Process Safety and Environmental Protection

Rok 2018, Volume 115

April

Jechan Lee, Insoo Ro, Hyung Ju Kim, Yong Tae Kim, Eilhann E. Kwon, George W. Huber. *Production of renewable C4–C6 monoalcohols from waste biomass-derived carbohydrate via aqueous-phase hydrodeoxygenation over Pt-ReOx/Zr-P*. Pages 2-7.

A bifunctional catalyst, Pt-ReOx supported on zirconium phosphate (Pt-ReOx/Zr-P), was prepared and tested for aqueous-phase hydrodeoxygenation (APHDO) of waste biomass-derived carbohydrate (e.g., sorbitol) to produce C4–C6 monoalcohols such as butanol, pentanol, and hexanol in a high-pressure continuous flow reactor. For steady-state operation, the reaction parameters were optimized to achieve the highest yield of C4–C6 monoalcohols from APHDO of sorbitol. Approximately 30% yield of C4–C6 monoalcohols was reached at optimal reaction conditions (temperature: 453K, pressure: 6.21MPa, weight hourly space velocity (WHSV): 0.16h−1) for APHDO of sorbitol over the Pt-ReOx/Zr-P catalyst. The effect of catalyst support for monoalcohol production was also evaluated by comparison between the Pt-ReOx/Zr-P and carbon supported Pt-ReOx (Pt-ReOx/C) catalysts. The Zr-P supported catalyst exhibited a four times higher yield of C4–C6 monoalcohols than the carbon supported catalyst, suggesting that acid sites atomically separated from metal sites play a crucial role in producing monoalcohols via CO bond cleavage of chemical intermediates produced during APHDO of sorbitol.

- **Keywords:** C4–C6 monoalcohols; Hydrodeoxygenation; Pt-ReOx/Zr-P; Sorbitol; Biofuels

Sonia Mbarki, Artemi Cerdà, Marek Zivcak, Marian Brestic, Mokded Rabhi, Mejid Mezni, Naceur Jedidi, Chedly Abdelly, Jose Antonio Pascual. *Alfalfa crops amended with MSW compost can compensate the effect of salty water irrigation depending on the soil texture*. Pages 8-16.

The availability of water resources of marginal quality such as drainage water or high-salt containing groundwater is turning into an important issue in Tunisia and other countries with scarce water resources. A pot experiment was carried out to evaluate plant production, nutrient content and heavy metal bioaccumulation in agricultural soils amended with MSW compost and irrigated with salty water, by using two different soil textures (clay and sandy). Salt water supply decreased plant dry yield in both soils. Salt stress had significantly reduction in plant biomass in sandy soil compared to those in clay soil (biomass of dry weight is significantly higher in clay soil than those in sandy soil in presence of salt: percentage of growth compared to control was 55% for clay soil and 45% for sandy soil). The application of Municipal Solid Wastes (MSW) Compost increased

significantly alfalfa productivity in both soils (Dry weight is significantly higher in presence of compost: 140% for clay soil and 125% for sandy soil). In non-amended soil, the growth was reduced significantly by salt stress (50% in clay soil, 26% in sandy compared to the soils without salty water application). Plants irrigated with salty water accumulated much more sodium on sandy soil (1.74mmolg−1) than on clay one (0.87mmolg−1 DW). Compost did not reduce sodium accumulation in aerial parts on sandy soil, whereas it slightly reduced it in those grown on clay soil. Zinc (Zn), Copper (Cu), Lead (Pb) and Cadmium (Cd) concentrations showed the same trend for both soil types. They increased statistically significant by salinity to 124–189%, the highest rise was found in Cu concentration on clay soil. The order of metal uptake was: Zn>Cu>Pb>Cd. A higher significant shoot accumulation of heavy metals (up to 305% of the control) was noticed in the presence of compost with no difference between salt-treated and non-treated. MSW compost amendment caused an increase of the studied heavy metals in alfalfa shoots grown that was higher on sandy soils than clay soils. Heavy metals in plants remained lower than phytotoxic level and these level of accumulation did not restrain the enhancement of alfalfa yield. MSW compost at 40tha−1 was convinent to do not attend phytotoxic level. These results suggest that MSW compost compensates, at least partially, the negative effect of salinity on plant growth and nutrient uptake and that it is important to know soil texture to apply compost to remediate salty degraded soils.

