Modernization and Capabilities of the Lawrence Livermore National Laboratory Pilot Facility for Remotely Controlled Energetic Materials Synthesis

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Abstract:
Lawrence Livermore National Laboratory has invested in the modernization of their synthesis pilot facility for the kilo-scale preparation of energetic materials and precursors. This capability will serve to accelerate the research and development progression toward new energetic materials as well as for the optimization of processes for existing conventional materials. The first two planned campaigns for the facility will include the nitration of 2,6-diaminopyrazine-N-oxide (DAPO) to 2,6-diamino-3,5-dinitropyrazine-N-oxide (LLM-105), and the amination of 1,3,5-trichloro-2,4,6-trinitrobenzene to TATB. The presentation will focus on the design and agile capabilities of the pilot facility, the transition from all glass vessels to the new two-story integrated skid with glass-lined carbon steel reactors, and the efforts to provide optimal operator safety by utilizing a custom Wonderware® platform for reagent additions and the majority of process manipulations.

Keywords: LLM-105, TATB, Pilot Scale Synthesis, SCADA

Introduction

The energetic materials synthesis group of Lawrence Livermore National Laboratory delivers research capabilities for the development of new and conventional high explosives, with a primary focus on insensitive high explosives.[1-4] Our synthetic chemists work primarily within Livermore's High Explosives Applications Facility (HEAF), which provides

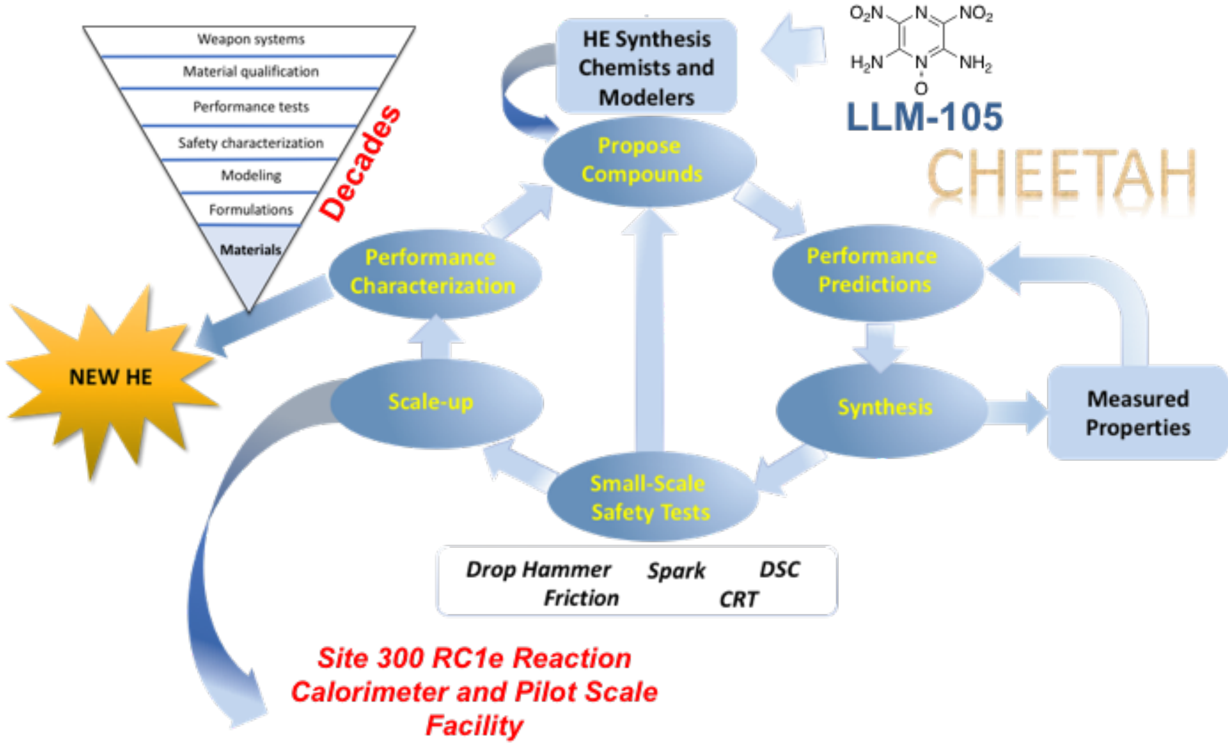

Figure 1 LLNL HE synthesis developmental process.

