Process Safety and Environmental Protection

rok 2011, ročník 89

Číslo 1 (January 2011)

Zoltán Török, Nicolae Ajtai, Adrian-Teofil Turcu, Alexandru Ozunu. *Comparative consequence analysis of the BLEVE phenomena in the context on Land Use Planning : case study : the Feyzin accident*. Pages 1-7.

Several technological accidents have occurred in the oil/gas refining and petrochemical industries, involving large quantities of LPG (Liquefied petroleum Gas), all having in common BLEVE (Boiling Liquid Expanding Vapor Explosion) phenomena. The new Member States of the European Union have to adopt the Seveso Directives, but after 3 years of membership there is still a gap in the Romanian legislation regarding a specific methodology for the calculation of Land Use Planning (LUP) distances in case of Seveso-type industrial sites. These distances were calculated for a BLEVE event, considering the French, Italian and Austrian LUP methodologies. The results were compared to establish which methodology is more adequate for the development of Romanian LUP methodology. The paper also presents an innovative approach of BLEVE modeling with the purpose to compare the measured consequences of the Feyzin (France) accident with the simulation results obtained using three available BLEVE models: static, dynamic and rupture of vessel. The investigations and simulation results demonstrate the theory that in case of BLEVE the thermal effects of the fireball are more severe than the effects of the blast wave, therefore, the recommended approach is to calculate the heat load from the fireball, using the French LUP threshold limits. **Research highlights:** ▶ Determination of the propane quantity involved in the BLEVE at Feyzin accident. ▶ Comparative analysis of static, dynamic and "vessel rupture" BLEVE models. ▶ Comparative study of French, Italian and Austrian Land Use Planning safety limits. ▶ Proposal of BLEVE modeling technique for Romanian Land Use Planning methodology. ▶ Results show that values obtained by dynamic modeling are the most adequate for LUP.

- **Keywords:** LPG; BLEVE; Simulation; Feyzin; Land Use Planning

Seyed Morteza Zamir, Rouein Halladj, Bahram Nasernejad. *Removal of toluene vapors using a fungal biofilter under intermittent loading*. Pages 8-14.

To investigate the performance of a compost biofilter treating toluene vapor during intermittent loading, a biofiltration system was set up. This system was inoculated with a special type of white-rot fungus, *Phanerochaete chrysosporium*. The system was loaded 10 h per day on 0.096, 0.024, 0.06 m^3/h of air flow rates, and 173.1 and 52.6 mg m^{-3} of

pollutant concentration while there was no aeration to the system during the remaining 14 h of the day. Maximum removal efficiency and elimination capacity obtained were about 92% and 1913.7 mg m^{-3} h^{-1}, respectively. The fungal biofilter showed its robustness to the alterations in inlet toluene concentration and gas flow rate. The kinetic of biological reaction was studied by application of Monod type equation. The kinetic constants K_m and r_m are evaluated as 3.495 g m^{-3} and 50 g m^{-3} h^{-1}, respectively. The results confirmed that the fungal system could effectively remove toluene in such a harsh condition without adding excess nutrient solution and during intermittent loading. **Research highlights:** ▶A biofilteration system was set up using fungus *Phanerochaete chrysosporium.* ▶The biofilter was loaded intermittently 10 h per day during 60 days of operation. ▶Maximum removal efficiency and elimination capacity obtained were about 92% and 1913.7 mg m^{-3} h^{-1}, respectively. ▶By application of Monod type equation the kinetic constants K_m and r_m are evaluated as 3.495 g m^{-3} and 50 g m^{-3} h^{-1}, respectively. ▶The effect of residence time was more significant than changing the inlet concentration on the biofiltration of toluene.

- **Keywords:** Biofilter; Toluene; *Phanerochaete chrysosporium*; Compost; Intermittent loading

Rashmi Sanghi, Awantika Dixit, Preeti Verma. *Evaluation of Coriolus versicolor for its tolerance towards toxic sulphonic azo dyes in sequential batch mode*. Pages 15-21.

