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Influence of cell properties on rheological characterization of microalgae suspensions

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HIGHLIGHTS

- Rheological properties of two algal strains suspension were reported.
- Algal suspensions displayed a shear thinning non-Newtonian behavior.
- Smaller algal cells caused higher effective viscosity of microalgae suspensions.
- Cell charge played a negligible role in affecting effective viscosity.

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ABSTRACT

The influences of algal cell size and surface charge on rheological properties of microalgae suspensions were investigated. The effective viscosity of two microalgae suspensions, i.e., the freshwater *Chlorella* sp. and the marine *Chlorella* sp., was measured as a function of their volume fractions in the range of 0.70–4.31%. The hydrodynamic diameters of the freshwater *Chlorella* sp. and the marine *Chlorella* sp. were measured to be 3.13 and 6.00 μm, respectively. The Zeta potentials of these two algal cells were measured to be −23.73 and −81.81 mV, respectively. The intrinsic viscosities of these two microalgae suspensions were further determined to be 24.7 and 16.1, respectively. Combining with theoretical models, these results indicated that the algal cell size has a predominant effect over cell surface charge in affecting rheological properties of microalgae suspensions. Smaller algal cells result in a higher effective viscosity of the microalgae suspension.

1. Introduction

Safe sustainable liquid biofuels are imminently needed to displace fossil oil in the near future, which contributes to global warming and is of limited availability (Amaro et al., 2011). The biofuels produced from renewable resources such as oil crops, animal fat, waste cooking oil and microalgae could help to reduce the world's reliance on petroleum fuels and CO_2 emissions (Naik et al., 2010). Compared with other oil crops and animal fats, microalgae have many advantages, such as high photosynthetic efficiency and oil productivity, short life cycles, easier to scale up, and less labor required for production (Li et al., 2008). Previous study (Chisti, 2007) suggests that biofuels produced from microalgae appear to be the only renewable energy source that has the potential to completely displace petroleum-derived transport fuels without adversely affecting the food supply and other crop products.

Despite the fact that microalgae have some clear advantages over conventional biofuel sources, broad commercialization of microalgae biofuel has been restrained due to large energy requirements and high costs in the process of cultivation, harvesting and oil extraction, which is mainly owing to the dilute nature of microalgae cultures (Beal et al., 2012; Laurent et al., 2009; Schenk et al., 2008). The rheological properties of microalgae suspensions affect not only the transport phenomena in bioreactors but also the downstream bioprocessing technologies such as harvesting and dewatering, thus directly impact the energy requirements and costs of algae biofuel production. For example, at present, the biomass concentration of microalgae suspension is only 0.5 g/L in open raceway ponds and 5 g/L in photobioreactors (Pulz, 2001). The harvesting culture suspensions need to be dewatered as much as possible to simplify the subsequent lipid extraction steps. Generally, in the primary dewatering step, the suspensions are

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concentrated by 100–200 times and become algal slurries (Uduman et al., 2010). And then these concentrated microalgae slurries will be pumped to the next biomass processing unit. Consequently, it is important and necessary to understand the rheological properties of microalgae suspensions in a broad concentration range from dilute suspensions to concentrated algal slurries for designing effective photobioreactors and enhancing downstream processes toward a large scale production of biofuel.

Microalgae suspensions are complex fluids that consist of water, dissolved salts, polymeric substances, and algal cells. Rheological properties of microalgae suspensions are in large dependent on the biomass concentration, physical properties of the algal cells and the rheological properties of liquid phase. Previous study found that, below a critical concentration, most microalgae suspensions displayed a Newtonian behavior (Sirin et al., 2013; Wilemana et al., 2012), and above a certain concentration, some microalgae suspensions exhibited non-Newtonian fluid behavior (Al-Asheh et al., 2002; Chen et al., 1997; Fernandes et al., 1991; Wayne et al., 1993; Wilemana et al., 2012). Compared to the effect of algal cell concentration, the influence of cell properties on rheological behavior of microalgae suspensions is still poorly understood.

The objective of this paper is to study the influence of algal cell size and surface charge on the rheological properties of microalgae suspensions. Two widely-used algal strains for biofuel production, i.e., the freshwater *Chlorella* sp. and the marine *Chlorella* sp., were used in this study. As will be shown later, these two algal cells share the same shape but different sizes and surface charges. By combining experimental data of algal characterization, rheological measurement and theoretical colloidal models, the effects of cell size and surface charge of these two algal strains on the effective viscosity of the microalgae suspensions were studied.