interdisciplinary collaboration in all facets of energetic materials science. The HEAF is a unique facility that allows for the conception and testing of new energetic materials, all under one roof (Figure 1). Within the HEAF, HE synthesis chemists can produce several gram quantities of new materials to determine its safe handling conditions (small-scale safety testing), density, heat of formation, and small-scale performance testing (Disc Accelerating eXperiment, DAX[5,6]). As the inverse pyramid depicts in Figure 1, in order to progress from the bottom (materials) to the ultimate goal of weapons systems, candidate materials must be scaled to multi-kilogram quantities to allow for the refinement of formulations, scaled performance, and large-scale safety testing. For multi-kilogram scale syntheses of energetic materials and their precursors, the Livermore Experimental Test Site (Site 300) contains a newly renovated and modernized pilot facility scheduled to be complete in 2018. With the newly renovated facility and future plans to add new capabilities such as continuous process equipment, LLNL hopes to accelerate and streamline the transition of new HE materials to our production partners.

Discussion

With the intent to be a fully sufficient HE R&D institution, LLNL began the modernization and renovation of the Site 300 pilot facility in 2015, with design and demolition completed by mid-2016 in partnership with the Hart Design Group.[7] The re-establishment of LLNL's pilot scale HE synthesis capabilities was a safety driven effort to transition from fully contact synthesis operations with large glass reactors, to a modernized and industrial class design with remote and automated features (Figure 2). The incorporation of remote capabilities and automation while still maintaining flexibility for a wide variety of synthetic processes (current and future) required a careful balance and compromise for the ultimate design and materials of construction. Eight comprehensive processes were evaluated to develop the final agile facility design. As will be discussed, the control of such a system requires a specialized, integrated software package.

