Biomass and Bioenergy 100 (2017) 108–115

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

New algal lipid extraction procedure using an amphiphilic amine solvent and ionic liquid

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ARTICLE INFO

Article history:
Received 10 August 2016
Received in revised form
1 March 2017
Accepted 17 March 2017

Keywords:
Microalgae
Biofuel
Amine
Extraction

ABSTRACT

Lipid extraction is a key step in microalgal biofuel production. However, economical microalgal biofuel production is limited by the high energy consumption of the extraction process. Therefore, in this study, we employed N-methylcyclohexylamine (MCHA) as a switchable solvent to directly extract a wet microalgal slurry, and an ionic liquid, [C_4-mim][PF_6] (1-butyl-3-methylimidazolium hexafluorophosphate), was used to recover the extracted algal oil through a simple phase separation method. CO_2 was used to trigger the separation of MCHA from [C_4-mim][PF_6], and MCHA was regenerated by heating and purging with N_2. Our extraction procedure differs from conventional solvent extraction, which requires drying algal slurries before extraction. The new extraction procedure adopted in this study can be used to extract wet algal slurries directly and recycle the solvent by using a low-energy consumption method. In addition, water-soluble MCHA was investigated for DHA(docosahexaenoic acid) wet algal slurries with 85% water content, and the extraction yield could reach 85% at low stirring speeds (200 rpm). Using [C_4-mim][PF_6] to separate algal oil from the crude extraction liquid, algal lipid recovery was approximately 77%. In summary, the results showed the feasibility of utilizing MCHA and [C_4-mim][PF_6] as extracting and separating agents, respectively, for algal oil exaction.

1. Introduction

Because of global warming and the continual increase in crude oil prices, identifying green energy alternatives has received substantial attention. Biofuels are good alternatives to fossil fuels because they are renewable and carbon neutral. Countries worldwide are implementing proactive green energy policies and biofuel development is expanding rapidly. Biofuels can usually be categorized into first, second, and third generation biofuels [1]. They are characterized by their biomass source, their limitations as a renewable energy source, and the technological progress of their use [2]. First generation biofuels are produced directly from food crops containing with high starch and oil such as soybeans, sugarcane, corn, rapeseed, sunflower, and others. Fermentation and transesterification are performed to produce ethanol and biodiesel, but food supply and biodiversity questions are raised when using first generation biofuels. Second-generation biofuels were developed to address the increasing demand for biofuels; however, they are more complicated to produce than their first-generation counterparts because they involve extraction from agricultural residues and forestry waste, such as bagasse, straw, wheat, and wood. Some difficulties remain regarding the enzymatic and chemical transformations used for selectively converting cellulose, hemicellulose, or lignin into useful products [3–5]. If such difficulties can be overcome, there is still much space for future development and the market implementation of microalgae, a third-generation biofuel.

Microalgae are a species of phytoplankton that exist worldwide.

Abbreviations: [C_4-mim][NTf_2], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [C_4-mim][PF_6], 1-butyl-3-methylimidazolium hexafluorophosphate; DCHA, dicyclohexylamine; DHA, docosahexaenoic acid; DMCHA, N,N-dimethylcyclohexylamine; IL, ionic liquid; MCHA, N-methylcyclohexylamine; SHS, switchable hydrophilicity solvent.

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http://dx.doi.org/10.1016/j.biombioe.2017.03.018
0961-9534/

One ton of microalgae can capture 1.83 tons of CO_2; hence, they are essential to energy conversion and the carbon cycle [6]. Compared with other oleaginous plants (e.g., soybean, rapeseed, and palm), microalgae exhibit a quicker growth rate, higher biofuel yield, and higher CO_2 consumption. Moreover, microalgae do not compete with other crops for land use; hence, algal biofuel is considered a crucial third-generation biofuel and an alternative to fossil fuels. In general, converting microalgae into biofuel has to be performed in four steps: microalgae harvesting, cell wall disruption, lipid extraction, and conversion of lipid oil into fatty acid methyl esters (FAMEs, also known as biodiesel) [7]. Microalgae are advantageous for biodiesel production because of their high oil productivity. Their biomass has a relatively high water content; thus, they must be dried after harvesting and before extraction [8,9]. Using a common lipid-soluble organic solvent (e.g., hexane, ethyl acetate, or chloroform) to directly extract wet microalgae can result in a low algal oil extraction yield, because the presence of water impedes the interaction between the hydrophobic solvent and algal lipids [10]. Using a hydrophilic organic solvent (e.g., methanol) as the cosolvent promotes the interaction between the hydrophobic solvent and algal oil, thereby increasing the algal oil extraction yield [11]. However, high-energy consumption fractional distillation is used to recycle the mixed solvent, and the amount of consumed energy substantially exceeds the energy value derived through algal oil production [12]. Hence, the large-scale production of microalgal biofuels is greatly restrained.

