Applied Energy 226 (2018) 461–468

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Effect of water content on [Bmim][HSO_4] assisted in-situ transesterification of wet *Nannochloropsis oceanica*

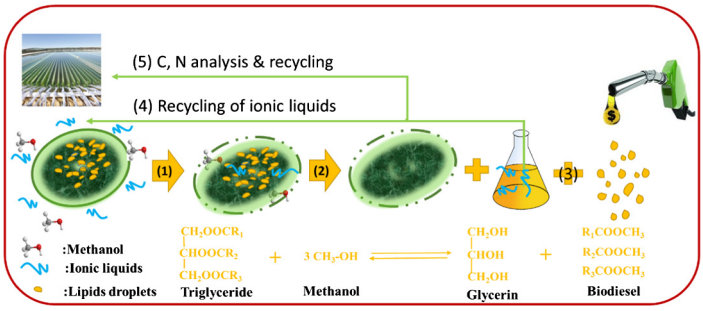
Yingqiang Sun[a,1], Chunyan Xu[b,1], Thomas Igou[b], Peilu Liu[c], Zixuan Hu[b], Steven W. Van Ginkel[b], Yongsheng Chen[b,*]

[a] Department of Chemical Engineering, Anhui University, Anhui 230039, China
[b] Department of Environmental Engineering, George Institute of Technology, Atlanta, GA 30332, USA
[c] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA

HIGHLIGHTS

- Water content was negative to algae dissolution and in-situ transesterification.
- FAME yield was affected by both ILs' catalyzation and negative effect of water.
- [Bmim][HSO_4] neutralized the negative effect of water on biodiesel yield.
- The decomposition of carbohydrates and proteins enhanced biodiesel production.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Water content
Wet algae
In-situ transesterification
Ionic liquid
Biodiesel

ABSTRACT

1-Butyl-3-methylimidazolium hydrogen sulfate ([Bmim][HSO_4]) was employed to catalyze the in-situ transesterification of wet *Nannochloropsis oceanica*. Algal cell wall was dissolved by [Bmim][HSO_4] according to TEM analysis of untreated *Nannochloropsis* sp. cells and lipid extracted algae (LEA). The temperature and time are favorable to biodiesel production in 100–200 °C, time of 0–70 min, with methanol: algae, however, it decreased to 10.64% at time of 90 min. The biodiesel and energy production of [Bmim][HSO_4] catalyzed in-situ transesterification varied due to the competition of catalytic property and algal dissolution ability with variation of water content. The catalytic property of [Bmim][HSO_4] was the dominate parameter affecting biodiesel production, therefore, total energy production of in-situ transesterification, as a parameter of biodiesel production, was slightly increased from 13.12 kJ to 14.51KJ with water content of wet algae varied from 0 to 15 wt%. However, it decreased to 8.37 at water content of 20 wt% due to the weakened algal dissolution ability, which was proved by the decrease of hydrogen bond acceptor capacity(β) from 0.942858 to 0.942851 in water content of 0–30 wt%. The decomposition of carbohydrates and proteins in IL – water mixtures enhanced biodiesel production according to elemental analysis of LEA.

* Corresponding author.
E-mail address: yongsheng.chen@ce.gatech.edu (Y. Chen).
[1] These two authors contribute equally in this manuscript.

https://doi.org/10.1016/j.apenergy.2018.06.029
Received 18 August 2017; Received in revised form 16 May 2018; Accepted 3 June 2018

1. Introduction

According to BP Energy outlook 2017, global liquids demand (oil, biofuel, and other liquid fuels) will increase by around 15 Mb/d, to reach 110 Mb/d by 2035 [1]. Therefore, the development of renewable liquid energy is urgent to provide energy security in the face of depletion of fossil fuel [2]. Biodiesel, as a promising alternative to regular diesel, is a renewable fuel consisting of alkyl esters [3]. It is an environmental friendly and sustainable fuel since it can be obtained from a variety of sources including vegetable oils, waste cooking oils, algae, and animal fats [4,5]. Also, it can be substituted in modern diesel engines without modification.

Algae are considered one of the most promising feed stocks for biofuel due to their rapid growth rate, high lipid content ($60\ m^3\ ha^{-1}$), ability to utilize non-arable land, lower water requirement, and environmental friendly properties in comparison to first and second-generation biofuel stocks [6–8]. Nannochloropsis, as one of important marine microalgae, is usually selected to do in-situ transesterification due to its high lipid content (31–68% by dry weight) [9]. Various methods used for algal biodiesel production, including solvent extraction, hydrothermal liquefaction, enzymatic & microwave pyrolysis, fermentation, and transesterification have been reported extensively [10–12]. However, the extensive upstream and downstream processes of harvesting, dewatering, conventional lipid extraction, purification and high energy demand make algal biodiesel production an expensive process [13]. According to a previous report, harvesting cost is 20–30% to the total cost of algal cultivation [14]. And energy consumption during drying is responsible for up to 59% of the total energy demand [15]. The net energy of 1 kg biodiesel production by in-situ transesterification of wet algae is about 105 MJ, while it is negative when using dry algae [16]. Thus, the in-situ transesterification method, in which lipids are simultaneously extracted and converted to biodiesel without drying and extraction, would be a promising alternative for biodiesel production from algae [17]. However, it is not widely utilized because water content has a negative effect on biodiesel yield due to following reasons [16,18–20]: Firstly, water can hydrolyze biodiesel to methanol and free fatty acids because transesterification is a reversible reaction [21]. Secondly, water content within the biomass prevents lipids from its extractive reaction with methanol [18]. Finally, water content can deactive acid catalysts due to its competition for available protons in the reaction [22].