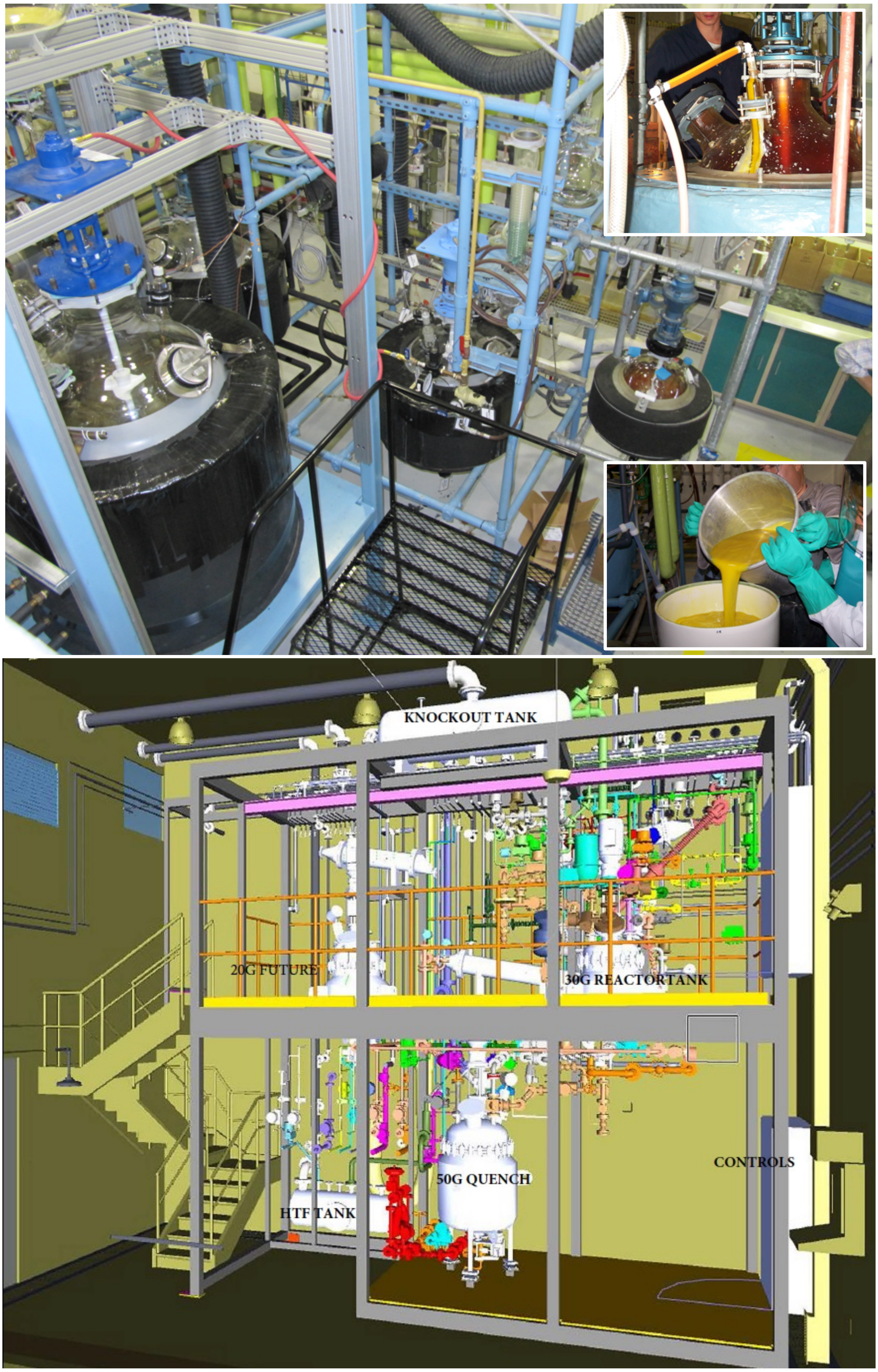

Figure 2 *Top:* Past LLNL pilot scale setup and contact manipulations. *Bottom:* 3D rendering of the modernized LLNL pilot facility with remote handling.

Facility and Pilot Skid Design

The safe scale-up of energetic materials syntheses reactions requires thorough planning, proper facilities, and an understanding of calculated risk. The last factor of calculated risk relates to the typical reaction processes for the preparation of high explosives, including nitration and oxidation conditions that generate high heats of reaction, unwanted, yet unavoidable decomposition pathways, and relatively unstable reaction products. In many instances, high explosive synthetic processes cannot be modified to a level of severity practiced in the majority of industrial production facilities.[8] One example is in the preparation of the TATB precursor 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB), which requires a one-pot trinitration of 1,3,5-trichlorobenzene in mixed acid at temperatures up to 150-155 ºC. Reports studying the ideal synthesis conditions indicate that temperatures exceeding this range by only 5 ºC leads to significant product loss through decomposition[9], and 5-10 ºC more leads to a runaway reaction and loss of containment.[10] This example and the nature of high explosives chemistry dictates the attention that must be factored into facility design and process safety.

The layout of the LLNL pilot facility is shown in Figure 3. The building was originally constructed and designed to contain explosive materials with earthen berms surrounding three sides of the structure. All electrical and mechanical utilities were removed and replaced, and the two-story pilot skid components are in compliance with Class I/Division I electrical ratings for explosive proof electrical equipment. Where available, dual rated equipment was also used for both explosive vapor and dust.

In order to minimize hazards of contact transferring of reagents to the pilot reactors, the former storage room was converted to a remote reagent delivery room. Contained within a fume hood are air operated diaphragm pumps, a metering pump, and vacuum/nitrogen pressure delivery options from two weigh stations. Each weigh station is connected to the control software for either remote operation from the control room (separate building), or from two other human machine interfaces (HMI) located within the pilot facility. Depending on the nature of the liquid addition, full flow, temperature, and rate-controlled additions can be locally or remotely controlled with minimal worry of operator exposure. Remote chemical transfers are a simple way to minimize risk as many of the reagents would pose significant hazards to operators during a standard contact transfer operation.

