Scale-up of Energetic Materials Using Principles of Model-based Control*

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Abstract:

Development of novel ingredients has been demonstrated to be a lengthy and costly process. An entire spectrum of pitfalls threatens the steady progress of a material. Two recent efforts by us will be used as examples of avoidance strategies to two of the most common pitfalls.

The application of much vaunted model based control system requires an accurate model. A study of the nitration of an intermediate for the synthesis of CL-20 was undertaken. This study was designed to provide an accurate model for a future model based control system. The responses of yield, purity, and kind of impurities to a range of reaction conditions were determined. The specific functions led to prediction of the best reaction conditions to ensure optimal reaction output. Then, the utilization and verification of this data set in a state-of-the-art nitration facility was completed. The extremely large data stream gathered in this facility allows the confident scale-up of any new process with sufficient data collected to allow rapid verification of process chemistry. The utilization of a programmed scale-up based on the data from the model-based control effort will be reported and the positive effects of this approach are briefly described.

Introduction:

The advantages of model-based control systems in the chemical industry at large has long been understood and exploited widely. The theory and practice is taught in undergraduate course work for chemical engineers. Industry standard software such as that available from Aspen Technology have achieved wide acceptance. The use of this approach to optimal production of a chemical has often been touted as a potential source of significant cost savings for our industry. A broad based effort in this direction is a thrust led by ARDEC with a coordinated team of investigators they have assembled.[1] This effort focuses on bringing the best scientific principles to bear on the current and future needs of the US military. In times of reduced production and sporadic purchases, an intelligent system and network of systems will be able to provide a degree of confidence in future capability that cannot be economically maintained otherwise.

In a typical application of a model based control system, such as an oil refinery, detailed process information is gathered over a period of time to build a process database. This database catalogs the manipulated variables, the controlled variables, and the way the manipulated variables affect the controlled variables. Typically, the function each controlled variable is of the corresponding manipulated variable will be determined in a painstakingly detailed process. From these data, the control system will be able to predict the future condition of a process based on any given set of existent conditions. But, most importantly, it can also manipulate the future outcome and

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“choose” the direction it wants to go in control of a set of variables based on the current conditions. This is in contrast to simpler process controllers that only respond to current error conditions and try to bring the system back to some set point.

Also critical to a model based control system is as complete an understanding as possible of all disturbance variables. These are those factors that change the controlled variables or product quality but cannot be manipulated or, often, even predicted. If all relevant factors could be completely manipulated then an absolute prediction could be made of the conditions in the process at any given point in time, past, present or future. In the ideal extrapolation of the system, the model would be “intelligent” and “learn” from what happens. If brought to fruition, this adaptive system would become better and better at running the process. The variability would get smaller and smaller with a more and more consistent product resulting. Naturally, the closer we can come to this, the better for the products we are producing.

Application of these general principals to a new material will require significant adaptation since the detailed data for an immature process are not available. This leaves us with the need to generate an early data set based on chemical intuition and understanding. In the rest of this document, the data gathering and initial determination of function on product yield and purity will be described. From this, a focus into a desired set of outcomes was made and verified.

Results:

CL-20 has been prepared by a variety of synthetic routes with the first invented by Arnold Nielson at NAWC/China Lake.[2] A route (figure 1) that has shown considerable promise is the nitration of TADA.[3,4] Compared to some other routes to CL-20, the nitration of TADA has not been examined and scaled-up. It, therefore, serves as a clean canvas on which to build a data set for nitration conditions. Based on previous experiments with TADA and other substrates that serve as CL-20 precursors, a set of critical process parameters had been identified. These include, but are not limited to, concentration of sulfuric acid in nitric acid for the mixed acids, loading of TADA in mixed acids, and amount of moisture in the acids.

