

Safety & Health News

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Thoughts on Risk Criteria Dennis C. Hendershot

Late last year CCPS published a new book in the *Guidelines* series titled *Guidelines for Developing Quantitative Safety Risk Criteria*¹ (I was the CCPS Staff Consultant on the project). The book discusses risk based decision making for process safety and the use of quantitative risk criteria. It does not recommend specific criteria, but rather surveys existing published criteria from various regulatory authorities and companies around the world, and discusses how this information might be used for any organization to establish such a risk management and decision making strategy. Convincing people that risk criteria are useful risk management tools can be difficult. How do you avoid the issue of “putting a value on life” and keep focus on using risk criteria to direct scarce resources to the areas where they will have the greatest benefit? Here are some personal thoughts.

You can never do everything. Many of us have heard someone say that we will do **everything possible** to make sure that _____ (fill in whatever incident occurred) never happens again. **Everything!**² Do you really mean that? Perhaps we want to stand up and say that this is not true (but that might not be a good career move!). Whatever is done to reduce risk, you can always identify something else that could be done in addition. And if that is done, you can identify still another thing that could be done. And so it goes on, forever. You can never do “everything possible”! You have to stop someplace. So the issue is how to decide when to stop. Risk criteria can be helpful in making this decision. Perhaps, at some point, the additional things that you do to address the risk you are focusing on managing will create new risks or increase the magnitude of other existing risks. Overall risk, considering all hazards, may actually be increased. Risk criteria can help focus attention on the idea that when you get down to a defined low level on a particular risk that you are working on, it becomes likely that there are other risks that are as high or even higher, and it is time to change your focus to looking at those risks. You are in an area where additional changes to whatever you are working on are not likely to make any real improvement.

You should never use risk criteria solely as an absolute tool. Just because you meet the criteria doesn't mean that you should not stop looking for potential improvements. The philosophy of continuous improvement still applies. If you meet the criteria and there are obvious further improvements that are easily affordable, you should not use the fact that you meet the criteria as an excuse for not doing things that make sense. Meeting the criteria means that it no longer makes sense to make “heroic” efforts and changes to get further marginal improvements. These take up a lot of resources that could more effectively be used somewhere else. But if something is obvious, not too difficult, and make sense, you should do it even if you meet the criteria.

¹ Center for Chemical Process Safety. *Guidelines for Developing Quantitative Safety Risk Criteria*. John Wiley & Sons, Inc., Hoboken, NJ, and American Institute of Chemical Engineers, New York, 2009.

² “You can't have everything. Where would you put it?” – Comedian Steven Wright

Finally, way back in 1983, Trevor Kletz made a very relevant comment on the morality of risk calculations and risk based decision making. I can't say it any better than Trevor did nearly 30 years ago, so I will finish by quoting him:

"To many people the calculations may seem cold-blooded or even callous. Safety, like everything else, can be bought at a price. The more we spend on safety, the less we have with which to fight poverty and disease or to spend on those goods and services which make life worth living, for ourselves and others. Whatever money we make available for safety, we should spend in such a way that it produces the maximum benefit. There is nothing humanitarian in spending lavishly to reduce a particular hazard which has been brought to our attention and ignoring the others. Those who make the sort of calculations described, far from being cold-blooded or callous, are the most effective humanitarians, as they allocate the resources available in a way which will produce the maximum benefit to their fellow men."³



Engineers and Divergent Thinking

Peter Lodal, AIChE Safety and Health Division Chair

As the world was justifiably captivated by the success in rescuing 33 Chilean miners trapped for more than two months underground, my thoughts drifted in another direction (my thoughts drift more and more these days), back to that day in April 1971, when, getting ready for school, I heard the words that chilled everyone who heard them; "Houston, we have a problem....."

In both instances, clear-headed thinking, combined with unparalleled engineering expertise, turned what could have been a tragedy into a triumph. Of course, not all crises end well, as *Challenger*, *Columbia*, and the litany of process safety incidents that we all can recite by heart illustrate. One salient question, then, is why do some turn out well, while others do not? There are as many reasons as incidents, but to me, several common themes emerge:

1. Luck—there is no denying that sometimes, we benefit from a favorable combination of circumstances beyond our control. While I believe this to be true, I think it is far less a factor than sometimes claimed.
2. Preplanning—General Eisenhower is reported to have said "Plans are worthless, but planning is everything." I believe his actual words were harsher (and not for general publication), but the concept is sound—thinking through what can happen helps you both prepare for the "expected" issues, as well as preparing you for the unexpected.
3. Developed expertise—The Chilean miners would not be alive today if their rescue had been based on the wishes and goodwill of people worldwide. The Chilean hard-rock miners, mobilized by the country's dynamic president, and Chile's willingness to seek out expertise to help them wherever they could find it, were at the core of the successful rescue. Experts estimate that it takes at least 10,000 hours of active engagement in any field of expertise to

³ Kletz, T. A. *HAZOP and HAZAN - Notes on the Identification and Assessment of Hazards*. Rugby, Warwickshire, England: The Institution of Chemical Engineers, 1983.

develop the skills necessary to become expert at it. And that's 10,000 hours of intense work, not 10,000 hours of putting in your time.