With the eight processes evaluated, the ideal design for the pilot skid would have contained three reactors of 50 (future), 100, and 200 L. At a minimum, two reactors (100 and 200 L) were needed to perform the majority of processes including the first two campaign materials of LLM-105 and TATB. Attention then turned to material of construction and configuration design.

Material of construction for high explosives chemistry is a challenge as the three major reaction categories of nitration, oxidation, and amination require rather different materials of construction under ideal conditions. Glass is more than acceptable for these processes in a wide range of temperatures, and a certain degree of glass lining loss over time is expected. However, metal components are not unavoidable and further compromises must be made. All attempts were made to use hastelloy C (276 and 22), PTFE, ETFE, tantalum, stainless steel, and glass as wetted parts. Additional constraints for construction came into play due to the limited space above and below the reactors. Limited space is exemplified by the use of a single port and common header for all reagents into the reactor, including sparge nitrogen, liquids, and reactive gases. Multi-purposing was a key component used by Hart Design Group to fit all the required needs for reagent addition by utilizing a tube within a tube approach.

In a typical nitration reaction, for example the nitration of 2,6-diaminopyrazine-1-*N*-oxide (DAPO) to LLM-105, the 100 L vessel serves as the nitration pot and the 200 L reactor serves two purposes: 1) emergency or off-normal quench, and 2) normal quench/product precipitation. Under normal controlled quench conditions, the precipitated product would be filtered, rinsed, and collected. The pilot skid utilizes a Nutsche-type filter for additional processing of the final product by allowing temperature controlled re-slurrying of the product for a purer material, ultimately limiting additional handling and reprocessing of the explosive material.

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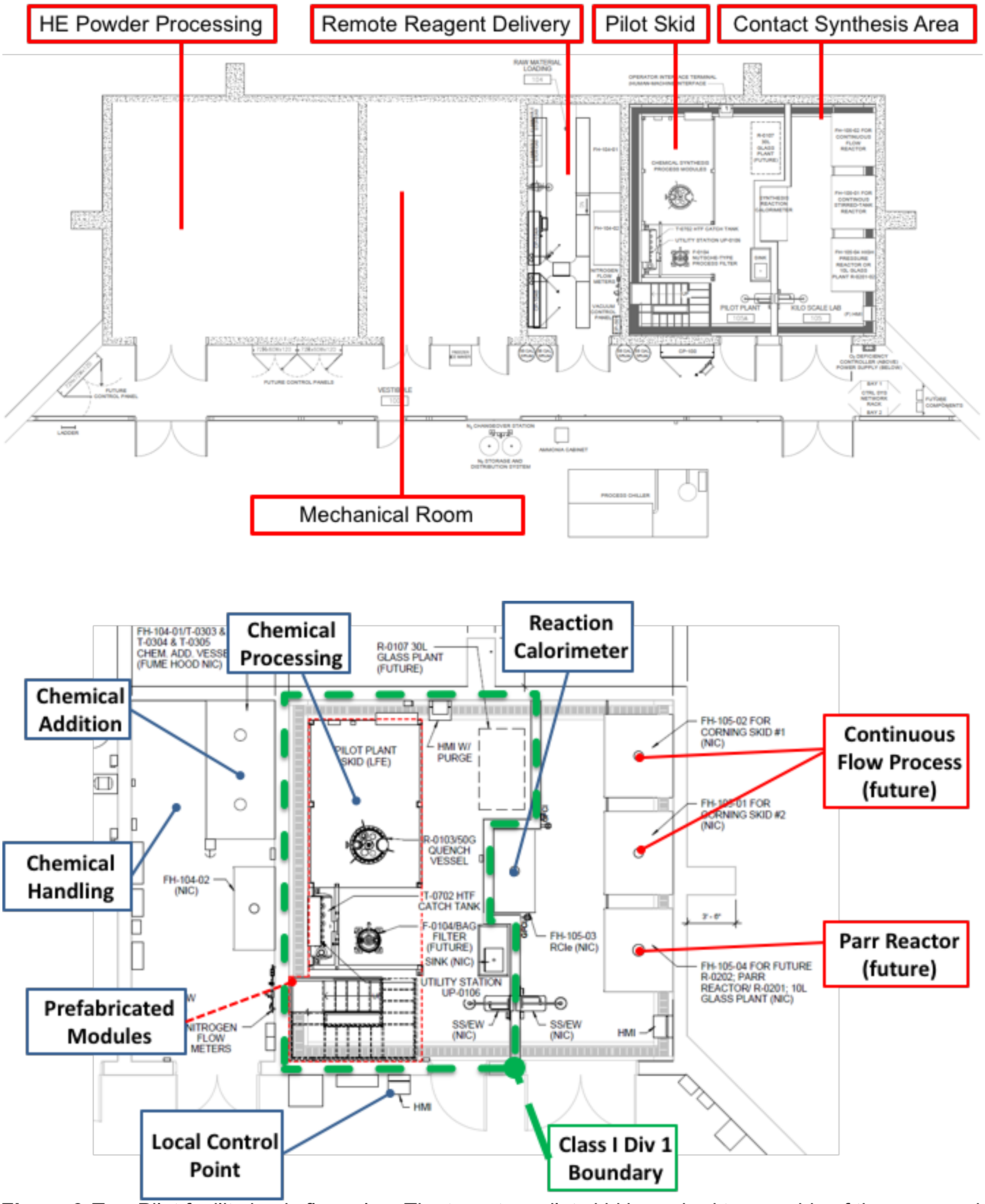