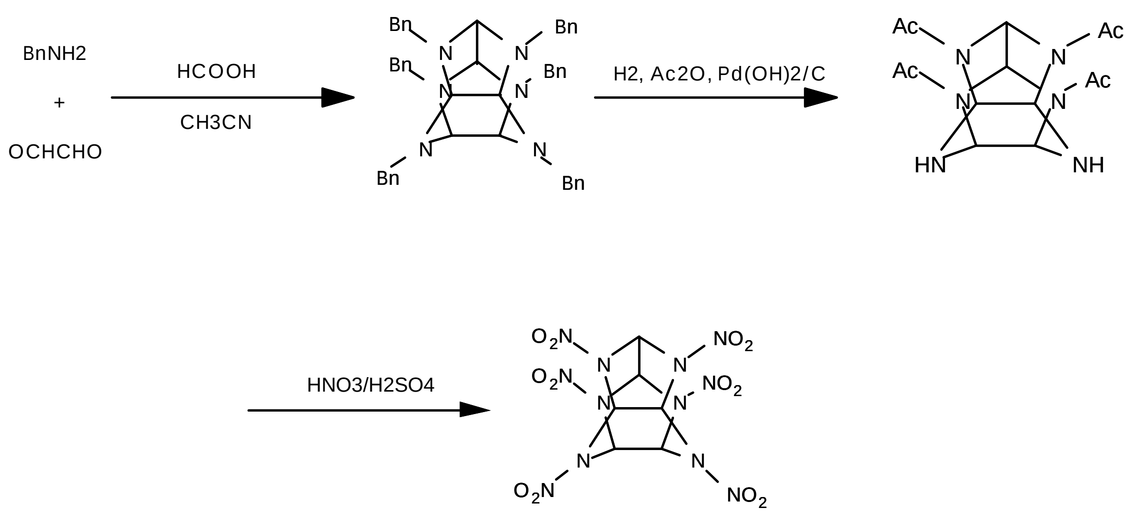

Figure 1. Synthesis of CL-20 through TADA. This three-step route is under investigation in the study reported here. This process is simple without either a two-step nitration or a two-step hydrogenation.

Initially, laboratory scale nitrations of TADA were performed according to the matrix in table 1. This work was performed in preparation for scale-up to the pilot plant facility. This early work disclosed that the acid ratio, acid to precursor ratio and water concentration can have a significant effect on the purity and yield of CL-20. The latest data on this program assists in establishing the optimum window for purity and yield of CL-20 made from TADA. This work will also help to establish the amount of error that will be acceptable in the quantities of materials used in the TADA nitration process.

Identical procedures were used on all nitrations. The acids were mixed prior to use. One hundred milliliters of acid were used in each nitration. The appropriate amount of water was added to attain either baseline or baseline plus 4 percent in each reaction. The amount of TADA added was determined from the pre-selected loading ratios of nominal or minus 25% acid relative to TADA. All reactions were run for the same period of time and at the same temperature.

The graphs shown below in figures 2-5 show the results of the nitration matrix. Percent yield was determined gravimetrically. Percent purity was determined by HPLC. The data in these figures indicates that it is possible to attain purity in excess of 99% while maintaining percent yield and increasing mass yield. This will allow a cost reduction in CL-20 from its current level, while increasing the purity at the same time. The increase in purity was attained by using TADA as the CL-20 precursor rather than TADF, and also using an optimal acid ratio and loading. The cost reduction occurs because of being able to produce more CL-20 per batch (higher loading capability). In the past, CL-20 made from TADF was 97% to 98% pure. The data show that CL-20 of greater than 99% purity was attainable in the lab scale matrix evaluation.

Table 1: TADA NITRATION MATRIX

SULFURIC (%)	ACID LOADING	WATER (%)
plus 20	Nominal	Nominal
plus 20	Nominal	plus 4
plus 20	minus 25%	Nominal
plus 20	minus 25%	plus 4
plus 10	Nominal	Nominal
plus 10	Nominal	plus 4
plus 10	minus 25%	Nominal
plus 10	minus 25%	plus 4
Baseline	Nominal	Nominal
Baseline	Nominal	plus 4
Baseline	minus 25%	Nominal
Baseline	minus 25%	plus 4
minus 10	Nominal	Nominal
minus 10	Nominal	plus 4
minus 10	minus 25%	Nominal
minus 10	minus 25%	plus 4

