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# Applications of Green Chemistry for Sustainable Future

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**ABSTRACT:** For more than three decades, Green Chemistry has provided a framework for chemists and chemical engineers to do their part in contributing to the broad scope of global sustainability. American Chemical Society journals are a great venue for these scientists to share their latest results and provide a resource to the chemistry community and beyond for understanding current problems and envisioning solutions. We believe this is an opportune time to highlight some of the leading articles on the broad theme of Green Chemistry being published today through a Virtual Issue of selected works from nine ACS chemistry and engineering journals.

**KEYWORDS-**green,chemistry,chemical,sustainability,global,future

## I. INTRODUCTION

The inception of this Virtual Issue is no coincidence. We have timed it to the 2021 Green Chemistry & Engineering Conference taking place virtually June 14–June 18. Now celebrating its 25th edition, we have seen progress toward more sustainable chemistries being showcased and celebrated at each GC&E conference. (1) The theme of this year’s meeting, “Sustainable Production to Advance the Circular Economy”, is particularly bold. It highlights the recognition that contributions must take into account a systems approach to reducing environmental impact through intentional design of chemical products, not just considering how raw materials are sourced and in the manufacture and use of industrial and consumer goods but also how these materials and goods may be reused, recycled, or upcycled. The embrace of life-cycle thinking as a goal among the Green Chemistry community comes at the backdrop of the realization of limited resources and a climate crisis the likes of which most of us still fail to fully comprehend. We believe these selected articles are stepping stones on the pathway to advance closed-loop economies while still serving as models for innovation at a fundamental level within their respective chemistry subdisciplines.

The drive for efficiency in organic synthesis merges the best of the idealisms of the Enlightenment and the Renaissance. Certainly, there is a premium on rationalism, with an aspiration of mechanistically sound reaction design and process development. But at the same time, the aesthetic appeal of the new ideas that culminate in the advances we now see routinely is unmistakable. There is no constraint on curiosity when we consider the boundary conditions of efficient, environmentally benign processes. On the contrary, these considerations spawn new concepts and approaches, ranging from postmodern expansions of photochemistry, reconsideration of seminal thinking about solvation, importation of physical and mechanical phenomena, to reaction development—the creativity born of efficiency considerations now drives major technology innovation in chemistry. The Journal of Organic Chemistry and Organic Letters are delighted to participate in this Virtual Issue with a selection of perspectives, research articles, and letters that highlight just some of the most impactful science in this arena, across a very wide swath of chemical space. Organometallics, a journal with a long-standing history of reporting fundamental advances in organometallic chemistry, catalysis, and materials, has selected contributions to this Virtual Issue that best highlight the diverse nature of this type of organometallic chemistry and that are likely to impact development of more sustainable chemical processes and the transition to a circular economy.

ACS Sustainable Chemistry & Engineering is a world leader in publishing groundbreaking research that addresses the challenges of sustainability, advancing the principles of Green Chemistry and Green Engineering with global reach and impact. Key coverage includes catalysis with emerging feedstocks and synthetic methods for preparing materials and chemicals in a sustainable way to help bring critical innovations from a research setting to commercialization. The journal takes pride in its central role in promoting innovations that will enable the implementation of a circular economy. Industrial & Engineering Chemistry Research publishes many, many papers in the Green Chemistry and sustainability space as these are core considerations in applied chemistry and chemical engineering. The ten articles in this Virtual Issue are just the tip of the iceberg and represent the types of papers readers can find in I&EC Research. We would encourage those interested in the Virtual Issue to browse through other recent issues of the journal, where they

will quickly find other articles aligned with the themes of the conference. Contributions from Environmental Science & Technology and Environmental Science & Technology Letters clearly illustrate the interdisciplinary systems approach that is required to address key environmental challenges that impede sustainability efforts—from remediation of pollution to design of next-generation safer and functional chemicals. Several of the high-impact contributions selected have been the subject of media coverage. Contributions from ACS Omega, an interdisciplinary open-access journal, were selected to highlight the potential impact of open-source publications and their importance in connecting scientists across industry and academia. With a similar goal, Organic Process Research & Development has a tradition of bridging industrial and academic research. Its focus on process chemistry as the science that enables the safe, environmentally benign, and economical manufacturing of chemicals is evident in the selected articles for this Virtual Issue, which highlight aspects of catalysis, synthetic methodology development, and synthetic strategy exploration that are needed to enable circular economies.(2,3)

### Minimizing Dependence on Fossil Fuels

The contributions from across these journals demonstrate that the design of methods for circularity necessitates multidisciplinary approaches and careful definition of the problem being addressed. (2) One of the key challenges we face continues to be decreasing our dependence on fossil fuels for chemical and fuel production. This entails both the efficient and clean transformation of renewable (biobased) raw materials into functional chemicals and fuels, as well as efficient CO<sub>2</sub> capture and conversion into fuels and chemicals. A number of exciting advances in this Virtual Issue highlight our progress on both fronts. In a critical review, Wang and Su et al. (DOI: 10.1021/acs.est.9b01453) discuss the development and application of engineered multifunctional nanohybrids of carbon nanomaterials and metal/metal oxide nanoparticles, which exhibit promising multifunctionalities for addressing the critical energy–water–environment (EWE) nexus.