4. Divergent Thinking—Of all the factors that I considered this is by far the most important, and for engineers, the most difficult. Why so hard? Engineers of all disciplines are trained to be convergent thinkers—gather data, do experiments, run calculations, so that in the end, the “best” solution is arrived at. Note that “best” almost always takes on the connotation of “only acceptable”. When dealing with unplanned, unscripted emergency situations, this type of thinking often leads to tunnel vision, and if circumstances either change on the fly (as they often do in fluid emergency situations), or if our size-up of the situation is flawed (also often a common occurrence due to lack of time to generate sufficiently accurate information), we can easily head down a blind alley, using up valuable time and resources, often irreversibly. The divergent thinker looks at a multitude of potentials, some which can be executed in parallel, some which will serve multiple solutions, and seeks to maximize potential solutions, instead of converging on just one. Both convergent and divergent thinking have their place, but in emergencies, divergence usually pays dividends.

So, to me, successful engineering support of emergency operations requires us to think differently than many of us were trained. While possible, it takes effort, discipline and intentionality to alter long-established patterns of behavior, which have served us well throughout our careers. Let's let the Chilean mine rescue stand as the example of why we should cultivate a different way of thinking.

Peter N. Lodal

Book Reviews

25 Years Later: The largest industrial disasters with hazardous material

By ir. C.M. Pietersen, Published by Gelling Publishing Co. PO Box 249, 2910 AE Nieuwerkerk aan den IJssel, The Netherlands. ISBN 978-90-78440-42-0. English version available on as a pdf at www.safety-sc.com/en.

This title presents an in-depth analysis of two 1984 disasters: the LPG explosions (BLEVES) that occurred near Mexico City, and the Bhopal, India MIC gas release. The author, Chris Pietersen, was the project manager at TNO (The Netherlands Organization for Applied Scientific Research) who led independent investigations of both events partially funded by the Dutch government. The author writes in the opening “Who is interested in a book about these old disasters? My reply is anyone who works in the process safety field. The underlying root causes of these accidents trace back to underlying cause of many accidents that have followed. Walt Howard summarized these as “Management decisions.” More broadly, the author writes that “these disasters occurred because large companies and governments did not follow the principles of safety.” The author has significant experience in the investigation of serious incidents. He writes that “It is sometimes as if time has stood still since 1984. ... Unfortunately, all of these [safety] systems are not effective if management is not alert enough. ... Prevention of victims of course, but also focus on victims after the event. That is an important responsibility that must be taken seriously.” The author discusses industrial safety 25 years later and what have we learned after these two events. What then follows are 10 short appendices that cover a wide range of topics from definition of BLEVES, to HAZOPs, to a reviews of

a number of recent incidents that have parallel situations similar to the two 1984 disasters. I recommend the book to any process safety supervisor or entry level engineer entering the process safety community.

Ron Willey, Sept 2, 2010

LNG Risk Based Safety : Modeling and Consequence Analysis

John L. Woodward and Robin M. Pitblado, John Wiley & Sons, Hoboken, NJ, 374 pages, \$115, April 2010, ISBN-13: 978-0-470-31764-8

Since the early 2000s, the LNG industry has grown by leaps and bounds globally as a clean fuel alternative to oil. Parallel to such growth, we have also witnessed lots of debates concerning the hazards or risks that LNG will bring to the society. In the preface of this book, the authors (John L. Woodward and Robin M. Pitblado) claimed that the full cycle of possible hazards and consequence mechanisms associated with loss of containment accidents or deliberate breaches has been reviewed. The underlying science governing discharge, pool formation and evaporation, dispersion, ignition and flash fire, and resulting pool fire is presented. Also presented are special hazards such as rapid phase transition, boiling liquid expanding vapor explosion (BLEVE), and vapor cloud explosions that are only possible under certain special circumstances.

Though there have been some literature reviews of the information in the public domain related to LNG safety, notably by Luketa-Hanlin⁴ and Cleaver et al⁵, no study has been conducted to review both the experimental data and prediction models with objectivity and exhaustiveness as this book. Woodward and Pitblado not only provide experimental data and modeling results for each LNG hazard, but also explain the science with theoretical equations. Risk and consequence analyses are presented for some potential hazard scenarios such as vapor dispersion and pool fire. Moreover over 440 literature citations have been listed in this book. Indeed this book is timely to compile all the literature information of the LNG properties and its hazards, based on known experimental data and theoretical modeling results, in order to provide current scientific understanding of the predicted behavior of any accidental LNG spills.

