

Manuscript

by Martomo Setyawan

Submission date: 11-Oct-2022 10:22PM (UTC-0500)

Submission ID: 1923130778

File name: manuscript_frontier_of_re.docx (4.46M)

Word count: 6242

Character count: 34089

MATHEMATICAL MODELING OF HYDRODYNAMIC CAVITATION AS LOW ENERGY EXTRACTION TECHNIQUE FOR LIPID REMOVAL FROM NANNOCHLOROPSIS SP.

⁵ Martomo Setyawan^{1,2}, Panut Mulyono², Sutijan², Razif Harun³ and Arief Budiman^{2,4,*}

¹ Faculty of Industrial Engineering, Ahmad Dahlan University, Jalan Prof DR Soepomo SH Yogyakarta, Indonesia

² Chemical Engineering Department, Gadjah Mada University, Jalan Grafika 2 Yogyakarta, Indonesia

³ Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 Serdang Selangor, Malaysia

⁴ Center for Energy Studies, Gadjah Mada University, Sekip K I A, Yogyakarta, Indonesia

* Corresponding Author: abudiman@ugm.ac.id

Abstract

² Lipid extraction assisted by hydrodynamic cavitation (HCLE) is one of the promising processes with low energy requirements. This study aims to reduce the extraction energy requirement using discrete flow system of HCLE and evaluate HCLE model to calculate the volumetric lipid mass transfer coefficient. The value of extraction energy requirement (E) can be adjusted by manipulating the number of repetition, cavitation number, microalgae concentration and temperature with the intention of E value is lower than the HHV of biodiesel. There were two models proposed, the first using total lipid mass transfer (Model 1) and the second using the separated lipid mass transfer (Model 2). It was found that Model 1 gave the best finding when the process was divided into three sections and the value of total volumetric lipid mass transfer ($k_T a_T$) for section 1, 2 and 3 were 1.855, 0.415 and 0.146 1/min with coefficient of determination (R^2) is 0.933, respectively. Whereas, the best result of Model 2 was achieved when the process divided into three sections, with the value of volumetric lipid mass transfer from disrupted microalgae ($k_f a_o$) for section 1, 2 and 3 were 2.137, 0.997 and 0.277 1/minute, respectively. The volumetric lipid mass transfer from the intact microalgae ($k_s a_s$) was 0.051, 0.039 and 0.026 1/min with R^2 of 0.971. Therefore, discrete flow system of HCLE is a promising technique to be developed and scaled up for extracting lipids from microalgae.

Keyword : Hydrodynamic cavitation, Lipid extraction, Microalage, Energy extraction, Volumetric mass transfer coefficient

1. Introduction

The increasing human population and modern human lifestyle cause the increasing energy demand. The fulfillment of world energy demand currently still rely on petroleum resources. This situation has forced the world to face some energy problems because of the contradiction between energy demands and supplies (Pradana et al., 2017; Sudibyo et al., 2017). The energy demands are increasing but the stocks of petroleum are estimated to decrease because they are non-renewable energy resources. Another problem caused by petroleum consumption is global warming due to greenhouse gas emission such as carbon dioxide. One solution to solve those problems in the future is using some new and renewable energy resources such as biomass and vegetable oil to fulfill the energy demands in the future. It will solve not only energy problems but also environmental problems, because to produce energy resource, they need carbon dioxide to grow so it will form the closed chain of carbon (Maity et al., 2014; Mata et al., 2010).

However, there are some potential problems in using biomass and vegetable oil as the energy resources such as the threat against food and land security. To avoid this problem, it is preferred to choose either non-edible vegetable oil or waste of biomass to serve as energy resources (Suganya et al., 2016). Some researchers had investigated some fuels from non-edible and waste renewable resources. For instance, bio-oil from palm empty fruit branch (EFB) (Sunarno et al., 2018), biodiesel from palm fatty acid distillate (Sawitri et al., 2016), gas from sugarcane baggase (Danyanto et al., 2016), bio-oil from wood, vegetables and fruits waste (Wicakso et al., 2017), bio-oil from microalgae waste (Jamilatun et al., 2017) and biodiesel from non-edible seeds such as jatropha and papaya seed (Kusumaningtyas et al., 2016). Nowadays, the production of the third generation of biodiesel from microalgae lipid is investigated by some researchers (Suganya et al., 2016).

