Efficient and clean production of fuels and biofuels: a summary

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This special issue (SI) offers selected papers from the PRES'11 conference, on exergy and process integration methodologies, integrated membranes and fibrous separation. Areas covered by these papers are related to renewables and include: biofineries, bioethanol, biogas, biodiesel, biowaste treatment, carbon and nitrogen trade-offs, decarbonised coal energy system, solar energy integration and CO₂ capture. The manuscripts have been selected to provide insight into various fields related to environmental policies and pollution reduction technologies. The methodologies and applications presented here demonstrate important diversity of technical and policy issues.

Crude oil atmospheric distillation columns in oil refineries consume huge amount of energy taken from crude oil, generating emissions including large amount of CO₂. A group of researchers: Amir Hossein Tarighaleslami from Islamic Azad University, Mahshar, Iran; Mohammad Reza Omidkhah, from Tarbiat Modares University, Tehran, Iran; Ali Ghannadzadeh from University of Toulouse, France; Roozbeh Hosseinzadeh Hesas from University of Malaya, Kuala Lumpur, Malaysia tackled this problem in their work *Thermodynamic evaluation of distillation columns using exergy loss profiles: a case study on the crude oil atmospheric column* (Tarighaleslami et al. 2012). They presented a case study on the crude oil atmospheric distillation

column of Tabriz refinery plant and showed the applicability of exergy loss profiles in thermodynamic examination of retrofit options. Exergy as a comprehensive thermodynamic property has been chosen to evaluate the distillation column thermodynamically (e.g. Benali et al. 2012). The exergy loss profile of the base case, can serve as a scoping tool to pinpoint the source of inefficiencies and has been used for screening from a list of retrofit options proposed by the industry for reducing inefficiencies. The exergy profile identifies the better retrofit option with 17.16 % reduction of exergy losses which finally lead to 3.6 % reduction of fuel consumption. With a significant reduction in primary fuel consumption of the furnace reduced CO₂ emission (Bulatov and Klemesš 2010) for crude oil refining.

The problem of the environmental impact was further dealt with by Lidija Čuček and Jiří Jaromír Klemesš from University of Pannonia, Veszprém, Hungary and Zdravko Kravanja from University of Maribor in Slovenia. Their work *Carbon and nitrogen trade-offs in biomass energy production* (Čuček et al. 2012a) provides an overview of carbon—CFs (Čuček et al. 2012b) and nitrogen footprints—NFs (Bakshi and Singh 2011) concerning their measures and impacts on the ecosystem and human health. The adversarial relationship between them is illustrated by the three biomass energy production applications, which substitute fossil energy production applications: (i) domestic wood combustion where different fossil energy sources (natural gas, coal, and fuel oil) are supplemented, (ii) bioethanol production from corn grain via the dry-grind process, to supplement petrol and (iii) rape methyl ester (RME) production from rape seed oil via catalytic transesterification, to supplement diesel. Life Cycle Assessment (LCA) is applied to assess the CFs and NFs resulting from different energy production applications from “cradle-to-

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grave". The results highlighted that all biomass-derived energy generation processes have lower CFs and higher NFs whilst, on the other hand, fossil energies have higher CFs and lower NFs (Kravanja et al. 2012). It can be seen that when only one FP is considered and evaluated, it most likely leads to inaccurate conclusions and incorrect decisions. Therefore, a complete set or at least more than one FP (also the potential environmental impact) has to be considered for LCA to provide valuable results and conclusions. The additional assessment of social and financial footprints should also be included. This could be done as an extension of the environmental performance strategy map towards a sustainability performance strategy map (De Benedetto and Klemeš 2010).

The majority of current sugarcane mills in Brazil are combined plants, producing both ethanol and sugar; the remaining ones being dedicated only to ethanol production. Otávio Cavalett, Tassia L. Junqueira, Marina O. S. Dias, Charles D. F. Jesus, Paulo E. Mantelatto, Marcelo P. Cunha, Henrique C. J. Franco, Terezinha F. Cardoso, Rubens Maciel Filho, Carlos E. V. Rossell and Antonio Bonomi from CTBE Campinas and Universidade Estadual de Campinas, Brazil present their contribution *Environmental and economic assessment of sugarcane first generation biorefineries in Brazil* (Cavalett et al. 2012). They focus on the technical, environmental and economic impacts of first generation sugarcane processing facilities in Brazil. They use an innovative framework called virtual sugarcane biorefinery. Their optimisation identifies a potential for reducing environmental impacts and improving economic results compared to base scenarios for both combined plants and distilleries. They observed that combined plants diverting more sugarcane juice for sugar production were more profitable, considering the average prices in Brazil for the past 10 years. This favours sugar production. Combined plants present higher IRR for both flexible and fixed plants. World sugar demand is probably not keeping up with increase in ethanol demand. Environmental impact results using the Life Cycle Assessment indicate (Bare 2011) that optimisation technologies in this study have a potential for a significant decrease in the environmental impacts of present and novel sugarcane biorefineries (in both autonomous distilleries and combined plants). Ethanol production in combined plants presented lower environmental impacts (Chouinard-Dussault et al. 2011) in comparison to autonomous distilleries in most of the impact categories evaluated in this study.

