CHEMICAL REVIEWS

Editorial

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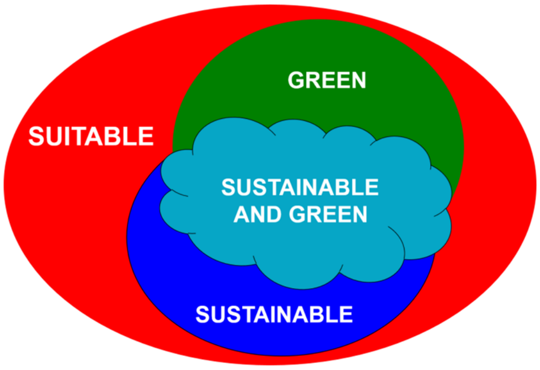
Introduction: Sustainable Chemistry

The fast and sometimes rampant expansion of human endeavors has resulted in unexpected and dynamic interactions between the growing population, food consumption, industrial development, and environmental damages.[1] In particular, the environmental and health impacts of the production, distribution, use, and discharge of chemicals at larger and larger quantities in a practically closed environment[2] have raised global concerns and resulted in the definition of sustainable development in the 1980s. The World Commission on Environment and Development stated in their report, entitled "Our Common Future", that sustainable development *″should meet the needs of the present without compromising the ability of future generations to meet their own needs”*.[3] While short-term needs can be identified with high certainty, long-term predictions have been unreliable due to the end of history illusion[4] and the extremely fast rate of scientific and technical advances.[5] Although our track record for predicting economic changes or societal transformations has been even more unreliable, most of the next generation definitions and metrics combined ecological, economical, and societal components at different portions.[6] In 2015, the United Nations identified 17 sustainable development goals (SDGs) with specific targets for the next 15 years.[7] The SDGs require the cooperation of all corners of life and will be measured by global, regional, and national indicators. The EU has also developed a set of sustainable development indicators, which were defined by 10 sustainable development strategy objectives.[8] Since the UN's development goals and the EU's strategy objectives have intermingled ecological, economical, and societal issues, "sustainable development" could be easily replaced by "suitable developments" by the stake holders, due to their vested or even conflicts of interests to generate profits for businesses, secure funding for NGOs (nongovernmental organizations) and environmentalists, or get elected or re-elected as politicians at the expense of the environment. Thus, the definition of sustainability should be an intrinsic property of a molecule, a material, a reaction, a process, or a technology. An alternative definition of sustainability was recently proposed, which is indeed independent of economic and social aspects: *resources, including energy, should be used at a rate at which they can be replaced naturally, and the generation of wastes cannot be faster than the rate of their remediation.*[9] This definition is similar to the first two principles, or system conditions, of the four sustainability principles of Robèrt et al.[10]

Chemist and chemical engineers have had the privilege to work on chemistry with very little, if any, limitations for a very long time and synthesized suitable[11] chemicals by suitable[11] reactions, which were the basis of suitable[11] processes. In the glorious days of the 1950s and 1960s, chemistry was envisioned as the solution to a host of society's needs, and it became a central science.[12,13] Natural and synthetic chemicals, including materials and their production technologies, enabled mankind to achieve longevity and much better quality of life.



While most of the emerging environmental and health problems caused by chemicals in the 1970s and 1980s have been addressed and fixed locally, several issues transformed to global phenomena (DDT and dioxin contamination, greenhouse gas emission, ozone depletion, ocean acidification, climate change, and micro- and nanoplastic pollution, just to name a few). One of the original responses to the escalating environment issues was the evolution of green chemistry, which started in the 1980s and has grown to be a guiding concept by the end of 1990s.[14] The first responders defined green chemistry by shifting the focus from cleaning up the wastes to pollution prevention.[15] The environmental and health impacts of hazardous chemicals, materials, and practices were addressed by the 12 principles of green chemistry,[16] which did not change at all in the last 25 year, indicating their timeless nature.