- **Keywords:** Salinity; Remediation; Restoration; Desertification; Arid; Irrigation; Crop; Alfalfa

María Dolores Víctor-Ortega, Diego Airado-Rodríguez. *Revalorization of agro-industrial effluents based on gallic acid recovery through a novel anionic resin*. Pages 17-26.

Gallic acid is a natural polyphenol with important biological implications. Nevertheless, gallic acid present in agro-industrial wastewaters is considered like a micropollutant, due to its toxicity above certain levels. Therefore, recovery of gallic acid from these effluents is interesting both from industrial and environmental points of view. Industrially, it is attractive the recovery of polyphenols and the obtainment of added value products. On the other hand, from the environmental point of view it is always welcome the decrease of the contaminant charge of an effluent, which could be, for instance, further reused for irrigation. In this work, the adsorption of gallic acid on a novel anionic resin has been investigated. In first place, thermodynamic studies have been carried out. The adjustment of experimental data to Langmuir, Freundlich and Temkin isotherms has been checked. Results evidence that the Langmuir model offers the best fitting (coefficient of determination, R2=0.9961). Secondly, in an attempt of understanding the kinetic behaviour of the system, the fitting of experimental data to three different kinetic models has been carried out. Namely, pseudo-first order, pseudo-second order and Weber–Morris intraparticle diffusion models have been considered. The highest coefficients of determination (R2) are obtained when a pseudo-second order model is assumed (R2 in the range 0.9840–0.9997). Lately, the evaluation of Gibbs free energy revealed that gallic acid uptake is a spontaneous process for the considered Dowex 21K XLT resin (ΔG°=−11.30kJmol−1). Desorption studies have been also conducted and it has been found that after 120min recovery efficiencies of gallic acid close to 100% are obtained. It has been proven that the resin performance is not altered at least for ten complete adsorption/desorption cycles.

- **Keywords:** Gallic acid; Anionic resin; Agro-industrial wastewater; Adsorption isotherms; Kinetics; Thermodynamic studies

Lucas Tadeu Fuess, Marcelo Zaiat. *Economics of anaerobic digestion for processing sugarcane vinasse: Applying sensitivity analysis to increase process profitability in diversified biogas applications*. Pages 27-37.

Abstract: Anaerobic digestion (AD) is the most suitable approach for managing vinasse, the main wastewater from ethanol production, based on potential biogas applications. However, despite significant improvements in both scientific and technological aspects of the AD of vinasse, specific aspects of the global process require a better understanding to facilitate the scale-up of treatment systems. In this context, this study aimed to identify the main factors that affect the economic performance of the AD of vinasse in sugarcane biorefineries using a techno-economic approach. The energy recovery potential, as well as economic parameters were obtained for different biogas applications. Sensitivity analysis was also used to assess the impacts of different factors on the profitability of the process. Overall, biomethane production economically outperformed electricity generation, regardless of the biorefinery type (autonomous or annexed) and AD layout (single- or two-phase). In turn, investment costs on AD-power plants and product (electricity or biomethane) prices characterized the primary factors governing the economic performance of biogas reuse, regardless of the proposed application. These results confirm the key role of external agents in encouraging the implementation of AD plants in ethanol biorefineries by establishing specific funding for biogas projects, imposing environmental restrictions and/or developing competitive AD-related technological packages.

