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Review article

Sustainable green solvents and techniques for lipid extraction from microalgae: A review

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ABSTRACT

Energy security is a serious concern for a sustainable economy where it has necessitated alternative renewable energy that can have the potential to meet the futuristic needs. Among renewable energies, carbon neutral biofuels from microalgae appear to be a promising move towards sustainability and cleaner fuels owing to its attributes of high CO_2-sequestering capability, high lipid productivity and being easily cultivable in an open pond and waste/marine/brackish water. However, the commercial viability of algae-based fuels suffers mainly from the cost incurred during the process. Among the steps involved in the biodiesel production from microalgae, lipid extraction in particular consumes not only a significant amount of energy and time but also causes environmental contamination by usage of toxic solvents. Conventional solvents used in lipid extraction process may further aggravate the quality of the product by dissolving other compounds like chlorophyll that may lead to erroneous results of lipid content. To circumvent the problem, green solvents and process intensification methods/techniques (green extraction technologies) potentially improve the characteristics of energy reduction, eco-friendliness, non-toxicity and efficient lipid extraction. Hence, this review focuses on the prospects of green solvents and extraction techniques that could improve the commercial viability of biodiesel production.

Contents

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1. Introduction

The biodiesel production process from microalgal lipids involves several steps including cultivation, harvesting, drying, lipid extraction, transesterification and purification of fatty acid methyl esters (FAME) [1,2]. Based on life cycle assessment studies, the oil extraction process consumes 90% of the energy, which signifies a need to improve the economic viability of the process [3].Although, on the one hand, microalgae have an unprecedented potential to cater future energy needs, on the other hand, the commercial viability of the process is jeopardized by the cost incurred particularly in lipid extraction [4]. Intriguingly, a recent study reported that the solvents (chloroform/methanol) used for lipid extraction from *Chlorella vulgaris* dissolved chlorophyll pigments along with the lipids [5]. In such cases, it leads to unpredictable results and deteriorates the quality of the product which ultimately impedes the biorefinery process. Hence, to ensure lipid extraction efficiency, suitable green solvent systems coupled with leveraging green techniques may circumvent any step involved in the conventional process, thereby, reducing the cost.

So far, current literature reviews have mainly focused on comprehensive lipid extraction methods from microalgae; however, recent studies consider the implications of green solvents and techniques that could be adopted to make the process more efficient. Hence, in this review, 'green solvents and extraction techniques' that have potential to replace conventional solvents and also some process intensification steps (energy-intensive approaches) for lipid extraction are discussed.

2. Essentiality for green solvent systems and process intensification techniques for lipid extraction from microalgae

Lipid extraction from microalgae is traditionally carried out by Folch et al. [6] or Bligh and Dyer [7] followed by lipid quantification using gravimetric estimation of lipid content. Folch et al. [6] developed a simple method for extracting total lipids from animal tissues. However, the efficiency of the method relies on the presence of mineral salts in the crude extract and use of large volumes of solvent. In the absence of mineral salts, most of the acidic lipids are washed out during the washing step. On the other hand, Bligh and Dyer [7] developed a rapid lipid extraction method to determine the lipid composition of frozen fish tissue. This method applies only to tissues that have 80% of water content, and the efficiency depends on the maintenance of chloroform, methanol, and water proportions according to the water content of the tissue. Chloroform and methanol are toxic and flammable, which detrimentally affect health and the environment. These solvents affect the quality of the product by dissolving undesired products (chlorophyll) during the extraction process [5]. In such cases, the quality of the lipid not only deteriorates but also impedes the biorefinery's goal of a more cost efficient process. Moreover, it is imperative that for biodiesel production, more emphasis has to be given to saponifiable lipids, which upon transesterification result in fatty acid methyl esters (FAME) but not the whole lipids [8]. Hence, suitable solvent systems for lipid extraction that are sustainable, non-toxic and yield higher lipid content without interference of non-lipid compounds should be considered [9].

In the lipid extraction process, essentiality of green solvents was placed in the above discussion. In addition to this, some new 'green or process intensification techniques' that facilitate time and energy reduction, less usage of solvent and minimization of downstream processing steps are essential to make the process viable. These techniques make the process simple and cost effective. For instance, wet algae biomass extraction is mostly preferred as it may render unnecessary drying steps. Similarly, transesterification which is used for ester and glycerol synthesis apart from biodiesel process of wet algae biomass may preempt not only the dewatering and drying steps but also the lipid extraction process (in situ transesterification). The potential of green solvents and process intensification technologies and their interventions can be compared with a conventional process for extraction and transesterification to biodiesel (Fig.1).

3. Existing technologies for lipid extraction

3.1. Lipid extraction by green/renewable solvents

3.1.1. Bio-derived solvents for solvent extraction (terpenes/FAME of plant origin/ethyl lactate)

In search of suitable alternative solvent systems, recent studies have shown that lipid extraction can be done with bio-based solvents that are efficient, eco-friendly and cost effective. Terpenes are extracted from plants and citrus species and possess excellent chemical and technical properties. Several terpenes such as D-limonene, *p*-cymene, and gum turpentine are derived from citrus peels, pine trees, and tree leaf oils respectively. Among the terpene solvents, D-limonene has been used for lipid extraction of *Chlorella vulgaris* and it was observed that the quality and yield obtained is similar when compared with hexane [10]. Moreover, it satisfies not only the Hansen solubility properties (HSP) but also considered as an alternative solvent owing to its low cost, degreaser, and cleaner properties [11–13]. Tanzi et al. [10] reported a two-step process in which Soxhlet extraction coupled with solvent elimination from the medium using Clevenger distillation resulted in almost the same quality and quantity of lipid content between *n*-hexane and D-limonene (Fig. 2).

In addition to terpenes, a new type of green solvents termed bio-derived solvents, originated from agricultural or bio-based feedstocks has emerged. The introduction of these solvents as a replacement for conventional organic solvents not only provides environmental benefits but also avoids the costly petroleum-based route of production. Recently, commercialized bio-based solvents include ethyl lactate and methyl soyate, produced from renewable resources such as corn, citrus, and soybeans. There are many products under development such as Gevo's renewable isobutanol that use proprietary technology to manufacture solvents which mimic petroleum-derived products [14]. Lower viscosity and vapour pressures (except DMF) make them easy to handle in solvent extraction applications without any evaporation. Soybean oil methyl esters and algal lipid extraction were carried out to evaluate the suitability of bio-derived solvents [15,16]. Their advantages such as low toxicity, biodegradability, and renewability characterized them as ideal solvents for lipid extraction. Eventually, these solvents could replace the conventional and other green solvents in different industrial extraction processes. Nevertheless, the major concern for bio-derived