



Mary Kay O'Connor Process Safety Center

Strategic Research Plans

Safety climate safety culture

The Center submitted a proposal to the National Science Foundation, addressing the effects of safety climate, safety culture, and personal propensities on safety decision making. The proposal was submitted in collaboration with the departments of psychology and political science. Parallel to the proposal activities, the Center is collaborating with the department of psychology in an attempt to define the relationships between safety climate, safety behavior, and safety performance. Safety culture refers to shared underlying values and assumptions that organizational members hold regarding safety issues while the perception of safety climate can influence the way employees behave and perform their work, which can have a direct impact on safety outcomes such as accidents, near misses, and daily safety behavior (MKOPSC, 2005a). Due to the complexity of these relationships, intensive research is required to address a variety of safety performance outcomes in addition to relying primarily on self-reporting instruments, as being conducted by psychologists and by department of managers. The Center is trying to address the following hypothesis:

“Safety performance outcomes are significantly correlated with safety climate and with safe culture”.

The study will address the hypothesis in the context of the process industries. Safety performance outcomes will consist of “leading” and “lagging” indicators, and will include information on safety performance outcomes from publicly available incident databases (given that this information is deemed useful). The antecedents, correlates, and consequences of safety climate and safety behavior will be addressed in an effort to demonstrate the systematized nature of safety issues.

The ultimate goal of this research is to develop key features of a good safety culture or operational discipline. Once a set of guidelines or identifiable indicators for a good safety culture are decided, the organizations can develop and implement programs to achieve and maintain safe operation and avoid potential disasters.

LNG Safety Research

LNG safety is back in the headlines as over 40 LNG importation terminals have recently been proposed to meet the projected USA natural gas demand. Controversy over LNG facilities siting has focused attention on LNG safety issues, particularly the potential impact of large fires on adjacent areas.

Participation in LNG projects over the past thirty years sparked the interest in updating LNG process safety R&D for several MKOPSC staff. Sam Mannan, Bob Nalbone, Mike O'Connor, Mike Stafford, and Harry West have a long history in LNG research, education and specific project experience, resulting in a continuing involvement in LNG safety issues.

The growth in use of LNG would be unexceptional were it not for the unusual behavior when accidentally released to the environment. Because of the low boiling point compared with ambient temperatures, spilled LNG quickly vaporizes to the gaseous form. If encountering an ignition source in the presence of air, a subsequent fire or explosion results that can cause catastrophic consequences for life and property.

The massive size of LNG storage tanks and LNG tankers means that any containment releases may have the potential for a very large incident. The hazards posed by LNG can be minimized by good engineering design and an understanding of the physical properties of LNG. Experimental investigations of LNG spills have showed its dominant features to be: rapid boiling of the liquid whether spilled on land or on the surface of water, horizontal spreading of the spilled liquid and the evolving vapor cloud, dilution of the vapor as it drifts downwind by mixing with ambient air, and ignitability of the vapor cloud.

MKOPSC has one of the largest LNG literature libraries in the world based upon the donation of Profession C. M. Sliepcevich. It contains the only copy of many older materials and experimental data that may be valuable to our researchers and the industry because it helps explain the basis for a present practice that is not well documented. MKOPSC is cataloging our holdings and soliciting hard to gather papers and reports documenting LNG research and development.

MKOPSC has signed a contract with BP for “LNG Vapor Cloud Control and Mitigation Research”. This project will focus on improved detection, suppression, protection and vapor control methods. Some aspects of LNG vapor cloud control have been investigated in the 1970s. Water mists or sprays have been used previously to suppress/extinguish flames emanating from spilled LNG pools. Significantly reduced water drop sizes are expected to allow water systems to extinguish flames through high cooling and evaporation rates. Fire-fighting foams have been used to control vapor emission from spills and to reduce thermal radiation from flames. However, no definitive guidelines on the engineering design criteria have been formulated relating to their use in fire safety and flammable cloud suppression. The results from this research will help developing definitive guidelines on the engineering design criteria for mitigating the consequences of LNG spill and/or fire. In addition, results of this R&D will be used to improve the BP – Texas A&M LNG Fire Fighting School curriculum and training methods. And lastly, the results may assist in alleviating some of the causes of public concern about LNG safety and emergency preparedness.

Department of Transportation (DOT) has approved the use of DEGADIS and FEM3A for LNG consequence modeling. The DEGADIS freeware can calculate dense gas diffusion from area sources and vent stacks. The simulation results were compared with wind tunnel experimental

data and showed good agreement. While this consequence model has been validated against experimental data, it is not appropriate to be applied to all LNG release scenarios.

LNG release source term modeling is the basis of the subsequent vapor dispersion modeling and pool fire modeling. The type and nature of the LNG release will have a significant effect on the ensuing dispersion estimate. DEGADIS is approved by DOT/NFPA for LNG consequence analysis, however, it does not have a source term integrated with it. Hence it may not be appropriate for use in evaluation of long trench or high pressure jet releases scenarios.

In the 80s NFPA considered the GRI SOURCE model, but was later abandoned when many problems surfaces. GTI's SOURCE5 code still does not have material balance and therefore can lead to incorrect and misleading results. A series of models for LNGF source terms would assist LNG industry to evaluate the many potential LNG spill scenarios.

The use of Computational Fluid Dynamics (CFD) to model LNG vapor clouds, is gaining increased acceptance as an efficient tool for the prediction of large-scale effects that include flammable cloud characteristics, combustion product dispersion, and heat effects to adjacent objects. Specifically, a number of CFD modeling tools such as FLUENT, FLACS, FEM3A, and FDS have been used recently to predict vapor cloud behavior. MKOPSC proposes to extend our work done with FLUENT on pyrophoric chemical releases to LNG releases. Preliminary results are encouraging. This is particular relevant since Department of Energy (DOE) has announced their internal CFD project also using FLUENT. MKOPSC also has a working copy of the DOT authorized FEM3A consequence model, hence comparison between FEM3A and FLUENT will be made. The use of CFD modeling in this research would open up new avenues to explore for both industry and academia.

Flames above a pool of LNG differ significantly from those of other liquid fuels due to the high surface flux, higher liquid regression rates, and higher length to diameter ratios. Several researchers have proposed correlations for LNG pool fire models. However, all these models are produced from small-scale experiments. The largest LNG pool fire experiment conducted was about 40m³. These correlations are being extrapolated to predict large-scale LNG spill events, greater than 25,000 m³. The LNG industry needs experimental data on large fire columns to validate large LNG pool fire model, also determine if there is a size where air entrainment ratios become limited, hence causing smoky (less thermal radioactive) fires. Good science and engineering insists on knowing the validity of extrapolating the mathematical model from experimentally verified data. Experimentally verified data on large fire columns to validate large LNG pool fire models are desired. While science always wants better experimental data to validate models over wider range of potential conditions, large LNG pool fire experiments are expensive and difficult to carry out. MKOPSC suggests not using LNG for initial large fire tests and proposes to design a field of orifices with gas nozzles that can be spread apart with for a more controllable experiment. Preliminary design of the experiment is underway, and LNG spill fire tests may be considered later. European regulations suggest rollover models avoid excessive (100 x normal boil-off) handling capability. Sensitivity / SIS data on LNG linear temperature probes and densitometers are needed. Also needed is mixing efficiency models for circular and rectangular tanks and a comparison of effectiveness of bottom mixing jets and proposed vapor injection systems.

Rollover following density stratification in LNG storage tanks was considered a problem, which required careful monitoring following several unexpected rollover events in the 1970s. However, today, density stratification is routinely used to reduce high LNG boil-off gas rates, particularly when tank filling through the top loading nozzles is required for heavier LNGs.

Thus boil-off gas compressor and pre-heater costs can be reduced both during and after unloading LNG Tankers.

LNG rollover predictive models are widely used tools in conjunction with internal tank traveling temperature and density instrumentation to predict and update the behavior of LNG stratification. Several proprietary and commercial rollover software models are identified and the potential use of Computational Fluid Dynamics (CFD) models for the non-circular tanks proposed for off-shore applications are under development.

Resilient Engineered Systems

With the increase in complexity of chemical plants and increase in the difficulty of predicting potential failures, the desire to design systems resilient to potential faults has increased. It is critical to understand the resilience of engineered systems, especially those that support the critical infrastructure of the nation, across all engineering and design disciplines (Mitchell and Mannan, 2005). While research has been performed to increase the resiliency of specific systems, the concept of resiliency as a property of a system has yet to be explored. Until now, no academic organization has devoted its mission to developing the methodologies and technology needed to identify potentially catastrophic failures, evaluate and improve the design of important engineered systems.