Ionic liquids (ILs), types of molten salts composed of organic cations and organic/inorganic anions, are organic salts melted below 100 °C [23–25]. They are widely used as promising solvents for biomass treatment due to their negligible vapor pressure and high thermal stability properties [26]. Recently, ILs are applied in lipid extraction from wet algae because of their ability to alter the fibrillary structure of cell walls, decrease cellulose crystallinity, and increase cellulose surface accessibility [25]. The mixture of [Emim][$MeSO_4$] and polar organic solvents was firstly applied to extract lipid from algae in 2010 [27]. Lee et al. (2012) demonstrated that [Bmim][CF_3SO_3] and [Emim][$MeSO_4$] were more effective to lipid extraction than Bligh and Dyer's method [23]. Ohno et al. (2013) dissolved wet and saliferous marine microalgae (WSM) by [C2mim][$MeO(H)PO_2$] under room temperature. To et al. [28] found ionic liquid-water mixtures were effective to carbohydrate and lipid extraction from algae. Yang et al. [29] reported that N-methylcyclohexylamine and [C_4-mim][PF_6] can be used to extract wet algal slurries with 85% water content directly with low-energy consumption. Deng et al. (2016) [30] found lipid extraction efficiency from wet microalgae under microwave-assisted lipid extraction with [Bmim][HSO_4] was over 10 times higher than traditional solvent extraction method.

Recent studies on ILs' application in biofuel production showed that acid ionic liquids were also promising alternatives of inorganic acid or base to catalyze esterification and transesterification. Rafiee et al. [31] conducted BrØnsted acidic ionic liquid-catalyzed esterification of oleic acid with methanol for biodiesel application. Yang et al. [32] catalyzed transesterification of Koelreuteria integrifoliola oil using a magnetically recyclable acidic ionic with fatty acid methyl ester (FAME) yield of 93.7% under optimal conditions. Sun et al. [33] firstly reported the catalytic in-situ transesterification of wet Nannochloropsis using 1-butyl-3-methylimidazolium hydrogen sulfate with FAMEs yield of 95.28%. Comparing with other catalysts, ILs are more effective to in-situ transesterification of wet algae because they avoid the mass transfer limitation of water content [34].

Water, a primary factor affecting energy consumption in harvesting, dewatering, and extraction stages, is usually negative to biodiesel production because it acts as a retardant or inhibitor to catalysts [35]. The interactions of ILs/water mixtures, which are usually described by Kamlet-Taft polarity parameters, α, β, and π*, vary with different water content in ionic liquid/water mixture [36,37]. Unlike the interactions of water with other catalysts, the hydrogen acidity and basicity, which are excellent predictors of pretreatment efficiency of cellulose, will vary with water content. On the other hand, ionization of ILs would be affected by water content in algae slurry. H^+ ions released from hydrolyzation of acid ILs can catalyze the transesterification process according to our previous work [33]. The concentrations of H^+ ions increase with increased amount of water content initially, leading to an increase of FAME yield due to its enhanced catalytic property. The enhanced catalytic property of acid ILs in a proper water content range will compete with the negative effect of water content on biodiesel yield. Therefore, the negative effect of water content on in-situ transesterification of wet algae is not significant observed due to the competition of catalytic property of H^+ ions from hydrolyze of acid ILs in a proper water percentage range. However, the concentrations of H^+ ions start to decrease when water contents keep increasing after the balance of hydrolyzation of acid ILs was reached. And thus, the catalytic property of acid ILs is weakened, which leads to decrease of FAME yield.

Most of the ILs studies on algae biomass have concentrated only on lipid extraction due to its solubility of cellulose and hemicellulose compositions of algal cell walls. Acid ionic liquids catalyzed in-situ transesterification of wet algae has not been investigated thoroughly. Also, using hydrolyzed acid ILs to catalyze in-situ transesterification of wet algae to "neutralize" negative effect of water content on mass transfer and hydrolysis of products has never been investigated.

Herein, the main purpose is to investigate the effect of water content on [Bmim][HSO_4] catalyzed in-situ transesterification of wet Nannochloropsis. The algae cells before and after IL catalyzed in-situ transesterification are characterized by Transmission Electron Microscopy (TEM). The compositions of crude biodiesel products were determined by a gas chromatograph (GC) connected to an Agilent 5973 series Mass Selective Detector (MSD) to investigate the effect of water content on biodiesel composition. The effects of reaction temperature, reaction time, mass ratio (wet algae: [Bmim][HSO_4]), and water content on biodiesel yield are also investigated thoroughly. The negative effect of water on biodiesel production is "neutralized" in the range of 0–15 wt%. To further assess the effects of water content on in-situ transesterification of wet *Nannochloropsis* sp. biomass, elemental analysis is performed to determine C, H, N, and S contents in lipid extracted residuals.

2. Materials and methods

2.1. Materials

Nannochloropsis oceanica biomass (received from Cellana, HI) was cultured indoors in 2′ × 2′ 15L flat panel bioreactors at ambient temperature, continuously illuminated with a light path of 5 cm and aerated with 2% CO_2 to provide pH control and adequate mixing. Cultures were inoculated in artificial seawater modified F/2 medium, with a starting nitrogen concentration of 12.6 mg NO_3-N. F/2 medium was