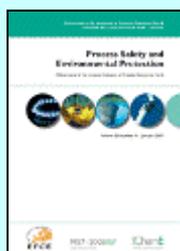


# **Process Safety and Environmental Protection**

**rok 2011, ročník 89**

**Číslo 3 (May 2011)**



**Samith Rathnayaka, Faisal Khan, Paul Amyotte. *SHIPP methodology : predictive accident modeling approach : part I : methodology and model description*. Pages 151-164.**

Many process accidents are controlled and mitigated before they escalate to major events. Unfortunately some do go on to produce catastrophic consequences. As the size and complexity of processing facilities increases, the risks posed by accidents are alarming. Operational safety could be improved by giving emphasis to the prevention of incidents, rather than relying on control and mitigative measures. This method is referred to as an "inherently safer design approach". To prevent major, though infrequent, event occurrence, it is important to consider accident precursors (symptoms of hazards) such as operational deviations, mishaps, and near misses, in order to prevent events at source rather than controlling or mitigating them. This paper describes a recently developed process accident model with predictive capabilities. It uses a combination of event and fault tree concepts to model the cause-consequence relationship. The model relies on process history, accident precursor information, and accident causation modeling. The model is able to capture the process operational behavior, and update the accident likelihood using the Bayesian updating mechanism. The predictive abilities of the model, along with risk estimation, help to develop and prioritize inherently safer design and operational strategies. This is Part I of two papers, focusing on implementation of this methodology. Part II deals with application of the methodology. **Highlights:** ► The SHIPP methodology provides an easy and effective mechanism to model process accident and integrates its results in process safety management system. ► Process accident model is developed with predictive capabilities using safety barriers concepts. ► The developed model is able to capture the occurrence behavior of an accident and update the accident likelihood using the Bayesian updating mechanism. ► The predictive model help to forecast the number of abnormal events in the next time interval given operation characteristics of the process system and accident precursor information. ► Application of the proposed methodology and developed accident model is demonstrated on a gas processing facility using real life plan data.

- **Keywords:** Accident precursors; Process accident model; Predictive model; Bayesian updating

**M.H. Chakrabarti, M. Ali, S. Baroutian, M.Saleem. *Techno-economic comparison between B10 of Eruca sativa L. and other indigenous seed oils in Pakistan*. Pages 165-171.**

*Eruca sativa* L. (known as *taramira* in South Asia) oil biodiesel shows good fuel properties when tested against ASTM D 6751 standard. Environmental performance of taramira oil B10 (10% (v/v) biodiesel blends with mineral diesel fuel, which is based upon the target set by the Government of Pakistan for 2025) in terms of engine exhaust emissions of CO<sub>2</sub>, CO, SO<sub>2</sub>, NO<sub>x</sub> and PM<sub>10</sub> is compared with jatropha, castor and canola oil B10 fuels and found to be better. However, its calorific value is low thus resulting in poor engine performance in comparison to other B10 fuels. In addition, due to the high cost of taramira oil at present, it is not economical to produce in comparison to jatropha biodiesel. Study suggested that these drawbacks may be circumvented by growing taramira plants on large scale on marginal lands across South Asian countries and conducting further research to increase its calorific value. **Research highlights:** ▶ Environmental emissions of taramira B10 are less than jatropha and castor B10 fuels. ▶ Engine performance of taramira B10 can be improved by increasing calorific value. ▶ Cost of taramira biodiesel can be reduced by growing the plant in marginal lands. ▶ Taramira biodiesel is easy to produce and can bring plenty of benefits for Pakistan. ▶ Jatropha biodiesel is also suggested as a feasible fuel for Pakistan and South Asia.

- **Keywords:** B10; Taramira; High speed diesel (HSD) fuel; Castor; Jatropha

**Alex Souza Ferreira, Marcelo Borges Mansur. *Statistical analysis of the spray roasting operation for the production of high quality Fe<sub>2</sub>O<sub>3</sub> from steel pickling liquors. Pages 172-178.***

Statistical tools were used to analyse the spray roasting operation so as to identify the main operating variables for the production of commercial value iron oxide (Fe<sub>2</sub>O<sub>3</sub>) by pyrohydrolysis from steel pickling liquors. The study was carried out using a 2<sup>4</sup> factorial design of experiments and the effects of the following variables were investigated based on large scale experimental data: temperature, liquor feed flow rate, pressure and feed air/COG (coke oven gas) ratio. The quality of Fe<sub>2</sub>O<sub>3</sub> was evaluated according to the contents of Cl, Fe, Si, Mn and H<sub>2</sub>O, as well as pH and granulometry. For the conditions investigated, the major influencing variables were temperature and feed flow rate; in fact, commercial value Fe<sub>2</sub>O<sub>3</sub> was obtained solely at higher evaluated levels of temperature and flow rate. The contents of Fe, Si and Mn in the Fe<sub>2</sub>O<sub>3</sub> were affected by the content of respective species in the feed liquor, which in turn depends on the type of steel treated in the pickling line. Simple statistical models were proposed to describe some Fe<sub>2</sub>O<sub>3</sub> characteristics. Before this study, only 10% of the Fe<sub>2</sub>O<sub>3</sub> produced at USIMINAS was commercialized, due mainly to the high content of chloride (approximately 0.45%, w/w). Today, all oxide produced meets quality requirements. **Research highlights:** ▶ A large-scale pyrohydrolysis process was evaluated statistically. ▶ Temperature and feed flow rate were found the major influencing factors. ▶ Simple statistical models valid at industrial scale were proposed. ▶ Production efficiency was improved and environmental pollution reduced considerably. ▶ Commercial value Fe<sub>2</sub>O<sub>3</sub> powder from the effluent of steel pickling line was obtained.

