

# Process Safety and Environmental Protection

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**Jianfeng Song, Xuhong Niu, Xue-Mei Li, Tao He. *Selective separation of copper and nickel by membrane extraction using hydrophilic nanoporous ion-exchange barrier membranes. Pages 1-9.***

Hydrophilic nanoporous ion exchange barrier membrane, based on polyethersulfone (PES)/sulfonated polyphenylether sulfone ketone (SPPEK), was utilized for the pH dependent separation of copper and nickel ions with a commercial extractant, LIX84-I. The extraction and stripping performance of the membrane was demonstrated in a single stage membrane contactor as well as in an integrated extraction/stripping system. By adjusting the feed pH to 2.9, a complete separation of copper and nickel was achieved using the membrane contactors, where a copper flux of  $1.10 \times 10^{-8} \text{ mol/cm}^2\text{s}$  was observed. In an extraction/stripping integrated sandwiched membrane extraction contactor, significantly higher copper flux was observed due to the coupling of copper stripping. In addition, the PES/SPPEK barrier membrane prevented the loss of the organic extractant, exhibiting high stability in 30 days dynamic test. The results indicated that the membrane extraction contactor system is of great potential for selective extraction of metal ions.

- **Keywords:** Membrane extraction; Nanoporous membrane; Ion exchange membrane; Copper; Nickel; LIX84-I

**Seong-Nam Nam, Hyekyung Cho, Jonghun Han, Namguk Her, Jaekyung Yoon. *Photocatalytic degradation of acesulfame K: Optimization using the Box-Behnken design (BBD). Pages 10-21.***

In this research, photocatalytic degradation of acesulfame K, one of the most popular artificial sweeteners, has been carried out under variations of the initial concentration, pH, concentration of persulfate, and amount of natural organic matter (NOM). The removal efficiencies for 30-min, 60-min and 180-min reaction time have been applied to response surface methodology using the experimental responses obtained by a four-factor-three-level Box-Behnken design (BBD). This provided 29 experimental data for the initial concentration of acesulfame K ranging from 300 to 900  $\mu\text{g/L}$ , pH of solution ranging from 4 to 10, persulfate concentration ranging from 0 to 10  $\text{mg/L}$ , and amount of natural organic matter (NOM) ranging from 0 to 5  $\text{mg/L}$ , which were consecutively coded as A, B, C, and D at three levels (-1, 0, and 1). The analysis of variance (ANOVA) tests with 95% confidence limits determined the significance of independent variables and their interactions consisting of the polynomial regression equation. The optimum values of the selected variables were determined by numerical optimization, and the experimental

conditions were found to reach complete mineralization for 30min and thereafter, at initial concentration of 887.2 $\mu$ g/L; pH of 4; persulfate concentration of 9mg/L, and NOM concentration of 5mg/L.

- **Keywords:** Acesulfame K; Box–Behnken design (BBD); Optimization; Photocatalysis; Persulfate; Response surface methodology (RSM)

**Jinxing Lan, Juncheng Jiang, Yong Pan, Zhan Dou, Qingsheng Wang. *Experimental measurements and numerical calculation of auto-ignition temperatures for binary miscible liquid mixtures. Pages 22-29.***

Auto-ignition temperature (AIT) is one of the most important parameters to assess potential fire and explosion hazards for chemicals. In this work, the AITs of 132 groups of binary miscible liquid mixtures were measured. Experimental results show the AITs of binary miscible liquid mixtures vary with their volume ratios. Three types of trends representing the relationship between AITs and volume ratios were found. A computational model was established to calculate the AITs of methanol+toluene, ethyl alcohol+toluene, ethyl alcohol+methanol and n-heptane+ethyl alcohol in 6 volume ratios. The calculation results showed that the calculated deviations were within 8% of the experimental results. For higher hydrocarbons, the model suffers from a lack of accurate chemical kinetic data to properly predict the AITs of the mixtures.

- **Keywords:** Binary miscible mixture; Liquid mixture; Auto-ignition temperature; Experimental measurement; Numerical calculation

**Farzan Sasangohar, S. Camille Peres, Jason P. Williams, Alec Smith, M. Sam Mannan. *Investigating written procedures in process safety: Qualitative data analysis of interviews from high risk facilities. Pages 30-39.***

Written procedures can play an integral role in mitigating risks and hazards in industries such as petrochemical, nuclear, and aviation. However, failure to adhere to procedures has resulted in major incidents. While there have been multiple studies investigating procedures in the aviation and nuclear industries, a comprehensive study of the high-risk industries' use of written procedures is largely absent. This paper documents one part of a large-scale project that addresses this gap by investigating the issues with procedure forms, usage, adoption, and challenges in a wide range of high-risk industries. A grounded theory approach in qualitative data analysis was used to examine 72 interviews with operators of varying roles and experiences across 6 countries and an offshore drilling vessel. Findings reaffirm previous research, suggesting an explanation for the lack of use of procedures due to the abundance of outdated procedures and procedures plagued by information overload. New findings suggest that frequency of the task and the experience level of the worker would impact workers' procedure use. Other unintended consequences associated with written procedural systems included reactive organizational behavior surrounding procedures and a general disconnect between the users and the writers of these documents.

- **Keywords:** Operating procedure; Petrochemical; Process industries; Interview analysis; Process safety management; Grounded theory

**Huawei Wang, Ya-nan Wang, Yingjie Sun, Xiangliang Pan, Daoyong Zhang, Yiu Fai Tsang. *Differences in Sb(V) and As(V) adsorption onto a poorly crystalline phyllosmanganate ( $\delta$ -MnO<sub>2</sub>): Adsorption kinetics, isotherms, and mechanisms. Pages 40-47.***

The environmental behavior of antimony (Sb) in soils is often considered to be similar to that of arsenic (As). Comparing the adsorption behavior of these two elements on soil minerals is important because both elements coexist in contamination areas. In this study, the differences in antimonate (Sb(V)) and arsenate (As(V)) adsorption reaction kinetics and isotherm characteristics on a poorly crystalline phyllo-manganate ( $\delta$ -MnO<sub>2</sub>) were studied. The potential mechanisms were identified using zeta potential, Fourier transform infrared spectrometry (FTIR), and X-ray photoelectron spectroscopy (XPS) analyses. The adsorption isotherm results indicated that the maximum adsorption capacity for As(V) was 1.5 times higher than that for Sb(V). The adsorption kinetics of Sb(V) and As(V) were well fitted using pseudo-first-order model, and the adsorption rate of Sb(V) and As(V) significantly depended on  $\delta$ -MnO<sub>2</sub> dosage and pH. At all tested pH values (3.0–9.0), the adsorption rate of As(V) was 4.0–7.7 times faster than that of Sb(V) at the same  $\delta$ -MnO<sub>2</sub> dosage and pH conditions. FTIR and XPS analysis confirmed that M (metal)-O was bonded with Sb(V) and As(V). The adsorption capacity and rate of As(V) were significantly higher than those of Sb(V), suggesting that  $\delta$ -MnO<sub>2</sub> had higher affinity toward As(V). The different adsorption behaviors of Sb(V) and As(V) onto  $\delta$ -MnO<sub>2</sub> should be considered in soils.

- **Keywords:** Adsorption kinetics; Antimonate; Arsenate; Poorly crystalline phyllo-manganate;  $\delta$ -MnO<sub>2</sub>; Environmental behavior

**Sergi Garcia-Segura, Joey D. Ocon, Meng Nan Chong. *Electrochemical oxidation remediation of real wastewater effluents – A review. Pages 48-67.***

Fate and health risks associated with persistent organic pollutants present in water effluents are one of the major environmental challenges of this century. In this paper, the electrochemical advanced oxidation process electrochemical oxidation is reviewed for its performance over the treatment of actual industrial and urban effluents. The electrochemical treatment of industrial effluents resulting from textile dyeing, petrochemical, paper mill, tannery industry as well as the treatment of domestic and urban wastewaters are discussed. Furthermore, the combination of electrochemical oxidation with other water treatment technologies as pre-treatment, post-treatment, and integrated treatment is also examined.

