Rapid Identification Of Reactivity Hazards In A Multi-Use Facility

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Abstract: Multi-use pilot scale plants often run production campaigns in parallel, requiring frequent changes in the chemistry from campaign to campaign and modified procedures to match the new production needs within a short time span. The facility must also match the client's product chemistry and process demands with their equipment capabilities.

These campaigns are likely to occur several times a year with considerable overlap of projects. Several basic but important questions arise for the facility manager. For example, how do the facility personnel:

- Pay adequate attention to all of the safety issues associated with the chemical reactivity?
- Ensure that the facility's equipment and the new process chemistry fit together safely?
- Verify emergency relief and vent sizing, estimate cooling duty needs, and implement the necessary process safety changes?

This presentation introduces a new approach and procedure that assesses each unit's operation of the batch record, identifies potential hazards, and recommends a methodology to evaluate the nature and extent of the hazard. A user-friendly software tool has been developed and will be compared to the use of other hazard analysis tools in this presentation.

1. Chemical Reaction Hazard Identification and Assessment

1.1 Introduction

Its Friday afternoon and the phone rings in the Plant Manager's office of Notlob Chemical Inc (NCI)., a well-known contract manufacturing facility. The Premier Chemical Company (PCC) wants Notlob to manufacture 100,000lbs of their new rat poison within the next six months. Dennis Bloodknock, never being one to pass up a challenge, accepts the campaign and the rush is on. There can be a number of predictable outcomes at this point, ranging from a successful completion to tragic failure.

Contract (Toll) manufactures, such as NCI, are required to produce chemical products under less than ideal conditions. NCI must move from project to project rapidly learning new chemistries; modifying their procedures to fit the next client's needs; matching the technology transfer package with NCI's equipment capabilities; and manufacturing the requested material(s) within a short time span. Successful navigation through this sequence of events requires reliable hazard information for the target chemical process.

It is possible to obtain reliable estimates of the nature and extent of chemically related hazards in an operation involving the storing, handling, or reactions of chemicals, in a reasonable amount of time, from a variety of readily available sources. Viewed as a whole, this data gathering exercise provides more than just clues to the risk potential of the new process.

Important data about the process may be found from many sources, such as Material Safety Data (MSD) sheets and the open literature, molecular functional groups, chemical compatibility considerations, thermokinetic information, consequences of planned and unplanned mixing, checklist assessment and calculational tools, and finally hazards testing.

A systematic approach to analyzing the safety of a particular process involves recognizing the various aspects of a manufacturing process that are opportunities for loss of control of the manufacturing process. They maybe summarized as:

- the chemistry and unit operations that together yield the desired result;
- upsets in the chemistry that could lead to an undesired result;
- upsets in the unit operations that could lead to an undesired result;
- upsets in the chemistry, or in a unit operation, that could trigger an upset in the other.

Reviewing each of these general failure scenarios could reveal a serious problem that may occur due to undesired reactivity and/or loss of process control. Typically, information required for this analysis includes knowledge of:

- the desired reactions for the chemicals involved;
- the side reactions that lead to yield loss;
- undesired reactions between reactants, process chemicals and materials;
- reactions that can occur in storage.

This data gathering exercise should be done even if the operation is only blending or mixing. Several serious accidents, some including fatalities, have occurred because the consequence of reactions between chemicals involved in blending operations were not known.

1.2 Information Sources for Chemical Reactivity

1.2.1 Material Safety Data Sheets

MSD sheets do not supply the level of information required to perform an information-based hazard analysis and should not be used as the sole source of process safety information. However, MSD sheets do provide guidance on toxicity, physical properties, stability and reactivity, fire fighting and spill management, safety conditions required, and specific chemical interactions to avoid.

1.2.2 Open Literature

There are many excellent sources of information that can provide assistance at all stages of a hazard assessment. Bretherick's Handbook[1] for chemical reactivity, Sax[2] for general chemical hazards, and NFPA[3] for fire protection from hazardous materials. The Center for Chemical Process Safety has produced two books[4,5] specifically on managing chemical process safety of reactive materials. These resources are frequently used for the initial assessment.

