Safety & Health News



SAFETY AND HEALTH DIVISION

WINTER 2010

John F. Murphy and Dennis C. Hendershot, Editors

INHERENT SAFETY – IN THE NEWS AGAIN! Dennis C. Hendershot

On November 6, 2009, the United States House of Representatives passed the Chemical & Water Security Act of 2009 (H.R. 2868), and the bill will be sent to the United States Senate for consideration in 2010. As passed by the House, some of the provisions of the bill include:

- Chemical Facility Antiterrorism Standards (CFATS), issued in 2007 by the Department of Homeland Security (DHS) based on temporary authority to regulate chemical facility security, become permanent.
- An evaluation of inherently safer technologies (IST) would be required for facilities which have the potential for a toxic release which could impact the surrounding community.
- DHS can require implementation of IST for the "highest risk" facilities, where it is determined to be feasible and cost effective.

It is difficult to project what will happen to this bill in the Senate. There will certainly be a lot of debate on the IST requirements, which are strongly opposed by industry. In particular, there is concern about giving the government the authority to dictate chemical manufacturing processes and synthesis routes.

My personal opinion is that engineers and chemists should be thinking about IST as a way of managing security and process safety risks. Many of us already do, and many companies have made it a part of their process development protocols. For these companies, a regulatory requirement for consideration of options does not have to be onerous. They are already doing it, and just need to document it. For those chemists, engineers, and companies who are not familiar with IST, perhaps a regulation requiring evaluation will help educate them. I do have concern with a regulatory mandate that a company use a particular technology identified by outside "experts". The real experts are people who have spent years developing an understanding of the technology of their process, not regulators who, at best, have a cursory understanding of each of the many different technologies they will be charged with regulating. This is not a comment on their competence or capabilities, but just recognition that the job they are asked to do is not really possible.

If you have an opportunity to share your thoughts with your elected representatives on this subject over the next few months, they might welcome some technical expertise in this area. A good place to start to get a basic understanding of inherently safer design concepts is a recent (October 2009) CCPS summary document titled "An Introduction to Inherently Safer Design". You can download this document from http://www.aiche.org/ccps/webknowledge/inherentlysafer.aspx. And, if you will be attending the 2010 Global Congress on Process Safety in March, there are a number of sessions which will discuss inherently safer design.

– Dennis C. Hendershot Editor, *Safety and Health News*

AICHE SAFETY & HEALTH DIVISION UPDATE Kathy Pearson, 2009 Chair, Safety and Health Division

I hope you are scheduled to attend the Global Congress on Process Safety (GCPS) in San Antonio, TX. It looks like another excellent conference! The work for the GCPS is almost done. The session and symposia chairs have done a lot of work to get everything organized. All the authors have been busy. Draft papers have been submitted to the session chairs, and I know the folks that are late are working hard. The final paper deadline is almost here. Confex (the on line conference organization system used by AIChE) is up to date and registration is on-line. This year, we had so many good papers submitted that during most of the conference will have 4 simultaneous tracks instead of 3. (Editor's Note: The complete program grid for the 2010 GCPS is attached to the end of this newsletter.)

If you are coming to the Spring Meeting, I encourage you to attend both the Safety & Health Division dinner on Monday evening (March 21) and the division's annual meeting on Tuesday evening (March 22). Both of these events are great opportunities to get to know other champions of Process Safety and to get involved.

The Division's annual dinner has always been a special occasion. The dinner will be held Monday night, March 21st, at the Casa Rio. Tickets are \$50. A cash bar will be provided. After dinner, Jack McCavit will give a short, lighthearted talk. Jack is now his own boss after a distinguished career with Celanese. Jack is a frequent consultant to CCPS and a familiar face at the Global Congress.

The annual Safety & Health Division meeting is how the division keeps up with all the division activities. The S&H Division sponsors may excellent projects and programs. The Loss Prevention Symposium and the Process Plant Safety Symposium are both under the division umbrella. We are always looking for new volunteers to work on the conference. The *Process Safety Progress* journal is an excellent publication of the division. The reviewers for the publication are from the division. The S&H Division also sponsors awards for the AIChE college student design competition, and judging the student design competition is very interesting. By attending the annual meeting, you can find out what is going on and consider volunteering.

If you can't travel to attend, please consider watching the Global Congress webinars. The papers of all consenting authors in the Global Safety Congress will be available by webinar. The presentations will be available individually through ChemE on Demand. If you are an AICHE member, you have 6 free webinar credits each year.

"I Remember One Time..." Stefan Wawzyniecki, CIH, CHM, University of Connecticut 2010 Chair, ACS Division of Chemical Health & Safety

How many of us have started or continued a conversation with that line? I use it all the time when I teach a class on hazardous waste. I tell the students to sit back, relax, and not worry about taking notes. Then I begin telling stories.

I find that when you engage an audience with an event that they can relate to, or even envision themselves in, it serves two purposes: 1) it entertains them and 2) it can be used as a learning tool.

Whether it's an incident that occurred on the shop floor, or during a particularly dangerous event, people are inclined to listen. When talking about OSHA standards, the subject matter is, admittedly, boring. The regulations are not written for the common man, and to convey their importance becomes a challenge. Time for storytelling.

"Back when I was working summers to pay for college...." We all could probably fill in the rest of the story here. My summer jobs began in the 1960's, before OSHA, so they do tend to be entertaining. ".... I worked in a wood-working shop, making louvered doors. The operator needs to align all the horizontal slats so that when the press is activated, they engage into the openings on the side members. Once, the guy operating the machine saw that one slat was misaligned, so he reached in just after he activated the press....."

At 17, I saw my first occupational accident of a finger being separated from the hand. Even if you have never worked in a wood-working shop, everyone is familiar with a louver door. And the making of one can now be visualized as well, and, finally, the bloody result of the accident.

When conducting safety training, whether it is a chemical operation involving batch processing of highly corrosive materials, or, the maintenance of a machine that requires the use of solvents, telling stories brings the audience into the scene, and, provides a better incentive to listen to the message, whether it is wearing the proper PPE, or following a set of guidelines in performing a task.