- **Keywords:** Sugarcane biorefinery; Vinasse management; Biodigestion; Bioenergy recovery; Techno-economic assessment; Sensitivity analysis

Sabry M. Shaheen, Christos D. Tsadilas, Nabeel Khan Niazi, Zeng-Yei Hseu, Yong Sik Ok, Magdi Selim, Jörg Rinklebe. *Impact of biosolid application rates on competitive sorption and distribution coefficients of Cd, Cu, Ni, Pb, and Zn in an Alfisol and an Entisol*. Pages 38-48.

We investigated the effect of biosolid application rates (0 (control), 20 (BS1), 50 (BS2), and 100Mgha−1 (BS3)) on competitive sorption and distribution coefficients (Kd) of Cd, Cu, Ni, Pb, and Zn in an acidic Alfisol and in an alkaline Entisol originating from Greece. Sorption of all metals was stronger in the Entisol than that in the Alfisol. Lead showed the highest Kd followed by Cu, Cd, Zn, and Ni in both soils. Sorption of Cd, Cu, Ni, Pb, and Zn increased significantly with increasing biosolid application rate in the Alfisol. Although sorption of Cd, Ni, Pb and Zn in the Entisol incremented significantly, sorption of Cu decreased significantly with increasing the biosolid application rate compared to control. Sorption of Cd, Cu, Ni, Pb, and Zn enhanced with raising the added metal concentrations under the three rates (BS1, BS2, and BS3) in both soils. The impact of biosolid rates on metal sorption was more pronounced in the Alfisol than in the Entisol. Lead and Cu were more affected by biosolid than Cd, Zn, and Ni in both soils. This study shows that biosolid application enhanced sorption of the studied metals in the Alfisol at the three rates, while it enhanced Cd, Ni, Pb, and Zn sorption in the Entisol at high rates, thereby decreasing their mobilization. However, application of biosolid to the Entisol at the three rates decreased Cu sorption and thus might increase its mobilization.

- **Keywords:** Potentially Toxic elements; Retention; Sewage sludge; Bioavailability; Remediation; Soil groups

Qiyong Xu, Siqi Tang, Jingchen Wang, Jae Hac Ko. *Pyrolysis kinetics of sewage sludge and its biochar characteristics*. Pages 49-56.

In this study, a comprehensive research was conducted for pyrolysis kinetics and biochar characterization with sewage sludge. Pyrolysis kinetics were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using sludge samples divided into four particle size ranges. Also, surface properties and Cu(II) adsorption capacities were determined for biochars produced at 300, 500, 600, 700, and 900°C. Similar thermogravimetric analyzer (TGA) profiles were observed with the tested particle size ranges (<2mm). Using a reaction model, estimated kinetic parameters

indicated that sludge particle size and heating rate affected activation energy. In biochar characterization study, it was observed that the surface chemical functional groups of biochar was reduced with increasing pyrolysis temperature. The maximum BET surface area was measured from biochar produced at 600°C as 92.3m2/g. Also, the biochar produced at 600°C showed the maximum Cu(II) adsorption capacity (146.7mg/g biochar). Electrostatic adsorption was the main mechanism of Cu(II) adsorption for biochar produced at 600°C, but complexation/precipitation was the main mechanism of Cu(II) adsorption for biochar produced at 300°C and 900°C. These adsorption results indicated that the adsorption mechanism and capacity of biochar could be modified by controlling pyrolysis temperature.

- **Keywords:** Sewage sludge; Pyrolysis; Temperature; Adsorption characteristics; Kinetics; Copper

Rock Keey Liew, Wai Lun Nam, Min Yee Chong, Xue Yee Phang, Man Huan Su, Peter Nai Yuh Yek, Nyuk Ling Ma, Chin Kui Cheng, Cheng Tung Chong, Su Shiung Lam. *Oil palm waste: An abundant and promising feedstock for microwave pyrolysis conversion into good quality biochar with potential multi-applications*. Pages 57-69.