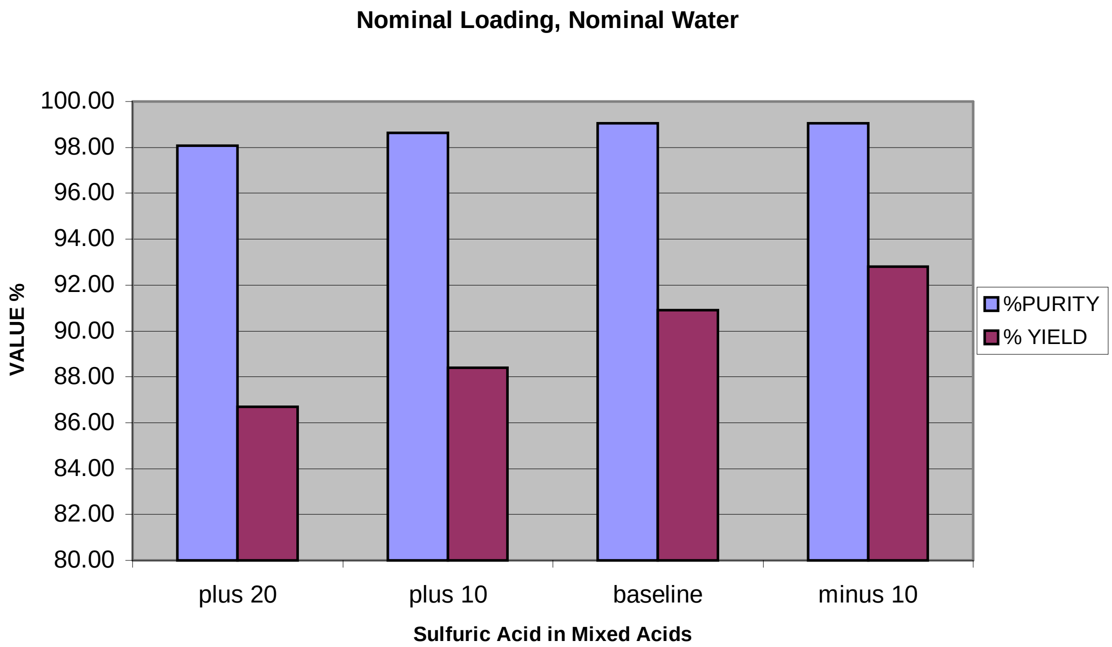

Figure 2. Summary of data from TADA nitration matrix. First of four figures depicting results from matrix in Table 1.

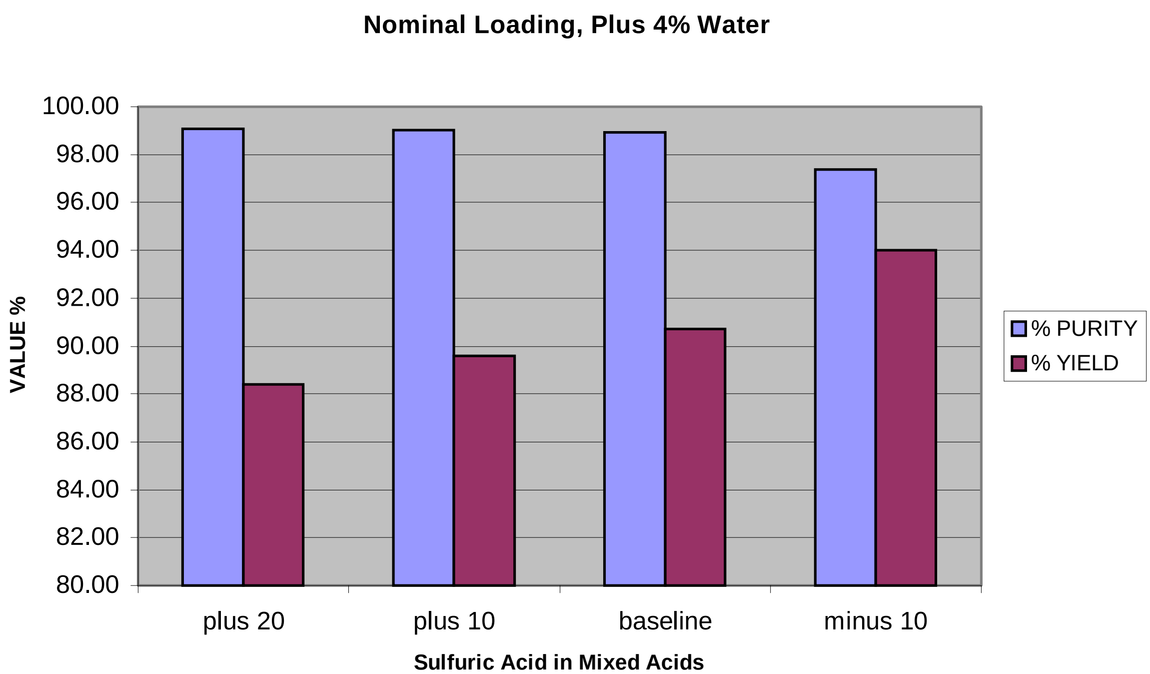

Figure 3. Summary of data from TADA nitration matrix. Second of four figures depicting results from matrix in Table 1.

