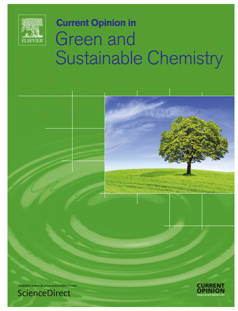

A Closer Look on Sustainable Solvents and Processes

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PII: S2452-2236(19)30035-5
DOI: https://doi.org/10.1016/j.cogsc.2019.07.003
Reference: COGSC 281

To appear in: *Current Opinion in Green and Sustainable Chemistry*

A Closer Look on Sustainable Solvents and Processes

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In 2015, 17 sustainable development goals (SDGs) were outlined by the UN ("Transforming Our World: The 2030 Agenda for Sustainable Development"), representing a plan of action for people, planet and prosperity [1]. Several of these goals highlight the need for sustainable chemistry and engineering, where green and sustainable solvents play a pivotal role. High quantities of organic solvents in respect to the products obtained are essential for chemical reactions to proceed. Furthermore, separation processes depend on the use of high amounts of solvents to accomplish high purity levels of the target compounds. As a result, the annual industrial-scale production of organic solvents has been estimated at ca. 20 million metric tons [2]. Although the current society cannot proceed without solvents, a growing awareness of the impact of solvents on human health and environment has been faced in the past decades. To overcome these drawbacks, while keeping our society standards, a range of greener and sustainable solvents has been proposed and the sustainability of some industrial processes has been improved.

The understanding of solvent properties is a core part of sustainable development; in this line, several solvents guides (mainly published by pharmaceutical companies) have been proposed to rank solvents according to their environmental, safety, and health (ESH) characteristics [3]. These guides can be used to help researchers and companies to identify solvents with low ESH impacts, while discouraging the use of nonrenewable and toxic solvents. Among some well-known and currently used solvents with low ESH impact, such as water, ethanol, ethylacetate, anisole, among others, examples of neoteric solvents that have been studied in a sustainable perspective include solvents derived from biomass, ionic liquids (ILs), deep eutectic solvents (DES), liquid polymers, supercritical carbon dioxide ($scCO_2$), gas expanded solvents and switchable solvents. Nevertheless, if a common volatile solvent can be replaced by a neoteric solvent, it does not mean that it should be. There are several barriers that need to be addressed before such neoteric solvents can be adopted at a large-scale, namely cost, availability, purity, safety regulations, disposal procedures, recycling procedures, among others. Furthermore, the entire life cycle of the solvents used and proposed processes is a critical issue that must be considered. Ideally, to improve processes sustainability, the following strategies should be considered: processes should be carried out without solvents at all (e.g. mechanochemistry), water should be considered as a primordial solvent, and solvents should be selected based on their ESH impact and able to display a multiple role (e.g. as solvent and reagent, as solvent and for product separation, etc.). Given the critical need of improving sustainability of both solvents and processes, this issue covers state-of-the-art reviews on neoteric and greener solvents and their application in several fields.

Jimenez-Gonzalez (https://www.sciencedirect.com/science/article/pii/S2452223618301147) provides an overview on life cycle considerations of solvents. The author clearly highlights that “the most sustainable solvent is the solvent that is not used”. However, when this approach is not possible, efforts are critically needed to minimize the solvent footprint, both by minimizing the amount of solvents used and their health and environmental impact. Their impact could be addressed by the solvent's life cycle analysis, which considers raw material extraction and production, manufacturing, transportation, use, recycling, and final disposal. This review describes key aspects to be taken into account when evaluating and selecting solvents by a life cycle assessment approach.

Li and co-workers (https://www.sciencedirect.com/science/article/pii/S2452223619300215) gives an overview on the greenest solvent overall: water. In this review, the advantages and disadvantages of several neoteric solvents are described and compared with the features offered by water, including supercritical or subcritical water. The combination of solvent strategies and separation technologies is also overviewed. The authors conclude that there is no perfect solvent for all chemical applications. However, the use of water as a solvent, if no solvent at all cannot be applied, should be always considered. Within the field of green solvents, **Marrucho and co-workers** (https://www.sciencedirect.com/science/article/pii/S2452223618301135) disclose and overview the potential of deep eutectic solvents as promising solvents in clean water, clean energy, and biotechnology fields. The remarkable properties of these solvents, namely their chemical versatility, which allows their tailoring for target applications, easy preparation and no need of purification steps are highlighted. Current challenges and opportunities arising from the use of deep eutectic solvents aligned with the scope of today's major concerns are described. **Giner and co-workers** (https://www.sciencedirect.com/science/article/pii/S2452223618301342) outline solvents derived from biomass and their potential as green solvents. Their environmental impact and other key physicochemical properties, such as vapor pressure or solubility, are described and compared with those displayed by conventional volatile organic solvents. The toxicity of these chemicals in several organisms is compiled, described and analyzed according to the type of endpoint studied. Although solvents from biomass have some green credentials, genotoxicity is a crucial property that still needs to be considered. In addition to ionic liquids as neoteric solvents, mixtures of two ionic liquids have been gaining momentum to tailor their properties. **Dhakal and Shah** (https://www.sciencedirect.com/science/article/pii/S2452223618301159) overview the knowledge gathered using molecular simulations applied to ionic liquid–ionic liquid mixtures. With the continuous rise in the computational power and accessibility of software packages supporting the implementation of polarizable models, future accurately modeling is expected aiming at tailoring the properties of ionic liquids and other green solvents for target applications.

