Status of AIChE Initiatives to Promote Effective Management of Chemical Reactivity Hazards

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NO ABSTRACT

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A Systematic Approach for Identification and Management of Chemical Reactivity Hazards

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ABSTRACT

An effective systematic approach for identifying and managing chemical reactivity hazards and implementing safe, robust, and plant-ready processes for the large-scale manufacture of specialty chemicals is described.

This approach includes: (1) a preliminary desktop screening (using group contribution, quantum chemistry, and advanced computational and modeling software) to assess fire and reactivity hazard potential; (2) experimental testing with a reaction calorimeter and automatic multiple reactors to evaluate normal processing conditions and the operating envelope for the desired reaction; (3) experimental testing with adiabatic calorimetry to evaluate thermal stability, the potential for thermal runaway, secondary decomposition reactions, gas evolution, and emergency relief scenarios. Experimental methods are usually supplemented with modeling, simulation, and kinetic calculations. A variety of online and offline analytical methods are also utilized.

This approach effectively integrates a range of conventional and modern tools. It has served well for hazard evaluation and screening of a broad range of process situations. Additional benefits include well optimized processes, guidance for process equipment and plant design, and the successful implementation of a range of protective, preventive, and mitigation systems to minimize process risks. Examples are included to illustrate this systematic approach.

Managing Chemical Reactivity - Minimum Best Practice

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ABSTRACT

A minimum best practice (MBP) is proposed to provide enough information to process, store and transport chemicals safely. The primary objective of the MBP is to reduce the frequency and consequences of runaway reaction-generated accidents, particularly those occurring within companies with limited technical and financial resources.

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SuperChems Reactivity Expert System for Screening Chemical Reactivity Hazards

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ABSTRACT

Recognizing reactivity hazards posed by pure chemicals and mixtures is critical for managing risks in processing industries, waste-treatment facilities, and emergency response activities. A binary interaction matrix is a simple but effective technique for summarizing chemical reactivity information. The construction of such an interaction matrix is a complex task and may involve several man-hours. A variety of data sources have to be consulted to generate a good quality chemical interaction matrix.

This paper discusses the development of the SuperChems Reactivity Expert system - a computerized algorithm that utilizes several databases of chemical interactions to generate a binary compatibility matrix along with a hazard report. The reactivity expert system also displays available regulatory and toxicity information for a chemical, if available.

We applied the reactivity expert system for screening the 167 CSB incidents and were successful in screening 126 of 127 incidents where the chemicals involved were specified.

Recommended Practice RP-101 Controlling the Hazards Associated With Reactive Chemicals

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ABSTRACT

Highly hazardous reactive chemicals pose a significant risk to chemical plant workers and the communities around them. These chemicals have the potential to create explosions, fires and releases of toxic materials. Unfortunately, the OSHA PSM regulation only covers a small fraction of these chemicals and in addition, the requirements of the regulation are not well understood by many companies. Recommended Practice – 101 is intended to fill this gap. It provides guidance on how to identify highly hazardous reactive chemicals and the recognized and generally accepted good engineering practices needed to control their hazards.

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Design Criteria for Reactive Hazard Screening Tools

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ABSTRACT

Screening for Reactive Hazards is an important part of a chemical process safety program. There are a number of screening tools available in the marketplace. The instrument design provides these tools with unique advantages and disadvantages. These tools should be used appropriately and within the operating conditions dictated by the design.

Several different types of screening tool are reviewed and evaluated to include Differential Scanning Calorimetry, Adiabatic calorimetry and a new technique, VariPhi, which combines attributes of the first two techniques.

Thermal Hazards Evaluation Using the ARSST

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ABSTRACT

Potential reactive chemical hazards are identified and quantified quickly and safely using the Advanced Reactive System Screening Tool (ARSST). This compact calorimeter has proven reliability for obtaining directly scalable rates of energy and gas release during a runaway chemical reaction as demonstrated over the last 15 years through consistently good performance in a variety of DIERS “round-robin” studies. More recently the ARSST has been used to investigate chemical compatibility, characterize foamy/nonfoamy behavior (reactive or non-reactive), evaluate isothermal stability, and estimate SADT values. This paper illustrates a number of applications where routine ARSST testing has provided an inexpensive and practical solution for evaluating thermal hazards.