This research focuses on understanding the underlying relationship of modes and causes of failures and developing techniques that apply to many types of systems, structures, and products. We propose to equate the resiliency of a system to a well-established concept, the resiliency of a material. Like a material, the resiliency of a system can be seen as the total amount of energy it can store before the system fails. While total energy storage within a material is relatively easy to calculate, the wide variety of different energy forms within systems makes determining total system energy challenging. Also, systems may fail due to lack of resilience of one component of the system. The unified approach to physics developed by Schmid and Fuchs will be used to establish a simplified overall energy balance for system in terms of characteristic “substance-like” quantities. The approach, combined with past research on resilient materials and systems, will also be used to determine variables that dominate the resiliency of systems. The system’s yield stress will be determined by identifying the point at which each sub-system fails and then using the unified approach to find the energy contained within the system at that point. These yield stresses, the dominant variables, and the overall energy balance will be used to develop correlations to determine the resiliency of different systems. These system correlations will be calibrated against material resilience expressions by using recently developed “smart” materials that can be classified as either materials or systems. Finally, the correlations will be applied to various equipment, units, and processes to aid in the development of tools and heuristics that can be used to improve the resiliency of chemical processes.

Flammability and Combustion Research

Flammability Research

Many manufacturing processes involve flammable chemicals, therefore flash points and flammability limits are information that is essential to maximize safety in process design and operational procedures. Even though there are regulations and standards that use the flash point

temperature as a criterion, most of the experimental standard test methods are for pure compounds. Most of the flammability information available in the literature applies to pure fluids. Generally, in the industry, the flash point of the mixture is taken as the flash point of the mixture component with the lowest value. It is thought that this practice adds a layer of protection, since the more “hazardous” compound is selected as the threshold value. However, the flash point of a mixture can deviate considerably from the flash point values of the individual mixture components (Vidal et al, 2004). This is the case of non-ideal mixtures which exhibits a minimum flash point behavior (MFPB). There are many mixtures (non-ideal solutions) having flashpoints below the flashpoint of any component. Therefore, a complete characterization of the liquid mixture is needed, especially for non-ideal mixture.

Prediction methods for the evaluation of the flash point of mixtures are desirable. There are some models available for the prediction of the flash point of mixtures, but they are functions of some basic data and/or parameters. Due to the large quantity of chemicals manufactured as well as the infinite combination of mixtures, reliable prediction tools are needed to predict mixture flash point when experimental data are not available especially for non-ideal mixtures which exhibit a minimum flash point behavior (Vidal, Rogers, and Mannan, 2005). For gases mixtures, flammability limits are needed. These limits are needed for various mixtures over various temperature and pressure ranges as well as over various oxygen atmospheres.

The flammability research at the Center is a combined theoretical and experimental study that will develop methods for predicting flash points (flammability limits) for liquid mixtures, and test those methods using experimental data (Vidal, 2005). A new apparatus capable of measuring flammability over wider ranges of temperatures and pressures has been designed and constructed for this purpose. This equipment is capable of measuring flammability limits over wider ranges of temperatures and pressures. At the same time various scenarios rich in oxygen concentration can be tested. (higher than 0.21, the composition of O₂ in air). A procedure to estimate the flash point of binary mixtures with limited vapor-equilibrium data was developed. The identification of mixtures exhibiting MFPB was assessed in this procedure. This study focused primarily in non-ideal liquid mixtures composed of alcohol-water and alcohol-hydrocarbon mixtures.

As a future direction, this research will be extended to other chemical groups as well as mixtures with more than 2 components. To identify specific functional groups with the tendency to form flammable mixtures, more experiment data are needed, especially for non-ideal binary flammable mixtures and aqueous mixtures. At the same time, it is important to study if water has the same effect on the flash point of other flammable chemicals such as hydrocarbons. If a series of chemicals from a specific chemical family are tested, some conclusions can be made for that chemical family as a function of chain length or molecular weight. Mixture flash point predictions with the UNIFAC model should be performed for non-ideal mixtures with different functional groups to test the flash point prediction capabilities of UNIFAC for various mixtures. This research can be expanded by incorporating the modified UNIFAC model. This model differentiates from the original UNIFAC model by using a modified combinatorial part and by incorporating temperature dependent interaction parameters that permit better description of the real behavior (activity coefficients) of mixtures.

Mixtures with more than two components should be studied experimentally and theoretically. The concept of pseudo components, which are lumps of components, can be useful in the flash point predictions. In the case of a three-component mixture, the 2 components with more effect on the non-ideality of the mixture are recommended as a first guess for the mixture flash point prediction. The prediction results should be validated with experimental data. A

systematic method to estimate the difference in flash point temperature between ideal and actual mixture as a function of mixture composition should be developed based on the flammability research of binary and multi-component mixtures.

This work is important because currently there are no reliable methods to assess the flammability of mixtures. In the case of liquid mixtures the flash point property is very important since it is used by regulatory agencies. The best way to obtain flash point information is by experimentation, however, for mixtures, a complete characterization of the mixture is necessary due to MFPB behavior. The chemical industry will benefit from this work because most of the chemicals handled in industry are mixtures instead of pure components. The development of theoretical methods to estimate flash points and flammability limits as well as the availability of experimental data will help in the characterization of flammability hazards.

Aerosol Research

Process fluids are capable of forming aerosols when they leak under high pressure. Mist or aerosol explosions have resulted in enormous losses to the chemical process and other manufacturing industry. Such aerosol explosions have been well documented, but little is known about the mechanisms for explosions of heterogeneous mixtures of vapor and droplets in air. Flammability limits for vapors are well defined. However, it has also been recognized that aerosols can explode at temperatures well below their flash points (Sukmarg et al, 2002). It is therefore critical that the hazardous nature of aerosols be studied in depth and strategies developed for reduction of aerosol explosion hazards and increased safety of handling fluids that can produce aerosols.

While it is postulated that heterogeneous aerosol mixture explosions can be more devastating than homogeneous vapor explosions, there is presently no concrete experimental evidence to support this theory. At issue is the prediction that the flame propagation speeds in aerosols are higher for a transition range of droplet sizes than speeds in vapor-air mixtures. Existing theory specifies a kinetically controlled premixed combustion mode for fine droplets below 8 microns, where the aerosol behaves like a vapor, and a mass transfer controlled diffusion mode for larger drops above 15 microns, where the aerosol first vaporizes and then combusts. Whereas, in the 'transition range', the flame speeds are significantly enhanced. It is therefore essential that this proposed transition range be studied experimentally to verify and understand the mechanism of aerosol explosions, though the existence of the transition range is anticipated by considering all facets of related theory and analysis.

Research conducted by the Center has established correlations between the operating conditions and the drop-size distributions of heat transfer fluids (HTF) aerosols and has developed predictive models to relate aerosol droplet sizes and formation distances to bulk pressures, temperatures, fluid properties, orifice sizes, and ambient conditions (figure below) (Sukmarg et al, 2002, Krishna et al, 2003, Krishna, 2003, and Sukmarg, 2000). Predictive correlations from this research will be useful to determine conditions at which HTFs can generate a large proportion of aerosol droplets in its transition range for enhanced flame propagation. This information will help determine the less hazardous HTF for set design operating conditions (Krishna, Rogers, and Mannan, 2003). Knowledge of the atomization process will help guide the proposed research on the explosive nature of aerosols. As potentially hazardous conditions are identified, effective prevention and control measures will be developed.

Future emphasis of aerosol research includes aerosol dispersion, aerosol combustion behaviors, fluid selection indices based on aerosol explosion hazards, anti-misting agents for

aerosol formation suppression, modeling aerosol rainout, and electrostatic effects on aerosol ignition energy. HTFs are generally low volatile with high boiling points and would offer us a more observable flame speed enhancement. Experimental support for the aforementioned theory would prove that aerosol explosions are more devastating than vapor explosions. A better understanding of aerosol combustion behavior is vital to the prevention of aerosol explosions. Identifying the transition range for various fluids would help develop strategies to prevent such droplet sizes from being generated. Aerosol droplets sizes generated through leaks in process systems are closely related to the operating conditions and the fluid and thermal properties. Using correlations that predict aerosol formation as a function of atomization conditions, safety guidelines for selecting less hazardous HTFs and their operation conditions will be established. Experimental and theoretical studies of other fluids will be carried out later.

Dust Explosion Research

Every process involving combustible finely divided solids or dusts is associated with explosion hazards. Although detailed statistical records of dust explosion are not generally available, it is known that approximately 70% of the dusts or powders processed in the chemical process industry are combustible and ignitable. Data from the Health and Safety Executive indicate one dust explosion every day in Europe, with damages from each incident in the range of millions of dollars, not including the damage and loss caused by injuries, fatalities, production stoppages, and marketing losses. In the United States, some recent incidents where dust explosions were most likely the root cause include incidents in Indiana (October 2003), Kentucky (February 2003), and North Carolina (January 2003).