Abstract: Oil palm waste (OPW), comprising mainly of empty fruit bunch, mesocarp fiber, frond, trunk, and palm kernel shell generated from palm oil industry, was collected, characterized, and then pyrolyzed to evaluate their potential to be converted into biochar with desirable properties for use in multi-applications. The OPW was detected to have considerable amounts of carbon (43–51wt%) and fixed carbon (30–39wt%), showing potential to be converted into carbon-rich biochar. Microwave pyrolysis of palm kernel shell as the selected OPW produced a biochar with zero sulphur content and high heating value (23–26MJ/kg) that is nearly comparable to conventional coal, thus indicating its potential as an eco-friendly solid fuel. The biochar obtained was also showed low moisture (<3wt%) and ash (3wt%), and a highly porous structure with high BET surface area (210m2/g), indicating the presence of many adsorption sites and thus showing desirable characteristics for potential use as pollutant adsorbent in wastewater treatment, or bio-fertilizer to absorb nutrient and promote plant growth. Our results demonstrate that OPW is a biowaste that shows exceptional promise to be transformed into high-grade biochar rather than simply disposed by landfilling or burned as low-grade fuel in boiler.

- **Keywords:** Oil palm waste; Microwave pyrolysis; Biochar; Adsorbent; Bio-fertilizer; Solid fuel

Nana Ren, Yuanyuan Tang, Mi Li. *Mineral additive enhanced carbon retention and stabilization in sewage sludge-derived biochar*. Pages 70-78.

Biochar is getting increasing attention due to good performance in carbon retention and strong stability, and has been proposed as a promising material for long-term carbon sequestration. In this study, sewage sludge was used as feedstock, and Ca(OH)2 was added to improve carbon stability in biochar through pyrolysis at temperature range of 300–700°C. A systematical analysis was conducted for the sludge-derived biochar with and without Ca(OH)2 addition, with respect to physiochemical properties, molecular structure, and chemical stability. Results indicated an obvious increase of DOC content and carbon retention in biochar when the Ca(OH)2 was added in the sludge feed. The CaCO3 formation and an increase in carbon-containing functional groups were evidenced from X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectra, respectively. Furthermore, the amount of carbon loss decreased over 3 times when H2O2 was added to the biochar as chemical oxidant, showing an obvious increase in carbon

stability with mineral additive. Moreover, the Ca(OH)2 addition also improved the surface area and alkalinity of the biochar, which may enhance the potential application of biochar products. Therefore, from effective increase in carbon retention and biochar stability, a novel idea can be provided for further production of sewage sludge-derived biochar with high carbon sequestration capacity and stability, and will help to further promote the utilization of pyrolysis as a promising strategy for the management of bio-waste.

- **Keywords:** Sewage sludge; Biochar; Ca(OH)2; Carbon retention; Carbon stability

Zhuang Ma, Jiajun Hu, Guodong Yao, Jia Duo, Binbin Jin, Fangming Jin. *Valorization of wheat straw: Rapid reduction of CuO into Cu and production of organic acids under mild hydrothermal conditions*. Pages 79-84.

Resource utilization of biomass waste has attracted considerable attention as an important method to reduce greenhouse gas emissions and also to alleviate the current dependence on fossil fuels. Herein, wheat straw, an abundant agriculture waste, was employed as a green reducing agent for direct reduction of CuO into metallic Cu under mild hydrothermal temperatures. Meanwhile, wheat straw was converted to value-added organic acid such as lactic acid and acetic acid. More than 90% yield of Cu with 40–80mmol/L lactic acid was obtained at 220–250°C for 1–3h. This study provides a promising low-carbon and energy-saving approach for Cu smelting and an alternative route for the chemical production from renewable resources.

- **Keywords:** Wheat straw; Valorization; CuO reduction; Organic acid; Hydrothermal conversion; Smelting

Chandrakant R. Holkar, Saransh S. Jain, Ananda J. Jadhav, Dipak V. Pinjari.. Pages 85-98.

