Challenges and Directions for Green Chemical Engineering—Role of Nanoscale Materials

Challenges and Directions for Green and Sustainable Chemical Engineering

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Role of Nanoscale Materials

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Andrew Livingston,[1,*] Bernhardt L. Trout,[2] Istvan T. Horvath,[3] Martin D. Johnson,[4] Luigi Vaccaro,[5] Joaquin Coronas,[6] Callie W. Babbitt,[7] Xiangliang Zhang,[8] Thalappil Pradeep,[9] Enrico Drioli,[10] John D. Hayler,[11] Kam C. Tam,[12] C. Oliver Kappe,[13,14] Anthony G. Fane,[15,16] Gyorgy Szekely[17,18,*]

[1] Barrer Centre, Department of Chemical Engineering, Imperial College London, London, United Kingdom
[2] Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States
[3] Department of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
[4] Small Molecule Design and Development, Eli Lilly and Company, Lilly Research Laboratory, Indianapolis, Indiana 48525, United States
[5] Laboratory of Green S.O.C., Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto, 8-06123 Perugia, Italy
[6] Chemical and Environmental Engineering Department, Instituto de Nanociencia de Aragón (INA) and Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC, 50018 Zaragoza, Spain
[7] Golisano Institute for Sustainability, Rochester Institute of Technology, 1 Lomb Memorial Drive, Rochester, New York 14623, United States
[8] Machine Intelligence & kNowledge Engineering; Computer, Electrical and Mathematical Science and Engineering Division (CEMSE), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
[9] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India
[10] Institute on Membrane Technology (ITM-CNR), Via P. Bucci 17/C, 1-87030 Rende, Cosenza, Italy
[11] Chemical Development, GlaxoSmithKline, Stevenage, Hertfordshire, SG1 2NY, United Kingdom
[12] Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada
[13] Research Center Pharmaceutical Engineering GmbH (RCPE), Center for Continuous Flow Synthesis and Processing (CC FLOW), Inffeldgasse 13, 8010, Graz, Austria
[14] Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010, Graz, Austria
[15] UNESCO Centre for Membrane Science & Technology, University of New South Wales, Australia
[16] Singapore Membrane Technology Centre, Nanyang Technological University, 637141, Singapore
[17] Advanced Membranes and Porous Materials Center, Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal, 23955-6900, Saudi Arabia
[18] School of Chemical Engineering & Analytical Science, The University of Manchester, The Mill, Sackville street, Manchester, M13 9PL, United Kingdom

* a.livingston@imperial.ac.uk, gyorgy.szekely@kaust.edu.sa

Table of Contents

1. Introduction

Nanotechnology and nanomaterials are among the most significant scientific and industrial research breakthroughs of the 21st century. With the rapid globalization of science, chemists, materials scientists and chemical engineers are synergistically working together worldwide to understand how to manipulate matter for the benefit of humankind. The Sustainable Development Goals set by the United Nations provide a blueprint through which a thriving and more sustainable future can be achieved for all (Figure 1).[1] These goals address the global challenges we face, and most of them are directly affected by chemical manufacturing. Consequently, it is our responsibility to design, manufacture and recycle chemicals, and develop processes, considering sustainability. Although there is a lack of consensus on the detailed meaning of the concept,[2] *sustainable manufacturing*, we take here a working definition by the United States' Environmental Protection Agency (EPA) as the creation of manufactured products through economically-sound processes that minimize negative environmental impacts while conserving energy and natural resources.[3]

Figure 1. The United Nations' Sustainable Development Goals covering 17 ambitions, most of which are impacted by chemical manufacturing. The chemicals, materials and processes developed today will either make or break these ambitions. Reprinted with permission from [1].

There are several emerging areas of nanoscale engineering with great promise for sustainable chemical engineering. Enzymes, Nature's biocatalysts, have outstanding selectivity and activity and facilitate a broad range of chemical transformations under mild reaction conditions. Besides their natural aqueous environment, there is a need for exploring and exploiting enzymes in organic solvents. The work on directed evolution to engineer enzymes earned the 2018 Nobel Prize in Chemistry for Frances Arnold. Enzymes engineered through directed evolution have great potential in the sustainable processing of a wide variety of chemical products, from pharmaceuticals to biomass. In parallel to the advancement of enzyme catalysis, the field of organocatalysis has emerged. Organocatalytic reactions exploit small-molecule enzyme mimics that are robust, safe, sustainable, metal-free and scalable.[4] Further developments in the field of catalysis both at nanoscale and process scale are crucial to advancing sustainability, since more than 90% of chemical engineering processes utilize catalysts globally.[5]

There are a plethora of innovative methodologies, all with the potential to enable sustainable industrial development, on the rise. The World Economic Forum, the International Union of Pure and Applied Chemistry, and the MIT Technology Review have published their own selections of the top 10 emerging technologies improving sustainability.[6,7,8] The unique advantages offered by flow chemistry and flow reactors have already triggered companies to invest in research and development, pilot scale tests, and implementation in production lines. Solvent-free reactive extrusion for mechanochemical synthesis and 3D printing of advanced engineering materials are emerging fields, with implementation and scale-up challenges yet to be solved. For about half-a-century, there has been a race to develop artificial leaves to efficiently mimick photosynthesis, and transforming carbon dioxide into liquid fuel.[9,10] The production of liquefiable hydrocarbons from excess carbon dioxide, water and other sustainable resources such as sunlight will create new opportunities for energy storage. Despite the tremendous efforts, these ideas are in their infancy, and it is essential that the enabling process development keeps pace with the scientific breakthroughs. Speaking about his startup using hydrogen-producing artificial leaves, Nocera lamented that "I did a holy grail of science. Great! That doesn't mean I did a holy grail of technology",[11] highlighting the importance of scale and engineering.

Recent breakthroughs in artificial intelligence (AI), in particular deep-learning and generative adversarial networks, have allowed machines to mimic imagination (Figure 2), which is a big leap toward unsupervised learning.[12] These advanced methodologies have much to offer scientists and engineers working with large databases, albeit suffering from limitations such heavy reliance on quality data. The power of these advancements in AI can only be exploited if research data is reported in a machine-readable manner and managed in online databases accessible to everyone. Most of the research data is mostly reported in image formats, which results in the loss of precise data points. Options for interactive plots are on the rise, and they ought to become mandatary in the near future.

