Process Safety in the Future – A View from the Chemistry

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ABSTRACT: This paper advances the thesis that a complete assessment of the chemical process safety must be founded on specific chemical hazards data. Usually, these data can only be obtained from appropriately designed experiments using the correct testing techniques. The basis of safety and the window of safe operations arise from the relevant process safety data.

Our experience with the chemical processing industry (CPI) has shown that the PSM elements Safety Information, Process Hazards Analysis, and Operating Procedures may be documented without adequate hazards test data for the covered process. The information is often qualitative; it may be taken from inappropriate laboratory data, and may not address the specific process deviation or worst-case situation(s). This lack of hazards test data represents an information void that tabletop or literature process hazard analyses alone cannot fill.

We make five recommendations:

- Chemical process safety supported by hazards testing is the right thing to do, whether the process is covered or not, and whether the process is at the manufacturing stage or not.
- Hazards testing to identify and evaluate potential upset conditions should be an integral part of a company's process safety program. It is the major information source for process hazard analyses.
- The information obtained is specific to the thermodynamics and kinetics of the process chemistry.
- The information enables clear identification of *operational, thermal and reactivity* hazards of processes involving highly hazardous chemicals.
- The scope of the testing scope should be matched with the quantities of chemicals involved and the development stage of the product.

Process Safety Management – The View from the Chemistry

David J. Leggett

1. Introduction

The intention of this paper is to argue that a complete assessment of the safety of a chemical process must be founded on specific hazards test data for the desired, and undesired, chemistry and process operations. These data can only be obtained from appropriately designed experiments using the correct testing techniques. The data are then transformed into relevant process safety information, by expert interpretation, to generate the basis of safety and the window of safe operations for the target process.

We have found that the OSHA Process Safety Management Process elements, Safety Information, Process Hazards Analysis, and Operating Procedures (29CFR1910.119) are often performed and documented in the absence of hazards test data applicable to the specifics of the covered process. At times, the hazard information is qualitative, taken from inappropriate laboratory data, and may not address process deviations or typical worst-case situations. This lack of hazards test data represents an information void that tabletop or literature process hazard analyses alone cannot fill.

1.1. Background

The Chemical Process Industry (CPI) is governed by legislation, in the form of standards and rules that cover the day-to-day, year-to-year, and cradle-to-grave operations for projects. They include "hard-hat" and chemical process safety, industrial hygiene, environmental, fire regulations, facility siting, etc. For the most part, the regulations are detailed and proscriptive. Compliance requires written responses describing the company's program(s) and activities relevant to the particular rule or standard. Inspections and un-announced inspections are a part of determining compliance. An additional chemical process safety standard was implemented in 1990. The standard is detailed in Occupational Safety and Health Administration (OSHA) process safety management (PSM) 29CFR 1910.119, Process Safety Management of Highly Hazardous Chemicals. These regulations are performance-based not proscriptive.

The Environmental Protection Agency (EPA) has a rule, "Risk Management Program", 40 CFR 68. This rule is similar to OSHA's PSM standard from a technical viewpoint. However, there are administrative differences with additional sections to address worst-case scenarios for major events and community right-to-know. For the purposes of this paper, OSHA's 29CFR1910.119 will be the focus of discussion. The points made are applicable, to EPA's RMP rule, at the technical level.

Table 1 lists the titles of each section, or element, of OSHA's process safety standard. Of these fourteen elements, five address aspects of the process that require the employer to have reliable and pertinent hazards data addressing process safety issues.

Fourteen elements of OSHA's PSM Rule	
Employee Participation: (c)	Mechanical Integrity: (j)
Process Safety Information: (d)	Hot Work Permit: (k)
Process Hazards Analysis: (e)	Management of Change (l)
Operating Procedures: (f)	***Incident Investigation: (m)***
Training: (g)	Emergency Plan & Response: (n)
Contractors: (h)	Compliance Audits: (o)
Pre-Startup Safety Review: (i)	Trade Secrets: (p)

Typically, large companies establish a process safety and loss prevention group of experienced individuals, that reports directly to senior management. Small companies have a similar approach with usually one person accountable for all HSE functions.