More specifically on the topic of CO<sub>2</sub> capture and use, Hatton et al. (DOI: 10.1021/acs.iecr.0c04512) identify a key challenge for carbon capture and storage (CCS)—the quest for net-negative emissions. They report that bioenergy with carbon capture and storage (BECCS) with molten sorbents offers a unique opportunity to realize net-negative emissions with minimal indirect emissions and low-cost separation of CO<sub>2</sub> from other gases. BECCS could remove 300–850 kg of CO<sub>2</sub> equivalents from the atmosphere per megawatt-hour of electrical output (kg/MWh<sub>e</sub>), making it advantageous to other low carbon technologies and allowing the offset of emissions from hard-to-abate industries. In the search for efficient materials for carbon capture, Sun et al. (DOI: 10.1021/acs.iecr.0c04126) report the development of light-responsive metal–organic frameworks (LMOFs), which have tunable structures and performances. While conventional amines cannot achieve controllable adsorption separation, these LMOFs have tunable amine-based active sites, which enhance CO<sub>2</sub> capture and control adsorption and separation. Several advances also highlight the improvement of technologies for reduction of CO<sub>2</sub> based on electrocatalytic methods, including the use of Ru and Re catalysts (DOI: 10.1021/acs.organomet.9b00815) and the use of ionic liquids for this application (DOI: 10.1021/acs.iecr.0c04037), as well as exploration of Earth-abundant iron catalysts (DOI: 10.1021/acs.organomet.8b00711). Complementary to electrochemical methods, enzymatic (DOI: 10.1021/acs.est.9b05284) and photocatalytic (DOI: 10.1021/acs.iecr.0c04126) methods are also shown to have a niche in the toolbox for conversion and utilization of CO<sub>2</sub>, as highlighted in reports by Sun et al. and Jin and Kim et al., respectively.

The efficient and clean transformation of renewable raw materials into functional chemicals and fuels has blossomed from a theoretical construct to an interdisciplinary field that is fueled by fundamental innovations in synthetic chemistry and guided by practical applications of biorefineries. The requirements of biorefineries for flexibility of feedstocks, relatively mild operational conditions, and low environmental impact have resulted in highly innovative methods for defunctionalizing and refunctionalizing biomass feedstocks to value-added chemicals and materials. On the defunctionalization front, Stephenson et al. report an organocatalytic method for photochemical C–O bond cleavage of the β-O-4 linkage in lignin scaffolds. This method offers a metal-free strategy to prior reports and is applicable to continuous flow processing (DOI: 10.1021/acs.orglett.0c03029). Cellulose-derived platform chemicals can also be obtained more efficiently from using a redox-switchable biocatalyst for controllable oxidation or reduction of 5-hydroxymethylfurfural (HMF) into high-value derivatives (DOI: 10.1021/acsomega.0c02178).

Expanding the gamut of new platform chemicals that can be obtained from biomass, Rio et al. describe the presence of valuable phenolic compounds incorporated into lignins, such as flavonoids, hydroxystilbenes, and hydroxycinnamic amides, which behave as authentic lignin monomers and are potentially available in large amounts from the abundant in

waste products from processing of agricultural or forest biomass (DOI: 10.1021/acssuschemeng.0c01109). Tomishige et al. discuss the utility of erythritol as a C4 platform in biomass refinery, derived from fermentation of sugars and glycerol (DOI: 10.1021/acsomega.9b04046).

The direct valorization of lignin to functional chemicals presents potential new avenues for efficiently converting lignin to chemical products. (5,7)Yin and Huang et al. report a lignin–carbohydrate complex that is a potent antioxidant for scavenging reactive oxygen species in vitro and zebrafish in vivo (DOI: 10.1021/acssuschemeng.9b05290). Lignin was also used in the manufacture of polyurethane formed by oxidative liquefaction (DOI: 10.1021/acsomega.1c00285). Many other transformations of biomass to functional chemicals and materials are discussed in two timely reviews on biomass-derived carbonaceous materials (DOI: 10.1021/acssuschemeng.8b06550) and bacterial cellulose-based composite scaffolds for biomedical applications (DOI: 10.1021/acssuschemeng.0c00125). On the critical front of transforming our polymer platform to renewable materials, consistent with the circular economy, Vodovotz et al. discuss how we can narrow the gap for bioplastic use in single-use food packaging, focusing on the most recent development successes in bioplastic materials and highlighting the “gaps” between bioplastics and their conventional counterparts with respect to their properties (DOI: 10.1021/acs.est.9b03755).

#### Minimizing the Impact of Chemical Synthesis and Manufacturing

Another key challenge in developing manufacturing infrastructure for a circular economy remains the minimization of the overall environmental footprint, which must minimize both the environmental impact of the manufacturing processes of chemicals as well as their potential hazard and persistence of the commodity chemicals produced. While the former has been a cornerstone of research in Green Chemistry from its inception in the early 1990s, it is still a fertile area of research, and we see evidence of that in this Virtual Issue. The latter will be addressed in further detail later in this Editorial.

Sustainability in organic chemistry, especially in organic synthesis, has been driving innovation for decades. With the amount of waste generated in many synthetic chemistry routes, especially at scale in manufacturing, we are faced with not only an ethical imperative to develop more sustainable chemical processes and products but also a financial imperative. Metrics to gauge our progress, including process mass intensity (PMI), have been developed that allow all aspects of a process to be compared. For example, conducting a reaction in water may not necessarily be an improvement if several volumes of an organic solvent are needed to extract/purify the product. One could even argue that water can be problematic because its high boiling point makes recycling energy intensive, but we do not know these details without consciously thinking about them. A recent perspective highlights the need to explicitly include the assessment of sustainability using Green Chemistry metrics. (3)

A number of studies highlight advances in catalysis and reaction engineering that have led to waste and energy minimization for processes that still pose significant challenges. Four of the contributions from Organic Letters focus on use of less harmful reagents, catalysts, or routes (e.g., DOI: 10.1021/acs.orglett.1c00850; DOI: 10.1021/acs.orglett.0c03272; and DOI: 10.1021/acs.orglett.0c01043). On the catalysis front, we see an increase in the scope of synthetic transformations facilitated by supported catalysts (DOI: 10.1021/acs.organomet.9b00082; 10.1021/acs.orglett.1c01058). In one example, Pei, Lu, and Cai et al. described the preparation of a reusable magnetic Ag–Fe<sub>3</sub>O<sub>4</sub> catalyst supported on cellulose microspheres for reduction of nitrophenols (DOI: 10.1021/acsomega.0c00437). We also see increased exploration of the utility of base metals in catalysis and organocatalytic processes being performed under mild conditions and with low catalyst loading: for highly enantioselective epoxidation of  $\alpha,\beta$ -unsaturated ketones, Jarczak et al. employed an amide-based Cinchona alkaloid at loadings as low as 0.5 mol % as a hybrid phase-transfer organocatalyst (DOI: 10.1021/acs.orglett.0c03272).

