Algal Research 33 (2018) 78–83

Contents lists available at ScienceDirect

Algal Research

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

Rheological properties of microalgae slurry under subcritical conditions for hydrothermal hydrolysis systems

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ARTICLE INFO

Keywords:
Microalgae slurry
Rheological properties
Subcritical temperatures
Biochemical reactions
Formula fitting

ABSTRACT

Hydrothermal hydrolysis is an effective pretreatment for biogas production from microalgae via fermentation. The rheological properties of microalgae slurry under subcritical conditions significantly affect the heat transfer performance and hence the energy requirement of hydrothermal reactors. In this study, we investigated the rheological properties of microalgae slurry under subcritical conditions (2 MPa, 100–200 °C). For the first time, we found that the apparent viscosity of microalgae slurry under subcritical conditions first drastically increased, and then gradually decreased with the increasing temperature, which is quite different with the variation trend at low temperatures (< 70 °C). In addition, the temperatures corresponding to the maximum apparent viscosities were different at different shear rates, which was probably due to the combined effects of starch gelatinization and protein denaturation at high temperatures. Finally, the relationship of the apparent viscosity of microalgae slurry with the temperature and shear rate was obtained.

1. Introduction

Biofuel production from biomass is an alternative technology towards sustainable energy and CO_2 emission reduction. Microalgae, as the "third-generation" biomass feedstock, have been extensively studied [1], due to their short growth period, high photosynthetic efficiency, and high organic matter accumulation [2]. Current commonly used methods for biofuel production from microalgae include pyrolysis, gasification, hydrothermal liquefaction, and fermentation [3–7]. The pyrolysis and gasification technologies are energy intensive due to the involvement of centrifugation and drying processes of microalgae biomass [7], while the hydrothermal liquefaction system is relatively complex for large-scale application because of its requirements for high temperature and high pressure (374 °C, 22 MPa) [5,8]. On the other hand, microbial fermentation process is a potential approach for biofuel production from microalgae slurry, as it can directly use wet microalgae biomass as feedstock and eliminate the drying process of microalgae biomass [9–11]. In addition, fermentation processes usually operate at room temperatures, much lower than that of the technologies mentioned above. However, the compact structures of microalgae cell wall hinder the organics to release out from the microalgae cells, severely reducing the performance of fermentation. Therefore, pretreatment of microalgae biomass is required to release out the organics from microalgae cells before the fermentation processes.

A promising pretreatment technology is hydrothermal hydrolysis, which uses the thermochemical properties of water under subcritical conditions (water belongs to aqueous phase with temperature > 100 °C) to treat the microalgae cells. It had been reported that the biogas yield of fermentation with marine microalgae (*Nannochloropsis salina*) after pretreatment with hydrothermal hydrolysis was enhanced nearly three times in contrast to that without pretreatment [11]. In addition, hydrothermal hydrolysis process can be easily used for large-scale applications due to the medium low temperature and low pressure requirements (temperature < 200 °C, pressure < 4 MPa) [12]. Notably, in large-scale hydrothermal hydrolysis applications, continuous reactors are commonly used for the reaction [13]. The rheological properties of microalgae slurry significantly affect the flow and heat transfer characteristics, which can affect the energy requirement of hydrothermal hydrolysis. Therefore, it is important to understand the rheological properties of microalgae slurry for high-efficient reactors design.

In previous studies, the rheological properties of microalgae slurry at low temperatures (< 70 °C) had been investigated [14–18]. It

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https://doi.org/10.1016/j.algal.2018.04.026
Received 3 January 2018; Received in revised form 23 March 2018; Accepted 27 April 2018
2211-9264/

showed that the microalgae slurry behaved shear-thinning non-Newtonian properties and the apparent viscosities decreased with the increasing temperature. Yet, the rheological properties of microalgae slurry under subcritical conditions (temperature ranging 100–200 °C, and pressure ranging 2–4 MPa) had never been reported. Notably, the rheological properties of microalgae slurry under subcritical conditions have a large difference with that of microalgae slurry at low temperatures, due to possible biochemical reactions and release of organics from microalgae cells [12]. Therefore, it is important to investigate the rheological properties of microalgae slurry under subcritical conditions.

In this study, the rheological properties of microalgae slurry under subcritical conditions (temperature ranging 100–200 °C) were investigated using an Anton Paar Rheometer. In addition, the effects of temperature and microalgae mass fractions on the apparent viscosities of microalgae slurry were investigated. The relationship between the apparent viscosities of microalgae slurry and temperature were obtained based on the experimental results, which may provide useful information on the future application.

2. Materials and methods

2.1. Microalgae biomass

The microalgae biomass used in this study was *Chlorella pyrenoidosa*, provided by Fuqing King Dnarmsa Spirulina Co. LTD (Chengmai, Hainan, China). The *Chlorella pyrenoidosa* was cultivated in open ponds with air agitation. The microalgae suspension was converted to microalgae powder via centrifugation and heated-air drying after cultivation process. The organics of the microalgae powder were carbohydrate, protein and lipid (shown in Table 1). Carbohydrate was measured by phenol–sulfate acid method [19], protein was measured by Lowry's assay [20], and lipid was measured by chloroform–methanol method [21].

