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Chai Siah Lee, John Robinson, Mei Fong Chong. *A review on application of flocculants in wastewater treatment*.

Flocculation is an essential phenomenon in industrial wastewater treatment. Inorganic coagulants (salts of multivalent metals) are being commonly used due to its low cost and ease of use. However, their application is constrained with low flocculating efficiency and the presence of residue metal concentration in the treated water. Organic polymeric flocculants are widely used nowadays due to its remarkable ability to flocculate efficiently with low dosage. However, its application is associated with lack of biodegradability and dispersion of monomers residue in water that may represent a health hazard. Therefore, biopolymers based flocculants have been attracting wide interest of researchers because they have the advantages of biodegradability and environmental friendly. But, natural flocculants are needed in large dosage due to its moderate flocculating efficiency and shorter shelf life. Thus, in order to combine the best properties of both, synthetic polymers are grafted onto the backbone of natural polymers to obtain tailor-made grafted flocculants. This paper gives an overview of the development of different types of flocculants that were being investigated for treatment of industrial wastewater. Furthermore, their flocculation performance will be reviewed and the flocculation mechanism will be discussed.

- **Keywords:** Coagulation–flocculation; Direct flocculation; Bio-flocculants; Grafted flocculants; Flocculation mechanism; Wastewater treatment

Ezerie Henry Ezechi, Mohamed Hasnain Isa, Shamsul Rahman Mohamed Kutty, Asim Yaqub. *Boron removal from produced water using electrocoagulation*.

Produced water is the largest wastestream of oil and gas exploration but its chemical composition hinders its beneficial use. Effective treatment and reuse of produced water can mitigate scarcity of fresh water, especially in arid areas. Presence of inorganic compounds such as boron in produced water renders its beneficial use difficult. In this study, boron removal from produced water was investigated. Synthetic wastewater was prepared simulating the range of boron concentrations in produced water. Four operating parameters pH (3–11), charge loading (1200–3600 Ah/m3), contact time (15–90 min) and concentration (10–30 mg/L) were selected and their optimum conditions investigated. The obtained optimum conditions were applied to treat real produced water. Residual boron concentration of 0.3 mg/L was obtained from initial boron concentration of 15 mg/L in real produced water at optimum

conditions of pH 7, charge loading 2400 Ah/m3 and contact time 90 min. Boron adsorption could be represented by Langmuir and Freundlich isotherm models. Electrocoagulation can be used for the effective removal of boron from produced water.

- **Keywords:** Boron; Electrocoagulation; Produced water; Adsorption; Isotherms

Pey Yi Toh, Bee Wah Ng, Abdul Latif Ahmad, Derek Chan Juinn Chieh, JitKang Lim. *Magnetophoretic separation of Chlorella sp. : role of cationic polymer binder*.

Cationic polyelectrolyte promoted effective attachment of iron oxide nanoparticles (IONPs) onto microalgal cells through electrostatic attraction. Poly(diallyldimethylammonium chloride) (PDDA) and chitosan (ChiL), both are cationic polymer, are feasible to act as binding agent to promote rapid magnetophoretic separation of Chlorella sp. through low gradient magnetic separation (LGMS) with field gradient ▿B less than 80 T/m in real time. Cell separation efficiency up to 98% for the case of PDDA and 99% for the case of ChiL can be achieved in 6 min when 3 × 107 cells/mL Chlorella sp. are exposed to 300 mg/L surface functionalized-IONPs (SF-IONPs). Different polyelectrolytes do not give significant effect on cell separation efficiency as long as the particle attachment occurred. However, the PDDA is more preferable as the binder for all type of microalgae medium than the chitosan (ChiL) since it is not pH dependent. SF-IONPs coated with PDDA guarantee the cell separation performance for all pH range of cell medium, with 98.21 ± 0.40% at pH 8.84. On the other hand, the ChiL performance will be affected by the cell medium pH, with only 22.93 ± 31.03% biomass recovery at pH 9.25.

- **Keywords:** Microalgae; Renewable fuel source; Magnetophoretic separation; Polymer binder; Electrostatic interaction; Sustainable

M.A.A. Ahmad, M.R. Kamaruzzaman, S.Y. Chin. *New method for acrylic acid recovery from industrial waste water via esterification with 2-ethyl hexa*nol.

Acrylic acid (AA) is an important component for the production of acrylate polymer. In a typical acrylic manufacturing unit, waste water contains AA in a range of 4–15 wt.% contributes to the high values of chemical oxygen demand. Due to the toxicity of AA to the aquatic organism, this wastewater should be treated before it is discharged to the environment. The waste water could be evaporated before sending to the incineration which was neither economic feasible nor environmental friendly. Esterification of wastewater containing carboxylic acid with alcohol could be a promising method to recover the acid by converting it to ester while purifying the wastewater. In the present study, recovery of AA via esterification with 2-ethyl hexanol (2EH) was investigated. The model industrial wastewater with various concentration of AA (10–100% w/w) was reacted with 2EH to produce 2-ethyl hexyl acrylate (2EHA) in the setups with total reflux and continuously water removal. These Amberlyst-15 (ion exchange resin) catalyzed reactions were carried out under the mass transfer resistance free region. The performance of both systems was compared. The yield for the reactions of the AA solutions with the AA concentrations of 30–80% was enhanced significantly when the reactions were carried out using the second setup. The kinetic data of the esterification of dilute AA was well described by the Eley–Rideal (ER) kinetic model incorporated with a correction factor to consider the catalyst fouling effect and pseudo-homogeneous (PH) kinetic model for the AA polymerization. The findings have shown the potential of recovering AA from the waste water stream via esterification. The concentrated AA solutions or larger amount of inhibitor should be adopted to prevent the catalyst fouling by the deposition of poly-acrylic acid on the catalyst surface.

- **Keywords:** Acrylic acid; 2-Ethyl hexyl acrylate; Esterification; Amberlyst 15; Waste water; 2-ethyl hexanol

Cheng-Liang Chen, Hui-Chu Chen. *A mathematical approach for retrofit and optimization of total site steam distribution networks*.

This paper presents a generic mathematical model for retrofitting the steam power plants in an industrial site. The industrial sector under review consists of one steel mill, one oil refinery, and several petrochemical plants, where only small-scale steam integration has been implemented before this study. The relevant unit models in a typical steam power plant are established, and the steam plant retrofit problem is formulated as a mixed-integer nonlinear program (MINLP). Feasible retrofit alternatives suggested by experienced field engineers are investigated in sequence to examine the revenue of those possible modifications. The first scenario examines operational optimization of existent plants; the second option allows installation of one new turbine and replacement of several boilers and turbines with lower efficiency; the third scenario considers using a steam ejector to upgrade the disqualified import steam in the oil refinery. The significant merits from these three retrofit alternatives show that the proposed MINLP formulation has been a great help to enhance the inter-plant steam integration in an industrial sector.

- **Keywords:** Steam power plant; Mathematical programming; Total site integration; Mixed-integer nonlinear programming (MINLP); Process integration; Retrofit; Optimization

John Frederick D. Tapia, Raymond R. Tan. *Fuzzy optimization of multi-period carbon capture and storage systems with parametric uncertainties*.

Carbon capture and storage (CCS) is an important technology option for reducing industrial greenhouse gas emissions. In practice, CO2 sources are easy to characterize, while the estimation of relevant properties of storage sites, such as capacity and injection rate limit (i.e., injectivity), is subject to considerable uncertainty. Such uncertainties need to be accounted for in planning CCS deployment on a large scale for effective use of available storage sites. In particular, the uncertainty introduces technical risks that may result from overestimating the limits of given storage sites. In this work, a fuzzy mixed integer linear program (FMILP) is developed for multi-period CCS systems, accounting for the technical risk arising from uncertainties in estimates of sink parameters, while still attaining satisfactory CO2 emissions reduction. In the model, sources are assumed to have precisely known CO2 flow rates and operating lives, while geological sinks are characterized with imprecise fuzzy capacity and injectivity data. Three case studies are then presented to illustrate the model. Results of these examples illustrate the tradeoff inherent in planning CCS systems under parametric uncertainty.

