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Bio-Solvents: Synthesis, Industrial Production and Applications

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Abstract

Solvents are at the heart of many research and industrial chemical processes and consumer product formulations, yet an overwhelming number are derived from fossils. This is despite societal and legislative push that more products be produced from carbon-neutral resources, so as to reduce our carbon footprint and environmental impact. Biomass is a promising renewable alternative resource for producing bio-solvents, and this review focuses on their extraction and synthesis on a laboratory and large scale. Starch, lignocellulose, plant oils, animal fats and proteins have been combined with creative synthetic pathways, novel technologies and processes to afford known or new bio-derived solvents including acids, alkanes, aromatics, ionic liquids (ILs), furans, esters, ethers, liquid polymers and deep eutectic solvents (DESs)—all with unique physiochemical properties that warrant their use as solvation agents in manufacturing, pharmaceutical, cosmetics, chemicals, energy, food and beverage industries, etc. Selected bio-solvents, conversion technologies and processes operating at commercial and demonstration scale including (1) Solvay's Augeo™ SL 191 renewable solvent, (2) Circa Group's Furacell™ technology and process for making levoglucosenone (LGO) to produce dihydrolevoglucosenone (marketed as Cyrene™), (3) Sappi's Xylex® technology and demonstration scale processes that aim to manufacture precursors for bio-solvents and (4) Anellotech's Bio-TCat™ technology and process for producing benzene, toluene and xylenes (BTX) are highlighted.

Keywords: bio-solvents, renewable resources, green chemistry, biorefinery, biomass

1. Introduction

Air quality deterioration, environmental, health and safety issues have raised serious concerns over continued processing of fossil-based feedstocks in producing chemical products such as fuels and solvents. As such, many efforts are being made to reduce the use of hazardous substances (particularly volatile organic solvents (VOCs)) and to eliminate or minimize waste generation in chemical processes. Switching from the currently widely used fossil-based solvents to greener ones derived from renewable resources constitutes a key strategy to drive sustainability as well as clean and safer chemical procedures in both industry and academia [1, 2].

Solvents are central to many chemical processes as they dissolve reagents and ensure sufficient interactions, at a molecular level, for chemical transformations to take place. For instance, the pharmaceutical industry is heavily reliant on solvents for

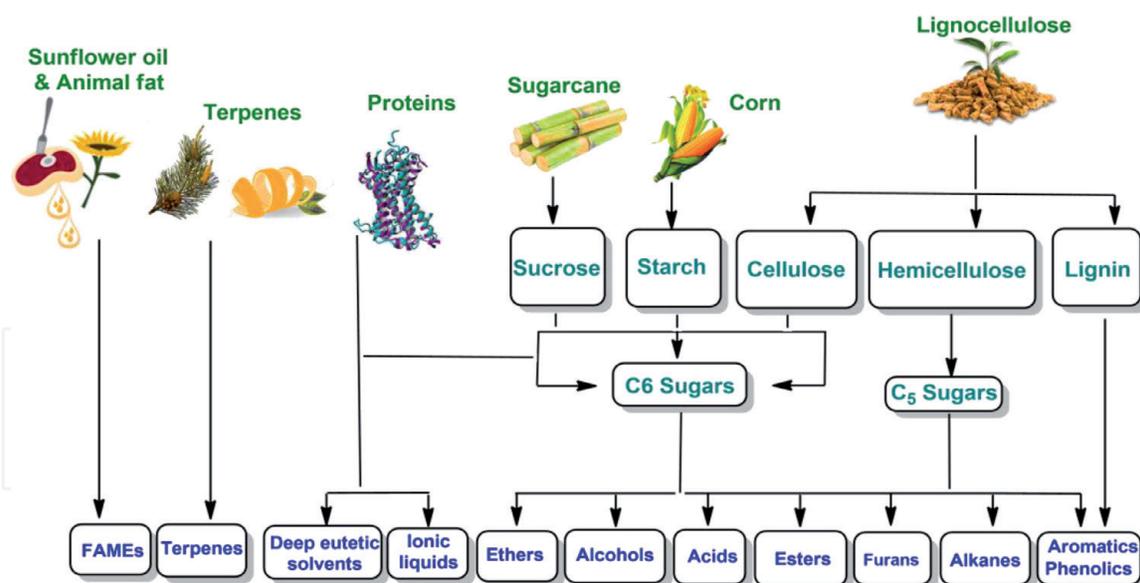


Figure 1.
The various sustainable solvents derived from biomass.

drug discovery, process development and drug manufacturing processes [3]. They are also used to extract and separate compounds from mixtures or natural products. Solvents are also important for performing compound purifications and form part of many manufacturing protocols as well as consumer products including fragrances, cleaning agents, cosmetics, paints, flavors, adhesives and inks, to name a few [1].

Many organic solvents are volatile, flammable and toxic; therefore, their use poses safety and health risks and impacts negatively on the environment. In order to address these issues, ‘solvent-free’ chemistry has been proposed, to mitigate against solvent exposure risks, and for chemical manipulations and formulations that absolutely require solvents, a system of ranking them by their environmental, safety and health (ESH) attributes has been introduced. This system aims to aid in selecting and using those solvents with minimum ESH risks and good green profiles [4–6].

Making use of renewable resources in producing solvents is a promising and important strategy to move towards sustainable chemical processing and to replace organic solvents derived from fossil raw materials. To this end, bio-based feedstocks such as carbohydrates, carbohydrate polymers, proteins, alkaloids, plant oils and animal fats have been used to produce bio-based solvents (**Figure 1**). This often requires prior processing of the raw materials (typical by thermochemical and biochemical conversion methods) to give familiar solvents or to provide completely new and innovative solvent entries [7, 8]. There are some, such as essential oils extracted from citrus peels (which are rich in terpenes), that are used directly.

The main processing methods include biochemical and thermochemical conversion [7]. Using one or a combination of these processing techniques, several classes of bio-based solvents (including alcohols [9–11], esters [12, 13], ethers [14], alkanes [15], aromatics [16] and neoterics [17, 18]) can be manufactured (**Figure 1**).

