Green Solvents: Past, Present and Future Viability

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October 19, 2021

Abstract

Green alternatives to integral processes must be adapted in order to move towards a sustainable future. Green solvents are non-toxic materials that have been used in many industrial and chemical-based applications. Unique and tunable properties of specialized green solvents such as bio-solvents, ionic liquids and supercritical fluids are key advantages of green solvents. Additional areas of interest include the incorporation of green solvents into green processes such as photovoltaic cell synthesis and biomaterial recycling. Despite several minor disadvantages in comparison with typical solvents, green solvents are tools of a forward-thinking approach to reducing humankind's toll on the environment, which is in a near-critical state. If green technologies are not adapted and the tolls of carcinogenic processes are not reduced, the planet faces serious lasting consequences.

1 Introduction

In recent years, safer alternatives to widely used materials have become highly sought after due to the threats of industrial processes on the planet. Green solvents have emerged as increasingly desirable solutions to this problem due to their limited environmental impact and efficacy in chemical dissolutions. The criteria for classifying a chemical as a green solvent has been a subject of debate for an extended period of time; however, studies have shown that simple alcohols and alkanes are favorable over acetonitrile, acids, dioxane, formaldehyde and tetrahydrofuran based on an in-depth comparison of chemical properties. Furthermore, mixtures of ethanol or methanol with water are preferable to mixtures of propanol-water or pure alcohols [K.07]. What underpins green solvents as a whole is that these chemicals can be utilized without the risk of harmful products forming and accumulating in nature that can lead to environmental degradation.

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Due to the broad capabilities of green solvents in chemistry, these chemicals have been utilized in a variety of applications. Notable areas of research include the usage of green solvents in solar cell coatings, as supercritical fluids (specifically CO2) in polymer synthesis and for the dispersion of carbon materials such as graphene. Additional green solvents of interest include biosolvents and ionic liquids: biosolvents such as ethyl lactate have yielded promising results in organic synthesis [KR16] and ionic liquids have been shown to be excellent catalysts while also offering a low environmental impact [R.13].

Biosolvents are solvents consisting of organic materials that have very low environmental impact. While these solvents achieve the same eco-friendly goal as green solvents, their constituents allow for a reduction in expenditures during synthesis. Despite the relatively narrow categorization that these solvents fall into, biosolvents have been useful in many applications such as biofuels, various consumer products and medicines [B.19]. This flexibility and lower environmental toll makes biosolvents an especially promising facet of green chemistry.

Ionic liquids are liquid salts that can be tuned both physically and chemically due to their charged components, a feature which offers select advantages over other green solvents [dlRAIAHFFF13]. Ionic liquids allow for very efficient and quick catalysis, high extraction efficiencies and lower risks due to the green compositions of the materials. Ionic liquids can be applied to organic chemistry, synthesis and biodiesel formulations, all of which have become increasingly prominent in the last several decades.

The overarching goal of the field of green solvents is to effectively utilize solvents in chemical applications without the repercussions of toxic materials. The negative impacts of industrialization have been seen globally and have inspired change within all areas of manufacturing and technology. The usage of green solvents in solar cells and biodiesel is notable in that it promotes green modes of transportation and energy accumulation. Assessing the viability of these key areas and others in the field of green chemistry is necessary in a rapidly developing world as it prioritizes efficiency and functionality.

Green solvents have evolved greatly in the past several decades; however, they have not yet reached the prominence of more typical solvents in mass markets. Besides being lesser known, green solvents have other features that render them less desirable in some circumstances, especially when considering efficiency. The aim of this examination is to identify the structure and function of green solvents, identify which fields they are being employed in and how they are utilized, compare the cost and functionality of green solvents in comparison with abrasive solvents and ultimately assess their viability.

2 Common Green Solvents

By definition, green solvents are solvents with a minimal environmental impact. The lack of specificity in this general classification has yielded complications with classifying green solvents. In 2007, C. Capello et al. compiled the various effects of different solvents to determine the boundaries of a green solvent. The

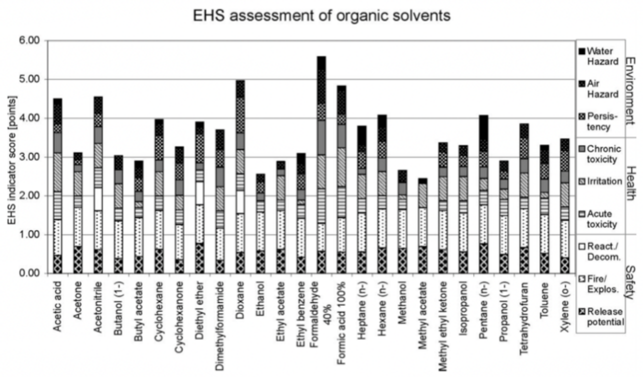


Figure 1: EHS assessment of organic solvents compiling hazardous properties and potency of each solvent [K.07].