On the application front, the quest for reducing traditionally high E-factors in the pharmaceutical sector continues. In two critical perspectives, colleagues from major pharmaceutical companies highlight the need to develop less wasteful and toxic methods for peptide and oligonucleotide synthesis and purification methods, in light of the growing utility of biological peptide-based pharmaceuticals (DOI: 10.1021/acs.joc.0c02291; 10.1021/acs.joc.8b03001). In another perspective in The Journal of Organic Chemistry, Rossen highlights insights from process chemistry that can reduce the impact of synthetic chemistry at smaller scales (DOI: 10.1021/acs.joc.9b00344). In Organometallics, Leahy and colleagues provide a perspective from the pharmaceutical industry on the role of catalysis with Earth-abundant metals (DOI: 10.1021/acs.organomet.8b00566).

Catalysis with Earth-abundant rather than precious metals continues to be an active area of research and key component of sustainable chemistry research. Manuscripts in Organometallics focus on cobalt (DOI: 10.1021/acs.organomet.0c00241) and iron (DOI: 10.1021/acs.organomet.1c00200) catalysts for hydrosilylation and nickel precursors (DOI: 10.1021/acs.organomet.0c00485) and heterogeneous catalysts (DOI: 10.1021/acs.organomet.9b00082) for Suzuki–Miyaura coupling, one of the most widely used methods for C–C bond formation. Pidko et al. also report the role of manganese in mediating C–C bond formation from organoboranes (DOI: 10.1021/acs.organomet.0c00781).

Waste reduction also continues to be tackled on the solvent front in the development of alternative solvents, such as less hazardous task-specific ionic liquids (DOI: 10.1021/acsomega.9b04091), deep eutectic solvents (DOI: 10.1021/acs.joc.0c02039; 10.1021/acssuschemeng.8b03520), and increasing the scope and efficiency of reactions in water, such as amidation (DOI: 10.1021/acs.orglett.0c01676), amine synthesis, and transfer hydrogenation (DOI: 10.1021/acs.organomet.0c00554; 10.1021/acs.organomet.1c00133). We also see the development of new biomass-derived solvents with greener profiles, such as glycerol-derived 1,2,3-triethoxypropane and systematic solvent selection protocols for “greener” solvents (DOI: 10.1021/acs.iecr.0c03789; 10.1021/acs.oprd.0c00326).

#### Designing Chemicals with Minimal Hazard

While minimizing the impact of chemicals through use of renewable resources and cleaner process technologies remains critical, the importance of the toxicological profile of the chemicals being circulated is now increasingly being recognized. The challenge of efficiently assessing the toxicological risks of thousands of chemicals at the design stage and for chemicals already in use requires interdisciplinary research efforts. Many toxicological mechanisms of interaction remain poorly understood and therefore unregulated. In this Virtual Issue, Shi et al. describe how in silico methods of molecular dynamic simulations will help to define molecular initiation events and identify toxicological mechanisms, enabling quick and effective screening of a wider range of chemicals (DOI: 10.1021/acs.estlett.9b00073). Blum et al. and Kwiatkowski et al. further propose that individual testing of thousands of chemicals is unrealistic, and chemical “classes” should be screened, using broad subclasses as required.<sup>(8,9)</sup> Venier et al. (DOI: 10.1021/acs.estlett.9b00582) provide excellent examples of the regrettable substitution of polybrominated diphenyl ethers (PDBEs) with organophosphate ester flame retardants (OPFRs), resulting in undesirable toxicological outcomes, and Kwiatkowski et al. consider the scientific bases for dealing with perfluoroalkyl (PFAS) chemicals as a class (DOI: 10.1021/acs.estlett.0c00255).

The design of plastics to be both biodegradable and sustainably produced from nonpetrochemical sources is another critical circular design area requiring urgent research input. The ES&T paper by Napper and Thomson (DOI: 10.1021/acs.est.8b06984) reports a lack of biodegradable plastic formulations used for carrier bags that offered rapid rates of decay compared to conventional plastic bags. For environmental concerns, Nguyen et al. (DOI: 10.1021/acs.estlett.8b00671) provide a novel and simple method in ES&T Letters to assess the quantities of microplastic fragments in environmental matrices, using hydrophobic iron nanoparticles to extract microplastics from soil, sediments, and water magnetically, and could be used as a sustainable remediation tool.

#### Sustainable Water Resources

The sustainable supply of potable drinking water is a global imperative and was identified as a United Nations Sustainable Development Goal in 2015. Just last month in ACS Omega, Gude et al. provided a critical evaluation and perspective of two major routes for developing more sustainable and circular-economy-based wastewater treatment and showed that integrating both concepts may result in superior energy and resource efficiency for wastewater treatment systems (DOI: 10.1021/acsomega.0c05827). Zdrow et al. (DOI: 10.1021/acs.estlett.0c00019) report on the use of self-healing bacterially formed cellulose fiber networks creating sustainable biological membranes (Live Filtration Membranes) capable of filtering water for drinking water purposes. Alternative energy-efficient and sustainable remediation approaches include the application of UV/sulfite water treatments to offer effective degradation of persistent PFAS chemicals in raw water for onward drinking water use, reported by Liut al. in ES&T Letters (DOI: 10.1021/acs.estlett.0c00236).

Environmentally sustainable and energy-efficient nanotechnology membranes also have water purification applications, often in combination with other environmental uses, including energy harvesting, environmental sensing, and remediation. Desalination technologies with superior high efficiency are based on selective desalination membranes

(Geise et al.; DOI: 10.1021/acs.estlett.9b00351) and reduced graphene oxide membranes with minimal impact of nanowrinkles (Zhang et al.; DOI: 10.1021/acs.estlett.0c00143). In addition to desalination, the degradation of persistent organic pollutants is also a key priority for water purification. Li, Li, and Zhang et al. (DOI: 10.1021/acs.est.8b05685) report on the use of a porous, coral-like nanostructure photoelectrode for this purpose while simultaneously producing electricity. Luo et al. describe mechanisms of carbo-catalysis in carbon nanotubes with persulfate oxidation for water treatment applications (DOI: 10.1021/acs.est.0c02645).