- **Keywords:** Carbon capture and storage; Technical risk; Fuzzy mixed integer linear programming; Data uncertainty; Source-sink matching; Optimization

Evgeniy Burlutskiy. *Numerical analysis of phase behavior during rapid decompression of rich natural gases*.

The effect of the condensation process on the gas and liquid phase behavior during rapid decompression of rich natural gases is studied in the paper numerically. A one-dimensional mathematical model of transient thermal two-phase flow of compressible multi-component natural gas mixture and liquid phase in a shock tube is developed. The set of mass, momentum and enthalpy conservation equations are solved for the gas and liquid phases. The approach to model a liquid condensation process during rapid decompression of rich natural gas mixture is proposed. The mass transfer between the

gas and the liquid is taken into account by introducing the appropriate terms into the governing equations. Thermo-physical properties of multi-component natural gas mixture are calculated by solving the Equation of State (EOS) in the form of the Soave–Redlich–Kwong (SRK-EOS) model. The proposed liquid condensation model is integrated into the GDP model. A simple case of GDP model, where the liquid was not considered, was extensively validated on base and dry natural gases. The proposed two-phase model is validated against the experiments where the decompression wave speed was measured in rich natural gases at low temperature. It shows a good agreement with the experimental data.

- **Keywords:** Mathematical modeling; Multiphase flow; Mass transfer; Condensation; Gases; Rapid decompression

Qinglei Tan, Guoming Chen, Lei Zhang, Jianmin Fu, Zemin Li. *Dynamic accident modeling for high-sulfur natural gas gathering station*.

Dynamic accident modeling for a gas gathering station is implemented to prevent high-sulfur natural gas leakage and develop equipment inspection strategy. The progress of abnormal event occurring in the gas gathering station is modeled by the combination of fault tree and event sequence diagram, based on accident causal chain theory, i.e. the progress is depicted as sequential failure of safety barriers, then, the occurrence probability of the consequence of abnormal event is predicted. Consequences of abnormal events are divided into accidents and accident precursors which include incidents, near misses and so on. The Bayesian theory updates failure probability of safety barrier when a new observation (i.e. accident precursors or accidents data) arrives. Bayesian network then correspondingly updates failure probabilities of basic events of the safety barriers with the ability of abductive reasoning. Consequence occurrence probability is also updated. The results show that occurrence probability trend of different consequences and failure probability trend of safety barriers and basic events of the safety barriers can be obtained using this method. In addition, the critical basic events which play an important role in accidents occurrence are also identified. All of these provide useful information for the maintenance and inspection of the gas gathering station.

- **Keywords:** Fault tree; Event sequence diagram; Accident causal chain theory; Bayesian theory; Bayesian network; Dynamic risk

Shuwen Gong, Lijun Liu, Junling Zhang, Qingxin Cui. *Stable and eco-friendly solid acids as alternative to sulfuric acid in the liquid phase nitration of toluene*.

Liquid-phase nitration of toluene was carried out using a silica supported Cs salt of phosphomolybdic acid (Cs2.5H0.5PMoO40) as catalyst with dilute nitric acid under mild conditions. The Cs2.5H0.5PMoO40 particles with Keggin-type structure were well dispersed on the surface of silica, and the catalysts exhibited strong acidity, which may be responsible for the high catalytic nitration activity. The effects of various parameters on nitration were tested, which included reaction temperature, reaction time, catalyst amount and reactants ratio. Under suitable conditions, the nitrations gave high toluene conversion (99.6%) and good mono-nitration selectivity. Compared to the conventional process, there was no other organic solvent or sulfuric acid used in the reaction system, which made it more environment-friendly. Moreover, the supported catalyst was proven to have excellent stability in the nitration process.

- **Keywords:** Liquid-phase nitration; Toluene; Solid acid; Catalysis; Supported

Genserik L.L. Reniers, Amaryllis Audenaert. *Preparing for major terrorist attacks against chemical clusters : intelligently planning protection measures w.r.t. domino effects*.

Chemical industrial areas or so-called chemical clusters consist of hundreds, and sometimes thousands, of chemical installations situated next to each other. Such areas can thus be seen as the summation of a large number of structures exhibiting danger to a certain degree for initiating or continuing accident domino effects or knock-on effects. In this article, an approach to investigate in a systemic way the vulnerability of each installation within the larger chemical cluster context, is developed. Our suggested method results in a prioritization of chemical installations with respect to their vulnerability for domino effects. The method can be used for intelligently designed protection of chemical industrial areas against terrorist attacks.

- **Keywords:** Chemical cluster; Security; Process industries; Security management; Domino effects

Sávio S.V. Vianna, Robert Stewart Cant. *Initial phase modelling in numerical explosion applied to process safety*.

The utilisation of computational fluid dynamics (CFD) in process safety has increased significantly in recent years. The modelling of accidental explosion via CFD has in many cases replaced the classical Multi Energy and Brake Strehlow methods. The benefits obtained with CFD modelling can be diminished if proper modelling of the initial phase of explosion is neglected. In the early stages of an explosion, the flame propagates in a quasi-laminar regime. Proper modelling of the initial laminar phase is a key aspect in order to predict the peak pressure and the time to peak pressure. The present work suggests a modelling approach for the initial laminar phase in explosion scenarios. Findings are compared with experimental data for two classical explosion test cases which resemble the common features in chemical process areas (confinement and congestion). A detailed analysis of the threshold for the transition from laminar to turbulent regime is also carried out. The modelling is implemented in a fully 3D Navier–Stokes compressible formulation. Combustion is treated using a laminar flamelet approach based on the Bray, Moss and Libby (BML) formulation. A novel modified porosity approach developed for the unstructured solver is also considered. Results agree satisfactorily with experiments and the modelling is found to be robust.

- **Keywords:** Chemical process safety; Explosion; Unstructured mesh; Computational modelling

Esteban J. Bernechea, Josep Arnaldos. *Optimizing the design of storage facilities through the application of ISD and QRA*.

Four strategies can be used to achieve safety in chemical processes: inherent, passive, active and procedural. However, the strategy that offers the best results is the inherent safety approach, especially if it is applied during the initial stages of a project. Inherently Safer Design (ISD) permanently eliminates or reduces hazards, and thus avoids or diminishes the consequences of incidents. ISD can be applied using four strategies: substitution, minimization, moderation and simplification. In this paper, we propose a methodology that combines ISD strategies with Quantitative Risk Assessment (QRA) to optimize the design of storage installations. As 17% of major accidents in the chemical industry occur during the storage process and cause significant losses, it is essential to improve safety in such installations. The proposed method applies QRA to estimate the risk associated with a specific design. The design can then be compared to others to determine which is inherently safer. The risk analysis may incorporate complex phenomena such as the domino effect and possible impacts on vulnerable material and

human elements. The methodology was applied to the San Juanico tragedy that occurred in Mexico in 1984.

- **Keywords**: Inherently Safer Design; Quantitative Risk Assessment; Process optimization; Storage installations; Domino effect; Land Use Planning

Mohammad Dadashzadeh, Faisal Khan, Rouzbeh Abbassi, Kelly Hawboldt. *Combustion products toxicity risk assessment in an offshore installation*.