2. Current Practices: Analysis and Commentary

2.1. Current Practices in Chemical Process Industry (CPI)

The rest of this paper makes the case that the five elements, highlighted in Table 1, together provide a sound basis for generating the required level of chemical process safety. However, when the standard was written it was not made clear that a hazard assessment, generated by considering only data from the open literature, MSD sheets, and proprietary information, might not be sufficient to generate a complete process hazard analysis. We contend that a full assessment of the safety of a chemical process should be founded on specific hazards test data for the desired, and undesired, chemistry and process operations. These data, obtained from appropriately designed tests, are then transformed into relevant process safety information by expert interpretation to generate the basis of safety and the window of safe operations.

Availability of Hazards Test Data: In our experience many companies, with the exception of the large companies, may not have the complete experimental data needed to specifically and fully address the five elements of Table 1. We also find that some companies, who do have this level of process safety information, may fail to fully appreciate the consequences of not having this process safety data.

Worst Case Scenarios, Basis of Safety and Consequences of Process Deviations: Identifying, evaluating, and controlling process hazards is the outcome of the following actions:

- Establishing the worst case scenario(s) (WCS);
- Defining the most severe credible worst case scenario(s) (MSC WCS);
- Development of the appropriate lines of defense for MSC WCS;
- Defining the basis of safety;
- Setting the envelope or window of safe operations.

These actions involve, directly or indirectly, much information that can only be generated by hazards testing designed to closely mimic the target chemical process.

Operating Procedures: Operating procedures are designed to keep the process within the window of safe operations by ensuring that normal process deviations do not compromise the basis of safety. For example, temperature, pressure, feed rate or time limitations for the process are reliably determined from the interpretation of the test data for the desired and undesired process and chemistry.

When asked why the (smaller) company's PHAs do not have these vital parts of the safety analysis the reply is often that there are not the resources within the company to conduct, or commission, this depth of safety analysis. Too often there is little hard information about the consequences of process deviations from the written standard operating procedures.

Incident Investigations: The incident investigation is usually in the form of a fault tree analysis but sometimes lacks hard data related to the cause(s), nature and extent of the incident as defined by the thermodynamics and kinetics of the process. However, if there has been a severe accident hazards test data will often be obtained at the direction of the investigating agency(s).

Pre-startup reviews: If hazards test data is not present in the process safety information or hazard analysis sections of the PHA then it is most likely not available for this stage in the manufacturing process.

The large chemical companies typically have internal resources for the great majority of process hazard evaluations and thermal hazards testing. Outside consultancies are still used for specialized requirements. As the size of the company decreases the need for outside technical support tends to increase. We have found that many of the small companies may not recognize the need for this aspect of hazard assessment and analysis.

2.2. Current Practices of Consultants to CPI

Chemical engineering consultancies divide into two main groups. The first group employs seasoned engineers as their senior consultants who have gained their experience in large chemical or petrochemical companies. Typically, these consultancies provide services that are generically listed as process safety, risk management, loss prevention, plant reliability and OSHA/EPA regulatory planning. These consultancies range from two to four people offering limited services to companies with 100 employees, and more, capable of providing the full compliment of process safety support.

The second group of consultancies offer a combination of process hazards testing and process safety, risk management and loss prevention services. Process hazard testing capabilities include operational hazards testing (flammability of gases, vapors and dust), chemical reactivity, thermal stability testing, and explosion testing up to 5 kilogram scale. Some consultancies offer large scale (10 kg minimum) testing to full size and testing for blast effects. There are less than 10 such hazards testing consultancies in the U.S. Both groups often provide modeling of blast effects and dispersion modeling services.

