Process Safety and Environmental Protection

rok 2012, ročník 90

Číslo 2 (March 2012)

C. Liebner, J. Fischer, S. Heinrich, T. Lange, H. Hieronymus, E. Klemm. *Are micro reactors inherently safe? : an investigation of gas phase explosion propagation limits on ethene mixtures*. Pages 77-82.

A method for the determination of safety properties for micro reactors and micro structured components is presented. Micro structured reactors are not inherently safe but the range of safe operating conditions of micro reactors are extended since the explosion region is reduced. The λ/3 rule was demonstrated to be applicable to micro scale tubes for stoichiometric mixtures of ethane–oxygen and ethane–nitrous oxide. Furthermore first results from an investigation concerning detonation propagation through a micro reactor of non-ideal geometry are shown. Initial pressure investigated is ranging from low pressure up to 100 kPa.

Highlights: ► Micro reactors are not inherently safe. ► Explosion propagation limits. ► Investigation method for the determination of safety properties. ► First results from explosion propagation through a micro reactor of non-ideal geometry.

- **Keywords:** Micro reactor; Explosion propagation limits; Chemical safety; Investigation method

G.H.A. Shirali, M. Motamedzade, I. Mohammadfam, V. Ebrahimipour, A. Moghimbeigi. *Challenges in building resilience engineering (RE) and adaptive capacity : a field study in a chemical plant*. Pages 83-90.

Safety issue in a chemical plant is absolutely critical because loss of control can result in a catastrophic consequence which is not limited to the boundaries of the plant. Thus, a risk assessment system is required for (a) preventing accidents by anticipation, (b) surviving disturbances by recovery, and (c) handling disruptive events by adaptation. RE is a proactive approach claiming to achieve all these objectives. The present research tries to identify challenges in the procedure of building RE and its adaptive capacity in a chemical plant. Primary data were collected through on-site observations and interviewing personnel. The results indicated the main challenges could be classified into nine categories of: lack of explicit experience about RE, intangibility of RE level, choosing production over safety, lack of reporting systems, 'religious beliefs', out-of-date procedures and manuals, poor feedback loop, and economic problems. Finally, it is concluded that the management insight about safety in such systems should avoid

hindsight bias and tend to create foresight. Changing this insight can lead to achieve high reliability and resilience in the plant.

- **Keywords:** Resilience engineering (RE); Chemical plant; Safety; Adaptive capacity

Ruifeng Qi, Katherine P. Prem, Dedy Ng, Morshed A. Rana, Geunwoong Yun, M. Sam Mannan. *Challenges and needs for process safety in the new millennium*. Pages 91-100.

Process industries have made quite a bit of progress in process safety since the tragic night of December 2, 1984 in Bhopal. Nonetheless, incidents continue to occur on a regular basis due to insufficient understanding of the urgency to identify best practices and drive for process safety improvements in the organization. This paper addresses some of the critical challenges in implementing effective safety programs: (a) failure to learn from past incidents and to capture those lessons into process design, procedures, training, maintenance, and other programs, (b) insufficient attention to leading indicators, and (c) an increase in complexity of process operations and lack of communication. In the presence of these challenges, there is a great need to develop better solutions by utilizing good science based approaches and best practice studies. Potential research areas include, but are not limited to, incident database analysis, reactive chemicals, inherently safer design, combustible dust explosion, facility siting, and the flammability of fuel mixtures and aerosols. In addition, an example was presented on LNG industry safety to illustrate that science-based research is needed to ensure the safe operation and to avoid or mitigate unintended consequences.

Highlights: ► Changes in industry, society and technology can cause new hazardous event scenarios. ► Optimizing production and ensuring process safety is daunting and complex task. ► Consequence modeling of LNG release for determining potential hazard zones. ► Experimental investigation of water curtain and expansion foam. ► Characteristics of chemicals & reaction mixtures to trace possible runaway pathways.

- **Keywords:** Bhopal; Process safety; Leading indicators; LNG

L. Gooijer, N. Cornil, C.L. Lenoble. *An international comparison of four quantitative risk assessment approaches : a benchmark study based on a fictitious LPG plant*. Pages 101-107.

In order to compare the quantitative risk assessment (QRA) methods for land use planning and licensing used in France, the United Kingdom, The Netherlands and the Walloon Region of Belgium, a benchmark exercise was performed. Based on a description of a fictitious LPG storage plant, INERIS from France, HSE from the United Kingdom, the Faculté Polytechnique de Mons from the Walloon Region of Belgium and the RIVM from The Netherlands used their own quantitative risk assessment approach to perform the exercise. The risk assessment approaches to determine third party risks of a LPG plant used by the four partners are very different. In France the assessment is based on a specific on-site analysis performed by experts. HSE uses a simple consequence based approach to determine safety distances. In The Netherlands and the Walloon Region a generic and standardized method for determining the risk contours is used. The differences relate to the calculation methodologies and the types of consequences that are calculated (such as lethal effects or irreversible effects). Despite the differences, the methods yield to similar safety distances between houses and companies: distances between 200 and 280 m. However, similar safety distances can still have different policy implications. For instance, the safety distances in The Netherlands and France are used as limit values, whereas in Belgium and the United Kingdom they are used to give an advice.