- **Keywords:** Wastewater treatment; Boron-doped diamond; Dimensionally stable anodes; Disinfection processes; Persistent organic pollutants; Anodic oxidation

**Sana Mallek-Ayadi, Neila Bahloul, Nabil Kechaou. *Chemical composition and bioactive compounds of Cucumis melo L. seeds: Potential source for new trends of plant oils. Pages 68-77.***

Studies were conducted on the chemical composition of melon (*Cucumis melo* L.) seeds, Maazoun variety. Melon seeds were found to contain (on a dry weight basis): moisture (7.16%), oil (30.65%), protein (27.41%), ash (4.83%), carbohydrate (29.96%), fibers (25.32%) and considerable amounts of antioxidant substances as phenolic compounds. The major mineral elements were: potassium, magnesium and calcium. The chemical composition of oil extracted from melon seeds was investigated. The main fatty acids of melon seed oil were linoleic acid and oleic acid. The chromatographic analysis of phenolic compounds showed that flavonoids were the most important group with predominance of amentoflavone (32.80 $\mu$ g/g). Besides, melon seed oil presented considerable amounts of phytosterols in which  $\beta$ -sitosterol was the major sterol accounting for 206.42mg/100g. The seed oil was also found to be rich in tocopherols with a predominance of  $\beta$ + $\gamma$ -tocopherol fraction. The obtained results revealed that melon seeds presented an alternative source of plant oil which may serve as raw material for food applications.

- **Keywords:** Melon (*Cucumis melo* L.) seeds; Seeds oil; Fatty acids; Bioactive components; Phenolic compounds;  $\beta$ -Sitosterol; Tocopherols

**Qing Zhao, Chengjun Liu, Baokuan Li, Ron Zevenhoven, Henrik Saxén, Maofa Jiang. *Recovery of chromium from residue of sulfuric acid leaching of chromite. Pages 78-87.***

The sulfuric acid leaching process is widely considered to be a cleaner technology to prepare chromium salt from natural chromite as no Cr(VI)-bearing wastes are generated or discharged. However, some insoluble anhydrous chromium sulfate could precipitate causing a serious chromium resource loss and potential pollution problems. For the purpose of recovery of chromium from leaching residue, a Box–Behnken design (BBD) based ammonium leaching treatment is investigated and optimized. A second-order polynomial regression model that reveals the functional relationship between processing parameters and recovery time is established and verified by the analysis of variance (ANOVA). Predicted results show a good agreement with the experimental data. The main and interactive effects of the processing parameters on the recovery time are illustrated by three-dimensional (3D) response surfaces. It was found that increasing temperature (from 70 to 90°C) and acidity (pH value from 0 to –0.5) of solution have positive effect on the leaching efficiency, and the plot of recovery time versus ammonium dosage shows a parabola-shape. On the basis of the findings in this study, an advanced sulfuric acid leaching process of chromite is proposed. Experimental results showed that hydrous and anhydrous chromium sulfate were completely recovered, and the average difference between the predicted and actual recovery times was less than 4%. All of the chromium resources can be utilized in the novel process, and no hazardous wastes or potential pollutants are discharged to the environment.

- **Keywords:** Anhydrous chromium sulfate; Chromium recovery; Box–Behnken design; Remediation; Cleaner production; Chromium slag

**Joyce T. Lopes, Artur Z. Francesconi, Sávio S.V. Vianna. *Modelling of source term from accidental release of pressurised CO<sub>2</sub>. Pages 88-96.***

Storage and transportation in carbon capture and sequestration (CCS) technology involve dealing with CO<sub>2</sub> at high pressures, which can lead to accidental releases. To assess and control risks and to calculate the minimum safe distance from tanks and pipelines to populated areas, the source term model of the leakage is extremely important, as it serves as input to model the dispersion of CO<sub>2</sub> into the atmosphere. The modelling of high pressurised CO<sub>2</sub> releases is relatively complex due to its thermofluidynamics particularities. Its triple point pressure is higher than the atmospheric pressure and it has a relatively high Joule–Thomson coefficient depending on the temperature and pressure conditions. Hence, it might lead to a two-phase flow and to solid formation when the depressurisation to atmospheric pressure occurs. Also, the molecular vibration of CO<sub>2</sub> might be important in some leakage scenarios. There are several approaches in the literature which address differently the aspects of the flow, specially regarding thermal and mechanical equilibrium or non-equilibrium. The present work provides an innovative approach for the discharge calculation in accidental high pressure releases. The Homogeneous Non-Equilibrium Model (HNM) is proposed, which accounts for non-equilibrium effects regarding not only metastability but also vibrational relaxation of the molecule. It considers the possible phase transitions and dry ice formation and it is applicable to steady-flow conditions. The model was tested with experimental data from CO<sub>2</sub>PIPETRANS project, HSE experiments and Cooltrans research programme. It was found that the model works well leading to results which agree with available experimental data. The proposed source model is relatively simple to implement and it does not demand numerical effort. The discussed discharge approach for CO<sub>2</sub> releases emerges as a good alternative to existing models.

- **Keywords:** CO<sub>2</sub>; Accidental releases; Source term; Multiphasic flow; Non-equilibrium; Vibrational relaxation; Metastability

**Leila Ekhlasi, Habibollah Younesi, Alimorad Rashidi, Nader Bahramifar. *Populus wood biomass-derived graphene for high CO<sub>2</sub> capture at atmospheric pressure and estimated cost of production. Pages 97-108.***

In the present study, populus wood biomass (PWB), as a precursor, was first carbonized under a nitrogen atmosphere and the obtained carbon was used to prepare graphene via chemical activation using KOH. The graphene samples were used to study as adsorbents for CO<sub>2</sub> capture. The effect of different parameters, such as various KOH/C weight ratios (2:1–4:1g/g), different heating temperatures (750–950°C) and heating time (30–90min), on the surface characteristics and CO<sub>2</sub> uptake capacity of the as-synthesized graphene was investigated. Various characterization techniques including elemental, TGA, BET, TEM, FT-IR and Raman were used. Under the experimental conditions of KOH/C impregnation ratio of 3:1, heating temperature of 850°C and heating time of 60min, the graphene sample showed a BET surface area of 1317.1m<sup>2</sup>/g, total pore volume of 0.604m<sup>3</sup>/g, up to 94% microporosity, and an average micropore diameter size of 1.84nm. The measured uptake capacity of 7.2mmol/g at a pressure of 1bar and 293K by sample G-3-850-60 was among the highest reported values in the literature data for carbon base materials. The isosteric heat of CO<sub>2</sub> adsorption onto the graphene samples were computed from the Clausius–Clapeyron equation, which was consistent with the physical nature of adsorption. Furthermore, these nano-adsorbents exhibited a high CO<sub>2</sub> adsorption capacity, thus proving to be good candidates for cost-effective CO<sub>2</sub> capture and storage for the downstream application on an industrial scale. In addition, the results of our laboratory investigations explore a process for scaling-up a complete flow diagram of graphene production from populus wood biomass and an economic evaluation of graphene production is estimated at a cost of about \$25per kg.

- **Keywords:** Populous wood; Graphene; CO<sub>2</sub> adsorption; KOH activation; Isosteric heat; Cost estimation

**L. Elsellami, F. Dappozze, N. Fessi, A. Houas, C. Guillard. *Highly photocatalytic activity of nanocrystalline TiO<sub>2</sub> (anatase, rutile) powders prepared from TiCl<sub>4</sub> by sol-gel method in aqueous solutions. Pages 109-121.***

In this piece of research, we have synthesized titanium dioxide (TiO<sub>2</sub>) powders from titanium tetrachloride (TiCl<sub>4</sub>) as an inorganic precursor by applying the sol-gel method. The effect of the calcination temperature in the range 400–800°C on the photocatalytic performance of TiO<sub>2</sub> nanoparticles was studied. The samples were characterized by TEM, BET surface area measurement, DRS and XRD. They were then used for the photodegradation of two model pollutants – phenol and formic acid – under exposure to UV-A radiation. Despite the fact that the adsorption of both phenol and formic acid on the various TiO<sub>2</sub> nanomaterials followed the Langmuir model, their degradation kinetics followed the Langmuir–Hinshelwood model. The results emphasized a strong increase in the adsorption and in the photocatalytic activity with the TiO<sub>2</sub> calcined at 600°C which was nearly 1.5 times higher than that of TiO<sub>2</sub>-P25 in the case of formic acid. For the degradation of phenol, TiO<sub>2</sub>-600 had a similar activity as TiO<sub>2</sub> P25. This is related to their tendency to degrade the intermediate products than the phenol itself. A formal mechanism scheme of phenol degradation has been proposed. The maximum photocatalytic efficiency was reached with the sample calcined at a temperature of 600°C, while a further increase in temperature depleted the photocatalytic response. The highest photocatalytic activity of the sample calcined at 600°C can be attributed to the improvement of the crystallization and the optimal anatase/rutile ratio (96/4).