2.3. Consequences of Lack of Appropriate Process Hazards Test Data

When analyzing worst-case scenarios the consequences of a particular scenario are as important as the frequency of the event. In other words, the risk-based approach to process hazard analysis and process safety management is key when reviewing credible worst cases and designing lines of defense. The nature and extent (consequences) of the worst case can only be determined from factual data. These data may be available from the company's loss prevention files, sometimes from the open literature, or from industry specialty associations. However, for many situations the exactly relevant data are not available. This is especially true if the intention is to design an emergency relief system (ERS) using the DIERS (Design Institute for Emergency Relief Systems) approach, or to determine the adequacy of a cooling system. A typical ERS design problem illustrates these points.

A common worst-case scenario is a reactor, or storage tank, surrounded by fire. The fire often originates from a pool fire where some amount of flammable material is present and burning. The task is to determine the adequacy of the in-place ERS under these fire conditions. The required (by calculation) area of the vessel's emergency vent is compared to the in-place nozzle area to establish, or verify, adequacy. The set pressure and other design information for the emergency relief system also arise from these calculations. A comprehensive physical properties database provides all the needed data. It is rare that any experimental work is needed to complete the ERS design for this situation.

However, this approach has an embedded assumption, which may not be challenged, that the contents of the vessel do not undergo chemical reaction(s), including decomposition, during the course of the fire and solvent loss. The undesired (or secondary) reactions that occur are characterized by rapid evolution of large quantities of gases and vapors. The decomposition products discharged from the vent will be either gassy, liquid or some combination of gases and liquids. Calculations using DIERS equations reveal that vent areas up to ten times the vent area for a "vapor only" system may be needed to accommodate these types of releases.

The data needed for the DIERS equations require temperature and pressure rise rates during the desired and undesired reaction(s), the maximum temperature and pressure reached during these reactions, and the type of material flow through the vent. Most of this data is unavailable from the public domain. Therefore, it is normally generated experimentally for the target chemical system and the worst-case scenario identified during the process hazard analysis. The consequences of not identifying the need for the DIERS approach, and therefore incorrectly sizing the emergency vent, can be a catastrophic loss of containment.

We have found that companies are often initially reluctant for a number of reasons to consider, or commission, hazards testing. However, once the company begins to appreciate the potential consequences of uncontrollable process upset(s), the need to identify, evaluate, and control these events seems more relevant. At that point, making the case for ERS design based, if needed, on the DIERS approach, and the overall need for hazards testing, becomes clear and justifiable to the company.

3. Intent and Coverage of New Approach to Chemical Process Safety

3.1. Introduction

It is our contention that an entirely adequate and cost effective hazards analysis, for the five OSHA PSM elements, may be gained through a diligent examination of the safety and potential hazards of the process. A "diligent examination" implies that the desired (or intended or primary) process chemistry and unit operations and the undesired events, or mal-operations, are examined in sufficient detail to provide at least quantitative limits on maximum or minimum temperatures, pressures, feed rates, temperature and pressure rise rates. Included in this examination is hazard testing for the raw materials, intermediates, and final product. Figure 1 provides an overview of desired and undesired chemistries and processes.