study rated different solvents based on their environmental impact in several different categories: release potential, fire/explosion and reaction/decomposition, acute toxicity, irritation and chronic toxicity, persistence, air hazard and water hazard. The assessment was carried out via two programs: the EHS method (Fig. 1) and the LCA method (Fig. 3): the first judges immediate hazards and gives a total score out of 6 (solvents closest to 6 are the least favorable), whereas the latter measures the threats posed by the entire lifespan of the solvent and energy required for disposal. While there was not a clear point to distinguish between toxic solvents and green solvents, the results clearly split the solvents into two different categorizations based on their locations on a graph of comparison. Many of the solvents considered green solvents were below 3.00 on the EHS scale and had negligible cumulative energy demands (CED) on the LCA. Based on the data, it was determined that simple alcohols such as methanol and ethanol or alkanes such as heptane or hexane are preferable, as shown by their much lower toxicity and long-term impact. Solvents such as dioxane, acetonitrile, acids, formaldehyde and tetrahydrofuran were not considered green solvents because of their high EHS indicator scores and significant CED, which reflected high levels of immediate toxicity as well as long term impact and difficulty to dispose of from an environment [K.07]. Many solvents classified as green solvents, notably those in the study, have simple structures and properties, allowing for flexibility despite their specific qualities (Fig. 2).

One of the most well-known solvents/green solvents is water (H2O). In addition to being able to break down ionic compounds and polar molecules due to its separation of charge, water has no environmental impact when used as a solvent. However, water is ineffective in interactions with nonpolar molecules. In situations like this, other types of solvents are required, increasing the im-

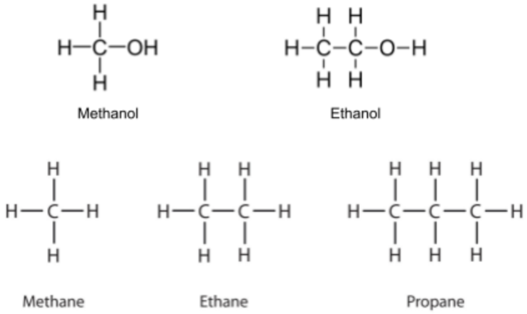
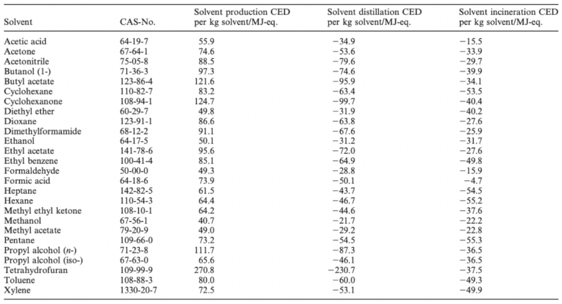


Figure 2: Chemical structures of common green solvents methanol, ethanol, methane, ethane and propane.



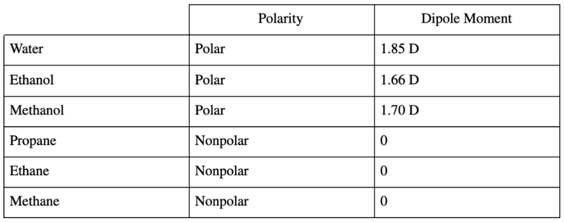
Solvent	CAS-No.	Solvent production CED per kg solvent/MJ-eq.	Solvent distillation CED per kg solvent/MJ-eq.	Solvent incineration CED per kg solvent/MJ-eq.
Acetic acid	64-19-7	55.9	−34.9	−15.5
Acetone	67-64-1	74.6	−53.6	−33.9
Acetonitrile	75-05-8	88.5	−79.6	−29.7
Butanol (1-)	71-36-3	97.3	−74.6	−39.9
Butyl acetate	123-86-4	121.6	−95.9	−34.1
Cyclohexane	110-82-7	83.2	−63.4	−53.5
Cyclohexanone	108-94-1	124.7	−99.7	−40.4
Diethyl ether	60-29-7	49.8	−31.9	−40.2
Dioxane	123-91-1	86.6	−63.8	−27.6
Dimethylformamide	68-12-2	91.1	−67.6	−25.9
Ethanol	64-17-5	50.1	−31.2	−31.7
Ethyl acetate	141-78-6	95.6	−72.0	−27.6
Ethyl benzene	100-41-4	85.1	−64.9	−49.8
Formaldehyde	50-00-0	49.3	−28.8	−15.9
Formic acid	64-18-6	73.9	−50.1	−4.7
Heptane	142-82-5	61.5	−43.7	−54.5
Hexane	110-54-3	64.4	−46.7	−55.2
Methyl ethyl ketone	108-10-1	64.2	−44.6	−37.6
Methanol	67-56-1	40.7	−21.7	−22.2
Methyl acetate	79-20-9	49.0	−29.2	−22.8
Pentane	109-66-0	73.2	−54.5	−55.3
Propyl alcohol (*n*-)	71-23-8	111.7	−87.3	−36.5
Propyl alcohol (iso-)	67-63-0	65.6	−46.1	−36.5
Tetrahydrofuran	109-99-9	270.8	−230.7	−37.5
Toluene	108-88-3	80.0	−60.0	−49.3
Xylene	1330-20-7	72.5	−53.1	−49.9