- **Keywords:** TiO<sub>2</sub> nanoparticles; TiCl<sub>4</sub>; Sol-gel method; Photocatalytic activity; Anatase/rutile; Mechanism.

**Yih-Wen Wang. *Evaluation of self-heating models for peracetic acid using calorimetry.* Pages 122-131.**

Thermal analysis of peracetic acid (PAA) with respect to the explosive properties was performed using calorimetry. The exothermic characteristics and thermal runaway profiles of PAA solutions were acquired through differential scanning calorimetry (DSC) and vent sizing package 2 (VSP2). The results revealed significant enthalpy changes and gas eruption for PAA solutions that were subjected to free-radical induced and autocatalytic reactions. The reaction kinetics and order of various PAA solutions were elucidated using calorimetry.

- **Keywords:** Thermal analysis; Peracetic acid (PAA); Autocatalytic reaction

**Wende Tian, Guixin Zhang, Huiting Liang. *Alarm clustering analysis and ACO based multi-variable alarms thresholds optimization in chemical processes.* Pages 132-140.**

In chemical process, excessive alarms, high false alarm rate (FAR), and high missed alarm rate (MAR) generated by unreasonable setting to variable alarm thresholds are the main causes of affecting operation stability and device safety. In this paper, a clustering analysis based method was proposed to optimize the variable alarm thresholds. Variables are first clustered into groups using standardized Euclidean distance before variable weights are given by entropy weight method. Second, the probability density functions of the variables are fitted with process data under normal and abnormal conditions. An objective function about the FAR, MAR, and average alarm delay (AAD) is then established with variable weight and alarm delay. Finally, the objective function is optimized to find the optimal alarm thresholds using ant colony optimization (ACO) method. Case study of an industrial atmospheric-vacuum crude distillation shows that the proposed method can effectively reduce FAR and MAR.

- **Keywords:** FAR; MAR; Alarm threshold optimization; Clustering analysis; ACO; Variable weight

**Surindra Suthar, Rashmi Verma. *Production of Chlorella vulgaris under varying nutrient and abiotic conditions: A potential microalga for bioenergy feedstock.* Pages 141-148.**

Oleaginous microalgae *Chlorella vulgaris* has been identified as potential algal species for biodiesel production. The information on behaviour of this algae under abiotic (pH, ambient temperature and photoperiod) and nutrient stress is limited. This study aimed to investigate the effect of pH (2, 5, 7, 9 and 11), temperature (10, 20, 30 and 40°C), photoperiod (continuous light, 24:0h; light and dark, 18:6h; and continuous dark, 24:0h) and nutrient load (N-NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup>) on growth and chemical composition of harvested biomass of *Chlorella*. Result indicates the optimum ranges of abiotic conditions as 18:6h light/dark regimes (photoperiod), 7-9 pH and 20-30°C temperature for algal cultivations. After optimizing the abiotic culture conditions, the second experiment (the role of nutrient load on algal biomass yield) was conducted. Results suggested the maximum biomass (dry-weight basis) production 0.439g/L at 50mg/L N-NO<sub>3</sub><sup>-</sup> and 0.34g/L at 25mg/L PO<sub>4</sub><sup>-3</sup> loads in media. The maximum biomass yield was 159mgL<sup>-1</sup> day<sup>-1</sup> and 114L<sup>-1</sup> day<sup>-1</sup> with optimum loads of N-NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup>, respectively at the end. The chlorophyll (a and b) and, sugar contents in algal biomass showed the direct relationships with nutrient loads in the culture media. Results suggest that growth

and chemical quality of *C. vulgaris* biomass can be scaled by optimizing the abiotic and nutrient loads in algal reactors.

- **Keywords:** Algal technology; Biofuel; Lipid; Biodiesel; Photoperiod; Microalgae

**Fatine Berdouzi, Claire Villemur, Nelly Olivier-Maget, Nadine Gabas. *Dynamic simulation for risk analysis: Application to an exothermic reaction. Pages 149-163.***

Currently, there is a strong demand for quantitative process risk analysis. There is a challenge in describing the process dynamic behaviour in case of failures. We suggest a methodology that combines dynamic simulation (Aspen Plus Dynamics tool), risk analysis (HAZOP review) and risk matrices. The hazardous scenarios leading to major accidents are identified, some of them are simulated which allows the determination of consequences and quantification of severity. Moreover, the knowledge of the process dynamic behaviour and the evolution of the operating parameters during a degraded mode permits adequate safety barriers recommendation. In this paper, the aim is to apply this methodology to a case study concerning an exothermic reaction in a semi-batch reactor. The chosen reaction is the oxidation reaction of sodium thiosulphate by hydrogen peroxide. Advantages and limitations of the proposed approach are revealed and discussed.

- **Keywords:** Process safety; Dynamic simulation; Risk assessment; HAZOP method; Runaway scenario

**Song Xue, Wenhe Chen, Mingjia Deng, Hui Luo, Wensheng Huang, Yunping Han, Lin Li.. Pages 164-173. *Effects of moisture content on the performance of a two-stage thermophilic biofilter and choice of irrigation rate***

The stabilization, innocuity, and reutilization of sludge can be obtained via the co-combustion of sewage sludge in cement producing kilns. Off-gases containing odours and volatile organic compounds (VOCs) are generated during the process of sewage sludge drying. A two-stage thermophilic biofilter was constructed in a cement plant to remove SO<sub>2</sub>, NH<sub>3</sub>, and total VOCs (TVOCs) from the plant's exhaust. The average concentrations of TVOCs, NH<sub>3</sub>, and SO<sub>2</sub> in the inlet stream were 164.33, 38.46, and 51.12mg/m<sup>3</sup>, and in the outlet stream were 44.54, 9.18, and 3.91mg/m<sup>3</sup>, respectively. During biofilter operation, nutrient solution was circularly pumped onto the packing material to ensure the packing material remained moist. The moisture content of the packing material increased from 40 to 85% as the irrigation rate varied from 0.05 to 0.42m<sup>3</sup>/h. The removal efficiencies of NH<sub>3</sub> and TVOCs changed accordingly. When the irrigation rate was 0.3m<sup>3</sup>/h, removal efficiencies were 88.71% for NH<sub>3</sub> and 81.38% for TVOCs. More than 90% SO<sub>2</sub> removal occurred throughout the operation. The polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) method was used to assay the microbial population. Both microbial counts and diversity increased when the irrigation rate increased.

- **Keywords:** Off-gas treatment; Thermophilic biofilter; Irrigation rate; Moisture content; Microbial population; DGGE analysis

**Dragana Štrbac, Christos A. Aggelopoulos, Goran Štrbac, Marinos Dimitropoulos, Mladenka Novaković, Tamara Ivetić, Spyros N. Yannopoulos. *Photocatalytic degradation of Naproxen and methylene blue: Comparison between ZnO, TiO<sub>2</sub> and their mixture. Pages 174-183.***

Photocatalytic (PC) methods based on advanced oxidation processes have shown great potential for removal of water pollutants. Oxide semiconductors stand out as the most promising materials for UV-mediated photodegradation of persistent pollutants in wastewater. Although an immense number of studies have appeared so far concerning the PC activity mostly of TiO<sub>2</sub> but also of ZnO, the efficiency of these and other mixed oxides in degrading a wide range of organic pollutants has not yet been extensively explored. In this work we compare the efficiency of ZnO, TiO<sub>2</sub> and the 2ZnO–TiO<sub>2</sub> mixed crystal prepared by mechanochemical solid-state treatment, to decompose a pharmaceutical (Naproxene) and a dye (methylene blue) compound. The phase morphology, composition, specific surface area and crystalline structure of the nanopowders were characterized in detail. The photocatalytic activity of ZnO under UV irradiation was systematically higher than the other materials. The activity of the mixture was found to depend on the type of the analyte molecule, being, however, higher than that of pristine TiO<sub>2</sub> nanoparticles.