Highlights: ► Four risk assessment approaches (QRA) are compared and they are very different. ► The differences relate to the calculation methods and the calculation effects. ► Despite the differences, the final safety distances are quite similar. ► But similar safety distances still have different policy implications.

- **Keywords:** Quantitative risk assessment; QRA; Benchmark study; LPG; Third party risk

Barbara Joan Lowesmith, Geoffrey Hankinson. *Large scale high pressure jet fires involving natural gas and natural gas/hydrogen mixtures*. Pages 108-120.

A series of six large scale high pressure jet fires were conducted using natural gas and natural gas/hydrogen mixtures. Three tests involved natural gas and three involved a mixture of natural gas and hydrogen containing approximately 24% by volume hydrogen. For each fuel, the three tests involved horizontal releases from 20, 35 and 50 mm diameter holes at a gauge pressure of approximately 60 bar. During the experiments, the flame length and the incident radiation field produced around the fire were measured. The fires also engulfed a 1 m diameter horizontal pipe placed across the flow direction and about halfway along the flame. This pipe was instrumented to measure the heat fluxes to the pipe. The data obtained is compared with previous data obtained for various hydrocarbons at large scale.

Highlights: ► Data from large scale jet fires are presented. ► The fuel was natural gas or natural gas with 24% hydrogen added. ► The flame length related to release net power and agreed with an existing correlation. ► The thermal radiation field and fraction of heat radiated were similar. ► Heat loads to a pipe were measured and found to be 15% higher for the hydrogen mixture.

- **Keywords:** Jet fires; Large scale experiments; Natural gas/hydrogen mixtures; Heat loads

E. Palazzi, B. Fabiano. *Analytical modelling of hydrocarbon pool fires : conservative evaluation of flame temperature and thermal power*. Pages 121-128.

As well known, risk is a combination of probability and consequences of an accident. In analyzing the consequence of accidental hydrocarbon fires and the potential for domino effects, the evaluation of the flame extent and temperature are of the utmost importance. Since the primary effects of pool fires are connected to thermal radiation and issues of interplant/tank spacing employees' safety zones, firewall specifications are to be addressed on the basis of a proper consequence analysis. By means of real scale experimental tests it was verified that both the thermal power and the flame temperature, Tf, increase as the pool area increases, up to reach maximum values in connection with a "critical pool dimension". Dealing with pool areas higher than the critical one, experimental results, performed by different researchers at different scales, show a decrease of Tf. An in-depth analysis of the different concurring phenomena connected to a pool fire development allowed identifying the limiting step controlling the flame temperature. In fact, the trend of Tf is mainly determined by the increasing difficulty of oxygen diffusion within the internal bulk of gaseous hydrocarbons. In this article, we propose a novel pool fire modelling approach based on the simplified physical phenomena occurring in a circular turbulent diffusion fire and suitable to provide a theoretical insight into the above-mentioned experimental trends and to obtain the maximum values of the flame temperature and of the thermal power. The geometry of the pool is dictated by the surroundings (i.e., diking) and the analytical models here presented were successfully applied to the common situation of circular pools. However, it must be remarked that the developed model, matching fairly well experimental data for

different hydrocarbons, can be applied in modelling similar scenarios characterized by different geometric or environmental conditions (e.g. road and rail tunnel fires).

Highlights: ► Novel analytical approach to hydrocarbon pool fire modelling. ► Analytical model based only on stoichiometry, thermodynamics and mass, momentum, energy balances. ► Good agreement experimental vs. theoretical trends of flame temperature and height. ► Conservative estimation of the thermal power of pool fires larger than 5–6 m.

- **Keywords:** Accident; Flame; Hydrocarbon; Model; Pool fire; Surface emissive power

Spyros Sklavounos, Fotis Rigas. *Advanced multi-perspective computer simulation as a tool for reliable consequence analysis*. Pages 129-140.