2. Alcohols

2.1 Methanol, ethanol, propanol and butanol

Bio-based ethanol is currently the most produced of all bio-solvents and is produced through biological transformation of sugars. These processes use either edible (sugarcane and corn) or nonedible (cellulose) feedstocks [19]. However, due

to concerns over edible feedstock causing the rise of food prices, there has been a move towards optimizing processes that produce cellulosic ethanol [20, 21], and indeed the world's first cellulosic ethanol commercial-scale production plant was commissioned in 2013 by Beta Renewable. This plant is situated in Milan, Italy, and uses Proesa™ technology for the pretreatment of agricultural waste (such as rice straw, giant cane (*Arundo donax*) and wheat straw) for production of ethanol at 60,000 tons/year [9].

Ethanol's most common uses are as a biofuel and solvent in consumer products such as perfumes, food coloring and flavoring, alcoholic drinks and in certain medication. The latter can be in both synthetic medicines and natural products. For example, highly efficient ethanol-assisted extraction of artemisinin, an active antimalarial drug, from *Artemisia annua*, has been demonstrated [22].

The presence of the hydroxyl group in ethanol makes it capable of hydrogen bonding, and it is therefore miscible with water and other solvents such as toluene, pentane and acetone.

Large-scale production of methanol is currently achieved using fossil-derived sources, by hydrogenation of carbon monoxide in the presence of a catalyst such as ZnO/Cr₂O₃ and Cu/ZnO/Al₂O₃ [23]. It can be obtained in small amounts in fermentation broths and from the gasification of biomass to produce bio-based syngas for subsequent conversion to methanol. The commercial viability of the latter is still under investigation [24].

Due to the structural similarity of methanol to ethanol, the former is often used in place of ethanol in synthetic procedures. However, its toxicity has limited its widespread application as a solvent in consumer products. Still, other useful applications where methanol features not only as a solvent but as a reagent and fuel do exist. For instance, methanol is used in methanol fuel cells and is a key reagent in the manufacture of fatty acid methyl esters (FAMES) (biodiesel) through transesterification of triglycerides and in dimethyl ether (DME) (diesel substitute) production [24]. It is also used in acid-catalyzed formation of methyl levulinate from bio-derived furfural alcohol (FA) and 2,5-hydroxymethylfurfural (HMF) [25].

Thermochemical synthesis of alcohols such as methanol, ethanol and propanol (1-propanol and 2-propanol) from glycerol raw materials (**Figure 2**) is also known. This process is often promoted by a catalyst through a hydrogenolysis reaction [26–28].

n-Butanol production was first commercialized in the early 1900s, in the Weizmann process (ABE fermentation). Here, *n*-butanol, acetone and minute amounts of ethanol are produced from starch feedstock using *Clostridium acetobutylicum* [10, 29]. Later, fossil-based production of *n*-butanol became more cost-effective which led to abandonment of the Weizmann process. Today there are some ABE fermentation production units; however, most *n*-butanol is produced mainly from petroleum by either (1) the oxo synthesis which involves hydroformylation of propene and then hydrogenation of the afforded butraldehyde, in the presence of a rhodium or cobalt homogeneous catalysts, (2) the Reppe synthesis (which involves the treatment of propene with CO and H₂O) in the presence of a catalyst such as iron or (3) a multistep, catalytic hydrogen borrowing, cascade process involving self-aldol condensation of acetaldehyde, dehydration and then hydrogenation of the resultant croton aldehyde [30].

n-Butanol has a low order of toxicity and has an energy density of 29.2 MJ/L, which is comparable to that of gasoline (32.5 MJ/L). It is also miscible with gasoline, and so it is not surprising that this alcohol is sometimes blended with gasoline to improve its properties. *n*-Butanol is also used as a solvent for coatings (varnishes, resins and waxes), paints and cosmetics and is an intermediate for making solvents (e.g. butyl propanoate, dibutyl ether and butyl acetate), polymer monomers (e.g. butyl acrylate and butyl vinyl ether) and plasticizers (e.g. butyl phthalates) [31].