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[1] Urben, P.G.; *Bretherick's Handbook of Reactive Chemical Hazards, Vol 1 & 2, 6th Edition*, Butterworth Heinemann (1999).
[2] Sax, N. I., *Dangerous Properties of Industrial Materials,* 7th ed., Van Nostrand Reinhold: New York (1987)..
[3] National Fire Protection Association, *Fire Protection Guide to Hazardous Materials, 10th Edition*, NFPA (1991). (Complete text of NPFA 49, 325M, 491M, and 704).
[4] Center for Chemical Process Safety; *Guidelines for Safe Storage and Handling of Reactive Materials,* American Institute of Chemical Engineers, New York, 1995
[5] Center for Chemical Process Safety; *Guidelines for Design Solutions for Process Equipment Failures,* American Institute of Chemical Engineers, New York, 1997

As the process hazard evaluation proceeds, specialized texts on dust explosions[6], emergency relief design[7], managing runaway reactions[8], and self-heating in solid materials[9] become important. CCPS has at least 40 specialist monographs on a wide range of process safety subjects.

1.2.3 Functional Groups, Chemical Identity, and Reaction Hazard Potential

The structural features of the chemical molecule (bond groupings) are indicative, often strongly, of instability or high reactivity within the molecule. Trends among the constituent atoms of these molecular groupings show, for example, that groups of the non-carbon atoms, such as -N-O- or -N-N≡N-, $-NO_2$, or multiply bonded carbon atoms may be hazardous.

Reactions may be classified as having a high hazard potential for one or more of the following reasons:

- Reactants or products contain functional groups or atom groupings that confer explosive properties;
- The reaction rate becomes explosive if cooling, agitation, addition controllers, etc fail;
- The reaction has a long and unpredictable initiation period *and* is strongly exothermic;
- Reactants or reagents are highly toxic or have very low personal exposure limits;
- Reactants react vigorously /explosively with air or moisture, under ambient or near-ambient conditions;
- Reactants or reagents, in particular catalysts, are pyrophoric;
- Side reactions can over-run the main reaction leading to thermal explosion or detonation;
- Product workups involve highly exothermic quenches.

Drawing the line between highly hazardous and moderately hazardous is, to a large degree, linked with the experience that lab personnel may have with the particular chemical process. A synthesis that involves the introduction of an functional group known to confer explosibilty, and has only been performed a few times should be considered as non-routine (Table 1, section 11) and identified as requiring a formal hazards review. [10]

1.2.4 Checklist Tools

Checklists are a straightforward way of reviewing the potential hazards of a chemical manufacturing process. They provide the inexperienced reviewer with a wealth of questions to ask about the intended process, or unit operations, as well as the causes, consequences, and probabilities of an upset condition arising. There are many checklists are available.

1.2.5 Chemical Compatibility Charts

Compatibility charts provide a quick reference guide to the consequences of inadvertent mixing and provide an excellent training tool for operators focusing on the areas of the operation that may have a high hazard. The US Coast Guard[11] has a widely used compatibility (inter-reactivity) chart that provides information for about 40

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[6] Bartknecht, W., *Dust Explosions Cause Prevention Protection*, Springer-Verlag, 1989

[7] Fisher, H.G. *et al*; *Emergency Relief System Design Using DIERS Technology, The Design Institute For Emergency Relief Systems (DIERS) Project Manual*, American Institute of Chemical Engineers, 1992

[8] Center for Chemical Process Safety; *International Symposium on Many Aspects of Runaway Reactions*, American Institute of Chemical Engineers, New York, 1990 - 2002

[9] Bowes, P. C.; *Self-heating: Evaluating and Controlling the Hazards*, 1984

[10] CCPS, *Guidelines for Hazard Evaluation Procedures,* 2nd Edition, AIChE (1991).

[11] 46CFR150 – Part 150 – Compatibility of Cargoes (COC) with useful background information provided by the Department of Energy at http://www.eh.doe.gov/chem_safety//chem_comp.html

chemical classes or mixtures. CAMEO, developed jointly by the EPA and NOAA provides on-line chemical compatibility information. Full details are available from the CAMEO website.[12]

1.2.6 Calculational Tools

A hazard analysis based on fundamental parameters requires quantitative information about both the thermodynamics and kinetics of the key reactions. There are some straightforward calculational tools that can estimate of these parameters well enough for hazard ***assessment*** purposes. CHETAH[13] allows estimates to be made of formation heats of molecules in the gas phase. These calculations also lead to reaction heats, estimates of the plosive characteristics of molecules and reactions, and adiabatic temperature rises for reacting mixtures.