The proliferation of finer powders in industry increases the explosion risks. As stated by the U.S. Chemical Safety Board in regard to the June 18, 2003, dust explosion in Kinston, NC, there is a critical need for research to characterize the explosion behavior of dusts to make possible strategies for handling dusts safely and to minimize the possibility and severity and therefore the risk of industrial dust explosions.

Safe handling of these dusts or powders is required which entails characterization of their chemical and physical properties such as particle size distribution, minimum ignition energy, turbulence etc. Fundamental research in the field of dust explosions has been classified into dust cloud formation process, dust cloud ignition process, flame propagation in dust clouds, and blast waves generation by burning dust clouds. Although, all the aforementioned aspects of dust cloud behavior have been studied in great detail both experimentally and numerically in the past, there is a specific need to develop rigorous mathematical models that relate some of the essential parameters of the dust cloud generation process such as, dust concentration, dust dispersion quality, dust velocities etc. Knowledge of the various ignition mechanisms that govern a typical dust cloud combustion/explosion process is limited and hence need to be identified accurately. Turbulence in a dust cloud is one of the major contributors of dust cloud combustion and flame propagation. This however turns out to be a difficult problem to solve owing to the chaotic and rather unpredictable nature of turbulence, wherein statistical treatments of various parameters are required due to a wide range of length and time scales.

In recent years, numerical modeling of dust explosions has been performed using Computational Fluid Dynamics techniques (CFD) that are based on finite volume, finite element or spectral methods. Preliminary results seem encouraging but there are still a lot unresolved issues that need to be investigated further. It needs to resolve all scales in the flow field and hence a large number of control volumes are required to obtain the desired resolution. On the

experimental front, large-scale tests need to be conducted on dusts that are able to mimic typical industrial explosion scenarios.

Reactive Chemical Research

Since its inception in 1995, the Mary Kay O'Connor Process Safety Center (MKOPSC) has researched the chemical behavior of industrial chemical reactions and processes. Reactive chemical hazards are seldom the characteristic of the chemical by itself but are highly dependent on the process conditions and modes of operation. The thermal behavior of a reaction system is analyzed to identify and assess potential hazards for likely scenarios in which process variables are exceeded or reaction components encounter incompatible materials or contaminants.

An Automated Pressure Tracking Adiabatic Calorimeter (APTAC) and a Reactive Systems Screening Tool (RSST) are currently used for the thermal analysis of reactive systems at the MKOPSC Reactive Chemical Laboratory. The RSST is used for preliminary screening analysis, while the APTAC is used for more advanced adiabatic thermal analysis to measure overall thermodynamic and kinetic parameters. Reactions are selected for investigation based on their industrial importance and on major incidents involving injuries or large losses. Experimental data are supplemented with computational methods to estimate measured properties and to guide subsequent tests to the most important system and conditions. Therefore, the reactive chemical research ongoing at the Center consists of three major parts: experimental tests, computational analysis, and development of systematic approach to evaluate reactivity hazard.

Experimental Research

Traditional Calorimetric Experimental Research

The exothermic behavior of a substance is influenced by the presence of functional groups, which also forms a basis for reactivity classification. This behavior suggests that there is an inherent structure-property relationship between the observed calorimetric properties and molecular structure. Chemical groups involved in current research and planned for future research include (Rogers, Liu, and Mannan, 2004):

Organic peroxides	Di-tert-butyl peroxide, Hydrogen peroxide, Benzoyl peroxide, Dicumyl peroxide, Di-tert-amyl peroxide, Cumene hydroperoxide, Tert-butyl hydroperoxide
Organic Nitrites, Nitrates, and Nitros	Nitropyrene, Nitroglycerine, Dinitrophenol, Trinitrotoluene, Dinitrotoluene, Nitropropane, Amyl nitrate, Nitrobenzene, Dinitrocresol, Dinitroaniline, Ethyl nitrate, Glyceryl trinitrate, Dinitrobenzene, Nitrocellulose, Nitroanisole, Nitrocyclohexane, Nitroethane
Unsaturated Hydrocarbons	Butadiene, Pentadiene, Butyne, Butene, Pentene, Acetylene, Amylene, Cycloheptatriene, Cycloheptane, Cyclohexane, Cyclooctadiene, Isobutylene, Dipentene, Ethylene, Hexene, Isohexene, Isoprene, Methyl pentadiene
Epoxides	Propylene oxide, Ethylene oxide
Hydrides and Hydrogen	Hli, HB, HC, HN, HO, HF, HNa, HAl, HSi, HP, HS, HCl

Reactivity and runaway behaviors of the above substances have been studied or will be studied experimentally using APTAC. The effects of contaminants (homogeneous catalysis) have been or will be studied experimentally as well (CISNEROS, 2002).

A reactive chemical experimental database is highly desired for reliable process safety information and safe handling of reactive chemicals. The Center proposes to establish a reactive chemical experimental database based on the published reactivity data and the experimental research at the Center. Thermo-kinetic parameters include onset temperature, adiabatic temperature increase, energy of reaction, maximum self heating rate, maximum pressure rate, etc. However, reactive chemical hazards are seldom the primary characteristic of the chemical by itself but are highly dependent on the process conditions and modes of operation. Therefore, the design of database structure and taxonomy is challenging. This database must incorporate parameters such as container and operating conditions other than the chemical involved.

Development of a Nanocalorimeter for Material Characterization

Calorimetric techniques are widely used to characterize materials. Thermal analysis of minute samples will greatly impact the development of high-throughput screening technologies to aid in the rational design of materials with tailored chemical and biochemical properties. This research focuses on developing a nanocalorimeter to characterize energetic materials for chemical process safety, homeland security, and military applications (Liu et al, 2005).

Key tasks are divided among design, fabrication, and characterization phases while we are focusing on the design and testing of the nanocalorimeter prototype currently. Fabrication of the calorimetric cell consists of (i) a thermal control module incorporating arrays of microfabricated heaters and temperature sensors, as well as necessary electronic interconnections, and (ii) a sample encapsulation module incorporating etched enclosures designed to accommodate either solid or liquid samples. These two components will be fabricated separately and assembled to form the completed calorimetric cell. This modular fabrication approach provides an enhanced level of flexibility by allowing the same thermal control module design to test a variety of samples through selection of an appropriate encapsulation module. The control algorithm and associated data acquisition system was implemented via a modular distributed I/O system (FieldPoint; National Instruments) and controlled by a Windows-based PC. Calibration of the temperature sensors was performed by placing each device in an oven and monitoring the resistance temperature detector at a series of temperatures. The thermal transition associated with the boiling point of acetone ($T_{b,p.}=56.2^{\circ}\text{C}$) has been studied.

A portable nanocalorimeter will be developed to provide technology capable of performing rapid detection and characterization of energetic materials in the field environment so that an appropriate threat management response can be quickly initiated. The device will be capable of performing thermal analysis on nanogram/nanoliter samples in a few minutes and can be used for fingerprinting explosives or energetic materials. Each disposable nanocalorimeter chip will cost less than \$1, and the cost of the complete system will be < \$2,000. A companion software package will also be developed to recognize explosive potential within a system. In addition, the software will enable chemical fingerprinting to be performed on the basis of thermal characterization data obtained from the calorimeter. This convergence between nanoscale calorimetry hardware and chemical fingerprinting software will be harnessed to

produce an inexpensive (< \$1 per chip) and field-deployable system offering greatly expanded capabilities to detect and characterize energetic materials in a complete self-contained package.

Computational Analysis

An important purpose of the computational methods is to provide values under conditions when the substances are unstable and cannot be measured accurately or safely, such as the heat of formation of hydroxylamine. Another important need is to supplement experimental data to determine reaction mechanisms for reactive hazard assessment. From these computations and experimental investigations, correlations are developed to extend at lower cost and expertise the detailed results to other systems. At the Mary Kay O'Connor Process Safety Center, we employ a variety of molecular modeling techniques to estimate thermo-physical properties, predict calorimetric data, and assess potential hazards due to chemical reactivity which is summarized in the following paragraphs.

HA Computational Study

As mentioned earlier, calorimetric studies on aqueous solutions of HA indicate that it is a highly reactive compound, but its properties have been insufficiently characterized. More specifically, a reliable HA heat of formation needed for reaction energy determinations was not available due to its instability. Quantum mechanical calculations involving isodesmic reactions were used to estimate HA heats of formation. To test the computed HA values, the heat of formation for hydrogen peroxide, a similar species for which reliable experimental data are available, was calculated by the same methods and compared with experimental data. Based on our calculations with a standard deviation of 0.3 kcal/mol, a value of -11.4 ± 0.6 (2σ) kcal/mol is recommended for HA heat of formation at 1 atm and 298.17 K (Saraf et al, 2003). The agreement and the consistency of the calculated hydrogen peroxide average value with the experimental value suggests that the calculated average value for the heat of formation of HA is more reliable than the available experimental value, -9.6 kcal/mol, which cannot be properly assessed.