2. Materials and methods

2.1. Algal strains and sample preparation

The algal strains used in this study were freshwater *Chlorella* sp. and marine *Chlorella* sp. Freshwater *Chlorella* sp. was provided by the Department of Biological Science and Technology at the University of Science and Technology Beijing (Jia et al., 2011). Marine *Chlorella* sp. was obtained from the Center for Collections of Marine Algae (CCMA) at the Xiamen University. The freshwater *Chlorella* sp. was cultivated in the Bold's Basal medium and the marine *Chlorella* sp. was cultivated in the f/2 medium. Both culture media were prepared according the recipes described by Andersen (Andersen, 2005). Both of the microalgae were cultivated in a 5 L photobioreactor at 25 ± 1 °C under continuous irradiance of 100 μmol m^{-2} s and continuous aeration rate of 15 mL/min by a pump. The suspensions were cultured for 7 days before cells were harvested for experiments. Samples used in this study were prepared from actively growing cultures during their exponential growth phase.

The cultivated algal cells were centrifuged at 4000 rpm (1070*g*) for 4 min at room temperature followed by washing with the 0.1% NaCl solutions. After three rounds of centrifugation and washing, the suspensions were resuspended in fresh nutrient media and mixed by a stirrer to prepare concentrated homogeneous samples which would be used for dilution in the experiments.

2.2. Sample calibration

The shapes of the algal cells were firstly observed by scanning electron microscopy (SEM). And then the cell shape and mean physical dry diameters D_{MD} were derived using the image processing software Image J1.44p basing on the SEM pictures. Furthermore, the measurements of the cell hydrodynamic size and surface charges were conducted. The hydrodynamic size distribution and mean volume diameters D_{MVD} of microalgae cells which were used to determine the volume fractions of microalgae suspensions were measured by a laser particle sizer (Microtrac Inc., USA, MicrotracS3500SI). Surface charges of algal cells were obtained from the Zeta potential measurements (Microtrac Inc., USA, Nanotrac wave). Before the measurements of D_{MVD} and Zeta potential, algal suspensions were filtered through a polyether sulfone filter paper with a pore size 15 μm to remove large algal flocculations and to have a single cell algal suspension for measurements.

The volume fractions of microalgae suspensions φ were derived by,

$$\varphi = N\pi D_{MVD}^3/6 \quad (1)$$

where φ is the volume fraction of the cell suspensions, D_{MVD} is the mean volume diameter which can be obtained from the measurement of the size distribution, N is the cell number concentration per cubic meter liquid. N was measured using a Neubauer counting chamber. In order to improve the precision and accuracy of the cell number concentration, the numbers of microalgae within all small cells were obtained, and the error of N is less than 1.5% (Hua, 1986).

For the convenience and accuracy of volume fractions of microalgae suspensions, the relationships between N and the optical density OD of microalgae suspensions were measured using a 1 cm pathlength cuvette visible spectrophotometer. Firstly, the characteristic spectra for the freshwater *Chlorella* sp. and the marine *Chlorella* sp. were determined. Then the calibration curves of N as a function of OD at the characteristic spectrum were developed.

2.3. Rheological measurement

The effective viscosity of microalgae suspension was determined at 25 °C using a Brookfield programmable LVDVII + digital viscometer fitted with a ultralow adaptor (Brookfield Engineering Laboratories Inc., USA). To assess the accuracy of the rheological measurement, the effective viscosity of polystyrene microbead suspensions (Aladding Reagent Inc., Shanghai, China) with the same size distributions as the freshwater *Chlorella* sp. suspension were measured. Effective viscosities of polystyrene microbead suspensions with a volume fraction of 4.77%, 3.53%, 2.35%, 1.18% were measured. The results indicated that the relative viscosity of microbeads suspensions μ_{rel} as a function of volume fractions matched to the Einstein equation well ($\mu_{rel} = \mu_{eff}/\mu_0$, where μ_{eff} is the effective viscosity of suspensions and μ_0 is the viscosity of suspending medium), which indicates that the rheological measurements in this study were reliable and the precision was enough.

During the rheological measurements of microalgae suspensions, experiments were conducted for shear rate γ from 5.0 to 100 s^{-1}, which correspond to values expected in field applications (Mitsuhashi et al., 1995). All measurements were performed three times and the arithmetic averages of the results were reported. The maximum standard errors for the shear rate and shear stress were 3.7% and 2.6%, respectively.

3. Results and discussion

3.1. Algal cell properties and microalgae suspension concentration

Fig. 1 shows the hydrodynamic size distribution of freshwater *Chlorella* sp. and marine *Chlorella* sp. determined by a laser particle sizer. The mean volume diameter of these two algal cells was measured to be 3.13 ± 0.80 and 6.00 ± 0.95 μm, respectively. Morphology of dehydrated cells of these two microalgae was determined