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Applications of the VSP2 in Process Safety

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ABSTRACT

This paper discusses the use and application of the VSP2 adiabatic calorimeter in several areas of process safety related to reactivity screening and pressure relief design. Several experiments are presented and discussed relating the reasons for the tests and the analysis and application of the resulting data. The systems presented include runaway reaction studies, relief sizing studies (vent sizing for non-tempered systems using the Omega approach) and thermal stability screening scans. In one of the thermal stability examples, the results were much more energetic than anticipated based on readily available information and the MSDS. Also, the use of the VSP2 in screening for dust hazards is discussed. Examples are presented on how the VSP2 is being used for determining if self-heating issues with dusts and powders are present and on how the VSP2 is used to get an estimate of the onset temperature for self-heating.

In addition to being informative for the technical personnel already doing work in this area this paper could provide insight and concepts to chemical companies with limited resources who want to be more active in process safety screening activities.

Runaway Reaction Characterization: Further Round-Robin Study on Five More Systems

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ABSTRACT

Five more reactive systems have been evaluated as part of the DIERS Users Group Design/Testing Committee round-robin testing activities. These include (1) dicumyl peroxide, (2) esterification involving isopropanol and propionic anhydride, (3) styrene/acrylonitrile copolymerization and (4) styrene/methyl methacrylate copolymerization. The round-robin data obtained in various equipment - ARC®, VSP/VSP2, APTAC™ and ARSST – are compared and any discrepancies are noted. Published data in the open literature, if available, are also included in the comparison. In addition,(5) an emulsion polymerization involving styrene and butadiene was attempted and the difficulties encountered are discussed.

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MIXTURES of ISOPRENE with butadiene-DERIVED popcorn polymer: CHARACTERIZATION OF REACTIVITY

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ABSTRACT

The reactivity of isoprene with butadiene-derived popcorn polymer has been examined via adiabatic calorimetry. The presence of popcorn polymer leads to the occurrence of reaction at 20-30°C lower temperature than observed for isoprene alone. The reactivity appears to be affected modestly by the presence of tert-butyl catechol inhibitor. For sufficiently-high popcorn polymer concentrations, the low temperature reaction is followed by an exotherm above 180°C reflecting reaction of the popcorn polymer itself.

The reactivity behavior of isoprene with popcorn polymer resembles that found previously for 1,3-butadiene with butadiene-based popcorn polymer.

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Experimental and Theoretical Modeling of Runaway Polymerization Under Free-radical Initiation

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ABSTRACT

This paper presents an experimental study of runaway polymerization of some common acrylic and vinyl monomers using the VSP2 adiabatic calorimeter. These monomers include methyl methacrylate, butyl acrylate, methyl acrylate, ethyl acrylate, vinyl acetate, vinyl pyrrolidinone and styrene. The free-radical initiators consisted of azo type and organic peroxide type. Modeling of the runaway self-heating behavior is attempted based on the classical free-radical polymerization kinetics. Comparison between model predictions and experimental data are shown to yield good results for many monomer systems, however, some deviations are noted.

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Venting of a Runaway Organic Peroxide Decomposition in Viscous Solvents on Pilot-Scale

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ABSTRACT

Polymerisation reactors are widely used in the chemical industry and runaway reactions continue to occur in them. Those of greatest concern include highly viscous multiphase mixtures. Considerable uncertainties exist in the design of emergency pressure relief systems for such reactors, as there is very limited experimental data available on the flow of such fluids in relief systems.

Venting experiments are reported here that have been carried out in a 350 litre pilot-scale reactor for the runaway decomposition of an organic peroxide in xylene solvent, with batch volumes of 150 and 200 litres and with a range of concentrations of polystyrene dissolved in the xylene to modify the viscosity. Measurements were made, as a function of time, of pressure in the reactor, vent line and catch tank; temperature at different levels in the reactor and in the vent line and catch tank; viscosity in the reactor; mass in the catch tank; and two-phase density in the vent line.