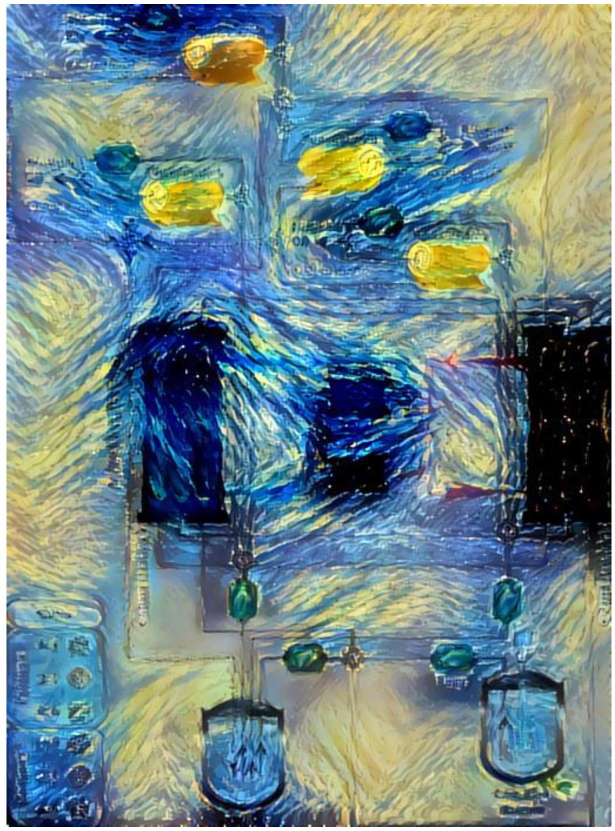

Figure 2. A schematic piping and instrumentation diagram (P&ID) consisting of stirred vessels, pumps and membrane modules, thermostats and adsorption columns reimagined by an artificial intelligence using deep neural networks.[13,14] The weirdly fascinating result is due to the fact that the understanding of the ingested data does not precisely translate into the ability to generate similar data, which is one of the main limitations of AI.

There are numerous technical, engineering and financial challenges associated with developing new, or re-purposing conventional and existing, materials and processes to sustainable alternatives. Thanks to the increasing efforts of the industrial sector, in particular the pharmaceutical manufacturers, the 'sustainability' buzz word has started to manifest in actions. Several companies have explicitly and publicly started using green chemistry and engineering as key drivers, and to innovate around sustainable initiatives. The next subsections and chapters in Sustainable Nanoscale Engineering highlight the sustainability potential of state-of-the-art materials ranging from smart polymers, through 2D materials, to metal-organic frameworks considering both their fabrication and application (Figure 3). Moreover, the potential of continuous-flow processes, life cycle optimization, and artificial intelligence directed towards sustainable nanoscale engineering are also evaluated.

Besides the direct research and development initiatives aiming at sustainable solutions, it is equally important that we incorporate these initiatives into the chemistry, materials science and chemical engineering curricula so as to equip our future generations to tackle challenges with a sustainable mindset. Surely, in the not-too-distant future, we will live in a sustainable world enabled by the fascinating materials, processes and methodologies described in this book.

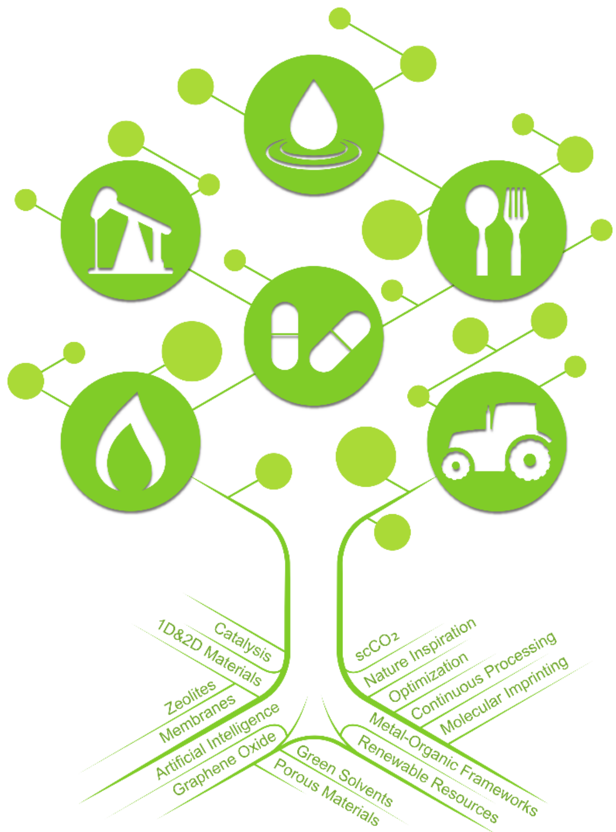

Figure 3. The relationship of industries and the state-of-the-art tools enabling them to be sustainable. Image credit: Ivan D. Gromicho @ KAUST.

2. From Green Chemistry to Sustainable Chemical Engineering

In the Green Chemistry arena, scientists are contributing to creating chemical and technological innovations enabling more sustainable and competitive chemical production. To reach this goal, waste minimization is a priority and the adoption of catalytic protocols are preferred.[15] While much industrial manufacturing may currently still employ classic homogeneous methods,[16] this tendency is mainly based on economic reasons, and therefore on regulations and price/availability of materials. While not always economically sustainable at present, in the future heterogeneous catalytic approaches will become the norm, enabling recovery of the catalytic system so that its durability is preserved over a sufficient number of runs. Accordingly, the design of novel materials for catalysis and suitable platform technologies for their use, plays a pivotal role in the route towards a sustainable chemistry.

Due to their easy separation from the reaction mixture, heterogeneous systems based on metals,[17,18,19] acid[20] or base[21] catalysts have been developed using both organic and inorganic supports. Among the heterogeneous catalytic systems, nanomaterials and metal nanoparticles-based catalysts have been widely studied in the last ten years thanks to their high surface area. In fact, it is well-known now how particle size is related to surface energy which in turn is directly connected with the catalytic activity.

