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New perspectives for green and sustainable chemistry and engineering: Approaches from sustainable resource and energy use, management, and transformation.

Special Volume. Introduction.

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Abstract

Chemicals are ubiquitous in everyday activities. Their widespread presence provides benefits to societies' wellbeing, but can have some deleterious effects. To counteract such effect, green engineering and sustainable assessment in industrial processes have been gathering momentum in the last thirty years. Green chemistry, green engineering, eco-efficiency, and sustainability are becoming a necessity for assessing and managing products and processes in the chemical industry. This special volume presents fourteen articles related to sustainable resource and energy use (five articles), circular economy (one article), cleaner production and sustainable process assessment (five article), and innovation in chemical products (three articles). Green and sustainable chemistry, as well as sustainable chemical engineering and renewable energy sources are required to foster and consolidate a transition towards more sustainable societies. This special volume present current trends in chemistry and chemical engineering, such as sustainable resource and energy use, circular economy, cleaner production and sustainable process assessment, and innovation in chemical products. This special volume provides insights in this direction and complementing other efforts towards such transition.

1. Introduction

Chemicals are ubiquitous in everyday activities. The chemical industry has generated considerable wealth and economic growth during the last two centuries (Arora et al. 1998). The Centre for Industry from the University of York reported, for 2013 and 2014, total sales of chemicals of 3.57 and 3.56 trillion US dollars for 2011 and 2014 respectively; located in China, Europe, rest of Asia and North America, these regions represent 82.3% and 76.5% of total sales for 2011 and 2014 (Healthon 2015; Lozano et al. 2016). While the top 50 worldwide chemical companies had sales of 961 and 775 billion US dollars in 2014 and 2015 respectively; though there is a sales decrease of 10.8%, profits actually increased for 2015 with a value of 96.7 billion US dollars representing an increment of 15.1% (Tullo 2015).

Innovation in the chemical industry has been foundation for its evolution highlighted in the centennial anniversary of the American Institute of Chemical Engineers a list of 100 market innovations related to chemicals (Chemical Engineering Progress 2008). A comprehensive and detailed account for the evolution of the international chemical industry, based on scientific breakthroughs during the 19th century and continuing with innovation in the 20th century, is presented by Aftalion (2001).There have been many examples of such innovations, such as in the energy, chemicals, and process sectors (including thermal cracking of heavy oil to produce gasoline, synthetic jet engine lubricants, high energy lithium batteries, anaerobic bioreactors for cleaning up wastewater in the production of terephthalic acid), and in products (e.g. Teflon and polycarbonates). Such innovations have also been fostered by political, social, and public policy support (Horstmeyer 1998; Arora et al. 1998).

The widespread presence of chemicals provides benefits to societies' wellbeing, but can also have some deleterious effects. To counteract such effects, green engineering and sustainable assessment in industrial processes have been gathering momentum in the last thirty years. The European Chemical Industry Council (CEFIC) made a clear commitment towards sustainability across the value chain (CEFIC 2015) and the World Business Council for Sustainable Development (WBCSD) has a specific project for chemicals where life cycle metrics, and social life metrics for chemicals have been established (WBCSD 2015; WBCSD 2014; WBCSD 2016).

Green chemistry, green engineering, eco-efficiency, and sustainability are becoming a necessity for assessing and managing products and processes in the chemical industry. Green chemistry can be used as a basis for assessing chemical processes in their early conceptual and design stages (Anastas & Warner 1998). Green engineering can help in selecting appropriate chemical processes that can help modulate decision making (Anastas & Zimmerman 2003). Eco-efficiency can help evaluate environmental and economic issues for goods and services in businesses (OECD 1998; Verfaillie & Bidwell 2000). There are quite a few examples of application of the deliberate drive to measure progress towards more sustainable chemical processes. The Institute of Chemical Engineers from the United Kingdom has a set of sustainability metrics for assessing a process (IChemE 2002). The chemical company BASF has applied eco-efficiency and sustainability metrics to assess their processes and products (Saling et al. 2002; Bradlee et al. 2009; BASF 2015). A similar concept, cleaner production, has been used in preventing leaks and redesigning processes based on resources efficiency (UNIDO 2017).