#### Closing the Loop

The environmentally sustainable recovery of resources from wastes is also a burgeoning area of research. In a highly cited account, Suh and Scott et al. report benchmarks for degradation rates of common plastics, which will help prioritize future research efforts on chemical degradation to close the loop (DOI: 10.1021/acssuschemeng.9b06635). In *Organometallics*, O’Hair and Ryzhov et al. explore the depolymerization of ethylene with palladium catalysts to understand approaches to remediation of polyolefins(10,11) (DOI: 10.1021/acs.organomet.0c00782). Li et al. report on the recovery of lithium from spent batteries using an acid-free mechanochemical process that utilizes salt and sodium carbonate as the sole reagents (DOI: 10.1021/acs.est.9b01919). Lo et al. provide a critical review on the use of selective sorbents for the removal and recovery of phosphates from water and wastewaters (DOI: 10.1021/acs.est.9b05569). Munasinghe-Arachchige and Nirmalakhandan (DOI: 10.1021/acs.estlett.0c00355) describe the recovery of nitrogen from sewage sludge and livestock manure as offering some circularity to the high global demand for nitrogenous fertilizers. The capture and conversion of carbon dioxide to bicarbonate is reported by Kim and Jin et al. (DOI: 10.1021/acs.est.9b05284) using an environmentally simple system of stabilized carbonic anhydrases loaded onto electrospun polymer nanofibers.

#### Lifecycle and Systems Thinking

The ability to apply life-cycle thinking to prioritize research and propose truly long-term, sustainable solutions is critical for identifying feasible ways to address circularity. Two common life-cycle assessment (LCA) methods—process LCA and economic input–output LCA—both suffer from different shortcomings. As a result, many hybrid methods are used to improve the overall accuracy. Luo and Ierapetritou analyze different hybrid LCA methodologies through a case study of two biomass-based p-xylene production technologies and provide key insights applicable to future LCA analysis (DOI: 10.1021/acs.iecr.0c04709). LCA analyses of the synthesis of widely used titanium dioxide nanoparticles (DOI: 10.1021/acs.est.8b06800) and butyl acetate (DOI: 10.1021/acs.iecr.0c04233) provide theoretical guidance for more sustainable production of both. Parkinson and Hunt apply such an approach in proposing the conversion of agricultural land in groundwater-stressed areas from irrigated crop types to rain-fed crop types combined with diversification to solar harvesting, so-called “agrivoltaics” (DOI: 10.1021/acs.estlett.0c00349).

#### Future Research Needs in Developing a Circular Economy

The selected publications in this Virtual Issue exemplify the diverse and interdisciplinary contributions surrounding the theme of this year’s conference. They also allow us to identify areas that will require further emphasis in order to strategically advance the field toward applications that facilitate circularity. Some of these areas include:

- Depolymerization and defunctionalization methods for existing chemicals that can allow circularity, especially for plastics;
- Design of circular systems with consideration of human health and ecotoxicity, ideally via rational design of benign commodity chemicals;
- Systematic application of life-cycle analysis, or thinking, and process metrics in developing new manufacturing/synthetic routes;(12,13)
- Implementation of machine learning and other big-data methods to drive innovation toward new paradigms of circularity.

In order to allow future contributions to highlight the potential application to circular economies, authors may want to consider explicitly addressing some of following questions in their manuscripts. First, consider the source of the

materials being used, and if it is fossil-fuel-derived, consider if there is a biobased alternative that could provide the same chemical insights. If elements are used that are facing limited supply, consider whether the synthetic routes and processes could help reduce the use of such materials. Second, discuss whether the method described could impact different stages of a chemical's life cycle. For example, is it a step that is potentially reversible based on kinetics and thermodynamics? If it produces byproducts, could those be a valuable resource? And finally, consider whether the method or product constitutes a safe product that can be either recycled, reused, or remanufactured. Addressing such questions forces the authors to apply life-cycle thinking and to broaden their discussion of the prior art most closely related to the advances presented. We look forward to future fruitful contributions to this field from the innovative authorship of the ACS family of journals.

## II. DISCUSSION

Sustainable development goals (SDGs) have been adopted by the United Nations to provide guidelines that address the three pillars of sustainability: environmental sustainability, economic sustainability, and social sustainability. A clear agenda composed of 17 SDGs with 169 targets aims at utilizing natural resources (water, energy, and raw materials) in a sustainable and eco-friendly manner.

This agenda, known as Agenda 2030, complies with the principles and fundamental aspects of green chemistry. In particular, the green chemistry approach has been developed in governmental, industrial, and educational fields worldwide to minimize the use of chemical reagents and prevent waste production and hazardous substance generation. This main objective of this approach is to promote resource sustainability, economic growth, environmental protection, social inclusion, and human well-being.