Figure 3: Life-cycle assessment of organic solvents measuring cumulative energy demand (CED) of solvent removal methods over solvent lifetime [K.07].

portance of environmentally friendly solvents with different properties (Fig. 4). Alkane molecules, for example, are nonpolar molecules which can be used as green solvents of nonpolar/low polarity molecules as a result of the lack of a polar charge. While the use of a green solvent may offer less flexibility in specific materials that can be utilized, this limitation can be mitigated in many situations by choosing simple solvents with appropriate qualities and avoiding toxic solvents with profound negative environmental impacts.

3 Biosolvents

Biosolvents are one of many groups of chemicals which meet the criteria to be considered a green solvent. In addition to being eco-friendly, biosolvents are biodegradable and synthesized from organic materials. A popular example of a biosolvent is ethanol, which is used frequently as a biofuel and an ingredient in consumer products [B.19]. Ethanol can be obtained from edible or non-edible



	Polarity	Dipole Moment
Water	Polar	1.85 D
Ethanol	Polar	1.66 D
Methanol	Polar	1.70 D
Propane	Nonpolar	0
Ethane	Nonpolar	0
Methane	Nonpolar	0

Figure 4: Polarities and dipole moments of common green solvents.

sources: fermentation can be employed to produce bioethanol from edible fruit feedstock (a primary product of the process) and cellulose can be used as a nonedible feedstock to produce the biosolvent [AM15].

Other biosolvents of note include ethyl lactate and glycerol. Ethyl lactate offers select advantages over other biosolvents and green solvents due to its tunable polarity, the ability to dissolve most organic reactants and full recyclability. In addition to these beneficial properties, ethyl lactate is relatively inexpensive and accessible, allowing for a wider reach in usage. Despite these attractive features, ethyl lactate has not been widely incorporated into chemical applications as of yet (a trait that many green solvents share to some degree). As a result, volatile compounds will maintain prominence in similar applications for the time being [KR16]. Glycerol is another prominent biosolvent which is unique in that it is able to exhibit properties that are similar to water, meaning that. Hydroxyl groups surround central carbon atoms, allowing for strong interactions with polar substances. A common form of this biosolvent is glycerol carbonate, which has ionizing and dissociating abilities that allow for the chemical to be a safe solvent in organic reactions. Due to its neutral and non-toxic state, glycerol carbonate fosters proteins and organic matter without the threat of decomposition [J.12]. The versatility and recyclable nature of biosolvents allow for these materials to boast advantages and further increase the desirability of green solvents.

4 Ionic Liquids

Ionic liquids are salts in a liquid state and are most commonly used at room temperature. Ionic liquids are considered green solvents due to their negligible vapor pressure, meaning that reactive gas will not be produced with the potential to interact with environmental reactants. Ionic liquids are commonly used as catalysts for reactions or extractants in separation processes [dlRA-IAHFFF13]. Y. Xiong et al. utilized phosphonium salts as catalysts in a study aimed at synthesizing cyclic carbonate. Ultimately, a high yield was produced and the ionic liquid catalyst was able to be separated from the products for repeated uses [R.13]. This process can be achieved through simple evaporation.

The recyclability of ionic salts exemplifies the potential of these materials in a variety of applications.

Similarly to biosolvents, ionic liquids have great flexibility in properties. This is due to the variety of cations and anions that can be selected as constituents of an ionic liquid. Ionic liquids tend to be utilized for similar processes to those of biosolvents: biodiesel and organic composite materials are commonly synthesized with ionic liquids acting as solvents. In a study conducted in 2015 by S. Wahidin et al., microalgae was converted into an eco-friendly biofuel when exposed to three ionic liquids and two organic solvents acting as cosolvents under microwave irradiation. After 15 minutes of simultaneous reaction, a biodiesel yield of 36.79% per dried biomass was achieved [S.16]. Biodegradable composite materials have also been synthesized with the usage of ionic liquids: in 2017, C. M. Patil et al. synthesized an organic biocomposite from cellulose, guar gum and PVA (polyvinyl alcohol). A strong biocomposite was created due to the strong interactions between the materials and the ionic liquid and the end product was superior to regenerated cellulosic film [J.18]. Despite being a niche grouping of green solvents, ionic liquids offer a range of properties that highlight the versatility of green chemistry.