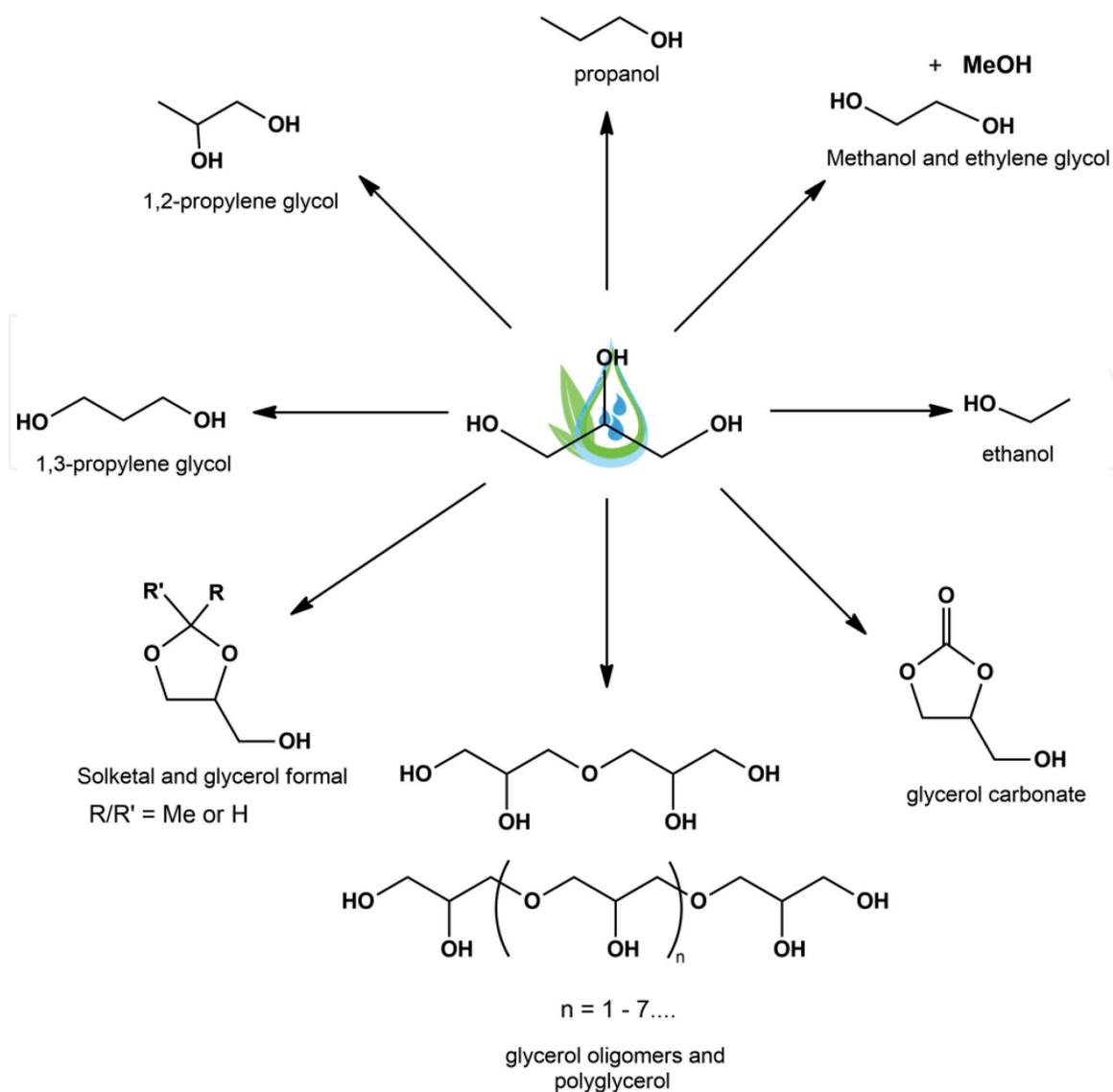


Figure 2.
Bio-based solvents derived from glycerol.

2.2 Furfuryl alcohol

The production of furfuryl alcohol involves two stages: (1) the pentosan is first hydrolysed to pentoses, e.g. xylose, and (2) cyclodehydration of the pentoses into furfuryl alcohol. The reaction is catalysed by acids such as dilute sulfuric or phosphoric acid, and the furfuryl alcohol is recovered by steam distillation and fractionation. Yields are generally between 30 and 50% [32].

Furfuryl alcohol is a solvent used in the refining of lubricating oils [33]. During the production of butadiene, an extractive distillation step is required to remove impurities [34]. Furfuryl alcohol is one of the extractive solvents that have been used for this purpose on a commercial scale, for example, at TransFuran Chemicals, USA. Furfuryl alcohol is also used as a solvent during crystallization of anthracene oils and during the modification of high phenolic molding resins to improve the corrosion resistance of the cured resin [35].

2.3 Glycerol and its derivatives

Global biodiesel production has increased from 0.78 billion (in 2000) to 32.6 billion liters by 2016 [36]. This has made large quantities of glycerol widely available, since biodiesel production generates 10,000 liters of glycerol for every 100,000

liters of fuel produced. This oversupply of glycerol, and its low toxicity, has driven many efforts to increase the portfolio of glycerol applications both directly and indirectly (by using it as a raw material to access value-added products). Because of its sweet taste, it can be used directly as a sweetener in processed foods. It is also used as a thickener and stabilizer for foods containing water and oil. Glycerol functions well as a solvent for processing cosmetics (this is where most glycerol is used) and forms part of pharmaceutical formulations to name a few [37].

More recently, glycerol has been used as a sustainable replacement for fossil-derived monoethylene glycol in purification of bioethanol by extractive distillation. Using glycerol, up to 99% purity of bioethanol is recovered [38]. Although its high viscosity and boiling point complicate reaction workups, several examples of successful Aza-Michael addition and Suzuki-Miyaura and Mizoroki-Heck reactions in glycerol have been reported [38, 39].

The conversion of glycerol leads to a variety of other products with solvent properties such as solketal, glycerol formal, glycerol carbonate, glycerol oligomers and polymers, deep eutectic solvents (DESs) as well as diols (**Figure 1**) [37, 40].

Solketal and glycerol formal are the products of acid-catalyzed acetone and formaldehyde reactions with glycerol, respectively [41], and currently solketal is sold commercially under the name Augeo™ SL 191. It is used as a solvent in interior-scenting products and household cleaners [42]. Another route to solketal is by metal-catalyzed condensation of glycidol with acetone [43].

Solketal is polar and has a very high boiling point (188°C), which makes it useful as a coalescent solvent in paints and inks and in controlled release systems (where gradual release of species like pesticides and drugs is required). It is a good heat transfer fluid and fuel additive, especially in gasoline and biodiesel where it favorably reduces the latter's viscosity [41]. Its high sensitivity to acid has limited its use as a solvent for reactions.

2.3.1 Glycerol oligomers and polymers

The main route for preparing di-, tri-, tetra- and polyglycerol is by direct oligomerization or polymerization of glycerol using acid or base catalysts, such as potassium carbonate or sulfuric acid. The base catalyst is usually more efficient due to its better solubility in glycerol, albeit with poor selectivity [44]. Glycerol oligomers and polymers have hydrophilic heads which makes them useful for surfactant applications. By careful control of their length and branching during syntheses, desirable physiochemical properties can be built into them such that they can be used as lubricants, polymers and solvents. They have also been earmarked as replacement solvents for fossil-derived glycol ethers in paints, inks and cleaning agents [45].

2.3.2 Diols

In addition to methanol, ethanol and propanol [46], the hydrogenolysis of glycerol can lead to formation of ethylene glycol (EG) and propylene glycol (PG, 1,2-propanediol and 1,3-propanediol) (**Figure 1**) [47]. It is worth mentioning that diols can also be obtained from thermochemical conversion of fructose in the presence of homogeneous osmium and ruthenium catalysts [48] and from cellulose using a nickel-tungsten carbide catalyst [49]. Recently, Sappi Ltd. acquired Plaxica's Xylex® technology which they plan to utilize in valorizing the hemicellulose component of their pulp processing waste, in producing, furfural and xylitol [50]. Changchun Dacheng Industrial Group operates a commercial integrated biological and thermochemical process that manufactures EG, PG

and 2,3-butanediol (2,3-BDO) from starch. Ten thousand tons of 2,3-BDO are produced annually [51].

Diols serve as dehumidifying and antifreeze agents. They have important applications as monomers (in polyester production) and work as solvents in the cosmetic and coating (varnishes and waxes) industries [46, 49].

3. Esters

3.1 Acyclic esters

Lactates are a class of non-toxic and green solvents obtained from treating lactic acid with various alcohols, such as ethanol, propanol and butanol. Lactic acid feedstock for making these solvents can be obtained *via* biochemical and thermochemical routes. The latter is economical but uses toxic hydrogen cyanide and gives a racemic mixture of lactic acid, while the biological process uses microbial fermentation technology and is more selective.