Microalgae have been proven as potential feedstock to produce future energy resource accompanied with numerous attractive features such as higher productivity and oil content than other energy crops. Lower

consumption of freshwater and utilization of arable land to obtain microalgal biomass ignite researchers interest to exploit them for product development e.g. biofuel (Chatsungnoen and Chisti, 2016). Most importantly, they use carbon dioxide for photosynthesis hence reducing global warming effects. The other added value from using microalgae as energy resource beside its oil content is to produce bio oil from microalgal biomass waste (Jamilatun et al., 2017) .

Previous studies of biodiesel production from microalgae have been concluded that microalgal biodiesel is not profitable at an industrial scale (Collet et al., 2014; Suali and Sarbatly, 2012). One of the issues is caused by higher extraction energy requirement compared to the potential energy from biodiesel itself. The high-energy input accounting for more than 30% of the total cost for extracting lipids makes current commercial microalgal biofuel production economically unfeasible. It has been reported that the energy requirement to extract microalgal lipid via mechanical technique is around 529 kJ/g dry microalgae (Lee et al., 2013) and the lowest is 3 kJ/g dry microalgae , whereas the High Heating Value (HHV) of biodiesel is only 42 kJ/gram, respectively (Lee et al., 2015). If it is assumed that lipid yield is 10% g/g, the lowest energy requirement will equal to 30 kJ/g lipid. This energy comparison shows that the extraction energy requirement plays a crucial role to provide enough gap to get both positive and large net energy to be consumed for further processing.

Most conventional extraction techniques of microalgal lipids involve longer processing steps and time and sometimes consume high energy. This hinders the application of the lipids products to be fully commercialized (de Boer et al., 2012). Therefore, a need for economical, fast and robust approach to extract the lipids from microalgae is essential. One of the extraction methods possessing much lower energy for extracting considerably high amount of lipid is hydrodynamic cavitation (Yen et al., 2013). The technique provides fast extraction rate (Setyawan et al., 2018) and low energy cell disruption using cavitation that generated by dropping flow pressure which are caused by increasing flow velocity (Lee et al., 2013), so this technique is easy to scale up (Lee and Han, 2015). This technique follows a solid-liquid mass transfer principle due to the cell disruption process. It was found that the initial concentration of microalgae is a crucial factor to improve the efficiency of lipid recovery. Higher microalgal concentration affects the rate of solid-liquid mass transfer (Paulo et al., 2014) hence the distribution between 5% to 10% gram microalgae per gram of feed mixture is recommended (Lee and Han, 2015). Therefore, this study investigates the correlation between the initial concentration and the convective mass transfer parameters during the extraction of microalgal biomass via discrete flow system of hydrodynamic cavitation. The energy requirement for the extraction process using discrete flow system of hydrodynamic cavitation is measured and a mathematical modeling is developed to understand the overall extraction process.

2. Materials and Methods

2.1. Microalgae

The microalgae that used in this experiment was *Nannochloropsis sp.* It was purchased from Balai Budidaya Air Payau in Situbondo East Java Indonesia. This microalgae was delivered in green powder. The powder was used as received and stored in a desiccator until further analysis.

2.2. Solvents

The solvents that used in this experiment were n-hexane (PT. Brataco Chemica, Indonesia, MW 86.18, 99.5%), and methanol (CV. Multi Kimia, Indonesia, MW 32.04, 99.5%)

2.3. Equipment

The experiments were carried out using a batch discrete flow system of hydrodynamic cavitation. The unit consists of a compressor, sample chamber, venturi and product chamber as shown in Figure 1. The compressor is used to supply compressed air and drive the solvent-sample mixture to the chamber. The venturi is used to generate cavitation and the product chamber is used to store feedstock and collect product. At the end of the process, the centrifuge is used to separate the fluid from solid products and the distillator is used to separate the solvent from lipid by evaporating the solvent.