Thanks to this property, several non-noble metal catalyzed processes have been developed[22,23] in order to reduce the consumption of exhaustive metals. In these endeavors, the careful design of the support and the final catalyst has been found to be crucial for the catalytic process, indeed for example, the acid-base properties of inorganic supports can affect the reactivity, or the support can be compromised by the reaction conditions, including temperature or pH. We must also recognize that whilst heterogeneous catalysts should be totally recoverable and recyclable, it can happen that, due to the agitation and mixing used in batch conditions, the materials can be partially crushed which makes their separation difficult.

Meeting this challenge, to reduce attrition and provide thermal and mechanical stability of heterogeneous supported catalysts, flow technology is proving an effective tool.[17,19,20,24,25] In addition, the use of a flow technology has multiple advantages including safety, temperature control, mixing of reagents in two phase systems, easy scale-up and space economy. The use of flow reactors reduces exposure to toxic intermediates or dangerous reagents or additives, allows operation at high temperature and pressure in a safer manner, and guarantees a cleaner reaction mixture minimizing metal leaching of the catalysts with subsequent minimization of purification waste.[17,19,24,25] Moreover, by increasing the number of combined flow reactors (the "numbering-up" approach) it is possible to scale-up processes without any of the common problems found in batch scale-up scenarios. Heterogeneous catalytic systems, based on nanomaterials with high surface energy, are ideal partners for flow technologies which can effectively be useful for the definition of greener processes.

3. The Promise of Continuous Processing and Monitoring

The International Union of Pure and Applied Chemistry (IUPAC) recently released their "Top Ten" List of emerging technologies that will contribute to the sustainability of Planet Earth in the 21st century.[26] Flow chemistry is highlighted as a critical technology to achieve the United Nation's Sustainable Development Goals (SDGs) by 2030, in particular for tackling SDG12: responsible consumption and production.[26,27]

Enhanced heat and mass transfer, precise residence time control, shorter process times, increased safety, reproducibility, better product quality and easy scalability are the main advantages of continuous flow versus conventional batch processing, and reason for the increasing implementation of continuous processes in the fine chemical manufacturing sector.[28,29] A green process needs to be scalable for the greatest environmental impact, and ideally a direct translation from lab- to industrial scale is desirable.[27] Continuous flow processing specifically addresses these needs, and for a large number of processes, distinct advantages over batch processing have been demonstrated in terms of cost, equipment size, energy consumption, waste generation, safety, efficiency and product quality.[27,28,29]

In particular, for the highly regulated manufacturing of pharmaceuticals, there is currently a strong trend towards continuous manufacturing techniques.[28,29,30,31] This ideally entails the development of safe, robust and cost effective processes in the earliest design stages, by merging ideas stemming from both green chemistry and green engineering.[27] A key green engineering concept in this context is the telescoping of multi-step syntheses accompanied by in-line separations to reduce solvent waste.[32,33,34,35] Therefore, virtually all pharma companies and contract manufacturing organizations (CMOs), are currently adopting this technology, as highlighted in a recent survey[31] and review.[36]

Furthermore, continuous flow processing techniques are beginning to have a profound impact on the production of functional materials ranging from quantum dots, nanoparticles and metal organic frameworks (MOFs) to polymers and dyes.[32] Flow chemistry provides robust procedures which not only enable accurate control of the product material's properties. but are also ideally suited to conducting experiments on scale. Importantly, the modular nature of flow and continuous processing equipment facilitates rapid reaction optimization and variation in function of the products.[32]

A more recent trend in continuous processing is the adoption of the "Industry 4.0" ethos, whereby simulation, system integration and the generation of large datasets are key enablers for a greater focus on quality, safety, cost effectiveness and sustainability. Key to this initiative is the real-time acquisition of data for chemical process development and in-process monitoring by process analytical technology (PAT).[37] Several recent reviews have highlighted the successful implementation of PAT within continuous flow environments, for example for enabling feedback loops for process control, automated self-optimization, kinetic model discrimination and parameter estimation.[38] The application of PAT principles to the monitoring of fine chemical synthesis is changing the way in which pharmaceutical processes are evaluated by regulatory authorities. These developments, although so far limited mainly to the pharmaceutical sector, will undoubtedly push the field of flow chemistry further in the years to come.

Continuous manufacturing of pharmaceuticals and the benefits it can provide are long overdue. In its true sense, it incorporates continuous flow with a systems approach to design, integration, and model-based control. While there are now five approved continuous pharmaceutical processes in the US, these all focus on making the final product, as opposed to chemical synthesis, and they are all partial continuous processes. The benefits are immense, including higher quality, reduction of risk of stock-outs, flexibility, lower footprint, substantial savings of both CapEx and OpEx, and, of course, substantial green benefits. Solvent recycle seamlessly fits into continuous processes, and with more efficient energy utilization not to mention reduction of chemical waste and more efficient use of equipment, all interested in green manufacturing should be interested in continuous manufacturing of pharmaceuticals. Given all of the benefits, why has the industry been so slow to adopt? A major reason for this is mental inertia. The batch approach of the industry has led to procedures for process development and manufacturing that need to be modified to move to continuous, in addition to the need for new investments in continuous equipment. As managers embrace the benefits of continuous more and more processes will get submitted and approved, and at one point a critical mass will be achieved leading to the transformation of the industry.