Ethyl lactate is the most common of the lactate esters, and Archer Daniels Midland Company, USA, operates a commercial production plant. Ethyl lactate has excellent physical properties, including a low vapor pressure and high boiling point (151–155°C) and solvent power (Kauri-butanol value > 1000). This makes it a good replacement for halogenated solvents, acetone and toluene and an excellent solvent for solubilizing resins and polymers. As such, it is used to dissolve plastics and to remove salts from circuit boards. Ethyl lactate also dissolves grease, inks and solder paste and strips paint [52].

Fatty acid methyl esters are produced by the transesterification of triglycerides, from vegetable oils or animal fats, with methanol for biodiesel applications. However, FAMES can also be used as bio-based solvents and have been found to possess high solvent power. When mixed with ethyl lactate, evaporation is aided post utilization in dissolution or in cleaning industrial parts [53].

3.2 Glycerol carbonate and γ -valerolactone

Glycerol carbonate can be synthesized via direct or indirect routes. With direct routes, carbon monoxide and oxygen [54] or carbon dioxide [55] is treated with glycerol in the presence of metal catalysts such as Pd and Sn, respectively. The use of CO₂ is more desirable due to its abundance and lower toxicity in comparison to CO; however, this route is low yielding (7–35%). The indirect route involves carbonation of glycerol with an activated carbonation source such as urea, dimethyl carbonate or phosgene, and among these dimethyl carbonate is preferred from an industrial production perspective [56].

Due to its favorable properties which include high polarity, boiling point (110–115°C) and flash point (109°C) and low vapor pressure, glycerol carbonate has interesting applications as a polar protic solvent, electrolyte liquid carrier, detergent solvent, humectant and nail polish/gel stripper [57]. It has also been demonstrated to serve as a promising solvent in pretreatment of sugarcane bagasse [13].

γ -Valerolactone (GVL) can be produced from 5-hydroxymethylfurfural or furfural alcohol via their dehydration and hydrolysis, respectively [58]. The resultant levulinic acid can then be converted to GVL in the presence of hydrogen and a suitable catalyst [59, 60]. This therefore links the cost of GVL production to the production of hydrogen. This has resulted in the limited widespread production and use commercially. The increased number of hydrogen production plants by water electrolysis (or use of transfer hydrogenation techniques) should aid in improving the process and economics to favor GVL commercial-scale production in the near future.

The physical and chemical properties of GVL favor its application as a solvent and illuminating fuel. It has a low melting point, high boiling and flash point and low toxicity and has a characteristic herbal smell that can be used to identify leaks or spills [61]. GVL has been used as a solvent in many biomass conversion reactions. For example, it was used as a solvent in the pretreatment of lignocellulose, hydrolysis of lignocellulose and dehydration of carbohydrates to furans [61, 62]. It has also been used as solvent in cross-coupling reactions such as Sonogashira [63], Hiyama [64] and Mizoroki-Heck [65].

3.3 Cyrene™

Cyrene (dihydrolevoglucosenone or 6,8-dioxabicyclo[3.2.1]octanone) is a ketone functionality containing solvent that can be prepared in a two-step process from cellulose [66]. The common starting point in its synthesis is from levoglucosenone (LGO), which can be obtained from a variety of cellulosic starting feedstocks such as Bilberry presscake [67], corn cob [68], poplar wood [69] or bagasse [70]. LGO has been successfully obtained from cellulose [71–73], by the patented Furacell™ process discovered by Circa Group Ltd., Australia. The process gives 40% yield of LGO and has consequently been scaled up to a 50 ton/year production [74]. The next step after the production of LGO is its hydrogenation to afford Cyrene™ (Figure 3). The hydrogenation of levoglucosenone to Cyrene has been largely dominated by heterogeneous Pd catalysts [75, 76].

Concerns over the use of toxic solvents (such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP)) in the industry have led to the exploration of Cyrene™ as a potential replacement. These dipolar aprotic solvents have very similar properties to those of Cyrene™ [77]. As a result, more examples of its use as solvent in syntheses are becoming popular. For example, metal organic frameworks that were previously prepared in DMF solvent have been successfully synthesized in Cyrene™ [78]. Cyrene™ has also been used in amide bond formation reactions [79].

3.4 Alkanes and aromatics

3.4.1 Alkanes

Furfural and hydroxymethylfuran can react with acetone (derived from fermentative processes) resulting in aldol-condensed products with longer carbon chain lengths. Subsequent hydrodeoxygenation of the aldol condensation products using a supported Pd catalyst, H₂ (plus acetic and/or Lewis acid cocatalysts), produces alkanes as shown in Figure 4 [80–83].

Alkanes are useful for reactions requiring nonpolar medium because they are generally unreactive. Consequently, they have been used as reaction medium during

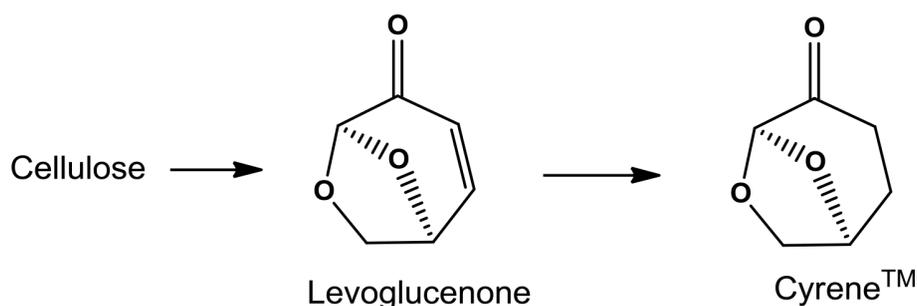


Figure 3.
Synthetic steps of Cyrene™ from cellulose.