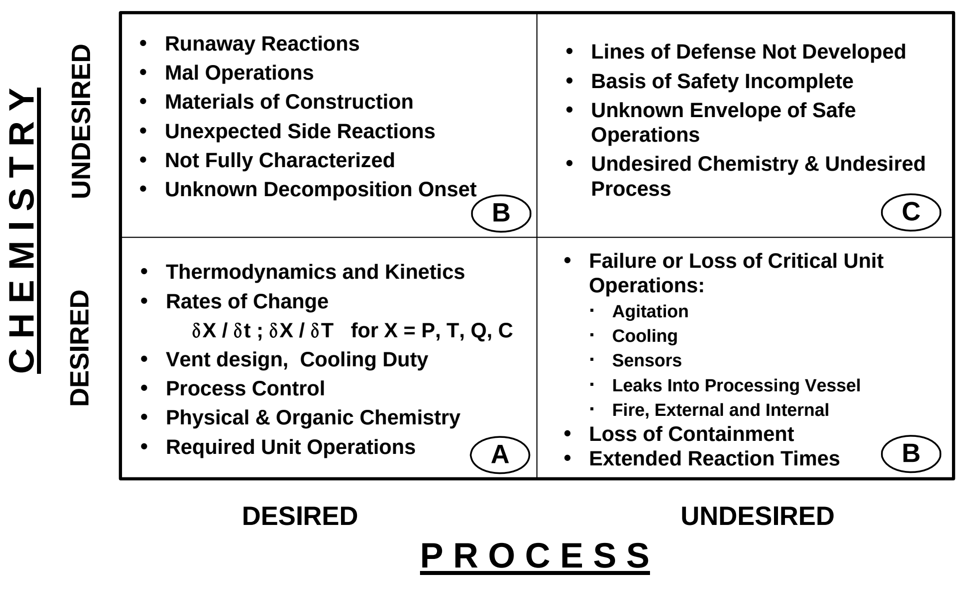

Figure 1. Relationship between Desired and Undesired Processes and Chemistry.

3.2. Desired and Undesired Processes and Chemistries; Levels of Hazard Evaluation

There are three levels of hazard evaluation that pertain to an evaluation of the desired and undesired processes and chemistries.

Hazard Evaluation of the Desired Process: Box A, figure 1, suggests that during the course of developing a chemical manufacturing process the topics shown in this box are generally understood and quantified to a reasonable level of detail. The essence of this level, directly related to the range of operating conditions and design options considered, may be summarized as:

- For raw materials, intermediates, and products:
  - Thermal stability;
  - Reactivity to common process materials;
  - Reactivity towards water, moisture and air;
  - Flammability (gases, vapors and mists, liquids and solids);
  - Impact and friction sensitivity.
- Specific, fixed values for T, t, P, concentrations;
- Variations in operating parameters for normal process are also considered;
- Temperature +/-10 °C;
- Feed rate at higher, or lower, than planned levels;
- Hold time variations;
- Specific, allowed process variations.

These data are relevant to hazard evaluation of the desired process. This level of hazard analysis provides an adequate assessment for processes operating normally and therefore the basic data for the Process Safety Information paragraph (element d). In other words, the elements of box A are the definition of Process Safety Information.

Hazard Analysis of Process Upsets: In other words, the consideration of known failure situations or worst-case scenarios that are credible for the target process. Examples of typical worst-case scenarios are:

- Loss of, or inadequate, cooling;
- High local temperature caused by loss of, or inadequate, stirring;
- Fire, or external heating, of the vessel or storage tank;
- Lack of adequate heat conduction;
- The pressurization of an enclosure by an oxidizing gaseous intermediate;
- Phase separation of a previously homogenous mixture;
- Sudden, or rapid, mixing of previously separate phases;
- Extended reaction and/or cycle time favoring auto-catalytic reactions;
- The unexpected introduction of a reactant, catalyst, or other material;
- The unexpected depletion of an inhibitor, or other material;
- Accumulation of reactants because reaction is rate limited.

Level B hazard analysis is the minimum standard that can lead to acceptable levels of process safety for most processes and is the basis for providing the information and data for Process Hazard Analysis and Operating and Procedures.

Hazard Evaluation of Abnormal Conditions: Box C considers of specific, abnormal conditions leading to unwanted exothermic activity not covered in level B.

This level concentrates on situations revealed by HAZOP, etc. that generate specific testing strategies. The information obtained at this level provides additional information for Process Hazard Analysis and Operating Procedures.