- **Keywords:** Photocatalysis; Naproxene; Methylene blue; ZnO; TiO<sub>2</sub>; Zinc titanate

**Nurull Muna Daud, Siti Rozaimah Sheikh Abdullah, Hassimi Abu Hasan. *Response surface methodological analysis for the optimization of acid-catalyzed transesterification biodiesel wastewater pre-treatment using coagulation–flocculation proces. Pages 184-192.***

Biodiesel wastewater is known as one of the most highly polluted wastewaters with high organic load, high amount of oils and fat contents and other compound such as chloride. The aim of this study is to optimize the coagulation–flocculation process prior to pre-treat biodiesel wastewater. This paper reports the optimal process conditions which were obtained using the Response Surface Methodology (RSM) analysis. This study was done using jar test apparatus. The Box–Behnken design was demonstrated beforehand to optimize this process. The investigated operating variables were coagulant dosage, initial pH, rapid mixing rate and contact time. The optimal process conditions obtained were alum dosage of 2g/L, initial pH of 7.13, rapid mixing rate of 200rpm and settling time of 65min. From the validation test conducted, the results were in reasonable agreement with the modeled values. The coagulant used in this study managed to reduce the COD, SS and turbidity contents by 34.5, 39.0 and 32.0%. respectively. Optimization of coagulation–flocculation can be done using the Response Surface Methodology (RSM) analysis and this proving that coagulation is capable of pre-treating biodiesel wastewater.

- **Keywords:** Biodiesel; Optimization; Alum coagulant; Jar test; Response Surface Methodology (RSM) method; Box–Behnken design

**Nepu Saha, Rashid Al-Muhannadi, Abdulla Al-Mohannadi, Luc N. Véchet, Marcelo Castier. *Is it the time to say bye to the  $\phi$ -factor? Pages 193-203.***

This paper presents a procedure to fit kinetic parameters of runaway reactions using data measured in Phi-TEC II adiabatic calorimeters. The parameter fitting is based on running multiple dynamic simulations of calorimeter experiments using a model that considers the compositional description of the fluid within the calorimeter cell and uses accurate thermodynamic models to evaluate the fluid properties, including changes to the amounts and compositions of each phase present inside the cell. In addition, the model accounts for the heat capacity of the calorimeter cell, which is considered to be temperature-dependent. This rigorous method represents a considerable departure from the simplifying assumptions embedded in the usual approach of adopting constant  $\phi$ -factors for treating data measured in adiabatic calorimeters. An example of the model's application shows that the parameters fitted using the proposed method are capable of an accurate representation of the dynamics of di-tert-butyl peroxide decomposition.

- **Keywords:** Reaction kinetics; Runaway reaction; Phase equilibrium; Equation of state; Dynamic simulation; Pressure relief

**Yixian Chen, Xiaosan Jiang, Yong Wang, Dafang Zhuang. *Spatial characteristics of heavy metal pollution and the potential ecological risk of a typical mining area: A case study in China. Pages 204-219.***

The goal of the presented research was to evaluate the possible heavy metal pollution in soil by applying Hakanson risk evaluation method with adjusting assessment domain combined with ArcGIS technology. The assessment standards were adjusted based on the amount and types of studied heavy metals. Topsoil samples in mining area were collected and tested the content of five kinds of heavy metals, Arsenic (As), mercury (Hg), copper (Cu), lead (Pb) and zinc (Zn). The area of different risk levels and the area ratio in each township were accurately calculate, and the regions with high pollution risk were further precisely located. The results indicate the following: (1) It was observed that the accuracy of soil-heavy metal assessment in Suxian was evidently improved by using Hakanson potential ecological risk with assessment domain adjustment. (2) The single factor and Nemero pollution indexes showed an evident contamination of five types of heavy metals in Suxian. (3) There is a high index of comprehensive ecological risk in Suxian; approximately 82.9% of Suxian is at a strong (level 3 or higher) risk level, demonstrating serious soil pollution. The quite strong risk region with the portion of 18.33% of total area is primarily concentrated in the area of the large Polymetallic mine and coal mining area. Using the single factor ecological risk index, the distribution of large areas of As and Pb high-risk pollution were explored. More than half of the soil in Suxian presents a strong Hg (level 3 and higher) risk level, and the primary strong ecological risk and quite strong ecological risk townships were identified as well. (4) A more finely characterized pollution status was achieved from this pollution assessment in Suxian based on the township level, rendering the study results a more practical guide and increasing their significance.

- **Keywords:** Mining area; Soil pollution assessment; ArcGIS; Potential ecological risk; Heavy metal pollution; Assessment standard adjustment

**Samir M. Deyab, Mohammed Taleb-berrouane, Faisal Khan, Ming Yang. *Failure analysis of the offshore process component considering causation dependence. Pages 220-232.***

Offshore oil and gas processing equipment operating in harsh environments poses high risk. This risk is further increased by the susceptibility of the equipment to natural disasters such as hurricanes and snowstorms due to harsh environments. When equipment functionality is compromised, it can become a hazard to personnel as well as to other equipment. The key safety practice on the offshore facility is to isolate the equipment and minimize consequences associated with processing equipment failures. When and how to isolate vulnerable equipment is a challenge due to limited understanding of the equipment's susceptibility and dependency to failure causes and consequences. This paper presents a methodology to analyze potential failure scenarios considering causation dependency and also determine which parameter(s) have the most impact on the failure. The results of the analysis are used to identify most sensitive equipment and their potential failure causes. This analysis will help to develop effective risk management strategies focusing on critical equipment.

- **Keywords:** Sensitivity analysis; Offshore safety analysis; Bayesian network; Causal dependency; Probabilistic modelling; Failure Analysis; Accident Model

**Cong Li, Lu-Kwang Ju. *Enhancement of resource recovery and sludge digestion by cultivation of phagotrophic algae with alkali-pretreated waste activated sludge and waste ketchup*. Pages 233-241.**

The reclamation of waste activated sludge (WAS) organics is often impeded by the long time required for the solid organic matter to solubilize. Here we introduce a fast approach to reclaim WAS by using phagotrophic algae. Phagotrophic algae have unique ability of growing by ingesting insoluble organic particles, which makes the solubilization of WAS organic matter unnecessary and largely accelerates the WAS digestion rate. To facilitate this approach, alkali treatment was evaluated at different pH and time and optimized at pH 10 for 6h to release microbial cells and other organics from the WAS flocs. Then the alkali-treated WAS was fed to phagotrophic algae. In later experiments, the addition of readily consumable organics, such as waste ketchup (WK), was found to enhance the percentage reduction of WAS organics and algae yield. With WK addition at 0.118:1 (w/w) WK-to-WAS organics, 46–49% of the WAS organic matter was digested within 22h. The lipid content was 20.8% in the treated biosolids, increased from 6.8% in the original WAS. With the fast digestion rate and high lipid production ability, this new approach has strong potential to improve WAS digestion and utilization.

- **Keywords:** Algae cultivation; Lipid production; Waste activated sludge treatment; Food waste treatment; *Ochromonas danica*; Sludge floc disintegration

**Roberto Bubbico, Barbara Mazzarotta. *Dynamic response of a tank containing liquefied gas under pressure exposed to a fire: A simplified model*. Pages 242-254.**

A simplified mathematical model representing the dynamic response of a tank containing a pressurized liquefied gas exposed to an external heat source, is presented. This scenario is of great practical interest in the process industry because it can result in the catastrophic failure of the tank with the explosive vaporization of the stored material (Boiling-Liquid Expanding-Vapour Explosion, BLEVE). The model has been validated against experimental data available in the literature and then applied to a number of reference cases, to assess the influence of the main parameters involved in the phenomenon on the evolution of the accident. This approach can be very helpful in various applications, such as risk analysis, where a large number of different scenarios must be simulated and/or the most critical conditions must be quickly identified. It has been found that the temperature of the tank wall in contact with the vapour phase is the most critical parameter. The time-to-failure of the tank is mainly affected by the received heat flux, while the time for the first opening of the pressure relief valve is very sensitive to both the initial storage temperature conditions and the heat input.

- **Keywords:** BLEVE; Mathematical modelling; Pressure liquefied gases; Accident prevention; Hazardous materials

**Y. Mortezaei, T. Amani, Sh. Elyasi. *High-rate anaerobic digestion of yogurt wastewater in a hybrid EGSB and fixed-bed reactor: Optimizing through response surface methodology*. Pages 255-263.**

Dairy production industry is one of the most polluting industries since it generates large volumes of high-strength wastewater. In this research, we studied the interactive effects of chemical oxygen demand (COD), hydraulic retention time (HRT), and COD/nitrogen ratio (COD/N) on the performance of a hybrid expanded granular sludge bed (EGSB) and fixed-bed (FB) bioreactor treating yogurt effluent was studied. For this purpose, response surface methodology (RSM) was applied to predict the behaviors of the system in term of COD removal and biogas production rate (BPR). RSM showed that the best models for COD removal and biogas production rate were the cubic and quadratic models,

respectively. The optimum region of the hybrid EGSB-FB reactor was acquired at influent COD of 11,200mg/L, HRT of 27h, and COD/N ratio of 51. These variables resulted in a 90% COD removal efficiency and a 180mL/h BPR. COD/N ratio (relevant coefficient=4.37) and influent COD (relevant coefficient=29.99) resulted respectively as the most effective parameters on COD removal and BPR.

