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Review Article

Green Solvents for Sustainable Chemistry: A Futuristic Approach

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ABSTRACT

Green solvents can be used to replace traditional solvents, which can be a long-term solution for minimizing environmental depletion. Citing "The Twelve Principles of Green Chemistry" as a main basis, this paper examines conventional solvents, their sources, and the associated environmental and health risks. Green solvents, their various varieties, industrial and general uses, applications, and reactions are briefly discussed in this article. Completely replacing conventional solvents with green solvents have a deleterious impact on industrial performance and chemical synthesis, several successful substitutes have proved their chemical efficiency as well as their widespread use and application. Review also discusses the future of green solvents, their efficacy, and how to make bio-based solvents an effective alternative in high demand chemical sectors to lessen the environmental hazard on the ground level.

Key words: Alternatives, Biodegradability, Conventional solvents, Green solvents, Hazards, Ionic liquids, Supercritical liquids, Sustainability.

1. INTRODUCTION

Conventional chemical processes contribute to major amount of environmental and health hazards. To reduce these hazards and attain more eco-friendly outcomes, the search for alternatives has always been an area of interest. Green chemistry is found as best possible alternative holding the future of chemical industry. It is the new emerging field that in order to achieve sustainability strives to work at the molecular level. The field reportedly possess the ability to harness chemical innovations to achieve the economic and environmental goals. In the beginning of the 1990s, nearly 20 years ago, the concept of green chemistry was first formulated and it was defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances."[Figure 1] [1-3].

Green chemistry has a framework of set of 12 principles. These principles act as a guiding framework for synthesis of new chemicals considering a holistic approach toward green technology with safety, efficiency, and biodegradability [Figure 2] [1].

The twelve principles are summarized below [1] –

1. **Prevention:** It is better to prevent the generation of waste than its removal after formation.
2. **Atom Economy:** There must be synthetic methods to incorporate all raw materials into final products.
3. **Less Hazardous Chemical Synthesis:** Whenever possible such methodologies should be used that pose little or no toxicity to human health and environment.
4. **Designing Safer Chemicals:** Chemical products should be such that preserve efficacy of the reaction and minimize toxicity.
5. **Safer Solvents and Auxiliaries:** The use of auxiliary substances should be avoided whenever possible and when used should be in minimal amounts.
6. **Design for Energy Efficiency:** The impact of energy requirements of reaction on environment should be recognized and minimized or replaced if possible.
7. **Use of Renewable Feedstocks:** Whenever practicable, raw materials should be renewable rather than depleting.
8. **Reduce Derivatives:** Derivative formation should be minimized or avoided if possible, as it requires more reagents and can produce waste.
9. **Catalysis:** Switching from stoichiometric reagents to catalytic reagents can improve reaction efficacy and lower energy requirements.
10. **Design for Degradation:** Reactants used should be such that break down into simpler biodegradable materials after the reaction and do not persist in environment.
11. **Real Time Analysis for Pollution Prevention:** Analytical methods should be developed that provide real-time, in-process monitoring and control of hazardous substances before they are generated.
12. **Inherently Safer Chemistry for Accident Prevention:** Substances for chemical reactions should be chosen to minimize any sort of chemical accidents including fires, explosions, and releases.

2. CONVENTIONAL SOLVENTS AND THEIR HAZARDS

Conventional solvents are general laboratory solvents that we routinely use for laboratory and industrial purposes because of their volatility, melting point, better dissolving power, and yield. Apart from their direct exposure to laboratory workers, when released in environment (air, water, and soil), these can cause potential threat to plants, animals, and humans from ground level reaching to mass level

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when left untreated [4]. Majority of chemicals can cause hazards if not handled carefully. Direct contact (inhalation, skin, and eye contact) and prolonged exposure (occupational) are the two major routes of chemical toxicity to humans. Damage to health can, depending on the chemical composition, damage to organs, weakening of the immune system, development of allergies or asthma, reproductive disorders and birth defects, effects on the psychological state, intellectual or physical development of children, cancer, etc. [5].