Since some parts of green chemistry may not be sustainable at all, a definition of sustainable chemistry should be established and applied for the assessment of each chemical or reaction or process. In general, *sustainable chemistry should use resources, including energy, at a rate at which they can be replaced naturally, and the generation of waste cannot be faster than the rate of their remediation*. It should be noted that not all sustainable chemicals or reactions or processes could be green. Therefore, the selection of chemicals, reactions, and processes, which are sustainable and green at the same time, should be preferred or the target of design and innovation. This thematic issue of *Chemical Reviews* is dedicated to Sustainable Chemistry with eight articles written by leading scientists and engineers from four continents. The topics cover some of the greatest challenges of sustainability including energy storage, carbon dioxide, and biomass conversion to chemicals, sustainable solvents and catalysts, and renewable and biodegradable polymers. The cover of this special issue shows a *yin* and *yang (yīnyáng or "dark—bright" or "negative—positive")*, one of the dominant concepts of Chinese philosophy focusing on the process of harmonization to ensure a constant, dynamic balance of all things considered. Indeed, this should be the overarching goal of sustainable and green chemistry.

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Fossil resources have offered the opportunity to build a supply demand energy system across the planet, regardless of the size and geographical position of the population. The transition to renewable energy resources, especially to photovoltaics and wind, requires the development of efficient and reversible energy storage systems. Although hydrogen gas could be used for energy storage, its low density as well as hazardous nature limits safe and efficient applications.

Formic acid, formate salts, and alcohols could be attractive alternatives for energy storage provided efficient catalytic processes are developed for the facile release of hydrogen from these molecules, as well as their regeneration from CO_2 and hydrogen. Laurenczy, Beller, and co-workers reviewed the progress in homogeneous catalytic hydrogenation of carbon dioxide to formic acid and methanol and the reverse dehydrogenation reactions. The dehydrogenation of biomass-based higher alcohols was also discussed. Particular attention was given to the sustainability aspects by focusing on additive-free processes and earth abundant metal catalysts. Detailed mechanistic insights were also given to demonstrate the development of superior catalytic systems.

The successful replacement of fossil resources in the production of carbon chemicals by renewable resources, such as carbon dioxide and biomass, is required for the development of a sustainable chemical industry. Some of the options to convert carbon dioxide to fuels, bulk and commodity chemicals, and even pharmaceuticals were evaluated by Leitner, Bardow, and co-workers. The environmental footprints of carbon dioxide and fossil resources based applications were assessed by analyzing the synthetic methodologies and/or processes and performing life cycle assessments. It was demonstrated that the conversion of carbon dioxide to chemicals does not constitute a carbon sink over the life cycle of the products since carbon dioxide is released at the end of life, but it can lead to more environmentally friendly production processes.

Biomass is a globally available, carbon-neutral, renewable feedstock for the production of carbon chemicals, which could completely replace the recently utilized fossil-based chemical processes even in this century. Mika and co-workers have reviewed the recent status of various catalytic transformations of carbohydrates to platform chemicals including the relevant mechanistic information as well as the biochemical production routes and techniques. The sustainability of the biomass based chemical industry will depend on the availability of the resources, the viability of the conversion processes, as well as the location and weather dependent replacement time of the different feedstocks. Sustainability will be influenced by the energy requirements, wastes generation during production, and their remediation in the natural environment. An overview of the different sustainability metrics was also provided.

Lignin is a major component of lignocellulose with a robust and irregular polymeric structure, which can serve as a sustainable source of aromatics. Emerging strategies for the depolymerization of lignin to well-defined products using catalytic or biocatalytic processes were reviewed by Barta and co-workers. The potential application of new aromatics for the synthesis of polymers or pharmacologically active molecules was discussed. Existing strategies for the functionalization or defunctionalization of lignin based compounds were also summarized. Following the whole value chain from raw lignocellulose through depolymerization to application whenever possible, specific lignin based compounds were identified which could be considered as potential lignin derived platform chemicals.

Solvents are important for chemists to provide one or more liquid phases for chemical reactions and processes. While some solvents are available from Nature even in large quantities, most of the solvents are man-made. Historically, solvents were selected to help the chemists' objectives only. With the increasing importance of local and global health and environmental issues, the potential impacts of solvents became important selection tools. The use and development of sustainable solvents are important for both the research community and the chemical industry.

Kobayashi and co-workers reviewed the advances in catalytic reactions using water as a reaction medium over the past decade. The use of water could benefit chemical processes by simplifying operations, allowing milder reaction conditions, and sometimes delivering unexpected reactivities and selectivities. After the "watershed" in organic synthesis revealed the importance of water, the development of water-compatible catalysts has flourished. One of the main advantages is that the product organic compounds are practically insoluble in water and simple extractive workup can readily separate a water-soluble homogeneous catalyst from the product that is soluble in organic solvents.