The detailed information and analysis related to LNG safety should be a useful resource for any engineers involved in LNG, teachers and students as well as folks in the legal and regulatory profession.

Ben Ho
Technical Advisor, BP

⁴ A. Luketa-Hanlin, "A Review of Large-Scale LNG Spills: Experiments and Modeling," *J. Hazardous Mat.*, A132, (2006), 119-140.

⁵ P. Cleaver, M. Johnson and B. Ho, "A Summary of Some Experimental Data on LNG Safety," *J Hazardous Mat.*, A140, (2007), 429-438.

7th Global Congress on Process Safety – Chicago, March 13-16, 2011

The 7th Global Congress on Process Safety (GCPS) will be held on March 13-16, 2011, in Chicago. Information on the Congress, including updates on the program and plans for other activities will continue to be provided on the Congress web site at:

<http://www.aiche.org/Conferences/Specialty/GCPS.aspx>

Here is a summary of the topics currently planned for the GCPS. The full agenda of papers for each session, and also abstracts for each scheduled paper, can be found at the GCPS web site above.

Loss Prevention Symposium:

- Case Histories and Lessons Learned
- Combustible Dust Hazards
- Fires, Explosions and Reactive Chemicals
- GCPS Poster Session
- Impact of Sustainability Efforts On Loss Prevention
- Risk Assessment - Release Modeling
- Consequence Modeling and QRA

Process Plant Safety Symposium:

- Facility Siting – for Existing Operations and Their Permanent, Temporary and Tent Structures
- Inherent Process Safety – Experience Applying the Discipline in Operating Facilities
- Layer of Protection Analysis (LOPA) – Case Studies and Application Experience
- Management of Change – the Most Difficult PSM Challenge
- Management of Combustible Dust Hazards
- Mechanical Integrity – Critical Line of Defense
- OSHA's National Emphasis Programs for Refineries and Chemical Plants – Experiences and Challenges
- Process Safety Culture – Impact of the Baker Panel Report to BP
- Risk Assessment – Revalidations
- Things Every Plant Engineer Should Know about Process Safety

Center for Chemical Process Safety International Conference:

- Application of Process Safety Principles
 - Emerging Issues in Global Process Safety – Impact On Industry From Recent Accidents
 - Integrating Reliability with Mechanical Integrity Programs
 - Lessons Learned From Facility Siting Studies
 - Lifecycle Management of Independent Protection Layers
 - New Relief System Solutions
 - Process Safety Knowledge, Competence, and Human Performance
 - Reinvigorating and Evolving Process Safety Implementation
 - Surgical Strikes vs. Blanket Approaches to Enterprise-level Risk Management
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ACS DCHAS-L Email List

DCHAS-L is the e-mail list of the Division of Chemical Health and Safety of the American Chemical Society. It is intended to facilitate the conduct of division business and provide the opportunity for members to make contacts with other members to share technical questions. List membership is for division members and, on a six month trial basis, non-members interested in divisional activities. This list is moderated to ensure that discussions do not stray from its intended purpose, but no technical review of the material on the list should be inferred from this editorial process. As this list is a public activity of the Division of Chemical Health and Safety, we expect that list discussions will be conducted in a professional tone. Information presented on the list is provided by the person writing the e-mail based solely on the information given in the question they are responding to. For this reason, e-mail list postings should not be considered professional advice, but rather helpful hints on issues to consider in addressing the question. The list is managed by Divisional secretary, Ralph Stuart. List traffic can be as high as 5 and 10 messages/day. If you prefer to receive all of the day's postings in a single e-mail, you can sign up for the DIGEST format. Contact Ralph for assistance with this. The DCHAS-L archive is available on the Web at:

<http://list.uvm.edu/archives/dchas-l.html>

New CCPS Books and Other Publications

Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, 2nd Edition

Published August 2010.

Providing an overview of methods for estimating the characteristics of VCEs, flash fires, and BLEVEs for practicing engineers, this guide has been updated to include advanced modeling technology, especially with respect to vapor cloud modeling and the use of computational fluid dynamics.

Guidelines for Acquisition Evaluation and Post Merger Integration

Published July 2010.

Written by a committee of industry experts, this book will provide a single, comprehensive reference that addresses acquisitions and merger integration issues related to process safety.

A Practical Approach to Hazard Identification for Operations and Maintenance Workers

Published June 2010.