The ability of the white rot fungus *Coriolus versicolor*, to produce enzymes during its growth and decolorise five chemically different sulphonic azo synthetic dyes was evaluated under the operating conditions which had already been optimized. An increase in the initial dye content, led to a slow decrease in the decolorisation efficiency. Sequential batch culture studies were performed in the laboratory for the long-term utilization of this fungus, to decolorise the individual dyes over repeated exposure (respike) of four cycles of 8 days each. The fungus showed high decolorisation capacity and was able to tolerate high concentrations of the dyes and sustain the decolorisation process for long. Under sequential batch reactors, very high degrees of decolorisation of the four reactive dyes were repeatedly achieved. The decolorisation potential of the fungus could be correlated to the glucose consumed by the fungus as well as the structure of the dyes. Dyes with a naphthalene di sulphonic chromophore having the SO_3H group para to the azo bond were easily degraded compared to the dyes with a benzene disulphonic acid chromophore which was difficult to degrade. **Research highlights:** ▶Decolorisation and degradation of dyes using White rot fungus *Coriolus versicolor*. ▶Sequential batch reactor. ▶Tolerance for the toxic respiking of the dyes. ▶ Sustain decolorising potential of the fungus for continuous cycles. ▶Structure of dyes.

- **Keywords:** *Coriolus versicolor*; Dye; Degradation; Decolorisation; Enzyme assays; Sequential batch reactor

Ming Yang, Faisal I. Khan, Rehan Sadiq. *Prioritization of environmental issues in offshore oil and gas operations : a hybrid approach using fuzzy inference system and fuzzy analytic hierarchy process*. Pages 22-34.

To implement an environmental management system (EMS) in offshore oil and gas (OOG) operations, decision makers always encounter a problem of how to prioritize the environmental issues for establishing an environmental policy. Analytic hierarchy process (AHP) is a popular method to perform multi-attribute decision-making to solve this problem. In order to deal with vague information, various fuzzy AHP methods have been proposed. However, these methods suffer four serious limitations: (1) there is a tremendous computational requirement; (2) sometimes only triangular fuzzy numbers can be used; (3) adding or deleting criteria/attributes is not easy to operate in the algorithm; (4) inconsistent judgments is more likely to be expected with fuzzy numbers.

This paper proposes a hybrid approach using fuzzy inference system (FIS) and fuzzy AHP which not only eliminates the above limitations but also serves as a robust tool for the prioritization of environmental issues in OOG operations. In this approach, a five-level hierarchy is developed. The highest level of the hierarchy corresponds to the goal – prioritization of significance of environmental issues, and the lowest level corresponds to environmental issues, whereas intermediate levels correspond to major concerns (environmental risks) and sub-parameters of risk. The FIS is applied at the lower levels of the hierarchy to infer the major risk parameters. After this, the scores representing the extent of risk are calculated. Fuzzy AHP is used at the higher levels to synthesize the Significance Scores that will help to prioritize environmental issues. An application of the proposed approach is demonstrated through a numerical example. **Research highlights:** ▶This work helps to set priorities under constrained and uncertain situation. ▶Integrating FIS with FAHP effectively reduce the computational requirement. ▶ Application of the tool in offshore oil and gas environment is illustrated.

- **Keywords:** Prioritization; Fuzzy inference system (FIS); Fuzzy analytic hierarch process (FAHP); Offshore oil and gas (OOG); Environmental issues

Guillaume Vincent, Eric Schaer, Paul-Marie Marquaire, Orfan Zahraa. *CFD modelling of an annular reactor, application to the photocatalytic degradation of acetone*. Pages 35-40.

This study deals with the photocatalytic degradation of acetone, which is a typical pollutant of indoor air, in an annular photoreactor. The TiO_2 photocatalyst is deposited on a fiberglass support and irradiated by a commercial fluorescent tube placed at the center of the device. Acetone conversion extents up to 90% are obtained for low initial concentrations. Neither external mass transfer nor internal diffusion limitations are observed, and the annular reactor is first assimilated to a plug flow reactor. The Langmuir Hinshelwood model gives a good description of acetone degradation, and kinetic and adsorption parameters can be analytically deduced of the performed experiments. A Computational Fluid Dynamics description of the reactor is then proposed. The classical Navier–Stokes equations describe the flow in the free zone, whereas the Brinkman equation is used for the description of the flow in the porous zone. From an hydrodynamic point of view, a very good agreement between theoretical and measured Residence Time Distribution or upward velocities is obtained, testifying for the good description of the photocatalytic reactor. For a given illumination, the variations of acetone concentration inside the reactor can then be modelled. Comparison between theoretical and experimental outlet concentrations allows finally a better precision in the determination of the Langmuir Hinshelwood kinetic parameters. A relative difference of about 15% appears between the two sets of kinetic parameters (obtained assuming a plug flow or deduced from the CFD modelling). CFD simulations of photocatalytic reactor can thus address a better design of such air treatment devices. **Research highlights:** ▶ CFD modelisation of an annular photocatalytic reactor. ▶Hydrodynamic validation by comparison between experimental and theoretical RTD and upward velocities. ▶Kinetics modelling of acetone photocatalytic degradation. ▶Better accuracy in the determination of the Langmuir Hinshelwood kinetic parameters.