Products of a hydrocarbon fire accident have both chronic and acute health effects. They cause respiratory issues to lung cancer. While fire is the most frequent phenomenon among the offshore accidents, predicting the contaminants' concentration and their behavior are key issues. Safety measures design, such as ventilation and emergency routes based only on predicted contaminants' concentration seems not to be the best approach. In a combustion process, various harmful substances are produced and their concentration cannot be added. The time duration that any individual spends in different locations of an offshore installation also varies significantly. A risk-based approach considers the duration a person is exposed to contaminants at various locations and also evaluates the hazardous impacts. A risk-based approach has also an additivity characteristic which helps to assess overall risk. Through the current study, an approach is proposed to be used for risk assessment of combustion products dispersion phenomenon in a confined or semi-confined facility. Considering CO, NO2 and CH4 as the contaminants of concern, the dispersion of the substances over the layout of the facility after a LNG fire is modeled. Considering different exposure times for three major parts of the facility including the processing area, office area and the accommodation module, the risk contours of CO, NO2 and CH4 over the entire facility are developed. The additivity characteristic of the risk-based approach was used to calculate the overall risk. The proposed approach helps to better design safety measures to minimize the impacts and effective emergency evacuation planning.

- **Keywords:** CFD; Pool Fire; Combustion products; Toxic dispersion; Acute effects; Risk-based approach

Sergey E. Galushin, José María Izquierdo, Miguel Sánchez Perea. *Transmission Functions and its application to the analysis of time uncertainties in Protection Engineering*.

In this paper we explore the concept of transmission Functions and its application to the resolution of the problem posed by the uncertainty in the time to take manual protective actions due for instance to different operator abilities. This time uncertainty is a very special kind of uncertainty with obvious relevance in Protection Engineering problems. Tackling it involves a large amount of simulations of transients associated to sequences of system transitions, resulting from those actions, where the only difference from one simulation to another is the time interval between transitions, the evolution laws being always the same. In order to solve such type of problems, a new formalism is proposed based on the concept of transmission Function. We prove that for a large class of Multiple Input–Multiple Output (MIMO) piecewise linear systems, the output may be obtained as additive contributions of each interval of the sequence, each one characterized via a Transmission Function. We then provide efficient methods to compute Transmission Functions of sequences of canonical Single Input-Single Output (SISO) piecewise systems, and to find the locus of protective action times that lead to damage (damage domain).

- **Keywords:** Piecewise linear systems; Damage domain; Time uncertainty; Simulation; Transmission Function; Protection *Engineering*

***Zhilin Xi, Manman Jiang, Jinjun Yang, Xian Tu. Experimental* study on advantages of foam–sol in coal dust control.**

In China, more than 2.65 million coal mine workers are exposed to coal dust. Every year, new pneumoconiosis cases amount to 25,000, among which 6000 cases die of this disease. The figure is twice the death toll in production safety accidents. Occupational diseases seriously endanger life and health of coal mine workers, and restrict the healthy growth of the coal industry. The paper presented a study of foam–sol-based coal dust control. This was an experimental study of characteristics of foam–sol-based coal dust control, which features dust capture, suppression, and isolation. Comparative wettability experiments were carried out to determine contact angles of water, aqueous foam, and foam–sol solution. A new foam–sol generating system with a conical diffuser outlet was proposed. The experiment results clearly showed that the foam–sol features dust capture, suppression, and isolation. The wettability of the aqueous foam solution was better than the foam–sol solution, but the foam–sol technology had the better ability to capture the airborne dust, suppress the static dust and enclose the dust source, due to the excellent surface viscosity, strong cohesiveness and less volatile property. The paper concluded that the foam–sol could greatly improve the dust control efficiency and did not have main deficiencies that the aqueous foam technology had.

- **Keywords:** Aqueous foam; Coal dust; Contact angle; Dust control; Foam–sol; Foam–sol generating system

Lianfang Cai, Xuemin Tian. *A new fault detection method for non-Gaussian process based on robust independent component analysis*.

Conventional fault detection method based on fast independent component analysis (FastICA) is sensitive to outliers in the modeling data and thus may perform poorly under the adverse effects of outliers. To solve such problem, a new fault detection method for non-Gaussian process based on robust independent component analysis (RobustICA) is proposed in this paper. A RobustICA algorithm which can effectively reduce the effects of outliers is firstly developed to estimate the mixing matrix and extract non-Gaussian feature called independent components (ICs) by robust whitening and robust determination of the maximum non-Gaussian directions. Furthermore, a monitoring statistic for each extracted IC is constructed to detect process faults. Simulations on a simple example of the mixing matrix estimation and a fault detection example in the continuous stirred tank reactor system demonstrate that the RobustICA achieves much higher estimation accuracy for the mixing matrix and the ICs than the commonly used FastICA algorithm, and the RobustICA-based fault detection method outperforms the conventional FastICA-based fault detection method in terms of the fault detection time and fault detection rate.

- **Keywords:** Fault detection; Non-Gaussian process; Independent component analysis; Mixing matrix; Robust whitening; Outliers

Sabrina Copelli, Marco Derudi, Carlo Sala Cattaneo, Giuseppe Nano, Massimo Raboni, Vincenzo Torretta, Renato Rota. *Synthesis of 4-Chloro-3-nitrobenzotrifluoride : industrial thermal runaway simulation due to cooling system failure*.

In pharmaceutical and fine chemical industries, fast and strongly exothermic reactions are often carried out in semibatch reactors (SBRs) to better control the heat evolution by the feeding rate. In fact, for such processes, a thermal runaway event may be triggered whenever the rate of heat removal becomes lower than the rate of heat production. Such a dangerous phenomenon consists in an uncontrolled reactor temperature increase that, occurring in practically adiabatic conditions, can trigger secondary undesired exothermic

reactions or, worse, decompositions of the whole reacting mixture with consequent reactor pressurization due to uncontrollable gases formation. In this work, dedicated software has been developed and used to simulate a cooling system breakdown in an industrial SBR where the nitration of 4-Chlorobenzotrifluoride is carried out. The mathematical model is able to simulate both reactor temperature and pressure vs. time profiles thanks to a complete description of both the desired reaction and the unwanted reacting mixture decomposition kinetics. Different accidental scenarios have been simulated, showing both the wide different consequences that can arise from the same initiating event and, therefore, the usefulness of a complete simulation of the hypothesized accidental scenario in the frame of a Quantitative Risk Analysis.

- **Keywords:** Thermal runaway; Cooling system failure; Aromatic nitrations; 4-Chlorobenzotrifluoride; Semibatch reactor; Decomposition kinetics

Nicola Paltrinieri, Faisal Khan, Paul Amyotte, Valerio Cozzani. *Dynamic approach to risk management : application to the Hoeganaes metal dust accidents*.

Several major accidents caused by metal dusts were recorded in the past few years. For instance, in 2011, three accidents caused by iron dust killed five workers at the Hoeganaes Corp. facility in Gallatin, Tennessee (USA). In order to prevent such accidents, a dynamic approach to risk management was defined in this study. The method is able to take into account new risk notions and early warnings and to systematically update the related risk. It may be applied not only in the design phase of a system, but also throughout the system lifetime as a support to a more precise and robust decision making process. The synergy of two specific techniques for hazard identification and risk assessment was obtained: the Dynamic Procedure for Atypical Scenarios Identification (DyPASI) and the Dynamic Risk Assessment (DRA) methods. To demonstrate its effectiveness, this approach was applied to the analysis of Gallatin metal dust accidents. The application allowed collecting a number of risk notions related to the plant, equipment and materials used. The analysis of risk notions by means of this dynamic approach could have led to enhanced hazard identification and dynamic real-time risk assessment. However, the approach described is effective only if associated to a proper safety culture, in order to produce an appropriate and robust decision making response to emerging risk issues.

- **Keywords:** Dynamic risk management; Hazard identification; DyPASI; Dynamic Risk Assessment; Dust explosion; Early warning

Xi Wu, Zhao Yang, Tian Tian, Mengxue Qin. *Experimental research on the flammability characteristics of several binary blends consisting of 1-Chloro-1,1-difluoroethane and extinguishing agents*.