Bioethanol produced from lignocellulosic resources is a promising candidate for the replacement of fossil fuels. Philipp Kravanja, Kurt Könighofer, Lorenza Canella, Gerfried Jungmeier and Anton Friedl from Vienna University of Technology and Joanneum Research Graz both in Austria dealt with this issue in their work *Perspectives for the production of bioethanol from wood and straw in*

Austria- technical, economic and ecological aspects (Kravanja et al. 2012). Technical, environmental and economic aspects to produce lignocellulosic ethanol in Austria are considered. Their previous research has been extended from (Kravanja and Friedl 2010, 2011). Concepts using 13 biotechnological processes from straw and softwood were formulated and simulated with the steady state flowsheeting software IPSEpro. The emission of greenhouse gases along the entire bioethanol production chain are compared to two reference systems producing the same amounts of by-products. In all processes, considerable amounts of by-products—electricity, heat, pellets, C5 molasses or biomethane could be obtained from residual biomass. Compared to a reference system driven by fossil energy, greenhouse gas emissions can be reduced by up to 76 %. The production cost of ethanol was found to be between 0.66 and 0.94 €/L of petrol equivalent. The next step appears to be a demonstration scale plant. They concluded that a key issue for lignocellulosic ethanol success in Austria could be the integration into existing infrastructure as the pulp and paper industry in the case softwood or conventional ethanol production in the case of straw.

An increase of agricultural investments in Croatia leads us to the implementation of new technologies and also to an increase of public awareness towards modern agricultural production (Bauer et al. 2010). Renewable energy sources, especially biogas, are becoming more attractive. An assumption of a total biogas potential for the farming sector in Croatia becomes important. One of obstacles is geographical spread and the small size of the Croatian farms. This is the reason why Tomislav Pukšec and Neven Duić from the Faculty of Mechanical Engineering and Naval Architecture University of Zagreb developed their work titled *Economic viability and geographic distribution of centralized biogas plants: case study Croatia* (Pukšec and Duić 2012). Centralised biogas plants are a possible solution for smaller family farms in Croatia. Farmers would have the opportunity to process their manure and get fertilizer substrate and earn money from selling manure on the side. For the largest biogas plants studied about 100,000 t/y of manure- the manure price at the biogas plant location would go up to 7 €/t while manure price on farm's location, for bigger farms, would go up to almost 3 €/t. Higher feed in tariffs would allow more centralised biogas plants and their wider regional distribution since they could retain the same profitability with smaller plant sizes. One of the future issues that needs investigation is transport (Ucekaj et al. 2010). With transport modelling and routing minimal farm sizes participating in the centralised biogas plant could be determined.

A team from State University of Campinas and State University of Maringa in Colombo, both in Brazil, deals with bio-diesel production from vegetable oils. Carla C.

R. S. Rossi, Lúcio Cardozo-Filho and Reginaldo Guirardello provided the contribution titled *Parameter estimation and thermodynamic model fitting for components in mixtures for bio-diesel production* (Rossi et al. 2012). They attempted to fill the information deficiency about parameter values for the models of phase equilibrium, which could lead to incorrect design of the reactors and separation processes and consequently to low efficiency caused by low mass transfer rates due to the presence of heterogeneous mixtures. They described two algorithms for fitting the model and estimating the parameter values in the UNIQUAC and NRTL model for a mixture of vegetable oils and bio-diesel. The first algorithm uses simulated annealing (SA) whilst the other—successive quadratic programming (SQP). In both algorithms, the equilibrium is calculated using the direct global minimisation of the Gibbs free energy. Bio-diesel impact on the environment has been studied by numerous workers. Chouinard-Dussault et al. (2011) presented a new approach for incorporating process-integration tools into life cycle analysis (LCA) for biofuel production. Mata et al. (2011) presented a sustainability analysis for bio-diesel. The complete life cycle was evaluated, comparing alternative raw materials such as microalgae. Elms and El-Halwagi (2010) presented a systematic approach for design and scheduling for bio-diesel production processes. Based on these works the authors presented an optimisation model for maximising profit accounting for greenhouse gas emissions, with economical and environmental evaluation. Also carbon footprint helps with the assessment of the carbon life cycle (Čuček et al. 2012b). The presented two step algorithmic approach was declared by the authors as a useful start to be followed by fine fitting. The fitted parameters are able to reproduce the experimental values more accurately than those obtained in previous works.