The aim of this Special Issue is to bring together original research and review articles discussing recent advances in meeting sustainable development goals (SDGs) by employing the fundamentals and applications of green chemistry. In particular, the Special Issue focuses on the implementation of green chemistry for water and air pollution mitigation, solid waste management, wastewater treatment, reagent recycling and reuse, and valuable metal refining. Accordingly, this Special Issue should be based on recent findings, current challenges, and future directions to simultaneously achieve environmental quality improvements and economic benefits. The ecological (water, land, biodiversity, and greenhouse gases), financial (energy, investment, and industrialization), and social (human health, awareness, and educational) related SDGs, supporting all features of fundamental and applied chemistry, are comprehensively covered.(15,17)

Potential topics include but are not limited to the following:

- Sustainable bioproduction of safer chemicals from food waste
- Bioconversion of food waste into environmentally friendly reagents
- Production, importation, utilization, development, adoption, and disposal of safer chemicals
- Risk assessment and management associated with human health effects from chemical reagents
- Green chemistry application to manage water engineering and water quality
- Environmental chemistry approaches for pollution and accident prevention, safety and resource sustainability, and energy and resource sustainability
- Management of local, regional, and global impacts of air pollutants, including SOX, NOX, PM10/2.5, and trace metals, with the design and implementation of safer chemicals, materials, and products
- Environmental pollution and conservation, along with economic development, based on green chemistry
- Regulatory aspects and hierarchy concepts of chemical waste management and pollution prevention principles, utilizing knowledge of treatment, storage, and disposal facilities
- State and federal agencies that govern the role of chemical technology in the industrialization of developed and developing countries
- Efficient use of natural resources through the utilization of renewable feedstocks(18,19)

### III. RESULTS

Green Chemistry is not a lab-curiosity; instead it aims at big objective of creating a sustainable tomorrow. Increasing number of green methodologies developed by academic and industrial researchers enables companies to commercialize these ideas. Industry, from small businesses to large corporations, has already made strategic moves towards sustainability by adopting the principles of green chemistry. The development of less hazardous processes and commercial products, the shift from inefficient chemical routes towards bio-based synthesis, and the replacement of oil-based feed stocks by renewable starting materials are only a few examples of the major decisions taken that will ultimately have vast consequences for the world chemical markets.

As per the analysis of Environmental Protection Agency, the US drug industry has decreased the use of VOCs by 50% between 2004 and 2013 by adopting principles of green chemistry. In the same time span, the amount of chemical waste released to air, land and water decreased by 7% as per Toxics Release Inventory (TRI) of EPA.

Recently four industrial drug units located in Hyderabad region of India has been closed on account of creating pollution [9]. China, too, has strict environmental concerns and has taken regulatory action on 40% of the industrial units located in thirty provinces [10]. These changes in policy suggest that it has become imperative to follow green practices.

Plastics, in spite of several uses, have a bad reputation owing to their origin from polymers derived from non-renewable petrochemicals and their non-bio-degradable nature. However, the same can be made from renewable feedstock as shown by a study carried out by Utrecht University [11]. Studies by Utrecht University also show that the market of bio-plastics will grow by approximately 37% per year till 2013 and at a rate of 6% between 2013 and 2020. Many marketing hubs have joined the initiative to replace plastics with bio-plastics. Wal-Mart has been using bio-plastics in packaging wherever possible [12]. On similar lines Nokia, a mobile making company, used 50% bio-plastics in Nokia 3111 Evolve phone cover as well as in Nokia C7 phone [13].

Procter & Gamble replaced most of the PVC based materials with greener alternatives [14]. Along with other companies P&G have taken the initiative to develop new solvents so as to replace volatile organic carbons in glossy paints.

Greener synthesis of Ibuprofen launched by BASF involves half the number of steps as compared to traditional method. Atom efficiency of new process is almost double than the old synthesis. In pursuit for the development of sustainable methodologies, BASF developed BASIL™ (Bi-phasic Acid scavenging utilizing ionic liquids) process involving the production of generic photo initiator precursor alkoxyphenylphosphine [15]. Using this technology the yield increased from 50 to 98%.

The Warner Babcock institute for Green Chemistry has developed a green hair-dye “Hairprint” which is a non-toxic, vegetable based product providing an alternative to the toxic, skin irritating and carcinogenic dyes [16].

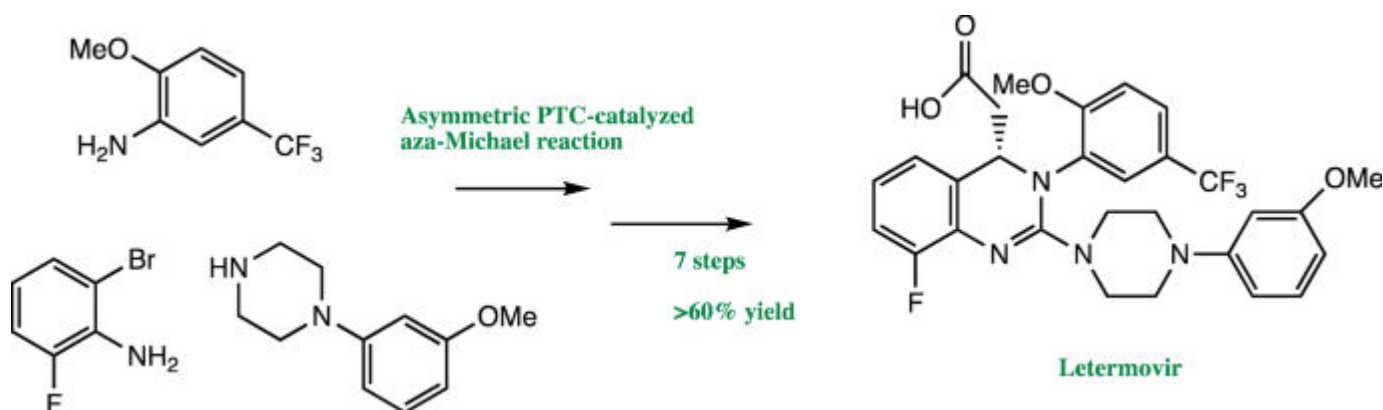
USA based Merck & Co., Inc. has successfully applied the principles of green chemistry to the synthesis of antiviral drug (cytomegalovirus infection) Letemovir which is currently in phase III of clinical trials. Cytomegalovirus (CMV) is a common virus whose infections are generally asymptomatic in healthy individuals but can cause severe damage in patients with immuno-depressed systems. The importance of this drug can be judged from the fact that it has been granted Fast-Track status by FDA and Orphan product designation by European Medicine agency for the prevention of CMV viremia in high risk population.



An evaluation of its traditional synthesis scheme revealed several areas for improvements like a very low overall yield of 10% due to a late stage resolution to access a stereogenic center, the use of nine different solvents, high palladium loading in Heck coupling. Moreover, no recycling of solvents and reagents had been there in the scheme.