European Solvent Industry Group advice to follow EU guidelines to improve air quality by contributing to the reduction of total volatile organic compound (VOC) emissions since 1990 [6]. Persistent accumulation of organic chemicals in the environment and improper waste management is the root cause of environment pollution since decades and cause severe toxicity to land, air, and water life [7]. Ozone depletion, water and soil pollution, groundwater contamination, BOD, and COD are major results of wide consumption of conventional solvents. The Solvents Industry Association offers advice and guidance to producers, distributors, and consumers of solvents to help to minimize the potential environmental impact [8]. Industrial and manufacturing firms commonly rely on solvents for a multitude of tasks such as making products, cleaning and degreasing machinery and surfaces, working with materials such as coatings and paints, and facilitating chemical reactions. Many corporate sustainability programs are seeking eco-friendly solutions around the employment of organic solvents, which are VOCs and have environmental and health effects. Table 1 lists different conventional solvents, their sources, and related risks to human health and environment.

3. GREEN SOLVENTS – TYPES, SOURCE, AND USES

Solvents used in different chemical processes are found to be of major environmental concern [14]. According to annual growth report (2020–2021), the production volume of the chemical industry in Europe is expected to increase by around 3.1% indicating more solvent involvement, leading to environment depletion [15]. Thus, the reduction of the use of solvents or replacing them with less toxic green solvents is two major aims of green chemistry [16].

According to Fisher, the green solvent expresses the objective of minimizing the environmental impact of the consumption of solvents in chemical production [17,18]. Effective utilization of green solvents such as water, supercritical fluids, liquid polymers, and ionic liquids (ILs) can help achieve the aim to reduce environment degradation. Low toxicity, phase behavior, chemical, thermodynamics, biodegradability, and non-flammability are some of the properties of novel green solvent or biosolvents [19]. Figure 3 shows different types of green solvents along with their respective examples and Table 1 discusses different solvents their sources, industrial, and general uses.

In extraction of natural products and oils, terpenes can be a good replacement to petroleum solvents like n-hexane [20]. Water being universal solvent and non-toxic can be used in various reaction medium, extraction, separation, and organic synthesis [21]. Deep eutectic solvent is another eco-friendly solvent which is widely used in dispersive liquid-liquid microextraction [22] and as green absorbents for volatile organic pollutants [23]. Another wonder class of solvents includes the ILs, which is commercially used in desulphurization of fuel oils [24] and carbon capture [25]. Instead of using n-hexane, n-butane can be used as a sustainable solvent for natural product extraction [26]. For processing of polymer melts [27] and pre-treatment of lignocellulosic biomass [28], super-critical fluids can be a good replacement to traditional solvents. For carotenoid extraction, fatty acid esters are good choice as solvent part [29]. Bioethanol, for its low toxicity and reliable availability, is used as green solvent in various synthesis and industrial production [30]. For its renewable nature, biodegradability, low costs, and eco-friendliness, castor oil serve as a promising green solvent for nanoparticle synthesis [31], agriculture, food, textile, paper, plastic, rubber, cosmetics, perfumeries, electronics, pharmaceuticals, paints, inks, additives, lubricants, and biofuels [32].

Table 1: Conventional solvents and their environmental and health hazards.

S. No.	Chemical	Physical State	Where it is found	Related risks to humans and environment	References
1	Benzene	Liquid	Crude oil and gas. Benzene is also used to make plastics, detergents, pesticides, and other chemicals. Benzene is produced naturally by volcanoes and forest fires	Human – Bone marrow damage, anemia, excessive bleeding, weakened immune system Environment – create smog	[9]
2	Toluene	Liquid	Paint thinners, nail polish removers, glues, correction fluids (white-out), explosives, printing, leather tanning, inks, stain removers	Human – Dizziness and confusion, anxiety, muscle fatigue, insomnia, numbness, dermatitis, liver and kidney damage Environment – Membrane damage to leaves, chronic toxicity to aquatic life	[9,10]
3	Zinc	Solid	Pipe organs, auto parts, sensing devices, sunblock, ointments, concrete, paint. Also used to form alloys with other types of metals.	Human – Nausea, vomiting, cramps, diarrhea, headaches, kidney, and stomach problems Environment – sufficient levels in soil and water cause prolonged contamination	[9,11]
4	Lead	Solid	Often found near mining sites as well as in-car batteries, roofing materials, statues, electronics, ammunition, sailboats, and scuba diving gear	Human – Health risks: anemia, brain damage, kidney disease, birth defects Environment – lead as dust contaminate air, water and soil at ground level	[12]
5	Ammonia	Gas	Laboratory industry	Exposure to higher concentrations cause respiratory distress, throat irritation	[13]