"I knew a guy, who" Everyone knows a guy who did something which resulted either in a funny anecdote, or an accident. Remember that lab technician who was re-distilling ether, and walked away to get a cup of coffee, got involved in a conversation, and then heard an explosion coming from his lab? Lesson learned? Leave no potentially dangerous operation left unattended.

I usually try to get a sense of who is in my classroom; sometimes they are employed in a blue collar job, but returning to school to aspire to a higher position. I try to get them to tell their own stories, because that involves them in classroom discussion. It beats reading from a slide presentation sometimes. It also results in the audience "buying-in" to the message- "why should I care about regulations?"- because they may save you from harming yourself.

Telling stories based on experiences offers lessons learned. Whenever an event is scheduled which you feel others could learn from- say, an ammonia offloading into a tank at a plant - take pictures. That way, others benefit from the experience. As they say, 'Every picture tells a story...." Much effort is put into developing SOPs- Standard Operating Procedures- What to do, How to do it, When to do it, and Why one does it a certain way. But reading from a script is enhanced by providing a story that goes with it.

"There was that time when "

I got called in to help a researcher, who had a cylinder of ammonia gas. The regulator appeared to be installed correctly, but after opening the valve, and then closing it, they noticed the regulator still registered pressure. All attempts to close the valve with the valve wrench were unsuccessful. What to do....

The person in the machine shop suggested an option he usually did for stuck connections. He brought in a piece of pipe, slid it over the handle of the wrench, thereby extending it, and providing more leverage. It worked. Done carefully, with emergency personnel alerted, the problem was solved. As a story, it provided a learning experience.

As with all stories, especially in these litigious times, many would offer such anecdotes with the caveat, "Don't try this at home". And there are times when the storyteller may dig a little too far back in his or her memory, and come up with a tale such as

"I remember when we took some cans of old ether and brought them down an abandoned road. Placed them on a platform, , and the guy with the best aim shot them with his rifle. They drained into an open vat, and then the guy with the best softball pitch, threw a flare into it to ignite it."

Definitely, do not try this at home.

William J. (Bill) Bradford

Bill Bradford died on October 12, 2009 in a nursing home in Newton, Massachusetts. Bill was a pioneer in safety and loss prevention in industry and in the American Institute of Chemical Engineers.

Bill was born in New Rochelle, New York and grew up in Lynn & Swampscott, Massachusetts, graduating from Swampscott High School. He served in the US Army in World War II. After his time in the service, he attended Northeastern University in Boston, graduating in 1950 with a degree in Chemical Engineering. He immediately went to work for the Factory Insurance Association. By 1955 he was working for William H (Bill) Doyle as a supervisor in the Chemical Department. Bill Bradford was always forthright in his approach to loss prevention and safety. For example, he was lightly censured for describing conditions in an insured's plant as "appalling." Bill Doyle thought he might use a softer term.

Bill left the FIA and went to work for FIA's competitors, Factory Mutual Engineering. After a few years with FM, Bill left and went to work for Exxon Research and Engineering. He often said his time with Exxon was spent "sitting on a sand dune in Libya." However, during his time with Exxon he did publish a ground-breaking paper with Tom Culberson on designing explosion resistant control rooms.

Leaving Exxon, Bill went to work for Olin Corporation in their Safety and Loss Prevention Department. During his time with Olin, Bill designed and managed some innovative full scale fire tests on containers for calcium hypochlorite, developing a fire resistant container.

During his time with FIA, FM, Exxon and Olin, Bill was a supporter and contributor to the efforts of Bill Doyle, Russ Miller and Walt Howard to form the AIChE Loss Prevention Symposium Committee and the Health and Safety Division of AIChE. He was a "founding father" of the Air and Ammonia Plant Safety Series. He served as chair of several Loss Prevention Symposia and contributed several papers. He was the Treasurer of the Loss Prevention Symposium Committee for a number of years. During that period of time, the committee's treasury continually increased because of Bill's tight fisted financial management.

The AIChE sponsored a continuing education course on "Loss Prevention Management" which was taught by W.H. Doyle and R.F. Schwab for a number of years. After Bill Doyle had to give up this activity because of ill health, Bill Bradford took over this task and carried on for a number of years,

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Bill officially retired from the AIChE 11a committee in 2002 and had been living a life of a retiree in his home in Brookfield, Connecticut, and later in a retirement home in Newton, Massachusetts. Until a few years ago, he and Betty, his wife of 59 years, spent their summers in a home in Maine.

Bill Bradford will be missed by those who knew him and those that benefited from his pioneering Safety and Loss Prevention efforts. His entire career was devoted to the cause of improving process safety in the chemical industry.

John Davenport and Richard Schwab

AIChE Safety and Health Division and SACHE Student Awards

The following student awards were presented at the AIChE Annual Meeting, November 2009, in Nashville, TN:

<u>SACHE Individual Safety Award - Walt Howard</u> <u>Award</u> Brian Ashenfelter Trine University Advisor: Dr. Majid Salim

<u>SACHE Team Safety Award - Jack Wehman</u> <u>Award</u> Rhiannon Quirk, James Sims, and Elizabeth

Wienslaw Northeastern University

Advisor: Barry Satvat

<u>Safety and Health Division Award - Ted Ventrone</u> <u>Award</u> Brian Ashenfelter Oklahoma State University Advisor: Majid Salim 2009 Safety and Health and SACHE Safety Design Contest Award Winners, from left to right, Wendy Smades, SACHE Chair, Brian Ashenfelter, Rhiannon Quirk, and Elizabeth Wienslaw, and Ron Willey, representing the Safety and Health Division (Photographer: Miranda Gray)

<u>Safety and Health Division Award – Ephraim Scheier and Walt Silowka Award</u> Jared Clark, Kristin Wallace, and Afshan Samli Oklahoma State University Advisors: Jan Wagner and Rob Whiteley

PAPERS OF INTEREST

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

1. "The Important Role of Pressure in Supercritical Fluid Process Development Revealed by Reaction Calorimetry" by Montelis, C. A. and Meyer, T., *Process Safety Progress*, Vol. 28, No. 3, pp. 244-249 (September 2009).