Abstract: Keratin is considered a major ***Valorization of keratin based waste*** animal product. It can be obtained from the sources such as animal feathers, hair, hoof, and nails. Such keratinous materials have high protein content, consisting of at least 17 amino acids which can be used for purposes such as nutrition in animal feed or fertilizers. However, these materials are hardly digestible because of the highly-structured di-sulphide linked polypeptides which must be cleaved before utilization. Degradation of keratin waste can therefore provide an inexpensive source of digestible protein and amino acids. Methods known to degrade keratin include hydrolysis under pressure while using steam, enzymatic hydrolysis or chemical hydrolysis with e.g. base, acid or other reactive agent such as ozone, hydrogen peroxide etc. Current paper is a review of the recent trends in the valorization of the keratinous substances, namely wool, feather and hair. In this review, various upcoming and established techniques to utilize these wastes are studied and their methods, advantages and disadvantages are compiled. A near-complete degradation is deemed possible using certain methods as in the cases of the ionic liquids, the reduction using thiols and tertiary-phosphines, the High Density Steam Flash Explosion, and the enzymatic keratinolysis. The cost and time required however, may make them infeasible. Thus, the optimum method may be chosen based on their product, its value, cost of the process and the time required for its completion.

- **Keywords:** Keratin waste; Wool; Hair; Feather; Reduction; Oxidation; Advanced oxidation processes (AOPs)

Samia Qadeer, Shahid Mahmood, Muzammil Anjum, Noshin Ilyas, Zulfiqar Ali, Azeem Khalid. *Synchronization of lipid-based biofuel production with waste treatment using oleaginous bacteria: A biorefinery concept*. Pages 99-107.

The use of oleaginous bacteria to produce lipid-based biofuels from organic waste is an emerging approach. The present study was designed to isolate oleaginous bacteria capable of growing on food-processing waste to produce bio-fuels on a sustainable basis. About 26 oleaginous bacteria were isolated from natural crude oils using Luria-Bertani (LB) medium under nitrogen-deficient conditions. The GC–MS analysis confirmed the ability of 10 isolates to produce free fatty acids, where oleic acid appeared to be the most recurring compound among the identified fatty acids. The results of aerobic wet digestion (batch mode) showed the potential of the strain KM15 for simultaneous lipid accumulation and waste treatment. Among different types of waste, removal of volatile solids (VS) up to 38.5% and oxidizable organic matter removal (COD-based) up to 48.9% was achieved by strain KM15, while simultaneously showing an accumulation of lipids up to 41.5% in 96h. The degradation efficiency of organic matter was 30.9% and 31% for apple and orange waste after 96h with a lipid accumulation of 21% and 25% respectively. Overall, Bacillus cerus strain KM15 was the most effective strain in the degradation of mango waste and, correspondingly, the production of biolipids from waste. This study illustrates the concept of biorefinery for sustainable waste management and simultaneous production of lipid-based biofuels. The use of waste as the sole source of nutrition could be a key factor in reducing the total production cost of lipid-based bacteriological biorefineries.

- **Keywords:** Biorefinery; Oleaginous bacteria; Food processing waste; Lipids

Jianwen Lu, Jamison Watson, Jianli Zeng, Hugang Li, Zhangbing Zhu, Meng Wang, Yuanhui Zhang, Zhidan Liu. *Biocrude production and heavy metal migration during hydrothermal liquefaction of swine manure*. Pages 108-115.