From an industrial perspective, 10 kg day^{-1} is a practical limit for fully continuous processes using mobile skids easily re-arranged in laboratory fume hoods. Continuous formulations are more advanced than continuous synthesis in terms of implementations for marketed products. The US and EU regulatory authorities have approved 5 continuous processing of drug products: Vertex continuous OSD manufacturing,[39] Vertex Symdeko,[40] Janssen's Prezista,[41,42] Lilly,[43] Pfizer.[44] Fully continuous processes for production in laboratory fume hoods have been developed by researchers at MIT, Continuus Pharmaceuticals, Zaiput, Snapdragon, On Demand Pharmaceuticals, among others.[30,45,46] Some of the key differences compared between the continuous processes for drug products and drug substances may have mean residence times and residence time distributions orders of magnitude longer, lower required analytical frequency, decoupling with surge vessels in the middle of the flow train, and a final batch drying step. From a manufacturing perspective, benefits of continuous-flow synthesis have included chemical process safety, containment, elimination of isolations, quality assurance of on-line analytical, and chemistries or process separations not feasible batch. A continuous process developed at the Continuous Drug Substance Manufacturing facility of Eli Lilly and Company earned the 2019 FOYA Process Innovation Category Award.[47]

4. Green and Sustainable Raw Materials for Chemical Manufacturing

Since the invention of the steam and internal combustion engines, the growth in the manufacturing of chemicals and materials from non-renewable resources has exponentially increased. In a similar manner, the automotive (vehicles) and consumer electrical sectors (e.g. refrigerators) have also generated a huge demand for fossil fuels, resulting in the release and accumulation of greenhouse gases. These activities have impacted the environment and society in ways that we could not have imagined or anticipated. The industrial revolution has transformed the manner in which materials are derived and utilized to produce products that improve the lives of mankind. Unfortunately, many of these innovations focus on the transformation of fossil fuels into petrochemicals and engineering materials that have permeated all aspects of human activity. As a consequence, the modern world is now plagued with many new challenges, such as climate change, environmental pollution in oceans, rivers, and lakes. For instance, an increasing problem is the unsustainable practices in the generation and disposal of synthetic polymers, leading to alarming polymer pollution at global scale and significant materials value loss.[48] To mitigate these environmental and economic issues, the development of sustainable polymers with closed-loop life cycles are emerging by shifting from a linear materials economy to circular materials economy (Figure 4).

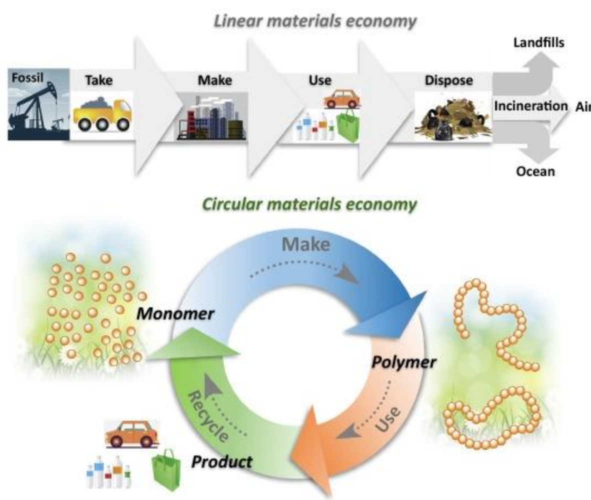

Figure 4. Towards circular materials economy frameworks by the development of sustainable polymers with full chemical recyclability. Reprinted with permission from [48].

The concerns over climate change and global warming have propelled scientists and engineers to explore innovative solutions that minimize their impact on the environment. Hence, sustainable use of technology and materials has become a major consideration for governments, NGOs and the private sectors. Consequently, a cradle-to-grave approach including the environment, and health and safety aspects is necessary when developing and selecting nanomaterials. Owing to the ongoing international debate on how to regulate nanomaterials and the lack of risk assessment data, the market for nanomaterials is somewhat uncertain.[49] Although nanomaterials hold great promise for a wide variety of engineering fields, their long-term environmental and health impacts could significantly undermine those advances. A framework for sustainable nanomaterials selection has been recently proposed with the aim of mitigating any unintended consequences.[50,51]

Research on the utilization of renewable resources in the production of cellulose nanomaterials and lignin from the forest and agriculture biomass has intensified, and new innovations in these sectors have spawned many new opportunities which will contribute to the reduction of greenhouse gases. A major challenge that needs to be addressed is the role of government, academic institutions, industry and non-governmental organizations in finding a common platform that fosters the adoption of these innovations. Should the demands of sustainable nanomaterials increase due to these partnerships, investment in the manufacturing of sustainable nanomaterials will grow rapidly. It is heartening to know that industrial scale applications of cellulose nanocrystals in sectors such as oil and gas, coatings, adhesives, and personal care have been reported. Additionally, the synthesis and production of sustainable nanomaterials has accelerated, and many demonstration plants for the production of cellulose nanocrystal, cellulose nanofibril, and lignin have been commissioned in countries including Canada, USA, Europe, Brazil, China and Japan. Thus, the supply of these materials is now at a scale where it is economical to utilize them in product development.

The increasing rate of carbon dioxide emission to the atmosphere in the second half of the last century has resulted in ever faster expansion of the renewable energy portfolio.[52] Consequently, the amount of fossil resources used for energy applications will decrease, although the utilization of fossil-based energy for the production of renewable energy generating devices must be also replaced with renewable energy. Significantly lower scale production and distribution of gasoline, diesel, and aviation fuel may result in increasing production costs to the point that fossil based carbon fuels and chemicals will become uneconomical. Biomass based carbon resources could are available alternatives, but they can only replace fossil resources successfully if their production processes and facilities are based on green and sustainable chemistry and engineering concepts. Green chemicals, materials, and processes could be developed by applying the definitions and principles of green chemistry[53] and green engineering.[54] The sustainability of green chemicals, materials, and processes could be secured by using resources, including energy, at a rate at which they can be replaced naturally, and the generation of associated wastes should not be faster than the rate of their remediation.[55] Therefore, companies should use sustainable chemistry,[56] ensure reliable biomass production by owning enough land to produce the required amount of biomass, and develop water management systems[57] for their production to avoid flooding or drought. If climate change threatens conventional agricultural practices, sustainable agricultural technologies have to be developed,[58] such as intensification and hydroponics.[59]