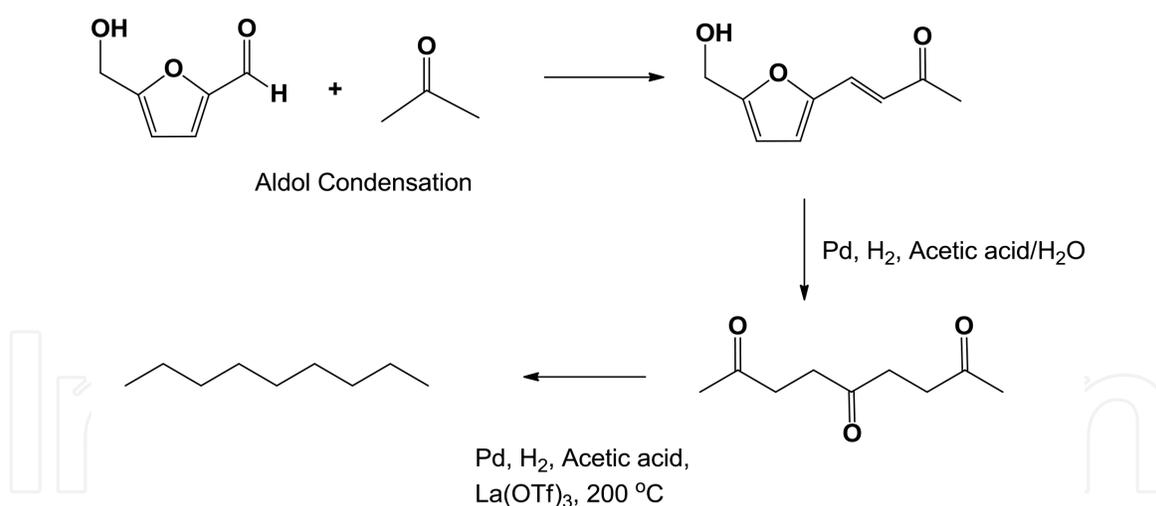


Figure 4.
Synthetic steps for straight-chain alkanes from bio-derived furan compounds.

the synthesis of drugs, pesticides and other chemicals. Their use as fuels varies depending on the length of the carbon chains. Generally C₃ and C₄ alkanes are used as liquefied petroleum gas for cooking and in cigarette lighters, respectively, while C₅–C₁₈ alkanes are used in gasoline, diesel and aviation fuel.

3.4.2 Benzene, toluene and xylenes

Benzene, toluene and xylene (BTX) can be derived from wood and agricultural waste [84]. Anellotech, a US-based company, has scaled up a process that converts biomass, using their Bio-TCat™ technology, into BTX mixtures. Benzene, toluene and xylene have identical properties as their fossil-derived counterparts [85]. Benzene is used in the manufacture of resins, rubber lubricants, synthetic fibers, detergents, pesticides, drugs and plastics. Toluene is used in printing and leather tanning processes and as a solvent in paint, a nail polish remover, thinners and glues, while xylene finds use as a cleaning agent, ingredient in pesticide manufacturing, disinfectants, paints, paint thinners, polishes, waxes and adhesives.

An elegant multistep route to renewable *p*-xylene was proposed. It begins with (1) the conversion of glucose to fructose, (2) followed by dehydration of the fructose to HMF, (3) hydrodeoxygenation of HMF to 2,5-dimethylfuran (2,5-DMF) and (4) subjecting the resultant 2,5-DMF to Diels-Alder cycloaddition with ethylene to afford the product [86].

3.4.3 Terpenes

Terpenes are a class of natural solvents obtained from essential oils found in plants. They have C₅H₈ isoprene units and can be acyclic, bicyclic or monocyclic; therefore, they have varying physical and chemical properties. Extraction using water hetero-azeotropic distillation at low temperatures affords terpenes, and they in turn have been utilized as green alternative solvents for the extraction of oils from microalgae [87].

D-Limonene is extracted from citrus peels and pulp by steam distillation and alkali treatment [88]. Industrially, limonene is used as a solvent in place of various halogenated hydrocarbons. By 2023, the demand of D-limonene is expected to be 65 kilotons/year [88]. It is also used as solvent to degrease and grease wool and cotton wool and in the dissolution of cholesterol stone, where its performance is better than chloroform and diethyl ether (DEE) in the latter. The catalytic isomerization

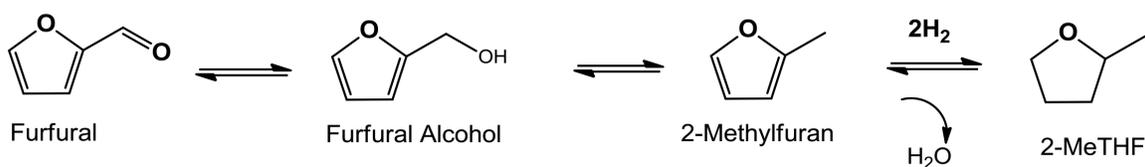


Figure 5.
The successive hydrogenation of furfural to 2-methyltetrahydrofuran.

and dehydrogenation of D-limonene give *p*-cymene, an aromatic hydrocarbon with equally good solvent properties [89].

α -Pinene is the most widely available terpenoid and is mostly found in essential oils of coniferous trees, or it can be recovered from paper pulping by-products, i.e. from crude sulphate turpentine [90]. Alpha-pinene is used as a household cleaning solvent and repellent for insects and in the production of perfumes. It also has medicinal properties as an anti-inflammatory and antibiotic agent.

3.5 Ethers

Bio-derived ethers are produced by the dehydration of bio-alcohols, mainly ethanol and methanol to form diethyl ether and dimethyl ether, respectively. These ethers are usually used as fuel additives to improve its octane rating and reduce emissions (NO_x and ozone) and engine wear.

2-Methyltetrahydrofuran (2-MeTHF) is a biodegradable, non-toxic, non-ozone-depleting, easy-to-recycle ether solvent with a good preliminary toxicology report [91]. It is produced from either furfural or levulinic acid *via* catalytic processes. For instance, the successive hydrogenation of furfural over Ni-Cu, Fe-Cu, Cu-Zn or Cu-Cr produces 2-MeTHF as illustrated in **Figure 5** [92, 93].

The first two hydrogenations have been reported to quantitatively convert furfural alcohol to 2-methylfuran using Ni-based catalysts followed by 2-methylfuran conversion over a Cu-Zn catalyst. 2-MeTHF can also be prepared from levulinic acid *via* consecutive hydrogenation and dehydrogenation steps. Here, Ru-based catalysts are the most active.

Pfizer, USA, has reported the application of 2-MeTHF as a solvent in two-phase reactions due to the poor solubility of water in 2-MeTHF [94]. This bio-derived solvent has also been used in place of dichloromethane (that has unfavourable environmental effects) because of its low boiling point, which makes it difficult to contain on a large scale. Using 2-MeTHF, high yields of product were afforded for amidations, alkylations and nucleophilic aromatic substitutions reactions.