Figure 3 *Top:* Pilot facility basic floor plan. The two-story pilot skid is pushed to one side of the room and the room was then divided in half to allow for fume hood contained equipment for contact HE synthesis research. *Bottom:* Expansion of pilot skid/reagent delivery rooms and HE contact operations room. The pilot skid area is outfitted with explosives rated electronic equipment and enclosures. Directly next to the pilot skid is the reagent delivery fume hoods to allow remote transfers of liquid reagents. The general purpose contact synthesis area will contain a RC1e calorimeter and room for future expansion equipment.

Figure 4 Pilot skid installed at LLNL Site 300.

Pilot Reactors

— 50L Pfaudler w/sample loop (future)
— 100L Pfaudler w/sample loop
— 200L Pfaudler

Process Analytical Technology (PAT)

— Raman spectrometer
— pH Meter
— Canty particle sizer
— Reaction monitoring camera

Ancillary Equipment

— Solids addition conveyor
— Molten addition funnel
— Remote liquid reagent addition
    — Air operated diaphragm pumps
    — Piston metering pump
— Ammonia gas cabinet
— Nutsche filter
— Bag filter
— Tantalum condensers
— RC1e reaction calorimeter

Industrial Control SCADA Software

From reagent addition, process monitoring, to material collection, the new pilot skids provide significant reductions in operator contact operations and the likely risk of chemical and related exposure to employees is greatly reduced. This is all made possible by the careful design of the Supervisory Control and Data Acquisition (SCADA) control software (CS) developed by LLNL and Avanceon.[11]

The complexity of the required control software is portrayed in the P&ID below (Figure 5, top), which is only one subset of many components in the pilot skid (excluding weigh stations for reagent delivery, quench reactor, and all other connected components). In summary, the control software contains over 1,180 alarms, 800+ I/O points, 100+ automated control valves, 160 phase operations (temperature control, transfer segments, agitation speed, etc.), and 111+ interlocks, which are all detailed in the control system functional specification of greater than 415 pages. The complexity of the control software leads to a simplified and safer process for the operator, as can be seen in the depiction of the same P&ID of the 100L reactor in the top of Figure 5 (bottom).

One may notice that although the control screen in Figure 5 is simplified, there is an absence of vibrant colors. This is done intentionally to follow the practice of HMI "situational awareness" whereby color is used in a consistent manner to draw attention to items of need. For example, alarms have different levels of severity, and yellow, light blue, pink, and red will all have different meanings for an alarm event. Essentially, in a generally bland background of light and dark grey, the operator is more likely to have their attention drawn to an event with a flashing color that is consistently utilized.