- **Keywords:** HCl regeneration; Pyrohydrolysis; Iron oxide; Spray roaster; Statistical tools

**Wenbin Xu, Xiaobin Li, Qiusheng Zhou, Zhihong Peng, Guihua Liu, Tianguai Qi. *Remediation of chromite ore processing residue by hydrothermal process with starch. Pages 179-185.***

Hydrothermal remediation (HR) of chromite ore processing residue (COPR) was studied using starch as a reducing agent. X-ray powder diffraction (XRPD) analysis and the Toxicity Characteristic Leaching Procedure (TCLP) tests were used to evaluate the mineralogical changes of the untreated and treated COPR and the remediation effectiveness of COPR, respectively. The influencing factors for the reduction rate of Cr(VI) in COPR were investigated. The findings indicate that reaction temperature (T),

reaction time ( $t$ ), stoichiometric ratio of starch to Cr(VI) ( $X$ ) and sulfuric acid dosage ( $\text{mol-H}^+/\text{kg-COPR}$ ) are the main factors, whereas liquid–solid mass ratio ( $L/S$ ) is the minor one. The results obtained from HR by starch ( $X = 0.375$ ) with  $\text{H}^+$  dosage of  $10.80 \text{ mol/kg-COPR}$  at  $453.15 \text{ K}$  for  $120 \text{ min}$  prove effective in meeting the TCLP regulatory limits of China Environmental Protection Agency (CEPA), and all the Cr(VI)-bearing minerals in COPR are completely destabilized. Compared with the room-temperature hydro-remediation (RTHR), reduction of Cr(VI) in COPR is complete by HR process, and the consumed dosage of starch is much less. Results also suggest that brownmillerite is the last completely destabilized Cr(VI)-bearing mineral and its complete destabilization is the key to the full success of the remediation of COPR. **Research highlights:** ►Hydrothermal remediation of COPR was presented for the first time. ►Hydrothermal reduction of Cr(VI) in COPR using starch is extremely effective. ►The destabilization of brownmillerite is the key to the full remediation of COPR. ►The reducing agent of starch is abundant, cheap and renewable.

- **Keywords:** Chromite ore processing residue (COPR); Starch; Hydrothermal remediation; Hexavalent chromium; X-ray powder diffraction (XRPD)

**Gaik Tin Ang, Geik Hoon Toh, Mohamad Zailani Abu Bakar, Ahmad Zuhairi Abdullah, Mohd Roslee Othman. *High sensitivity and fast response SnO<sub>2</sub> and La-SnO<sub>2</sub> catalytic pellet sensors in detecting volatile organic compounds.* Pages 186-192.**

The characteristic and effectiveness of pure and modified tin dioxide catalytic pellets as volatile organic compound sensors are discussed. The pure and La-doped SnO<sub>2</sub> thick film sensor pellets exhibited highest sensitivity to ethanol, methanol and acetone vapour at sensing temperature  $300 \text{ }^\circ\text{C}$ . The highest sensitivity towards  $500 \text{ ppm}$  of ethanol, acetone and methanol was achieved by  $5 \text{ at.}\%$  of La-doped SnO<sub>2</sub> with values of  $\sim 57$ ,  $\sim 55$  and  $\sim 59$ , respectively. The enhancement of the sensitivity of La-doped SnO<sub>2</sub> can be explained by the increase of surface areas; decrease of crystallites sizes and the basicity of the lanthanum dopants. The response times for the developed sensors were about  $13\text{--}15 \text{ s}$  for both pure SnO<sub>2</sub> and La-doped SnO<sub>2</sub> illustrated a fast response sensor that could be used as VOC sensors. **Research highlights:** ►SnO<sub>2</sub> and La-SnO<sub>2</sub> catalytic pellets were developed by using modified sol–gel method. ►The optimum operating temperature was  $300 \text{ }^\circ\text{C}$  for both SnO<sub>2</sub> and La-SnO<sub>2</sub> pellets. ►The response times for both SnO<sub>2</sub> and La-SnO<sub>2</sub> pellets were in the range of  $13\text{--}15 \text{ s}$ . ►The highest sensitivity towards VOCs was achieved by the  $5 \text{ at.}\%$  La-SnO<sub>2</sub> pellet. ►Lanthanum in SnO<sub>2</sub> had increased the pellet's sensitivity in detection of VOCs.