A switchable hydrophilicity solvent (SHS) is an innovative solvent, and its polarity can be triggered by adding CO_2. Nitrogen-containing organic compounds, including primary, secondary, and tertiary amines, amidines, and guanidines, are often used as SHSs [13,14]. In an aqueous solution, a SHS reacts with CO_2 to form ammonium bicarbonate salt, thus increasing the polarity and hydrophilicity of the solvent. The solvent can be reconverted into its original state by heating and gas purging. A SHS can be used to separate and purify chemical reaction products or extract nonpolar substances such as oil [15–17]. Such a process involves utilizing the compatibility of SHS with a target isolate or extract before the solvent is switched. After the SHS is switched by adding CO_2 to increase its polarity, the target isolation or extraction can be separated from the solvent. Therefore, for microalgal lipid extraction, a SHS can be employed at normal pressure and a moderate temperature (40–70 °C) instead of in a high-temperature and low-pressure vacuum environment to separate and recycle the solvent. This approach reduces the operating cost and energy consumption, providing a potential strategy for extracting microalgal oil [12].

Previous studies have mostly used a SHS to extract algal oil by utilizing its hydrophobicity before polarity switching [18–21]. A two-phase (solvent phase and algae aqueous phase) extraction approach has been mostly used, and the algal slurry must be evenly stirred to increase the interaction between the solvent and extract (algal biomass). In this study, an amphiphilic amine, N-methylcyclohexylamine (MCHA), was used as the SHS. A specific ratio of the SHS was used to extract wet algae through a single-phase approach, in which the solvent and water of the algal slurry were mixed and dissolved completely, thereby facilitating the interaction between the solvent and algal lipids. However, if a switchable solvent is hydrophilic before switching (under normal temperature and pressure), removing CO_2 in subsequent steps prevents separation between the solvent and water; hence, the SHS becomes unrecyclable. Therefore, this study adopted a suitable ionic liquid (IL) as an intermediate extractant. Because an IL easily dissolves polar substances (e.g., amine compounds) [22–24] but only slightly dissolves nonpolar substances (e.g., algal oil) [25], this study first employed an IL to separate algal lipids from the algal solution containing the SHS. Subsequently, CO_2 was used to recycle the SHS in the IL. Fig. 1 presents the flowchart of the proposed novel method for wet algal lipid extraction and solvent recycling.

2. Materials and methods

2.1. Materials

The microalgae, which were commercial DHA algae, were purchased from Far East Bio-Tec Co., Ltd. in Taiwan. The dry powder was generated using a direct spray dryer and was stored in a refrigerator. The dry algal powder was mixed with deionized water until 85% water content was achieved.

The ILs include 1-butyl-3-methylimidazolium hexafluorophosphate [C_4-mim][PF_6]) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_4-mim][NTf_2]), solvents, and chemicals used in this study were purchased from Sigma-Aldrich (Missouri, USA) Chemical Co. Inc. and used as received. All purchased chemicals were of reagent quality. Soybean oil was purchased from Taiwan Sugar Co., Ltd. (Tainan, Taiwan). Nitrogen (99.99%) and CO_2 (99.95%) were supplied by Chiah Lung Enterprise Co. (Hsinchu City, Taiwan).

2.2. Methods

2.2.1. Wet algal lipid extraction

For lipid extraction by using amine solvents, MCHA, N,N-dimethylcyclohexylamine (DMCHA), or dicyclohexylamine (DCHA) (60 mL) was mixed with the algal slurry (30 g, water content = 85 wt%) and stirred at room temperature for 1–3 h. After completing the extraction, the residual algal biomass was removed by centrifugation, and the crude solution was collected. Subsequently, 100 mL of hexane and 150 mL of 10 wt% citric acid were used to anti-extract the algal lipid. The hexane layer was collected, dried over anhydrous sodium sulfate, filtered, and had its solvent removed by vacuum evaporation to obtain the crude lipids. Thereafter, transesterification and gas chromatography analysis of the crude lipids were performed.

For lipid extraction of volatile organic solvents, chloroform–methanol (2/1 v/v), chloroform, or hexane (60 mL) was mixed with the algal slurry (30 g, water content = 85 wt%) and stirred at room temperature for 1–3 h. After completing the

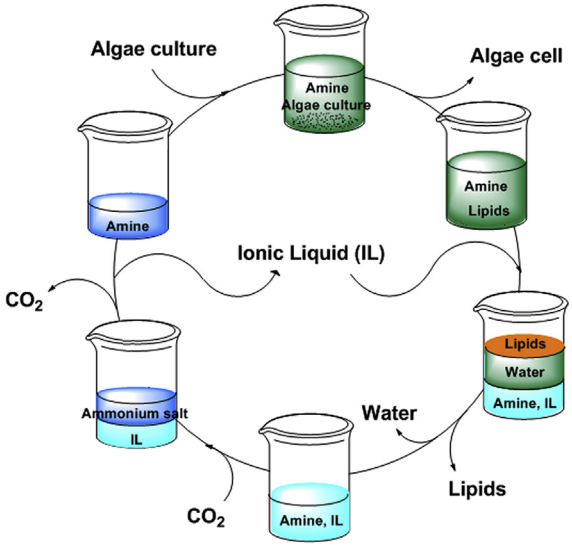

Fig. 1. Flowchart of the novel method for algal lipid extraction and solvent recycling.