This portable reference and practical guide to hazard identification is ideal for process operators, maintenance workers, and supervisors who are at the front lines in preventing fires, explosions, and toxic releases in chemical plants and refineries.

Inherently Safer Technology (IST) Definition

The US Department of Homeland Security's Chemical Security Analysis Center (CSAC), part of the Directorate of Science and Technology, has initiated an effort to enhance the safety and security of hazardous chemicals. As a first step, AIChE's Center for Chemical Process Safety (CCPS) was contracted to develop a formal scientific and technical definition of Inherently Safer Technology (IST). This definition is intended to help inform discussions of the role of IST in chemical plant and refinery security.

"It is clear that the concept IST can be, and has been used to address process safety issues in chemical plants and refineries," said Scott Berger, Executive Director of CCPS. "When considered in the security context, we must also think about the broader supply chain so that risk is not shifted from one site to another with no net reduction in risk. We must also consider the degree to which IST impacts security, as the impact on safety and security may be different."

"IST is one tool in the toolkit for improving security and safety within the chemical supply chain," said George Famini, Director of CSAC. "Understanding all of these tools and how they can be used to reduce the risk of a terrorist or catastrophic incident on a chemical facility or on chemicals in transit is critical."

You can read the final report "Definition for Inherently Safer Technology in Production, Transportation, Storage, and Use," at the CCPS web site:

<http://www.aiche.org/Conferences/Specialty/GCPS/IST.aspx>

Papers of Interest

Thanks to Stan Grossel for providing the following list of recent papers which might be of interest to Division members.

1. "Reactive Hazard Analysis of Cumene Hydroperoxide and Dicumyl Peroxide" by Wu, S-H and Shu, C-M, *Process Safety Progress*, Vol. 20, No. 2, pp.162-165 (June 2010).

This article covers the thermal properties of cumene hydroperoxide (CHP) and dicumyl hydroperoxide (DCPO). DSC was employed to determine the reaction kinetics, heat of decomposition (ΔH_d), exothermic onset temperature (T_o), reaction order (n), etc. A thermal activity monitor (TAM) also used to detect the storage index and thermal hazard parameters under various external temperatures. The onset temperature of CHP and DCPO were determined to be 110°C using DSC. This article describes the best operating conditions when handling CHP and DCPO.

2. "Runaway Reaction on Tert-Butyl Peroxybenzoate by DSC Tests" by Cheng, S.-Y. et al, *J. Thermal Analysis and Calorimetry*, Vol. 93, No. 1, pp. 121-126 (July 2008).

Tert-butyl peroxybenzoate (TBPB) is one of the sensitive and hazardous chemicals which

have been popularly employed in petrification industries in the past. This study attempted to elucidate its unsafe characteristics and thermally sensitive structure so as to help prevent runaway reactions, fires or explosions in the process environment. We employed DSC to assess the kinetic parameters [such as exothermic onset temperature (T_o), heat of reaction (ΔH), frequency factor (A), and the other safety parameters, using four different scanning rates (1, 2, 4, and $10^\circ\text{C}/\text{min}$)], combined with curve-fitting methods. The results indicated that TBPB becomes very dangerous during decomposition reactions; the onset temperature and reaction heat were about 100°C and 1300 J/g , respectively. Through this study, TBPB accidents could be reduced to an accepted level with safety parameters under control. According to the findings in this study and the concept of inherent safety, TBPB runaway reactions could be thoroughly prevented in the relevant plants.

3. "Feasibility Study for a Passive Trip System to Prevent a Runaway Reaction in a Batch Reactor" by Jablonski, D. and Hauptmanns, U., *J. Hazard. Mater.*, Vol. 167, Issue 1-3, pp. 1095-1099 (August 15, 2009).

Reactors for carrying out exothermic reactions are, amongst others, equipped with trip systems. Normally these are active systems requiring a number of components such as sensors, pumps, or valves to function for a successful trip. They may, for example, use the injection of a reaction inhibitor or the dumping of the reactor contents into a knock-out tank. The availability of such systems, i.e., their probability of functioning on demand, largely depends on their degree of redundancy. However, the possibility of common cause failures places a limit on increasing their availability by raising their degree of redundancy. Nevertheless, a trip system may reach a high availability if instead of stepping up its redundancy, a passive systems is used. The design of such a passive trip system for batch reactors is described and its feasibility is demonstrated by experimental investigations of three different types of reactions.

4. "Planning Protection Measures Against Runaway Reactions Using Criticality Classes" by Stoessel, F., *Proc. Safety and Environ. Protect.*, Vol. 87, Issue 2, pp. 105-112 (March 2009).