- **Keywords:** Anaerobic digestion; Yogurt wastewater; Hybrid EGSB-FB; Response surface methodology (RSM); COD removal; Biogas production

**Yan Cuiping, Zhang Mingxing, Lin Longyuan, Chen Haiyan. *An analysis of a reverse pulse cleaning process using high-flow pleated fabric filter cartridges. Pages 264-274.***

A high-flow fabric filter cartridge with a high pleat ratio, along with a large diameter, and a large filtration area, showed increased susceptibility to incomplete cleaning, caused by the greater variation of pulse airflow in the filter cartridge. In order to investigate the cleaning characteristics of high-flow pleated fabric filter cartridges, a pleated fabric filter cartridge ( $\Phi 325 \times \Phi 215 \times 1000$ mm) was used to the experiment. Then, the peak pressure distribution along the height of the filter cartridge with five measurement locations was recorded using five pressure transducers. The process of dust cake born off the filter cartridge was photographed using a high-speed camera. The cleaning process of a high-flow filter cartridge was examined, and the peak pressure variation on the filter cartridge was determined during the pulse cleaning. The results show the following: the process duration of the dust cake born off the filter cartridge was 372ms. The maximum peak pressures were 4932, 14,026, 3998, 8813, and 1962Pa from the top to the bottom along the height of the filter cartridge, respectively. The peak pressure and duration formed by the pulse airflow are indicative of the cleaning process of dust cake born off filter cartridge. Although a peak pressure high to 673Pa appears at location one with the first transient time, only a minor amount of dust particles was born off filter cartridge. Therefore, the process of quartz particles born off the entire filter cartridge was not only related to the peak pressure, but also to the duration. Meanwhile, the experiment shows that an increase in the pulse width can decrease the likelihood of dust particles being reattached on the bottom of the filter cartridge. The peak pressures increase on the filter cartridge when the pleat number decreases from the 155 to 125. This can decrease the incidence of incomplete cleaning.

- **Keywords:** Filter cartridge; Pulse cleaning; Reverse airflow; Static pressure; Dust cake born off; High-flow

**Ruozhu Dong, Zhongmin Jia, Siyue Li. *Risk assessment and sources identification of soil heavy metals in a typical county of Chongqing Municipality, Southwest China. Pages 275-281.***

Eight heavy metals (HMs: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were measured from 337 top and 80 deep soil samples in Tongliang District (Chongqing, SW China), and consequently multiple statistics and indices (PI — pollution index; Igeo — geoaccumulation index; EF — enrichment factor, and RI — potential ecological risk index) were employed for risk evaluation of HMs in soils. The concentrations of Cd and Hg in top soils exceeded threshold values for China's State Environmental Quality Standards for soils. PI suggested the contamination of HMs in top soils was ranked as:  $Cr < As < Cu < Ni < Pb < Zn < Hg < Cd$ , while deep soil showed a different order as:  $Cr < As < Cu < Hg < Cd < Pb < Zn < Ni$ . EF showed moderate enrichment of Cd in top soils, and top soils were unpolluted to moderately polluted by Cd and Hg, as indicated by Igeo. However, minimal enrichments of HMs in deep soils were found. It should be noticeable that several sites in top soils showed As, Cd and Hg with  $I_{geo} > 1$ , indicating moderate pollution. RI showed that 59% of top soils and 8% of deep soils were moderate risk, while 3% and 1% of top soils were considerable and high risk, respectively. PCA

(principal component analysis) identified two possible sources for HMs, which explained 69% and 71% of total variances in top and deep soils, respectively. The sources for Ni, Zn, Cu, Cd, and Pb could be fertilizers, pesticides, and domestic wastes. The sources for Hg and As enrichment could be industrial activities.

- **Keywords:** Multiple indices; Geoaccumulation index; Enrichment factor; Potential ecological risk index; Heavy metal pollution; Anthropogenic activities

**Tao Fan, Gang Zhou, Jiayuan Wang. *Preparation and characterization of a wetting-agglomeration-based hybrid coal dust suppressant*. Pages 282-291.**

Driven by the advancement of science and technology, the number of safety incidents in coal mines has been steadily declining. Nonetheless, a small-scale killer, i.e., coal dust, has become a dominating factor threatening the safe production in coal mines. Therefore, the control of coal dust has become the key to the safe and efficient production of coal mines. The present paper discusses the preparation of a type of hybrid dust suppressant by cross-linking sodium ligninsulfonate and acrylamide, which generates a type of macromolecular product. Subsequently, Fourier infrared spectroscopy, X-ray diffraction spectroscopy and scanning electron microscopy experiments are conducted to analyze the structure of the product. Moreover, the TG-DSC experiments are carried out to analyze the thermal stability of the product. It is found through a single factor experiment that the optimal synthesis condition is: the mass ratio of lignin to acrylamide is 2:7; the mass ratio of cross-linking agent to acrylamide is 3%; the optimal reaction temperature is 65°C; an examination of the product through a high-power microscope with ultra depth of field reveals that the prepared macromolecular product can cause the coal dust particles to undergo an agglomeration process; however, the prepared product cannot sufficiently wet the coal dust; to enhance the wettability of the production, 0.15% (by mass fraction) of dodecyl dimethyl betaine (DDB) is added to the system. An experiment concerning the interaction between coal dust and the prepared product indicates that the present suppressant can effectively suppress the dispersion of coal dust through a combination of wetting and agglomeration effects.

- **Keywords:** Coal dust control; Agglomeration agent; Wetting agent; Grafting polymerization; Environmental friendliness; Surface active agent

**Mohamed Guerfali, Ines Ayadi, Ameni Belhassen, Ali Gargouri, Hafedh Belghith. *Single cell oil production by *Trichosporon cutaneum* and lignocellulosic residues bioconversion for biodiesel synthesis*. Pages 292-304.**

Barley hull hydrolysate was used as the fermentation feedstock of *Trichosporon cutaneum* CTM-30125 yeast strain for production of microbial lipid as the potential raw material of biodiesel. An effective hydrolysis process based on the combination of dilute acid hydrolysis and enzymatic saccharification was developed to maximize recovery of total sugars. On synthetic media, CTM-30125 can assimilate glucose and xylose simultaneously and accumulated intracellular lipid up to 43.6% (w/w). However, when grown on acid barley hull hydrolysate (ABHH) the lipid content was low (16.6% w/w) and a detoxification step was required. Overliming by Ca(OH)<sub>2</sub> treatment and adsorption by activated charcoal improved the fermentability of ABHH significantly by removing the inhibitors and reducing the nitrogen content. The solid fraction resulting from the acid treatment of the barley hull was treated with hydrolytic enzyme complex produced by the hyper-cellulolytic fungal strain *Trichoderma reesei* Rut C-30. Enzyme production and hydrolytic conditions were optimized to enhance the saccharification. The structural changes in native and treated raw material were monitored using FTIR spectra. Detoxified ABHH and enzymatic hydrolysate were successively fermented by the CTM-

30125 strain in fed-batch bioreactor without addition of external nitrogen source. A total biomass of 17.5g/L with a lipid content of 38.2% (corresponding to a lipid yield of 6.7g/L) could be achieved after 168h of culture. The relative fatty acid composition indicates the presence of increased levels of saturated (41.2%) and monounsaturated (52.5%) fatty acids in the oil, making it ideal for biodiesel production.

- **Keywords:** Lignocellulosic residues; Bioconversion; Microbial lipid; *Trichosporon cutaneum*; Cellulases; Biodiesel

**Augustine O. Ifelebuegu, Esiwo O. Awotu-Ukiri, Stephen C. Theophilus, Andrew O. Arewa, Enobong Bassey. *The application of Bayesian – Layer of Protection Analysis method for risk assessment of critical subsea gas compression systems. Pages 305-318.***

Subsea gas compression system (SGCS) is a new critical subsea-to-shore field development solution that could reduce costs and environmental footprint. However, this system is not without inherent and operational risks. It is therefore, vital to evaluate the possible risks associated with SGCS to ensure the safe operation of the system. To this end, Layer of Protection Analysis (LOPA) is a suitable method for the estimation of possible risks. However, the failure rate data from SGCS required for LOPA is sparse and mostly developed from experimental testing. Bayesian (BL) logic is an effective tool that could be used to resolve this shortfall. In this paper, generic data from a secondary database was updated with SGCS specific data using BL logic to give a better risk frequency value. The key findings show that the posterior values derived from the BL-LOPA methodology are safer and more reliable to implement for an event scenario when compared to literature, expert judgement and generic data; therefore recommending an improved judgement in the application of safety instrumented systems for a required safety integrity level. The case studies used demonstrated that the BL-LOPA risk assessment method is sufficiently robust for quantifying uncertainties in new process facilities with sparse data.