5. The Role of Green Solvents in Chemical Manufacturing

Approximately half of all materials used in the manufacture of small molecule active pharmaceutical ingredients (APIs) are organic solvents.[60] The analysis excluded solvent used the preparation and cleaning of, typically, multi-purpose batch reactors. Apart from inclusion in some APIs as solvates, the solvent is an auxiliary material that may be used in all unit operations of a process; and as such it should ideally be "innocuous when used".[61] Classical solvents with few environmental, health and safety (EHS) issues, i.e. that could be considered "greener" are generally oxygen containing hydrocarbons: alcohols, esters and ketones.[62] In addition, many of these solvents either are, or can be derived from, sustainable feedstocks. Their disadvantages are that they are not inert for all chemistries; are volatile, and thus potential atmospheric pollutants; and are not the most powerful solvents for many intermediates and APIs. The converse holds: the stronger (polar aprotic) and more chemically inert (chlorinated, hydrocarbon and ether) solvents generally have the most severe EHS issues. Some solvents are claimed to be green for a single issue, e.g. low volatility or obtained from renewable feedstock, but do not score as "green" in solvents guides when considered holistically.[62,63]

Progress is being made to identify alternative, primarily bio-derived, solvents for the most problematic solvent classes such as polar aprotic solvents: propylene carbonate,[64] cyrene,[65] *N*-butylpyrrolidinone,[66] polarclean.[67] and hydrocarbons.[68] In particular, a number of solvents have been demonstrated as drop-in replacements for polar aprotic solvents in pharmaceutically relevant chemistries. Adoption of new solvents by the pharmaceutical industry is slow with several hurdles to overcome. The time taken to develop a complete understanding of human and/or environmental toxicology means they are considered with caution. The specified limit for the residual amount of a new solvent that is unclassified under ICH guidelines present in an API must be justified.[69] Many polar aprotic replacement solvents have high boiling points making removal by evaporation or recovery/ purification by distillation energy intensive. Solvent recovery for reuse in API manufacture is permissible under ICH, provided the recovered solvent meets the appropriate specification for its intended use. Recovery for other industrial uses is also feasible. The cost of solvent recovery is a consideration for low volume APIs.[70] Ultimately, the ability to recover solvent depends on process design, and while high water miscibility can aid separation by partition, it presents challenges for either solvent recovery or water treatment. In addition, security of supply is a concern. The use of water or alternative solvents, e.g. deep eutectic solvents (DES)[71] and Natural Deep Eutectic Solvents (NADES)[72], prepared from natural products with fewer EHS issues is increasing, and these solvents are showing some surprising reactivity.[73,74]

The application of chemo- and biocatalysis is aligned to green chemistry principles[75] and can be more compatible with the "greener" solvent classes. The use of nano-particulate metal catalysts is emerging in the field of chemo-catalysis and applied to reactions commonly used in API synthesis.[76,77] Such approaches offer the prospect of lower catalyst loadings, catalyst separation and ligand free catalysis which can be advantageous because, while precious metal recovery is achievable, ligands are often lost during work-up. Like adoption of new solvents, the use of nano-particulate catalysts presents some challenges to the industry, especially with concern about exposure to toxic metals during preparation and handling and decontamination of reaction vessels. Replacement of toxic metals with benign alternatives is a long-term green chemistry objective[78] where the use of nanoparticles and organocatalysts could be advantageous. The toxicity profile of any supporting media used in nanoparticle preparation or stabilization, if unknown, presents similar challenges to new solvents if present as a residue in API. Nanotechnology has been tested for materials sequestration, oxidative and/or photo-degradation in waste water treatment and extensively studied in areas of drug delivery and in therapeutic use for some cancers.

6. The Quest for Clean Water

Access to clean water is one of the most important indicators of development. This water has to be affordable to create a meaningful impact on the society. Chemistry of nanomaterials due to their enhanced surface area, confinement of the active nanostructures in nanoscale cages, exposure of specific surfaces with desired geometry for interaction with contaminants, optimum combination of properties such as surface area and electrical conductivity, control of phenomena such as droplet condensation, permeation, etc., have led to the creation of new methods for efficient water purification. Creation of affordable materials for constant release of silver ions[79] is one of the most promising ways to make water microbially safe. Combining the capacity of diverse nanocomposites to scavenge toxic species such as arsenic, lead, and other contaminants along with the above capability can result in affordable, all-inclusive drinking water purifiers that can function without electricity. A critical problem in achieving this is the complex species usually present in drinking water which deposit and cause scaling on high energy surfaces of nanomaterials. Such constant release/adsorbing materials can be synthesized in a simple and effective fashion in water itself, without the use of electrical power. The nanocomposite produced exhibits river sand-like properties, such as higher shear strength in loose and wet forms.[79] The ability to prepare nanostructured compositions at near ambient temperature has wide relevance for adsorption-based water purification. Such properties are even more significant as active nanomaterials do not get into the flowing water, eliminating nanotoxicity concerns. Materials composed of metastable iron oxyhydroxides[80,81] are currently used to supply arsenic-free clean drinking water to about 1000,000 people in India daily, at a cost of US$0.3 per KL, delivered in the kitchen. Translation of such materials to affordable filters across the world could eliminate the arsenic menace, which affects close to 120 million people globally. Extension of such science to other contaminants such as fluoride, uranium, mercury, chromium, etc., can solve drinking water problems across the world in many resource-limited regions. Materials with high electro-adsorption properties have been used to develop capacitive deionization units.[82,83] New technologies using nanostructures have been used to create efficient water harvesters from air.[84], while new nanocomposite structures with graphene are claimed to be able to reduce desalination costs substantially.[85] Nanopores made in MoS_2 nanosheets can produce H_2O_2 efficiently using visible light, causing disinfection of flowing water.[86] While new technologies for clean water are essential, contaminants have to be detected and measured quantitatively at ultra-trace levels. Many nanostructures can effectively perform these functions[87,88], making affordable sensing and removal possible.