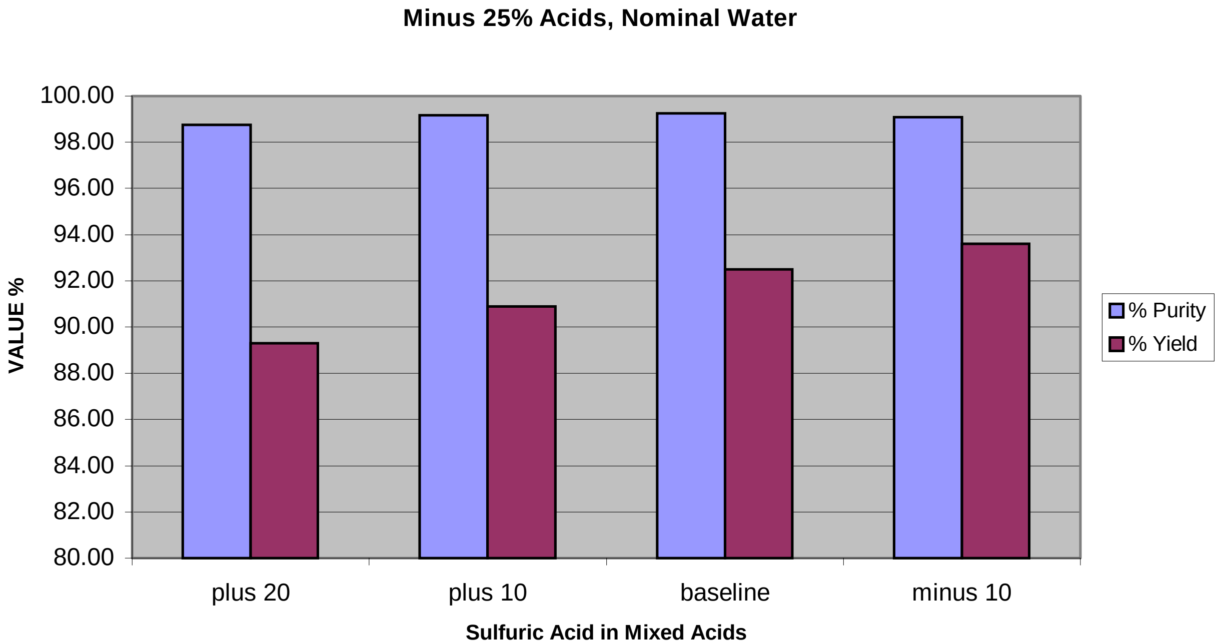

Figure 4. Summary of data from TADA nitration matrix. Third of four figures depicting results from matrix in Table 1.