- **Keywords:** Bayesian; LOPA; Risk assessment; Subsea systems; Gas compression

**Kosar Hikmat Hama Aziz, Ali Mahyar, Hans Miessner, Siegfried Mueller, Dieter Kalass, Detlev Moeller, Ibrahim Khorshid, Muhammad Amin M. Rashid. *Application of a planar falling film reactor for decomposition and mineralization of methylene blue in the aqueous media via ozonation, Fenton, photocatalysis and non-thermal plasma: A comparative study. Pages 319-329.***

The efficiencies of ozonation and different advanced oxidation processes (AOPs) including photocatalytic ozonation, Fenton, photo-Fenton, photocatalytic oxidation, UVA/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, and non-thermal plasma generated by a dielectric barrier discharge (DBD) were compared in terms of the energy yield ( $G_{50}$ ) for decolorization of MB and total organic carbon (TOC) removal using a planar falling film reactor. Fenton oxidation and ozonation were found to be the most efficient methods for the decolorization of MB, although these techniques attained rather low mineralization. A combination treatment of the ozonation with the photocatalysis demonstrates a synergistic effect on the mineralization efficiency. The photocatalytic oxidation and UVA/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> provide only a moderate MB decolorization. The degradation efficiency of the DBD plasma is significantly dependent on the composition of gas atmosphere. The addition of Fe<sup>2+</sup> to the solution in the DBD plasma under argon atmosphere improves the degradation efficiency due to the occurrence of Fenton reaction. The energy yield for 50% conversion of MB is calculated between 0.13 and 20.5g/kWh, and the maximum and minimum values were obtained by the ozonation and photocatalytic oxidation, respectively. Ozonation with the highest

energy yield provided a moderate mineralization by only 19%, while the DBD plasma obtained the highest TOC removal by 88%.

- **Keywords:** Advanced oxidation process; Decolorization; Mineralization; Energy yield; Dielectric barrier discharge; Falling film reactor

**Mohammad Kavand, Elahe Fakoor, Saeed Mahzoon, Mansooreh Soleimani. *An improved film-pore-surface diffusion model in the fixed-bed column adsorption for heavy metal ions: Single and multi-component systems.* Pages 330-342.**

The present work was investigated the adsorption of heavy metal ions including lead ( $Pb^{2+}$ ), Cadmium ( $Cd^{2+}$ ) and Nickel ( $Ni^{2+}$ ) onto a commercial activated carbon (AC) in single and multi-component aqueous fixed bed column. The model, named film pore-concentration dependant-surface diffusion (FPCDSD), was able adequately to consider the details of inter- and intra-pellet transport mechanisms in column mode and predict film, pore and surface diffusivities of the adsorption process considering a nonlinear isotherm model. A diffusional kinetic model was developed, to investigate the effects of several parameters like initial concentration, flow rate, and bed height, and also to explain the adsorption kinetics and evaluation of the mass transfer coefficients. The detailed calculation methods to determine the contribution of each resistance against mass transfer were addressed in the paper. The model with mass transfer parameters (with the order of magnitude of  $D_p \approx 10^{-10} m^2 s^{-1}$ ,  $D_s \approx 10^{-15} m^2 s^{-1}$ ,  $D_z \approx 10^{-5} m^2 s^{-2}$ , and  $k_f \approx 10^{-5} m s^{-1}$ ) was found successful in correlating adsorption data in single, and multi-component system under different operating conditions. Sensitivity analysis revealed that the value of  $D_p$  and  $k_f$  dictate the model performance. The Biot number was found to increase with increasing flow rate and initial concentration, indicating an increase in intraparticle diffusion resistance.

- **Keywords:** Kinetic modeling; Heavy metal; Adsorption; Fixed bed column; Diffusion; Desorption

**Ahmin Park, Yoonae Ko, Sijin Ryu, Youngsub Lim. *Numerical modeling of rapid depressurization of a pressure vessel containing two-phase hydrocarbon mixture.* Pages 343-356.**

Blowdown or rapid depressurization of pressure vessels is a well-known safety process that removes overpressure at an emergency situation. Since the thermodynamic and transport properties in a vessel change remarkably during depressurization, rigorous estimation of the properties with respect to time is essential. Particularly, the temperature drop due to the expansion would cause the wall of the vessel to become brittle, and hence, it should be evaluated in an early stage of the design process. This study developed a numerical model to simulate the phenomenon of the rapid depressurization and estimate the non-equilibrium temperature changes of the vapor, liquid and vessel wall during the depressurization process, considering combined convection, nucleate boiling and transient multilayer conduction through the vessel wall. The results of this study were compared with experiment, numerical models from literature and several commercial software and showed good agreement with experimental results.

- **Keywords:** Blowdown; Depressurization; Non-equilibrium; Numerical modeling; Simulation; Flare system

**Zhian Huang, Chuanwu Sun, Yukun Gao, Yucheng Ji, Hui Wang, Yinghua Zhang, Rui Yang. *R&D of colloid components of composite material for***

***fire prevention and extinguishing and an investigation of its performance. Pages 357-368.***

Because the existing fire prevention and extinguishing materials for coal mining cannot adhere to coal for long periods of time, this study investigated their colloid components. A colloid recipe of sodium silicate as the base material, sodium bicarbonate as the coagulation accelerator and sodium polyacrylate as the polymer additive was determined. An optimum proportion was obtained by orthogonal tests, whereby the ratio of water to solid was 4:1, sodium silicate accounted for 4%, sodium bicarbonate accounted for 5% and sodium polyacrylate accounted for 0.75‰. Comparing the performance of four other typical materials of fire prevention and extinguishing through contrast experiments, we observed that the new material has advantages of dropping the temperature, lowering the concentration of oxygen and carbon monoxide and increasing the concentration of carbon dioxide. In addition, a field test was conducted with the new material. After injection, three zones of spontaneous combustion showed clear changes: the oxidation temperature rise zone was ahead by 8m, its length was shortened by 20m and the choking zone moved up by 28m. These changes indicated the improvement of colloid could significantly increase the effect of fire prevention and extinguishing materials.

- **Keywords:** Compound material; Spontaneous combustion; Colloid components; Choosing experiment; Orthogonal experiment; Optimal proportion

***Gang Guo, Fei Wang, Guo-Qiang Liu, Sheng-Jun Luo, Rong-Bo Guo. Calculation on the phase equilibrium and critical temperature of CH<sub>4</sub>/CO<sub>2</sub>. Pages 369-377.***

The phase equilibrium and critical temperature are the pivotal parameters for the application of biogas, especially the liquefied biogas. In this work, rapid estimation methods for the phase equilibrium (e.g. SRK, PR and PC-SAFT equations of state (EOS)) and critical temperature (e.g. MF, CVF, CP, GT, RK, MW and GC methods) of synthetic biogas (CH<sub>4</sub>/CO<sub>2</sub>) were summarized based on previous studies and the accuracy was then verified according to the experimental data. The results showed that PR EOS gave more accurate results when estimating the phase equilibrium of CH<sub>4</sub>/CO<sub>2</sub>. For the estimation of critical temperature of CH<sub>4</sub>/CO<sub>2</sub>, in the region with low CH<sub>4</sub> composition (<50%), all the estimation methods except GC method gave the results close to the experimental data, while GC method produced obviously lower values. While in the region with high CH<sub>4</sub> composition (>60%), only MF and CP methods gave the most accurate results.

- **Keywords:** CH<sub>4</sub>/CO<sub>2</sub>; Phase equilibrium; Critical temperature; Rapid estimation; Equations of state; Peng-Robinson EOS

***Li Huang, Xiaochun Li, Teng Cai, Manhong Huang. Electrochemical performance and community structure in three microbial fuel cells treating landfill leachate. Pages 378-387.***

Electrochemical performances and pollutants removal characteristics of synthetic landfill leachate were investigated using three dual-chambered microbial fuel cells (MFCs). An open circuit MFC, aerated MFC and non-aerated MFC were used to compare the performance of the different modes. Results showed that aerated MFC was superior to the open circuit MFC and the non-aerated MFC in generating electricity and removing pollutants. High-throughput sequencing of the bacterial and archaeal communities revealed that electricigen of *Enterobacter* and *Comamonas* was found in three MFCs. *Methanobacterium* was the genus of archaea present at the highest proportion in the open circuit MFC, non-aerated MFC and aerated MFC, at 56.67%, 51.62% and 58.37%, respectively. Diversity of the bacterial and archaeal community in open circuit MFC is

higher than that of closed circuit MFC. Richness goes by contrary. The circuit connections and growth conditions can help to control the species of biomass and change the performance of MFCs.