If differential scanning calorimetry (DSC) data have been obtained for a pure material or a reaction mixture, several thermal stability indicators[14] may be estimated from the data. These include adiabatic decomposition temperature rise, ΔT_{ADIAB}; critical half thickness, a; critical temperature, T_C; impact sensitivity, SS; explosion potential, EP; time-to-thermal-runaway, t_{NR}; instantaneous power density, IPD; and NFPA instability rating, IR.

1.2.6.1 Initial Screening Calculations

In the absence of real hazards test data there are a number of numerical, semi-quantitative methods available to assist in the assessment of chemical stability. The information provided by these methods should be used to determine the severity of the risk that might be incurred by proceeding without knowledge of reliable values of E_a, A, and ΔH (activation energy and pre-exponential factor in Arrhenius equation, heat of reaction).

Oxygen balance: The oxygen balance (OB) of a compound is the difference between the oxygen content of the compound and that is required to fully oxidize the carbon, hydrogen and other oxidizable elements present to carbon dioxide, water, etc. It is known empirically that explosives with an oxygen balance close to zero are the most powerful having maximum energy release at this equivalence point. A conservative use of this approach is to be concerned about molecules that show a positive OB but do not be unconcerned about molecules that have a negative OB.

Reaction Heat Estimation: The energy that is involved in a reaction, $\Delta H_{reaction}$ can be estimated by Hess's Law if the enthalpies of formation of the reactants and products are known. The theoretical methods include those that use bond contributions, for example average bond summation methods, and ones that use group contributions, (e.g., CHETAH).

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[12] CAMEO website http://www.epa.gov/ceppo/cameo/what.htm

[13] CHETAH**:** Computer Program for Chemical Thermodynamics and Energy Release Evaluation, Version 7.3." Developed by ASTM subcommittee E27.07.
See also http://www.chetah.usouthal.edu/index.html and http://www.astm.org/COMMIT/CUSTOM1/E27.htm

[14] ASTM Standard "E1231-01 Standard Practice for Calculation of Hazard Potential Figures-of-Merit for Thermally Unstable Materials." Developed by subcommittee E27.02.

1.2.6.2 Using Adiabatic Information to Derive Specific Engineering Quantities

Temperature of No Return, T_{NR}: The temperature of no return is the maximum temperature above which the heat generated by the reaction exceeds the cooling capacity available. Therefore, T_{NR} is an extrinsic property depending on the state and properties of the vessel such as the cooling capacity of the vessel, its size and geometry, fill level, rate of agitation, etc. This variable is frequently used to assess the safety of storage tanks and drums where cooling is by natural convection to air. However, if no hazards testing has been performed on the vessel contents none of these calculations can be performed with the result that "fire-fighting" efforts will be largely a matter of guess work.

Self-Accelerating Decomposition Temperature, T_{SADT}: This parameter is a measure of the maximum ambient (air) temperature that can be tolerated without thermal runaway, for a selected operating temperature. SADT is influenced by the size of the storage container, similar to T_{NR}. It is a parameter that specifically addresses the storage of potentially thermally unstable materials.

1.2.7 Transforming Information into the Process Hazard Potential

The information gathered from the sources and techniques described in section 1.2.1 through 1.2.6 are assessed as a whole and documented. Table 1 illustrates one way that the documentation may be accomplished. The table is also used as a decision aid in determining the need to perform a more advanced hazard evaluation. The major part of the hazard review table is outlined in the following sections.

Sections 1 to 5, 10, 13 to 15. Documentation of Hazard Review: These sections record basic information for documentation purposes, including the names of chemicals to be handled.

Sections 6 and 7. Physical Properties of the Chemicals: The physical properties of each chemical represent the basic information that is used for this initial hazard assessment. If all of the information requested in sections 6 and 7 is available it will be possible to obtain a reasonable overview of the potential hazards. Realistically, not all the data will be present. The melting and boiling points, flash point and flammable limits of the material constitute a minimum set of physical properties to establish the conditions for safe operations.

Sections 8. Chemical Overview, Mostly from MSD Sheets: This section gathers specific information about each chemical used in the synthesis. Several of the consequences of mishandling common solvents can be assessed from the flash point, the lower and upper flammable limits (LFL and UFL) and minimum ignition energy (MIE.)

Section 11: Classification of Process as Routine or Non-Routine
The final step in the process compares the gathered data with the company-defined safety boundaries and risk tolerance, in the form of a Window of Safe Operations (WSO) for the lab. For example, section 11 of the Review Form (Table 1) shows a typical set of flammability, temperature and pressure limits for the reaction conditions that define a typical WSO.