As mentioned before, ionic liquids are uniquely tunable and effective in the synthesis of biofuels, which can be used to power engines with a lesser (but still present) environmental impact. Biofuels are not an all-green solution to the fuel industry as they contribute to global warming. However, they produce less CO2 upon combustion than diesel fuels. While ionic liquids offer advantages as ingredients of biofuels, a major disadvantage of their usage is difficulty to retrieve and recycle the chemicals; additionally, ionic liquid residue can have detrimental effects on the efficacy of common enzymes used in biofuel synthesis such as cellulase [C.12]. The positives and negatives of ionic liquids in biofuels must be weighed against each other as the materials advance in order to maintain some level of efficiency in tandem with environmental gains.

5 Green Solvents in Photovoltaics

Currently, the leading material out of which photovoltaic cells are constructed is silicon due to the material's high stability and consistent efficiencies, which result from silicon's extremely strong crystal lattice structure. However, a series of new materials have been developed, notably perovskite (CaTiO3), with the potential to phase out silicon in the future. Perovskite has a unique crystalline composition which helps to maintain structure and be an effective semiconductor. In comparison with silicon-based photovoltaics, perovskite boasts a very high efficiency (over 29%) with the downside of a decreased stability [L.21]. Despite this, perovskite is generally much cheaper than silicon, making it easier to obtain and mass produce. Although the end result yields a source of green energy, the means of photovoltaic construction can be dangerous, notably the chemicals used for cell/interface synthesis. Researchers in the field of green chemistry have striven to make these processes much more efficient and envi-

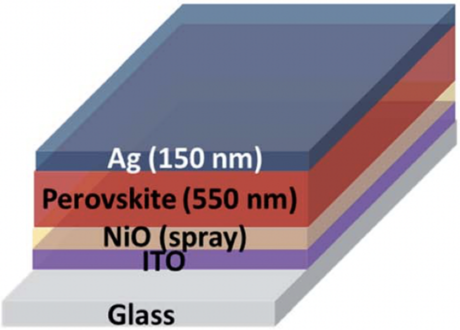


Figure 5: Thin-film perovskite solar cell schematic [J.20].

ronmentally safe in order to minimize the impact of photovoltaic production.

Common solvents utilized in metal halide perovskite photovoltaic cells are often toxic, such as chlorobenzene, and can have harmful effects when disposed of. Chlorobenzene is used as a medium for energy conversion. In a study conducted by T. Bu et al., researchers used the green solvent ethyl acetate in place of chlorobenzene and produced layered perovskite cells that championed an efficiency of 19.43% in small cells and 14% in larger cells. In addition to higher efficiencies, experimental cells exhibited higher stabilities than cells treated with chlorobenzene [J.17].

Other production strategies have been pursued in order to create a fast and efficient method of producing photovoltaics. In a 2020 study by S. Huang et al., researchers set out to fabricate mass-producible perovskite solar cells using a green solvent mixture of y-butyrolactone (GBL) and dimethyl sulfoxide (DMSO). Blade-coating was utilized for simple means of fabricating large interfaces and a final PCE of 17.02% was achieved. While the final PCE was unable to reach previous highs of perovskite cell performance, it is the highest recorded for blade-coated perovskite cells using green solvents [W.20a]. The positive results of this study highlight the promising potential of blade-coating in technology manufacturing.

Additional methods for increasing production in regards to perovskite solar cells include scalable spray methods. N. Kumar et al. used a combination of common green solvents in combination with nickel oxide films to produce high efficiency triple cation perovskite solar cells (Fig. 5). In addition to achieving a PCE of 17.3%, experimental cells were dopant-free and demonstrated potential for scalable production with a very high stability of 87% PCE [J.20]. With perovskite being very close to entering photovoltaic markets, benefits of perovskite solar cell production must be put at the forefront of their synthesis. The incorporation of green solvents into perovskite cells offers the opportunity to make cells more attractive to potential buyers from an ecological perspective while still maintaining high efficiency and yield potential.