3.3. Process Safety and Product Life Cycle

Products that are manufactured by a chemical company have reached commercial status by a number of routes. Three common situations are:

- Product and process development, from conceptual R&D through pilot scale, and process development to full scale manufacturing, is performed by the same company;
- License, or purchase technology; the product is close to commercialization;
- Toll manufacturing of an intermediate or final product for another chemical company.

Each situation presents a different set of challenges to providing a safe working environment free of unacceptable process and chemical hazards.

From R&D to Manufacturing: In this situation the manufacturer will likely design a compound or product of interest that may be a variant within an existing family, or is a new product family. The compound must be prepared, at the lab scale, in sufficient quantities to satisfy any number of commercial suitability screens. Although quantities are small, potential hazards to personnel exist and need to be identified and evaluated. Commercial success normally leads to scale-up. A hazards testing protocol, which follows the life cycle of a process, has several key advantages.

First, the testing is closely tied to the scale of the operation and the three hazard evaluation levels illustrated in Figure 1. For example, it important to know the flammability of the materials and the shock or friction sensitivity of any newly synthesized chemicals. Differential scanning calorimetry and adiabatic calorimetry provide valuable information about the desired and undesired reactions and some worst-case scenarios that are relevant at the lab scale.

Second, personnel responsible for the next step in product development can expect a full process safety package to be available from the previous level of operations. Hazards information is added to the package relevant to the new scale of operation. In other words, Process Safety Management, and its documentation, is an evolving and on-going activity integrated into product life cycle.

License or Purchase Technology: Companies license or purchase technology in order to shorten product development cycle time. Evaluation of the process safety information, a part of the technology transfer package, is necessary in order to safely integrate the new product within existing company standards. In order to provide adequate hazards information some testing during the R&D bench and pilot stages might be required.

Custom Manufacturing: In this situation the toll manufacturer frequently relies on the client to provide the process safety information. Rapid production of product is the hallmark of the successful toll manufacturer. Therefore, the need to reduce cycle time to the minimum and appropriately address the potential risks of the process presents a dilemma to the toll manufacturer. Recent accidents in this segment of the CPI indicate that potential hazards, which may arise from the chemistry of the process, may have been misidentified, unidentified or unknown, with tragic consequences. An appropriate level of preliminary hazards testing, recommended from an effective process hazard evaluation, is often all that is required to demonstrate the level of risk associated with the new chemical to be manufactured. The required hazards testing may need to focus on verifying that the custom manufacturer’s available equipment and the new chemistry are compatible. (Reference 11 provides more details)

Despite the obvious differences between cradle-to-grave product development, technology acquisitions, and toll manufacturing, the principles of tying the nature and extent of hazards testing to the product life cycle still hold. Several benefits accrue by coupling testing with product and process development:

- Ensures on-going personnel safety at all developmental stages of the product;
- Ensures up-to-date and relevant process safety is available to all personnel;
- Generates only information that is needed at the current scale;
- Lessens the process safety hazards testing and assessment work-load for the latter stages of product life cycle;
- Provides valuable process design information that will influence process design, at the design phase, rather than requiring last-minute process design change(s).

3.4. Process Safety and Hazards Test Data

The previous section presented the link between product life cycle and hazards testing tied to progress through the cycle. There is also a linkage of common hazards testing techniques with the five process safety elements is shown on table 2.

Table 2. Types of Hazards Test Data Needed to Satisfy Five OSHA PSM Elements

Hazards Testing Procedure	PS Info (section d)	PHA (section e)	Operating Procs (section f)	Pre-Start Up Rev (section i)	Incident Invest (section m)
Calculations/Books/Open literature	✓	○	○	○	✓
Flammable Limits and Flash Points	✓	○	○	○	✓
DSC / DTA	✓	✓	○	○	✓
Adiabatic High ϕ Calorimetry	✓	✓	○	○	✓
Reaction Calorimetry	✓	○	○	○	○
Adiabatic Low ϕ Calorimetry	✓	✓	○	○	✓
Venting requirements	✓	✓	○	○	✓
Flammability / Explosion	✓	○	○	○	✓
Impact Sensitivity	✓	○	○	○	✓
Dust Explosion potential	✓	○	○	○	○