A systematic approach to the assessment of thermal risks linked with the performance of exothermal reactions at industrial scale was proposed a long time ago. The approach consisted of a runaway scenario starting from a cooling failure and a clarification of these scenarios into criticality classes. In the meantime, these tools became quite popular and many chemical companies use them. Recently, the international standard IEC 61511 required the use of protections systems with reliability depending on the risk level. Since the criticality classes were developed as a tool for the choice of risk reducing measures as a function of the criticality, it seems obvious that the criticality classes may be used in the context of the standard IEC 61511, which provides a relation between the risk level and the reliability of protection systems. Firstly, the runaway scenario and the criticality classes are described. Secondly, the assessment criteria for severity and probability of occurrence of a runaway scenario are described, together with the required data and their interpretation in terms of risk. Thirdly, the assessment procedure is exemplified for the different criticality classes. Finally, the design of protection measures against runaway and the required IPL and SIL are based on the risk assessment obtained from the criticality classes. This approach allows minimizing the required data set for the safety assessment and for the definition of the protection system designed in order to avoid the development of the runaway.

5. "Numerical Comparison of Chemical Reactors Safety Criteria" by Molga, E. and Lewak, M., *Computer Aided Chem. Eng.*, Vol. 26, pp. 1159-1163 (2009).

The boundary safety criterion, which can be applied when the reaction kinetic information is scarce, has been compared to the model-based safety criteria: the divergence criteria and the criterion of derivatives, respectively. The results obtained for a homogeneous liquid reaction carried out in a semi-batch stirred tank reactor confirm abilities of this boundary safety criterion to predict safe operating conditions.

6. "Azodicarboxylates: Explosive Properties and Thermal Hazards" By Berger, A. and Wehrstedt, K. D., *Proc. 12th Annual MKOPSC Symposium*, October 27-28, 2009.

A large number of azodicarboxylates and their derivatives are produced and used in the chemical industries. The versatile application of these compounds in research institutes and in the chemical industries for chemical synthesis arouse additional hazards. The aim of this paper is to obtain a prediction about the structure-response relationships regarding the explosive properties and the thermal hazards of different versatile used azodicarboxylates. The substances were examined with DSC. Furthermore, different laboratory test materials, based on the UN Recommendations on the Transport of Dangerous Goods, were applied to determine the explosive properties of these aforementioned substances

7. "Secondary Decompositions in the N-Oxidation of Low-Order Alkylpyridines" by Saenz, I. R. et al, *Proc. 12th Annual MKOPSC Symposium*, October 27-28, 2009.

Decomposition reactions during runaway are of significant concern due to the rapid pressure rise that they could produce, subsequently leading to the potential catastrophic rupture of the reaction vessel. As such, the reliable identification of secondary decompositions is important in the prevention of undesired events. During the runaway reaction of the N-oxidation of alkylpyridines, hydrogen peroxide, which serves as the reaction oxidant, starts decomposing into oxygen and water at low temperatures. This decomposition can increase the temperature enough to trigger the decomposition of alkylpyridine N-oxide (product of the N-oxidation), leading to a subsequent exponential increase in temperature and pressure which can have severe consequences due to the continuous production of non- condensable gases. As hydrogen peroxide decomposition is condition sensitive, the runaway behavior of the N-oxidation depends on the conditions of the system as well. Thus, changes in concentration or modifications of operating conditions can significantly affect the onset temperature, the Time to Maximum Rate (TMR), and other parameters. In order to study the decomposition of low-order alkyl- pyridines, calorimetric studies for 2-picoline N-oxide were performed using the APTAC calorimeter in isothermal mode. The condition-sensitivity of these systems wads also studied under different temperatures and catalyst concentrations. The purpose of this work is to identify the runaway behavior Of the N-oxidation of low-order alkylpyridines under Different scenarios which allow for the development of appropriate safety and control measures.

8. "Evaluative Comparison of Two Methods for SADT Determination (UN H.1 and H.4)" by Malow, M., Michael-Schulz, H., and Wehrstedt, K. D., *Proc. 12th MKOPSC Symposium*, October 27-28, 2009.

The authors present their results on the comparison of two methods for the SADT determination. Both methods, UN test H.1 and UN test H.4 are recommended by the

international transport regulations from the UN. But during the last years the applicability of the UN test H.4 has been questioned for solid substances. Therefore, three organic peroxides and one self-reactive substance have been investigated in 5 kg and 20 kg packages as well as in the UN test H.4 in a 500 mL Dewar vessel. The SADT values determined with the different methods match. The UN test H.4 seems to be well suited for solid substances at least from 20 kg or 60 L.

