

Drying Characteristics of *Chlorella pyrenoidosa* Using Oven and its Evaluation for Bio-Ethanol Production

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Abstract. The objective of this research is to study the influence of temperature on drying and changes in carbohydrate composition during the drying. *Chlorella pyrenoidosa* was dried in oven at various temperatures and initial weight 2 g. The initial moisture content of *Chlorella pyrenoidosa* was 487.2% dry weight and the composition was hemicellulose (62.76), cellulose (2.39), and lignin (0.46% dry weight). Every 5 min, the moisture content was recorded. The critical moisture contents of *Chlorella pyrenoidosa* at 50, 60, and 70 °C are 7.2, 3.9, and 3.1% dry weight, respectively. Meanwhile, the equilibrium water contents are 0.53, 0.32, and 0.12% dry weight, respectively. The carbohydrate content in *Chlorella pyrenoidosa* cell as a result FTIR analysis indicates that the higher temperature of drying the carbohydrate content increases. Drying of *Chlorella pyrenoidosa* at temperatures of 50, 60, and 70 °C will decrease moisture content without disturb carbohydrate molecule, so the carbohydrate content increases. Therefore, drying of *Chlorella pyrenoidosa* before converting become bio-ethanol will give benefit to increase the carbohydrate content and initial rupturing of it's cell.

Introduction

Fuels have become humans' important need that must be fulfilled. This can be proven by a research conducted by Sirajunnisa and Surendhiran which stated humans' needs for fuel by 80-88% [1]. Their dependence on fossil fuels shows that only about 10% of fuel is produced from renewable energy sources [2]. Therefore, renewable fuels need to be improved. One alternative fuel is bio-ethanol derived from biomass. It is seen to be very potential as a fossil fuels substitution [3]. Until now, raw materials for bio-ethanol have been shifted to the third generation raw materials called microalgae [4].

Microalgae are promising biomass for bio-ethanol [5], because they have a high CO₂ fixation ability, 10 times more efficient than terrestrial plants and can produce 30-100 times more energy per hectare than agricultural crops [6]. One type of microalgae that can be used in the third generation bio-ethanol production is the genus *Chlorella*. These microalgae are rich in carbohydrates with a content of 37 to 55% dry weight, so that it can be used as a promising raw material for producing bio-ethanol [7-10]. This research used *Chlorella pyrenoidosa* with species cultivated in freshwater which makes them more potential, because it contains higher carbohydrates compared to *Chlorella vulgaris*. They are also easily cultivated.

Bio-ethanol production using *Chlorella pyrenoidosa* microalgae has stages from cultivation to harvest, drying, oil extraction, hydrolysis, fermentation, distillation, and finally purification [11]. *Chlorella pyrenoidosa* drying aims to reduce the post-harvest its water content which still contains water content of 480% dry weight [12]. This is done to prevent decomposing process and reduce the costs of handling, transportation, packaging, and storage [13]. Nearly 60% of the total energy consumed in bio-ethanol production is in the drying stage [14,15]. Therefore, it is important to learn the effect of temperature on drying and changes in carbohydrate composition during the drying.

There are several methods that can be used for drying microalgae, namely by sun, freeze drying, vacuum drying, using a dryer (oven, microwave oven, rotary dryer, drum dryer, spray dryer, and greenhouse) [16]. Previous research conducted by Biz was *Chlorella pyrenoidosa* drying using spray drying method, but this method still requires a lot of energy compared to drying using oven [17]. Besides being influenced by the type of drying tool. Microalgae drying is also strongly influenced by time and temperature. The drying rate is affected by time; the longer the drying time, the higher the drying rate [15]. Whereas temperature can affect the texture and humidity of microalgae; high temperatures can damage the active components contained in microalgae [18].

Materials and Methods

Drying *Chlorella pyrenoidosa* using an Oven. *Chlorella pyrenoidosa* microalgae were obtained at Ugo Plant Shop, Purworejo, Central Java in the form of 1 kg slurry. The slurry was stored in the refrigerator at 30 °C. Before starting the drying, ± 50 g of the slurry were filtered using filter paper (twice) and then left for 5 min to obtain its paste form. The drying was done with 2 g *Chlorella pyrenoidosa* paste in a porcelain mug using an oven (Ecocell 55, Standard Oven). Every 5 min, the paste was taken, removed from the oven, and cooled using a desiccator for 2 min. From the desiccator, the paste was weighed using a digital scale (OHAUS PA214, Analytical Balance) and then put back into the oven. The dried paste was carried out to achieve a constant weight. This drying was carried out at temperature variations of 50, 60, and 70 °C. After that, each powder obtained is screened using a sieve 500 μ m (Endecotts, S/Steel).