Analysis of the results shows that the venting behaviour of a high viscosity reaction system is complex. There is no simple relationship between maximum pressure and viscosity. The results indicate that the flow regime in the reactor is influenced by the fluid viscosity and that this is of primary importance in explaining the effects on maximum pressure. A comparison of the experimental results with the results of a simple approximate vent sizing method recommended by DIERS showed significant differences between the experimental and calculated maximum reactor pressures.

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Revisiting DIERS Two-Phase Methodology For Reactive Systems Twenty Years Later

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ABSTRACT

Building upon the original DIERS methodology presented twenty years ago, an easy to use design methodology for reactive vapor, gassy and hybrid systems has resulted that properly accounts for two-phase flow effects. The methodology is illustrated to be consistent with available experimental and incident information and examples of bad and good design practices are provided for vapor, gassy and hybrid systems.

A Detailed Kinetic Model for the Polymerization of Acrylonitrile

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ABSTRACT

Many useful papers and publications have appeared in the literature about the properties and free-radical polymerization of acrylonitrile (see references [1] through [31]). In particular, the publication entitled “The Chemistry of Acrylonitrile”, published by American Cyanamid [32] presents a very useful summary of acrylonitrile reactions with a myriad of other chemicals. The majority of published acrylonitrile free-radical polymerization and copolymerization rate data is measured at constant temperature, i.e., isothermally.

In this paper we present twenty four measured adiabatic calorimetry data sets for the bulk polymerization of acrylonitrile. The tests were conducted using pure acrylonitrile, as well as acrylonitrile in combination with aqueous solutions of ammonia, sodium hydroxide, hydrogen peroxide, t-butyl hydroperoxide and hydrogen cyanide.

Pure acrylonitrile has an exothermic heat of polymerization of 17.3 +/- 0.3 kcal/mol. It polymerizes in both the liquid and vapor phase. The formed polymer begins to decompose exothermically above 240 °C. Small amounts of sodium hydroxide and/or ammonia significantly increase the polymerization rates of acrylonitrile and lower the polymerization onset temperature. Contamination with these materials must be avoided.

Bulk polymerization of acrylonitrile is not practiced today because of the runaway reaction potential. Thermally-induced bulk polymerization data and rate models are necessary to establish pressure relief requirements for storage tanks containing acrylonitrile. Scenarios of interest include fire induced bulk runaway polymerization and process induced bulk runaway polymerization caused by contamination and/or excess charge of initiator. A recent study by the United States Chemical Safety Investigation Board revealed that storage vessels and drums of reactive chemicals account for 32 % of all accidents surveyed.

Specific Features of Kinetics Evaluation in Reaction Hazard Assessment

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ABSTRACT

The advanced approach to assessment of reaction hazards is principally grounded on the use of kinetics-based simulation of a process. First of all it concerns solution of such important challenges as design of emergency relief systems and rating reactivity. Apparently the validity of the results obtained strongly depends on the reliability of a kinetic model applied which, in its turn, is essentially defined by the proper choice of a mathematical model of a reaction and the correctness of the methods used for kinetics evaluation. This paper is aimed at discussion of these problems.

At first two classes of kinetic models - formal and concentration-based descriptive ones - are considered followed by demarcation of areas of their applicability.

Then we analyze pertinence of some assumptions many popular methods of kinetics evaluation are based on. It is shown that in many cases only sophisticated computational methods of kinetics evaluation can give adequate kinetic models that are appropriate for hazard assessment.

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Anticipate Pressure Relief Requirements for Tempered Systems Based on Process Data

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ABSTRACT

This paper considers emergency pressure relief vent sizing for a tempered system at the conceptual design stage. An evaluation procedure is developed for pressure relief scenarios with and without vapor-liquid disengagement. The key feature of this analysis is the reduction of vent sizing equations to a form with only overpressure as the independent solution variable. With such relations on can proceed from process data and reasonable assumptions to efficient estimation of pressure relief vent size for concept evaluation. The analysis also provides insight as to why relief vent sizes for tempered systems turn out the way they do.

