



Are ionic liquids eco-friendly?

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ABSTRACT

Ionic liquids are molten salts that have excellent chemical and thermal stability. Because they have qualities inherent to some precepts of green chemistry, they are identified as a potential substitute for traditional organic solvents. These useful physical and chemical properties have led to several promising applications in renewable energy technologies. Despite being classified as green solvents, these neoteric solvents present a number of problems related to their synthesis, toxicity and biodegradability, making their use questionable environment-wise. In this review, we analyzed the processes of synthesis, recovery and recycling, toxicity and biodegradability of different ionic liquids. A comparative analysis with some fossil-based solvents and organic-based green solvents was also undertaken. Through the construction of synthesis trees, it was found that all ionic liquids analyzed presented some problematic stage, mainly due to the use of volatile compounds containing C, N, S and halogens. On the other hand, several eco-friendly methodologies have been used for recovery and recycling, such as ultrafiltration and water extraction. One of the main critical points is related to toxicity and biodegradability, as most ionic liquids currently used are toxic and poorly biodegradable or non-biodegradable. Due to their infinite combination, computational modeling studies combined with life cycle assessment studies may, in the future, design new eco-friendly ionic liquids that largely comply with the 12 principles of green chemistry.

Abbreviations: [2-HEAA], 2-hydroxyethylammonium acetate; [2-HEAF], 2-hydroxyethylammonium formate; 2-METHF, 2-methyltetrahydrofuran; [2-TEAA], Tris(2-hydroxyethyl)ammonium acetate; Aliquat® 336, Methyl trioctyl ammonium chloride; [AMIM] [Cl], 1-allyl-3-methylimidazolium chloride; [APBIM] [Glu], 1-(3-aminopropyl)-3-butylimidazolium glutamic acid; [BMBIM] [Br], 1,3-dibutyl-2-methylimidazolium bromide; [BMIM] [Ace], 1-butyl-3-methylimidazolium acetate; [BMIM] [BF₄], 1-butyl-3-methylimidazolium tetrafluoroborate; [BMIM] [Br], 1-butyl-3-methylimidazolium bromide; [BMIM] [Cl], 1-butyl-3-methylimidazolium chloride; [BMIM] [HSO₄], 1-ethyl-3-methylimidazolium hydrogen sulfate; [BMIM] [OAc], 1-butyl-3-methylimidazolium acetate; [BMIM] [OSO₄], 1-butyl-3-methylimidazolium octylsulfate; [BMIM] [N(CN)₂], 1-butyl-3-methylimidazolium dicyanamide; [BMIM] [NTF₂], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [BMIM] [PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [BMIM] [TfO], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; [BMPyr] [NTF₂], 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; [BMPz] [N(CN)₂], 1-butyl-2-methylpyrazolium dicyanamide; [BSMIM] [HSO₄], 1-(4-sulfobutyl)-3-methylimidazolium hydrosulfate; [BVim] [Br], 1-butyl-3-vinylimidazolium bromide; CH₂Cl₂, Dichloromethane; C₂H₄Cl₂, 1,2-dichloroethane; CH₃CCl₃, 1,2-dichloroethane; [C₄(m-ABIM)₂] [PF₆]₂, 1,4-bis(3-(m-aminobenzyl)imidazole-1-yl)butane bis(hexafluorophosphate); [C₄(MIM)₂] [(2HSO₄)(H₂SO₄)₂], 1,1-bis(3-methylimidazolium-1-yl) butylene hydrogen sulfate-sulfuric acid cluster; [C₄Py] [Br], 1-butylpyridinium bromide; [C₄Py] [NTF₂], 1-butylpyridinium bis(trifluoromethylsulfonyl)imide; [C₅C₁IM] [NO₃], 3-pentyl-1-methylimidazolium nitrate; [ChCl]/urea, Choline chloride/urea; CPME, Cyclopentyl methyl ether; Cyphos® IL 101, Trihexyl(tetradecyl)phosphonium chloride; [DIPEAc], Diisopropylethylammonium acetate; [EAN], Ethylammonium nitrate; [EIM] [Cl], 1-ethylimidazolium chloride; [EMIM] [BF₄], 1-ethyl-3-methylimidazolium tetrafluoroborate; [EMIM] [Cl], 1-ethyl-3-methylimidazolium chloride; [EMIM] [EtSO₄], 1-ethyl-3-methylimidazolium ethylsulfate; [EMIM] [NTF₂], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [EMIM] [HSO₄], 1-ethyl-3-methylimidazolium hydrosulfate; [EMIM] [OAc], 1-ethyl-3-methylimidazolium acetate; [EMIM] [SCN], 1-ethyl-3-methylimidazolium thiocyanate; [EMIM] [TFA], 1-ethyl-3-methylimidazolium trifluoroacetate; [EtOHMIM] [PF₆], 1-(2-hydroxyethyl)-3-methylimidazolium hexafluorophosphate; [Et₃N-SO₃H] [Cl], N,N-diethyl-N-sulfoethan ammonium chloride (triethylamine-bonded sulfonic acid); [EtAN], Ethanolammonium nitrate; EtOAc, Ethyl acetate; [Hbet] [NTF₂], Betainium bis(trifluoromethylsulfonyl)imide; [HMIM] [Cl], 1-hexyl-3-methylimidazolium chloride; [HMIM] [NTF₂], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [HMPyr] [NTF₂], 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide; [HSO₃-bCPL] [HSO₄], 1-(4-sulfonic group) butylcaprolactamium hydrogen sulfate; MeCN, Acetonitrile; [MMIM] [DMP], 1,3-dimethylimidazolium dimethylphosphate; [MSBP] [HSO₄], 1-methyl-2-(4-sulfobutyl)-pyrazolium hydrosulfate; [OMIM] [BF₄], 1-octyl-3-methylimidazolium tetrafluoroborate; [OMIM] [Cl], 1-octyl-3-methylimidazolium chloride; [P4444] [OAc], Tetrabutylphosphonium acetate; [PIP14] [Br], 1-butyl-1-methylpiperidinium bromide; [PyBu] [OAc], N-butylpyridinium acetate; [TBAB], Tetrabutylammonium bromide; [TEA] [HSO₄], Triethylammonium hydrogen sulfate; [TETAH] [Lys], Triethylenetetramine l-lysine; THF, Tetrahydrofuran; [THPC], Tetrakis(hydroxymethyl)phosphonium chloride.