Development of clean coal technology expected to mitigate the CO₂ emission level while meeting the rising global energy demands which require highly efficient and economically compelling technology. The UK researchers Kok Siew Ng, Nan Zhang and Jhuma Sadhukhan from The University of Manchester, Manchester and University of Surrey, Guildford presented their research entitled *Decarbonised coal energy system advancement through CO₂ utilisation and polygeneration* (Ng et al. 2012). They started from the observation that integrated gasification combined cycle (IGCC) with carbon capture and storage (CCS) system is highly efficient and cleaner compared to the conventional coal-fired power plant. They proposed an alternative process IGCC scheme, which encompasses the reuse of CO₂ from the flue gas of the gas turbine into syngas generation, followed by methanol synthesis. The system performance has been enhanced through systematic energy integration—see e.g. (Klemeš et al. 2010). It has

been found that the thermodynamic and economic feasibilities have attained significant improvement through suitably balanced polygeneration scheme. The economic potential can be enhanced from negative impact to 317 M€/y (3.6 €/GJ). The results have demonstrated promising prospects of employing CO₂ reuse technology into IGCC system, as an alternative to CCS system. They consider imperative to evaluate the scope for decarbonised polygeneration from fossil fuels as well as system enhancement through process integration (Klemeš et al. 2007; Zhang et al. 2012). The other factors as global energy demand, economic aspects as well as government policies should be taken into consideration (Bulatov and Klemeš 2009; Klemeš and Friedler 2010).

Integration of solar thermal energy can reduce the utility cost and the environmental impact. A proper integration of solar thermal energy is required in order to achieve it. The objective of the work *Integration of solar thermal energy into processes with heat demand* (Nemet et al. 2012) is to maximise the solar thermal energy delivered to the process. It has been delivered by a group from the University of Pannonia in Hungary and the University of Maribor in Slovenia Andreja Nemet, Jiří Jaromír Klemeš and Zdravko Kravanja. The objective of their work is to maximise the solar thermal energy delivered to the process. It is a result of trade-off between the captured solar thermal energy and the magnitude of process demand. Two novel curves are introduced to present this trade-off: (i) the Captured Solar Energy Curve (CSEC), which represents the available amount of heat from solar source and (ii) the Minimal Capture Temperature Curve (MCTC), indicating the minimal temperature making the heat transfer feasible. The crossing point of these two curves presents the minimal temperature of the capture being still sufficiently high to be usable for processes. The capture potential is revealed in full when the CSEC and MCTC are used with the Grand Composite Curve. In Total Site Profiles (Klemeš et al. 2007, 2010) the heat recovery is first maximised and then the CSEC and MCTC tool is applied. The implementation of CSEC and MCTC approach is illustrated by two case studies. The integration of solar thermal energy has a great potential in reducing other utilities, originating from fossil fuels, and their impact on environment, represented by footprints (de Benedetto and Klemeš 2010; Čuček et al. 2012a). The results showed a possibility to obtain targets for the maximal amount of integrated solar thermal energy. A first case study an integration of solar thermal energy to a process is considered. The fossil fuel consumption is reduced by 373 kW, which is the load of solar thermal energy. In the second case study the integrated load of solar thermal energy was 174.4 kW. This reduces the fossil fuel requirement from 738 to 563.6 kW, which is a 23.6 % decrease. The curves are being further developed for

inclusion of economic analysis to become a comprehensive tool for targeting the minimum cost. The variation of the irradiation and the ambient temperature is included in the future work using Time Slices.