The aim of studying elementary reactions of HA decomposition is to understand the initiation steps leading to HA runaway reactions and explosive behavior. Such an understanding of the behavior of HA at the molecular level can lead to development of better inhibitors to prevent metal catalysis and consequently prevent or reduce thermal runaway reactions. Thermodynamic calculations for plausible steps were computed with the B3P86 density functional quantum model. The reaction network and mechanisms have been proposed in the presence of H^+ and OH^- (Wei et al, 2004; Wei, 2005). Calorimeters cannot provide concentration response but only temperature and pressure responses. In-situ measurement by GC, MS, or FTIR can provide valuable insights about the intermediates or gas products, which are needed to validate the predictions and to simplify the reaction network.

Our study showed that initial step of hydroxylamine decomposition is due to intermolecular hydrogen transfer instead of homolysis of N-O bond (Wei, 2005). This may also be true for hydrogen peroxide. In the literature, experimental evidence showed that shock initiation chemistry in nitroarenes proceeded through intermolecular hydrogen atom transfer rather than C-NO₂ scission. Some theoretical studies on H₂O₂ and CH₃NO₂ decomposition in both gas phase and aqueous solution can be carried out to reach a more general conclusion.

It is known in the industry that a trace amount of contaminants may have significant effects on the reaction rate. The center has conducted experiments on the effects of trace metals,

base, and acid in the HA decomposition (Cisneros, 2002; Saraf, 2003; Wei, 2005). Further efforts are desired to correlate contamination study with homogeneous and heterogeneous catalysis research. The catalytic behavior of HA will investigate potential reaction pathways in the presence of ferrous (Fe^{2+}) ions. The Stuttgart basis set (relativistic effective core potential) will be employed for modeling the Fe^{2+} ion. None of the steps investigated so far have predicted the initiation phase of HA decomposition, but research continues to determine probable mechanisms for HA catalysis in presence of metals ions at the molecular level.

Molecular Modeling for Runaway Behaviors

Current understanding and modeling of runaway reactions are usually inadequate for predictions of system behavior because they are based on overall behavior parameters and do not account for detailed chemical and transport events of branched-chain thermal processes. We plan to model energetic and runaway reaction systems using a synergistic combination of experimental methods to analyze the decomposition species and kinetics and theoretical methods to calculate missing kinetic parameters followed by scale-up to macro-scale advection-diffusion-reaction analysis capable of predicting hazard potential. Initially, we will focus on hydroxylamine but the techniques and protocols developed will be useful for other energetic and runaway reactions. We will measure the overall runaway reaction behavior using calorimetry, identify reactive intermediates, and measure rate constants using in situ FTIR for the liquid phase reactions and laser spectroscopy for the vapor phase reactions.

To supplement experimental information, ab initio quantum mechanical methods will be used to calculate thermodynamics properties of species involved in key chemical reactions. These results will be employed to determine rates using microcanonical rate theory. Based on the Reynolds number of the reacting flow, both laminar and turbulent flow will be considered in the macroscopic runaway behavior analysis. An important goal of this research is to enable accurate prediction of runaway reaction behavior, which is needed for designs of safer and more economic industrial processes involving highly energetic and reactive chemicals. Also, this research could contribute to an industrial protocol for analysis of rapid and energetic chemical reactions.

Prediction of Calorimetric Data

Calorimetric measurements to determine reactivity can be resource consuming, so computational methods to predict reactivity hazards present an attractive option. None of the available theoretical methods address the issue of chemical kinetics within a system that affects the rate of energy release and consequent hazards posed by the substance. It is well known that the structure of a substance affects its reactivity and this reactive nature of a compound is reflected in the calorimetric data. There are certain rules of thumb commonly employed for estimating reactive hazards. For example, the presence of a nitro (NO_2) group is regarded as a potential source of reactivity. This behavior suggests that there is an inherent structure-property relationship between the observed calorimetric properties and molecular structure. However, this dependence of observed behavior and molecular structure has not been satisfactorily quantified. Therefore, our aim is to develop theoretical methods to quantify both kinetics and thermodynamic based on molecular structure.

To predict reactivity of a substance it is intuitive to deduce probable reaction pathways, but it is difficult to predict the reaction pathways for a compound, especially at high temperatures. Also it is difficult to extract exact kinetics from calorimetric data, because the calorimetric data reflects only temperature (or temperature and pressure) vs. time behavior.

Therefore as an alternative to extensive kinetic modeling, we propose to employ quantitative structure-property relationship (QSPR) techniques to predict calorimetric data such as onset temperature, T_{onset} , and energy of reaction based on molecular structure.

QSPR techniques have been successfully employed for drug design and for correlating properties such as boiling point, autoignition temperature, and molecular properties. Our aim here is to correlate and predict DSC calorimetric data. The potential independent descriptors used to correlate calorimetric data, which are characteristics of a molecule and account for the chemical structure of the molecule, include highest occupied molecular orbitals, lowest unoccupied molecular orbitals, highest positive charge, highest negative charge, weakest bond, mid-point potential, delocalizability index, charge (bond strength descriptor), and dipole moment. The descriptor values can be obtained using the B3P86 density functional model.

This approach is useful as a screening tool for reactivity parameter predictions as a guide to identify the most significant systems that require more accurate values from experiment or computation.

Systematic Approach for Reactivity Evaluation

The Center has developed a structured approach for the evaluation of reactive chemical hazards that integrates literature data screening, computational estimations, theoretical modeling, and experimental measurements (Aldeeb, 2003). The main goal of this systematic approach is to focus the research on the most likely and most hazardous reaction stoichiometry and hence reduce the need for detailed experimental analysis for a large number of process reactions. More detailed and advanced experimental analyses may be required for the more complex and reactive systems. The Center employs calorimetric measurements and classical and quantum chemistry models to determine properties of chemicals and to analyze chemical systems.

Inherent Safety Research

Development of a Hierarchical Fuzzy Model for the Evaluation of Inherent Safety

Inherent safety has been recognized as a design approach useful to remove or reduce hazards at the source instead of controlling them with add-on protective barriers. It is widely accepted as a good engineering practice. However, inherent safety is based on qualitative principles that cannot easily be evaluated and analyzed, and this is one of the major difficulties for the systematic application and quantification of inherent safety in plant design.

During the last few years, several measurement techniques and analysis tools have been developed to estimate the degree of inherent safety of a plant or a process unit. These tools are based on traditional Boolean mathematical methodologies that are limited by the uncertain and subjective nature of the information analyzed.

To address this problem, here we propose the use of fuzzy logic for the measurement of inherent safety by proposing a hierarchical fuzzy model (Gentile, 2004). This project has the objective to bring inherent safety to systematic quantification and analysis by proposing a mathematical tool to work with subjective, uncertain, and imprecise data and to incorporate information from experience and heuristic knowledge. It can be applied to process design, process synthesis, evaluation of inherent safety, process simulation, and transportation of hazardous substances.

The proposed method is computer-based and process simulator-oriented in order to reduce the time and expertise required for the analysis (Gentile, 2004; Gentile, Rogers, and Mannan, 2003). The used fuzzy model is the Mamdani algorithm because it works with IF-THEN rules whose antecedents and consequents are based on linguistic variables defined in terms of fuzzy sets. The overall system is formed of 35 fuzzy inference systems arranged in a hierarchical tree where the outputs from the lower levels are used as inputs for the higher levels. The user is required to provide 25 input values for the chemical substance, operating conditions, and vessel design parameters. Other 11 parameters are required for the design of adaptive membership functions for the evaluation of dispersion hazard, corrosion potential, and vessel operating conditions. It is expected that in the future, by linking the present approach to a process simulator, process engineers can develop safety analysis during the early stages of the design in a rapid and systematic way.

Future work is required in order to expand the model including other factors and adapt the basic model for vessels to other equipment. Because the software relies on information that is available in the equipment datasheets, it will be useful to develop a Visual Basic application able to run in Excel and facilitate the application during the plant design stage. On the other hand, by linking the proposed methodology to process simulation and cost estimation, it will be possible to create a powerful engineering tool able to evaluate process units or plants from often conflicting criteria such as technical requirements, cost limitations, environmental, and safety aspects.

An additional fuzzy inference system can be developed in the future in order to evaluate the relation between the size of a plant and its overall inherent safety index. A large plant with a low safety index can have a lower hazard density than a small plant with a low index. Plants with high hazard density could have more opportunities for design improvement. Several tests must be performed before the set of rules for the consistency rules can be designed because it is necessary to analyze several case studies on real plants.

A more ambitious goal of this research is to break the traditional boundaries of safety ideology associated with the idea that safety is subjective and hence non-quantifiable. One of the ideas of the present research is that safety is not subjective because safety is not a matter of opinion. The laws of physics, chemistry, and thermodynamics govern safety and these laws do not care about what a design engineer thinks is or is not safe. Therefore the only aspect of safety that is subjective is associated with human factors.