1-Chloro-1,1-difluoroethane (R142b) can be used as the refrigerant, foaming agent and ORC (Organic Rankine Cycle) fluid. R142b was described as one of the interim substitutes in the Montreal Protocol (signed in 1987), and allowed to be used in developing countries until 2040. However the production and consumption of R142b were required to be frozen this year on the average data of 2009 and 2010 according to its latest amendment (signed in 2007). Binary alternatives R245fa/R142b, R227ea/R142b, R600a/R142b and R134a/R142b are possible substitutes in the initial transition period of frozen and phase-out R142b for the reason of pressure approach, which may be welcomed by the countries with wide use of R142b considering the technology and cost. This paper contributes to the flammability of these binary mixtures experimentally by using a self-made test rig built on the ground of Chinese National Standard. Not only the flammable limits of blends were studied, but also the related flame images were presented and analyzed. In addition, the flame suppression efficiencies of R245fa, R227ea and R134a have been

compared and the lower flammable limits of R600a/R142b has been estimated and tested at different ratios. The presented work is beneficial to environmental protection.

- **Keywords:** HCFC-142b; Substitute; Phase out; Refrigerant; Flammable limit

Martin J. Goodfellow, Jonathan Wortley, Adisa Azapagic. *A system design framework for the integration of public preferences into the design of large infrastructure projects*.

Large infrastructure projects such as new roads, railways and nuclear plants have often suffered from public opposition, causing significant delays and costs. In many cases poor engagement between the supporters of construction and the public have contributed to this. Therefore, this paper proposes a novel design framework with the aim of improving public engagement at an early design stage. Following a modified quality function deployment (QFD) process, it enables incorporation of public preferences into the design process, thus helping to improve the social acceptability of large infrastructure projects and reduce costs related to opposition and delays. The application of the framework is illustrated by a case study related to design of nuclear power plants.

- **Keywords:** Large infrastructure; Nuclear power; Participatory design; Quality function deployment; Stakeholder engagement; System design

A.D. Galeev, S.I. Ponikarov. *Numerical analysis of toxic cloud generation and dispersion : a case study of the ethylene oxide spill*.

The present study examined the accidental spill of ethylene oxide, and a sensitivity analysis of the corresponding consequences was conducted using computational fluid dynamics (CFD). A validation of the gas dispersion CFD model against the experimental data sets included in the model evaluation protocol (MEP) was performed. The effect of the variability of the wind velocity on the extension of the hazardous areas and pool evaporation characteristics was evaluated. Additionally, the mitigation effects of the dike walls surrounding a spill were discussed. CFD simulation results have shown that the mitigation effect of dike walls is determined by their influence on both gas dispersion and pool evaporation and depends strongly on wind velocity in terms of toxic impact distances.

- **Keywords:** Consequence analysis; Evaporation modelling; Dispersion modelling; Dike walls; Mitigation effect; CFD

Amirhosein Rad, Bahman Abdolhamidzadeh, Tasneem Abbasi, Davood Rashtchian. *FREEDOM II : an improved methodology to assess domino effect frequency using simulation techniques*.

The uncertainty and the complexity associated with the domino effect is a barrier to assessing the frequency of such accidents analytically. The use of simulation techniques, such as Monte Carlo, to examine the domino effect instead of analytical techniques has shown great promise. In this paper, a new method to assess the frequency of domino accidents is proposed—FREEDOM II—which is an improvement on the recent algorithm proposed by the authors (FREEDOM). The modifications on FREEDOM were carried out to overcome a limitation of the method and to extend its capabilities. A key shortcoming of the earlier method was its inability to handle multiple failure scenarios. This shortcoming has been overcome in FREEDOM II. A new and improved algorithm has been developed that carries out the simulation in a significantly shorter run time. The applicability of the new model is shown by performing a multi-scenario case study.

- **Keywords:** Domino effect; Frequency estimation; Simulation; Monte Carlo; Risk assessment; Multiple scenarios

Hossam A. Gabbar, Sajid Hussain, Amir Hossein Hosseini. *Simulation-based fault propagation analysis : application on hydrogen production plant*.

Recently production of hydrogen from water through the Cu–Cl thermochemical cycle is developed as a new technology. The main advantages of this technology over existing ones are higher efficiency, lower costs, lower environmental impact and reduced greenhouse gas emissions. Considering these advantages, the usage of this technology in new industries such as nuclear and oil is increasingly developed. Due to hazards involved in hydrogen production, design and implementation of hydrogen plants require provisions for safety, reliability and risk assessment. However, very little research is done from safety point of view. This paper introduces fault semantic network (FSN) as a novel method for fault diagnosis and fault propagation analysis by using evolutionary techniques like genetic programming (GP) and neural networks (NN), to uncover process variables' interactions. The effectiveness, feasibility and robustness of the proposed method are demonstrated on simulated data obtained from the simulation of hydrogen production process in Aspen HYSYS®. The proposed method has successfully achieved reasonable detection and prediction of non-linear interaction patterns among process variables.

- **Keywords:** Fault sematic network (FSN); Cu–Cl thermochemical cycle; Aspen HYSYS®; Genetic programming; Neural networks; Process variables interaction

A. Azhagurajan, N. Selvakumar. *Impact of nano particles on safety and environment for fireworks chemicals*.

Pyrotechnic devices, commonly known as fireworks, have a huge popularity. The sonic effect produced by the fireworks mainly depends upon the chemical composition of the mixtures and the particle size. Specifically this means that the larger the particle size, the more the quantity of powder mixture is to be used. Therefore, a high quality product which can produce the expected noise level with lesser quantity of chemicals is a major challenge faced by the pyrotechnic industry. This can be achieved by adopting either of the two approaches namely, one, by changing the chemical composition or, the other, by changing the particle size. At present the particle size of the chemical composition is at the micron level. However, by converting the composition into nano size, the volume of mixture used will be greatly reduced without compromising the sound level produced. The major advantage of using nano size powders is that it is essentially environmental friendly, producing less pollution and ensuring a cleaner environment. Concurrently, the major risk in using nano size powders is that it is a fire hazard. In this paper, the pros and cons of using nano powders in the manufacture of fireworks have been analyzed, collecting data from various research works and presenting the same as a review article.

- **Keywords:** Fireworks; Flash powder; Nano; Micron; Hazard; Explosivity; MIE

S. Thiyagarajan, S.P. Sivapirakasam, Jose Mathew, M. Surianarayanan, K. Sundareswaran. *Influence of workpiece materials on aerosol emission from die sinking electrical discharge machining process*.

Simultaneous investigation of environmental emissions and machining aspects of electrical discharge machining process is essential for achieving hygienic and efficient machining. The main objective of the present work is to experimentally investigate and analyze the aerosol emission rate and the material removal rate from a die sinking electrical discharge machining process for three commonly used work piece materials

viz., tool steel, mild steel and aluminum using Taguchi methodology of Experimental Design in order to suggest suitable process conditions for green manufacturing. The aerosol emission profile of all workpiece materials was found to be closely related to the material removal profile. A significant variation in emission and material removal rate was observed for workpiece materials which may be accorded to the variation in melting and vaporization temperatures. It was also observed that majority of aerosol constituents evolved from workpiece materials and that the constituents with low melting points were having high relative concentration in the aerosol emitted. The study introduced a parameter, the relative emission rate for comparing the emission for various process parameters and workpiece–tool material combinations. The favorable machining parameters for each material were then identified by employing signal to noise ratio analysis of the relative emission rate.