Another pharmaceutical company, Actelion Pharmaceuticals Ltd. in Switzerland, uses 2-MeTHF as solvent in the synthesis of 5-phenylbicyclo-[2.2.2] oct-5-en-2-one [95], an intermediate during the preparation of an important pre-clinical candidate. Furthermore, the reaction was successfully upscaled to kilogram scale, and the reaction still gave excellent yields (98%) in 2-MeTHF.

4. Ionic liquids

Ionic liquids (ILs), defined here as materials that are made up of cations and anions (salts) which melt at or below 100°C , evolved from the nineteenth century. This field started with a report by Paul Walden, in which he studied the physical properties of ethylammonium nitrate ($[\text{EtNH}_3][\text{NO}_3]$), a salt which melted at around 14°C [96]. Ionic liquids are commonly formed through the combination of an organic cation (usually heterocyclic), such as dialkylimidazolium, and either an

inorganic or organic anion (such as halides or methanesulfonate) [97]. The advantage with ionic liquids is their low vapor pressure, meaning the risk of atmospheric contamination and related health issues are reduced by using these solvents. It is for this particular reason that they are viewed as green solvents [98]; however, low volatility alone is not the only property that makes ionic liquids green. For instance, toxic and non-biodegradable ionic liquids will not be referred to as a green solvent even though they have negligible volatility [97]. In this regard, ionic liquids composed of bio-derived components have the added advantage and are outstanding candidates as sustainable and green solvents.

4.1 Sugar-based ionic liquids

Since the depolymerization of hard-to-dissolve carbohydrate polymers can be achieved using ILs, it would be beneficial to develop sugar-based ILs with the aim of employing these in a 'closed-loop' carbohydrate polymer depolymerization process [99]. Some sugar-based ionic liquids which have potential in this regard have already been synthesized, even though they have been used for various other processes. The glucose-linked 1,2,3-triazolium ionic liquids were synthesized by copper(I)-catalysed regioselective cycloaddition of a glucose azide to a glucose alkyne, followed by quaternization with methyl iodide (**Figure 6**) [100]. The ILs were used as reusable chiral solvents and ligands in copper(I)-catalysed amination of aryl halides with aqueous ammonia. The triazolium salt affords the compound in its liquid state at room temperature, and hence the compound can be used as a solvent, while the free hydroxyl groups of the glucose moiety aids in stabilizing the copper(I) species during the reaction.

Methyl-D-glucopyranoside has also been used to synthesize an ionic liquid with promising solvent potential [101]. The synthetic sequence involved uses *t*-butyldimethylsilyl chloride (TDSiCl) to protect the hydroxyl at the primary position. The other secondary hydroxyl groups were converted to methyl ethers followed by reduction of the anomeric position and further deprotection of the primary hydroxyl. After deprotection of the primary hydroxyl group, it was then converted to a triflate to form an intermediate. This triflate intermediate finally underwent a nucleophilic substitution reaction using diethyl sulphide to afford an ionic liquid, with a triflate anion and a sulfonium cation, which was a liquid at room temperature (**Figure 6**).

Handy et al. have used fructose to synthesize room temperature ionic liquids [102]. In their synthetic protocol, copper carbonate, ammonia and formaldehyde were used to ring-close fructose and form hydroxymethylene imidazole. This imidazole was then taken through a series of alkylation steps (with 1-bromobutane followed by iodomethane) to form an imidazolium cation. Anion metathesis was performed to give a series of room temperature ionic liquids (**Figure 7**), which were used as recyclable solvents for Mizoroki-Heck cross-coupling of aryl iodides with alkenes.

An arabinose-based imidazolium IL was synthesized in 2018 starting with 2,3,5-tri-*O*-benzyl-D-arabinofuranose [103]. The pentofuranoside starting material was prepared by benzylating all the hydroxyl groups of D-arabinose, except the hydroxyl group on the carbon adjacent the ring oxygen atom. The free hydroxyl group was then reacted with propane-1,3-diylldioxyphosphoryl chloride in the presence of 1-methylimidazole to form a mixture of anomeric phosphates. This was then reacted with 1-methylimidazolium chloride and trimethylsilyl triflate, in catalytic amounts, to give a pure anomeric ionic liquid with a chloride anion. Anion metathesis reactions gave two additional ionic liquids (**Figure 7**), which were used as co-solvents in the synthesis of alcohols from aromatic aldehydes.

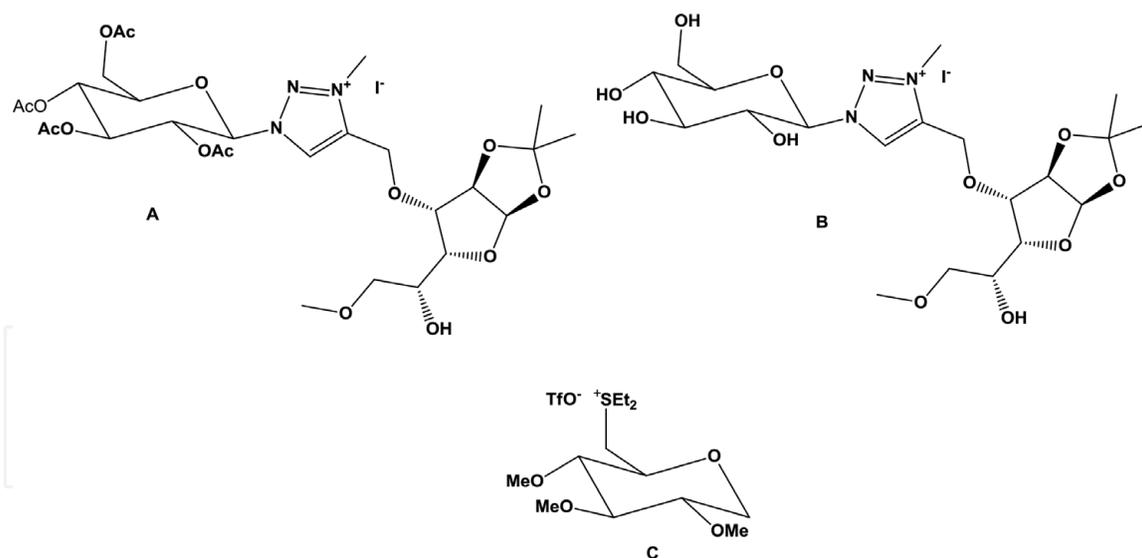


Figure 6. Glucose-based ionic liquids [(A and B) glucose-tagged triazolium ILs; (C) glucopyranoside-based IL].