7. Membranes for a Greener Future

Innovations in process technology are strategically necessary for realizing Sustainable Industrial Growth, minimizing environmental problems, energy consumption, costs, and increasing productivity and final high quality production lines. The principle and goals of process intensification describe well the actions necessary for reaching these goals.[89,90] It is interesting to emphasize the important contribution that Membrane Engineering is offering today to this strategy.[91,92] In a recent report published in Chemical Engineering News the example of the recent successes of “Made in China” in Chemical Process Technology describe the situation well. Most of the “case studies” reported are in fact related to the introduction of membrane operations in production lines.[93]

Nanofiltration, zeolite membranes, membrane bio reactors, microfiltration, pervaporation, and all pressure driven membrane operations are typical examples of technologies becoming dominant in various fields, from desalination to waste water treatment, from ethanol dewatering to gas purification. For instance, a membrane-assisted process for the conversion of carbon dioxide and methane into synthesis gas to reduce the carbon footprint of high-carbon fossil fuels was developed by Shanghai Advanced Research Institute (SARI) with the support of funds provided by Shell. Recently, Evonik Industries AG and the SINOPEC Beijing Research Institute of the Chemical Industry (BRICI) joined forces to build a process development laboratory for Organic Solvent Nanofiltration (OSN) membrane technology. Evonik stated that new technologies developed at the lab will be marketed to chemical, food, and drug producers in Asia. Recently, the Chinese Academy of Science finished the largest zeolite membrane separation system in the world for dewatering of ethanol with scale of 100,000 tons per annum. Approximately 70% of the membrane plants are employed in petrochemical (38%), power generation (22%), and steel industries (9%), while textiles, paper, food, and mining grasp 17% of the remaining plants.

Progress in utilization of new green solvents in membrane preparation, and in the use of advanced 2D materials including graphene, integrated with the development of emerging membrane operations including membrane distillation, membrane crystallizers, membrane condensers, membrane emulsifiers, offers important opportunities for overcoming existing limits to the traditional Chemical Process Engineering.

The most recent successes of membrane engineering has not been in new membranes but in the development of new membrane systems and of integrated membrane operations. The most interesting and visible case is membrane systems in seawater desalination where membranes systems are today the dominant technology, including in the Gulf and MENA Countries. Further interesting progress may be realized in the next years based on the utilization of graphene and other 2D materials in membranes and mixed matrix membranes production.

The growth of the overall membranes and membrane systems market might be related to the realization of emerging membrane operations including membrane distillation, membrane crystallizers, membrane condensers, membrane emulsifiers, based mainly on the production of hydrophobic microporous or nanoporous membranes serving as membrane contactors. These systems could contribute to realization of a process intensification in chemical processes. In all these operations hydrophobic microporous or nanoporous membranes with specific appropriate characteristic will have to be created, since at present there is no large-scale production at industrial level for these hydrophobic porous membranes.

Membrane technology has a major role to play in sustainable access to clean water for humanity. Our demand for water continues to increase due to population growth and climate change. However, there are limited sources of clean surface waters and supplies need augmentation from alternative 'infinite' sources, such as the oceans and wastewater. The dual membrane processes of ultrafiltration (UF) pretreatment followed by reverse osmosis (RO) purification is now the established platform for seawater desalination and wastewater reclamation; in the latter case the UF membrane could be the separation step in a wastewater membrane bioreactor (MBR). In terms of sustainability criteria, membrane technologies are attractive with potential for modest cost and modest energy demand, resource recovery, low ecological impact, low human health impact and high reliability and resilience. This particularly applies to decentralized systems,[94] favored by the modular nature of membrane systems.

The modest energy demand required for sustainable processing is a potential feature of membranes in the water domain. For example surface water treatment by UF can be achieved by the use of gravity-driven membranes (GDMs) which require very low energy use and generate no chemical residues.[95] Seawater desalination by UF+RO already operates relatively efficiently and there are prospects to almost halve energy demand by combining GDM pretreatment, use of next generation 'ultrapermeable' RO membranes in a staged cascade, and energy recovery from the brine using pressure retarded osmosis (PRO).[96] For wastewater reclamation the next step should be the anaerobic MBR (AnMBR) + RO process, with biogas production providing a net energy benefit for the MBR stage.[97] A feature of these examples is that there is a potential trade-off between capital and operating costs, where a more sustainable operation with lower energy and ecological impact typically requires more initial investment due to lower fluxes (GDM operation) and/or additional stages (PRO). For proper sustainability accounting these additional investments need to be balanced against the externalities.[98] Figure 5, adapted from T. Asano (Stockholm Water Prize, 2001), illustrates how membrane technologies fit into the 'engineered' water cycle. An important feature of this for the future is multiple reuse, which is made possible by sustainable membrane technologies.

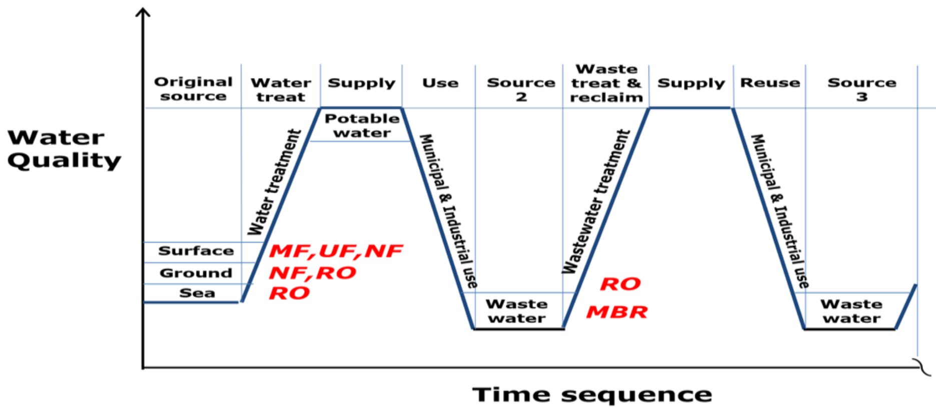

Figure 5. Water quality history for use and reuse – showing the role of membrane technologies.

8. Advanced Porous Materials for Energy-Efficient Processes

Porous materials consist of a solid matrix with interconnected pores. Porous structures are abundant in nature, with crucial functions across various aspects of our lives from biological tissues to rocks, and soils to zeolites. The long and winding road exploring these natural materials has resulted in the exploitation of porosity in advanced engineering materials covering separations, catalysis, sensing, petrochemicals and beyond (Figure 6). Precise control over the order and functionality of porous structures — *via* the utilization of structure-encoded molecular building blocks —enables the fine-tuning of materials for targeted applications.[99] These materials include zeolites, metal−organic frameworks (MOFs), polymers of intrinsic microporosity (PIMs), porous organic polymers (POPs) and covalent organic frameworks (COFs), all of which hold great promise for paradigm shifts in the energy, catalysis, separation and environmental fields. However, the need and challenges for scalable and sustainable synthesis of these materials have been highlighted.[100] Moreover, understanding the synthetic mechanisms, catalyst-assisted synthesis, solvent-free fabrication, process modelling and equipment design are all areas with room for improvement to achieve sustainable porous materials.