Not surprisingly, the progress on reducing the footprint of the chemical industry has been in areas that are key to the production of chemicals and their sustainability: sustainable energy and resources, circular economy, cleaner production and sustainable process assessment, and innovation in chemical products.

An important element for the chemical industry is its energy use. Energy is a key a factor for production, in the same terms as capital and labor. Oil, Coal, and Natural gas consumption for 2015 (BP 2016) was 11,306 million metric tonnes of oil equivalent, far larger than iron ore and grains for food. In 2015 worldwide consumption of fossil fuels was 11,306 million tonnes oil equivalent (which includes oil, natural gas, and coal) (BP 2016), which corresponds to 245 million barrels of oil equivalent per day.

Energy has also been linked to economic growth, through fossil fuels since the 18th century, particularly through their substitution of human and animal labour (Ayres & van den Bergh 2005). Energy inputs, as represented by "useful work", meaning the product of energy by conversion efficiency, have promoted development from the onset of the first industrial revolution to the present (Ayres et al. 2003). Energy sources are country specific. Hence, a first stage for transitioning towards a low-carbon economy is the efficient use of energy from fossil fuels.

Some of the fossil fuels are inextricably linked in their manufacture to chemical processing, where a paradigm change is needed related to green and sustainable chemistry. Worldwide chemical markets and economies rely on large materials flows, where energy is embodied (Laitner 2013). "*Since primary energy accounts for a very small fraction of the GDP –around 5 percent – it seems to follow that it cannot be an important factor of production. .....It follows that (1) energy is actually a much more important factor of production than its small cost share would indicate, and (2) that perpetual future growth cannot safely be assumed. A future scenario of shrinking reserves of fossil fuels and an increasingly stringent climate policy, with associated rising energy prices, has very negative implications for economic growth worldwide*." (Ayres et al. 2009). The World Business Council for Sustainable Development has published several reports taking into account Energy and Climate Change, as well as the possible scenarios towards a sustainable path (WBCSD & Corbier, L. Hone, D. Schmitz 2004; WBCSD & Corbier, L. Hone, D. Schmitz 2005). Shutting down the material flow of fossil fuels would bring World economies to a standstill. In this regard energy efficiency forms part of the path towards a low-carbon economy. Considering the commitment to extract as much as possible usable energy from fossil fuels becomes a necessity and can be considered as a mandate.

The European Commission (2011), in its Roadmap to a Resource Efficient Europe, asked to have proper and efficient use of resources, as well as consideration of sustainable production and consumption. For example, the European Union Ecodesign Directive set requirements for energy-related products and according to (Dalhammar et al. 2014) takes into consideration resource efficiency, they analyse advantages and disadvantages when applying the directive, as well as providing recommendations for future actions. The European Ecodesign Directive emphasises the focus on energy rather than on resource efficiency (Bundgaard et al. 2017).

A nascent concept in dealing with resource efficiency is 'circular economy'[1]. The Circular economy is a philosophical stance for changing the way economy is considered, taught and applied (MacArthur et al. 2015; MacArthur 2013). The WBCSD is fostering circular economy as a cluster (Frampton 2016) and identified environmental priorities that promotes a circular economy, along

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[1] It should be noted that the concept of 'circular economy' was first proposed by Leontief (1928) in the late 1920s, but it is until recently that it has been linked to resource efficiency.

with information on global material flow and carbon, water, and land footprints (Ecofys-WBCSD 2017), and the Journal of Industrial Ecology has a special issue dedicated to the concept (Bocken et al. 2017).

Parallel discussions on resource efficiency have taken place around the role in future energy supply and its impact on food availability if crops are used for fuel production, as well as the inherent capital and operating costs involved. Biofuels will help in reducing carbon dioxide emissions and represent an important energy source in future energy supplies (Caspeta et al. 2013). Biomass use is directly linked to markets, i.e. when fossil fuels price increase the outlook for biomass derived chemicals and biofuels appears promising, but when oil prices decrease then biomass use is discouraged by the markets (Quentin Grafton et al. 2012).