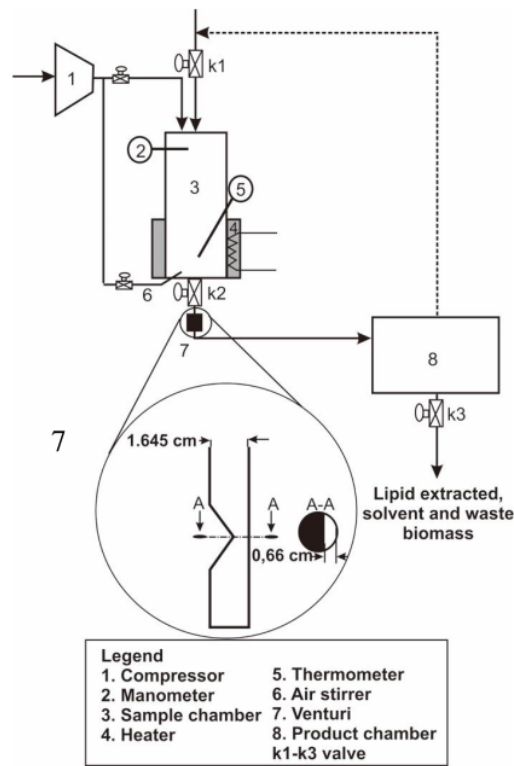


Figure 1. The Scheme of Hydrodynamic Cavitation Equipment

2.4. Experimental Procedures

The discrete flow system of HCLE experiments were carried out by varying microalgae concentration, cavitation number and temperature. Variation of microalgae concentration were done by varying the amount of *Nannochloropsis sp.* biomass of 5, 7.5, 10 and 12.5 grams. Variation of cavitation number were done by varying pressure booster 3.125, 4.167, 5 and 6.25 atm. And variation of temperature were done by varying temperature at 30, 34, 38, 42, 46 and 50 °C. A mixture of methanol and hexane were used as the extraction solvents in this study. The biomass and solvents were loaded into the sample chamber and then were flowed through the venturi with a pressure booster. The mixtures were re-flowed for several cycles (2, 3, 4, and 5.) to study the degree of cell disruption and lipid yields. Once the extraction was completed, the extracts and solid phase were separated using centrifugation process. To ensure the all of the lipids that extracted form microalgae was taken and weighed, the solids were washed with an equally amount of methanol and hexane. The lipids which were dissolved in the mixture solvent were recovered via vaporize the solvent to obtain lipids as the residue with a constant weight and it was weighed and recorded as w_1 . After the residue was weighed, get mass of lipids free of solids, the next step the residue was washed with 5 ml hexane three times and the remaining solids were dried until the weight remained constant and recorded as w_2 . The lipid free solids weight (w_p) obtained from the biomass was calculated using Equation 1.

$$w_p = w_1 - w_2 \quad (1)$$

Extraction yield is the weight of extracted lipids compared with the weight of dry microalgae as the sample as shown in Equation (2).

$$y = \frac{w_p}{w_{mi}} \quad (2)$$

where y is extraction yield and w_{mi} is weight of dry microalgae as the sample.

2.5. Extraction Energy Requirement and Mathematical model

2.5.1. The Extraction Energy Requirement Calculation

The discrete flow system of HCLE process requires energy to drive the microalgae and solvent to flow through the cavitator for generating the cavitation. This energy requirement is calculated by multiplying the air pressure booster with the cross sectional area of sample chamber and the sample depth. The energy requirement can be written as Equation (3).

$$E = 9.8P \frac{\pi}{4} D^2 L \quad (3)$$

where E is the extraction energy requirement (Joule), P is the pressure of the sample chamber (kg/cm^2), D is the diameter of the sample chamber (cm), L is the sample depth (cm) and 9.8 is the conversion factor from kgf to Newton.

2.5.2. Mathematical Model

The HCLE process is a lipids transfer process from solid (microalgae) to liquid (solvent) phase using hydrodynamic cavitation and assisting disrupting of microalgae wall as well. To generate the cavitation for this system, the value of inception cavitation number is 0.45 (Franc and Michel, 2005), and the value of Reynold number is more than 32,000, hence indicates the flow is fully turbulence. Those values were taken due to microalgae have a very small particle size, ranging from 1 to 10 μm (Beacham et al., 2014). There are some assumptions to govern the model:

- Diffusion mass transfer in microalgae body is neglected because of the small size of microalgae cells.
- Diffusion mass transfer in the fluid film is neglected because there is turbulent flow of the fluid.
- The convective mass transfer mechanism is the main process of the mass transfer.

There are two assumptions in governing the model based on the microalgae cells-type; disrupted and intact. The first assumption is the lipid mass transfer from the disrupted and intact microalgae are taken as the total lipid mass transfer from microalgae to the solvent. Thus, only one value of the volumetric mass transfer coefficient represents the lipid mass transfer from the disrupted and intact microalgae. This scheme is illustrated in Figure 2.a. The second assumption is the lipid mass transfer from the disrupted and intact microalgae are taken separately, so there are two different values of volumetric mass transfer coefficient from the disrupted and intact microalgae to the solvent. The illustration of this model is described in the Figure 2.b. Therefore, different models were developed based on those assumptions.