In addition to the works of Ng et al. (2012) and Matsuda et al. (2010), the integrated coal gasification combined cycle (IGCC) is studied to achieve higher power generation efficiency than conventional pulverised coal combustion power plants. A Japanese group including Akira Kishimoto, Yasuki, Kansha, Chihiro Fushimi, Atsushi Tsutsumi from The University of Tokyo in Japan present the article *Exergy recuperative CO₂ gas separation in pre-combustion capture* (Kishimoto et al. 2012). IGCC with a CO₂ capture process does not improve power generation efficiency, because CO₂ separation from gas mixtures requires huge amounts of energy (Decamps et al. 2010). For this reason the authors analysed the CO₂ separation process in the pre-combustion capture process using a process simulator (PRO/II) in the steady-state, and proposed a new process using a modularity based on self-heat recuperation (SHR) technology to decrease energy consumption. Pre-combustion capture was applied in the IGCC plant, which involved coal gasification and CO-shift conversion with CO₂ capture (Bandyopadhyay 2011). The results show that the energy consumption for the CO₂ separation process using SHR was decreased by two thirds. This means that the electric generation efficiency can be improved by SHR compared with conventional IGCC with a CO₂ capture process.

Petrochemical industry is highly energy and capital intensive. An interesting work from Paola Bernardo and Gabriele Clarizia, Istituto di Ricerca per la Tecnologia delle Membrane, ITM in Arcavacata di Rende (CS), Italy brings an attempt at the implementation of membrane operations for meeting environmental standards, controlling production cost and final products quality. The paper *Integrated membrane operations in the ethylene oxide production* (Bernardo and Clarizia 2012) investigates the conversion and separation sections of the plant, considering the use of membrane reactors for the separate feeding of the oxidant, membrane contactors for the absorption of ethylene oxide and CO₂ and gas separation membrane units for the hydrocarbon recovery before their recycle to the reactor. Design considerations are provided and the benefits from each membrane operation, as well as from their synergic integration, are outlined with particular attention to environmental impact, raw materials and energy consumption. The impact of industrial production is related to the extraction of resources and to the emission of waste (Diwekar and Shastri 2011). The authors claim that their approach to ethylene oxide manufacture is general and can be followed in all the processes where loss of valuable components, reduction of waste generation and utility consumption are important.

Wastewater effluents from textile industry mainly contain dyes used in the dyeing or printing of textiles yarns or fabrics. Many technologies can be adopted for dye removal from wastewater, among others biological treatments based on activated sludge, adsorption on activated carbon or membrane processes. None of these methods is suitable for all classes of dyes; treatment plants of great dimensions and difficult handling can be required, while cost can be prohibitive. Franco Ferrero and Monica Periolatto from Politecnico di Torino in Italy presented an extension of their previous work (Ferrero and Periolatto 2011) entitled in this case *Functionalized fibrous materials for the removal of dyes* (Ferrero and Periolatto 2012). They performed dye adsorption on low cost fibrous cellulose materials, submitted to a cationisation process using a quaternary ammonium reagent. These materials were characterised by FTIR-ATR spectroscopy, while the treatment efficiency was investigated through exhaustion and kinetic adsorption tests towards anionic and cationic dyes. The regeneration tests by bleaching show that regenerated material maintained good adsorption power. However, recently Hebeish et al. (2011) proposed the cationisation of sawdust for removal of direct dye. Further laboratory investigation is needed before proceeding to scale-up to a pilot plant. The proposed process seems promising; but the cost of the cationisation should be evaluated and minimised.

Conventional polymers are made of crude oil components through chemical polymerisation. The authors from Austria Michaela Titz, Karl-Heinz Kettl, Khurram Shazhad, Martin Koller, Hans Schnitzer, and Michael Narodslawsky from Graz University of Technology in Austria present the paper *Process optimization for efficient bio-mediated PHA production from animal-based waste streams* (Titz et al. 2012) reporting the achievements of the project ANIMPOL- to produce biopolymers by converting lipids into polyhydroxyalkanoates (PHA) in a novel process scheme in order to reduce dependence on crude oil and decrease greenhouse gas emissions. Waste streams from slaughtering cattle are used as substrate material. Lipids from rendering are used in this process scheme for biodiesel production. Slaughtering waste streams may also be hydrolysed to achieve higher lipid yield. Biodiesel then is separated into a high and low quality fraction. High quality biodiesel is for sale as fuel and the low quality one is used for PHA production as carbon source. Selected offal material is used for acid hydrolysis and is a source of organic nitrogen and carbon source for PHA-free biomass with high production rate in fermentation process. Nitrogen is a limiting factor to control PHA production during the fermentation process. It is available for bacterial growth from hydrolysed waste streams and as added separately as NH₄OH solution. Selected microbial strains are used to

produce PHA. The process design should minimise waste streams and energy losses through cleaner production. Ecological evaluation of the process design can be done by footprint assessment (Čuček et al. 2012b) and by sustainable process index methodology (Niederl-Schimidinger and Narodoslawsky, 2008).

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