Along this line, research has taken place on producing ethanol from biomass or biomass products (such as sucrose) has being done for many years. This has generally occurred through hydrolysis, then fermentation, and further separation, basically as mentioned from glucose, sucrose, starch or cellulose, as can be seen with biorefineries (Kamm et al. 2006). An alternative option is residual biomass gasification rendering a gas containing: carbon monoxide, hydrogen, some methane and carbon dioxide (called synthesis gas or syngas), which can be used as fuel or as raw material for chemicals. A potential technological change uses syngas as raw material, where several acetogenic and methanogenic bacteria produce ethanol and acetate (Vega et al. 1989), instead of the hydrolytic route, with experiments that maximise the ethanol to acetate ratio. The steel company Arcelor-Mittal, which aims to build a facility to produce 53 million litres per year of ethanol from steel manufacturing waste gases (Lane 2015). Upgrading lignocellulosic material to produce value added chemicals can also be achieved (Cheali et al. 2015) presenting strategies for production where economic and sustainability constraints are used to design a biorefinery network where profit is maximised and a sustainability criterion is minimised.

Biomass can be used to produce a vast number of chemical products that can substitute, in many choices, petrochemical compounds. This biomass potential use needs to be linked to resource use efficiency, as presented above. As oil is processed in a refinery to fuels, and chemicals; the "biorefinery" concept is equivalent to an oil refinery because biomass is transformed into various products, ranging from chemicals to biofuels (Kamm et al. 2006). Economic participation in chemicals production from bio-based materials will represent a 22% potential market share for 2025 (Biddy et al. 2016). Bioconversion and outlook for future biorefineries can be used to produce methane an ethanol for transport or heating (Lasure et al. 2004). Algae to produce biofuels is forecasted to represent a biofuel source capable of providing the global demand for transport (Demirbas 2010). Residual biomass has the potential to produce chemicals based on processes with zero waste approach (Arevalo-Gallegos et al. 2017).

Technological advances have taken place on biomass gasification. Some examples include: 1) the assessment of dual fluidised bed systems (Corella et al. 2007; Maniatis 2008; Molino et al. 2016), where heat for the gasification fluidised bed is provided by biomass combustion in a second fluidised bed, balancing the process energy requirements; then gasification products can be used in power systems and thermal processes; 2) an air-steam gasification process simulation, using Aspen Plus and Fortran programming, for a bubbling fluidised bed reactor, using gasification temperature, steam to biomass ratio, and particle size (Beheshti et al. 2015); 3) a simulation of a circulating fluidised bed for biomass gasification using a set of homogeneous and heterogeneous reactions, as well as hydrodynamic bed behaviour (Miao et al. 2013); 4) gasification with steam in an experimental fluidised bed gasifier to produce hydrogen with integrated catalytic adsorption and taking into account the influence on performance of several process variables, concluding that catalyst and adsorbent interaction improves gas heating values increasing hydrogen composition (Khan et al. 2014); and 5) the use of perovskite-type catalysts for steam gasification of a slurry mixture of bio-oil and bio char to maximise hydrogen yield (Yao et al. 2016).

In this sense recycling precious and scarce metals contained in waste electrical and electronic equipment will foster this strategy (Chancerel et al. 2009). Similarly experimental data is needed to design a recycling process for indium in liquid crystal display such experiments varying time, temperature and leaching agent concentration have been done by (Zeng et al. 2015). Operational sustainability metrics for electronic recycling are developed and applied by o a case study for electronics recycling, recommending the metrics during decision making between recycling and landfill option (Atlee & Kirchain 2006).