- **Keywords:** Microbial fuel cell; Landfill leachate; Community structure; Electrochemical performance; Archaea; Oxygen

**Fan Geng, Gang Luo, Yingchao Wang, Zhengbiao Peng, Shengyong Hu, Tiantian Zhang, Hongli Chai. *Dust dispersion in a coal roadway driven by a hybrid ventilation system: A numerical study.* Pages 388-400.**

Dust contamination to ventilation systems is a common issue for mine operators during underground coal mining. In the present study, dust dispersion driven by a hybrid ventilation system in an underground mine has been investigated via a computational fluid dynamics (CFD) model. Specifically, the numerical model was developed based on the Euler-Lagrange method where the trajectory of dispersed dusts was solved individually. Dust dispersion induced by turbulence was considered by a stochastic tracking model. Effects of key parameters (e.g., gas velocity and exhaust duct length) on dust dispersion characteristics throughout the coal roadway have been examined. The results showed that the distribution of dusts exhibited extreme non-uniformity with a significantly higher concentration present near the mining face, particularly on the exhaust side. The cross-sectional average dust concentration substantially decreased along the axial direction in the front part of the coal roadway. Intense circumfluence and secondary sedimentation of dusts were found to be the main mechanisms that drove the non-uniform distribution of dusts. The model is shown to be capable of reproducing the dust dispersion process captured in the experiments and the prediction results agree well with the experimental data.

- **Keywords:** Dust distribution; Coal roadway; Hybrid ventilation system; Respirable dust exposure; Euler-Lagrange method; Numerical simulation

**Yi Yang, Yun-Ting Tsai, Yanni Zhang, Chi-Min Shu, Jun Deng. *Inhibition of spontaneous combustion for different metamorphic degrees of coal using Zn/Mg/Al-CO<sub>3</sub> layered double hydroxides.* Pages 401-412.**

Layered double hydroxides (LDHs) have excellent physical and chemical properties and are thus widely and effectively used to inhibit spontaneous coal combustion. In this study, Zn/Mg/Al-CO<sub>3</sub> LDHs, which are metal ion-LDH complexes, were prepared through coprecipitation and synthesized using three types of coal with different metamorphic degrees to form Zn/Mg/Al-CO<sub>3</sub> LDH/coal. Additionally, the spontaneous coal combustion inhibition mechanism of added Zn/Mg/Al-CO<sub>3</sub> LDHs was investigated using scanning electron microscopy, in situ Fourier transform infrared spectroscopy, and differential scanning calorimetry to further elucidate prevention and control measures for spontaneous coal combustion. The results demonstrated that Zn/Mg/Al-CO<sub>3</sub> LDHs are extremely highly compatible with coal and form a crystalline structure on the surface of coal, which interrupts the diffusion of oxygen for combustion and, consequently, inhibits spontaneous coal combustion. Furthermore, the negative effects of various crucial functional groups on spontaneous coal combustion were weakened by the addition of Zn/Mg/Al-CO<sub>3</sub> LDHs. When decomposing, Zn/Mg/Al-CO<sub>3</sub> LDHs undergo an endothermic reaction and generate enormous amounts of CO<sub>2</sub> and H<sub>2</sub>O, which could effectively reduce the surface temperature of coal and dilute the oxygen concentration of the environment. A novel material, Zn/Mg/Al-CO<sub>3</sub> LDHs can be used to prevent the occurrence of severe accidents caused by spontaneous coal combustion.

- **Keywords:** Spontaneous coal combustion; Coprecipitation; Metamorphic degree; Inhibition mechanism; In situ Fourier transform infrared spectroscopy; Functional group

**Ranjana Rathaur, Sumit H. Dhawane, Amit Ganguly, Mrinal Kanti Mandal, Gopinath Halder. *Methanogenesis of organic wastes and their blend in batch anaerobic digester: Experimental and kinetic study.* Pages 413-423.**

The scarcity of the fossil fuels and increasing energy demand urges the production of sustainable source of energy. The uncontrolled generation of wastes and their easy accessibilities gained a significant attention towards its use for the synthesis of renewable energy like biomethane. In order to cope up with the energy demand and urgency of alternative non-conventional energy source, the present study is focused on improvisation of biogas production qualitatively and quantitatively from different substrates viz. paper waste, Parthenium hysterophorus, canteen waste, and their mixture. The enhancement of the methane potential is accomplished by treating these substrates with catalyst (poultry litter, silica gel and cow urine) and active inoculum (gobar gas slurry) under the standard anaerobic digestion condition. The methanogenesis process was carried out in a 1l batch digester at 1:1 ratio of water:feed under mesophilic temperature (37°C) for hydraulic retention time of 30 days. Moreover, cumulative gas yield for considered substrates were 167.32ml/g VS, 149.05ml/g VS, 197.72ml/g VS, 290.69ml/g VS respectively with methane content in biogas for each substrate of 25.5%, 56.8%, 60%, 62% respectively. Among various kinetic models studied, first order kinetic model was found to be best to describe the kinetics of biomethane synthesis for all employed wastes with maximum fitting accuracy ( $R^2=0.966$ ). Results of the study confirm the enrichment of quality and quantity of the product gas. The experimental study also revealed that the process is prominent for the efficient production of biomethane to meet the excessive energy thrust.

- **Keywords:** Biogas; Renewable energy; Organic waste; Anaerobic digestion; Kinetics

**Wei-Hsiang Chen, Tsung-Hsien Huang, Chung-Ya Wang. *Impact of pre-oxidation on nitrosamine formation from a source to drinking water: A perspective on cancer risk assessment.* Pages 424-434.**

Given the carcinogenicity of nitrosamines as nitrogenous disinfection byproducts, this study investigated the impacts of different pre-oxidation technologies on nitrosamine formation through different full-scale treatment approaches from a health risk assessment perspective. The cancer risk posed by six nitrosamines and their formation potentials (FPs) in a surface water source and three subsequent plants with comparable treatment approaches in southern Taiwan were estimated to investigate the total toxicity variations through different treatments. In the results, sufficient environmental exposure suppressed the risks by nitrosamine-FPs in the source, with appreciable risks (the median ranging from  $6.4 \times 10^{-5}$  to  $1.0 \times 10^{-4}$ ) present in the water near the intake. In three treatment plants, the risks decreased through the treatment processes (1%–84% reduction). Pre-chlorination suppressed the risk by nitrosamine formation during post-chlorination (dropped by 58%–86%), whereas pre-ozonation elevated the risk in the next oxidation steps. Removal of organic matter before ozonation reduces the risk increase during oxidation. Total organic carbon (TOC) ( $r=-0.89$ ) or dissolved organic carbon (DOC) variations ( $r=-0.86$ ) were negatively associated with the cancer risk variations in three DWTPs. The discrepancy between the risks estimated by using different toxicity data sources occurred. Effectively minimizing the formation of nitrosamines with proper source water quality, treatment approaches, and correct parameters to monitor are critical for minimizing the toxicity posed by various nitrosamines in drinking water.

- **Keywords:** Nitrosamine; Cancer risk; Pre-oxidation; Nitrogenous disinfection byproduct; Organic carbon; Drinking water safety

**Lalatendu Muduli, Prasanta K. Jana, Devi Prasad Mishra. *Wireless sensor network based fire monitoring in underground coal mines: A fuzzy logic approach*. Pages 435-447.**

Mine fire is one of the major hazards in underground coal mines. Continuous monitoring of underground coal mines for early detection of fires is very much important from the mines safety point of view. In recent years, wireless sensor network (WSN) has gained enormous attention for monitoring of underground coal mines. In this technique, the sensor nodes are deployed in coal mines for collecting various environmental data, such as temperature, relative humidity, concentrations of different gases, etc. and send these data to a base station (sink) directly connected to the ground monitoring centre. Since the monitoring data are uncertain and imprecise in nature, it is important to interpret and analyze the data for taking measures for preventing fire hazard. In this paper, we propose a WSN-based fire monitoring system for underground coal mines using fuzzy logic approach for enhancing the reliability in decision-making process to alleviate the mine fire hazard. Mamdani fuzzy inference system is used as fuzzy model for taking real-time decisions on monitoring data. The system is extensively simulated using Fuzzy Logic Toolbox in MATLAB. The simulation results revealed that the proposed system is more reliable and responsive to fire hazard as compared to the offline monitoring system used in underground coal mines.