5.1 Green Solvents in All-Polymer Solar Cells

Green solvents have been incorporated into photovoltaic cells of many varieties, with perovskite being one of the main focuses at the moment. Another relevant topic within the field is all-polymer (organic) solar cells. All-polymer solar cells utilize a blend of two polymers functioning as electron donors and acceptors, which interact with light to create a steady stream of electrons. Naturally, special chemicals must be applied to the polymers that make up these cells, which recently has included green solvents to provide an alternative to toxic chemicals. A large distinction in type and functionality of photovoltaic devices has been the usage of thin or thick films of the light-harvesting layer of the cell: generally, thick films are avoided due to constraints in light-harvesting capability and low PCE. A study by Z. Li et al. found that the usage of a green solvent in tandem with thick film solar cells yielded viable solar cells with a PCE of 9% despite the size of over 500 nm. The original non-halogenated solvent, cyclopentyl methyl ether, was used with the green solvent dibenzyl ether to yield promising results for the field as well as for future industrial prospects [Y.20].

The breakthrough of green solvent-based all-polymer solar cells has not been exclusive to thick film photovoltaic cells. Other studies with thinner films demonstrate positive results when utilizing green solvents in combination with all-polymer solar cells. In a 2015 study by S. Li et al., all-polymer cells used anisole as a green solvent with a perylene diimide base as the electron acceptor. Despite not reaching an efficiency to match the previously discussed experiment, a PCE of 6.5% was attained [J.15]. Anisole is also known as methoxybenzene, although it is not toxic like other benzenes (chlorobenzenes for example). The substitution of a methoxy group makes it much less toxic. Despite the presence of minor safety hazards when dealing with anisole, the material can be considered an effective green solvent.

Thin film solar cells, composed of several different layers to achieve greater efficiency and flexibility, have been studied in context with green solvents. Thin film photovoltaic cells have become prominent technologies and are synthesized by depositing layers of thin film upon substrate to create a photovoltaic device. Thin film solar cells are typically much more lightweight, flexible and cost-effective due to their lower usage (and thus wastage) of materials. T. Le et al. carried out an examination of the preparation of CIGSe (copper indium gallium selenium) thin film solar cells with the use of a nanocrystal ink deposition via spin coating. The green solvent ethanol was used to synthesize the nanocrystals, which were then deposited in a mixture of 2-propanol and 2-methoxyethanol for dispersion and eventual coating. These novel means of synthesizing thin film solar cells suggest further advancements in green technology and mass production from an environmentally-friendly standpoint [C.19].

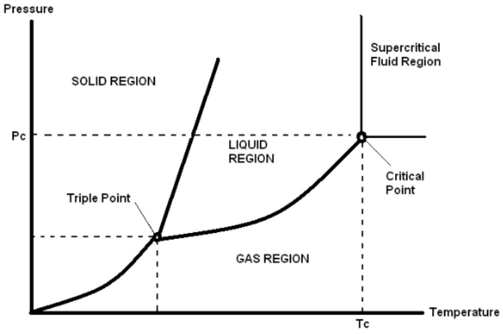


Figure 6: Ideal phase diagram [PA21].

6 Supercritical Fluids

Supercritical fluids have been utilized as green solvents because of their limited toxicity and their advantageous characteristics as materials. Supercritical fluids are substances with temperatures and pressures above their critical limits, yielding properties of both liquids and gases (Fig. 6). The material itself lies somewhere between the two and can be used for either in specific applications. In order to obtain a supercritical fluid, the material must be extracted after being subjected to very high temperatures and pressures for processing. This process creates eco-friendly and highly tunable materials that are able to be incorporated into many different applications.

Among the more common supercritical fluids is carbon dioxide, which typically acts as a gas at normal temperatures and a solid when frozen. Supercritical carbon dioxide has many uses in modern science, notably the synthesis of polymer melts with supercritical carbon dioxide acting as a solvent. Additional prevalent usage has come in the form of medicinal purposes. In 2004, N. Bandi et al. used supercritical carbon dioxide as a green solvent in the synthesis of budesonide–and indomethacin-hydroxypropyl-B-cyclodextrin (HP-BCD), a drug that can be used to prevent and slow the effects of neurological diseases. Chemicals were combined with supercritical carbon dioxide through the opening of containment vessels and mixing (Fig. 7). Ultimately, the special properties of supercritical carbon dioxide yielded an improved drug dissolution rate and reduced drug crystallinity, allowing for increased performance when ingested [U.04].