The technique of reaction calorimetry adapted for use with reactions in supercritical fluids was used to study some safety aspects of the free-radical dispersion polymerization of methyl methacrylate in supercritical CO2. The reaction heat rate profile was found to change very little once the dispersion was well formed. Furthermore, it provided valuable information for the calculation of the maximum temperature attainable by the synthesis reaction (MTSR) in the case of a hypothetical cooling system failure. Finally, a series of failure scenarios demonstrated the importance of the pressure as far as the safety of the process is concerned, due to the particularity of the supercritical period, since a cooling system failure during this phase leaves very little time before the pressure overcomes the operational limit of the equipment and results in an accident. Hence, the utility and the importance of defining the reaction heat rate profile become obvious and several safety features have to be taken into consideration when designing a SCF process.

 "Improvements in the Safety Screening of Resin Manufacturing Processes" by Kalfas, G., Krieger, T., and Wilcox, R., *Process Safety Progress*, Vol. 28, No, 3, pp. 275-281 (September 2009).

Consequences of acrylic resin reactor runaways can be devastating, as it is evident in investigation reports of industrial accidents. Critical in preventing major accidents is the safety screening of any acrylic resin formula to be manufactured in large scale. Computer model simulations facilitate the evaluation of "layers of protection" against acrylic polymerization runaways. This work describes the adaptation of a chemical process dynamic simulator (DuPont[™] TMODS[™]) for use in simulation acrylic polymerization runaways. "Loss of cooling" and "monomer pooling (accumulation)" scenarios are the causes of these runaways. Simulations show that scenarios leading to "monomer pooling" result in more energetic runaways and to larger emergency relief capacity requirements than "loss of cooling" scenarios.

3. "Estimation of Time to Maximum Rate under Adiabatic Conditions (TMRad) Using Kinetic Parameters Derived from DSC – Investigation of Thermal Behavior of 3-methyl-4-nitrophenol" by Roduit, B. et al., paper presented at the NATAS 37h Annual Conference, September 20-23, 2009, Lubbock, TX.

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 the case of cooling failure. The kinetics of the decomposition of different samples (different manufacturers and batches) of 3-methyl-4-nitrophemol were investigated by conventional DSC in non-isothermal (a 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 data. 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 course 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 a Φ -factor of 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 TMRad of 24 hours characteristic for a sample with initial reaction progress amounting to zero. The described estimation method can be verified by just one HWR-ARC, or by one correctly chosen ISO-ARC run of reasonable duration by knowing in advance the dependence of the TMR on the initial temperature for any Φ -factor. The 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.

4. "Validation of Two Models for Discharge Rate" by Woodward, J. L., *J. Hazardous Materials*, Vol. Vol. 179, pp. 219-229 (2009).

A substantial body of discharge rate data has been developed over the past half century applicable for validation of single and two-phase discharge models. This paper applies a wide range of test cases and compares predictions with test data for two types of discharge model: (a) the energy balance model, and (b) the non-equilibrium model of Diener and Schmidt. The latter enhances the original homogeneous equilibrium model of Leung. This exercise reveals possible inconsistency between experimental datasets as much as it provides confirmation of the accuracy of the models, but both models are shown to provide adequate predictions within a factor of two and generally better.

- 5. "Handling of Reactive Chemical Wastes A Review" by Etchells, J. C. et al, IChemE Symposium Series No. 154 (Hazards XX), Paper 56 (2008). A study has been made of 142 incidents reported to the HSE, caused by unintentional or inadequately planned mixing of incompatible waste chemicals, or the decomposition of thermally unstable wastes. 62% of the incidents occurred at waste producer sites, the remainder occurring during waste treatment and transit. The immediate effects of such incidents included fires, explosions, chemical releases, and drums rocketing off-site. In some case employees were killed or injured. Five common reaction types accounted for over 68% of incidents where the chemistry was known. In most cases these reactions could be linked to specific industry types, in particular the chemical industry and engineering/metal treatment. This paper reviews the incidents and their causes, many of which were failures to take simple precautions, such as properly characterizing, packaging and labeling the waste, particularly during 'bulking up' into storage containers. The guidance available to prevent such incidents has been identified and, where gaps were found, suggestions to take matters forward with industry are made. A particular issue is the screening procedures required before waste chemicals are mixed, particularly in large tanks and reaction vessels, both at waste producer and waste-treatment sites. An ongoing research project on scale-up, being carried out for the HSE by HSL, is described. The Environment Agency (EA) is taking an active interest in this project.
- 6. "Thermal Decomposition Behavior of Cumyl Peroxide Measured by FT-IR" by Iwata, Y. and Koseki, H., *Proc. MKOPSC 11th Annual Symposium*, pp. 153Ff (2008).

The purpose of this study is to investigate the hazardous evaluation method in which FT-IR is used in order to make the fire prevention and the safety handling countermeasures of chemical substances. The FT-IR equipment is used to measure the absorbance changes in the thermal decomposition. The absorbance of raw materials and products corresponds to their concentrations. The concentration change of the raw materials and products is the important information to predict when the runaway reaction occurs. Cumyl peroxide (CHP) was used as an example. The thermal decomposition of CHP is known as the autocatalytic decomposition type. The temperature of the self-reactive substances of the autocatalytic style is not observed obviously before the runaway reaction. The temperature and pressure of a sample were measured in a closed pressure vessel in order to investigate the decomposition of CHP. The thermal decomposition of CHP is the closed pressure vessel was examined by measuring the time history of absorbance of CHP. Di-tert-butyl peroxide (DTBP) was investigated in a previous paper. DTBP increases gradually in the thermal decomposition before the runaway reaction. The results of CHP were compared with those of DTBP.