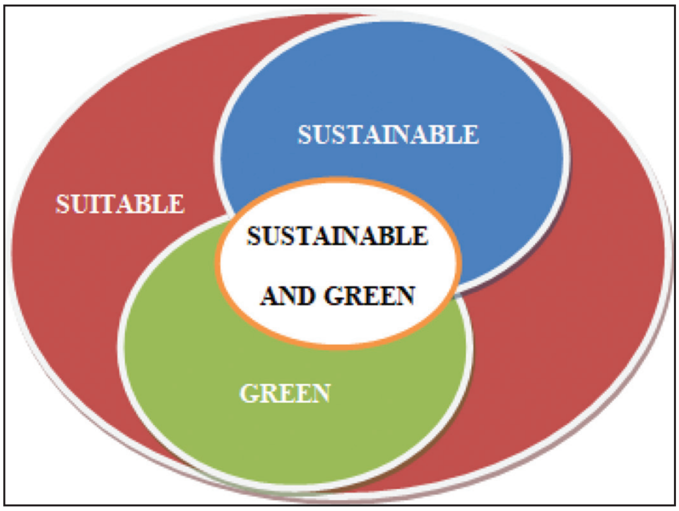


Figure 1: Sustainable and green chemistry.

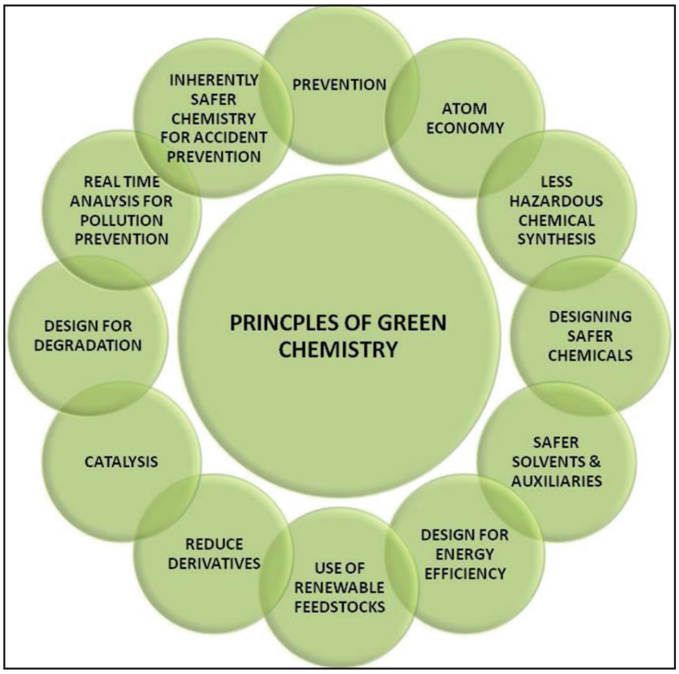


Figure 2: Principles of green chemistry [1].

Bio-based specialty solvents such as ethyl lactate are also a sustainable solvent in processing of green tea biomolecules [33] and extensively in organic reaction and synthesis [34]. Polyethylene glycol (PEG) is also an green substitute which is well known for its coupling reactions and carbon-carbon bond formation [35].

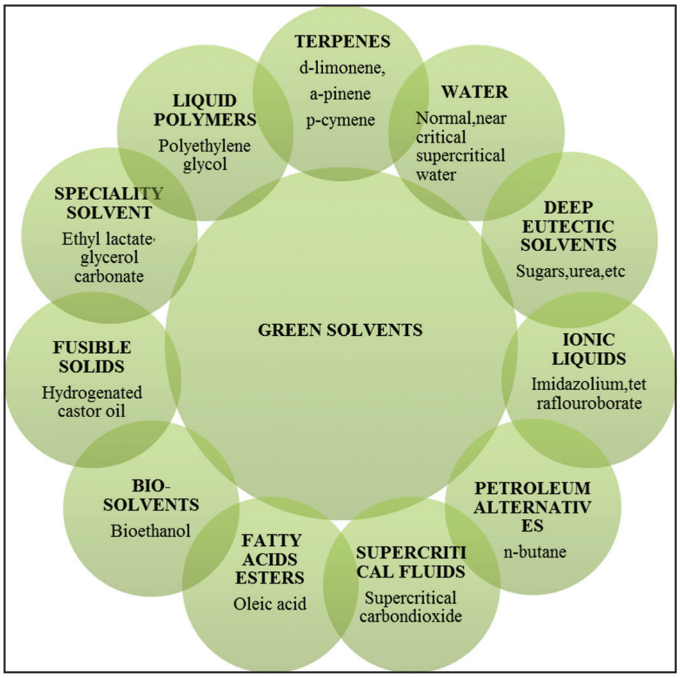


Figure 3: Different types of green solvents.