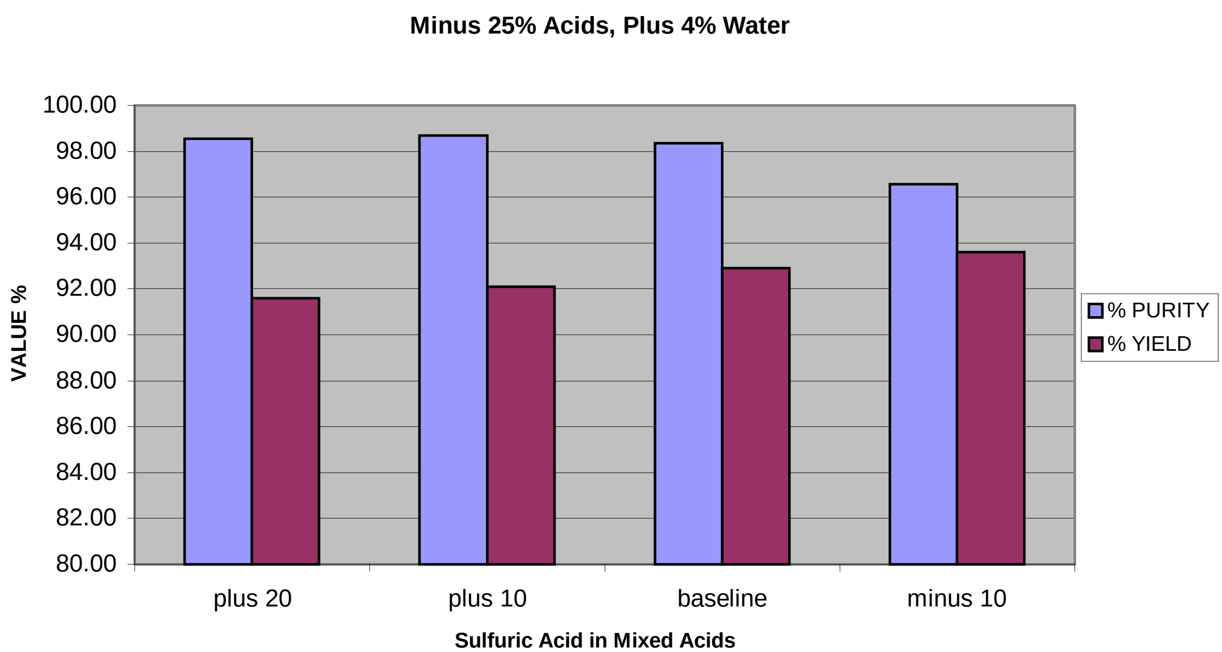

Figure 5. Summary of data from TADA nitration matrix. Fourth of four figures depicting results from matrix in Table 1.

A comparison of the four figures allows several significant conclusions. At the nominal loading and plus 4% water, an increasingly higher percent yield is recorded at each reduction in sulfuric acid. Percent purity decreases with increasing acid ratios, however, the purity is relatively constant at the higher sulfuric acid contents and drops significantly at the lowest sulfuric acid contents. With nominal water, the purity increases up to baseline sulfuric acid then remains fairly level from baseline to minus 10% sulfuric. At minus 25% acid loading, the percent yield increases with increasing acid ratios for both the nominal and plus 4 percent water. The purity remains fairly constant with nominal water when plus 10%, baseline or minus 10% sulfuric acid is used, although the baseline appears to be optimal. The purity appears to maximize at plus 10% sulfuric acid when plus 4% water is used. The data indicate that the highest purity material was obtained from the minus 25% acid loading, baseline acid ratio, and nominal water content nitration.

These results suggested that it might be possible to go to a higher loading than even the minus 25 percent on the acids. A comparison of the figure 2 graph to the figure 4 graph suggested that higher loadings might be possible since percent purity did not change at any acid ratio in going across this range. They also suggested that it may be possible to use less sulfuric acid if less water is present.

The results were verified in 20-gallon nitrations in a new nitration pilot facility. A second-generation nitration matrix was executed based on this lab matrix to verify the results and focus more on the ranges of greater interest in on reducing water content, increasing yield and reducing reaction time.

Conclusion:

A database has been developed for the nitration of TADA to form CL-20. These data form the foundation of a useful guide to ensure a high quality product. In considering the application of common principles of model based control, these data can be used to guide initial conditions including the amount of sulfuric acid in a reaction, the reaction period, and the concentration of TADA in acids to ensure maximum purity and yield. The application of these principles will improve product consistency and reduce cost as much as possible without compromising any critical product characteristics.

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[1] The team includes ARDEC, Geocenters, Stevens Institute of Technology and Thiokol. Related programs include the TIME effort. General direction on the effort is provided by Tom McWilliams whose specific leadership is acknowledged. Specific assistance of Mark Mezger and Steve Nicolich is particularly noted.

[2] Nielson, A.T.; U.S. Patent 5,693,794.

[3] Hamilton, R.S.; Sanderson, A.J.; Wardle, R.B.; Warner, K.F. “Studies on the Crystallization of CL-20,” 31st International Annual Conference of the ICT, June 27-30, 2000.

[4] Kodama, et.al.; WO/23792, 1996.