- 7. "Evaluating SADT by Advanced Kinetics-Based Simulation Approach" by Roduit, B. et al, J. Thermal Analysis and Calorimetry, Vol. 93, No. 1, pp. 153-161 (2008). This process study depicts the extension of the method of the application of the advanced kinetic description of energetic materials decomposition by its combination with the exact heat balance carried out by numerical analysis and the determination of the self-accelerating decomposition temperature (SADT). Moreover, the additional parameters such as thermal conductivity of the self-reactive substances, the type of containers and insulation layers, and different temperature profiles of the surrounding environment were taken into consideration. The results of DSC experiments carried out with different heating rates in the range of 0.25-4°C/min were elaborated by the Thermokinetics software. The application of the Thermal Safety software and the kineticsbased approach led to proper selection of experimental conditions for SADT testing. The applied approach enabled the simulation of such scenarios as the thermal ignition of self-reactive chemicals conditioned previously for 12 hours at 80°C and exposed later isothermally for 8 hours to temperatures between 120-180°C. The described method can be used for analysis of possible development of runaway during storage or transport of dangerous goods (TDG) and containers, and subsequent choice of the conditions that can prevent an accident.
- "Sizing of Safety Valves for Very Viscous Shear-Thinning Liquids" by Moncalvo, D., Friedel, L., and Jorgensen, B., Paper presented at the ExHFT-7 Conference, June 28-July 3, 2009, Krakow, Poland.

The extension of the actual sizing standards for safety valves from Newtonian liquids to shearthinning polymers is impeded by the lack of measurements. Here, liquid and two-phase flows of polyvinylpyrrolidone are discussed based on new experimental data. In liquid flows the mass flow rate is weakly affected by an increment in the polymer weight in the solution. This result suggests that the rate of viscosity increment with the polymer concentration between the seat and the disk is very slow. In support of this theory the distributions of the shear rates and of the viscosities are calculated computationally and that effect is evinced. In two-phase flows the total mass flow rates at constant relieving pressure and quality increases notably with the polymer weight in the liquid. A possible explanation considers both that air entrapment strains shearthinning liquids to very large shear rates and that a reduction in the void fraction following a redistribution of the phases occurs, when the viscosity of the medium increases.

9. "Thermal Stability at Elevated Pressure – An Investigation Using Differential Scanning Calorimetry" by Priestley, I. J. G. et al, *IChemE Symp. Ser.* No. 154, Paper 59 (2008).

During laboratory scale development of a new chemical process which is to be operated at elevated pressure a material was found to undergo an unexpected thermal decomposition. Initial DSC testing had indicated that melting appeared to be a prerequisite for decomposition and based upon this and the fact that melting points are elevated at increased pressures the material had been expected to be thermally stable under the proposed operating conditions. The unexpected thermal decomposition resulted in a more extensive investigation into the thermal stability of the material being performed. Work was carried out primarily at adiabatic pressure in order to obtain an understanding of the mode of the decomposition. The work was then extended to pressures of up to 30 bar and although this gave us a further insight into the decomposition with the University of Aberdeen has enabled DSC measurements to be carried out at 500 bar confirming predictions about the melting point behavior, but also giving an unexpected view of the thermal decomposition. A second collaboration with the University of Huddersfield provided a further insight into the thermal decomposition.

10. "Dewar Scaleup for Reactive Chemical Waste Handling" by Vechot, L. and Hare, J., *IChemE Symp. Ser.* No.154, Paper 57 (2008).

The use of non-pressurised Dewar flasks had been proposed by some parts of the chemical waste treatment industry to determine the exothermic reaction incompatibility of mixtures. Temperature rises of between 6-10°C in the Dewar vessel over a period of 10 minutes has been suggested by industry as criteria to indicate an exothermic reaction of concern. A literature review of the specific heat losses from Dewar flasks and large-scale vessels is compared to specific heat losses of Dewar flasks measured experimentally. Typical values of thermal characteristics of large-scale vessels used in the waste industries have also been assessed. The specific heat loss in the Dewar flask and large-scale vessels are very different. Scaleup limits of four types of Dewar have been calculated for different values of overall heat transfer coefficients for large-scale vessels. Thermal behavior of exothermic reactions in a Dewar flask has been compared to that predicted in large vessels using reaction kinetics and heat transfer models. For fast and highly energetic reactions the reaction energy release rate can be significant compared to the heat losses and the Dewar flask can detect runaway reactions. However, for low energy reactions or reactions with long induction time, the heat losses can be significant compared to the heat release rate and the Dewar test can then miss exotherms or give non-conservative results. It appears that the 6-10°C criterion proposed by the waste treatment industry might be observed when the heat losses do not have a significant importance compared to the reaction heat release rate. However, the reaction completion time at large scale would be shorter than at the Dewar scale. In some cases, 10 minutes might be sufficient to detect the exotherm but not the runaway reaction. The test should therefore be run to reaction completion in order to fully detect exotherms. Reliable conclusions about the scale-up of Dewar data can be obtained when the chemical reaction kinetics are well known. Unfortunately, this is not generally the case in the waste treatment industry. So, unless the specific heat loss of the Dewar has been shown to be less than large-scale vessels, this method in isolation is likely to be unreliable for scaleup to large vessels.

11. "Sizing of Safety Valves Using ANYSIS CFX-Flo" by Moncalvo, D. et al, *Chem. Eng. Technol.*, Vol. 32, No. 2, pp.247-251 (2009).

This work discusses the effect of the degree of fineness of the flow volume discretization and that of the turbulence model on the accuracy of reproduction of air mass flow rates in two safety valves using the CFD software ANYSIS Flo®. Calculations show that the degree of fineness of discretization is the decisive factor affecting the exactness of the calculations and that the best

reproduction is achieved with grids where at least two cells are built on the smallest edge. The selection of the turbulence model has by far in comparison a lower impact; however, the best accuracy is obtained using the standard k- ω model and the SST modification of Menter.