Information provided in sections 11 and 12 helps lab personnel decide if any of the proposed operational parameters are outside of the limits that have been pre-defined as constituting a "routine" synthesis. If one or more of these predetermined boundaries are crossed the synthesis is classified as Non-Routine and an additional detailed review is required before any laboratory work is started.

1.2.8 A Word of Caution

This approach does not explicitly address the synthesis reaction being performed, except by considering the type of reaction (esterification, nitration, Friedel Craft, etc.) being performed. Evaluation of the thermal hazards of a specific reaction requires a more detailed investigation of the desired reaction(s) and any undesired reactions, together with an analysis of possible equipment upsets or procedural short-comings.[15, 16, 17, 18]

2. Choosing the Appropriate Process Chemistry Hazards Testing

The preceding assessment approach focuses on obtaining a hazard assessment without gathering new experimental hazard test data. However, the assessment may highlight a potentially hazardous situation but without any indication of the severity of the upset. Quantifying the energy and power output resulting from an upset condition or the desired reaction requires specific quantitative data, as detailed in the previous section. If the data is not available it can be obtained by performing the appropriate hazards testing.

The three types of hazards detailed earlier are thermal stability hazards, chemical reactivity hazards, and operational hazards, as shown in Table 2. Choosing the correct hazard testing to perform is dictated by the information required, the type of process being studied and the chemicals involved. The following sections describes a tool that provides guidance and assistance to answering the questions "What information is needed to define the nature and extent of the potential hazard?" and "What hazard testing will provide the data that to answer this question?"

2.1 Introduction

Consider the chemical reaction that is the basis of a chemical manufacturing process:

$$A_{SOLUTION} + B_{LIQUID} \xrightarrow[85° C]{} \text{Crude Product, AB} \xrightarrow[\text{Vacuum Distill}]{} \xrightarrow[\text{Recrystalize}]{} \text{Pure Product, AB}$$

This chemical description of the process summarizes the chemical relations and the key condition(s) for reaction. We have already noted that the nature and extent of the reactivity hazard depends on the specific chemical reaction and the reaction conditions. However, the reaction as written implicitly includes a number of engineering steps each one of which could be hazardous. For example, the use of a solution of reactant A, $A_{SOLUTION}$, requires that the solution is prepared as part of the manufacturing process and will probably raise solvent handling concerns.

Therefore, looking at the chemical reaction from an engineering perspective the manufacture of "Pure Product" comprises the following steps:

1. Dissolve A_{SOLID} in solvent (DMF) using Day Tank DT-101 (Process Steps 1a to 1d)
2. Add B_{LIQUID} to reactor R-101 and heat to 85° C (Process Step 2)
3. Add $A_{SOLUTION}$ to R-101 over 2 hours (Process Steps 3a – 3c)
4. Stir out reaction mass at 120° C for 4 hours to form "Crude Product" (Process Step 4)
5. Remove excess solvent (DMF) by vacuum distillation and re-crystallize to "Pure Product"

The first step may be broken down further to the level of the batch record instruction, one action per step:

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[15] Leggett, D.J., *Runaway Reactions: Ignore the Chemistry at Your Peril*, Chem Eng., 107, #8, 78 (August, 2000).
[16] Barton, J. and R. Rogers, *Chemical Reaction Hazards: A Guide to Safety*, 2nd Edition, Gulf Publishing (1997).
[17] CCPS, *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*, AIChE (1995).
[18] Grewer, T. *Thermal Hazards of Chemical Reactions*, In Industrial Safety Series, Vol 4, Elsevier (1994).

1. Dissolve A_{SOLID} in solvent (DMF) using Day Tank DT-101
    a. Add solvent (DMF) rapidly to DT-101
    b. Turn on agitator
    c. Add A_{SOLID} slowly from sacks to DT-101
    d. Agitate slurry rapidly until dissolved

A similar detailing of the other main steps results in the complete batch record for the manufacturing process.

2.2 Deriving Hazard Testing Recommendations from the Batch Record Step

This section describes the software package, PHAROS, [19]developed to support engineers and chemists in deciding the need for process hazard information and in the selection of appropriate hazard testing. The basis of the approach implemented in PHAROS is the analyses of each step of the batch record and each word within each step. The software recognizes each chemical component, including solvents, the action performed, and the context of the action. Recommendations are made for the hazard assessment information needed for each step and the operational, reactivity or thermal stability hazards testing data that may be used to provide the necessary data. The recommendation is in the form of one or more tests; an explanation for the recommendation is also provided.