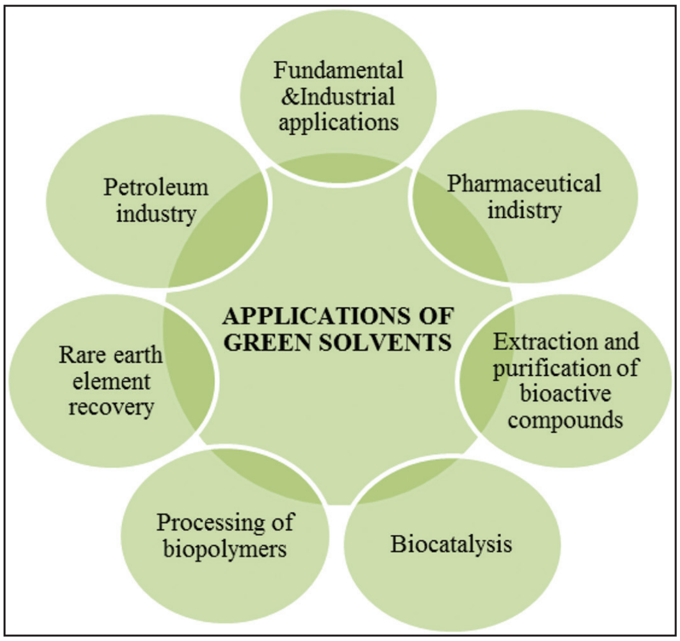


Figure 4: Applications of green solvents.

4. APPLICATIONS OF GREEN SOLVENTS

In petroleum industry, ionic liquids are used in desulfurization process to reduce SO_2 emissions [48]. Fundamental and industrial applications [Figure 4] of green solvents have wide range from reaction synthesis to oil extraction, sensors and biosensors, CO_2 capture, lignocellulosic biomass utilization, and bio-based chemicals [49]. Solvents used in the pharmaceutical field accounts for mass consumption in the range of 80–90%and biosolvents such as butanol, polyethylene glycol, biorenewable solvents, and supercritical solvents are widely used in the extraction and solubility of drugs [50]. In the past two decades, supercritical fluids, ILs, and deep eutectic solvents have been the most actively investigated as possible green solvents, especially in the domains of food, flavor, and fragrance, as well as medicinal plant processing [51]. Organic carbonates are a family of organic molecules and chemical intermediates that are known for their high biodegradability, low toxicity, and flexibility which lead to their wide application in biocatalysis [52]. Alternative solvents for biomass pre-treatment and extraction of natural polymers from resources include ILs, deep eutectic solvents, and bio-derived solvents [53]. Another interesting area is rare earth element recovery and ionic solvents, such as ILs and deep-eutectic solvents, have gotten a lot of interest since they offer an alternative to traditional metal recovery methods [54].

5. GREEN SOLVENTS IN CHEMICAL REACTIONS

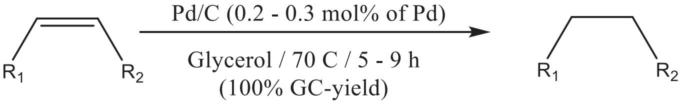
With the growing advancements in the field of chemical research, potential threat to environment and human health has increased considerably. Thus, to make chemical researches, more environment-friendly

Table 2: Green solvents: Sources, industrial and general uses.

S. No.	Solvent	Source	Industrial uses	General uses	Reference
1	Water	Naturally occurring	Petroleum and food industry	(Universal solvent) Extraction of solvents, industrial purposes, etc.	[36]
2	Glycerol	Animal fat	Food and cosmetic industry	Isolation of reaction products, personal care products, mouthwashes, etc.	[37]
3	Ethyl lactate	Processing of corn	Food and beverage industry	Paint industry, removing greases, adhesives, magnetic tape coatings, etc.	[38,39]
4	Supercritical carbon dioxide	Liquid state of CO2	Pharmaceutical industry	Polymer-related applications, Extraction of essential oils	[40,41]
5	Ionic liquids	Organic salts	Electronic industry	Biocatalysis	[42]
6	n-butane	Natural gases	Refinery and petrochemical industry	Aerosol propellant, fuel additives, etc.	[43]
7	Bioethanol	Fermentation of sugar and vegetable residues	Power and chemical industry	Motor fuel, additive in gasoline, etc.	[44]
8	Cyclopentyl methyl ether	Addition of methanol to the cyclopentene	Bio refineries	Biotransformations, bioextractions, chromatography, solid-phase peptide synthesis.	[45]
9	Dimethyl carbonate	Reaction of methanol with carbon monoxide and oxygen	Paint and cleaning industry	Raw material for organic synthesis	[46]
10	Ammonium	Volatilization of urea, manures, slurries	Fertilizer and pesticide industry	Textiles, dyes, etc.	[47]