Where ✓ - data needs to collected; ○ - data already gathered will be used

Table 2 makes the point that for a typical process a *thorough* examination of the process, yielding process safety information in compliance with section (d), contains most of the data for sections (e), (f), and (l). The assumption is that if the PHA turns up questions about worst-case scenarios they can usually be answered from the data and analyses of the hazard testing indicated in Table 2. In particular, operating procedure limits on temperature, pressures, and other parameters, which are elements of the basis of safety and window of safe operations, are also obtained from the test data. Again, little if any additional test data is required if the initial process information and PHA are complete. Plant pre-startup safety reviews are similar to PHAs with related data requirements. This level of hazards test information may also be used to improve the overall safety of the process through the experimental evaluation of various risk reduction strategies.

For an accident, or incident, in addition to the basic information of sections (d) and (e) it is probable that further hazards testing will be necessary to provide a definitive explanation of the cause of the accident.

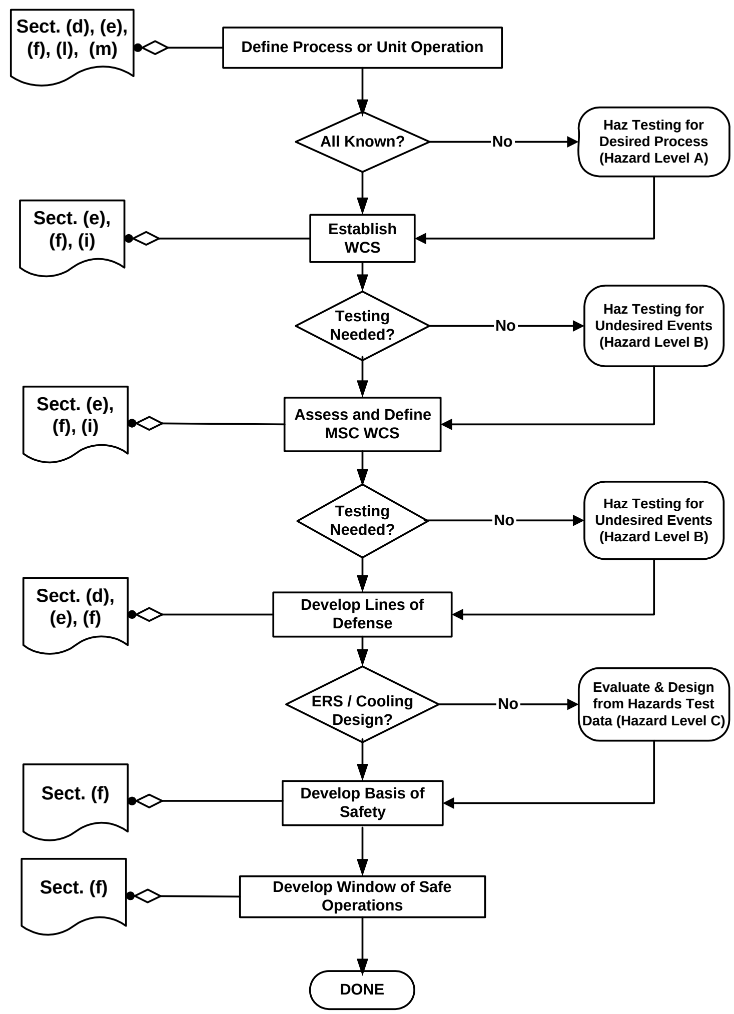

Figure 2. Flowchart Linking PSM Requirements, Hazards Testing and Hazard Assessment Stages

Figure 2 presents a typical order of conducting the hazards testing, linking the stage of product development, regulatory requirements and hazard testing sequence and complexity. The center column of the flow chart indicates that the desired process is assessed first and any missing information is provided by appropriate hazards testing. An assessment of the undesired events and process upsets is then performed, again obtaining hazards testing where needed. At that point, the lines of defense, basis of safety and window of safe operations can be defined from the data generated, and information gained from, sections (d) and (e).