Greener synthesis, as published by Merck, involves a novel cinchonidine based PTC-catalyzed Aza-Michael reaction for configuring the single stereocenter as shown in Scheme 1 [17]. Also, there is an increase in overall yield by 60%, reduction in raw material cost by 93% and reduction in water usage by 90%. It has been estimated that, once operational, this optimized process will lead to reduction of more than 15,000 MT of waste over the life time of Letemovir. Life-Cycle Assessment reveals that the green process is expected to decrease the carbon foot-print by 89%. It is quite evident from the green synthesis of Letemovir that the Green Chemistry is not only environmentally friendly but also economically lucrative. This scheme has won the EPA's Presidential green chemistry award under the category "Greener synthetic pathways" in 2017 [18].

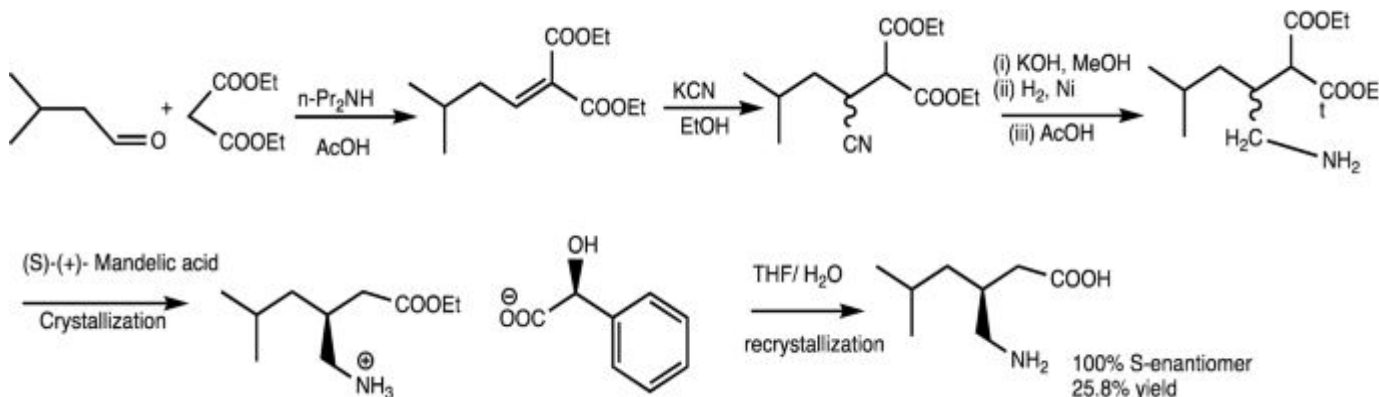
Scheme 1



#### Green synthesis of Letemovir

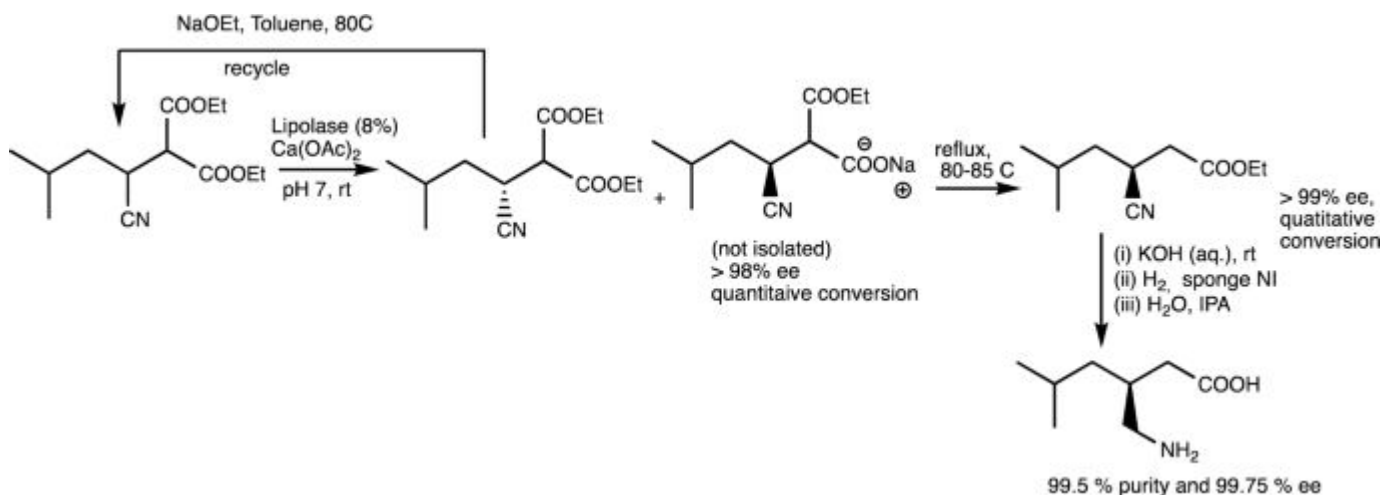
Of the various technologies used in green chemistry, biocatalysis holds an important place [19]. Most of the reactions occurring in physiological systems are catalyzed by enzymes which are nature's catalysts. Enzymes are not only biodegradable but are renewable as well due to the ease of production by fermentation of sugar etc. In order to achieve the aims of sustainability, more and more companies are working in the area of designing and using enzymes as biocatalysts. An impressive case highlighting the impact of biocatalysis on pharmaceutical manufacturing is the greener synthesis of Pregabalin, an active ingredient of neuropathic pain reliever Lyrica<sup>®</sup>. In 2008, Pfizer improved the classical route for the synthesis of Pregabalin by adopting biocatalysis as a key step which led to 90% reduction in solvent usage, 50% reduction in the requirement of raw materials besides energy savings [20]. Solvent and energy saving in the process is equivalent to reducing 3 million tons of CO<sub>2</sub> emissions which is actually equivalent to taking 1 million Indian cars off the road for a year. Schemes 2 and 3 compare the classical and greener route for the synthesis of pregabalin.