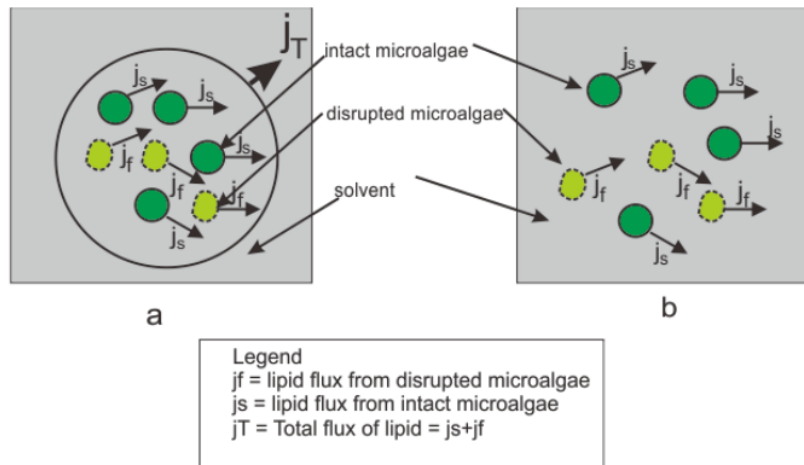


Figure 2. Illustration of Lipid Mass Transfer: a) Total Lipid Mass Transfer ; b) Lipid Mass Transfer From Disrupted and Intact Microalgae.

2.5.2.1. Model 1. Total Lipid Mass Transfer Approximation

This model is illustrated in Figure 2.a. with total lipid flux (j_T). At initial condition of the solid-fluid extraction, the concentration of lipid in the solvent (y) is zero, the changing value of y as a function of the time is equal to the number lipids released from the solid (j_T), so it can be written as Equation (4):

$$m_f \frac{\partial y}{\partial t} = j_T \quad (4)$$

where m_f represents the mass of fluid phase and t represents time. The amount of lipid release is equal to the mass transfer coefficient multiplying with the concentration gradient between microalgae surface and the bulk of the liquid, and it can be written as Equation (5):

$$j_T = k_T a_T \rho_f (y^* - y) \quad (5)$$

where $k_T a_T$ is total volumetric mass transfer coefficient, ρ_f is fluid density, and y^* is lipids concentration on microalgae surface. Value of y^* can be predicted by Equation (6):

$$y^* = K \cdot x \quad (6)$$

2.5.2.2. Model 2. Separately Disrupted and Intact Lipid Mass Transfer Approximation

In this model, lipid mass transfer from the disrupted and intact microalgae are taken separately. The changing lipid concentration in the solvent can be written as Equation (7):

$$m_f \frac{\partial y}{\partial t} = j_f + j_s \quad (7)$$

where j_f represents lipid mass flux from the disrupted microalgae and j_s represents lipid mass flux from the intact microalgae. The lipid mass flux from disrupted microalgae is a function of disrupted microalgae fraction and changing lipid concentration in the microalgae and can be written as Equation (8):

$$r m_s \frac{dx_1}{dt} = -j_f \quad (8)$$

where r represents fraction of disrupted microalgae, x_1 represents lipid concentration in the disrupted microalgae, m_s represents mass of dry microalgae, and the lipid mass flux from disrupted microalgae can be written as mass transfer equation, Equation (9):

$$j_f = k_f a_o \rho_f (y^*_1 - y) \quad (9)$$

where $k_f a_o$ represents volumetric mass transfer coefficient from disrupted microalgae, y^*_1 lipid concentration at the surface of disrupted microalgae. The lipid mass transfer from intact microalgae can be written as Equation (10):

$$(1 - r) m_s \frac{dx_2}{dt} = -j_s \quad (10)$$

where x_2 represents lipid concentration in the intact microalgae. And the lipid mass flux from intact microalgae can be written as mass transfer equation, Equation (11):

$$j_s = k_s a_s \rho_f (y^*_2 - y) \quad (11)$$

where $k_s a_s$ represents volumetric mass transfer coefficient from intact microalgae and y^*_2 represents lipid concentration at the surface of intact microalgae.

3. Results and Discussion

3.1. The Extraction Energy Requirement

The calculation results of the extraction energy requirement (E) as a function of repetition number is described in the Figure 3.a.