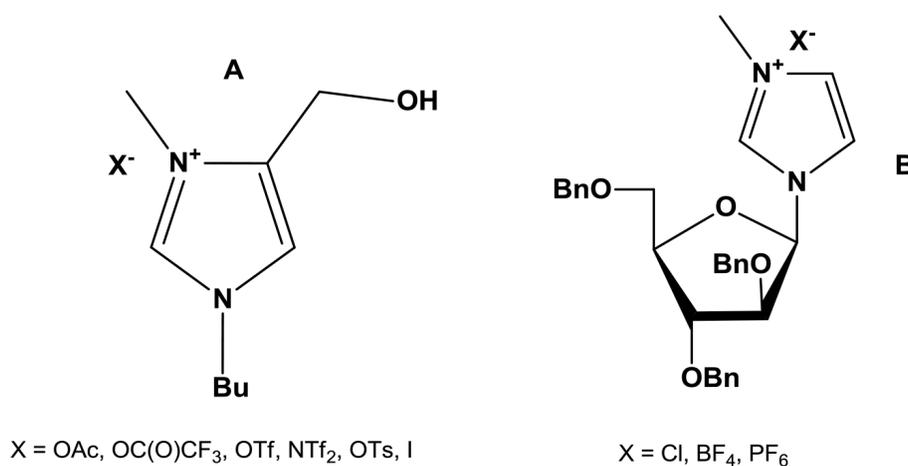


Figure 7. ILs based on pentoses [(A) fructose-based ILs; (B) arabinose-based ILs].

4.2 Alkaloid-based ionic liquids

Ionic liquids which contain ampicillin as active pharmaceutical ingredients were developed by Ferraz et al., by neutralizing basic ammonia solutions of ampicillin with different organic cation hydroxides. These ampicillin-based ILs may be useful in the development of bioactive materials [104]. A chiral IL derived from ephedrine was synthesized by Wasserscheid et al. N-methylephedrine was synthesized from ephedrine and alkylated with dimethyl sulphate followed by ion exchange to form the IL, with a melting point of 54°C [105]. Heckel et al. reported the synthesis of ionic liquids derived from nicotine by the quaternization of the pyridine ring of nicotine with methyl iodide and ethyl bromide. The resulting chiral nicotine-based ILs were examined as chiral solvating agents (Figure 8) [106].

4.3 Lipid-based ionic liquids

Linoleate and oleate were used in the syntheses of four ILs with melting points below -21°C (Figure 9). Unsaturated fatty acids were initially taken through neutralization reactions with NaOH followed by ion exchange with either

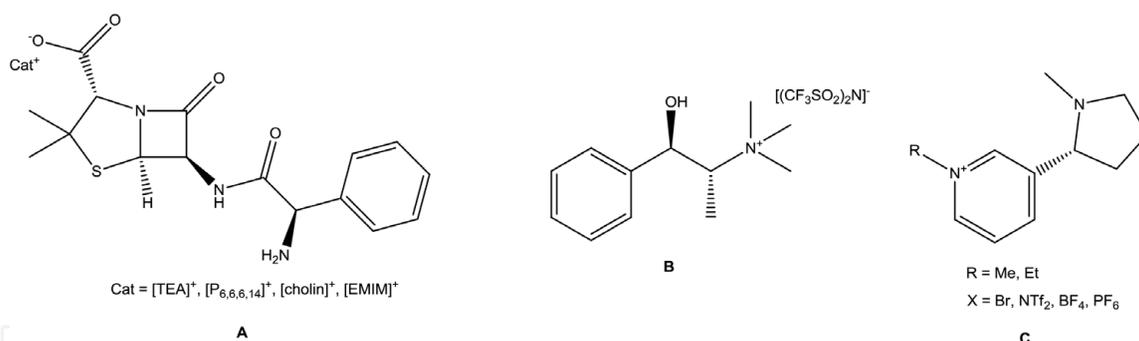


Figure 8. Alkaloid-based ILs [(A) ampicillin-based ILs; (B) ephedrine-based IL; (C) nicotine-based ILs].

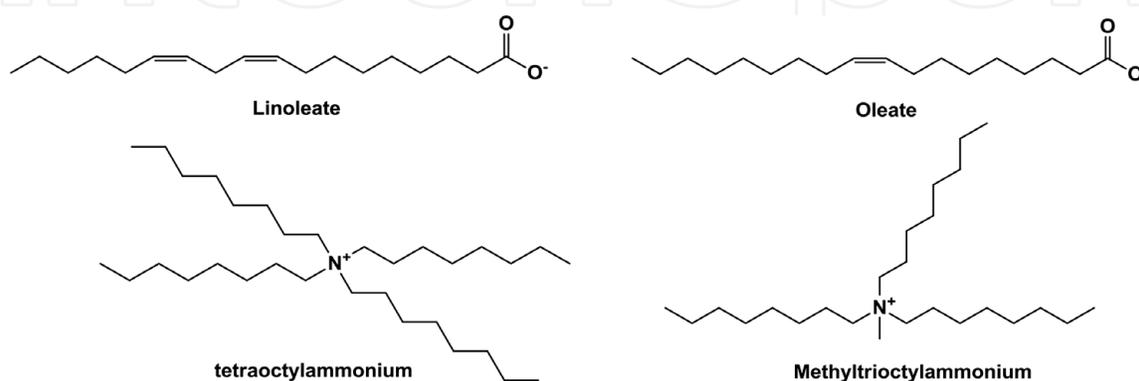


Figure 9. Anions and cations used in the syntheses of lipid-based ILs.

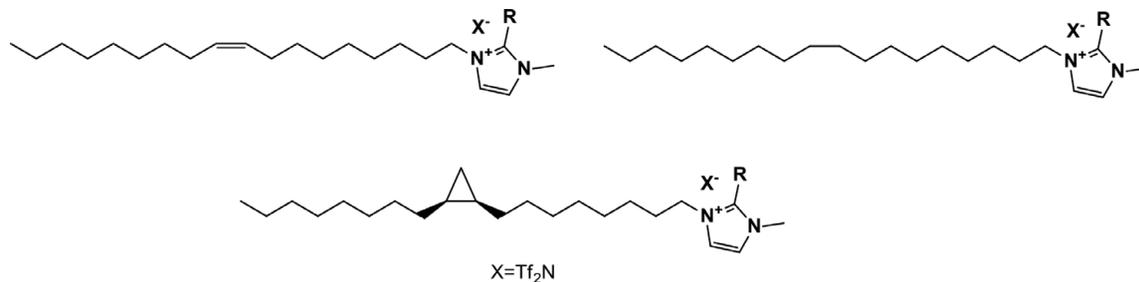


Figure 10. Lipid-based imidazolyl ILs.

tetraoctylammonium or methyltrioctylammonium chloride. The ILs were then successfully used as solvents in the extraction of metal ions from aqueous solutions [107].