- 12. "Influence of the Liquid Phase Physical Properties on the Void Fraction at the Inlet of a Full-Lift Safety Valve" by Moncalvo, D. and Friedel, L., Chem. Eng. Technol., Vol. 32, pp.273-282 (2009). This work studies the influence of the physical properties of a liquid on the void fraction at the inlet of a corner valve resembling a full-lift safety valve. The test media are mixtures of air and aqueous solutions of glycerin. Our own measurements evince a reduction in the void fraction when the relative weight of glycerin in the solution is increased. If the effects of density, viscosity, and surface tension on the void fraction are accounted for by increasing the relative weight of glycerin in the solution, it results that the observed reduction of the void fraction is primarily a consequence of the enhancement of viscosity. On the other hand, the increment of the liquid density is responsible for a modest increase in the void fraction and the effect of the reduction in the surface tension is almost negligible. The enhancement of either the density or the viscosity of the liquid phase increases the relative velocity of the gas in the two-phase mixture, and, therefore, the slip. The impact of the liquid properties on the void fraction in co-current vertical pipe flows is similar to that at the inlet of the corner valve. Among the most common correlations for pipe flows, the formulation of Rouhani and the homogeneous void fraction accurately reproduce the void fraction at the inlet of the valve only for two-phase flows with liquids of low viscosity. A new void fraction correlation is proposed here, which reproduces all measurements very well and correctly predicts the impact of the liquid phase properties. Despite numerical coefficients, which can be fitted to additional sets of measurements, the structure of the new correlation is also applicable outside the range of two-phase flows for which it has been explicitly validated.
- 13. "Advanced Kinetics-Based Simulation of Time to Maximum Rate Under Adiabatic Conditions" by Roduit, B. et al, J. Thermal Analysis and Calorimetry, Vol. 93, pp. 163-173 (2008). An adiabatic calorimeter is very often used for the investigation of runaway of exothermic reactions. However, the ideal adiabatic environment is a theoretical state which during laboratory scale testing cannot be obtained, but may only be approached. Deviation from the fully adiabatic state comes from (i) the thermal inertia of the test system or heat lost into the sample container, and (ii) the loss of heat from the container itself to the environment that reflects the 'operational adiabaticity' of the instrument. In addition to adiabatic testing, advanced kinetic approach based on the kinetic parameters determined from DSC data performed under different heating rates can be applied. It enables to simulate what may happen on a large scale by testing and upscaling results obtained with a small amount of the sample. The present study describes the method of the evaluation of kinetic parameters of the coupling reaction of aniline with cyanamide in water/HCI from the DSC signals measured in non-isothermal experiments carried out with the rates of 0.5-8°K per minute. The reaction rate and reaction progress in adiabatic conditions were predicted after introducing the kinetic description of the reaction into the heat balance equations. It enabled to calculate the thermal safety diagram depicting the runaway time as a function of the process temperature. The influence of thermal inertia of the system, expressed as the Φ -factor, on the reaction course in concentrated and diluted reactant solutions was determined and discussed.
- 14. "Evaluation of Runaway Reaction for Dicumyl Peroxide in a Batch Reactor by DSC and VSP2" by Wu, S-H et al, *J. Loss Prev. Process Ind.*, Vol. 22, pp. 721-727 (2009).

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Dicumyl peroxide (DCPO) is usually employed as an initiator for polymerization, a source of free radicals, a hardener, and a linking agent. In Asia, due to its unstably reactive nature, DCPO has caused many thermal explosions and runaway reaction incidents in the manufacturing process. This study was conducted to elucidate its essentially hazardous characteristics. To analyze the runaway behavior of DCPO in a batch reactor, thermokinetic parameters, such as heat of decomposition (Δ Hd), exothermic onset temperature (To), maximum temperature rise (dT/dt)max, maximum pressure rise (dP/dt)max, and self-heating rate, were measured via DSC and the VSP2. Meanwhile, adiabatic thermal runaway phenomena were then thoroughly investigated by VSP2. The thermokinetics of DCPO mixed with acids or bases were determined by DSC/VSP2, and the experimental data were compared with kinetics-based curve fitting of thermal safety software (TSS). Results from curve fitting indicated that all of the above mentioned acids and bases could induce exothermic reactions at even an earlier stage of the experiments. To diminish the degree of hazard, hazard information must be provided to the manufacturing process.

15. "2-Methylpyridine-N-Oxidation Runaway Studies" by Saenz, L. et al, *J. Loss Prev, Process Ind.*, Vol. 22, pp. 839-843 (2009).

Calorimetry has been used in order to identify the runaway behavior of 2-methypyridene-Noxidation (2-picoline-N-oxidation). Experiments were performed in an Automatic Pressure Tracking Adiabatic Calorimeter (APTAC), employing 2-methylpyridine-N-oxide (2-picoline-Noxide) with or without catalyst, 2-methylpyridine-N-oxide, hydrogen peroxide, 2-methylpyridine (2-picoline) and catalyst, and 2-methylpyrididine, hydrogen peroxide, and catalyst. Approximately 16.5 g of aqueous solutions were used in 100 ml closed glass cells, in all but one measurement. Measurements were performed isothermally or employing the Heat-Wait-Search (HWS) technique. During reaction runaway, any excess of hydrogen peroxide and the produced 2-methyl-pyridine-N-oxide decompose releasing non-condensable gases and raising the pressure. It was found that the reaction runaway is condition sensitive. Catalyst, the presence of 2-picoline and/or its N-oxide, affect hydrogen peroxide and/or 2-picoline-N-oxide decomposition rates. Further research accompanied by analytical measurements of the gas and liquid phase would provide indications in regard to the decomposition mechanisms followed in those cases.

16. "A Simple, Explicit Formula for the Critical Pressure of Homogeneous Two-Phase Nozzle Flows" by Moncalvo, D. and Friedel, L., *J. Loss Prev. Process Ind.*, Vol. 23, pp. 178-182 (2010). The critical pressure ratio of the homogeneous two-phase nozzle flow model known as the Omega method is expressed as a function of the Omega Parameter as the exact numerical solution of a transcendental equation. A well fitting, easy to use, explicit approximation for flashing and non-flashing flows is presented here. The validation against the exact numerical solution proves that this new formula is better fitting than the other ones in the technical literature for both single and two-component flows.