The use of green solvents has been a hot topic in the development of sustainable processes. In this line, **Sheldon** (https://www.sciencedirect.com/science/article/pii/S2452223618301172) provides an overview on the “greening of solvents” focused on the development of sustainable organic synthesis. Recent developments on the use of sustainable solvents in organic synthesis are critically reviewed, where the commonly used organic solvents and less common bio-based examples are assessed and ranked according to their waste disposal and environmental impact, health and safety parameters. The use of water as a solvent, including the use of aqueous biphasic catalysis, micelle-enabled catalysis and biocatalysis, is finally outlined as a more sustainable alternative to reactions in organic solvents. In quest of shifting to a sustainable bio-based economy, lignocellulose is becoming an increasingly important feedstock. However, its valorization demands for the effective and sustainable deconstruction of the lignocellulosic matrix and fractionation of its constituents. **Hummel and co-workers** (https://www.sciencedirect.com/science/article/pii/S2452223618301354) describe the use of ionic liquids and gamma-valerolactone as alternative solvents in the deconstruction and refining of biomass. The latest progresses in this field are described, as well as their feasibility in terms of costs and recyclability. Recent demands for the decrease, reutilization and valorization of waste have motivated research within a biorefinery and circular economy perspective. **Meireles and co-workers** (https://www.sciencedirect.com/science/article/pii/S2452223618301202) disclose the perspectives on the biorefining of plant matrices into marketable products using supercritical CO_2. A wide variety of products can be obtained from vegetable biomass, including extracts with relevant biological activities and biopolymers, which are overviewed. **Prasad and Sharma** (https://www.sciencedirect.com/science/article/pii/S2452223618301366) describe and analyze the use of green solvents, such as ionic liquids, deep eutectic solvents and bio-derived solvents, for the extraction, dissolution and processing of biopolymers. Biopolymers such as guar gum, tamarind gum, cellulose, agarose, κ-carrageenan, chitin and DNA are a target of this overview. Although neoteric solvents such as ionic liquids and deep eutectic solvents are suitable for the processing of various biopolymers and functional materials preparation, additional efforts are still need to scale-up the described processes, while turning them cost-effective and environmentally-friendly.

Within a circular economy perspective, **Billard** (https://www.sciencedirect.com/science/article/pii/S2452223618301123) overviews the use of green solvents in urban mining, namely by the use of green solvents in recycling processes and metal recovery from technological objects. Significant advances have been achieved in the recovery of metals from phosphor lamps, multilayer flexible packaging, permanent magnets, and used tires. **Pacheco-Fernández and Pino** (https://www.sciencedirect.com/science/article/pii/S2452223618301391) report on the use of green solvents in analytical chemistry. Among the neoteric solvents investigated, amphiphilic solvents, ionic liquids, and deep eutectic solvents received a significant attention. These have been investigated in liquid-phase microextraction methods (within sample preparation) and as additives or pseudo-stationary phases in liquid chromatography (within analytical separation methods). Given their potential, it is expected an increase in the number of analytical applications of green solvents in the following years. **Nematollahi and Carvalho** (https://www.sciencedirect.com/science/article/pii/S2452223618301160) provide a critical analysis on the use of alternative solvents (ionic liquids and related mixtures and deep eutectic solvents) for CO_2 capture. The limitations that have been hampering the development of separation units and processes capable of fulfilling industrial demands are described, as well as the steps needed to turn the carbon capture, utilization, and storage by neoteric solvents a reality. Within the application of green solvents to develop sustainable processes, **Schuur and co-workers** (https://www.sciencedirect.com/science/article/pii/S2452223618300919) provide an overview on solvent-based separation processes. These processes can reduce the energy input for separation, e.g. when compared with distillation, and improve biocompatibility. The authors conclude that for all solvent systems not only the primary separation operation should be considered, but instead all the entire process should be taken into account, including solvent recovery where most of the energetic input takes place.

In this issue, the green credentials of neoteric solvents are described, as well as their performance and potential in several applications, ranging from catalysis, biomass processing, urban mining, to CO_2 capture. A range of technical, economic, and environmental factors are summarized, giving a more complete picture of the current status of sustainable solvents and processes development. Although it is still a long path to take, due to their remarkable characteristics and performance, the use of neoteric solvents in industrial processes is becoming a reality, as appraised by some recent created companies.

Conflict of interest statement

Nothing to declare.

Acknowledgments

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES.

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