9. "Guidelines for Safely Handling Organic Peroxides and Inorganic Peroxides by Calorimetric Approaches" by Wu, S-H, Su, C-H, and Shu, C-M, *Proc. 12th MKOPSC Symposium*, October 27-28, 2009.

Organic peroxides (Ops) and inorganic peroxides (IPs) are usually employed as an initiator for polymerization, a source of free radicals, a hardener, and a linking agent in low density polyethylene (LDPE), polyvinyl chloride (PVC), controlled-rheology polypropylene (CR-PP), and styrene industries. Worldwide, due to their unstably reactive natures, OPs and IPs have caused many thermal explosions and runaway reaction incidents. This study was conducted to elucidate their essentially-hazardous characteristics. To analyze the runaway behavior of OPs and IPs in the traditional process, thermokinetic parameters, such as heat of decomposition (ΔH_d), exothermic onset temperature (T_o), self-accelerating decomposition temperature (SADT), half-life time to maximum rate (TMR), critical temperature (T_c), etc., were measured by calorimetric approaches and calculation methods. Generally speaking, safety and health handling information of hazardous materials and toxic substances are noted in MSDSs, but MSDSs do not provide many important handling safety data. In order to provide loss prevention information more useful safety data must be provided in MSDSs or safety guide books.

10. "Safer Management of Process Changes in Chemical Reactors" by Dellavedova, M. et al, *J. Loss Prev. Process Industries*, Vol. 23, No. 4, pp. 515-521 (July 2010).

Nowadays many chemical industries are SMEs (small and medium-sized enterprises) where multi-purpose batch or semi- batch reactors are commonly used. Vent sizing for realistic runaway scenarios is not an easy task for such enterprises since they have usually few resources and use multi-purpose reactors with fast process turnovers. As a consequence, these batch and semi-batch reactors are usually equipped with emergency relief systems sized once forever when the reactor is designed. This can lead to a large under- estimation of the vent area in case of runaway reactions occurring when processes different from the ones considered for originally sizing the vent are carried out. The approach proposed in this work aims to identify the maximum reactor load leading to safe conditions even in case of runaway phenomena to be handled with the emergency relief system already installed (or even with a smaller vent area). This approach allows avoiding the change of the emergency relief system with a larger vent area (as required every time a new more hazardous process has to be carried out in existing reactors) at the price of lower plant productivity.

11. "What Pressure Relief Really Means" by Kelly, B. D., *Chem. Eng. Prog.*, Vol. 6, No. 9, pp. 25-30 (September 2010).

This article was written to familiarize the novice engineer with some of the challenges in pressure relief systems – by first reviewing some important concepts that must be understood, then exploring relief system design. Among the topics discussed are: relief protection

strategy, pressure relief valves, safety valves, emergencies, staggering set pressures, the blowdown header, pilot-operated valves, preventing overpressure, testing, and closing thoughts.

12. "A Viscosity Correction Factor for Shear-Thinning Liquid Flows in Safety Valves" by Moncalvo, D. and Friedel, L., *J. Loss Prev. Proc. Ind.*, Vol. 23, No. 2, pp. 289-293 (March 2010).

At the moment there is a lack in the existing standards of a sizing procedure for media of more complex rheological behavior than Newtonian. A formulation for the generalized Reynolds number to calculate the viscosity correction factor and size safety valves for the flows of shear-thinning media is proposed in this work. The various formulations in the literature are validated in their accuracy of estimation of the mass flow rates of aqueous solutions of polyvinyl- pyrrolidone. Among them, the generalized Reynolds number defined using the wall viscosity of the annulus between the seat and the disk gives the highest accuracy without over- estimating the measured mass flow rates. On the base of these results, this generalized Reynolds number is recommended for introduction in the next review of both ISO 4126-1 Part 1 and API 520 for the sizing of safety valves for shear-thinning media.

13. "Estimation of Time to Maximum Rate Under Adiabatic Conditions (TMR_{ad}) Using kinetic Parameters Derived from DSC- Investigation of thermal Behavior of 3-Methyl-4-Nitrophenol" By Roudit, B. et al, Paper presented at the *Asia Pacific Symposium on Safety*, October 29-23, 2009, Osaka, Japan.