2009 ACS DIVISION OF CHEMICAL HEALTH AND SAFETY OFFICERS AND COMMITTEE CHAIRS

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6th Global Congress on Process Safety

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Beginning	Ending	LPS	PPSS	CCPS	GCPS Future Track
1	I		Monday, I	March 22	
8:00 AM	9: 20 PM		Opening Pler	nary Session	
8: 00 AM	8:15 AM	Introduction and	Welcome, Kathy Pearson (GCPS Ch	nair) and Scott Berger (Executive Di	rector of CCPS)
8:15 AM	8: 30 AM	Introductory Rei	marks, Ron Wiley (LPS Chair), Chi	p Howat (PPSS Chair), Don Connolle	y (CCPS Chair)
8: 30 AM	8:40 AM	Presentatio	on of William H. Doyle Award LPS B	est Paper Award and PPSS Best Pap	er Award
8: 40 AM	9:20 AM	Keynote Address: Gilles Co	ourtemanche, Global Manager for Ex Chem	xxonMobil's Safety, Health & Environ nicals	ment for Downstream and
9: 20 AM	10:00 AM		Cof	fee	
		Fires, Explosions and Reactive Chemicals	Management of Change - The Most Difficult PSM Challenge	LOPA Bloopers and Outtakes	CCPS - Inherently Safer Design/Inherently Safer Technologies
10:00 AM	10: 30 AM	A Fuel Ratio Method for Estimating MESG of Nitrogen-Diluted and Oxygen- Enriched Fuels (Samuel A. Rodgers)	Managing Management of Change (Jack Chosnek)	HAZOP, LOPA, SIL - Be Careful What You Ask For! (Mike Broadribb)	Overview of IST (Dennis Hendershot)
10:30 AM	11:00 AM	Fire Study of Melting Fiberglass Using Fluent CFD Software (Steve G. Rochelle, Gary S. Whittaker, J. Wayne Chastain, Michael J. Maness, Peter N. Lodal)	Are you tired of playing "Whack a Mole" with your process safety program results - If so, its time for a change (David Cummings)	LOPA - Going Down the Wrong Path (Robert F. Wasileski & Fred Henselwood)	The DHS Chemical Facility Anti- Terrorism Standards (Lawrence M. Stanton)
11:00 AM	11: 30 AM	Assessing the Burning Rate of Solid Oxidizers (Elizabeth C. Buc, Henry L. Febo)	Training Management of Change Approvers (Karen Study)	Chronic Pain Resulting from Your Relief Device Management Systems (Christie A. Arseneau)	IST Trade-Offs (Jatin Shah)
11:30 AM	1: 30 PM	Lunch - Deni	nis Hendershot - So, I've Done a Of	RA and Have a Bunch of Numbers -	Now What?
		Fires, Explosions and Reactive Chemicals	Layer of Protection Analysis (LOPA) - Case Studies and Experiences	Case Histories of Risk Assessment and Problem Solving	CCPS - Inherently Safer Design/Inherently Safer Technologies
1:30 PM	2:00 PM	Safety Considerations on Flameless Venting in Working Environments (Matthijs de Maaijer)	LOPA and Human Reliability – Human Errors and Human IPLs (William Bridges)	Quantitative Risk Assessment Case Study for Organic Acid Processes (R Wayne Garland)	Federal View of IST from the CSB Perspective (John Bresland)
2:00 PM	2: 30 PM	Thermal Stability of Chemicals Based on Kinetics and Vessel Parameters (Amy Theis)	Use and Misuse of Enabling Conditions and Conditional Modifiers in Layers of Protection Analysis (J. Wayne Chastain)	Learning from events: Major process safety incidents from waste water in process chemical plants. (Paul G. Lambert and John Woodward)	ACC Philosophy on the Appropriate Application of Inherently Safer Principles (Pete Lodal, Laurie Miller)

Beginning	Ending	LPS	PPSS	CCPS	GCPS Future Track
2:30 PM	3:00 PM	Prediction of the Reactivity Hazards for Organic Peroxides Using a Novel QSPR Approach (Yuan Lu, Dedy Ng, Dr. M Sam Mannan)	Is It Really An Independent Protection Layer? (Arthur Dowell III)	Modeling the National Chlorinated Hydrocarbon Supply Chain and Effects of Disruption (Dr. Margaret E. Welk, Dr. Amy Sun, Dr. P. Susan Downes)	Applying Inherently Safer Systems – Contra Costa County's Experience (Randall L. Sawyer)
3:00 PM	3: 30 PM		Bre	sak	
		Fires, Explosions and Reactive Chemicals	Layer of Protection Analysis (LOPA) - Case Studies and Experiences	Case Histories of Risk Assessment and Problem Solving	CCPS - Inherently Safer Design/Inherently Safer Technologies
3:30 PM	4: 00 PM	Dust or Gas Explosion: Case study of dryer explosion and design venting (Scott G. Davis, Derek M. Engel and Olav Roald Hansen)	Consistent Consequence Severity Estimation (Angela Summers, Bill Vogtmann)	A Guide to Developing and Implementing Safety Checklists: Plant Steam Utilities (Mark Fecke, P.E., John Martens, Ph.D., P.E., Joel Cowells, P.E., Delmar "Trey" Morrison, Ph.D., P.E.)	Facilitated Panel/Audience Question and Discussion Session (Hendershot, Stanton, Shah, Bresland, Lodal, and Sawyer)
4:00 PM	4: 30 PM	Revision of Facility Siting Recommended Practice and Implementation Guidelines (Wayne Garland, Quentin A. Baker and Raymond H. Bennett)	Instrumented Protective Systems for Distillation Operations (Jennifer Mize, Wayne Chastain)	Distillation Columns Risk Assessment: When The Regular Hazop Evaluation Is Not Enough (Dalva Janine Rita, Carlos Marenco, Ivan Mantovani, Fabiana Tedeschi, Claudio Takase)	Facilitated Panel/Audience Question and Discussion Session (Hendershot, Stanton, Shah, Bresland, Lodal, and Sawyer)
4:30 PM	5: 00 PM	Flammable Gas Dispersion in Offshore Platforms: Gas Detectors Location (André Fleck, Ricardo Medronho, Marcio Nele)	Using the ISA84 / HAZOP / LOPA Process to Design a Safety Instrumented System (SIS) For a Fumed Silica Burner (Jeffrey O. Mudd, Bryan E. Pierce, Bruce K. Vaughen)	Pareto Optimization on Component Inspection Interval for Level Control in an Oil/ Gas Separation System (Xiaole Yang, Carl Laird and M. S. Mannan)	Facilitated Panel/Audience Question and Discussion Session (Hendershot, Stanton, Shah, Bresland, Lodal, and Sawyer)