Scheme 2



## Conventional synthesis of Pregabalin

Scheme 3



## Enzyme catalyzed synthesis of Pregabalin

Not only in drug synthesis, biocatalysts also find important applications in the synthesis of plastics. Now a days, research is mainly targeted towards the synthesis of biodegradable plastics from renewable resources.

California based start-up “Newlight Technologies”, founded in 2003, took a funding of \$9.2 million for developing a carbon negative technology that combines air with methane emissions to produce Aircarbon™ a thermoplastic. Aircarbon™ is approximately 40% oxygen from air and 60% carbon and hydrogen from methane emissions. The technology itself was not new but the use of a proprietary biocatalyst by Newlight Technologies made it actually commercially viable by increasing the yield nine times and decreasing the cost by a factor of three thereby making Aircarbon cheaper than oil based plastics. With the commercial scale-up in 2013, Aircarbon™ was adopted by a number of leading brands like Dell, Hewlett-Packard, IKEA, Sprint, The Body Shop and Vinmar for manufacturing their respective products. In recognition of the company’s commercial achievements, Newlight was named “Most innovative company of the year” in 2013 and Aircarbon™ was named “Tech innovation of the year” by The American Business Awards [21]. For the green attributes of the process involving capturing and using greenhouse gases, Newlight technologies has been awarded the prestigious EPA’s Presidential Green Chemistry Challenge award in 2016 [22].

Most chemical processes involve solvents in the reaction and separation step to dissolve solids, reduce viscosity, modulate temperature, and recover products by means of extraction or recrystallization as reaction media or for cleaning purposes. Solvents not only dissolve the reactants but they also affect the rates, chemo-, regio- and stereoselectivities of reaction. However, majority of the organic solvents used in industry, despite their inherent advantages, are associated with several ill-effects on human health and environment. Moreover, these solvents are derived from non-renewable resources like petroleum. These parameters are in contradiction to the very basics of Green Chemistry. Due to these reasons, the only alternative available is to substitute these environmentally harmful solvents with some benign solvents. Hungerbuhler et al. [23] discussed the following four directions towards the development of green solvents

1. Substitution of hazardous solvents with one that show better EHS (Environment, Health, Safety) properties such as increased biodegradability or reduced ozone depletion potential [24].
2. Use of “bio-solvents” i.e. solvents produced from renewable resources such as ethanol produced by fermentation of sugar-containing feeds, starchy feed materials or lignocellulosic materials [25].
3. Substitution of organic solvents with supercritical CO<sub>2</sub> in polymer processing avoids the use of chlorofluorocarbons, and reduces the ozone depletion [26].
4. With ionic liquids that show low or negligible vapour pressure, and thus fewer emissions to air [27].

Fabric dyeing consumes a lot of water. About 7 gallons of water is used up to dye a T-shirt and lot of energy is wasted in drying the dyed material. A Dutch start-up recently launched water-free dyeing using supercritical carbon dioxide as a solvent under pressure and at elevated temperature. As no water is used so energy required in drying is also saved [28].

Elevance Renewable Sciences, Inc., used a nobel prize winning metathesis technology developed by Grubb’s to produce two green solvents

In collaboration with the surfactant manufacturer Stepan, Elevance produced a surfactant called STEPOSOL MET-10U as a replacement for N-methyl pyrrolidone and dichloromethane in adhesive removers and paint strippers. This surfactant can also be used in household and industrial cleaners in place of glycol ethers. STEPOSOL MET-10U is a unique unsaturated di-substituted amide derived from a bio-based feedstock [29]. With a Kauri-Butanol value greater than 1000, STEPOSOL MET-10U provides superior cleaning performance and is environmentally friendly due to a low vapor pressure, high boiling point, and Biorenewable Carbon Index (BCI) of 75%.

Another heavy-duty green degreasing solvent developed by Elevance Renewable Sciences is Elevance Clean™ 1200 which is a VOC free bio-based solvent [30]. In 2015, Elevance Clean™ 1200 was awarded bio-based product innovation of the year at WBM bio business awards for its out-standing cleaning performance. Being produced from natural oils this non-flammable solvent meets the various restrictive environmental regulations. Therefore, Elevance Clean™ 1200 is

- (i) VOC exempt (Directive 2004/42/CE of the European Parliament and the Council)
- (ii) REACH registered
- (iii) Readily biodegradable (by OCED method)
- (iv) Free of components listed in the EU dangerous substances directive (Regulation No. 1272/2008).

The various advantages of Eleavance Clean™ 1200 are enlisted below

- (i) Strong solvency characteristics greater than even of d-limonene, dibasic esters, vegetable esters and isoparaffins on the Kauri butanol (Kb) scale.
- (ii) Excellent performance across a broad range of cleaning applications which includes metal cleaning, industrial and institutional degreasing, transportation and food processing.
- (iii) Being non-flammable, it is easy to handle. It works very well in the neutral pH range (6–9) thereby eliminating the need of caustic cleaning products.

In 2014, Solberg Company won the first Insight Innovation award at the 3<sup>rd</sup> annual THINC for its environmentally-friendly fire-fighting foam concentrate RE-HEALING. Conventional firefighting foams use fluorinated surfactants which are hazardous for the environment. The RE-HEALING firefighting foam concentrate use a blend of non-fluorinated surfactants, sugars, solvent and corrosion inhibitor leading to far less environmental impacts. Control, extinguishing time, and re-ignition resistance are necessary for the safety of fire-fighters and RE-HEALING fulfills all these conditions. The company also won the 2014 EPA Presidential Green Chemistry award for this innovation. [31].