Integrating Process Safety into Process Design and Optimization

The principle of inherent safer design is the cheapest if applied at the early stage of process development and design. The integration of safety into process design and optimization is highly desired. This research proposes a procedure for integrating safety into design and optimization framework by using safety parameters as an optimization constraint (Suardin, 2005).

As a preliminary attempt, this research employs Dow's Fire and Explosion Index as a safety parameter to be integrated into process optimization. This project automates the calculation of F&EI. The ability to calculate the F&EI, to determine loss control credit factors and business interruption, and to perform process unit risk analysis is the unique features of this F&EI program. In addition to F&EI calculation, F&EI program provides the descriptions of each item of the penalties, chemicals/materials databases, the flexibility to submit known chemical/material data to databases, and material factor calculations. Moreover, the sensitivity analyses are automated by generating charts and expressions of F&EI as a function of material

inventory and pressure. The expression will be the focal point in the process of integrating F&EI into process design and optimization framework. The proposed procedure of integrating F&EI into process design and optimization framework is verified by applying it into process design and optimization of reactor-distillation column system.

As mentioned earlier, this research is focused on integrating safety, not the Dow's fire and explosion index, into process design and optimization framework. Dow's fire and explosion index employed in this research is not sensitive to temperature changes and some other process conditions. Process optimization requires optimization model in the form of mathematical expression. Therefore the availability of a proven safety hazards analysis with the ability to generate expression for the safety parameter will greatly increase the attractiveness of this methodology. Currently, most hazards analysis methodologies quantify safety parameter without generating expression represents the safety parameter. Developing or improving existing evaluation index to generate the safety expression gives better safety parameter representation, which couples this research with the inherent safety index research at the Center.

Practical risk reduction for refining processes

Process safety has been emphasized in the petroleum refining and petrochemical industry over the decades. This is especially true in the refinery unit processes, where reactive and hazardous materials are handled at elevated temperatures and pressures.

The guiding principles of inherent safety have been clearly illustrated by Trevor Kletz. While there is no argument against the concepts of inherent safety principles, the application of these principles often gives rise to a discussion of overall risk. The current research includes a literature review of the fundamental concepts and evaluation systems that have been applied to the petroleum industries for previously implemented risk reduction projects.

This project is an attempt to identify practical risk reduction options for the petroleum industry to make its operations inherently safer in a pro-active manner. Future directions of this research include an in-depth review of the hazards existing in the major processes in the petroleum industry and a comprehensive synthesis of the technology and equipment that have been used or proposed to enhance safety and reduce risk. General guidelines to evaluate a process in terms of the holistic impact to the greater system can be developed from this study.

Quantitative Risk Assessment

Risk analysis is a key feature of modern decision making, for both government and industry. While not yet mandated by government regulations, quantitative risk analysis is an increasingly preferred method of hazard evaluation based on numerical estimation of incident frequency and consequences. Internationally, there appears to be a gradual trend towards increasing use of quantitative risk assessment methods in the chemical process industry — fully for the relatively small number of instances where they can be applied, and partially in semi-quantitative approaches. This trend was evident in Europe ([reference?](#)).

MKOPSC has been long involved in the research in the area of quantitative risk assessment, as well as provided consultancy to the industry. For example, the Center conducted several comprehensive quantitative subsystem hazards analysis study covering process, Chemical Agent Transfer System, electrical power system, fire protection system, Heating, Ventilation, and Air Conditioning system, Ton container decontamination system, product offsite transportation, and their related support systems for Newport Chemical Demilitarization Facility,

which is designed to destruct VX stockpile. Fault Tree Analysis techniques were applied to all aforementioned systems and their related support systems. The identified major hazardous events, Agent Release, Personnel Injury and System Loss, were ranked according to the predefined Risk Assessment Code. Critical primary failures (basically equipment failures, operator errors and environmental conditions) and combinations of primary failures contributing to the potential occurrence of undesired top events are identified. The areas of safety concern were highlighted, primarily by the uncertainty caused by lack of available relevant reliability data. All the undesired events are reduced to an acceptable level with suggested changes of process design change, operating specifications, and maintenance procedures. The safety impacts of all risk reduction suggestions have been quantified and discussed as well.

Research activities in this area are highlighted in the following sections.

Development of A Computer-Aided Fault tree Analysis Methodology

Risk analysis and management is becoming increasingly important to the process industry to meet safety criteria and regulations. As a powerful and systematic tool, fault tree analysis (FTA) has been adapted to the particular need of chemical process quantitative risk analysis and found great applications. However, the application of FTA in the chemical process industry is limited. One major barrier is the cost of manual synthesis of fault trees. It requires a thorough understanding of the methodology as well as the process and is vulnerable to individual subjectivity. The quality of FTA can be highly subjective and variable.

The availability of a computer-based FTA methodology will greatly benefit the CPI. The central idea of this research is to capture the cause-and-effect logic around each item of equipment directly into mini fault trees (Wang, 2004). Special template fault tree models have been developed to manage special features. Fault trees created by this method are expected to be concise. A prototype computer program is provided to illustrate and test the proposed methodology against some examples. The results generated from the program have been compared to published results and verified to be correct. Ideally, FTA can be standardized through a computer package that reads information contained in process block diagrams and provides automatic aids to assist engineers in generating and analyzing fault trees.

This work proposes a computer-aided methodology for fault tree synthesis (Wang et al, 2002). Many special features are designed to prevent incidents, which are crucial in the synthesis of fault trees. Common process controls have been considered in this work, however, complex chemical processes may not only have process control loop and safety-related functions, but also process loops. Every loop in the process under study needs to be identified but also classified according to its structural characteristics and functionalities. It is rather difficult to automate the loop identification and classification. In this work, configuration of special features is entered manually by users. Though it has been recognized that a mechanistic approach for the recognition of all the special features is not appropriate for fault tree synthesis in the CPI, guidelines and taxonomy to help analysts in identifying and classifying special features systematically is valuable and highly desired.

Each chemical plant is unique. However, for many common devices, materials, and processes, we have accumulated sufficient knowledge of their failure mechanisms and fault propagation. Directed digraphs, failure modes and effects tables, and external events tables are used to incorporate fault propagation in chemical plants. These tables will be stored in a relational database to be used in the fault tree synthesis algorithm. It is desired to develop or

revise these common tables for a specific plant using a process simulator, which will provide the more accurate and complete fault propagation systematically.

The prototype program developed in this research was to illustrate and test the methodology against case studies. Emphasis has been placed on the chemical engineering side. However, for the proposed methodology to be realized commercially, it will involve not only fault tree models for equipment and special features, but also database design and implementation, graphics, computational algorithm, user interface, etc. Chemical engineer/researchers must work closely with computer scientists to accomplish this goal.

The final product of this research is to provide a computer package that standardize the procedure of quantitative risk analysis and help decision makers to decide more formally and more cost-effectively. Computer-aided fault tree analysis module, which is the focus of this research, will read information from electronic P&ID automatically and assist engineers in generating and analyzing fault tree models. It will significantly reduce, if not eliminate, subjective factors involved in the manual construction of fault trees. The computer will take up the dull part of fault tree generation, thus reduce the cost and human force required in traditional fault tree analysis. In particular, fault tree models will be well documented and easy to modify according to system changes. It will be ideal for this module to connect with electronic P&ID, process simulator, and consequence analysis softwares to computerize quantitative risk assessment procedure.

The last but not the least, though this work is originally developed for the application in the chemical process industry, it has the extendibility to other fields such as electrical systems, the nuclear industry, and the aerospace industry.

Transportation risk analysis for hazardous materials transportation

More than 3.1 billion tons hazardous materials (HazMat) are shipped in the United States annually. According to the Department of Transportation (DOT) statistics, 156,442 Hazmat transportation incidents occurred during 1995 to 2004, resulting in a total of 221 deaths and 3,143 injuries. The public and the agencies such as DOT and the Federal Emergency Management Administration show increasing concern with regard to the risk associated with the transport of HazMat. Optimization of HazMat transport involves comparisons of alternatives in the domain of risk, as well as an analysis of the tradeoffs between cost and risk. This optimization approach is possible as long as risk can be quantified.

The numerical methodology developed to assess the transportation risk was hard to employ directly by decision or policy makers. One reason is that the methodology was proposed without input data, or the methodology was too complicated to obtain available input data. For example, incident frequency and conditional release probability data were assumed to be available in most of the methodologies, but in fact the acquisition of the required data calls for considerable effort.

The methodology should be developed according to the availability of data. In this research, a procedure is developed to evaluate individual risk and societal risk associated with hazardous materials transportation. The basic incident frequency is estimated from DPS (Department of Public Safety) and DOT database as a function of lane number, weather, surface condition, and alignment. The basic incident frequency is then modified considering the effects of truck type, container capacity, container type, and driver experience. Fuzzy logic is employed to incorporate the expert's knowledge so that the effects from these factors can be estimated

(Qiao et al, 2004). The membership functions are built based on the data from the HMIS database or expert experience.

