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Biogas liquid digestate grown *Chlorella* sp. for biocrude oil production via hydrothermal liquefaction

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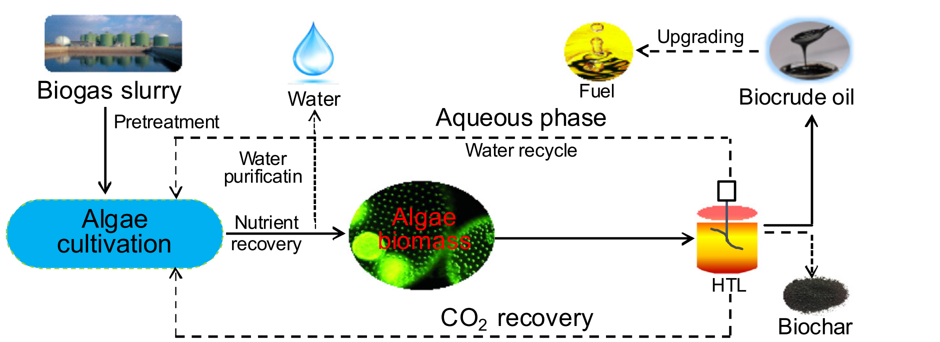
HIGHLIGHTS

- Valorization of biogas effluent coupling algae and hydrothermal liquefaction
- Higher oil yield using biogas effluent than standard medium
- Reveal potential of biocrude oil from biogas effluent grown algae
- Higher yield and similar properties of oil using 500 mL than 100 mL reactor

GRAPHICAL ABSTRACT



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ABSTRACT

Microalgae can not only purify and recover the nutrients from wastewater, but also be harvested as wet biomass for the production of biocrude oil via hydrothermal liquefaction (HTL). *Chlorella* sp. cultivated in the ultrafiltration (UF) membrane treated anaerobic digestion (AD) liquid digestate of chicken manure was used as the feedstock in this study. The present study characterized the products and investigated the elemental migration during HTL of *Chlorella* sp. fed with AD effluent wastewater (WW) and BG11 standard medium (ST) in 100 mL and 500 mL reactors under different operational conditions. Results showed that the highest oil yield of WW (38.1%, daf) was achieved at 320 °C, 60 min and 15% TS in 500 mL reactor, which was 14.1% higher than that of ST (33.4%, daf) at 320 °C, 30 min and 20% TS in the same reactor. WW had a similar carbon and hydrogen distribution in the four product fractions under HTL conditions compared with ST. 43.4% and 32.4% of carbon in WW11 and ST11 were released into the biocrude and aqueous phase in 500 mL reactor, respectively. As much as 64.5% of the hydrogen was transferred to the aqueous phase. GC–MS results showed that the chemical compounds in the biocrude oil from WW consist of a variety of chemical constituents, such as hydrocarbons, acids, alcohols, ketones, phenols and aldehydes. These two biocrude oils contained 17.5% wt. and 8.64% wt. hydrocarbons, and 63.7% wt. and 79.8% wt. oxygen-containing compounds, respectively. TGA results showed that 69.3%–66.7% of the biocrude oil was gasified in 30 °C–400 °C. This study demonstrates the great potential for biocrude oil production from microalgae grown in biogas effluent via HTL.

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1. Introduction

There were 31,696 medium and large-scale biogas projects amounting to an annual biogas yield of 1.46 billion m^3 in 2014 in China (Chen and Liu, 2017), which also produce a large amount of biogas slurry every day. High concentrations of anaerobic digested (AD) effluent pose a great burden to the land and environment (Singh et al., 2011; Huong et al., 2014). Previous research indicated that microalgae were a good candidate for the purification of wastewater (WW) (Mart Nez et al., 2000; Sydney et al., 2011). Microalgae cultivated in wastewater exhibits the advantages of having a high photosynthetic efficiency, high biomass productivity, and it benefits from having a rapid growth rate (Arbib et al., 2017). Further, microalgae also does not compete with the food supply, does not use arable land, and it is CO_2 neutral, leading to additional integrated benefits for sewage purification and nutrient recovery (Wijffels and Barbosa, 2010).

Hydrothermal liquefaction (HTL) has the advantage of converting a wide variety of feedstock into oil, including bacteria, wastewater sludge, and algae (Zhou et al., 2013; Patel et al., 2016). The HTL path for the production of renewable liquid fuels has no strict lipid content limitation (Savage, 2012). Furthermore, HTL also can produce biocrude oil directly without drying the feedstock, significantly decreasing the energetic input (Williams and Laurens, 2010). Many researchers have used microalgae as a feedstock for biofuels production in recent years (Halim et al., 2012; Huang et al., 2010). Previous studies have proved that algae biomass can be a suitable HTL feedstock for biocrude oil production (Rawat et al., 2011).