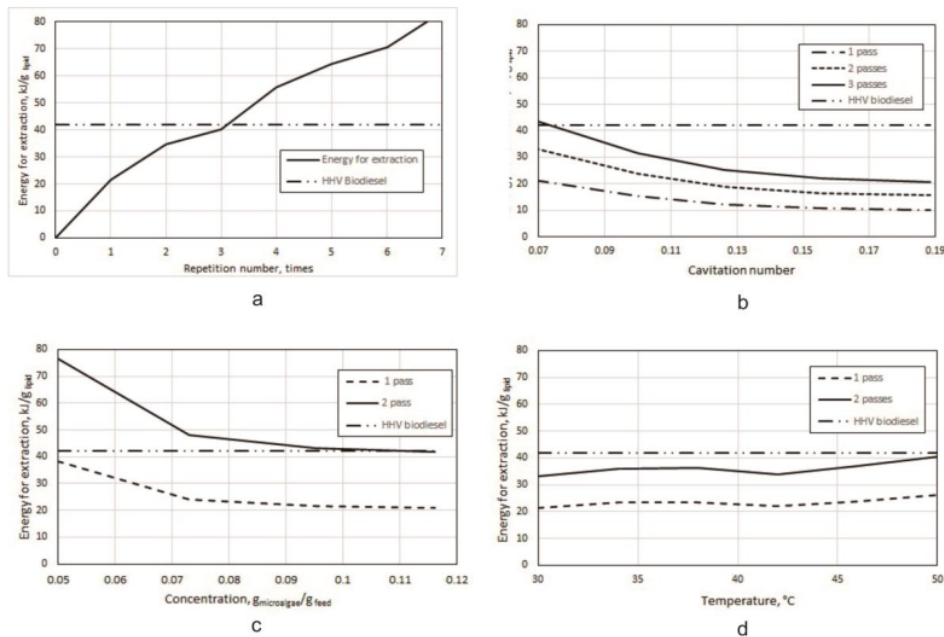


Figure 3. Extraction energy requirement (E) as a function of (a.) The number of repetition at the pressure of 6.8 kg/cm², temperature of 30°C and cavitation number of 0.068. (b.) Cavitation number at the pressure of 6.8 kg/cm² and temperature of 30 °C. (c.) microalgae concentration at the pressure booster of 6.8 kg/cm² and the temperature of 30°C (d.) Temperature at the pressure booster of 6.8 kg/cm² cavitation number of 0.068

Figure 3.a shows that the value of E was increased by the increasing number of repetitions. The increasing of E tends to linear with the increasing number of repetition because the number of energy for each extraction step was equal with the constant pressure booster. When comparing with the HHV of biodiesel, which is as high as 42 kJ/g biodiesel (Sivaramakrishnan and Ravikumar, 2011), the E value was 3 times lower than HHV of biodiesel for this condition. The influence of the pressure booster to E value can be represented as the influence of cavitation number (σ) to E value. The σ can be calculated using Equation (12) (Franc and Michel, 2005).

$$\sigma = \frac{p_2 - p_v}{\frac{1}{2}\rho v^2} \quad (12)$$

where P_{dw} is the pressure on the downstream, P_v is the vapor pressure of the fluid, and P_{up} is the pressure on the upstream. The calculation result of E value as a function of σ is described in Figure 3.b.

Figure 3.b. shows the E value tends to decrease by the increasing of σ . It indicates that at higher σ , the energy requirement is lower because the pressure is lower as well. In this case, the HCLE would find the limit or maximum value of σ while cavitation is still happening, called as an inception cavitation number (σ_i). The value of σ_i depends on the type of the channel, e.g. σ_i is 0.45 when elliptical form with axis ratio of $\frac{1}{4}$. Beside this limitation, at higher σ value, the value of E tends to be constant. It means that at higher σ , the amount of energy input is decreased and the constant value of E indicates lower yield extraction. Hence it is not an economically value if HCLE is done at the high σ value. The best value of σ is the point where the value of E starts to constant, around 0.13.

Microalgae and solvent will form a solid-liquid system with the type of fast settling slurries. In the system, the solid concentration will slip the velocity (Perry and Green, 2008). The influence of the solid concentration to the extraction energy is described in Figure 3.c. It shows that the extraction energy requirement tends to decrease by the increasing microalgae concentration. With the constant pressure booster, it means that the amount of energy input is equal for each concentration. Therefore, the decreasing value of E displays the increasing amount of extracted lipid. At the concentration above 0.073 g microalgae/g feed, the value of E tends to be constant and

indicating the amount of extraction lipid remains constant. The constant amount of the extracted lipid at a high microalgae concentration means that the reduction of the lipid yield compared to the microalgae feed. Therefore, the optimal concentration in this condition was 0.073 g microalgae/g feed.