- **Keywords:** CFD simulation; Photocatalytic reactor; Acetone degradation; Indoor air treatment

Tarrant J. Falcke, Andrew F.A. Hoadley, David J. Brennan, Sarah E. Sinclair. *The sustainability of clean coal technology : IGCC with/without CCS*. Pages 41-52.

Integrated gasification combined cycle power generation (IGCC) is one of the emerging clean coal technologies for reducing greenhouse emissions in coal-fired electricity generation. IGCC technology, both with and without CO_2 capture and storage (CCS) is

compared with conventional super-critical power generation based on pulverized coal. The comparison is based on an equal consumption rate of Queensland black coal. The sustainability parameters being investigated are: thermal efficiency, environmental performance, inherent safety and economics. The IGCC processes have been modeled using commercial steady-state mass and energy balance software. Both the gross and net thermal efficiencies of the IGCC power station are reduced when the plant is configured for CCS. The net efficiency is reduced from 32.1% to 26.1%, when 81% of the CO_2 is captured. This delivers an overall reduction in CO_2 emissions per unit of electrical energy output of 73.2% compared to the reference plant. However, environmental performance in other areas suffers as a result of switching to IGCC-CCS, particularly fresh water consumption is increased by 2.5 tonne/MWh for both coastal and inland locations. Inherent safety risks associated with IGCC are also greater with the gasifier being the highest risk unit in the facility with a Dow fire and explosion index of 168 compared with an index of 107 for a conventional boiler. Toxicity hazard also increases with carbon monoxide present at concentrations several thousand times higher than the TWA limit. The minimum viable selling price of electricity for a 7% IRR is calculated to increase from USD80 MWh^{-1} for a conventional power station to USD101 MWh^{-1} for IGCC and to USD145 MWh^{-1} for IGCC-CCS. It is concluded that the application of IGCC-CCS is highly effective in reducing carbon dioxide emissions, the highest-profile problem associated with coal-fired electricity. There is an economic penalty which has been previously documented. However, there are also drawbacks concerning inherent safety and other environmental factors apart from CO_2 emissions, which until now have been under emphasized. **Research highlights:** ▶The IGCC without CCS has a lower net efficiency (32%) compared to conventional power generation (37%). ▶IGCC has considerably higher water demands than conventional coal power generation for both inland and coastal locations. ▶The IGCC process reduces the atmospheric emissions of SOx and NOx. However, this is done by transferring the environmental burden to the wastewater system. ▶The risk associated with fire and explosion is increased in probability for IGCC due to the increased number of process units, and in severity due to the process conditions. ▶Risk associated with toxicity are almost nil in a conventional modern power station, but are significant in an IGCC process due to high concentrations of CO and H_2S. ▶The cost differential between the conventional plant and the IGCC-CCS plant is around USD100/tonne CO_2.

- **Keywords:** Coal gasification; Thermal efficiency; Environmental performance; Inherent safety; Process economics

Hui Wang, De Ming Wang, Karl T. Chuang. *A sulfur removal and disposal process through H2S adsorption and regeneration : breakthrough behaviour investigation*. Pages 53-60.

The breakthrough behaviours of H_2S adsorption in a fixed-bed reactor of iron oxide based adsorbent under elevated pressures were studied. The effects of variations in superficial gas velocity from 0.09 to 0.26 m/s, H_2S feed concentration from 0.5% to 6% (v/v), the operating pressure from 405 to 5070 kPa absolute, and the height of the fixed-bed from 11.7 to 24.5 cm on the breakthrough curves and sulfur loading capacity were investigated. It was found that the shape of the breakthrough curves depends on the superficial velocity and the inlet H_2S concentration in gas streams. Under both higher superficial velocity and higher inlet H_2S concentration, the shape of the breakthrough curve becomes steeper, and vice versa. The sulfur loading capacity decreases as the superficial velocity and the inlet H_2S concentration increase, but it increases as the bed height increases. The change of operating pressure does not have a significant effect on the shape of the breakthrough curve or sulfur loading of the adsorbent. The pressure drop across the bed follows the Ergun equation. The investigation was also extended to the use of the regenerated adsorbents. An empirical equation of exponential function can be used to describe the breakthrough curves. This work provides useful data for the adsorption tower design and process optimization. **Research highlights:** ▶The H_2S

breakthrough curve of the iron oxide based adsorbent is a non-S type. ▶H_2S flux through the bed determines the shape of breakthrough curves. ▶Operating pressure has no significant impact on breakthrough behaviour. ▶An empirical equation is used to predict the breakthrough curves. ▶The Ergun equation can predict pressure drop across the iron oxide adsorbent bed.