Hallett and co-workers have reviewed several aspects of the most prominent sustainable organic solvents in use today including ionic liquids, deep eutectic solvents, supercritical fluids, switchable solvents, liquid polymers, and renewable solvents. Besides examining each class of solvent within the context of the reactions or extractions for which it is employed, their process and system performance were also discussed. A wide range of technical, economic, and environmental factors were considered, providing a more complete picture of the current status of sustainable solvent research and development.

The contributions of biocatalysis to sustainable chemistry were reviewed by Sheldon and Woodley. Based on the principles and metrics of green chemistry and sustainable development, biocatalysis is sustainable and green! Protein engineering has improved the performances of existing enzymes and resulted in the invention of novel biocatalytic reactions. Biocatalysis has successfully been applied in the industrial synthesis of many active pharmaceutical ingredients. The sustainability of biocatalytic reactions can be further improved by substrate, medium, and reactor engineering. Immobilization of enzymes has increased their stability to enable facile recycling, resulting in better performance and commercial viability. Consequently, biocatalysis is widely applied in the production of pharmaceuticals and in some commodity chemicals. Moreover, its broader application will be further stimulated in the future by the merging petrochemical and biorefineries.

The widespread application of petroleum-based plastics and especially the formation micro- and nanoplastics in the environment represents a serious threat to wild life and humans. Their replacement with sustainable alternatives is a great challenge. Waymouth and co-workers have critically reviewed the sustainability of polymers including the characteristics of preferred feedstocks, production processes, and end-of-use options. Aliphatic polyesters and polycarbonates are very promising sustainable polymers based on renewable resources and have excellent biodegradability. The potential impact of catalytic transformations to develop more sustainable replacements for petroleum-based plastics was also addressed.

The eight articles presented in this special issue on sustainable chemistry demonstrate that both chemists and chemical engineers have responded to the challenges of sustainable development including the replacement of crude oil, natural gas, and coal to produce energy and chemicals from renewable resources and the application of novel reaction environments, catalysts, and materials. Finally, the *yin* and *yang* on the cover should be a visual reminder to design and develop chemical systems and processes in harmony between resource management and wastes remediation.

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Notes

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

Biography

István T. Horváth received his Diploma in Chemical Engineering (1977) and Ph.D. in Chemistry (1979) at the University of Pannonia, Veszprém, Hungary. He was an Assistant Professor at the Veterinary University, Budapest, Hungary (1979−1980) and a Research Engineer at Chinoin, Budapest, Hungary (1981). He was a Postdoctoral Research Associate at Yale University (1982−1984), a Scientific Coworker at the Swiss Federal Institute of Technology (ETH-Zürich), Switzerland (1984−1987), a Senior Staff Chemist at ExxonMobil Corporate Research, Annandale, New Jersey (1987−1998), and a Professor at the Institute of Chemistry, Eötvös University, Budapest, Hungary (1999-2009). He has been a Chair Professor of Chemistry at the City University of Hong Kong since May, 2009, and was the Head of the Department of Biology and Chemistry until July 31, 2015. He has published over 120 papers, 30 chapters, and 20 patents and gave 145 invited lectures and 220 seminars. He was the Editor-in-Chief of the “Encyclopedia of Catalysis” (Wiley, 2002), the Editor of “Fluorous Chemistry” (Springer, 2012), and the Co-Editor of Aqueous Organometallic Chemistry and Catalysis (Kluwer, 1995), Handbook of Fluorous Chemistry (Wiley-VCH, 2004), Multiphase Homogeneous Catalysis (Wiley-VCH, 2005), and Advance Green Chemistry (World Scientific Publishers, Singapore, 2018). He was the Chairman of COST Action D29 on Sustainable/Green Chemistry and Chemical Technology (2002−2007). He received the first Fluorous Technology Award in 2005, the Senior Humboldt Research Award in 2006, and the Green Chemistry Lecture Award in 2008. He is an RSC Fellow (2013), ACS Fellow (2014), and AAAS Fellow (2016).

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