PHAROS analyses each word of each batch step systematically because the each step is systematically constructed as a sentence of the following form:

Verb + Noun + Adverb +Preposition + Agent + Preposition + Agent

The "sentence " is assembled by selecting "words" from a list of verbs, nouns, adverbs, etc. in a definite order. Some of the Verbs, Nouns Adverbs, Prepositions, and Agents are:

Verb	Noun	Adverb	Preposition	Agents
Add	Pressure	Immediately	From	Day Tank 1
Agitate	Reactant 1	Quickly	Into	Pump
Pump	Slurry	Slowly	Under	Sack
Transfer	Solvent 1	Sub-Surface	Using	Weigh Scale

For example, the sentences for step 1 to 4 constructed from the menus of Verbs, nouns, etc are shown below:

Step	Verb	Noun	Adverb	Preposition	Agent	Preposition	Agent
1a	Pump	Solvent1		From	T-1011	To	DT-101
1b	Start	Agitator					
1c	Add	Reactant 1	Slowly	From	Sacks	To	DT-101
1d	Agitate	Slurry	Continuously	Until	Dissolved		
2	Pump	Reactant 2	Continuously	From	Drums	To	R-101
3a	Start	Agitator					
3b	Heat	Reactant 2	Continuously	Using	Heat Exchanger	To	Temperature
3c	Add	Solution	Continuously	From	DT-101	To	R-101
4	Agitate	Reaction Mass	Continuously	At	Constant T		

[19]

The software recognizes that Solvent 1 is DMF, that Reactant 1 is a specific chemical, and uses the supplied physical properties data to distinguish between solids, liquids, and gases. The hazards data required for each chemical and operation involving that chemical is therefore guided in part by the physical properties data. Information is also entered about the quantity and addition rate of chemicals, agitator speed, and heat-up rates.

As each process step is added the list of recommended tests increases. PHAROS reviews the total set of recommended tests to that point removing redundancies and adding hazard data and test recommendations. Additional information requirements and test recommendation(s) are added if the software detects that a mixture of chemicals has occurred in a vessel. The system has been designed to produce a conservative set of recommended tests. For example, every use of the noun "Reactant" recommends that thermal stability testing (DSC, Adiabatic Calorimetry) is needed and if the material is a solid or liquid impact and friction sensitivity is also recommended. The recommended test for each of the process steps are shown in Table 3.

Once all the process steps have been entered the third part of the software is run that accesses a large set of rules which address situations where an earlier step may have a consequence to a later step. For example, a reactant, dissolved in a solvent in a previous step, to a reactor containing the other reactant. Reaction calorimetry (Table 4: t)is needed to assess the potential hazard of step 3c but that does not become apparent until the software examines both steps 2 and 3c and detects that step 3c is the actual reaction step. Step 4, initially flagged for reaction calorimetry, is eliminated because this is a stir-out step. Adiabatic calorimetry is prudent at this point to assess the thermal stability of the crude reaction mass. The final report, produced by this third phase of the process, describes the type of hazard test information needed based on the complete process and the processing conditions, and recommends the testing that can provide the necessary data.

The final report for steps 1 through 4 is shown in Table 4. The content of the table should be viewed as information requirements that may be satisfied by reference to the open literature, especially in the case of flammability data. The data needs are not equally pressing. For example, it is normal to conduct the operational testing (Table 4:a – f, j - m) in stages. Dust flammability (Table 4:a and b) usually needs be obtained experimentally; liquid flammability (Table 4:c and m) may often be available in the open literature; MIT, AIT, MOC and charge accumulation are normally performed once the results of a, b, c, and m are known. A detailed examination of the material handling operations for this process did not show a need for friction or sensitivity testing. However, the software suggested that the solids addition to the reactor be reviewed for the static charge accumulation during the pouring-from-sacks operation.

The amount of thermal stability testing was reduced, in this instance, by electing not to perform DSC testing. If both DSC and adiabatic calorimetry are available it is usually reasonable to perform the more comprehensive adiabatic testing only. However, that decision is made on a case-by-case basis; PHAROS will always suggest that both should be performed. The reaction mass and crude product are tested using thermal inertia adiabatic calorimetry (Table 4:r and s) to provide data that may be used directly to size, or confirm the sizing of, the emergency relief system of the reactor.