The use of supercritical carbon dioxide in polymer melt synthesis has been explored in recent years: crude oil is expended in massive amounts due to the worldwide reliance on plastic, a reliance that contributes greatly to pollution and the various environmental problems facing earth. The field of bioplastics helps to lessen this problem by creating plastics that are easily biodegradable,

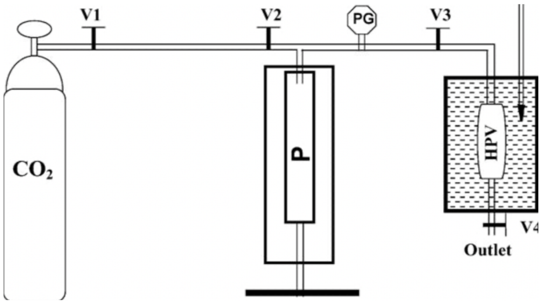


Figure 7: Supercritical fluid setup for cyclodextrin processing [U.04].

preventing landfill buildup over time. A 2018 study proposed the use of supercritical carbon dioxide as a grafting medium on which to combine polycaprolactone with monomers such as glycidyl methacrylate, maleic anhydride and methyl acrylate. The strength of the polymer produced with the supercritical carbon dioxide was much higher than that of earlier versions of the polymer which were produced with a mixture of starch, polycaprolactone and the various monomers incorporated into this study [F.18]. At this point in time, plastics are much more common than bioplastics due to the large differences in strength and functionality between the two; however, advancements shown to be effective such as those presented in this study will aid in making the field more tangible for consumers and investors alike.

6.1 Supercritical Fluids in Consumer and Hygeine Products

Despite having little recognition by the general public, supercritical fluids have been incorporated into many everyday products. A pertinent facet of this category of supercritical fluid usage is in antibiotics/antibacterial materials. An experiment conducted by T. Adamovic et al. used supercritical carbon dioxide to synthesize a cellulose acetate-based material with antibacterial properties. As with any synthesis utilizing supercritical fluids, very high pressures and temperatures were maintained during the chemical process. Cellulose acetate beads were impregnated with carvacrol, which is a phenol that has anti-toxic properties. The antibacterial halted bacterial activity by disrupting the cytoplasmic membrane of the bacteria and allowing all materials to permeate, resulting in cell death. When bacterial strains were tested in the presence of the antibacterial, there were significant declines in bacterial strains with a 60% carvacrol impregnation [I.17]. The main purpose of the study was to synthesize an antibacterial material to combat bacterial strains in the food industry (notably the heavily drug-resistant Staphylococcus aureus), though future applications in the field of biomedicine are projected. This study shows the possibilities of using supercritical fluids as impregnation devices in organic synthesis as well as new roles of green chemistry in antibacterial products.

Essential oils have been synthesized with supercritical carbon dioxide. The supercritical fluid, being non-toxic, cheap and non-volatile, is very desirable in regards to reaction processes. A 2012 study by Y. Sánchez-Vicente et al. exhibits an examination of applications of supercritical carbon dioxide in the synthesis of both citrus oils and eucalyptus oils, specifically the temperatures at which terpenes (unsaturated hydrocarbons found in plants) and supercritical carbon dioxide can effectively mix to create viable essential oils. An ideal compositional range of 313.15 and 323.15 K was found with a pressure of 7.64 MPa [C.13]. The usage of supercritical carbon dioxide is preferable over water and other polar solvents due to its nonpolar condition, which is favorable when dissolving terpenes, which are highly nonpolar. The overall flexibility of supercritical carbon dioxide and its many applications in common products should be of note as it highlights the many uses of the fluid as well as the already-established strengths of green solvents.

6.2 Environmental Applications of Supercritical Fluids

Supercritical fluids have been used to assist in the breaking down of lignocellulosic biomass, which is raw plant matter lacking constructive applications. Lignocellulose is very common due to the agriculture industry and is relatively difficult to dispose of due to its abundance; breaking it down can be very energy consuming. The material can be fermented and converted into ethanol, which is a very prominent and effective green solvent. In a 2015 paper, Tingyue Gu described the process in which supercritical carbon dioxide can be used to treat the lignocellulosic biomass prior to fermentation to save high extraction costs. Pretreatment is necessary as failure to do so will yield up to 20% less sugar from enzyme hydrolysis. Researchers chose supercritical carbon dioxide as it increases ethanol yield and is essentially carbon neutral, meaning that it does not contribute to the atmospheric carbon dioxide concentration and can be utilized in other processes. Additionally, supercritical carbon dioxide requires less energy and pressure for its synthesis. Energy expenditure is ultimately lower due to supercritical carbon dioxide lowering operation temperature and pressure compared with water [T.13].

6.3 Supercritical Water

Water is the most benign solvent: in an unaltered state, water is completely nontoxic. It is an incredibly effective solvent due to its high polarity (a result of its uneven charge/dipole moment). However, when subjected to large amounts of pressure and heat, water can gain new properties that allow for greater flexibility and tunability in reactions; changes in temperature or pressure lead to differences in density and phase. In a supercritical state, water presents a supercritical hydrothermal state best suited for materials synthesis, gaining the beneficial properties of both gases and liquids.