The microalgae slurry used in this study was prepared by mixing microalgae biomass powder with water. To understand the variation trend of the rheological properties of microalgae slurry with temperature, starch slurry, protein slurry, and the mixture slurry of starch and protein were also investigated. The starch slurry was mixed by water and corn starch, and protein slurry were mixed by water and whey protein. The specific mixture steps were the same to the mixture process of microalgae slurry. The selected concentrations of starch slurry, protein slurry and the mixture slurry were based on the content of carbohydrate and protein in 10 wt% microalgae slurry (shown in Table 1), thus the selected concentrations of starch and protein were 33.2 and 32.2 mg/mL, respectively.

2.2. Rheological measurements

The apparent viscosities of microalgae slurry were measured using an Anton Paar Rheometer (MCR302, Austria). The microalgae slurry with volume of 5.5 mL was added to the rheometer by pipetting. The temperature was controlled by an attemperator. The rheometer was pressurized with high-pressure nitrogen gas, and the pressure in the rheometer was controlled with a valve. The apparent viscosities were measured at a certain mass fraction, a certain shear rate, and a certain temperature. When investigating the effect of temperature on the apparent viscosity of microalgae slurry, the temperature increased from 80 to 200 °C in series. The mass fraction of microalgae slurry ranges from 5 to 15 wt%, the shear rate ranges from 21.5 to 1000 s^{-1}, and the temperature mainly ranges from 100 to 200 °C. The apparent viscosities of microalgae slurry with mass fraction of 15 wt% at the pressure of 2 and 4 MPa were also measured to investigate the effect of pressure on the rheological properties of microalgae slurry. The apparent viscosities of starch slurry, protein slurry, and the mixture slurry of starch and protein were also measured to investigate the reason of viscosity changing trend with temperature. All apparent viscosities were measured in twice unless specified. The standard errors were calculated by Eq. (1)

Table 1
Organic contents of the microalgae biomass powder used in this study (data shown is the mean ± SD, n = 3).

Organics	Content (%)
Carbohydrate	33.24 ± 1.32
Protein	32.20 ± 1.14
Lipid	35.92 ± 0.91

$$\sigma = \sqrt{\frac{1}{3}\sum_{i=1}^{3}(\eta_i - \overline{\eta})^2} \quad (1)$$

σ is the standard error, η_i is the measured apparent viscosity, $\overline{\eta}$ is the average apparent viscosity.

2.3. Formula fitting

The formulas of apparent viscosities of microalgae slurry at subcritical conditions were obtained by fitting. Based on the fit model ($\eta = K\dot{\gamma}^{n-1}$) of power law fluid, the certain values of K (consistency coefficient) and n (power law index) could be obtained at a certain temperature. Then, the formula of K and n changed with temperature were obtained by the fitting model of normal distribution. Finally, the residuals of K, n between actual value and calculated value were fit by the model of polynomial, and added to the fitting formula.

After the fitting results of microalgae slurry apparent viscosities were obtained, the goodness of the formula fitting results was analyzed by the correlation coefficient in statistics. It's the goodness of fit between line y = x and the points (experimental data, calculated data). When the correlation coefficient tends to 1, the residual error between the experimental data and calculated data was reduced.

The calculation formula of correlation coefficient (r) is shown in Eq. (2).

$$r = \sqrt{1 - \frac{S_{Y\cdot X}^2}{S_Y^2}} \quad (2)$$

$S_{Y\cdot X}$ is the standard error between Y and estimation of X (Y_{est}), calculated by Eq. (3). S_Y is the standard error of Y, calculated by Eq. (4).

$$S_{Y\cdot X} = \sqrt{\frac{\sum (Y - Y_{est})^2}{N}} \quad (3)$$

$$S_Y = \sqrt{\frac{\sum (Y - \overline{Y})^2}{N}} \quad (4)$$

3. Results and discussion

3.1. Shear-thinning phenomena of microalgae slurry under subcritical conditions

Medium-low pressure (from 2 to 4 MPa) of subcritical conditions was necessary in hydrothermal hydrolysis, thus the effects of pressure on apparent viscosities of microalgae slurry at various temperatures were first investigated. As shown in Fig. 1A, the variation of the apparent viscosities of microalgae slurry with temperature were almost the same at different pressures. Fig. 1B showed that the correlation coefficient of the apparent viscosities of microalgae slurry at pressure of 2 and 4 MPa was 0.981, and the difference value of apparent viscosities affected by pressure was < 6%. It suggested that pressure had no significant influence on the apparent viscosities of microalgae slurry, thus the pressure used in the further study was set as 2 MPa.

Fig. 2A shows the variation of apparent viscosity of microalgae slurry with the shear rate under subcritical conditions. The microalgae slurry