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Review article

Ionic liquids for the fractionation of microalgae biomass

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ABSTRACT

Microalgae have emerged as one of the most promising sources of renewable biomass. However, considerable challenges must be addressed in order to improve the commercial outlook for the production of commodity chemicals. The largest challenge remains the energy intensive and consequently costly process of microalgae harvesting and drying. Ionic liquids have found a niche application in this area by allowing the extraction of lipids from wet biomass at low temperatures in less time than traditional lipid extraction methods. A number of recent studies have advanced the study of wet extraction of microalgae using ionic liquids and elucidated some of the limitations of this process. However, the most promising avenue for ionic liquid-based wet extraction lies in the fractionation and recovery of multiple biomass products such as lipids, carbohydrates, and carotenoids, in a single process.

1. Introduction

Microalgae have received considerable attention in recent years as one of the most promising source of sustainable biomass for the production of fuels and chemicals. Microalgae present several advantages over terrestrial crops for sustainable biomass production. Firstly, microalgae do not require soil and are capable of photosynthetic growth using sunlight, carbon dioxide, water, and inorganic salts as their major nutrients, allowing for a potentially carbon negative growth process [4]. Algae are also capable of producing an assortment of desirable biochemicals for a variety of industries, but of particular interest is the accumulation of lipids by microalgae for the production of biodiesel. However, although they are capable of growth rates exceeding traditional land crops used for biodiesel production such as soya bean, their overall low cell density in their liquid growth media presents certain challenges for downstream processing. This has thus far limited their applications at the commercial scale to a handful of high end products such as the carotenoid astaxanthin, or as a source of protein and antioxidants [26].

Since the late 1990s, greater general awareness of the significant impacts of chemical refining processes on the environment has led to a shift from post-process remediation to the development of greener processes. As the overarching goal of algal-based products is to use a renewable resource for the production of chemicals and fuels, it is not surprising that the development of microalgae refining processes are also heavily influenced by the principles of green engineering [5,34]. Ionic liquids (ILs) which have been often touted as green solvents are becoming increasingly used as solvents for lipid extraction, refining of carbohydrates, or extraction of high value products from algal biomass [8,9,13,22,25,27,28,35].

ILs are salts which generally consist of a large asymmetrical organic cation which when combined with an anion have a melting point below 100 °C. They have often been described as *green solvents* due to their low volatility, however, they can vary considerably in their physiochemical properties such as polarity, hydrophobicity, toxicity, and thermostability [30,31]. Cation structures most commonly use nitrogen containing ring structures such as imidazolium or pyridinium structures with various alkyl substitutions, or in contrast alkyl substituted ammonium or phosphonium-based structures [30,31]. Anions can vary considerably from small alkali metals such as chloride or bromide ions, to more complex structures like alkyl esters, carboxylic acids, fluorinated anions, or amides [30,31]. Accordingly, a full life cycle analysis of the impacts of both the IL synthesis and the process application should be independently assessed before being classified as truly "***green***" [20].

Several specific applications of ILs in algal biomass processing have emerged and are the basis for the organization of this critical review. A guide explaining the acronym system used in this work is presented in Table 1. Firstly, an introduction to IL-based lipid extraction processes for biodiesel production are discussed, followed by the specific effects of IL structure and reaction conditions on extraction efficiency, IL extractions of wet biomass, and the use

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Table 1
Abbreviation guide for ionic liquids discussed in this review.

Cation structure	Abbreviation	Anion Structure(s)	Abbreviation
1-alkyl-3-alkyl-imidzolium	$[C_nC_nim]$	Methyl, ethyl, butyl	Me, Et, Bu
1-alkyl-3-methyl-imidazolium	$[C_nmim]$	Bis(trifluoromethylsulfonyl)imide	$[NTf_2]$
1-alkyl-4-methylpyridinium	$[C_nC_{1\beta}py]$	Thiocyanate	[SCN]
1-alkyl-3-methylpyridinium	$[C_nC_npy]$	Taurine	[tau]
Tetraalkylammonium	$[N_{n\,n\,n\,n}]$	Prolinate	[pro]
Tetraalkylphosphonium	$[P_{n\,n\,n\,n}]$		

of switchable solvents for lipid extraction (Fig. 1).