Notable research applications of supercritical water fixate around nanoparticle synthesis, which begins with an accumulation and fixation of metal salt monomers; a steady stream of supercritical water is introduced to synthesize equal-sized nanoparticles. Y. Zhu et al. used this method to synthesize chromium-doped CeO2 nanoparticles, which can be incorporated into reactions to increase the reaction rate. These particles have a wide range of environmental applications and can be used to combat pollution: examples include the treating of heavy oils, waste products from the paper industry and general unused plentiful biomass. Electron microscopy was used to identify nanoparticle size and configurations, confirming sizes between 5-8 nm and 15-30 nm as well as the presence of a crystal lattice. Additionally, high concentrations of oxygen were found within the nanoparticles, implying their potential as potent environmental catalysts [T.15].

Supercritical water, similarly to supercritical carbon dioxide, can be utilized in green processes to synthesize and break down plastics and other polymers. Important to this application of supercritical fluids in polymer synthesis is the strengthening of plastics, which can be achieved by reinforcing the plastic with materials such as carbon fiber. Besides being very mechanically strong, carbon fiber is extremely lightweight and resistant to degradation. In 2019, Y. Kim et al. aimed to use supercritical water as a green means to recycle this resistant material with a low environmental impact and low cost. Supercritical fluids are extremely strong solvents due to their high diffusion rate and low viscosity, among other properties. A notable point of focus in this study is the use of supercritical water as a lone solvent without cosolvents or catalysts. A decomposition efficiency of 99% was reached. After being decomposed, recycled carbon fibers were compounded with cyclic butylene terephthalate, a resin, to form composites with thermal and electrical applications, which was achieved through the use of a hot press [Y.19]. The results of this study highlight future environmental goals in regards to the full recyclability of carbon-strengthened polymers. Also of note is the strength of supercritical water as a solvent, which was able to achieve degradation without the aid of oxidants, cosolvents, or catalysts. Supercritical fluids offer cheap, efficient methods of breaking down or synthesizing materials with few lasting effects on the environment.

Supercritical water has been utilized in recycling processes besides those related to polymers and carbon material reclamation. The disposal of circuit boards and other technological parts is controversial due to the integral metals used in their construction; waste of this technology wastes the important materials as well. A 2013 study specifically focused on waste printed circuit boards, which are used in almost all electronics. Metals such as copper, tin, lead, cadmium, chromium, zinc, nickel and manganese make up a large portion of these circuit boards and are completely wasted once disposed of after usage. F. Xiu et al. proposed the usage of supercritical water instead of hydrometallurgical or pyrometallurgical processes, both of which leave toxins and large amounts of metal unretrieved. In the study, supercritical water methods utilizing depolymerization (conversion of polymers into monomers) and oxygen were employed to positive effect, although the depolymerization method was more effective than the method in the presence of oxygen as time and temperature increased. Acid leaching was then employed for metal extraction: the process was tested on untreated metals, supercritical water depolymerization-treated metals and supercritical water-treated metals in the presence of oxygen. Each method resulted in several metals exhibiting lower leaching efficiencies, though the depolymerization method had the most consistently high results out of the three. The results suggest that a combination of multiple methods could be employed to attain optimal results [F.13].

6.4 Extraction Applications of Supercritical Fluids

Supercritical carbon dioxide has potential in environmental applications as well as extraction. Metal ions chromium (III) and chromium (VI) are heavy metals that have several applications in consumer products such as dyes, pigments and leathers; additionally, chromium (III) and chromium (VI) have uses in coatings and platings for preservation. Both materials are very difficult to extract under normal conditions, however, as chromium (III) has a strong hydration with water molecules and chromium (VI) is highly toxic. These difficulties have prompted researchers to identify alternative methods of extraction, leading to the hypothesis that supercritical carbon dioxide can be used via chelation. The fluorinated chelating agent lithium bis(trifluoroethyl)-dithiocarbamate was used with supercritical carbon dioxide to achieve a high extraction efficiency of 90%+ for both materials [JK07].

Extraction of key nutrients and components of plants can be achieved through the use of supercritical fluids. Specifically highlighting soybeans, there are many compounds that are difficult to retrieve from plant biomass such as polyphenols and flavonoids. The latter of the two is a very effective antioxidant. Other compounds such as isoflavones have been shown to prevent or lessen the impacts of chronic diseases and cancers, making their extraction a high priority and incredibly sought after. A 2018 study sought to utilize the green solvent supercritical carbon dioxide in order to remove valuable constituents from soybean biomass for later use. Supercritical carbon dioxide is beneficial for extractions such as these due to its low temperature and pressure, low toxicity, low cost and recoverability; supercritical carbon dioxide does not chemically alter extraction materials. In the study, ethanol is used as a cosolvent due to its high polarity and low cost relative to its strength. This increased the slope of the extraction curve. Nonpolar extracts were lower but did not affect polar extraction. A maximum extraction yield of 2.1% was achieved at 12 kg CO2/ kg expeller [M.19].