- **Keywords:** Electrical discharge machining (EDM); Emission; Aerosol; Taguchi methodology; Relative emission rate

J.M. Ingram, A.F. Averill, P.N. Battersby, P.G. Holborn, P.F. Nolan. *Electrostatic ignition of sensitive flammable mixtures : is charge generation due to bubble bursting in aqueous solutions a credible hazard?*

Experiments have been conducted to gain insight into the credibility of sparging aqueous solutions as an electrostatic ignition hazard for sensitive hydrogen/air or fuel/oxygen mixtures (Minimum Ignition Energies of ~0.017 mJ and ~0.002 mJ, respectively, compared to ~0.25 mJ for hydrocarbon/air mixtures). Tests performed in a 0.5 m3 ullage produced electric field strengths between 125 and 560 V m−1 for air flows of 5–60 l min−1, respectively, comprised of 2–4 mm diameter bubbles. Field strength can be related to the space charge and fitting to an exponential accumulation curve enabled the charge generation rate from the air flows to be estimated. This was observed to be directly proportional to the air flow and its magnitude was consistent with literature data for bubble bursts. The charge accumulation observed at laboratory scale would not be a cause for concern. On the basis of a simple model, the charge accumulation in a 27 m3 ullage was predicted for a range of air flows. It is apparent from such calculations that ignition of hydrocarbon/air mixtures would not be expected. However, it would seem possible that field strengths might be sufficient to cause a risk of incendive spark or corona discharges in moderately sized vessels with sensitive flammable mixtures.

- **Keywords:** Bubbles; Aerosol; Space charge; Electrostatic; Ignition; Hydrogen

M. Sam Mannan, Simon P. Waldram. *Learning lessons from incidents : a paradigm shift is overdue*.

Drawing on historical data we show that the international community of process engineers has not been good at learning lessons from their past accidents. We call for a paradigm change in the way we approach this and the creation of a single new, multi-national, multilingual accident database that is free at the point of use and that includes immediate and underlying causes as well as "lessons learned". It must be user-friendly and provide links to key source documents. The purpose of this paper is to challenge those in authority, and with the power to do so, to make this happen. We give some preliminary views on what may be required. In countries that so choose this could include an element of compulsion to consult the database in specific circumstances and a sign-off procedure to verify that this has been done.

- **Keywords:** Accidents; Causes; Incidents; Lessons learned; Database; Multi-lingual; Free access

A. Azadeh, V. Salehi. *Modeling and optimizing efficiency gap between managers and operators in integrated resilient systems : the case of a petrochemical plant*.

The reliability issue in complex industrial systems such as oil, gas, petrochemical companies, nuclear and aviation industries has been of great importance. Resilience engineering (RE) is a new attitude toward the improvement of safety and reliability in the stated systems. One of the challenges a resilient system might face is the gap between work as imagined by managers and work as actually done by operators. This study will introduce a new framework named integrated resilience engineering (IRE) as a result of developing the concept of RE. The data used in this research have been obtained by means of questionnaire from a petrochemical company. Thereafter, the efficiency of operators and managers are calculated in RE and IRE frameworks through data envelopment analysis (DEA) approach. Then, the gaps between managers and operators are analyzed in two frameworks. The results are indicative of a significant growth in the number of efficient operators and managers in IRE framework compared to RE framework. Besides, the efficiency mean of managers and operators in IRE framework has experienced the growth of 1.8% and 5% compared to RE framework, respectively. The efficiency gap between managers and operators in IRE framework has also enjoyed the improvement of 88% compared to RE framework. Generally, it can be said that the suggested items of this research has led to the betterment of managers and operators' efficiency and of the efficiency gap between them. Therefore, these items can improve the resilience and safety of complex systems. The results of Spearman test show that there is a strong direct correlation between the DEA results in two frameworks. This is the first study that examines the efficiency gap between operators and managers based on the RE principles and by means of DEA approach.

- **Keywords:** Integrated resilience engineering (IRE); Petrochemical plants; Data envelopment analysis (DEA); Efficiency gap; Managers; Operators

G. Reniers, T. Brijs. *Major accident management in the process industry : an expert tool called CESMA for intelligent allocation of prevention investments*.

A tool (called CESMA) was developed to carry out cost–benefit analyses and cost-effectiveness analyses of prevention investments for avoiding major accidents. A wide variety of parameters necessary to calculate both the costs of the considered preventive measures and the benefits related with the avoidance of accidents were identified in the research. The benefits are determined by estimating the difference in (hypothetical) major accident costs without and with the implementation of a preventive measure. As many relevant costs and benefits as possible were included into the tool, based on literature and expert opinion, in order to be able to deliver an all-embracing cost–benefit analysis and cost-effectiveness analysis to assist in the investment decision process. Because major accidents are related to extremely low frequencies, the tool takes the uncertainty of the unwanted occurrence of a major accident into account through the usage of a so-called 'disproportion factor'. Compared with existing software, the CESMA tool is innovative by striving for an as-accurate-as-possible picture of costs and benefits of major accident prevention, and taking the uncertainties accompanying disastrous events into consideration. Furthermore, an illustrative example of CESMA is presented in the paper.

- **Keywords:** Cost–benefit analysis; Cost-effectiveness analysis; Major accidents; Disproportion factor; Expert tool; Process industries

Ramin Barati, Saeed Setayeshi. *On the operator action analysis to reduce operational risk in research reactors*.

Human errors during operation and the resulting increase in operational risk are major concerns for nuclear reactors, just as they are for all industries. Additionally, human reliability analysis together with probabilistic risk analysis is a key element in reducing operational risk. The purpose of this paper is to analyze human reliability using appropriate methods for the probabilistic representation and calculation of human error to be used alongside probabilistic risk analysis in order to reduce the operational risk of the reactor operation. We present a technique for human error rate prediction and standardized plant analysis risk. Human reliability methods have been utilized to quantify different categories of human errors, which have been applied extensively to nuclear power plants. The Tehran research reactor is selected here as a case study, and after consultation with reactor operators and engineers human errors have been identified and adequate performance shaping factors assigned in order to calculate accurate probabilities of human failure.

- **Keywords:** Operational risk; Human reliability analysis; SPAR-H method; Tehran research reactor; Probabilistic risk assessment

Ke-Wu Pi, Qu Xiao, Hui-Qin Zhang, Min Xia, Andrea R. Gerson. *Decolorization of synthetic Methyl Orange wastewater by electrocoagulation with periodic reversal of electrodes and optimization by RSM*.

Treatment of Methyl Orange (MO), an azo dye, synthetic wastewater by electrocoagulation with periodic reversal of the electrodes (PREC) was examined. Response Surface Methodology (RSM) was used to optimize the influence of experimental conditions for color removal (CR), energy consumption (ENC), electrode consumption (ELC) and sludge production (SP) per kg MO removed (kg(MOr)) with optimal conditions being found to be pH 7.4, solution conductivity (κ) 9.4 mS cm−1, cell voltage (U) 4.4 V, current density (j) 185 mA cm−2, electrocoagulation time (T) 14 min, cycle of periodic reversal of electrodes (t) 15 s, inter-electrode distance (d) 3.5 cm and initial MO concentration of 125 mg L−1. Under these conditions, 97 ± 2% color was removed and ENC, ELC and SP were 44 ± 3 kWh kg(MOr)−1, 4.1 ± 0.2 kg(Al) kg(MOr)−1 and 17.2 ± 0.9 kg(sludge) kg(MOr)−1, respectively. With the enhanced electrochemical efficiency resulting from the periodic electrode reversal, the coefficients of increased resistance and decreased current density between the two electrodes in the PREC setup were 2.48 × 10−4 Ω cm−2 min−1 and 0.29 mA cm−2 min−1, respectively, as compared to 7.72 × 10−4 Ω cm−2 min−1 and 0.79 mA cm−2 min−1 as measured for the traditional electrocoagulation process. The rate constant of decolorization was also enhanced by 20.4% from 0.152 min−1 in the traditional electrocoagulation process to 0.183 min−1 in the PREC process. These performance characteristics indicate that the PREC approach may be more promising in terms of practical application, as a cost-effective treatment, than conventional electrocoagulation for textile dye removals.