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Recent advances in lipid extraction using green solvents

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ABSTRACT

Green solvents are a new class of solvents mostly known for being environmentally friendly. The main green solvents besides water are organic-based solvents, some ionic liquids (including deep eutectic solvents) and CO₂, which is typically used in supercritical conditions (SC-CO₂). Recently, organic-based solvents and ionic liquids have been subjected to laboratory testing to estimate their potential as substitutes for fossil solvents in the process of lipid extraction. In the last decade, different pure or combined green solvents and different methodologies have been studied and compared with the standard methodology. Cell disruption of animal, vegetable or microbial samples, dry or wet, is a previous step that has been studied many times in association with extraction efficiency. Combined techniques of rupture and extraction using ultrasound, microwaves or maceration were also employed in the extraction process with green solvents. Other techniques such as pressurized liquid extraction and simultaneous distillation and extraction were also applied, sometimes not only with the objective of extracting more, but also of purifying the obtained product. Lipid extraction was performed mainly with the organic solvents cyclopentyl methyl ether and 2-methyltetrahydrofuran, while ionic liquid extractions were performed mainly with imidazolium-based ionic liquids. The advances obtained in this decade in lipid extraction using these three classes of green solvents were studied and evaluated in this review. Economic viability and future challenges were also analyzed with a view to using these solvents in extraction processes on an industrial scale rather than restricted to the extraction of products with high biological value.

1. Introduction

The growing use of chemical solvents in industry has been a subject of great concern in government sectors and environmental entities. Solvents are usually volatile organic compounds (VOCs) with countless properties such as high solubility and volatility, widely employed in the food, chemical and pharmaceutical industries for being mostly liposoluble. Examples include their use in the extraction of seeds for the production of edible oils and biodiesel [1].

Due to their high volatility, organic solvents pose a serious problem for human and environmental health. For humans their inhalation or absorption through the skin can have immediate negative effects such as skin and eye irritation, nausea and dizziness, among others, while in the long term there may be damage to the liver, kidney and central nervous system [2].