Using catalytic reagents over stoichiometric reagents is one of the principles of green chemistry. Developing recyclable and recoverable catalyst adds to the green profile of a technology. Exhausts from the automobile engines pose a major threat to the environment. Inside the engine, temperature being very high, oxygen and nitrogen react to form nitric oxide (NO). Conversion of NO to NO<sub>2</sub> is highly desirable for the removal of oxides of nitrogen. However, this reaction is, in general, quite slow. A team of scientists from U.S, China and South Korea developed the catalyst using Mn-Mullite (Sm, Gd) Mn<sub>2</sub>O<sub>5</sub>–manganese–mullite materials containing either Samarium or Gadolinium to convert the toxic diesel engine exhaust product nitric oxide to a more benign nitrous oxide [32]. Over a range of temperatures, the new catalyst performed better than platinum (around 64% better at 300 °C and 45% better at 120 °C).

RCHEM Pvt. Ltd. Hyderabad, in collaboration with Chaudhuri et al. [33] developed a green synthesis of anti-ulcer drug Ranitidine. The conventional synthesis generates dimethylsulfide which is a hazardous to human health. Prof. Chaudhuri, from IIT Guwahati, and Prof. Kantam from ICT Hyderabad developed vanadium–titanium and titanium phosphorous based solid supported catalysts. In the presence of these heterogeneous catalysts H<sub>2</sub>O<sub>2</sub> acts as an oxidant to convert the dimethylsulfide to colourless odourless liquid dimethyl sulfoxide (DMSO). The DMSO generated is further used in the manufacturing process of drug thereby reducing the cost of production by 20%.

There are numerous applications where green chemistry has marched beyond the research laboratories and finding commercial applications. However, a lot more efforts are required, particularly in the area of life-cycle analysis so as to evaluate the environmental impact of the various “green” drugs after these traverses the human physiological system. Terry Collins, from the University of Pittsburg, developed a series of tetra-amido macrocyclic ligand based catalysts modelled on peroxidase enzymes [34]. Collins proposed that addition of these at a late stage in the sewage treatment process could help break down a wide variety of chemical residues from the drugs before they can affect the environment.

## Challenges

Just being green is not enough for a process to be a commercial success. Regulatory, economic, political and technical challenges often impede the industrial implementation of a green process.

Current regulations are focused on reducing risk through reductions in exposure while green chemistry promotes the reduction of inherent risk by reduction of hazard. In U.S, the regulations require that every time a manufacturer changes the production process, it has to undergo a re-certification process with the FDA. This process is both costly and time-

consuming, and hence serves to dissuade firms that would otherwise invest in developing atom efficient chemistries that reduce waste. Changes to more benign processes are inhibited by cost-intensive, control-oriented regulation. Lack of awareness among the different stake-holder groups poses a barrier to the implementation of green processes. Developing a successful green process is not only about green chemistry, it involves the knowledge of green engineering, biotechnology, economics and above all toxicology. The chemists generally lack the training in these disciplines which further hampers the implementation of green chemistry on an industrial scale. Even if all factors are the in the favour of a green process, it can be rejected on a commercial-scale if it fails to be economically attractive. Green industrial processes should be comparable to the traditional processes in terms of costs of the products.

There are a number of examples of technically robust, environmentally-friendly processes that have been started at first but were withdrawn at a later stage due to commercial implications. It does not always pay to be green in the chemicals sector. Thomas Swan and Company in Consett, UK, implemented the work of Martyn Poliakoff (Nottingham University), to start world's first continuous-flow reactor using supercritical carbon dioxide as a solvent [35]. Sc-CO<sub>2</sub> system lead to selective hydrogenation of isophorone to 3,3,5-trimethylcyclohexanone without any by-product formation. This lead to elimination of an expensive and energy-intensive separation required by the conventional technique. But due to the lack of government subsidies, the plant could not provide chemicals more cheaply than those made by the traditional non-green methods. Therefore, after commercially running from 2002 to 2009, this plant was taken out of production.

Similar things happen with the process involving isomerization of 3,4-epoxybut-1-ene to 2,5-dihydrofuran in a phosphonium iodide ionic liquid developed by Eastman Chemical Company.

Capital investment also prevents the commercialization of a green technology. IFP (France) used ionic liquids, as solvent as well as co-catalyst, on a large scale for the nickel catalyzed dimerization of alkenes, named as Difasol process [36]. This is a biphasic process wherein the product forms a separate layer above the ionic liquid layer and thus can be easily separated. Compared to the conventional Dimersol process, this method has many advantages like better catalytic activity, ease of separation of product, better dimer selectivity and higher reactor space time yields. However, the cost of capital equipment posed a hurdle towards its commercial implementation.

The commercialization of green processes also requires many changes in all part of the long and global supply chain. Eden Organic foods developed a BPA-free coating for food packaging which was found to be compatible with some foods like beans but not for highly acidic tomato sauce. Switching to different coating type for different food type implies a smaller market size and change in manufacturing machines and consequently a higher cost. The implementation of such initiatives requires that everyone in the value chain agrees and is willing to accept the changes.

As most of the industries have been driven by monetary profits therefore voluntary adoption of the sustainable practices seems less feasible. A strong, attractive and balanced regulation is required so as to enforce the greener practices. The most promising and significant regulation is the REACH (Registration, Evaluation, Authorization and Restriction of Chemical substances) regulation framed and launched by European Union in 2007 [37]. On one hand REACH makes it mandatory for the chemical companies to disclose more information on the environmental and health risks of their products; on the other hand it grants potential exemptions on registration for five years for a process which favours new sustainable innovation. This move of European Union has motivated other countries to devise similar regulations so as to create a sustainable chemical industry.

#### IV. CONCLUSION

Green chemistry holds the key to a sustainable society. It has the inherent potential to bridge the gap between society and science. Innovations, backed by sound policies and regulations, will accelerate the large-scale implementation of green processes. Next generation of chemists should be taught the basics of green chemistry at a very early stage so that

they can think green and develop safer methodologies. Interdisciplinary and multidisciplinary research can help in solving the various technical hurdles for commercializing this philosophy. Subsidizing the greener initiatives and tax exemptions to the companies adopting green processes will have a positive impact. Industries should realize the fact that getting a new greener process registered and making capital investment is a one-time investment which can have positive impacts on various aspects of society and environment.

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