- **Keywords:** Electrocoagulation; Periodic reversal of electrodes; Response Surface Methodology; Decolorization; Methyl Orange wastewater; Electrolysis efficiency

Li Shi, Weiqiu Huang. *Sensitivity analysis and optimization for gasoline vapor condensation recovery*.

Volatile organic compounds (VOCs) are easily evaporated and discharged from everywhere into the atmosphere, especially in various operations of gasoline. The emission of VOCs is always a significant environmental problem, and the control of VOCs

pollution has been a hot topic in the field of air purification. In this paper, the condensation separation method for gasoline vapor recovery was investigated and four gasoline vapors of S1–S4 were selected for the sensitivity analysis and optimization of the condensation process, using the Model Analysis Tools from Aspen Plus. Generally, to control VOCs pollution efficiently, both the vapor recovery efficiency and the outlet vapor concentration of the condensation recovery system should be simultaneously considered. Then an optimized three-stage condensation process was proposed, whose condensation temperatures were optimized and designed at 1 °C, −40 °C and −110 °C, respectively. Further, based on the comprehensive consideration of both meeting the more strict VOCs emission standard and ensuring the condensation recovery system work stably and economically, it was recommended that the maximum total vapor recovery efficiencies for S1–S4 should be 99.73%, 99.79%, 99.82% and 99.19%, and the minimum outlet vapor concentrations be 2.87 g/m3, 2.75 g/m3, 3.04 g/m3 and 16.98 g/m3, respectively. Accordingly, the condensation temperature of the copious cooling stage should be set at −130 °C. Moreover, the total cooling duties for the single-stage and three-stage condensation processes were investigated and compared when the condensation temperature of the recovery system ranged from 20 °C to −110 °C. The total cooling duties of the three-stage condensation process for S1–S4 would be saved by 12.23%, 15.68%, 13.96% and 15.65%, respectively. Finally, a three-stage condensation system was developed for the industrial gasoline vapor recovery, which has performed well since its installation.

- **Keywords:** Gasoline vapor; Condensation; Vapor recovery efficiency; Outlet vapor concentration; Cooling duty

Abbas Jorsaraei, Mahdi Gougol, Jules B. Van Lier. *A cost effective method for decentralized sewage treatment*.

The aim of this research was to upgrade the performance of a conventional septic tank (CST) for on-site treatment of sewage with negligible costs. Although CST is known as an inexpensive pre-treatment system, a complementary treatment is required to reuse its output effluent. In this work, the quality of treated wastewater reached to the standard level for irrigation by the innovational changes made in the structure of CST for converting it into an advanced septic reactor (ASR). The modification consists adding some pipe and trays without using any mechanical or electrical equipment. ASR was operated at ambient temperatures in laboratory and pilot-scale. The effects of up-flow velocities (Vup) of 0.4, 0.5, 0.7, 1 and 1.5 m/h and hydraulic retention times (HRT) of 36, 24 and 12 h on the ASR treatment performance were studied. For optimum Vup of 1 m/h and HRT of 24 h and biomass specific methanogenic activity (SMA) of 0.31 mg COD/g VSS d the maximum removal of chemical oxygen demand (COD), biochemical oxygen demand (BOD5) and total suspended solids (TSS) were 86.2%, 79.4% and 95%, respectively. The results showed that ASR is an appropriate alternative for CST for sewage on-site treatment by a low cost modification.

- **Keywords:** Decentralized treatment; Anaerobic treatment; Advanced septic reactor; Wastewater treatment; Economy and reuse

Weiliang Han, Peng Zhang, Zhicheng Tang, Gongxuan Lu. *Low temperature CO oxidation over Pd–Ce catalysts supported on ZSM-5 zeolites*.

A series of Pd–Ce supported ZSM-5 zeolite catalysts for CO oxidation at low temperature were prepared by co-impregnation method. The effect of Pd–Ce synergistic function, Ce loadings, and properties of ZSM-5 zeolite on low temperature CO catalytic oxidation was investigated in detailed. The results showed that the Pd and Ce loading on ZSM-5 zeolite support at the same time enhanced catalytic activity compared with only Pd or Ce loading

on ZSM-5 zeolite support. The properties of ZSM-5 zeolite had a strong influence for CO oxidation. Through the research, the ZSM-5 zeolite with high silicon aluminum ratio and small size also was helpful for CO oxidation. Among these catalysts, the catalyst with 19 wt% Ce loading displayed the highest catalytic activity. Chemical and physical properties of catalysts were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). XRD and TEM showed that Pd species were highly dispersed on the surface of ZSM-5 zeolite, which was strongly dependent on the amounts of Ce loading and the interaction among Pd species, Ce promoter and ZSM-5 support. The addition of CeO2 improved the dispersion of Pd species over ZSM-5, and synergistic function of Pd and CeO2 enhanced the catalytic activity. XPS characterization indicated that as the addition of Ce increased, Pd species was easy to enrich on the surface of the catalyst.

- **Keywords:** Low temperature catalyst; ZSM-5; CO oxidation; Noble metal catalyst; Synergistic function

Yasir A. Elsheikh. *Optimization of novel pyrazolium ionic liquid catalysts for transesterification of bitter apple oil*.

In the present study, 4 different functionalized pyrazoliums based on sulfoalkyl-pyrazolium hydrogensulfate and alkylsulfo-alakylpyrazolium hydrogensulfate were explored to catalyze biodiesel production from bitter apple oil (BAO). The results demonstrated that a longer chains catalyst of 2-(4-sulfobutyl) pyrazolium hydrogensulfate (SBPHSO4) exhibited the highest catalytic activity, which is attributed to its strong acidity. The highest yield of esters was up to 89.5% when the reaction was carried out under the conditions of 5.2 wt% of SBPHSO4, molar ratio of methanol to BAO of 15:1, 170 °C, and 800 rpm for 6 h. These results demonstrated that ionic liquids offer a promising new type of pyrazolium catalyst for biodiesel production. The use of clean ionic liquids in preparing clean biodiesel could solve the drawbacks associated with using the old conventional catalysts and might be employed as an efficient catalyst for such relevance.

- **Keywords:** Bitter apple oil; Pyrazolium ionic liquid; Transesterification; Biodiesel

Gopal Chandra Sahu, Santanu Bandyopadhyay, Dominic C.Y. Foo, Denny K.S. Ng, Raymond R. Tan. *Targeting for optimal grid-wide deployment of carbon capture and storage (CCS) techno*logy.

Carbon capture and storage (CCS) techniques are considered as one of the promising approaches to reduce carbon dioxide (CO2) emissions from fossil fuel based power generation, which still accounts for a significant portion of greenhouse gas emissions in the world. CCS technology can be used to mitigate greenhouse gas emissions, with the additional advantage that it allows continuing use reliable and inexpensive fossil fuels. However, CCS retrofit entails major capital costs as well as a reduction of overall thermal efficiency and power output. Thus, it is essential for planning purposes to implement the minimal extent of CCS retrofit while meeting the specified carbon emission limits for the power sector. At the same time, it is necessary to plan for compensatory power generation capacity to offset energy losses resulting from CCS retrofit. In this paper, an algebraic targeting technique is presented for planning of grid-wide CCS retrofits in the power generation sector with compensatory power. The targeting technique is developed based on pinch analysis. In addition, the proposed methodologies are illustrated through case studies based on grid data in India and the Philippines. Sensitivity analysis is carried out to determine the suitable CCS technology and compensatory power source which satisfy emission limits.

- **Keywords:** Carbon capture and storage (CCS); Energy planning; Pinch analysis; Process integration; Targeting; Greenhouse gas emissions

Shaun Rimos, Andrew F.A. Hoadley, David J. Brennan. *Environmental consequence analysis for resource de*pletion.