The procedure takes into account the effects of hazardous materials type, environmental, truck configuration, and road conditions to both the accident frequency and consequence. A transportation route is viewed as a linear risk source constituted by a great number of risk source links. For each link the incident frequency occurred under various conditions is assessed by mathematical model based on the Department of Public Safety accident database. A numerical procedure, which allows the coupling of time effectiveness and mathematical accuracy, will be developed for the individual risk evaluation, and therefore provides criteria for the route selection of hazardous materials transportation.

User-friendly software on transportation risk analysis and the route selection can be developed based on this research. With sufficient data, the incident frequency of different road could be measured given the data of affecting parameters, and then the general models could be built to assess the incident frequency for any kind of road. The release frequency data could be obtained from HMIS, and the consequence would be assessed by CANARY or other commercially available software, then the user friendly software could be developed to assess the transportation risk for any possible route and decide the optimal route based on user requirements incorporating the incident frequency, release scenario, and consequence assessments.

The transportation risk analysis results can be used in a decision-making system. Both the transportation risk and cost are considered in the transportation route selection. User's preference on low risk or low cost would be considered in the optimized routing methodology. The decision support system can be set up based on this work. The environmental condition (including the population distribution) of the transportation should be obtained from GIS or other sources. The results from the risk assessment, cost evaluation, and routing methodology would be inputs to the system. Then the decision would be made about the emergency response, evacuation procedures, resource management, public protection and so on.

LNG Reliability Data

Quantitative risk assessment requires failure and event data. The ideal situation in quantitative risk assessment is to have sufficient in-house data, however, due to various restrictions, laboratory data or data from generic data sources are often used in reliability studies. Transferring data from laboratory or generic data sources brings uncertainty.

The failure rates of equipment can be influenced by a large number of factors, including design, specification, manufacture, application, operation conditions, maintenance, and environment. Reliability data can often deviate by a factor of three or four, and a factor of ten is not unusual, as suggested by Kletz (1999). In the process industry, the operating conditions and environment can change dramatically for the same equipment. The most desirable information is to have sufficient plant specific data. However, in many cases, equipment has not been operating long enough to provide statistically valid data, internal collection may not be appropriate, or for new plant designs there is no possibility to collect any in-house failure data.

In particular, there is few reliability or failure rate data collected for the equipment in the LNG industry. Usually failure rate data from nuclear, oil and gas industry like OREDA handbook are borrowed for reliability studies and risk assessment of the LNG facility. This

brings uncertainty which is hard to predict and makes the analysis results unreliable and easy to attack.

An LNG reliability database has been suggested by several LNG industry companies. A survey to update GRI's historical failure rate database (last data in 1980s) is being considered. Our idea is to gather available data from other industry such as oil and gas industry and cryogenic industry and adjust the data through Bayesian analysis to predict reasonable failure rate data for the equipment used in the LNG facilities. Unit operations fault tree models are being considered for the new plant designs, particularly the offshore facilities.

An industry consortium is being considered for this activity. Upon successful execution of this project, it may be expanded to the chemical process industry as well.

Making the Business Case for Process Safety

Every production practice has its positive or negative consequences. Cost Benefit Analysis (CBA) is a systematic approach of assessing the life-cycle costs and benefits of public or private projects. A proper cost and benefit analysis during the initial phase of the chemical processes is of the utmost importance for its successful realization. However, the methods available for evaluating a chemical plant are mostly based on an economic balance. In reality, every chemical process may involve job opportunity, environmental consequences, and other social effects. It is necessary to establish a framework for considering these costs and benefits so that decisions may be consistent with economical and social objectives. In this research, we propose the concept of value at risk (VAR) to evaluate social advantages and disadvantages of a chemical plant according to their consequences and significances (Fang, Ford, and Mannan, 2004). VAR is a method first introduced in the financial sector for modeling potential loss in a complex venture.

In order to achieve the goal, VAR principles are applied to the layers of protection analysis (LOPA) of an ethylene refrigeration compressor. Specially, the VAR loss probability distribution functions associated with different configurations of protection layers around an ethylene refrigeration compressor are analyzed. Our study shows that the benefits of a given layer of protection are not necessarily captured by a single average number, since the entire probability-value curve is affected. A distribution analysis of frequencies and probabilities at different cost levels can provide more insight than simple averages when deciding on the allocation of safety resources.

This project plan on having a visual basic based program on the process safety of a chemical plant. The program will project the costs of process safety compared with the risks of disasters during the life cycle of a plant/industry. Future studies would include various stochastic factors such as pegging a market variable on it and how stock prices would be affected. Human factors could be instituted as well based on various levels of training and experience affect process safety.

Layer of Protection Analysis

LOPA is a semi-quantitative risk analysis technique that defines a cause-consequence scenario and estimates the likelihood of the undesired consequence of occurring. Layers of protection are added to a system to lower the frequency of deviations and mishaps. The combined effect of the protection layers to reduce frequencies and consequences are compared with risk tolerance levels for the plant.

The measure of the risk associated with a scenario depends on the frequency of an event and the Probability of Failure in Demand (PFD) of the layers of protection. However, this information is sometimes uncertain, imprecise, qualitative or sparse. Therefore auxiliary methods should be used to complement LOPA in risk analysis. The Center's research includes exploration of auxiliary methods such as the Fuzzy Logic theory and Bayesian estimation, to use in combination with LOPA to analyze risk in the LNG Industry and Ammonia Refrigeration Systems.

Chemical Incident Data Systems

A national repository database for chemical accidents

A national repository of information on chemical accidents has been identified as the top priority of National Chemical Safety Program Roundtable ([MKOPSC Report](#)). The deficiencies of current data systems have been identified in a number of studies. Although data is increasingly available on-line much is not and the underlying consistency and quality of the data is still lacking.

Currently there are many federal, state and local agencies collecting and reporting chemical incidents. However, each agency can only collect information on incidents within their legislative authority. Rulemaking further limits the scope in many cases. Also, because of the varying focus amongst agencies the data collected and the terminology employed vary widely. The agencies are generally limited to certain chemicals, above threshold quantities, in particular facilities or transportation modes. These limitations stymie efforts to gain an overview of all chemical incidents.

Many of the systems rely on self-reporting of incidents by companies involved. While the reporting is mandated by law it is not known how many incidents go unreported. Independent means of checking for completeness are generally not available. Some agencies do use proactive means of searching for incidents, however, their scope is limited in other ways. For example, the NRC system focuses on early notification of incidents but lacks accurate and detailed follow-up information.

Present databases are limited in scope with regard to the information fields in them, consistency in collecting data over time and the type of incidents contained in them. The features of particular databases are generally determined by the agency responsible for collecting the data in accordance with their legislated responsibilities and authority. Because of the patchwork of collecting and reporting there are overlaps and gaps as previously described. The development of an integrated system must address this problem. Additionally, it is desirable to eliminate redundant reporting to multiple agencies.

There is presently no reliable means for evaluating the performance of industry in limiting the number and severity of accidental chemical releases. There is also limited data with which to prioritize efforts to reduce the risks associated with such releases. Without this information there is no means to measure the effectiveness of present programs or to guide future efforts.

In order to gain an overview of relevant risks across all industries, government facilities, fixed facilities, transportation modes, toxic, reactive, flammable and otherwise dangerous chemicals an integrated database is required (Mannan, 1998). The database could either be a series of databases or one all-inclusive one. However, the data in each portion of the database

would be tailored to meet the needs of all stakeholders. This would allow an analysis starting with the undesirable consequences of chemical releases, whether injury, ecological or monetary back through the technical, management and social causes of the releases.

The repository is to serve two basic functions:

1. Track progress in reducing chemical incidents.

Especially, to determine if existing programs of government, industry and other organizations are effective in reducing the number and consequences of chemical incidents.

2. Learn from past incidents to help reduce incidents in the future.

Especially, to identify patterns of management and system failure to guide and prioritize efforts in the areas of investigation, legislation, regulation, management, operation, training, and research.

There would be 5 primary phases to the work:

1. Establish a census of incidents for the past ten years of fixed facility and transportation incidents.
2. Create an integrated database of fixed facility incidents which would contain confidential information for use by government agencies and others by agreement. (This is required to incorporate HSEES data)
3. Create a public version for use by industry and the public.
4. Create public and private versions of transportation incidents.
5. In parallel with the above a “real-time” collection and vetting system would be established”.

The initial focus should be fixed facilities rather than transportation systems. Data sources for the fixed facility phase include NRC (Coast Guard), RMP (EPA), HSEES (ATSDR), AIS (OSHA), and NBIRS (News Based Incident Reporting System by MKOPSC – This system is in development and not yet available to the public). The existing data collection systems should be improved and integrated rather than attempting to implement a completely new system.