Studies have shown that higher solvent volumes are intended for extraction processes, with hexane being the most commonly used solvent for this purpose [3]. Authorities have demanded the urgent replacement of this solvent by a more environmentally suitable

(acceptable) option, since the volume of solvent employed in each extraction process constitutes a real problem for the environment.

As an alternative, a new class of solvents emerged in the market, less harmful to human health and especially to the environment. The so-called “green solvents” originate from renewable and organic/inorganic (ionic liquids) sources, and may even be of fossil origin, providing they satisfy the criteria of “green chemistry” [4–6].

Recently, laboratory tests have shown that different green solvents have the potential to replace chloroform and hexane in the extraction of lipids, mainly in the extraction of oilseeds and microbial fatty acids for the production of biodiesel and oil with high biological value, such as tocopherols and terpenes [7–11].

This objective of this review is to describe the main advances achieved in this decade in the extraction of different classes of lipids with the three classes of green solvents most commonly used nowadays: organic-based solvents, ionic liquids (including deep eutectic solvents) and CO₂ (supercritical CO₂, SC-CO₂).

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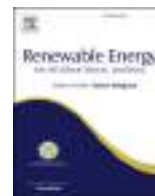
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Biodiesel production from microalgae by direct transesterification using green solvents

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ABSTRACT

This study evaluated the production of biodiesel from the microalgae *Chlorella pyrenoidosa* by direct transesterification using 2-methyltetrahydrofuran or cyclopentyl methyl ether co-solvents as an alternative to chloroform. Acid-catalyzed transesterification using hydrochloric acid was developed for biodiesel production. Biodiesel was purified by column chromatography using one of the two green solvents as eluents. The highly ecological biodiesel quality was compared to the biodiesel produced using chloroform as co-solvent. A 3³ factorial design was conducted to optimize the production of fatty acid methyl esters, being the independent variables investigated: solvent and catalyst volume, solvent and catalyst ratio (methanol:co-solvent:hydrochloric acid), and temperature, with a reaction time of 150 min. Biodiesel production was mainly influenced by temperature increase. The achieved yields using cyclopentyl methyl ether, 2-methyltetrahydrofuran, and chloroform were 71–92%, 67–91%, and 61–76%, respectively. The fatty acid methyl esters profile of biodiesel produced with 2-methyltetrahydrofuran and cyclopentyl methyl ether consisted of approximately 45% polyunsaturated components. The biodiesel obtained was within the ASTM D6751 and EN 14214 standards. The replacement of fossil solvents used in direct transesterification of biomass with a green solvent resulted in a further ecological biodiesel production process towards a circular bioeconomy.

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1. Introduction

For environmentalists and other researchers, the impact of fossil fuels and their combustion products on the environment is one of the biggest problems faced by humanity nowadays. Global warming and climate change, pollution (air, water, and soil) and its adverse effects on health stand out among these negative impacts. Recently, alternatives have emerged for the production of biofuels derived from oilseeds, wastewater, sugarcane, and microalgae. Unfortunately, biodiesel from oilseeds, as well as waste cooking oil and animal fat, cannot realistically satisfy even a small fraction of the existing demand for transport fuels [1]. The fact that the production of biofuels from oilseeds and sugarcane compete with the food production discourages the possibility of producing these biofuels on a large scale, even to meet the internal demand from any country. To date, biodiesel from microalgae is the most viable

alternative to meet the high demand, since it requires less space for production, in addition to increasing productivity per area of production. Thus, biodiesel from microalgae gained scientific and government support worldwide.

The biodiesel production from microalgae biomass is a recent technology mainly aimed to generate an ecological and economically viable fuel. Recent studies have shown the potential application of this fuel as a substitute for diesel supply for vehicles, ships, or even aviation [2–7]. Currently, several tests have been carried out with different compositions of biodiesel from different microalga species [2–7]. Companies, such as Solazyme (U.S.) and Euglena (Japan), have successfully carried out tests with microalgae biodiesel-powered cars [5–7]. On the other hand, the company Sapphire Energy (U.S.), along with the Continental Airlines, operated a 2-h flight using a mixture consisting of 50% petroleum-based jet fuel and 50% alternative biofuel produced from *Jatropha* and microalgae [5,6].

However, large-scale production still lacks a technology competitive with petroleum diesel. One of the biggest challenges to produce microalgae with a high percentage of lipids is their scaling-

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