The left hand column shows the link between the progress of the hazards testing and the contribution to the various elements of the process safety standard. It should be noted that the operating procedures, a key piece of the whole PSM standard, draw information from every step of the proposed hazards testing protocol. The right hand column indicates the type of hazard test data and interpretation needed for each step in the process hazard analysis.

4. Discussion

Process safety issues and concerns should be included in all aspects of process and product development including the design phase. It is axiomatic that accomplishing this goal requires the use of data about the performance of the desired, and undesired, process and applicable chemistries. It is not difficult to make the case that compliance with section (e) (*To develop a thorough, orderly, systematic approach for identifying, evaluating and controlling the hazards of processes involving highly hazardous chemicals.*) can only be accomplished if the employer (or process owner) possesses the relevant data.

A fundamental benefit of this shift in focus is a reduction in frequency of the type of incident seen, for example, at Napp Technologies, Inc. (*EPA/OSHA Joint Chemical Accident Investigation Report,* EPA 550-R-97-002, October 1997).

The five elements of OSHA's PSM standard together elaborate the following three key principles:

- Define and prioritize the credible worst case scenario(s);
- Design effective lines of defense for credible worst case scenarios;
- Develop the basis of safety and establish the window of safe operations.

Implementation of these principles requires accurate and pertinent hazards test data, obtained from appropriate hazards testing techniques.

4.1. Benefits of Proposal to CPI

Large companies do a good job of complying with the OSHA standard. Many have an internal hazards testing group that actively participates in the company's HSE programs. These companies are well aware of the benefits that hazards testing confers on process safety. Emphasizing that test data be used, regardless of company size, generates a more fundamental knowledge of the process. This in turn, leads to fewer upsets when running the processes, resulting in decrease injuries and fatalities to chemical workers and reducing adverse community and public reaction.

In three recent serious accidents where OSHA was involved (Napp Technologies; Morton International; Concept Sciences), lack of adequate process knowledge and lack of knowledge of the nature, extent and consequences of mal-operations were major causes of the accidents.

Large companies promote the value of hazards testing by presenting papers at professional conferences, and contributing time and effort to authorship of books on all aspects of the safety in, for example the CCPS "Guidelines for…" and articles in journals. However, these laudable efforts might be largely "preaching to the choir" if the mid-size, smaller, and toll manufacturing companies do not have the resources to expose their engineers to these sources.

5. Recommendations

There is no doubt that chemical process safety is the prudent and sensible approach lowering the accident and incident rate within the CPI. The OSHA standard has been in place, substantially unchanged, since 1990. During that time, many of the accidents involving chemical reactions occurred due to inadequate or missing data about the desired, and undesired, chemistry or process operations. Accidents occur in all types of chemical production facilities, including labs and pilot plants, even though the process (facility) is covered by the standard. In other words, both covered and not covered processes both present the same potential for hazardous situations. Three key points arise from this, and the body of the paper.

- Chemical process safety supported by hazards testing is the right thing to do, whether the process is covered or not, and whether the process is at the manufacturing stage or not.
- Hazards testing to identify and evaluate potential upset conditions should be an integral part of a company's process safety program. It is a major information source for process hazard analyses.
- The information obtained is specific to the thermodynamics and kinetics of the process chemistry.
- The information enables clear identification of *operational, thermal and reactivity* hazards of processes involving highly hazardous chemicals.
- The scope of the testing scope should be matched with the quantities of chemicals involved and the development stage of the product.

6. References

The following references provide the substantiation for this paper. They present excellent discourses, from various, related viewpoints, on the generation and application of hazards testing data.

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