Resource depletion is of concern to both present and future generations in terms of access to resources. It is a prominent impact category within life cycle assessment (LCA) and sustainability assessment. This paper examines existing resource depletion approaches and indicators in the context of natural gas depletion, and their limitations in modelling the wider environmental consequences of resource consumption. Some existing models assume substitution of scarce fossil fuels with an alternative fossil fuel or mix, but do not consider all of the subsequent change in impacts. An additional methodology is proposed to measure the impact changes when fossil fuel substitution occurs as a result of scarcity. The methodology will demonstrate the effect of resource scarcity for individual processes but also multiple processes which operate at different levels of resource consumption with varying degrees of impacts. The methodology is applied to a scarcity situation of natural gas in Australia, where black coal is substituted for gas. It is first applied to natural gas consumed for electricity generation only. In the second case, the methodology is applied to the substitution of natural gas for both electricity generation and hydrogen production. The varying impacts on emissions to air and water, together with solid waste generation and water depletion, as a result of the substitution are used to reflect the consequences of fossil fuel depletion. The indicators also provide information on the impacts of substitution in each product, thus enabling users to prioritise products based on the impacts produced during natural gas allocation.

- **Keywords:** Resource depletion; LCA; Sustainability; Natural gas; Environmental impacts

Orlando Jorquera, Ricardo Kalid, Asher Kiperstok, Elias Braga, Emerson Andrade Sales. *Effluent stream treatment in a nitrogenous fertilizer factory : an exergy analysis for process inte*gration.

The industrial processes used for the production of nitrogenous fertilizers are the main generators of reactive nitrogen compounds, chemicals and effluents that ultimately impact the biosphere. Exergy analysis has been performed to a nitrogen fertilizer factory in the State of Bahia, Brazil, where the Anaerobic Ammonium Oxidation (Anammox) and other physical–chemical processes are used to partially or totally handle the feed streams normally sent to a stripping tower. The results showed that the combined use of physical–chemical and biological process can improve the overall exergetic efficiency and avoid the emission of reactive compounds to the atmosphere allowing the recovery of the condensate lost as effluent, so that it can be reincorporated in the production of steam network, increasing energy efficiency and environmental performance of the process.

- **Keywords:** Nitrogen; Ammonia; Fertilizer plant; Exergy analysis

Maryam Hosseini, Ali Baradar Khoshfetrat, Eghbal Sahraei, Sirous Ebrahimi. *Continuous nitrifying granular sludge bioreactor : influence of aeration and ammonium loading rate*.

Granulation of nitrifying bacteria was investigated in a continuous bubble column bioreactor. Then, the combined effect of aeration and ammonium loading rates on dissolved oxygen (DO) concentration as well as nitrification process was evaluated in the system using an experimental design technique. After 120 days, stable nitrifying granules with average diameter of 1.4 mm and settling velocities of 55 m/h were obtained. The influence of increasing ammonium loading rate (ALR) was found to be more significant than decreasing aeration rate on the reduction of DO concentration inside the nitrifying bioreactor. The system could handle the ALR values of 0.48–1.92 gNH4+-N/L d with the ammonium removal efficiency from 65% to

nearly 100% at the tested airflow rates of 2.5 and 4.5 L/min. At the low aeration, the complete ammonium conversion to nitrate was replaced with nitrite when the ALR increased to 1.44 gNH4+-N/L d. At the high aeration, however, almost complete nitrification was achieved except the high ALR in which the nitrite accumulation was observed up to 38%. The study demonstrated that the continuous bioreactor had a considerable performance for obtaining stable nitrifying granules to have nitrite accumulation under control with changing the ratio of aeration rate and ALR.

- **Keywords:** Nitrifying granules; Nitrite accumulation; Ammonium loading rate; Aeration rate; Continuous bubble column bioreactor

Daisuke Tashima, Yuuki Urakawa, Yutaka Suenaga, John D.W. Madden. *Optimization of mixture ratio of electrolyte for reducing activation resistance of proton exchange membrane fuel* cell.

The purpose of this study is to find an optimal mixture ratio of the platinum-loaded carbon catalyst and the electrolyte in a membrane electrode assembly (MEA) of a proton exchange membrane fuel cell for reducing the activation resistance, which influences the electrochemical surface area, activation polarization, and maximum power density of the MEA. First, mixture ratios of 10, 20, 40, and 60 wt% platinum-loaded carbon catalysts and electrolyte were examined. The results indicated that the fuel cell performance improved for mixing weight ratios of 1.0:2.0 in 10 wt% Pt/C, 1.0:1.8 in 20 wt% Pt/C, 1.0:1.1 in 40 wt% Pt/C, and 1.0:0.5 in 60 wt% Pt/C. Next, we evaluated the activation resistances of the MEA from the AC impedance characteristics using the optimal mixing weight ratio of the platinum-loaded carbon catalyst and the electrolyte. It was found that the activation resistances of the anode and cathode decrease with an increase in the weight ratio of platinum-loaded carbon in the catalyst layer.

- **Keywords:** Proton exchange membrane fuel cell; Membrane electrode assembly; Platinum-loaded carbon; Catalyst; Activation resistance; Cole-Cole plot

Lipika Das, Uttam Maity, Jayanta Kumar Basu. *The photocatalytic degradation of carbamazepine and prediction by artificial neural networks*.

The three layer artificial neural network model was applied to predict the degradation efficiency for carbamazepine in photocatalytic oxidation under UV radiation. Titania–zirconia was employed as a catalyst for the photooxidation. The catalyst was prepared using titanium isopropoxide and zirconium oxychloride by sol–gel method and characterized by transmission electron microscopy and BET analysis. Different process parameters such as, initial concentration of carbamazepine, pH of the solution, catalyst concentration and time of UV irradiation were employed as the input to the artificial neural network model and the output of the network was degradation efficiency of carbamazepine. The multilayer feed-forward networks with the Levenberg–Marquardt (trainlm) backpropagation training algorithm was used for the network training. The smallest mean square error was obtained for three-layer network with 'logsig' transfer function and five neurons in the hidden layer gave optimal results. A comparison between the predicted values and selective experimental data of degradation efficiency showed a high correlation coefficient (R2) of 0.997.

- **Keywords:** Titaina–zirconia nanocomposite; Photocatalysis; Carbamazepine; Artificial neural network; Sol-gel method; Oxidation

Jun Ren, Chuanjin Xie, Jian-Ying Lin, Zhong Li. Co-utilization of two coal mine residues : non-catalytic deoxygenation of coal mine methane over coal gangue.

The deoxygenation of coal mine methane (CMM) is a necessary process for concentrating methane by pressure-swing adsorption technology. Removal of oxygen in CMM by the reaction between oxygen and carbon in coal gangue is a novel solution for simultaneously utilizing two kinds of byproducts of coal mine, CMM and coal gangue. Process conditions for the deoxygenation of CMM were investigated systematically by using a fixed-bed reactor. The results show that higher temperature and lower gas flow rate not only decreased the residual oxygen concentration in the outlet gas but also increased the methane loss, and that the particle size of gangue did not influence deoxygenation within the experimental conditions used. Under optimal conditions (650 °C and 250 mL/min), there was no residual oxygen in the outlet gas and the methane concentration decreased by less than 0.5 mol%. XRD results show that coal gangue was activated during deoxygenation, and that activated gangue was suitable for utilization as a main component in cementitious materials.

- **Keywords:** Coal gangue; Coal mine methane (CMM); Deoxygenation; Compressed natural gas (CNG); Cementitious material

C.M. Sheridan, D. Glasser, D. Hildebrandt. *Estimating rate constants of contaminant removal in constructed wetlands treating winery effluent : a comparison of three different methods*.