Part of the technological innovation has been the recent development of ionic liquids. Ionic liquids can be used for lubrication due to their tribological properties (Zhou et al. 2009), and in nanotechnology and surface engineering (Bermúdez et al. 2009). They present a "greener" alternative to standard solvents (Zhang et al. 2008). Technological advances on ionic liquids have included: experiments to obtain solubility data regarding four different ionic liquid compounds (Revelli et al. 2010); solubility for several gases besides CO_2 and modelling based on regular solution theory (Bara et al. 2009); adequate methods for designing ionic liquid molecules to be used for CO_2 capture (Hasib-ur-Rahman et al. 2010); and ionic liquid design for CO_2 capture as well (Zhang et al. 2011). From process design assessment perspective, a tool for bioethanol production from a gasification process; or as new chemical compounds we have the use of ionic liquids, in several applications, from tribology, to CO_2 capture or used as solvent to produce a chemical, with its advantages and possible environmental concerns.

This special volume presents fourteen articles related to sustainable resource and energy use (five articles), circular economy (one article), cleaner production and sustainable process assessment (five article), and innovation in chemical products (three articles).

2. Discussion of the articles in the Special Volume

Mazziotti et al. (in this volume) assessed Best Available Technologies (BAT) considering their energy efficiency. These technologies correspond to Italy's industrial sector with a high-energy intensity, such as iron and steel production, refineries for oil and gas, and large combustion power plants. The authors conclude that the facilities analysed have improved their efficiency, some facilities have done it replacing their processes, but there is still room for further improvement in energy efficiency for these Italian industrial sectors.

Gabaldon-Estevan et al. (in this volume) studied a process change to improve energy efficiency using a dry manufacturing path for ceramic tiles renders a lower energy and water consumption for the process. The importance lies in modifying the dry solid processing where a tile is produced of similar quality to the wet path, since the final product must be able to supply market demand regarding performance and quality. This implies that water does not need to be evaporated, and thus less energy is needed. This is a similar case when producing cement where there is a dry milling and a wet milling path for preparing the mixture that goes to the cement kilns; in the wet route energy has to be used to dry the wet solid and this implies an amount of around 2,200 kJ/kg of water present in the solid, adding to the energy budget.

Gaviao et al. (in this volume) developed a method to discriminate the most energy efficiency process for a sample of six bioethanol processes in China; based in a combination of Life Cycle Assessment and Data Envelopment Assessment, along a Probabilistic Composition Preferences (CPP) method, their analysis concludes that such methods combination enable better discrimination among the processes.

Magalhães de Medeiros et al. (in this volume) analysed the production of bioethanol through a fermentation route that uses synthesis gas (syngas) instead of the glucose or sucrose routes. They call it a second-generation route. The analysis considers the economic viability and conclude that with a selling price of 706 US $/m³ for ethanol there is a 10% rate of return. Presently[2] in USA the price fluctuates between 396 and 410 US $/m³, while in Europe it is 674 US $/m³. Underlining the importance of market price for the economic viability of bioethanol production.

Hinchliffe et al (in this volume) analysed the review processes, discussing their differences and shortcomings to improve any future review process. Within this article takes into account regulations of the European Union the framework for energy efficiency labelling (European Union 2015). The discussion considers that a consistent review will improve comparability and transparency, but it will imply that the timeline, as well as budgetary constraints need to be considered. The approaches taken for the review process have identified that more time is needed. The authors propose a scoping study (omnibus) prior to selecting a more thorough review process.

Tecchio (in this volume) addressed the concept of circular economy by taking into consideration the resource efficient European roadmap, and the European Union action plan for circular economy, where policy is set up to enhance material use efficiency, and where the frame of reference lies in the following actions: prevention, reuse, recycling and energy recovery as opposed to disposal and landfilling. This represents a paradigm shift for businesses, government and public in general. The author emphasised the framework proposed will help foster sustainable engineering, as well as promote adequate metrics, calculation procedures to mention a few issues. It is with this outlook that a circular economy will set part of the foundations for our future economies.

Saavalainen et al. (in this volume) proposed a selection of sustainability indicators to assess a new process design according to the principles of Green Chemistry. Seven indicators were chosen: 1) Materials efficiency, 2) Waste prevention, 3) Raw materials selection, 4) Product benign by design, 5) Fewer auxiliaries, 6) Energy efficiency, and 7) Risk and hazard management. These indicators allowed decision makers to discriminate between two formic acid production routes. The authors suggest that this type of method should be part of the academic curriculum in higher education institutions.