Microalgae has a strong ability to adapt to AD effluent, serving as a suitable alternative for wastewater treatment with accompanied benefits of being utilized for renewable biofuel production (Singh et al., 2011). Zhu et al. (2013)used diluted piggery wastewater for microalgae cultivation and biodiesel production. However, AD and biodiesel production have strict requirements for the C/N input value and lipid content, respectively. Singh et al. evaluated the growth potential of mixotrophic microalgae utilizing anaerobic digester effluent growth medium for bioenergy application and pollutant degradation (Singh et al., 2011). The biochemical components of wastewater-based microalgae were greatly affected by the nutrients of the wastewater, and a higher N content limited the accumulation of lipids while promoting the accumulation of proteins (Tsolcha et al., 2016). Current research utilizing wastewater-based microalgae has mainly used for biogas and biodiesel production (Yuan et al., 2012; Wiley et al., 2011). Most of the preceding studies focused on hydrothermal conversion of municipal wastewater cultivated microalgae (Neveux et al., 2016; Wang et al., 2016; Zhu et al., 2017); however, little information is available about the HTL of microalgae cultivated in AD effluent. This information is crucial towards developing a microalgae biofuel paradigm integrated with AD wastewater purification. In this study, *Chlorella* sp. cultivated in the AD effluent of chicken manure after UF membrane treatment was selected as HTL feedstock. The microalgae cultivation in anaerobic digested effluent provided multiple benefits to the local environment and the cultivated microalgae simultaneously could be used for biocrude oil production.

We have identified the feasibility of biocrude oil production from microalgae cultivated in after UF treatment (Wang, 2017). However, its performance over using standard medium (ST) is not clear. Furthermore, it is important to identify how the reactor volume impacts the performance of HTL considering its scale up. In light of these issues, the objectives of this study are: (1) to investigate the distribution of the four-phase products from *Chlorella* sp. fed with WW in comparison to ST, (2) to verify the organic elemental migration under HTL in a 500 mL reactor. (3) to compare the biocrude oil properties and energy recovery from the two kinds of microalgae via HTL both in 100 mL and 500 mL reactors.

2. Material and methods

2.1. Feedstock characterization

Chlorella sp. was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and was cultivated in a raceway pond in AD effluent in a greenhouse. The AD effluent was provided by Shandong Minhe Biological Technology Co., Ltd. (Penglai, China). The wastewater was then further treated by a UF membrane and diluted to a suitable concentration of TN, TC and NH_3-N, respectively. The same microalgae *Chlorella* sp. species was then cultivated in wastewater and BG11 standard medium and subsequently named WW (wastewater group) and ST (control group), respectively. WW and ST had distinctive biochemical and inorganic contents. As shown in Table 1, WW *Chlorella* sp. had a higher lipid content (14.6% ± 0.40%, dw) than ST *Chlorella* sp. (12.6% ± 0.60%, dw), which may be due to the high TC and TOC in the UF wastewater, which was beneficial for lipid accumulation. The protein content in ST *Chlorella* sp. (52.5% ± 3.52%, dw) was higher than WW *Chlorella* sp. (39.8% ± 2.04%, dw). The WW *Chlorella* sp. had a lower ash content (12.7% ± 0.03%, dw) compared to ST *Chlorella* sp. (25.4% ± 0.08%, dw) due to the differences in the harvest technology and medium properties. The main metal ion in the UF clear solution was potassium (108 $mg \cdot L^{-1}$), while the main metal ion in the BG11 medium was sodium (369 $mg \cdot L^{-1}$). The high content of Na (4.21 $mg \cdot L^{-1}$) in the microalgae *Chlorella* sp. cells usually resulted in a high ash content. The Ca ion concentration in ST *Chlorella* sp. (47.3%, dw) was also higher than that of the WW *Chlorella* sp. (23.4%, dw), which also contributes to a high ash content.

The higher heating values (HHVs) of the biocrude oil were calculated according to the Dulong formula (Neveux et al., 2016; Wang et al., 2016; Xu and Lad, 2008; Zhu et al., 2017):

$$HHV = (MJ/kg) = 0.3383\ C + 1.422\ \left(H - \frac{O}{8}\right)$$

where C, H and O were the weight percentages of carbon, hydrogen and oxygen in the feedstock and biocrude oil, respectively.

The HHV of feedstock was measured using a bomb calorimeter (Model 6200, Parr Instrument Co., Moline, Illinois, USA) (Li et al., 2014).

2.2. Experimental procedure

HTL experiments were performed in a 500 mL batch Parr reactor (4574, Parr Instruments Co., Moline, IL, USA) (Zhu et al., 2016) and a 100 mL batch reactor (Model 4593, Parr Instrument Company, Moline,

Table 1
Proximate and metals of two *Chlorella* sp. strains cultivated in AD wastewater (WW) and standard medium BG11 (ST).

Parameters	WW	ST
Proximate analysis		
Ash (%dw)	12.7 ± 0.03	25.4 ± 0.08
Crude lipid (% daf)	14.6 ± 0.40	12.6 ± 0.55
Crude cellulose (% daf)	11.7 ± 0.52	20.7 ± 0.36
Crude protein (% daf)	39.8 ± 2.04	52.5 ± 3.52
HHV ($MJ \cdot kg^{-1}$)	22.4 ± 0.03	20.7 ± 0.21
Metals ($mg \cdot g^{-1}$)		
Ca	23.4	47.3
Cu	0.01	0.04
Fe	1.62	3.86
K	8.45	6.39
Mg	3.02	3.49
Mn	0.08	0.58
Na	0.46	4.21
Zn	0.25	0.47

daf = dry ash free. Proximate analysis was performed in triplicates, and the mean values were presented.