Beginning	Ending	LPS	SSdd	CCPS	GCPS Future Track
))		Tuesday,	March 23	
		Combustible Dust Hazards	Mechanical Integrity – Critical Line of Defense	Consequence Modeling - Session Chair Antoinette Wenzel (Toni)	PPSS - The 'Soft Side' of Process Safety - Culture, Competency, Improvement
8:00 AM	8: 30 AM	OSHA's Experience with the Combustible Dust National Emphasis Program (Sanjeeva Kanth)	Using Root Cause Failure Analysis Results to Estimate Time to Failure & PFDavg for Pressure Relief Valves (Julia V. Bukowski, William M. Goble, Robert E. Gross)	Modeling Small Releases from Tanks (Rick Knack, Michelle L. Brown)	Implementing a Successful Conduct of Operations and Operational Discipline Program (James A. Klein, William Bradshaw, Lee Vanen Heuvel, Don Lorenzo, Greg Keeports)
8: 30 AM	9:00 AM	Practical Issues with Marginally Explosible Dusts – Evaluating the Real Hazard (Samuel Rogers, Erdem Ural)	Use of Multiple Non-destructive Examination (NDE) Methods in Life-cycle Evaluation of Process Equipment and Systems (F. Russ Davis CSP)	Atmospheric storage tank explosion modeling (Jerome Taveau, Jérôme Richard)	Process Safety in the Face of Significant Change (Leslie, J. May Ph.D., Don Pomraning)
9:00 AM	9: 30 AM	Property Insurance Company Evaluation of Combustible Dust Hazards (Henry Febo)	Risk-Based Mechanical Integrity – Beyond Fixed Equipment (Thomas J. Folk)	Update of "Guidelines to Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards" (Quentin A. Baker, Adrian J. Pierorazio, John L. Woodward, Ming Jun Tang)	How to Evaluate Process Safety Culture (Jerry Forest)
9: 30 AM 1	0:15 AM		Cofi	fee	
		Combustible Dust Hazards	Mechanical Integrity – Critical Line of Defense	Consequence Modeling - Session Chair - John Herber	Learning from our Systems
10:15 AM 1	0: 45 AM	Materials as Inherent Ignition Sources for Dust Explosions During Spray Drying (Vincent Van den Hoogenband)	Adjusting Spring Operated Pressure Relief Valve Proof Testing Intervals Using Statistical Modeling, and Comparing the Resulting Financial Risk assessments. (Stephen P. Harris, Robert E. Gross)	A Resilience Assessment Framework for Infrastructure and Economic Systems: Quantitative and Qualitative Resilience Analysis of Petrochemical Supply Chains to a Hurricane (Eric D. Vugrin, Drake E. Warren, Mark A. Ehlen)	Process Safety Management in the Energy Sector (Marc McBride, Harry Chen)
10:45 AM 1	1:15 AM	A Full-Scale Experimental And Modeling Investigation Of Dust Explosions In A Roller Mill (Kees Van Wingerden, Geir Pedersen, Brian Wilkins, Mogens Berg and Niels Otto Findsen Nielsen)	Strategies & Tactics for Mechanical Integrity Budget Battles (Daniel A. Long, Jack McCavit)	Modeling Dispersion and Deposition of Smoke Generated from Chemical Fires (Shahryar Khajehnajafi, Reza Pourdarvish, Hardik Shah)	Analyzing Historical Process Data to Identify Near Misses Warning Signs: Examples from the Buncefield Incident (Timothy J. Myers, Harri K. Kytömaa, Alfonso F. Ibarreta, Nicolas Ponchaut)