Kinetic parameters of the decomposition of hazardous chemicals can be applied for the estimation of their thermal behavior under any temperature profile. This paper describes the application of the advanced kinetic approach for the determination of the thermal behavior also under adiabatic conditions occurring, e.g., in batch reactors in case of cooling failure. The kinetics of the decomposition of different samples (different manufacturers and batches) of 3-methyl-4-nitrophenol were investigated by conventional DSC In non-isothermal (few heating rates varying from 0.25 to 8.0 K/min) and isothermal (range of 200-260°C) modes. The kinetic parameters obtained with AKTS-Thermokinetics software were applied for calculating reaction rate and progress under different heating rates and temperatures and verified by comparing simulated and experimental signals. After application of the heat balance to compare the amount of heat generated during reaction and its removal from the system, the knowledge of reaction rate at any temperature profiles allowed the determination of the temperature increase due to the self-heating in adiabatic and pseudo- adiabatic conditions. Applied advanced kinetic approach allowed simulation of the Heat-Wait-Search (HWS) mode of operation of adiabatic calorimeters. The thermal safety diagram depicting dependence of Time to Maximum Rate (TMR) on the initial temperature was calculated and compared with the results of HWS experiments carried out in the system with ϕ -factor amounting to 3.2. The influence of the ϕ -factor and reaction progress reached at the end of the HWS monitoring on the TMR is discussed. Presented calculations clearly indicate that even very minor reaction progress reduces the TMR_{ad} of 24 hours characteristic for a sample with initial reaction progress amounting to zero. Described estimation method can be verified by just one HWS- ARC run of reasonable duration by knowing in advance the dependence of the TMR on the initial temperature for any ϕ -factor. Proposed procedure results in significant shortening of the measuring time compared to a safety hazard approach based on a series of ARC experiments carried out at the beginning of a process safety evaluation.

14. "A Simple, Swift and Pragmatic Approach in the Use of Small Scale Laboratory Tests to Define Safe Drying Conditions for Manufacturing Scale Pressure Filters" by Anderson, K., Maude, D. and Wagner, S., *IChemE Symposium Series No. 155 (Hazards XXI)*, pp. 170-178 (2009).

It is relatively straightforward to determine the worst-case onset decomposition temperatures for liquids of low viscosity when scaling up from laboratory to plant of known size and natural cooling characteristics, as there are usually insignificant temperature gradients within the bulk mass of the liquid. However, the same cannot be said for solids (powders) or highly viscous liquids as these inherently have relatively poor thermal conductivity resulting in insulating effects that vary greatly depending upon the size and shape of the bulked mass. The Frank-Kamenetski model has been used and reported extensively in the literature, considering the balance between the heat of decomposition and the heat loss solely by thermal conduction and can be manipulated to give a critical layer thickness or volume at any temperature of interest. The approach adopted within AstraZeneca's development plants for the specification of safe bulk drying of Active Pharmaceutical Ingredients (API) and their intermediates is discussed with the main focus being on pressure filter drying. The various lab techniques and the respective sensitivities are used along with conservative estimations of various physico-chemical parameters to extrapolate, quickly and safely to larger-scale operating conditions. These conservative predictions are compared against larger scale test data as an initial step to ongoing corroboration of the simple pragmatic approach.

15. "Ignition of Bulk Solid Materials by a Localised Hotspot" by Caine, P. et al, *IChemE Symposium Series No. 155*, pp. 191- 200 (2009).

Thermal decomposition of combustible bulk powders poses a risk in the process and allied industry in operations, storage, and transport. Testing for storage and transport is well developed in establishing maximum possible pack sizes and safe ambient temperatures. However, current UN and EU tests are concerned with the maximum acceptable temperature for the whole bulk of the material, and do not consider the propagation from a hotspot (UN Manual of Tests and Criteria 2003, and BS EN 15188, 2007) This paper details the development of a small scale test method which has subsequently used to determine the ignition and subsequent combustion/decomposition characteristics for various bulk solid materials initiated by a local heat source. The results presented complement work undertaken by Brinkley et al to predict the ignition of weakly reactive solids by nearby heating sources via computational methods, and will also be used to assess the suitability of the small scale screening test, to be used as part of the thermal hazard assessment process to detect materials susceptible to this type of behavior.

16. "Reaction Hazard Analysis for Cumene Hydroperoxide with Sodium Hydroxide or Sulfuric Acid" by Chen-Y.-L. et al, *J. Thermal Analysis and Calorimetry*, Vol. 95, No. 2, pp. 535-539 (2009).

Organic peroxides (OP) are very susceptible to thermal sources, chemical pollutants, or even mechanical shock. Over the years, they have caused many serious explosions. Cumene hydroperoxide (CHP) is widely employed to produce Phenol and dicumyl peroxide (DCPO) in the manufacturing process. Differential scanning calorimetry (DSC) and thermal activity monitor (TAM) were employed to determine the potential thermal hazards and thermokinetic parameters [such as exothermic onset temperature (T_o), maximum temperature (T_{max}), and

enthalpy (ΔH) of CHP mixed with sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). High performance liquid chromatography (HPLC) was used to analyze the concentration vs. time of CHP, when CHP is mixed with NaOH; the T_o is induced earlier and reactions become more intricate than the pure CHP solution. CHP added to NaOH H_2SO_4 is more dangerous than pure CHP alone. Depending on the operating conditions, NaOH and H_2SO_4 are incompatible with CHP.