- **Keywords:** Fuzzy logic; Underground coal mines; Wireless sensor network; Mine environment; Mine fire monitoring; Fire intensity

**M.A. Martín-Lara, A. Ronda, G. Blázquez, A. Pérez, M. Calero. *Pyrolysis kinetics of the lead-impregnated olive stone by non-isothermal thermogravimetry*. Pages 448-458.**

The thermal behavior of the lead-impregnated olive-stone during pyrolysis was investigated via thermogravimetric analysis at different heating rates under an inert atmosphere of nitrogen to study the effect of the metal during the thermal process. Thermogravimetric curves showed a little increase of the degradation temperature of hemicellulose and cellulose because of the presence of the metal when the material impregnated with lead was tested. Therefore, calculated kinetic parameters varied slightly after impregnation with lead. Apparent activation energies were 119.72, 238.65 and 68.76kJ/mol for hemicellulose, cellulose and lignin fractions in raw olive stone and 119.40, 257.00 and 68.46kJ/mol for the same fractions in the lead-impregnated olive stone.

- **Keywords:** Isoconversional methods; Lead-impregnated biomass; Olive stone; Pyrolysis; Thermogravimetric analysis; Three independent reactions

**Kun Chen, Faisal Khan, Xiaofei Jing. *Safety assessment of natural gas purification plant*. Pages 459-466.**

With risks becoming more complex and diverse in natural gas purification plant (NGPP), safety evaluation approaches are required to quickly identify hazards, and effectively assess safety levels. NGPP-safety evaluation represents an essential analytic step in preventing catastrophic accidents and reducing losses. This paper presents a safety evaluation model for NGPP based on fuzzy comprehensive evaluation and improved analytic hierarchy process (F-IAHP). The assessment model is established based on the authors' years of work experience in this field. To correct the subjectivity of the traditional weighting method, a new method used to determine the relative weight is adopted, and an evaluating index system was established for NGPP. Then the F-IAHP methods were combined to validate the safety levels of 3 representative enterprises. The results show that three NGPP plants at Moxi, Wanzhou and Zhongxian have very low risk,

low risk and medium risk, respectively. These results reflect the actual safety situation of the facility. The application of this work can make the evaluation easy, effective and reliable. It is expected that this work may serve as an assistance tool for managers of enterprise in improving NGPP-safety level.

- **Keywords:** Natural gas production plant; Fuzzy comprehensive evaluation; Safety assessment; Improved analysis hierarchy process

**Xuecai Xie, Deyong Guo. *Human factors risk assessment and management: Process safety in engineering.* Pages 467-482.**

Human factors are the primary factors leading to accidents. Therefore, managing human factors is an important way to prevent accidents. This paper aims to introduce a new method to assess and manage human factors. First, the accident causation model was improved based on Reason's "Swiss-cheese" model, which was then combined with the Human Factor Analysis and Classification System (HFACS) to establish the human factors risk assessment model. The evaluation model includes 5 levels (organization influence, unsafe supervision, preconditions for unsafe acts, unsafe acts, and emergency influence) and 25 human factors. In the risk assessment process, the set pair analysis method was used to calculate the connection number and the partial connection number of each factor, level and whole system. The safety score and risk development interval were calculated by using the connection number, and the risk grade is determined. Thus, the dynamic quantitative evaluation of human risk is realized. By using the partial connection number, the risk development trend of each factor is predicted. Due to the lack of human managed enterprises, the safety status of people is approximately discrete. Therefore, this paper establishes the SPA-Markov chain risk prediction model to predict human risk. The verification results show that the prediction error is less than 2%. This indicates that the prediction model can be applied in practice. To reduce human risk, ABC analysis and the "S-O-R" model were used for human risk management. The application results show that this method has a significant effect on improving human safety factors. Finally, this paper summarizes 12 common unsafe factors and their effective safety "stimulus" measure, researching the accident path. According to the organizational level and individual level of human factors, different kinds of human factors management methods are suggested.

- **Keywords:** Human factors; Risk assessment and management; Set pair analysis; SPA-Markov risk prediction method; ABC analysis and "S-O-R" analysis model; Human factors risk assessment model

**Jing Hu, Juan Zhou, Shaoqi Zhou, Pan Wu, Yiu Fai Tsang. *Occurrence and fate of antibiotics in a wastewater treatment plant and their biological effects on receiving waters in Guizhou.* Pages 483-490.**

Wastewater treatment plants (WWTPs) are not designed for the removal of antibiotics. Thus, several studies have been conducted to evaluate the fate of antibiotics in wastewater treatment processes. However, most of these investigations did not consider the antibiotic contamination in the receiving waters. This study investigated the occurrence and fate of antibiotics in a wastewater treatment plant and the ecological risks posed by surface water receiving the effluent discharge. The results indicated that the levels of 18 antibiotics in the influent ranged from 37.21ngL<sup>-1</sup> to 2935.40ngL<sup>-1</sup>, and sulfamethizole (SMZ) was the major component among the 18 antibiotics; SMZ occurred most frequently and at the highest concentrations. Mass balance analysis was performed to explore the mechanisms of antibiotic removal, and the findings indicated that biotic and abiotic degradation are the major removal mechanisms; however, removal of quinolones is primarily ascribed to sludge adsorption. Because activated sludge consists of negatively charged colloidal particles, it is more inclined to adsorb quinolones, which contain positively charged nitrogen atoms. The resulting loading of

antibiotics from WWTP effluent discharge into the receiving water of the Yangjie River may result in their uptake by aquatic organisms and thus poses a risk to human health.

- **Keywords:** Antibiotics; Wastewater treatment plants; Removal mechanisms; Removal efficiency; Receiving waters; Ecological risk

**Mohammad Hossein Keshavarz, Mohammad Jafari, Karim Esmaeilpour, Mohammad Samiee. *New and reliable model for prediction of autoignition temperature of organic compounds containing energetic groups*. Pages 491-497.**

Autoignition temperature (AIT) is one of the most important safety specifications used to characterize the hazard potentials of a chemical substance. A simple model is introduced for reliable prediction of the AIT of organic compounds containing energetic functional groups nitro, nitrate, nitramine, and peroxide. It requires the only molecular structure of organic energetic compounds without using complex molecular descriptors and computer codes where they need expert users. Model building has been constructed on the basis of the measured AIT of 45 organic energetic compounds and compared with the predicted results of the best available group additivity method. For 9 compounds with unlike and complex molecular structures, the new model has also been checked that gives good predictions. The root mean square (RMS) deviations of the new model and group additivity method are 47.45 and 194.25K, respectively, for 54 compounds (corresponding to 111 data points).

- **Keywords:** Autoignition temperature; Organic compounds; Energetic functional groups; Correlation; Molecular structure; Safety; Correcting Functions

**Ya-li Cao, Xia Wang, Cheng-qi Yin, Wen-wen Xu, Wen Shi, Guang-ren Qian, Zhi-meng Xun. *Inland Vessels Emission Inventory and the emission characteristics of the Beijing-Hangzhou Grand Canal in Jiangsu province*. Pages 498-506.**

Currently, air pollution from vessel exhaust emission is increasingly prominent. In particular, Jiangsu province, as a large inland waterway transportation province, has a large amount of ship emissions; however, the amount of such emissions remains unidentified. Considering the importance of the Beijing-Hangzhou Grand Canal for Jiangsu province and for the country, the inland vessel emission inventory of the Beijing-Hangzhou Grand Canal in Jiangsu province in 2014 was established using activity-based approach, the total annual emissions of particulate and gaseous pollutants were quantified, and the emission characteristics of vessels were also discussed. Dry cargo ships are the largest source of air pollutants, with ships whose gross tonnage is between 200 and 600tons having the greatest contribution to exhaust emission. The order of the emission contribution for each vessel operation condition was as follows: normal navigation>passing through the shipping-lockage>berthing>mooring. Vessels running on the fairway made the greatest contribution in the aspect of the spatial distribution. Except in February, the monthly emissions not from ships presented a relatively steady trend.

- **Keywords:** Beijing-Hangzhou Grand Canal in Jiangsu province; Inland vessels; Air pollution; Emission inventory; Emission characteristics; Emission factors