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Adiabatic Runaway Reaction, Blowdown, Quench and Inhibition in Fire Engulfed Vessels: An Experimental Study

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ABSTRACT

Two linked PHI-TEC adiabatic calorimeters were used to simulate a fire heating and runaway reaction scenario. This was for plant-scale continuous flow reactors that are used for the production of acrylamide: two-phase venting from a "blocked in" reactor into a dump tank containing water and a chemical inhibitor was simulated. After venting both the reactor and the quench vessel were subjected to continued heat inputs from the fire. The main purpose of the study was to determine whether this could introduce any secondary decomposition reactions.

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Limiting Temperature and Fire Duration as a Means of Prevention of Energetic Decomposition Reactions

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ABSTRACT

This paper considers methods to address the condition which could arise when an existing process vessel – not a reaction vessel – is considered for a new service utilization. The emergency pressure relief vent has been previously evaluated in a traditional manner with the typical underlying assumptions (a) an external fire of unlimited time duration, and (b) a relief set pressure corresponding to the vessel design pressure. The new service application includes a new set of fluid properties, including a potential exotherm with an onset temperature which could only be attained by the considerations (a) and (b) above. This paper considers methods to avoid the exotherm onset temperature.

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Last Line of Defense, Only Line of Defense?

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ABSTRACT

A relief system is often referred to as the "last line of defense". However, it should not be the "only line of defense".

This paper provides an expert perspective and interpretation of today's legal climate with regard to projects involving pressure relief systems for reactive chemicals. A case study involving the storage of uninhibited butadiene is used to illustrate key concepts and recommendations. Recognized and Generally Accepted Good Engineering Practices (RAGAGEP) are cited to illustrate the importance of utilizing layers of protection. In other words, a pressure relief system should not be the only layer of protection, especially for reactive chemical.

A Heuristic Approach of Calculating Spray Water Flux Needed to Avert Fire Induced Runaway Reactions

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ABSTRACT

In general all reactions have some heat effects. When the ability of the equipment to remove the heat is exceeded by the heat generated by a reaction, a hazardous situation called a runaway reaction may take place.

Sometimes the exothermicity of runaway reactions is so high that the size of an emergency vent becomes impractical to install. Water sprinklers can sometimes be used to avert a fire induced runaway reaction.

Because the sprinkler system has a finite activation time, insulation helps to prolong the time required to reach the decomposition temperature.

This paper concludes that the required water flux to avert the fire-induced run away reaction may be conservatively estimated by adding the water flux necessary to maintain an unbroken water film on the external surface of the equipment and the water flux necessary to absorb the fire heat after allowing for the splash loss and the in-flight loss.

When adequate sprinkler water is used, the metal temperature of the insulation jacket cannot theoretically exceed the boiling point of water thereby assuring the avoidance of fire-induced runaway reactions whose adjusted onset decomposition temperature exceeds 100 ^{o}C. Fire-induced runaway reactions with lower onset temperature can also be avoided depending on the initial temperature of the contents, mass of the contents and equipment, insulation thickness, fire duration etc, but a detailed calculation including dynamic simulation is necessary, and the burden of proof lies with the designer.

The reliability of the sprinkler system must be maintained high in order to include its credit as an environmental factor to avoid the fire-induced runaway reaction as a scenario per NFPA 30. Although API RP 521 does not allow any credit for sprinkler water, it allows credit, unlike NFPA 30, for insulation thickness, and therefore, a runaway reaction can be avoided by using insulation alone per API RP 521.

ERS Design for Two-Liquid Phase Systems

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ABSTRACT

Two-liquid (immiscible) phase reactive systems are often encountered in industrial processes such as suspension polymerization and emulsion polymerization. Typically these reactions are carried out in a reactor comprising of one organic monomer phase and one aqueous phase. The organic phase usually of lower density can be either more volatile or less volatile than the aqueous phase. This paper discusses the runaway characterization of such immiscible systems and the concern over phase separation and potential phase inversion. Vent sizing equations are presented for two extreme cases with and without phase separation. The discharge of a two-phase flashing fluid containing two immiscible liquids is also presented using an extension of the omega method. Illustrations are given for the styrene-water and the vinyl chloride-water systems.