Moisture content data were used to evaluate the critical conditions and the drying equilibrium. FTIR (Fourier Transform Infra-Red) analysis was carried out for samples that were heated at the time before the critical conditions, after critical conditions, and at equilibrium conditions at each drying temperature. This was done to determine changes in the composition of compounds in *Chlorella pyrenoidosa* due to the influence of temperature and time. FTIR analysis was carried out at the Organic Chemistry Laboratory, Universitas Gadjah Mada.

Results and Discussion

The Effect of Time on *Chlorella pyrenoidosa* Drying. During drying, the moisture content of microalgae will continue to decrease [15]. The effect of time on decreasing water content of *Chlorella pyrenoidosa* drying using oven can be seen in Fig. 1. The initial moisture content was 487.2% dry weight. At 50 °C, after 5 h, the moisture content dropped to 259.5% dry weight, after 15 h the moisture content became 23.6% dry weight, and after 19 h the moisture content was 0.5% dry weight. The drying of *Chlorella sp.* has been studied using a greenhouse drying [19]. The initial moisture content was 79.66% dry weight, and after drying for 56 h it decreased to 20.70% dry weight. Besides using greenhouses drying, microalgae drying using oven has also been studied for *Gracilaria sp.* [20]. The results showed that at 40 °C with an initial moisture content of 80% dry weight, at 2 h, the moisture content was $\pm 20\%$ dry weight, at 5 h dropped to $\pm 8\%$ dry weight, and 7 h was $\pm 5\%$ dry weight. During the drying, the moisture content will drop dramatically, then drop slowly, and finally be constant [20]. In this study, at 70 °C for 5 h, the decrease in moisture content was 69.33% dry weight, then after 8 h was 96.44% dry weight, and after 10 h was up to 99.74% dry weight.

The Effect of Temperature on *Chlorella pyrenoidosa* Drying. Drying is affected by temperature, the higher the temperature, the faster the drying will be [15]. In *Chlorella vulgaris* drying using an oven, at 40, 60, 80, 100, 120, and 140 °C, the moisture content equilibriums dropped to 16.9 ± 2.0 , 99 ± 0.8 , 5.1 ± 1.4 , 3.0 ± 1.1 , 2.2 ± 0.9 , and $1.3 \pm 0.3\%$ dry weight, respectively [21]. This shows that the higher the temperature, the smaller the moisture content will be, which also means that *Chlorella vulgaris* is drier. In the study of Villagrancia et al. (2016), *Chlorella vulgaris* drying was carried out using a microwave, the moisture contents at the same time (5 min) at a power variation of 300, 600, and 900 W were 0.34, 0.15, and 0.06% dry weight. This shows that at the same time, at a higher power, moisture content will dramatically decrease [15].

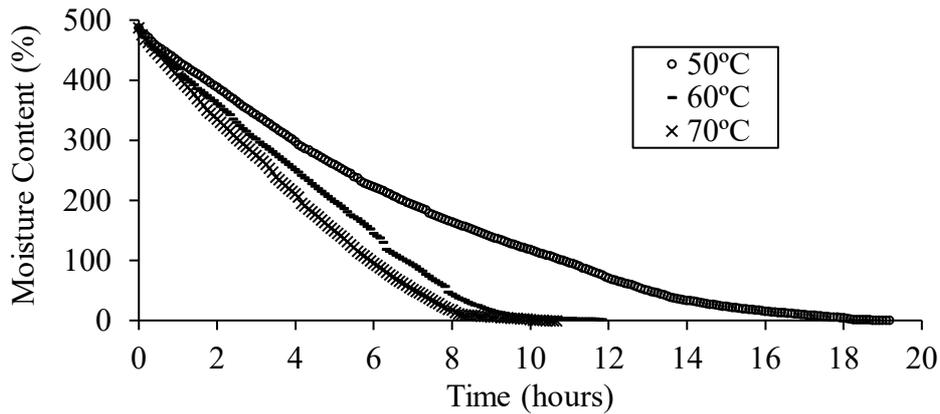


Fig. 1 The Effect of Time on *Chlorella pyrenoidosa* Drying using Oven ((\circ) 50, (-) 60, (x) 70 $^{\circ}$ C)

In this study, during the drying, the moisture content of *Chlorella pyrenoidosa* continued to decrease and then stabilize, which can be seen in Fig. 1. The initial moisture content was 487.199% dry weight. At 50, 60, and 70 $^{\circ}$ C, the critical moisture content reached 7.22, 3.90, and 3.05% dry weight, respectively, while for the equilibrium moisture contents reached 0.528, 0.323, and 0.117% dry weight, respectively. At 50 $^{\circ}$ C, the moisture content dropped dramatically to 7.22% dry weight at 850 min, and then reached 0.528% dry weight at 1050 min. At 60 $^{\circ}$ C the moisture content dropped dramatically to 3.9% dry weight at 650 min and reach 0.323% dry weight at 730 min. Meanwhile, at 70 $^{\circ}$ C the moisture content dropped dramatically to 3.05% dry weight at 585 min, and 0.117% dry weight at 640 min. At 50, 60, and 70 $^{\circ}$ C, the drying achieved more stable moisture content at 1150, 730, and 640 min, respectively. This shows that the higher the drying temperature, the faster it dries. This drying is also useful to keep *Chlorella pyrenoidosa* from being easily damaged, because it can be stored for a long time when it contains less than 10% moisture content [21].