3. Summary

This paper has reviewed a variety of preliminary hazard evolution procedures that may be used to rapidly evaluate the potential hazard of chemical manufacturing process. It is often the case that questions remain, after this preliminary hazard evaluation, as to the consequences of a process upset (loss of cooling, agitation, feed pump controllers, etc). The software system PHAROS has been developed to aid chemists and chemical engineers determine the hazard potential of each process step by answering the questions: "What information is needed to define the nature and extent of the potential hazard?" and "What hazard testing will provide the data that to answer this question?"

Table 1. Preliminary R&D Reactive Chemicals Hazard Review Form

1 Run Ref #	_____/_____	**2. Synthesis Type:**	_____	**3. Date**	_____
4. Description:	_____	**5. End Use:**	_____		

7. Physical Properties	**6. Chemicals to be used – Sample, Reactants, Solvents**		
B Pt / M Pt / VP @ 20 °C	____ / ____ / ____	____ / ____ / ____	____ / ____ / ____
Fl Pt / AI / MIE	____ / ____ / ____	____ / ____ / ____	____ / ____ / ____
LEL / UEL	____ / ____	____ / ____	____ / ____
Dust Explosion Severity			
8. Chemical Overview			
Stability/Reactivity			
Toxicity/Exposure			
NFPA/HMIS Ratings			
Incompatibilities			
Spill Clean-up Material			
PPE Required			
Specific Hazard (Note 1)			
9. Function in synthesis			

10. MDS Sheet Reviewed	Signed: _____	Date: _____

11. Classified as a Non-Routine Operation (check relevant categories)			
High toxicity / Low exposure limits		Chemical Handled (Air/water sensitive, Corrosive)	
Flammability (Fl Pt<10 °C; LFL<10%)		Extreme Reaction Temperature (> 150 °C; < -30 °C)	
Flammability (AI<200 °C; MIE < 0.5mJ)		High Temperature Feed (> 50 °C)	
High Hazard Reaction or Functional Group		High Pressure Reaction (>10 bar)	
High/moderate hazard reaction performed ≤ 2 times		High Pressure Feed (>2 bar)	

12. Potential Hazard Level	Routine: Y N	Non-Routine: Y N	
13. Synthesis by	Name: _____	Sign: _____	Date: _____
14. Hazard Review by	Name: _____	Sign: _____	Date: _____
15. Non-Routine Hazard Review	Schedule Date : _____	Date Completed : _____	

Note 1: Enter as many codes as needed to describe the Special Hazard: RDX – Oxidizer/Reducer; PYR – Pyrophoric; POL – Polymerizes; EXP – Reacts explosively; HS – Sensitive to heat; WAT – Water reactive; PER – Peroxide former; INH – Inhibitor required; IMP – Impact/ friction sensitive; TCN – Temperature control needed; GRP – Functional group

Instructions for Use of Form

Use this form as a check-list and review of potential hazards involved in the synthesis. Each section requires responses, as detailed below:
1. Reference number **2**. Technique **3**. Date filled out **4**. Describe Synthesis **5.** Product end-use **6.** List each chemical used in the run – use a new form as needed; **7**. Physical properties – use MSD sheet, Saxs, Merck Index and "Sources of Ignition" (Bond) **8**. Summarize listed properties as available from reference materials, mostly MSD sheets **9**. Function of each chemical in the synthesis, ie reactant, solvent, catalyst, etc. **10**. MSDS reviewer, when; **11**. What led to a Non-Routine classification? Check all appropriate boxes **12**. What is the assessed potential hazard – Routine or Non-Routine **13**. Who will perform the synthesis; when? **14**.This hazard review; when? **15**. If Non-Routine, when is detailed hazard review scheduled; when completed? Non-Routine hazard review notes must accompany this form with risk reduction recommendations activities as needed.