The production of swine manure has increased constantly with the continuing development of the livestock industry. Swine manure contains a large amount of nutrients, heavy metals, and pathogens, which may cause severe environmental pollution when released into the environment without proper treatment. Hydrothermal liquefaction (HTL) has been recognized as a promising technology to degrade wet biowaste and recovery energy in the form of biocrude oil. This study investigated the effects of the operational parameters, including the temperature (220–370°C), the retention time (0–90min) and the total solid content (TS) (10–30%) on the HTL of swine manure. The volatile solid (VS) removal rate of swine manure reached up to around 90%, whereas the highest biocrude oil yield was 25.58% (based on dry biomass). FT-IR analysis indicated that the biocrude oil mainly consisted of esters, acids, aldehydes and hydrocarbon compounds. The results of elemental distribution showed that over 70% of the heavy metal elements (Zn, Cu, As, Pb and Cd) were accumulated in the solid residue. This study provides a basic depiction of energy recovery and the mitigation of environmental concerns when utilizing swine manure as a feedstock for HTL.

- **Keywords:** Swine manure; Hydrothermal liquefaction; Waste treatment; Biocrude oil; Solid residue; Heavy metals

Duojiao Zhang, Na Duan, Hailin Tian, Cong Lin, Yilin Zhang, Zhidan Liu. *Comparing two enhancing methods for improving kitchen waste anaerobic digestion: Bentonite addition and autoclaved de-oiling pretreatment*. Pages 116-124.

The effects of different enhancement methods, including adding bentonite (1.25%, w/w, wet substrate) and autoclaved de-oiling pretreatment (121°C, 30min), on the anaerobic digestion of kitchen waste (KW) were comparably studied. Mesophilic continuous stirred tank reactors were used under different organic loading rates (OLRs) of 1.11–1.84gVS (volatile solid)L−1d−1 and two different hydraulic retention times (HRTs) (20d and 25d).

In this study, two enhancement methods and extending HRT could prevent volatile fatty acids (VFA) accumulation and obtain a high methane production at low OLR. Owing to the effect of providing nutrients and buffering capacity, the maximum methane yield was obtained with adding bentonite at OLR of 1.39gVSL−1d−1. However, for high OLR (1.84gVSL−1d−1), a decrease of the methane yield and system breakdown occurred due to the accumulation of VFAs. Engineering design and process evaluation of a CSTR biogas plant treating with KW based on the laboratory experiment was stated.

- **Keywords:** Anaerobic digestion; Kitchen waste; Bentonite; Autoclaved de-oiling

Poonam Tirkey, Tanushree Bhattacharya, Sukalyan Chakraborty. *Optimization of fluoride removal from aqueous solution using Jamun (Syzygium cumini) leaf ash*. Pages 125-138.

Removal of fluoride was done by adsorbent prepared from leaves of Syzygium cumini. Adsorbent preparation was done by calcination (500°C) and characterized by multiple physiochemical, and micro-analytical techniques including EDS, FT-IR, TGA and XRD. The adsorbent was mainly composed of calcium carbonate and calcium oxide/hydroxide. Adsorption study revealed a maximum fluoride removal efficiency of 77.8% with uptake capacity 4.56mgg−1, within 60min of contact time from an initial 6mgL−1 fluoride solution with adsorbent dose 6.5gL−1 at pH 6.5 and temperature 300K. Fluoride adsorption data obtained best fitted to the Freundlich isotherm model, signified a multilayer adsorption process. Additionally, the mean calculated adsorption energy (1kJmol−1) from the Dubinin-Radushkevich model suggested a physical adsorption process. The kinetic adsorption data showed agreement to the pseudo-second-order and intraparticle diffusion model, both signifying that the removal of fluoride involved boundary layer effect and intraparticle diffusion. Spontaneous and exothermic nature of the adsorption process was revealed by the thermodynamic parameters. Finally, the adsorbent successfully purified two real water samples contaminated with fluoride. The results suggested that physical adsorption with some effect of electrostatic interaction and anion exchange was also involved in the fluoride adsorption. This study will be useful in designing new calcium based low-cost adsorbent from biological wastes for removing fluoride from contaminated water.

- **Keywords:** Fluoride; Biosorbent; Drinking water; Adsorption equilibrium; Kinetics; Leaf ash