Fourier Transform Infrared Spectroscopy (FTIR) Analysis. This study refers to the research of Sert et al. (2018) to read the functional group type [22]. The functional groups of proteins, lipids, and carbohydrates in *Chlorella pyrenoidosa* before and after drying are shown by band peaks in the transmittance spectrum at certain wave numbers from FTIR analysis results, as in Fig. 2A and B, respectively. Before and after drying, carbohydrate compounds can be detected at wave numbers of 1242.16-925.83 cm^{-1} , which is indicated by the functional groups of C-O, C-O-C, and C-C. Protein compound at a wavelength of 3294.42-3695.61 cm^{-1} indicates the presence of N-H groups. Lipid compound at a wavelength of 1519.91-2924.09 cm^{-1} , indicates that there is a C=O group. The presence of carbohydrates makes *Chlorella pyrenoidosa* microalgae can be used as a raw material for making bio-ethanol. In the manufacturing process, before being hydrolyzed, the protein and lipid contained in *Chlorella pyrenoidosa* should be extracted first, so that its utilization is more optimal. This can be developed as a biorefinery concept.

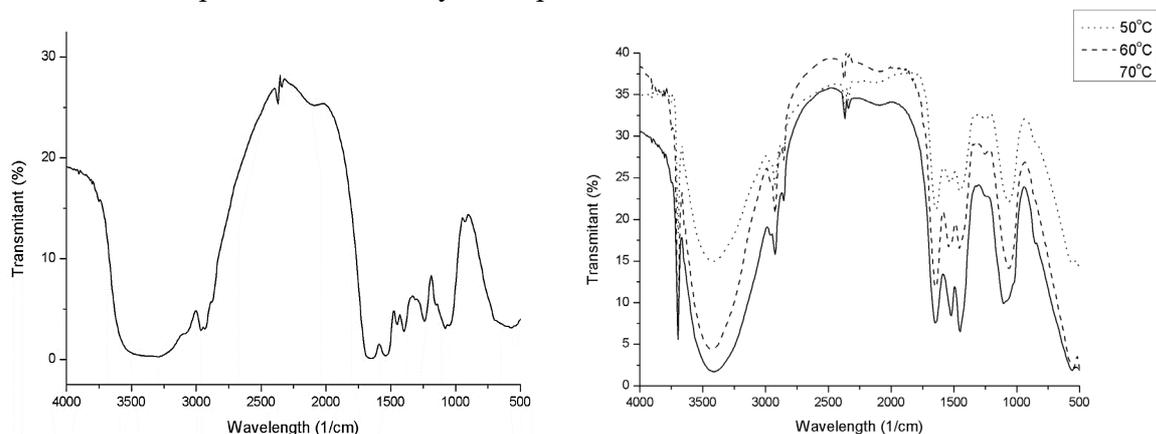


Fig. 2 *Chlorella pyrenoidosa* FTIR spectrum: (A) before drying and (B) after drying at various temperatures (50, 60 and 70 $^{\circ}$ C)

Fig. 2A and 2B show that at 50, 60, and 70 °C, the absorption curve shape is the same but the transmission decreases. This indicates that the higher the drying temperature, the higher the proteins, lipids, and carbohydrates content will be, because the water content decreases. This is in line with the research conducted by Villagrancia et al., who studied the *Chlorella vulgaris* drying using microwaves with a power variations of 300, 600, and 900 W. The results showed that the higher the power, the lower the lipid group transmittance will be, so that the lipids composition increase. Therefore, drying *Chlorella pyrenoidosa* at a temperature range of 50 to 70 °C will not affect its composition; the main component which is carbohydrate is not significantly reduced. This means that the drying is still safe.

Summary

At 50, 60, and 70 °C, the critical moisture content reached 7.22, 3.90, and 3.05% dry weight, respectively, while for the equilibrium moisture contents reached 0.528, 0.323, and 0.117% dry weight, respectively. Before the drying, carbohydrate compounds can be detected at wave numbers of 1242.16-925.83 cm^{-1} , which are indicated by the functional groups of C-O, C-O-C, and C-C. The presence of carbohydrates makes *Chlorella pyrenoidosa* microalgae can be used as a raw material for making bio-ethanol. The temperature variations of 50, 60, and 70 °C, the absorption curve shape is the same but the transmission decreases. This indicates that the higher the drying temperature, the higher the proteins, lipids, and carbohydrates content will be. This also indicates that drying *Chlorella pyrenoidosa* at 50 to 70 °C, the main component which is carbohydrate is not significantly reduced. This means that the drying is still safe.

Acknowledgments

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