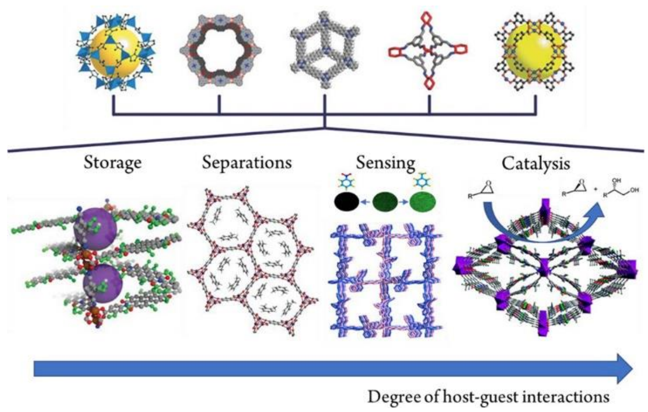

Figure 6. Rational design of porous materials has great potential to pioneer numerous engineering applications that are governed by host−guest interactions. Reproduced with permission from [[100]].

Zeolites are hydrated crystalline aluminosilicates with microporosity. There are more than 230 different zeolite type structures and only a few of them are industrially applied. Most important types of zeolites (FAU, MOR, etc.) have their natural counterpart, even the most applied MFI type structure (silicalite-1 and ZMS-5) has Mutinaite[101] as a counterpart, found in Antarctica years after its discovery in the middle 70's.[102] Thus it can be said that current commercial zeolites are inspired by minerals. Nature inspired synthetic zeolites, and zeolites in turn have inspired the development of several organized porous materials with different chemical composition and properties, such us ordered mesoporous silicas (OMS),[103] octahedral-pentahedral-tetrahedral (OPT) zeolitic materials,[104] metal-organic frameworks (MOFs),[105,106] and covalent organic frameworks (COFs).[107] Zeolites remain irreplaceable in fields requiring high performance (mainly high temperature and presence of moisture and acid gases) and optimum cost such as catalysis, and simultaneously zeolites have open new catalytic routes including those dealing with the transformation of renewable bio-feedstocks into valuable platform compounds.[108,109] However, times are changing and no one knows what the destiny of petrochemistry is, since alternative fuels (H_2, biomethane, simple alcohols) coming from sustainable sources generating mechanical power and electricity are increasingly competing with oil derivative fuels. Of course not only petrochemistry, related to the production of fuels (by FCC, hydrocracking, isomerization, etc.), demands zeolites - other materials (e.g. polymers and fine chemicals)[110] and processes (e.g. separations, pollution abatement and emerging applications)[111] require zeolites too. Zeolite-supported bifunctional catalysts can be used for biomass valorization through the selective hydrodeoxygenation of platform molecules.[112] In this field, there is a need for more research on the rational design of the catalysts for reactions in biomass conversion, and better understanding the synthesis-structure-performance relationships with regards to proximity and site balancing.

MOFs incorporating magnetic nanoparticles are emerging for the capture and energy-efficient triggered release of CO_2 *via* magnetic induction heating,[113] which is called magnetic induction swing adsorption (MISA). The selectivity of MOF-based separation materials can be tuned via molecular building block approach and reticular chemistry, which was demonstrated for natural gas upgrading,[114] and propane/propylene separation.[115] performance A promising class of emerging porous materials is zeolitic imidazolate frameworks (ZIFs) with more than 150 synthesized structures. They are a thermally and chemically stable subclass of MOFs with a great potential for energy-efficient separations.[116] A fluorinated nickel-based MOF was also reported for the energy-efficient removal of water from gas streams. Owing to its hydrolytic stability, it can be easily regenerated by heating to only 105 °C after the dehydration process.[117]

The US Department of Energy's National Energy Technology Laboratory (DOE-NETL) recently reported a research on improving the energy-efficiency of air separation using hollow fiber sorbents in a pressure swing adsorption (PSA) process.[118] The project focused on developing a low-cost technology to produce oxygen for use in coal gasification processes. High permeability and selectivity are required for membrane-based hydrogen separation to achieve sufficient throughput and purity. Polymers of intrinsic microporosity offer solution-processability, structural tunability and mechanical flexibility for gas separation. A series of promising triptycene-based ladder-polymer molecular sieves have been reported for hydrogen purification.[119] H_2S-selective and ultrapermeable glassy amidoxime-functionalized porous polymers were reported for sour gas separation using a ternary feed mixture (with 20% H_2S:20% CO_2:60% CH_4).[120] These membranes demonstrated 2–3 orders of magnitude higher permeability than commercially available competitors did.

9. Artificial Intelligence: A New Dimension in Chemical Engineering

In chemical engineering — from chemical, through materials, to process development, and parallel maintenance and logistics — artificial intelligence (AI) is emerging as a transformative power across the chemical manufacturing enterprise. Artificial Intelligence (AI) has been attracting increasing attention in the chemical engineering community. Recent advances in AI (including the availability of large-volume data, the development of sophisticated machine learning algorithms such as deep neural networks, and the support of powerful computing resources) have revolutionized many domains, one of which is chemical engineering.[121] Here we describe the chemical process as f(x)=y, where x are input variables (experimental parameters) and y is the target output variable to be optimized (e.g., yield, productivity, cost), which allows us to describe how AI has been introduced to chemical engineering, summarized in the following directions.

First, in most cases f(x) is unknown. That is to say how y depends on x is unclear. Machine Learning (ML, a subfield in AI) models are designed to have predictive power to map x to y by approximating the function f(.). Neural networks are popular ML models, which have been proved as general approximators of any non-linear function with appropriate setting of network architecture, and have been used successfully for prediction reaction results.[122,123,124] Data-driven chemical synthesis planning is another new trend, to seek help of machine learning.[125,126] Reaction rules are extracted from large reaction corpora (such as the United States Patent and Trademark Office (USPTO), Reaxys, and SciFinder databases). Machine learning models are trained on selected reactions, and then employed to predict the transformation rule used to produce a molecule.