The data collection and analysis would be performed for the 10 year period of 1994 to 2004 as well as in “real-time”. The major data sources would be EPA RMP, ATSDR HSEES and NRC. The 10 year period is consistent with the RMP data as well as the HSEES data. The 10 year period should be sufficient to establish whether any trends exist with time. The OSHA Accident Investigation Data will supplement the main data sources. The “real-time” effort will be based on NRC and Internet news searches.

If possible indicators will be developed by normalizing the data for such factors as chemical production, GDP, or number of workers.

Integration of Existing Sources into the national incident repository database

While it is easy to be critical of the existing systems it should be recognized that substantial resources are involved in data collection, vetting, investigation and reporting. These incident investigation and reporting efforts are often integral to the agency’s function. OSHA for instance has a database that summarizes all the accidents that they investigate. Thousands of

these involve chemicals. This content cannot be captured by a new reporting system, it has to be integrated into the system.

Because of the close coupling of the data gathering and investigation to the agency's function it appears impractical to replace the existing systems with one new system. In addition there are generally 10 to 25 years of previous data in these systems. Integrating the systems should allow for effective use of these existing resources.

Technical advancement is also making it easier to integrate data from diverse resources. Most database systems are or will be updated to systems that can convert data to commonly available standard formats. This data can then be readily transferred by electronic means to the integrated system.

This proposed plan seeks to capitalize on the existing data and systems while bringing them together in an integrated system, making them more complete, consistent, and accessible. The plan will also address the flow, tracking, filtering, and vetting of information from initial reporting, through the relevant agencies and into the repository.

Accessibility of incident reporting systems has improved dramatically in the last few years as information is made available on the internet. However, there is still a great deal of progress that can be made simply by making information more readily available online.

The proposed repository will also include collection of news accounts of incidents. This will serve several purposes. It will provide a check to see if all significant incidents are being reported to the NRC. It can also provide additional information that is not otherwise being collected, especially incidents that do not fall within the jurisdiction of any particular agency. It may also provide some insight into public and media perception of chemical incidents.

Incident Reporting System

Initial federal reporting of incidents is primarily through the NRC. Approximately 25,000 cases per year are reported in this manner. The NRC maintains these initial reports in a database called the IRIS Incident Reporting Information System. The NRC selectively forwards this initial information to approximately 16 other federal agencies and to state agencies. Some agencies such as ATSDR employ a number of additional sources such as local fire departments, industry, medical providers and news media. The various agencies process portions of this information, conduct investigations, and make reports within the scope of the agency. There is no overall summary or evaluation of the information.

A consistent reporting method should also allow tracking of trends for various industries, processes, chemical types, and consequences. This knowledge would allow prioritization of efforts by government, industry, researchers and others to promote progress in chemical process safety. Such an effort would dovetail with other activities such as investigations by the CSB which focus on an in depth analysis of the most severe accidents. A full understanding of chemical accidents is probably best served by having an overview of all accidents as well as in-depth understanding of severe accidents.

The NRC should continue to be the focal point of all reporting regarding chemical incidents. The database manager would notify the NRC of any incidents that were found through

news media and other sources and not previously reported. Every incident could then be followed through the system based on its NRC assigned number.

Each agency would continue to perform its normal functions of collection, filtering, vetting, investigation and reporting. The processed information would then flow into the Repository. The Center would perform additional filtering, vetting, translation of non-standard data, and identify and merge duplicate reports. Vetting would include telephone, fax and written follow-ups to confirm and correct data as needed. The data collection process would be proactive with the manager seeking out incidents and details of the incidents, similar to the ATSDR's surveillance system.

The Center would develop a taxonomy into which the existing data could be mapped. The basis would be a taxonomy used to enhance the NRC data based on the text descriptions. The resulting repository would then be made available on-line in a fully searchable system and for download or distribution on CD ROM in standard formats. The publicly available system would have identifying information redacted to be consistent with the requirements for HSEES data.

Abnormal situation management Research

Fault diagnosis is destined to hold central importance in maintaining a chemical industry after installation of Advanced Process Control system (APCS). It has been estimated that US-based petrochemical industry could save up to \$10 billion annually if abnormal process behavior could be detected, diagnosed and appropriately dealt with [Nimmo et al, 1995]. Further, it is highlighted [Vedam, 1999] that the same industry loses over \$20 billion annually due to inappropriate reaction to abnormal behavior.

The purpose of this research is to establish and maintain safety of processes through automation and analysis methodologies. Because modern chemical plants are large and complex, early and accurate fault detection and diagnosis is imperative. Effective application of these methods can reduce product rejection rates, limit downtime, and help to attain stringent safety requirements.

The central goal of abnormal situation management is to document all possible normal modes of a plant operation and detect deviations from normal behavior. Although this goal is complete in itself, attaining it requires the methods of "Fault Detection and Diagnosis," which analyzes unmanageable events that occur frequently. Fault detection and diagnosis have gained a central importance in the chemical process industries over the past decade. This is due to several reasons, one of them owing to instrument malfunctions in a heavily instrumented chemical process system and secondly because of process drifts due to parameter variation. Moreover, since industrial processes operate in a closed loop with appropriate output feedback to attain certain performance objectives, instrument faults have a direct effect on the overall performance of the automation system. This presents a need for fault diagnosis systems which use limited information of the process dynamics and accurately detect, isolate, and identify faults.

The focus of this research is on the development of a fault diagnosis framework for systems which can exhibit nonlinear characteristics and include uncertainty (Rajaraman, Hahn, Mannan, 2004). The methodology proposed in this research consists of a novel state and parameter estimator that operates in parallel with a model based fault diagnosis algorithm. The new estimator has the advantage that it is significantly less computationally intensive than traditional approaches and can easily be implemented for real time operations. In case of

unavailability of a first principles model of the process, subspace identification methods can replace the state and parameter estimator in the overall fault diagnosis algorithm. Thus, this approach is centered around two main components: the design of a nonlinear observer, which includes uncertain parameters as augmented states, and the choice of an appropriate fault isolation and identification filter for reconstructing the location and nature of the fault.

The observer design was performed based upon Kharitonov's theorem but takes into account the effect that changes in the parameters have on the steady state of the system. This resulted in a nonlinear, augmented observer, which has the property that it is locally stable for parametric uncertainty within a specified range. Additionally, it is possible to guarantee a certain level of performance for convergence of the states and parameters. The fault isolation and identification filter was designed based upon a linearization of the nonlinear model at each time step. Preliminary research on tuning the observer gains has been carried out for the state and parameter estimation to attain a faster rate of convergence of the estimation error has been presented. The effect of measurement noise on the developed state and parameter estimator has been investigated as well.

This research can be further developed in various ways which is highlight below. Recently the work by [Rajaraman et al, 2004] exposed the need for robust fault diagnosis methodology and suggested some improvements in the area of robust fault diagnosis. The main idea was to incorporate two-time scales for fault diagnosis and methodology. However, a thorough research has to be done to establish the frequency of model adaption vis-à-vis fault detection. Hence, this research would focus on developing robust fault diagnosis techniques when model parameters as well as fault signals are time-varying in nature.

Another front of this research that can be taken further is to develop fault diagnosis methodology which has the flavor of systems engineering but not extensively driven by the physical model of a system. One such work in this area was by [Rajaraman et al, 2005] in which empirical models were derived from real plant data of the process by Subspace Model Identification (SMI) and were used for sensor fault diagnosis. What remains to be done is to develop similar Subspace model based fault diagnosis for both actuator and sensor fault diagnosis.

Since feedback controllers use measurements to determine the actuation which result in faults propagating in the system in an unknown fashion. Therefore, another interesting area is to perform fault detection, isolation, and reconstruction in closed-loop systems.

Most of the abnormal situation in chemical plants arises due to misinterpretation of alarms. Even today, alarms systems are designed to respond to any abnormal readings of the instruments. Some research has to be done to determine the root cause of such alarms. As a first step this can be determined by using data driven fault diagnosis to distinguish between process upsets and hardware upsets. In essence subspace model-based fault diagnosis methodology can be used in each control loops to determine the effect of one measurement on the other.

This idea is related to process optimization and fault diagnosis. Typically, in a plant after the design stage, various streams (flow variables) are reconciled with the real plant measurement to determine whether the desired objective of design is achieved. This is typically called as Data reconciliation and gross error detection. A lacuna is this idea is that one has to believe in the quality of measurement. Therefore, there is a scope of research to achieve data reconciliation in the presence of faults in the measurement. Again as a first step this could be tackled by incorporating two-time scale approach, where data-reconciliation is performed at a lesser frequency than fault detection.