special attention has been paid to the properties and applications of green solvents in extraction and fractionation, chemical reactions, and material synthesis. Many processes that use green solvents have been commercialized [55]. Few examples of organic synthesis are discussed herewith using green solvents as an alternative [Table 2].

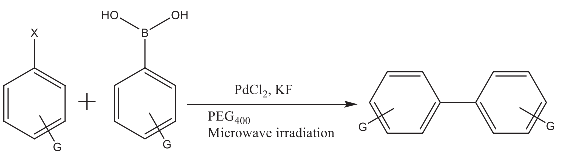
1. Glycerol can act as a reducing agent in metal catalyzed reactions, transfer hydrogenation of olefins, and can yield decent results and can be recycled later [55]



R_1R_2 = -$(CH_2)_4$-; R_1 = Ph, R_2 = H

eq1

2. In Suzuki reaction, the yield was best between 4-iodotoluene and phenylboronic acid in PEG400 (90%) compared to other solvents such as toluene and DMF [35]



G: electron donating or withdrawing groups
X: Br and I

eq2

3. Ethylene glycol is an abundant renewable biomass, low toxic solvent, which has huge industrial importance and an excellent green solvent for photocatalytic cascade cyclisation reactions [56].

6. FUTURISTIC APPROACH

Sustainability can be achieved through green chemistry in three key areas, first, renewable energy technologies, where chemists can contribute to the development of economically feasible conversion of solar energy into chemical energy. Second, the reagents used by the chemical industry are derived primarily from petroleum and increasingly must be sourced from renewable sources to reduce our dependence on fossil carbon. Third, technologies that are harmful to the environment must be replaced by harmless alternatives.

Since 2002, the biennial green solvents conference has been an important table of discussion of scientific progress and industrial implementation of advanced fluids for chemical syntheses and processes. This interdisciplinary meeting dealt with the development and application of alternative solvents, including aqueous phases of unconventional use, ILs and supercritical liquids, as well as green organic solvents and soluble polymers. Other topics included solvent-free processes, as well as materials processing solvents, phase separable reagents, and various separation strategies [57]. Their separation efficiency and organic nature suits well for industrial purposes.

Following are some of the replacement of conventional solvents –

- CPME and 2-MeTHF both can be produced from the furfural, which is a bio-derived compound. Both are very useful for the replacement of hazardous chemicals such as THF. 2MeTHF has the decisive advantage of a tight natural cycle. The solvent shutoff circuit is very important to ensure that no further damage to the environment occurs. There is a great opportunity to study the applicability of 2MeTHF in the chemical process industry [58]
- Propylene carbonate (PC) is also an important green solvent that will consume CO2 to produce. This CO2 can be derived from a number of biological processes like bioethanol. The PC is also found a suitable alternative for THF. 1,3-Propanediol is an important solvent for the cosmetic industry and has potential for a number of applications with the ketone group organic solvents. It can also be utilized for the production of biodegradable polymers [59]
- Ethyl lactate can replace DCM solvent. It also has high potential use for the extraction of caffeine from tea [60].

7. CONCLUSION

Our future environmental sustainability challenges require an efficient alternative, and green technologies pave the way for such an approach. Glycerol, water, and ILs can be considered the primitive green solvents, and their performance and good manufacturing results have shown that they are the most commercially used green solvents. Other solvents such as CPME, 2-methylTHF, and ethyl lactate also proved to be a green alternatives to reduce and prevent contamination from conventional solvents. The 12 principles of green chemistry form the basis for inventing green solvents in solid, gaseous, and liquid form with acceptable efficacy. European solvent industry group believes that complete VOC ban will harm the industry but their management is necessary to reduce the solvent-based environment harm.

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