7 Carbon-Based Applications of Green Solvents

The dispersion of certain carbon-based materials has been an area of difficulty and great attention due to the many beneficial properties that can be attained when dispersed in water. A material of focus is graphene, which consists of a

2D lattice of carbon atoms. Graphene can be used in composites, electronics and coatings, among other applications. This versatility is due to the many properties of graphene, including high conductivity, strength, flexibility and impermeability. Researchers have sought to extend these properties to water, which has proven to be very difficult due to the strength of its covalent bonds as well as its lack of polarity, which does not interact favorably with highly polar water molecules. At the moment, very little progress has been made towards fixing this problem through the use of green solvents, although work has been done by using organic solvents as well as through reduction by adding functional groups containing oxygen. Despite this, applications of graphene synthesized with green solvents have been explored with promising results.

7.1 Graphene Preparation Via Green Solvents

Graphene can be both prepared and processed with green solvents to produce positive results as well as mitigate a portion of the environmental impact that its synthesis can cause. A novel approach for the preparation of graphene is presented by M. Yi et al., in which multiple green solvents are mixed together to exfoliate graphite (in turn producing graphene). Ethanol and isopropyl alcohol were mixed in purified water, which became the medium into which graphite powder was deposited. The solvent mixture was chosen for toxicological reasons as well as their low boiling point and low cost. The combination of green solvents and an easily accessible liquid phase suggests the use of this process in the mass production of graphene from graphite in the future, with the cheapness of all materials factoring heavily into this process [W.20b].

The oxidized form of graphene, graphene oxide, has been shown to be a useful tool in the preparation of films with mechanical properties. In its oxidized state, graphene oxide is able to interact with other materials (notably water) at a much higher rate, albeit with a loss of several properties that make graphene so desirable in the first place. A 2019 study combines graphene oxide with cellulose to synthesize carbon nanocomposite films processed by green solvents. The primary green solvent used in this experiment was polyethylene glycol, which was mixed with sodium hydroxide and deposited into a system with cellulose and graphene oxide. The chemicals were stirred and then frozen, after which the film was cast, gelated and dried to form a film. The film was cross-linked with epichlorohydrin to promote adhesion with cellulose and stronger attraction between different materials. Following film synthesis, tensile strength was assessed and the film was examined for defects by an electron microscope, of which none were found. Additionally, the graphene oxide film was shown to inhibit harmful UV rays [S.20]. The strong covalent bonds that hold graphene together make the material incredibly strong (albeit brittle), which was applied to this film to positive effect. These results indicate scalable and inexpensive production in the future.

8 Conclusion

Green solvents represent a promising area of innovation in the chemical industry, with interesting topics ranging from biosolvents and ionic liquids to green solvents in solar cell films, supercritical fluids and green solvents used with carbon materials. Great strides have been made to incorporate these materials into as many modern technologies as possible. Green solvents have no major effect on the environment in case of deposition, spillage, or emissions release. In many instances, green solvents are very cost-effective as well, offering no significant increase in price over toxic/petrochemical solvents. However, the preparation of green solvents can be very costly, such as the supercritical fluid process, which requires expensive and potentially non-feasible equipment.

Environmental impact is the most important facet of green solvents. Whereas green solvents are essentially benign, toxic solvents can release harmful vapors, harm wildlife and contribute to water pollution when disposed of, all of which have severe repercussions over time. The tunability of green solvents such as ionic liquids and supercritical fluids allows for a very broad range of applicability, whereas simple ethyl containing solvents can be used in solar cells and polymer synthesis. When one has the opportunity to incorporate a green solvent into a reaction in the place of a toxic solvent, the green solvent should always take priority.

Green solvents are completely viable and necessary at this point in time. Because the threats of climate change have become impossible to ignore, measures must be taken to reduce the impact of humankind on its planet. Green solvents offer benign and effective solutions to toxicity in modern chemicals, which solidifies their viability in modern sciences. Despite minor inflexibilities in current applications, green solvents are completely necessary and beneficial in a rapidly changing world.

9 Acknowledgements

I would like to thank Dr. Thomas McCoy, Christine Leventhal, and Horizon Academic Research Program for the support of my scientific endeavors.

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