. The use of 1-butyl-3-methylimidazolium acetate with an organic cosolvent as an aid in the dissolution of LLM-105 has allowed for solutions above 10 wt% to be achieved. The resulting morphology continues to produce material with large aspect ratios. The particle size has been increased with modifications to the dosing rates of the antisolvent used to reprotonate the Meisenheimer complex of LLM-105. This process has been successfully scaled through a 5-L reactor at NSWC, IHDI.

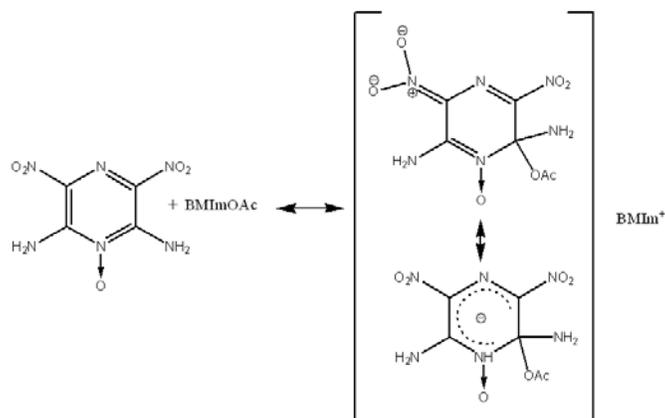


Figure 7: Formation of the meisenheimer complex of LLM-105 through the use of an ionic liquid

CONCLUSIONS

The use of cutting edge technology and application of sound chemical engineering principles resulted in the successful scale-up of a promising new energetic material. Modifications to the oxidation of ANPZ to LLM-105 resulted in the elimination of accumulated heat and afforded a safe process. These efforts were made possible through a scale down study using Mettler Toledo's RC1 and in-situ analytics. The use of ionic liquids is a promising method to recrystallize highly insoluble energetic materials. An improved solubility has been seen with the use of BMImOAc, but the ability to lower the aspect ratio of these materials remains a challenge.

RECOMMENDATIONS

Additional research to reduce the cost of producing LLM-105 through alternative synthesis or process modification is underway. Eliminating the expensive TFA is required to reduce overall cost. The optimal conditions for the reaction have yet to be identified and require additional chemical engineering support including studies on the decomposition of hydrogen peroxide and the trifluoroperoxy acid in the presence of ANPZ. This can be accomplished using gas flow measurements and heat flow measurements while monitoring conversion using high performance liquid chromatography. Recrystallization efforts will continue in an attempt to identify suitable solvents to reduce the aspect ratio of LLM-105 and grow crystals of desired particle size and distribution.

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