Major accidents involving hazardous materials are a crucial issue for the chemical and process industries. Many accidental events taken place in the past showed that dangerous substances may pose a severe threat for people and property. Aiming at loss prevention, a series of actions have been instituted through international regulations concerning hazardous installations safety preparedness. These actions involve efficient land-use planning, safety studies execution, as well as emergency response planning drawing up. A key factor for the substantial consideration of the above is the effective prediction of possible accident forms and their consequences, for the estimation of which, a number of empirical models have been developed so far. However, (semi-)empirical models present certain deficiencies and obey to certain assumptions, thus leading to results of reduced accuracy. Another approach that could be used for this purpose and it is discussed in this work, is the utilization of advanced computational fluid dynamics (CFD) techniques in certain accident forms modeling. In particular, composite CFD-based models were developed for the simulation of several characteristic accident forms involving isothermal and non-isothermal heavy gas dispersion, confined and unconfined explosion in environment of complex geometry, as well as flammable cloud fire. The simulation cases were referred to real-scale trials allowing us to conclude about the validity of the quantitative results. Comparisons of the computational predictions with the experimental observations showed that obtained results were in good agreement with the experimental ones, whereas the evaluation of statistical performance measures proved the simulations to be statistically valid.

Highlights: ► CFD models were developed for the simulation of chemical accidents. ► The models developed were validated with experimental data. ► Release and dispersion, fire and explosion phenomena were successfully approached. ► Critical quantities for consequence analysis purposes were effectively estimated. ► Shock wave attenuation within tunnels is given by new statistical models.

- **Keywords:** Loss prevention; Consequence analysis; Environmental impact; Gas dispersion; Explosion; Cloud fire

Man-hong Huang, Yu-dong Yang, Dong-hui Chen, Liang Chen, Hui-dong Guo. *Removal mechanism of trace oxytetracycline by aerobic sludge*. Pages 141-146.

To investigate the mechanism of removal of selected pharmaceuticals in activated sludge systems, laboratory-scale batch experiments were conducted to assess the adsorption and degradation behavior of trace oxytetracycline (OTC). The adsorption equilibrium of OTC was observed in 30 min and the adsorption process could be well described by a pseudo-second-order model with a rate of 0.362 L μg−1 min−1. The OTC adsorption rate decreased with increasing temperature and could be fitted by the Freundlich isotherm. The linear partition coefficients (Kd) were 1.19, 0.999, and 0.841 L g−1 at temperatures

of 15, 20, and 25 °C, respectively. Thermodynamic analysis revealed that the adsorption of OTC onto the inactivated sludge was spontaneous ($\Delta G = -16.7$ to -17.0 kJ mol−1), enthalpy-driven ($\Delta H = -24.9$ kJ mol−1), entropy-retarded ($\Delta S = -27.4$ J (mol K)−1), and predominantly a physical adsorption.

Highlights: ► We investigate mechanism of removal of trace oxytetracycline (OTC) by sludge. ► Adsorption of OTC by sludge is quick and fits the pseudo-second-order model. ► OTC sorption decreases with increase of temperature and could be fitted by the Freundlich isotherm. ► Adsorption of OTC onto the inactivated sludge was spontaneous and entropy-retarded. ► Most of the initial OTC was removed by adsorption during aerobic degradation.

- **Keywords:** Aerobic sludge; Kinetics; Oxytetracycline (OTC); Remove

Davor Dolar, Sanja Pelko, Krešimir Košutić, Alka J.M. Horvat. *Removal of anthelmintic drugs and their photodegradation products from water with RO/NF membranes*. Pages 147-152.

Photolytic reactions are often complex, involving various competing or parallel pathways and leading to multiple reaction products. Removal of anthelmintic drugs (AD) – levamisole (LEV), albendazole (ABZ), praziquantel (PZQ), febantel (FEBA) from water and their photodegradation products with reverse osmosis (RO) and nanofiltration (NF) membranes were investigated in this work. Simulation of photodegradation of ADs was carried out under laboratory conditions with UV lamp at a wavelength of 254 nm for 4 h. Reverse osmosis (LFC–1 and XLE) and tight nanofiltration (NF90) membranes showed good removal (>83%) of anthelmintic drugs in binary solutions and in mixture. Other nanofiltration (NF270, NF and DK) membranes had rejection between 22 and 45% for smaller drugs (LEV and ALB) and >90% for PZQ and FEBA. These results show that main rejection mechanism in binary solutions was size exclusion and in mixture additional physico-chemical interactions had influence. After the UV treatment anthelmintic drugs were degraded into several photodegradation products (5 for LEV, 2 for ABZ, 1 for PZQ and 8 for FEBA). Reverse osmosis and NF90 membranes removed >95% of all photodegradation products (except FEBA1 around 70%) and other nanofiltration membranes between 33 and 99.99%.

Highlights: ► Treatment of anthelmintic drugs (AD) in model waters with UV light for 4 h. ► We examined removal of AD and their degradation product with NF and RO. ► Excellent removal of AD with NF and RO membrane treatments. ► Degradation of compounds (up to 8% compound) after UV treatment. ► Good to excellent removal of degradation products with NF and RO.

- **Keywords:** Anthelmintic drug; Photodegradation product; Membrane; Nanofiltration; Reverse osmosis