- **Keywords:** Sulfur removal and recovery; Hydrogen sulfide; Iron oxide; Breakthrough

Simon Guštin, Romana Marinšek-Logar. *Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent*. Pages 61-66.

A stable continuous stripping of ammonia from the anaerobic wastewater treatment plant effluent was obtained in the ammonia stripping bench plant. The effects of temperature, amount of air and pH level on the removal of ammonium from the effluent were examined in the experiments. The operating parameters in the trials were chosen in respect of the economically feasible operating conditions in a biogas plant. The results of ammonium removal were compared with theoretically calculated values of free ammonia in these conditions. Ammonia stripping bench plant continuously removed up to 92.8% of ammonium and 88.3% of total nitrogen from the anaerobic digestion effluent. High pH had the most significant effect on stripping, causing the change of the ammonia/ammonium ratio in favour of ammonia. The second important factor was the amount of air passing through the stripping bench plant promoting the transition of ammonia from the liquid phase to the gas phase. The temperature within the examined range had the least significant effect on ammonia stripping. Continuous stripping of nitrogen from the anaerobic digestion effluent could considerably reduce the area required for the application of nitrogen-rich digestate after the biogas production and enable the treatment of the anaerobically digested effluent in the wastewater treatment plant. **Research highlights:** ▶A stable stripping of ammonia from the anaerobic wastewater treatment plant effluent was obtained. ▶Stripping of ammonia was continuous, with removal rate up to 92.8%. ▶The most influence on stripping had high pH level, then air flow rate and finally temperature. ▶High removal of ammonia nitrogen enables the final treatment of the anaerobic centrate in the municipal wastewater treatment plant.

- **Keywords:** Ammonia; Stripping; Anaerobic digestate; pH; Temperature; Air to liquid ratio

S. Clément, A. Gouiller, P. Ottenio, S. Nivelon, P. Huber, P. Nortier. *Speciation and supersaturation model in papermaking streams*. Pages 67-73.

Environmental responsibility of papermaking industry leads to intensive reuse of water streams. As well known in chemical engineering, this closure of loops causes the accumulation of soluble species, including calcium ions and inorganic carbon. The result is increased scaling, mainly by calcium carbonate. Due to complex behaviour, predicting scaling in papermaking streams is not straightforward and process water disposal should be kept at a high level in order to prevent scaling. This is contradictory with the objective of preserving the environment. Calcium carbonate precipitation is considered as complex since:

- speciation calculation must take into account several complexes and protonated species ($CaCO_3^0$, $CaHCO_3^+$, $CaOH^+$, HCO_3^-, H_2CO_3) in addition to Ca^{2+} and CO_3^{2-};

- several polymorphs can precipitate;

- the nucleation requires a rather high supersaturation to occur in homogeneous way.

We combined a mass balance approach using the CTP proprietary software PS2000 (Ruiz et al., 2003), specially developed for the simulation of actual papermaking plants and the USGS software PHREEQC (Parkhurst and Appelo, 1999), devoted to the speciation in complex aqueous solutions, to predict the local value of the Ionic Activity Product (I.A.P.) in the nodes of paper plants streams. These data were analysed using the results and methodology by Elfil and Roques (2004), comparing the I.A.P. with the solubility products of the three relevant polymorphs (anhydrous calcium carbonate, monohydrate calcium carbonate, calcite) to predict the risk of scaling. A campaign of analysis on an industrial site permitted to benchmark the calculation. **Research highlights:** ▶ Combination of iterative solutio of heat and mass balance equations with use of a powerful software for speciation allows to accurately model the chemical behaviour of water streams in an industrial plant for the production of recycled cellulose fibres. ▶ Speciation in papermaking aqueous streams must take Volatile Fatty Acids (VFA's) into account. ▶Prediction of scaling in papermaking circuits is possible and should be a useful tool in order to improve the closure of water circuit, a decisive challenge from the environmental point of view.

- **Keywords:** Water circuits closure; Scaling; Speciation; Supersaturation; Process simulation