The software platform chosen by LLNL as the basis for the Avanceon prepared CS is Wonderware®. This software platform provides a completely customizable and expandable product that allows for commercial off-the-shelf (COTS) instrument/part integration and is used by many industrial facilities worldwide. This aspect is important to LLNL as transitioning our processes to our industry partners is the overall goal of our pilot facility. Additionally, the pilot skids will utilize Wonderware's® InBatch software product, which is consistent with the ISA-88[12] standard for batch management processes, providing assurance that all necessary information from batch to batch is appropriately captured and documented. The use of InBatch will provide batch parameter control, but it will also provide operational safety by utilizing a set recipe for each run, which can limit the automation of each step as well as the level of approval at each step (dual sign-off requirements and custom security settings). As the pilot batch runs will still be R&D processes, flexibility to adjust the recipe or to have some leeway during a process is desired. Accounting for flexibility with upper and lower bounds and logic loops can be integrated into the recipe. However, the CS is also designed to allow overriding for manual operation of individual valves, if necessary.

Other key functions of the CS that are built in, are the integration of low-low, low, high, and high-high alarms for individual instrument responses depending on the process. For example, for exothermic reagent additions, the reaction temperature alarms can be adjusted to initiate different system responses based on the severity of the upper and lower bounds from stopping reagent addition, to initiating an immediate system cooldown. In addition to the CS safety functions are hardwire interlocks that are tripped in events such as power outage and seismic activity. These interlocks can also be tripped via operator initiated emergency stops, and facility door interlocks.

Over time, it is anticipated that changes/additions to equipment, modifications to control screens, and tweaking of automated valve sequence events will be necessary for improved performance and to enhance safety features despite our best efforts to put forth the best CS possible. The chosen software platform allows for this necessary flexibility and a refined system focused on operator safety, process safety, and process efficiency will evolve over time.

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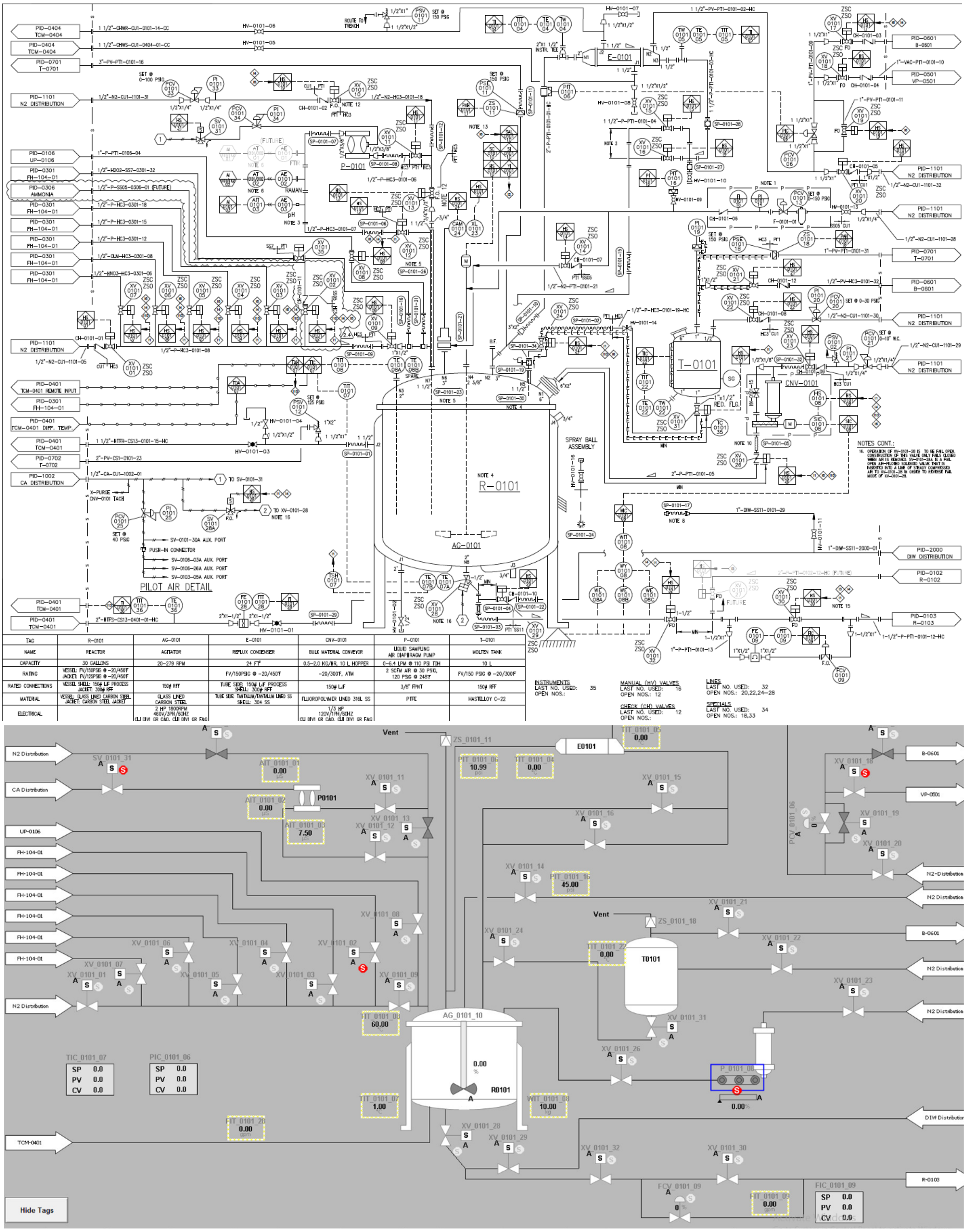