- **Keywords:** Sol–gel; Tin dioxide; Lanthanum; VOCs sensor

**Ali Baradar Khoshfetrat, Hossein Nikakhtari, Mohammad Sadeghifar, Mohammad Shaker Khatibi. *Influence of organic loading and aeration rates on performance of a lab-scale upflow aerated submerged fixed-film bioreactor.* Pages 193-197.**

The effect of organic loading and aeration rates on the performance of a lab-scale upflow aerated submerged fixed-film bioreactor, packed with polypropylene media, was examined in terms of dissolved oxygen (DO) concentration and chemical oxygen demand (COD) removal efficiency using an experimental design technique for a 6-month operation period. The system could handle the organic loadings of  $1\text{--}2.5 \text{ kgCOD/m}^3\text{d}$  with the COD removal efficiency from  $74$  to  $90\%$  regardless of aeration rate for synthetic municipal wastewater. In a low aeration rate of  $4 \text{ l/min}$ , increasing organic loadings to the values higher than  $2 \text{ kgCOD/m}^3\text{d}$  resulted in a  $16\%$  decrease in the system performance, most likely due to the DO concentration reduction (about  $57\%$ ). With increasing the aeration rate to  $8 \text{ l/min}$ , however, the COD removal and DO values

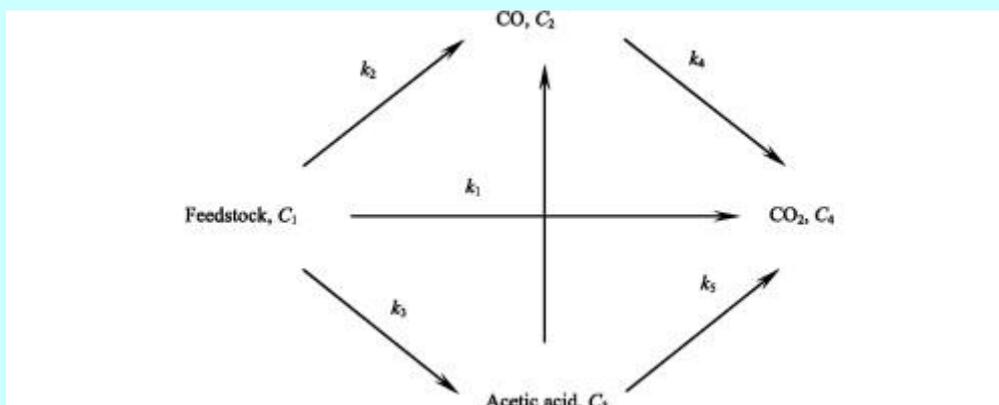
remained constant at about 90% and 5.8 mg/l, respectively, with a slightly decrease to 83% and 4.5 mg/l for the high loading rate of 2.5 kgCOD/m<sup>3</sup>d. The statistical analysis with a 90% confidence interval showed the interaction of main factors on the COD removal is important only when the both main factors of the aeration and loading rates were increased. It is concluded that the system used in the present study could show an acceptable stability and performance during the long-term period particularly at the high airflow rate. **Highlights:** ► There is the limit line for the aeration rate under high organic loading rates in the ASFF system. ► The ASFF system can show an acceptable stability and performance for a long-term operation period particularly at the high airflow rate. ► The DO values are in a good agreement with the COD removal efficiencies. ► Both the loading and the aeration rates as well as their interactions are important for the COD removal efficiencies.

- **Keywords:** Aerated submerged fixed-film (ASFF) system; Organic loading rate; Aeration rate; COD removal; DO concentration; Experimental design

**Bao-chen Cui, Shu-zhi Liu, Fu-yi Cui, Guo-lin Jing, Xian-jun Liu. *Lumped kinetics for supercritical water oxidation of oily sludge.* Pages 198-203.**

Oxidation of oily sludge in supercritical water was studied in batch reactor under the conditions of reaction temperature from 390 to 450 °C, pressure up to 25 MPa, and time from 1 to 10 min. The oily sludge oxidation undergoes a parallel-consecutive reaction pathways, in which it first decomposes to intermediates of aliphatic ketones, aldehydes and carboxylic acids with conjugated double bonds and via low molecular mass organic acids to the final product carbon dioxide. A 4-lump kinetic model was proposed to describe supercritical water oxidation of oily sludge. The experimental data obtained were used to estimate the six kinetic constants and the corresponding activation energies in the model. The model testing results revealed that the model predictions were in good agreement with the experimental results. The model helps us get good insight into the performance of the batch reactor that would be useful for optimization of supercritical water oxidation of oily sludge.

**Graphical abstract**



**Highlights:** ► Oxidation of oily sludge in supercritical water. ► 4-Lump kinetic model. ► Six kinetic constants and the corresponding activation energies in the model. ► The model predictions were in good agreement with the experimental results.

- **Keywords:** Oily sludge; Supercritical water; Oxidation; Lumped kinetics; Reaction pathway