Table 2. Relating Hazard Testing Technique with Type of Hazard

a. Thermal Stability Hazards	
Scenarios	*Typical Calorimetric Technique*
Self -reactivity Inappropriate storage conditions Runaway Reactions / Thermal Explosions Loss of utilities leading to loss of cooling, loss of agitation	Differential Screening Calorimetry Adiabatic Calorimetry Dewar Calorimetry
b. Chemical Reactivity Hazards	
Scenarios	*Typical Calorimetric Technique*
Water and/or air reactivity Inappropriate materials of construction Wrong chemicals added Wrong addition rates, or order of addition Hypergolic and pyrophoric properties of the reactants or products	(Mixing) Isothermal Calorimetry Heat Flow Reaction Calorimetry Iso-Peribolic Calorimetry
c. Operational Hazards	
Scenarios	*Typical Calorimetric Technique*
Flammability dusts, vapors and gases Mechanically induced hazards Static induced hazards	20-Liter Sphere Dust Explosion Severity MIE, MIT, AIT, COC, LFL, UFL, Layer Ignition Bulk Resistivity / Charge Relaxation Impact and Friction Sensitivity

Table 3. Recommended Tests Generated by PHAROS

Recommended Test	Process Step									Data Generated / Purpose of Test Data
	1a	1b	1c	1d	2	3a	3b	3c	4	
DSC	•		•		•		•	•	•	T_{ONSET}, T_{MAX}, T_{END}, $\Delta H_{ESTIMATE}$
Adiabatic Calorimetry, high ϕ	•		•		•		•	•	•	T_{ONSET}, T_{MAX}, T_{END}, ΔH_{DECOMP} $(T,P)_{TIME}$, $(dP/dt, dT/dt)_{TIME,TEMPERATURE}$,
Adiabatic Calorimetry, low ϕ	•		•		•		•	•	•	T_{ONSET}, T_{MAX}, T_{END}, ΔH_{DECOMP}, ERS Design, $(T,P)_{TIME}$, $(dP/dt, dT/dt)_{TIME,TEMPERATURE}$,
Isothermal Mixing Calorimetry			•					•	•	ΔH_{MIXING}
Reaction Calorimetry								•	•	$\Delta H_{REACTION}$, Power, Energy, Accumulation
MIE	•									Minimum energy required to ignite a dust, vapor or gas cloud
DE, 20 liter			•							Dust Explosion (20 liter) to determine severity of a dust explosion
LFL,UFL	•				•					Lower % of vapor (LFL) and Upper that will ignite in air
MIT	•									Minimum temperature required to ignite a dust, vapor or gas cloud
AIT	•									Temperature for spontaneous combustion of material
MOC	•									Minimum oxygen concentration required to sustain combustion
Charge Accumulation			•		•					Propensity of solids to accumulate and hold static charge during handling
Friction Sensitivity			•		•					Need to determine if any solids or liquids can detonate when processed mechanically
Impact Sensitivity			•		•					Need to determine if any solids or liquids can detonate when processed mechanically

Table 4. Final Set of Data Requirements and Recommended Process Hazard Tests

Recommended Test	Process Step									Data Generated / Purpose of Test Data
	1a	1b	1c	1d	2	3a	3b	3c	4	
DSC			**g**				**p**			T_{ONSET}, T_{MAX}, T_{END}, $\Delta H_{ESTIMATE}$
Adiabatic Calorimetry, high ϕ			**h**				**q**			T_{ONSET}, T_{MAX}, T_{END}, $(T,P)_{TIME}$, $(dP/dt, dT/dt)_{TIME,TEMPERATURE}$, ΔH_{DECOMP}
Adiabatic Calorimetry, low ϕ								**r**	**s**	T_{ONSET}, T_{MAX}, T_{END}, ΔH_{DECOMP}, ERS Design, $(T,P)_{TIME}$, $(dP/dt, dT/dt)_{TIME,TEMPERATURE}$,
Isothermal Mixing Calorimetry			**i**							ΔH_{MIXING}
Reaction Calorimetry								**t**		$\Delta H_{REACTION}$, Power, Energy, Accumulation
MIE	**a**									Minimum energy required to ignite a dust, vapor or gas cloud
DE, 20 liter			**b**							Dust Explosion (20 liter) to determine severity of a dust explosion
LFL,UFL	**c**				**m**					Lower % of vapor (LFL) and Upper that will ignite in air
MIT	**d**									Minimum temperature required to ignite a dust, vapor or gas cloud
AIT	**e**									Temperature for spontaneous combustion of material
MOC	**f**									Minimum oxygen concentration required to sustain combustion
Charge Accumulation			**j**							Propensity of solids to accumulate and hold static charge during handling
Friction Sensitivity			**k**		**n**					Need to determine if any solids or liquids can detonate when processed mechanically
Impact Sensitivity			**l**		**o**					Need to determine if any solids or liquids can detonate when processed mechanically