Second, a key problem in material design and laboratory exploration is to find the optimal set of parameters that lead to a satisfactory result. That is, finding x* that can maximize y=f(x). The traditional trial and error process optimization is cumbersome, takes a lot of time and consumes a lot of chemicals. Even with chemists' expertise in screening a set of predetermined experimental conditions, it is still expensive due to the high number of required experiments. Since f(x) is unknown, it is not feasible to use gradient-based optimization solutions. AI techniques open a new way to address the optimization problem in chemical laboratory studies. For example, using genetic algorithms, simulated annealing and direct search based on simplex to search the optimal parameter setting in recent work.[127,128] Also, the searching process can be integrated with the prediction model to provide a comprehensive materials discovery system using active learning.[129]

Third, a direction of study explores published articles and extracts useful information for understanding chemical concepts and reaction process. The main motivation is the exponential increase in the number of published articles, which reading all relevant papers in a topic less and less feasible. With the help of the branch of AI known as Natural Language Processing techniques, computers can be used to assimilate the information contained in these research papers. An example is their use to automatically extract synthesis information and trends from zeolite journal articles.[130]

10. The Drawback of Nanomaterials

The rapid pace of innovation in the nanotechnology sector has led to a new sustainability conundrum. On one hand, engineered nanomaterials offer novel chemical and physical properties that enhance the performance of renewable energy generation and storage systems, environmental remediation technologies, and agricultural and health applications. These benefits will likely translate into reduced fossil fuel consumption, greater potential for carbon mitigation and sequestration, and improved technologies for treating air, water, and soil emissions. On the other hand, the same unique properties that make nanomaterials attractive for so many applications also introduce the potential for unanticipated environmental, economic, and social risks.[131] Ensuring that the potential benefits of nanotechnology use outweigh possible impacts requires a more proactive approach to nanoscale design and manufacturing and overall systems analyses.

Some sustainability risks stem from the potential for nanomaterials to be released during processes associated with their manufacturing, use, or decommissioning. Once released to the natural environment, the ultimate transport, transformation, fate, and resulting ecological impacts of these materials are still poorly understood.[132] These impacts may include aquatic ecotoxicity in freshwater or benthic organisms, which is widely studied, albeit through highly variable methodological approaches.[133] At a broader scale, long-term accumulation of nanomaterials in nature may result in impacts to ecosystem function and services. While these risks are still uncertain, early research suggests that they may include increased predation, decreased population growth and reproduction, and shifts in underlying microbial ecology underpinning ecosystem processes.[134,135,136] While direct risks from nanomaterial release have raised significant scientific and public attention, the broader perspective on environmental impacts of nanotechnology is more complex and challenging to understand.

Ongoing nanomaterial design and development must take into consideration the entire life cycle of these materials, and the potential for environmental harm at this holistic scale. In particular, nanoscale material synthesis and nano-enabled manufacturing are critical points for environmental improvement. Carbon based nanomaterials like carbon nanotubes (CNTs), fullerenes (e.g., C60), and graphene have extremely energy intense manufacturing processes.[137] As a point of comparison, one kilogram of functionalized fullerene C60-PCBM has an “embodied energy” of 65 GJ,[138] which is over 300 times greater than that of aluminum produced from virgin resources (~200 MJ/kg). Even though these fullerene derivatives are only used in extremely small amounts in photovoltaic cells, their enormous energy footprint contributes almost 20% of the solar cell’s own life cycle energy footprint.[139]

Several life cycle assessment (LCA) studies have modeled the "cradle-to-grave" environmental impact of nanomaterial production, use, and disposal and have have generally shown that the downstream impacts of nanomaterial release are often dwarfed by much greater energy, emission, and ecotoxicity impacts stemming from upstream processing. For nanomaterials characterized by low yields and high energy intensity, the key life cycle impact driver is typically energy use directly in the synthesis process or further upstream in precursor preparation. In the case of titania nanoparticle production, life cycle impact increased proportionally to the complexity of organic precursors as compared to simple inorganic precursors.[140] Energy intensity of single-walled carbon nanotube production has greater life cycle risks than the potential release of these materials into the environment, even under extreme scenarios.[141] Upstream processing steps often require significant electricity inputs, which come from fossil fuel combustion, a process that emits greenhouse gases, heavy metals, and other air toxics. Nanomaterial production also causes environmental impacts due to acid mine drainage and metals emissions during mining operations, particularly for metallic materials like nano-silver.[142] Nanotechnology often has exacting technical specifications for materials used, resulting in significant organic solvent use during separation, cleaning, and purification processes.[138] In the limited literature yet to examine metal-organic frameworks and zeolite membranes, solvent use was identified as the key environmental impact driver for several processing routes.[143,144] These findings collectively underscore the importance of greener nanoscale manufacturing routes, wherein increased yield, reduced energy demand, solvent recycling, and green solvents are critical factors to minimize environmental impacts of nanotechnology.

However, when considering the environmental tradeoffs from nanomaterial manufacturing, it is essential to evaluate nano-enabled technology adoption through a holistic lens.[51] Modeling life cycle energy demand or ecotoxciity of manufacturing only begin to capture how material tradeoffs may ripple out to broader techno-ecological scales. Consider the use of nanotechnology in renewable energy systems like solar photovoltaics. Nano-enabled improvements could increase efficiency, reduce costs, or extend system lifetimes, all of which may further catalyze more adoption of solar technology. Greater deployment of renewable energy may in turn displace fossil fuel use, thereby reducing heavy metal and greenhouse gas emissions associated with extracting and combusting coal and natural gas. Considering both benefits and costs of nanotechnology has the potential to point out opportunities where use of these materials can lead to the greatest overall system result.[145146147] Unfortunately, life cycle thinking is rarely mentioned, much less applied in conjunction with research devoted to creating, characterizing, and integrating novel nanomaterials, and many of these technologies have yet to be fully evaluated via a life cycle assessment. To realize the full sustainability benefits of nanotechnology, future research must reflect greater integration of technological innovation with environmental assessment, eco-design, and green manufacturing.

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