Facility Siting

Facility siting and layout is a process for finding the optimal location for a chemical or petroleum processing site to reduce risk levels, including recognizing and assessing long-term risks, and layout of facilities and equipment within that site. Appropriate siting and layout establish the foundation for a safe and secure site with a lower potential for toxic impacts, fire escalation, and explosion damage. The risk to personnel and the surrounding community will be reduced, and additionally, maintenance will be easier and safer to perform. However, these benefits do not come without associated costs. Tradeoffs between initial capital investment, life cycle costs, and risk reduction are inherent in siting and layout decisions.

Wide range facility siting research includes explosion and dispersion modeling to calculate risks between facilities and residential areas or between facilities. The center's research on facility siting and layout include

1. Facility layout optimization based on risk analysis;

The purpose of this research is to combine optimization concepts and safety concepts in a facility layout. The objective function is the sum of the costs of land, piping, managing, protection devices and safety (risk). Optimal separation distances and directions will be obtained using real meteorological data and data from various hazardous facilities which have toxic gases or explosive materials.

2. Effect of explosions on confined buildings;

Experimental results for outside risks during an explosion are available; however, the risks that occur within confined buildings are not well quantified. Research using simulation methods will be conducted to better our understanding of the risks in confined buildings.

Engineering Sustainability

Engineering for Sustainable Development (ESD) is an integrated system approach, which aims at developing a balance between the requirements of the current stakeholders, without compromising the ability of the future generations to meet their needs. This is a multi-criteria decision-making process that involves the identification of the most optimal sustainable process, which satisfies economic, ecological, and social criteria as well as safety and health requirements. Certain difficulties such as ill-defined criteria, scarcity of information, lack of process-specific data, metrics, and the need to satisfy multiple decision makers can be encountered when ESD is applied. The Center's research will include developing a new approach/methodology to overcome these difficulties.

ESD can be broken down into three major steps, starting with the Life Cycle Assessment (LCA) of the process, followed by generation of non-dominating alternatives, and finally selecting the most sustainable process by employing an analytic hierarchical selection process. This methodology starts with the prioritization of the sustainability metrics (health and safety, economic, ecological and social components). The alternatives are then subjected to a pair-wise comparison with respect to each Sustainable Development (SD) indicator and prioritized depending on their performance. The SD indicator priority score and each individual alternative performance score together are used to determine the most sustainable alternative. Currently, the Center's research includes applying proposed analysis approach and metrics for ESD to alternative biofuel production and fuel cell system.

Reference:

- Aldeeb, A.A. (2003), Systematic Approach for Chemical Reactivity Evaluation, Ph.D. Dissertation, Texas A&M University, December 2003
- Cisneros, L. (2002), Adiabatic Calorimetric Studies of Hydroxylamine Compounds, Ph.D. Dissertation, Texas A&M University, August 2002
- EPA (1995), User's Guide to Federal Accidental Release Databases, EPA CEPPPO and NRT, September 1995
- Fang, J.S., D.M. Ford, and M.S. Mannan (2004), Making the Business Case for Process Safety Using Value-at-Risk Concepts, *Journal of Hazardous Materials*, 115(1-3): 17-26
- Gentile, M. (2004), Development of a Hierarchical Fuzzy Model for the Evaluation of Inherent Safety, Ph.D Dissertation, Texas A&M University, August 2004
- Gentile, M., W.J. Rogers, and M.S. Mannan (2003), Development of an Inherent Safety Index Based on Fuzzy Logic, *AIChE Journal*, 49(4): 959-968
- Kletz, T. (1999), HAZOP and HAZAN: Identifying and Assessing Process Industry Hazards, 4th edition, Warwickshire, UK: Institution of Chemical Engineer
- Krishna, K. (2003), Measurement and Prediction of Aerosol Formation for the Safe Utilization of Industrial Fluids, Ph.D dissertation, Texas A&M University, December, 2003
- Krishna, K., T.K. Kim, K.D. Kihm, W.J. Rogers, and M.S. Mannan (2003), Predictive Correlations for Leaking Heat Transfer Fluid Aerosols in Air, *Journal of Loss Prevention in the Process Industries*, 16(1): 1-8
- Krishna, K., W.J. Rogers, and M.S. Mannan (2003), The Use of Aerosol Formation, Flammability, and Explosion Information for Heat Transfer Fluid Selection, *Journal of Hazardous Materials*, 104(1-3): 215-226
- Liu, Y-S., V.M. Ugaz, W.J. Rogers, and M.S. Mannan (2005), Development of a Nanocalorimeter for Material Characterization, *Journal of Loss Prevention in the Process Industries*, 18(3): 139-144
- Mannan, M.S. (1998), Accident History Database: An Opportunity, 1998 Annual Symposium of the Mary Kay O'Connor Process Safety Center, March 30-31, 1998, College Station, Texas
- Mitchell, S.M. and M.S. Mannan (2005), Resilient Engineered Systems, *Chemical Engineering Progress*, June
- MKOPSC (2005a), safety culture white paper, Newsletter, Mary Kay O'Connor Process Safety Center, Summer 2005
- Nimmo, I. (1995), Adequately address abnormal situation operations. *Chem. Eng. Process*, 91(1):1361-1375
- Qiao, Y., M. Gentile, M.S. Mannan (2004), "Fuzzy Logic Methodology for Accident Frequency Assessment in Hazardous Materials Transportation," Proceedings of the CCPS 19th Annual International Conference, Orlando, Florida, June 29-July 1, 2004, pp. 215-224
- Rajaraman, S., J. Hahn, M.S. Mannan (2004), A Methodology for Fault Detection, Isolation, and Identification for Nonlinear Processes with Parametric Uncertainties, *Industrial and Engineering Chemistry Research*, 43(21): 6774-6786
- Rajaraman, S., J. Hahn, M.S. Mannan (2004), A Methodology for Fault Detection, Isolation and Identification for Nonlinear Processes with Parametric Uncertainties. *Ind. Eng. Chem. Res.*, 43(21):6774-6786
- Rajaraman, S. J. Hahn, M.S. Mannan (2005). Sensor fault diagnosis for time-varying systems using Subspace model identification. Submitted to *IEEE Transactions on Control Systems and Technology*

- Rogers, W.J., Y.-S. Liu, and M.S. Mannan (2004), "Experimental and Computational Methods for Process Safety Research," Proceedings of the 3rd NRIFD Symposium, Mitaka, Tokyo, Japan, March 10-12, 2004, pp. 55-66
- Saraf, S.R. (2003), Molecular Characterization of Energetic Materials, Ph.D Dissertation, Texas A&M University, December 2003
- Saraf, S.R., W.J. Rogers, M.S. Mannan, M.B. Hall, and L.M. Thomson (2003), Theoretical Thermochemistry: Ab initio Heat of Formation for Hydroxylamine, *Journal of Physical Chemistry, A*, 107(8): 1077-1081
- Suardin, J. (2005), The integration of Dow's Fire and Explosion Index into process design and optimization, Master thesis, Texas A&M University, August, 2005
- Sukmarg, P. (2000), Effects of Operating Conditions on a Heat Transfer Fluids Aerosol, Master thesis, Texas A&M University, August, 2000
- Sukmarg, P., K. Krishna, W.J. Rogers, K.D. Kihm, and M.S. Mannan (2002), Non-intrusive Characterization of Heat Transfer Aerosol Sprays Released from an Orifice, *Journal of Loss Prevention in the Process Industries*, 15(1): 19-27
- Vedam, H., . V. V. (1999), PCA-SDG based process monitoring and fault detection. *Cont. Eng. Prac*, 7(7): 903-917
- Vidal, M. (2005), Binary Mixture Flammability Characteristics for Hazard Assessment, Ph.D Dissertation, Texas A&M University, August, 2005
- Vidal, M., W.J. Rogers, J.C. Holste, M.S. Mannan (2004), A Review of Estimation Methods for Flash Points and Flammability Limits, *Process Safety Progress*, 23(1): 47-55
- Vidal, M., W.J. Rogers, M.S. Mannan (2005), Prediction of Minimum Flash Point Behavior for Binary Mixtures, *Transactions of the Institute of Chemical Engineers, Part B, Process Safety and Environmental Protection*, May
- Wang, Y. (2004), Development of a Computer-Aided Fault Tree Synthesis Methodology for Quantitative Risk Analysis in the Chemical Process Industry, Ph.D Dissertation, Texas A&M University, December, 2004
- Wang, Y., T.L. Teague, H.H. West, and M.S. Mannan (2002), A New Algorithm for Computer-aided Fault-Tree Synthesis, *Journal of Loss Prevention in the Process Industries*, 15(4): 265-277
- Wei, C. (2005), Title, Ph.D Dissertation, Texas A&M University, August 2005
- Wei, C., S.R., Saraf, W.J. Rogers, and M.S. Mannan (2004), Thermal Runaway Reaction Hazards and Mechanisms of Hydroxylamine With Acid/Base Contaminants, *Thermochimica Acta*, 421(1-2), 2004: 1-9