2. Lipid extraction

Several species of microalgae exhibit the ability to accumulate large portions of their dry weight as intracellular lipids (up to 75% wt.) [4]. Due to their small size, single celled algae must first be harvested from their liquid growth medium using solid liquid separation techniques. Traditionally, microalgae are then dried and subjected to organic solvent-based extraction. Cell disruption can greatly aid in facilitating the recovery of lipids by improving the mass transfer properties of the system as solvent extraction is primarily diffusion-based [15]. However, due to their small size, cell disruption processes, such as enzymatic degradation, ultrasonication, or microwave irradiation, can be either material or energy intensive processes [15,23]. Most solvent-based extraction processes are also incompatible with wet biomass, requiring extensive drying of the algae prior to extraction, which can add significant costs to the overall process. Dewatering and drying is thought to be responsible for up to 70% of the biodiesel production cost from microbial lipids [14].

ILs have been recently shown to facilitate the extraction of lipids from microalgae, primarily by disrupting microalgal cell structure [35,28] allowing either auto partitioning of the lipids or presumably improving access of co-solvents to the intracellular lipids. However, care must be taken to compare IL extraction techniques to the proper controls, particularly, lipids extracted should be compared to total cellular lipid content as determined by an appropriate analytical technique such as the Bligh & Dyer (B&D) method [1], the Folch method [11] or direct transesterification [37] using ground and dried biomass. One common issue in many publications is the application of the B&D method with wet microalgal cultures. This method was originally created to extract lipids from wet animal tissues containing up to 80% water [1], however, it has yet to be shown that this method is acceptable using a wet culture of single celled algae, which are much more resistant to cell lysis than animal tissues [24]. This method has also been shown to be less efficient when extracting lipids from fish tissues containing >2% lipids by dry weight, which brings into question whether this method is appropriate for use with microalgae as it is expected that industrial production of microalgae would contain >20% wt lipids [18].

It should also be noted that these methods do not necessarily represent the same fractions of lipids that can be extracted from biomass. For example, hexane extraction is highly specific for neutral lipids (triacylglycerides) [24], while the Folch method extracts an oil with a relatively higher level of non-lipid impurities [16]. In most cases, only the neutral lipids will be used for biodiesel production as transesterification yields from polar lipids require more expensive catalysts, longer reaction times, and higher reaction temperatures [17]. Whenever possible, direct transesterification methods such as the laboratory protocol developed by the National Renewable Energy Laboratory should be adopted as it uses an acid catalyst known to convert all lipids including free fatty acids and phospholipids to fatty acid methyl esters (FAME) and reduces lipid losses during extraction by adopting appropriate recovery standards [37]. Otherwise, transesterification of the oil to FAME using a base catalyst will allow identification of the relative

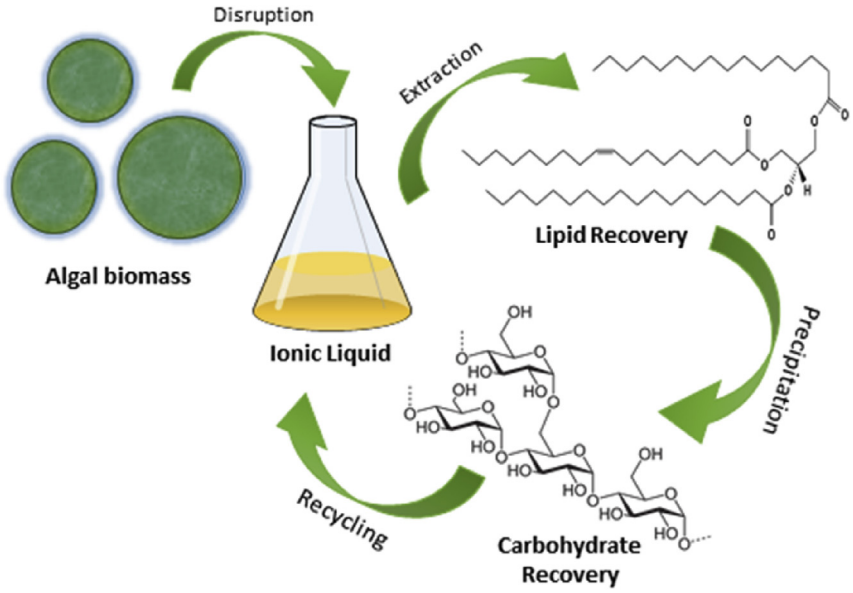

Fig. 1. Summary of an IL-based biomass fractionation process. After cell disruption with the IL, the lipids are recovered and the residual biomass containing carbohydrates and proteins is precipitated allowing for recycling of the IL.