In this paper we investigated the use of three different methods for determining the rate constants for degradation of winery effluent within a sub-surface flow constructed wetland (CW). These methods comprised of using a dispersed plug flow (the Peclet) equation; a tanks-in-series (TIS) equation; and analysing the residence time distribution (RTD) directly. The last of these is described by the convolution integral (CI). We demonstrated self-similarity of the RTDs, which meant that the system's hydraulics were similar throughout the CW. We therefore extrapolated the RTD data to develop a more complete understanding of the hydraulic properties of the CW and examine how they affected the kinetics of degradation. We found that whilst both the Peclet and the TIS equation were able to predict concentration within the CW, this required the optimisation of more than one variable at the same time rendering a result that was more of a modelling exercise than a useful design tool. The CI method could be applied to predict system parameters effectively. We used it to measure rate constants of removal for both ethanol and potassium (key species for tracking the degradation/treatment of the effluent). Acetic acid, however, did not degrade implying that the CW operated aerobically. The concentration of sodium increased very slightly, indicating that it is not bioremediated/removed and that there are some minor evapotranspirative effects. The rate constant found for the biodegradation of COD was found to have significantly more uncertainty associated with it than the measurement of the rate of degradation individual components and we therefore posit that it is better to describe the processes of degradation by tracking individual components rather than lumped parameters.

- **Keywords:** Modelling rate constants; Constructed wetlands; Convolution integral; Peclet Equation; Tanks-in-series; Wetland hydraulics

Denny K.S. Ng, Irene M.L. Chew, Raymond R. Tan, Dominic C.Y. Foo, Mike B.L. Ooi, Mahmoud M. El-Halwagi. *RCNet : an optimisation software for the synthesis of resource conservation networks*.

RCNet is a spreadsheet-based software for the synthesis of resource conversation networks (RCNs) for planning the efficient use of material resources (e.g., water, utility

gases, solvents) in industrial plants. The software is developed based on the well-established process integration tools, namely pinch analysis and mathematical programming techniques. In the first stage, pinch analysis is used to determine maximum resource conservation targets prior to detailed RCN design. In the second stage, mathematical optimisation is then used to determine the optimal flowrate allocation between process sources and sinks of the RCN, to achieve the performance targets. RCNet is applicable for various industrial applications. To date, no generic software has been developed to handle water minimisation, hydrogen recovery and property integration, which is the main subject of this work. In the developed software, same interface and platform can be used to solve abovementioned problems independently. For illustration, three literature examples on water minimisation, hydrogen recovery and property integration, as well as an industrial case study are solved using RCNet.

- **Keywords:** Targeting; Design; Waste minimisation; Process integration; Pinch analysis; Mathematical optimisation

Maryam Tamaddoni, Rahmat Sotudeh-Gharebagh, Shunji Nario, Mehdi Hajihosseinzadeh, Navid Mostoufi. *Experimental study of the VOC emitted from crude oil tank*ers.

Light hydrocarbons vaporize to the space between crude oil interface and roof of the storage tank during loading of crude oil tankers in marine oil terminals. When crude oil is loaded to the tank, these hydrocarbons are vented into the atmosphere which is considered as a main source of emission of volatile organic compounds (VOCs) in oil terminals. VOCs emitted from the crude oil not only create severe air pollution problems but also a considerable amount of valuable hydrocarbons are wasted to the atmosphere. On the other hand, VOCs are flammable which create major safety hazards to the loading process. Therefore, the oil industry has largely focused on control of VOCs. In this research, an experimental study was conducted to characterize VOCs emitted from storage tanks of crude oil in a large-scale oil export terminal. Using the industrial data and simple mathematical tools, effect of different parameters on the composition of emitted gases was investigated. Furthermore, an experimental procedure is proposed to assess the potential of a crude oil absorption process for recovering emitted gases. Experimental results showed that the crude oil absorption process can be adapted to the situation of considered marine terminal for recovering this vent stream of emitted gases. This work can help plant engineers to decide on an appropriate strategy to control VOCs.

- **Keywords:** Volatile organic compounds; Oil terminal; Crude oil; Oil tanker

R. Bahrami, H. Ale Ebrahim, R. Halladj. *Application of random pore model for SO2 removal reaction by CuO*.

In this work, mathematical modeling of SO2 removal reaction with CuO was accomplished by the random pore model. The partial differential equations, describing the reaction of a gaseous reactant with a single pellet and also a packed bed of solid reactant, were solved by the finite element method. The results of modeling consist of CuO conversion-time profiles at different temperatures and SO2 concentrations, and also break through curves which were compared with the literature experimental data in a good accuracy. The rate constants were estimated from the initial slope of the conversion-time curves, and the product layer diffusivities were evaluated from the whole conversion-time profiles.

- **Keywords:** SO2 removal; CuO; Random pore model; Mathematical modeling; Conversion profiles; Break through curves

Zohreh Fattah, Mehran Rezaei, Abolfazl Biabani-Ravandi, Abdullah Irankhah. *Preparation of Co–MgO mixed oxide nanocatalysts for low temperature CO oxidation : optimization of preparation conditions*.

In this study, a series of Co–MgO mixed oxides (30 wt.% Co) were prepared by co-precipitation method and employed as catalyst in low temperature CO oxidation reaction. The preparation conditions were optimized by the Taguchi method of experimental design to synthesize a sample with high catalytic performance toward CO oxidation reaction. The effects of four variables, pH of solution, aging temperature, aging time and molarity of precursor solution at three levels were investigated. The optimized sample was characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption of oxygen (O2-TPD), N2 adsorption/desorption, thermal gravimetric and differential thermal analysis (TGA/DTA), and transmission electron microscopy (TEM) techniques. The results revealed that the optimized sample showed a mesoporous structure with a narrow pore size distribution centered in the range of 7–17 nm and particle size about 5.5 nm. It was found that the molarity of solution and aging time had the most influence on the CO conversion, respectively. The catalytic results showed that the highest CO conversion obtained from samples synthesized by Taguchi orthogonal array was about 90% at 200 °C, while the CO conversion for optimized sample was 95%. In addition, the effect of operational conditions was studied over optimized sample.

- **Keywords:** Magnesium; Cobalt; Nanoparticles; Experimental design; CO oxidation

Debasree Banerjee, Ujjaini Sarkar, Sayantani Chakraborty, Debasri Roy. *Removal of a cationic bisbiguanide using Functionalized Activated Carbons (FACs)*.

Functionalized Granular Activated Carbons (FACs) are used as adsorbents for treating pharmaceutical wastewaters containing Chlorhexidine Gluconate. Chemical modifications of Granular Activated Carbons (GACs) using functionalizing agents like HCl and HF produce FACs. The adsorption capacity of each of FAC-HCl and FAC-HF is found to be higher than GAC. The modelled maximum adsorption capacity for FAC-HCl is 1.02 g/g of adsorbent, 3.49 g/g of adsorbent for FAC-HF and 0.0682 g/g of adsorbent for GAC. This is mainly due to the additional chemisorptions by surface complexation at the functionalized surface sites of the modified GACs. This is also supported by the well-known pseudo-second-order kinetic model. Formation of surface complexes with the functional groups and weakly polar Chlorhexidine Gluconate is well supported by the physical characterization using Energy dispersive X-ray spectroscopy (EDAX), Brunner–Emmett–Teller (BET) test and Fourier Transform Infrared spectroscopy (FTIR) analysis after adsorption. The adsorption capacity of GAC and the FACs increases in the order of FAC-HF > FAC-HCl > GAC conforming to the proportion of the total acidity of the carbon surfaces. Intra-particle diffusion is not the sole rate-controlling factor. An agreement to pseudo-second-order kinetic model, Elovich kinetic model and Boyd's film diffusion model proves that chemisorption is the rate-controlling parameter in this adsorption study.

- **Keywords:** Pharmaceutical wastewater; Chlorhexidine Gluconate; Adsorption; Functionalized Activated Carbon; Batch equilibrium analysis; Kinetics

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