Beginning	Ending	LPS	PPSS	CCPS	GCPS Future Track
11:15 AM	11:45 AM	Combustible Dust: A Practical Approach to Identifying and Mitigating Hazards (Richard C. Griffin, Paula A. Wiley)	Semi-Automated Work Process for Capturing Relief Valve Proof Test Data to Support Failure Rate Analaysis (Jared Gladney, Todd Horner, Bob Matthews, Harold W Thomas)	Consequence Modeling of Chlorine Release (Prakash Amulakh Shah, Chandrakant J Patel, Ms. Raja Kirthi Kalluri)	Journey towards PSM excellence (Ravi Ramasamy, Ruskin Damani, Debendra Das, Prasad P. Chaitanya, Vishal Patel, Prakash A Shah, Vikas Shori, Ramesh Solanki, Nemsingh Verma)
11:45 AM	1: 30 PM		Lunch - Scott Berger - Lessons Le	arned from CCPS' Next 25 Years	
		ORA and Risk Criteria	Preventing Loss of Containment Incidents - Beyond Mechanical Integrity	Improving Process Safety Regulations	PPSS - Risk Assessment - Expanding Horizons for the PSM Environment
1:30 PM	2:00 PM	Challenges in Developing and Implementing Safety Risk Tolerance Criteria (Walt Frank)	Preventing Loss of Containment through a Systematic Assessment of Hazards, Consequences, and Risks (S. Dharmavaram, James A. Klein)	Panel discussion with industry & government experts.	Lessons Learned from Real World Application of the Bow-tie Method (Steve Lewis, Kris Smith)
2:00 PM	2: 30 PM	Ensuring Consistency of Corporate Risk Criteria (Wayne Chastain)	Analysis of causes of hydrocarbon leaks from process plants (Stein Haugen)	Panel discussion with industry & government experts.	High Integrity Protective System Design Using A Risk Based Approach (Robert Stack)
2:30 PM	3:00 PM	Enhancing Offshore Safety: S Description of the Offshore Major Accident Risk (OMAR) Model (Mike Considine, Dave Fargie and Warrick Cooke)	A Decade of Loss Containment Lessons (Marc G. Sáenz)	Panel discussion with industry & government experts.	Graded Quality Assurance Approach to Risk Assessment and Asset Management (Ramanathan Bharathi Theertha Viswanathan, Steve Soos)
3:00 PM	3: 30 PM		Bre	äk	
		ORA and Risk Criteria	Preventing Loss of Containment Incidents - Beyond Mechanical Integrity	Improving Process Safety Regulations	PPSS - Risk Assessment - Expanding Horizons for the PSM Environment
3:30 PM	4:00 PM	Geographical Societal Risk: a Useful Method for Understanding Societal Risk (Hans Boot)	Improved Flange Joint Reliability Can Help Prevent Loss of Containment (Tom Sandbrook, John Ludman, Mike Emery)	Panel discussion with industry & government experts.	Successful Process Safety Management Requires a Barrier Risk Assessment Tool (Ronald G. Hallmark)
4:00 PM	4:30 PM	The Use of Quantitative Risk Assessments to Site Temporary Trailers and Portable Buildings (James M. Hudson, Alex M. See)	The Hazards of Thermal Expansion (Juan C. Ramirez, Russell A. Ogle, Andrew R. Carpenter, Delmar "Trey" Morrison)	Panel discussion with industry & government experts.	Optimizing Facility Siting and Layout through Mapping Risk Estimates on Plant Area and Monetizing (Seungho Jung, Dedy Ng, Carl Larid and Sam M. Mannan)
4:30 PM	5:00 PM	ORA - Legal Prespective in OSHA Proceedings (Mark S. Dreux)	Using Real Time Process Models to Detect Loss of Containment and Mitigate Hazards (Harri K. Kytömaa, Timothy J. Myers, Alfonso Ibarreta, Nicolas	Panel discussion with industry & government experts.	Evaluation Of Normative Barriers Through The Mads/Mosar Methodology (Laurent Perrin, Felipe Muñoz, André Laurent)
5:00 PM	6: 30 PM		Poster S	Session	

Beginning	Ending	LPS	SSdd	CCPS	GCPS Future Track
			wednesday	, March 24	
		Human Factors	National Emphasis Programs	Learning from the Past	LPS - Fires, Explosions and Reactive Chemicals
8: 00 AM	8: 30 AM	Evaluating Human Response to An Alarm For LOPA or Safety Studies (Robert J. Stack and Paul Delanoy)	OSHA's PSM National Emphasis Programs: A Review of Findings to Date (Lisa A. Long, James Lay, Michael Marshall)	Hazards of Unplanned Power Dutages: Implementing Appropriate Safeguard (Russel Dgle, Tara L. Henriksen, Delmar "Trey" Morrison III)	RIV and SSIV Installations on Deepwater Platforms: A Decision Making Screening Tool (Oingsheng Wang, Bryan F. Bennighof, Jaffee Suardin, Nilesh R. Popat, Jeff McPhate and Dr. M. Sam Mannan)
8: 30 AM	9: 00 AM	A Framework for Human Error Analysis of Emergency Situations (Travis JB Deacon, Paul R. Amyotte, Faisal I. Khan, Scott MacKinnon)	Preparing for the Chemical NEP (Mark S. Dreux)	Vear-Miss Management to Develop Dynamic Leading Indicators to ^P redict Incidents (Ankur Pariyani, JIku G. Oktem, Warren D. Seider)	Jet Flame Length & Themal Radiation: Evaluation with CFD Simulations (Arafat Aloqaily, Arnab Chakrabarty)
9:00 AM	9: 30 AM	Elements of Human Factors Missing from Process Safety (Bill Bridges)	Complying with NEP/VPP RAGAGEP (Chad Patschke)	-earning the Lessons from Buncefield (Ian Travers)	Burn Injury Caused by Mixing Incompatible Chemicals with Sodium Permanganate (Russell A. Ogle, Delmar "Trey" Morrison III)
9: 30 AM	10:15 AM		Coff	ee	
		Human Factors	National Emphasis Programs	Process Safety into the Future	LPS - ORA and Risk Criteria
10:15 AM	10:45 AM	Using Conduct of Operations Principles to Improve Human Performance Under Challenging Economic Conditions (William Bradshaw, Kerry C. Beidelman and Amy J. Stubos)	Its Coming Right For Us! What to Expect and How to Prepare for the Chemical NEP (Christie A. Arseneau, Mark L. Farley)	Evergreening Your PHA (Sheri Sammons, Steve Higgens)	Process Safety and Chemical Security - The Need for Company- Specific Risk Criteria (Brad A. Fuller)
10:45 AM	11:15 AM	An Integrated Toolkit for addressing human factors issues in process safety (David Embrey)	Challenges in Hosting an NEP Inspection (Ken Hanchey, Jim Thompson)	BART:A Comprehensive Risk Vanagement Tool for Asset Integrity (Paolo Cherubin, Stefano Pellino, Chiara Cerruti, Paolo Carnevale, Riccardo Bandini)	Modification of Risk using Barrier Technology (Robin Pitblado, Cynthia Spitzenberger, Kjellaug Litland)
11:15 AM	11:45 AM	Modular Procedural Automation Addressing the Post Recession Skills Gap (Maurice Wilkins)	OSHA Chemical NEP Panel Discussion (Christie A. Arseneau, Mark S. Dreux, Mark L. Farley, Ken Hanchey, Lisa Long and Chad Patschke)	Dbjective Analysis of PSM Audit Data (Jerry Forest)	A Simplified Approach to Risk- Based Facility Siting (Ahmad Shafaghi, Mark Whitney)
11:45 AM	1: 30 PM		Lunch - US Nuclear Regulatory (commission - Human Reliability	