Figure 5 *Top:* P&ID of 100 L glass-lined carbon steel reactor with associated inputs, outputs, valves, and utilities. Key components include reagent header with ammonia and hydrogen peroxide capabilities, and a molten addition tank. *Bottom:* Rendering of the industrial control software graphical user interface for the same reactor depicted above. Colouring is in line with "situational awareness" scheme where shades of grey indicate on/off and red, yellow, blue are meant to draw attention to immediate needs.

Conclusion

LLNL's new energetic materials synthesis facility provides a safe, remotely controlled skid for a variety of synthetic processes. The following is a summary of the skid capabilities. The reactors are rated for operating pressures of up to 135 psi and all wetted parts include glass-lined carbon steel vessels, hastelloy, tantalum, and PTFE. Reaction temperatures of -10 to 170 ºC are possible with the current combination of heat transfer fluid and thermal control units. The ability to add ammonia (vaporizer) to both 100L and 200L vessels will allow for the synthesis of energetic compounds such as TATB. Hydrogen peroxide dosing can be used with the incorporation of a special PTFE coated line. Solids can be metered via conveyor, which is also rate controlled capable through the CS. All liquid reagent additions are remotely controlled via metering pump, diaphragm pump, vacuum, or pressure. Flexibility for various synthetic methods is available through the ability to phase separate, distill, and recirculate between vessels. A sample loop on the 100L vessel contains three inputs for the in-situ monitoring of reaction conditions with Raman and pH currently installed. Clean in place (CIP) is available with InBatch® automated recipe development. Final product isolation and impurity removal is accomplished with a Nutsche and bag filter respectively.

Acknowledgements

The authors would like to thank funding sources from DOE and NNSA Headquarters as well as contributions from LLNL's Mark Coons, Jeff Packard, Steve Chan, Kenn Knittel, Veronica Harwood, Lou Bertolini, Lou Ferranti, Mao Xi Zhang, Spencer Vartanian, Levi Merrell, Yong Han, Lara Leininger, Jon Maienschein, Sabrina DePiero, Mark Zagar, Kevin Vandersall, Kevin Merrell, Barbara Jesus, Hiroshi Saito, Dawn Kramer, Shari Brigdon, Alex Gash, George Overturf, Ken Newman, Wes Davis, Dave Hill, John Scott, Deanna Kahmke, Kim Elam, Donovan Day, Annette Warner, Cameron Cornell, and Trini Gonzalez, as well as subcontractors Hart Design Group, Hart Engineering (facility design and fabrication), RORE Inc. (construction installation), Total Facility Solutions (mechanical systems), Wilhite (electrical), Avanceon (control software), Nalas Engineering (process hazard analysis). This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-PROC- 749068.

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