Kwan et al. also synthesized ILs using lipids through alkylating a tertiary amine (**Figure 10**). The lipids used in this instance were methyl oleate and methyl stearate. In a third instance, cyclopropanated oleic acid methyl ester synthesized the reaction of the double bond of the oleate with diiodomethane, and diethylzinc was used to alkylate the tertiary amine. After reacting the obtained alkyl iodide with the imidazoles, anion exchange of the iodide with bistriflimide gave imidazolium bistriflimide ILs [108].

5. Deep eutectic solvents

Deep eutectic solvents are analogous to ILs in the sense that they possess similar properties of low melting point and non-volatility, but they are, however, two different types of solvent systems. Unlike ILs, which are made up of one type

of discrete cation and anion [17], DESs are formed from an eutectic mixture of a hydrogen bond acceptor (HBA), mostly quaternary ammonium salts, and a metal salt or hydrogen bond donor (HBD). The mixture forms a eutectic phase which has a lower melting point than the individual components [109]. There is a charge delocalization created through hydrogen bonding between, for example, a halide anion of the HBA and the HBD which causes the decrease in the melting point [18]. DESs are usually formed from relatively inexpensive bio-based components which makes them biodegradable and affordable [17]. Abbott et al. initially developed DESs based on choline chloride and zinc chloride as cheaper alternatives to imidazolium-based ionic liquids, which would make them readily accessible for bulk applications in syntheses. These new solvents were made by heating mixtures of the choline chloride and zinc chloride in molar ratios of 1:1, 1:2 and 1:3 until clear colorless liquids were obtained, with the 1:2 mixture giving the lowest freezing point of 25°C [110]. Choline is a provitamin which is derived from lecithin, found in plants and animal organs [111]. As such, choline-derived

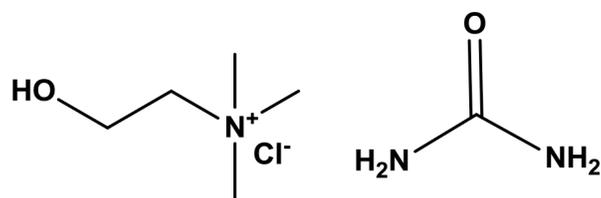


Figure 11.
 DES based on choline chloride and urea.

Hydrogen bond donor (HBD)	ChCl/HBD ratio (mol/mol)	M.p. of HBD/°C
 Levulinic acid	1:2	32
 Xylitol	1:1	96
 D-Sorbitol	1:1	99
 D-Isosorbide	1:2	62

Table 1.
 Novel room temperature liquid DESs derived from renewable sources [119].

DESs are bio-based solvents, particularly where it is paired up with bio-sourced HBDs such as lactic acid, levulinic acid, glycerol and sugars. On a large scale, choline is produced by a single-step reaction between HCl, ethylene oxide and trimethylamine [17].

DESs based on urea (**Figure 11**) were prepared by mixing choline chloride (m.p. 302°C) and urea (m.p. 133°C) in different molar ratios. This showed that a eutectic phase occurs at a choline to urea ratio of 2. This DES has a very low freezing point of 12°C, which was significantly lower than its constituents, thus giving a room temperature solvent [112]. The choline chloride-urea DES has been used as both a catalyst and solvent for the selective *N*-alkylation of various aromatic primary amines. This method avoids the complexity of multiple alkylations, which is a problem encountered when polar volatile organic solvents are used. After the reaction, DES recycling by simple biphasic extraction with ethyl acetate was carried out, and the DES was reused at least five times (with just a slight loss in activity) [113]. This same group have used the choline chloride-urea DES as a solvent and catalyst for the bromination of 1-aminoanthra-9,10-quinone [114] and for the Perkin reaction [115].

DESs based on choline chloride and glycerol or ethylene glycol have also been used as extraction solvents to remove excess glycerol from biodiesel [116–118]. Also, new choline chloride-based DESs with levulinic acid and sugar-based polyols as renewable hydrogen bond donors were synthesized. The best ratios of choline chloride (ChCl) and HBD which gave liquid DESs at room temperature are shown in **Table 1** [119]. DESs based on different bio-based HBD (oxalic, lactic and malic acids) and HBA (choline chloride, betaine, alanine, glycine, histidine, proline and nicotinic acid) have also been prepared and tested as solvents for the dissolution of lignin, cellulose and starch. Majority of the resulting solvents exhibited high lignin solubility but poor cellulose solubility.

This was advantageous since DESs can be used in separating lignin from cellulose [120]. DESs can be viewed as a more environmentally friendly alternative to volatile organic solvents—they are affordable, easily prepared and scalable, inflammable and also biodegradable [121].

6. Conclusions

Rising concerns over depletion of fossil reserves and the drive towards sustainable and responsible consumption of resources have presented a challenge and opportunity for scientist and engineers to work together in developing methods, technologies and processes for producing of bio-based products. These include commodity chemicals, fuels and materials of which many of the chemicals have solvent properties. As such, they have been widely used in extractions and in solvating a range of physiochemical processes and numerous consumer goods (by either dissolving, stabilizing or modifying the latter's properties) across the manufacturing research and development landscapes. This review has contextualized and discussed some existing and emerging approaches in these areas.

Even though most bio-solvents are still volatile like their petroleum counterparts, the bio-solvents have the advantage of being biodegradable, derived from renewable resources, and their production often results in CO₂ emission savings. A novel array of ionic liquids and deep eutectic solvents based on inexpensive bio-derived components has been developed, and because these solvents have low volatility, it presents a solution to the volatile organic solvent concern. Additionally, they are usually recyclable after use, with the benefit of tunability to bring about smart solvents for tailored applications.

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Conflict of interest

The authors declare no conflicts of interest.

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