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Process Control in Multipurpose Plant – Sufficient to Prevent a Runaway Reaction in all Cases?

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ABSTRACT

When determining the Basis of Safety for a multipurpose plant, all products to be manufactured in that plant have to be taken into account. Different possible maloperations must be considered in conjunction with the various products and the process control measures that may be in place. One product may potentially prove to give the worst case for one scenario, but for a different scenario it may be another product that poses the greater risk. Therefore, detailed in depth knowledge/experience is required for consideration of the implications and consequences of the reaction in a maloperation situation; which may be significantly different to the normal operation.

The new plant that was being investigated was to manufacture 22 isothermal emulsion polymerisation products with a range of feed times from one to four hours. The exothermic nature of these products also varies widely with up to four different monomers being fed from bulk storage. Due to the wide difference in heat output from

these reactions, it was deemed that one product would have to be manufactured at a reduced batch size of 12te instead of 18te in order to provide adequate cooling capacity.

For this new plant, the fundamental way it differs from our existing plants is that instead of the monomers being mixed in a monomer vessel prior to the start of the reaction and then fed to the reactor, there is a direct feed of monomer during the reaction phase. This system has advantages in that a monomer mixture, which could potentially destabilise, is not held for long periods of time. But this system introduces other issues that must be resolved.

Therefore, experimentation using the Vent Sizing Package (VSP) apparatus was used to investigate the various credible maloperations for the different products. During this investigation various phenomena were highlighted that had not been obvious during the initial worst case identification study. By using these VSP experiments in conjunction with engineering design, sufficient process control measures were attained to prevent a potential major runaway reaction from occurring.

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Containment System Design

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ABSTRACT

This paper deals with the design considerations for several plant containment systems which were installed as part of the emergency pressure relief system. In all cases, the quench tank approach with vapor suppression was utilized. The examples presented include (1) multiple batch reactors handling vinyl monomers, (2) multiple initiator charge vessels and (3) multipurpose batch reactors with possible Grignard–type reactions. The design considerations include quench fluid selection, sizing of the quench tank, fluid mixing, sparging dynamics, vapor condensation efficiency and post relief heatup.

Pressure Safety Valve Thrust Forces for Compressible Gas or Vapor Flow

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ABSTRACT

When a pressure safety valve actuates, thrust forces are developed. These thrust forces must be considered for the proper installation of the relieving device. For gas or vapor compressible flow, Simpson developed thrust force plots that can be utilized to calculate the magnitude of the thrust force. Although these charts are available in the open literature, the assumptions behind the charts and the derivation of the underlying equations are not. This paper addresses this issue by re-deriving the equations necessary for reproducing the charts. All fundamental assumptions are stated and all flow models are explained. The limitations of the equations are clearly stated. Numerical examples are given to illustrate the use of the equations and the corresponding Simpson Charts.

The examples are also used to compare calculated results from other methods. In addition, several important modifications to the original charts are noted. The thrust force equations for a relief valve operating with a subcritical nozzle and a subcritical outlet, which are absent from the original Simpson Charts, are included here. The extent of the region where the relief valve operates with a critical flow nozzle and a subcritical flow outlet is modified to account for backpressure effects. Finally, the concept of a minimum relief valve outlet to nozzle area ratio is introduced.

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Relief Vent Sizing For Deflagrations

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ABSTRACT

Many gas-phase reactions result in a pressure build-up which is very fast, but slower than that for an explosion (i.e. a deflagration). Sizing a relief vent by the conventional method which assumes steady state conditions at the vent throat can result in an unacceptably large vent size. A method previously proposed by DuPont based upon an experimental

rate constant for the deflagration (e.g. a “violence coefficient”) and an expression for the experimental flow capacity of the valve results in more realistic vent sizes. This paper compares the results of these two methods, as well as a method using a more general relation for the valve flow capacity with data for an ethylene decomposition reaction reported by DuPont.