Scarazzato et al. (in this volume) applied the principles of cleaner production to electroplating industries. The authors concluded that electrodialysis can provide a better way of handling wastewater containing copper, nickel and zinc enhancing processes cleaner production. This is achieved by water reuse, heavy metals recovery, and increasing the electrolytic bath's operational life.

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[2] http://markets.businessinsider.com/commodities/ethanol-price; https://tradingeconomics.com/commodity/ethanol; http://www.nasdaq.com/markets/ethanol.aspx?timeframe=1y; https://www.afdc.energy.gov/fuels/prices.html; http://www.eubia.org/cms/wiki-biomass/biofuels-for-transport/bioethanol/

Li et al. (in this volume) reviewed the widespread use of electronic gadgets and its fleeting life time can generate large amounts of waste, and recovering some of the chemicals elements used is relevant due to environmental impact, toxicity concerns, and material scarcity. The simplified method proposed can provide further insights and proper foundations to recycling e-waste.

Iqbal et al. (in this volume) emphasised that processing marine-derived bioactive compounds is a way to add value to algae and marine by-product streams, arguing that research is being redirected towards safer and natural alternatives, instead of the chemical-based synthetic compounds.

Esfahani et al. (in this volume) presented experimental results where a blend of coal and biomass are gasified to produce a cleaner syngas, and where tar concentration is decreased with the help of a catalyst containing potassium salts. The paper illustrates a typical transition between a technology using coal, a fossil fuel, and biomass (wood) wherein there are opportunities to improve process performance, but that eventually a biomass-based process will evolve and have technical maturity avoiding the use of fossil fuels.

The paper by Rahim et al. (in this volume) provides an analysis regarding the use as lubricants, partly because they can be custom made according to specific needs but also due to its physical and tribological properties. There are still certain concern regarding their environmental impact and sustainability characteristics, but research is an ongoing task that will provide an evolving path for improvement.

Flores-Tlacuahuac et al. (in this volume) sets out a proposal for ionic liquid design methods, coupled with optimization to estimate those ionic liquids with a higher CO_2 solubility, in order to test them in processes that consider CO_2 capture from fossil fuels combustion; stating that designing ionic liquids is strongly linked to the process where they will be used. The authors propose an optimization procedure that considers economic and sustainability issues in its formulation.

Alvarez et al. (in this volume) compared a process where a traditional organic solvent is used, such as toluene, with a process using an ionic liquid. Their analysis, through LCA, is an attractive solution for substituting toluene, especially regarding solvent recovery; however, ionic liquids have a higher toxicity than the standard solvent, and thus, the authors recommend that further research is needed in developing ionic liquids for this type of application.

3. Conclusions

Presently, humanity is at a milestone regarding the intensive use of natural resources and their corresponding transformation through chemistry and industrial chemical processes. Such use is causing imbalances and reaching thresholds where the Earth´s carrying capacity is compromised. Chemicals production is inextricably associated with energy use, like warp and weft in a fabric. In this special volume, the various contributions underline resource and energy efficiency. The European Union has established a policy roadmap that considers resource efficiency. Some European countries have started to substitute coal for renewable energy sources that will need an advanced set of materials, considering the appropriate use of scarce ones, thoroughly linked with sustainable chemical processes. Green and sustainable chemistry, as well as sustainable chemical engineering and renewable energy sources are required to foster and consolidate the transition. (Leontief 1928). The papers in this volume provide insights in this direction, complementing other efforts towards achieving more sustainable societies.

Our planet is finite; it is a closed system for material resources hence the need to use them sensibly, but an open one for energy having the opportunity to harvest the sun's energy output.

The present generation of humans owes this important decision to future generations, there is a moral mandate to modify the "business as usual" stance, and engaged in a sustainable manner to do business, as well as provide education for the future professionals, and the population in general.

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