17. "Hazard Evaluation for Redox System of Cumene Hydroperoxide Mixed with Inorganic Alkaline Solutions" by Hou, H.-Y. et al, *J. Thermal Analysis and Calorimetry*, Vol. 95, No.2, pp. 541-545 (2009).

In petrochemistry, dicumyl peroxide (DCPO) is used in various resins for improving physical properties, which was produced by cumene hydroperoxide (CHP) with an oxidation reaction, redox reaction, and dehydration reaction. The reactant, CHP, is a typical organic hydroperoxide and has been intrinsically unstable and reactive due to its bivalent O-O structure which can be broken readily with bond-dissociation energy. This sequence on sensitivity study aimed at the thermal hazard evaluation for the reactive and incompatible characteristics of CHP mixed with various inorganic alkaline solutions. DSC and vent sizing package 2 (VSP2) were used to analyze the thermal hazards and runaway reaction of redox systems, such as decomposition of CHP in cumene solution and CHP reactions with inorganic alkaline solutions. Exothermic onset temperature, peak power, heat of decomposition, adiabatic self-heating rate, pressure rise rate, maximum temperature, maximum pressure of the reaction system, etc. were determined. The results of the tests have proven helpful in establishing safe handling, storage, transportation, and disposal guidelines.

18. "Thermal Runaway Hazards of tert-butyl Hydroperoxide by Calorimetric Studies" by Wang, Y.-W., Duh, Y.-S., and Shu, C.-M., *J. Thermal Analysis and Calorimetry*, Vol. 95, No. 2, pp. 553-557 (2009).

Thermal runaway reactions associated with exothermic behavior of tert-butyl hydroperoxide (TBHP) solutions and TBHP reacting with alkaline contaminants were studied. A DSC apparatus was used to characterize these inherent behaviors of TBHP solutions with KOH, NaOH, LiOH, and NH_4OH . The exothermic peak in thermal curves of TBHP solutions with different alkalis were detected by DSC thermal analysis. By thermal analysis, the authors compared various heats of decomposition of TBHP solutions with alkaline impurities, and determined the incompatible hazards of various TBHP solutions with alkaline contaminants. Comparing with TBHP in various diluents, the adiabatic runaway reaction via vent sizing package 2 (VSP2) indicated that aqueous TBHP intrinsically possesses the phenomena of thermal explosion with dramatic self-reactive rate and pressure rise under adiabatic conditions. Many commercial peroxides may have different hazard behaviors. Therefore, using thermal methods to classify the hazards is an important subject.

19. "Chemical Reaction Hazards of Distillation Processes" by Arthur, G, Williams, C. and Lugnbuehl, M., *ICHEM E Symposium Series* No. 155, pp. 700-703 (2009).

Distillations are used for many reasons, including purification, solvent recovery, concentration, and even reaction. There are a number of factors that should be considered when assessing the chemical reaction hazards associated with distillations. These include: thermal stability,

gas evolution, peroxidation, sublimation, materials compatibility, thermal history, air ingress, pyrophoricity, and control. This paper discusses the potential hazards associated with distillation processes on lab, pilot plant, and production scale, by asking and answering pertinent questions, illustrated by using examples from the authors' experiences.

20. "Lessons Learned from a Thermal Runaway Incident Involving An Organic Peroxide Intermediate During a Power Outage" by Morrison, D., Dillon, S. E. and Fecke, M., paper presented at the *AICHE 2010 Loss Prevention Symposium*, March 22-24, 2010, San Antonio, TX.

A small specialty chemicals plant experienced an unusual power outage as the result of a nearby lightning strike. The lightning strike damaged several of the electrical distribution systems, local controls, and instrumentation systems in such a way that the extent of the damages was not apparent. During the ensuing period of less than 10 hours, the facility personnel attempted to identify and repair the damaged systems to bring the plant back online. Unbeknownst to the operating personnel due to the damaged controls and instruments, a large oxidizing reaction vessel, which was in use at the time of the outage, contained a sufficient enough quantity of hot organic peroxide intermediate that it had started to undergo self- sustained thermal decomposition. Without the ability to cool the material in the reactor vessel, the organic peroxide underwent thermal runaway leading to uncontrolled venting of hot reaction byproducts that were ignited leading to an internal flash fire followed by a large pool fire in the operating unit. Personnel were injured and significant facility damages were caused. This paper will describe the accident investigation, provide comparisons to other recent thermal runaway incidents, like the T2 accident, and discuss lessons learned from thermal runaway accidents.

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