It is known that the extraction process is affected by temperature (Islam et al., 2014). It was reported that the extraction of *Jatropha* oil using a mixture of methanol and hexane solvent showed a decreasing in extraction efficiency when reducing the solid concentration (He et al., 2017). The effect of temperature shows a significant contribution on distribution coefficient and the relationship is determined according to the Van't Hoff Equation (Dagostin et al., 2015).

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (13)$$

where K is the distribution coefficient, ΔH° is the enthalpy change in the standard condition (kJ/mole), ΔS° is the entropy change in the standard condition (J/mole/K) and R is the universal gas constant (J/mole/K) with the value of ΔH° and ΔS° in the common extraction process are both positive (Dagostin et al., 2015).

Based on our previous study, we found that the value of K was influenced by temperature, indicating the increasing of temperature will lead to increase the K values (Setyawan et al., 2018). The temperature effect on extraction energy requirement in the HCLE process is described in the Figure 3.d. It shows the value of E was slightly increased from 30 to 37°C, followed by decreasing at 42°C, and the value was increased back afterwards. It was found that the minimum extraction energy requirement was at 30°C with the value of E of 21.464 kJ/kg lipid for 1 pass extraction, thus the optimum temperature for this process was 30°C.

3.2. Lipid Release Mechanism

Microalgae lipids are entrapped and protected by cell walls. To make an efficient lipid extraction, it is required to disrupt their cell walls and then recover lipids from the matrix using solvent. The understanding of the mechanism of lipids release from microalgae in the HCLE is the important step to take the right assumptions in the mass transfer model evaluation. The difference between the lipids release rate from the disrupted and intact microalgae were done to understand the mechanism. This study was investigated by comparing the HCLE and conventional extraction techniques and the comparison is shown in Figure 2. It shows that the yield of the HCLE was higher than the conventional process, indicating the lipid release in the HCLE was not only from the intact microalgae but contributed by the disrupted microalgae as well (Yamamoto et al., 2015). In the HCLE, there are extraction of lipid from disruption and intact microalgae simultaneously and the conventional method is assumed only from the intact microalgae. In the HCLE, there are two conditions of microalgae: the disrupted microalgae and the intact microalgae, and the lipid was released from both disrupted and intact microalgae simultaneously (Lee and Han, 2015).

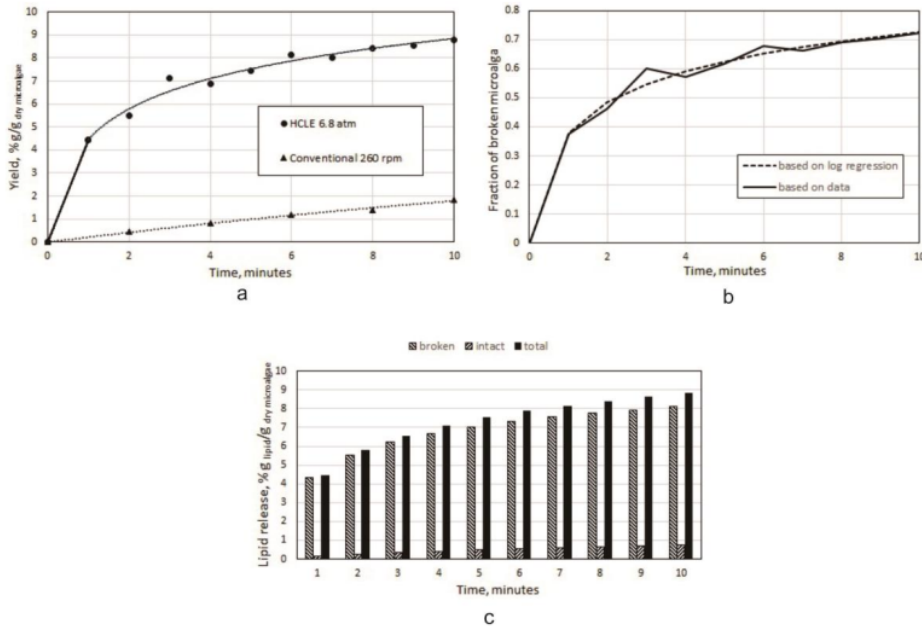


Figure 4. (a). Comparison of extraction curve between HCLE and conventional extraction. (b). Fraction of disrupted microalgae as function of time. (c). Comparison of lipids release from disrupted and intact microalgae

Figure 4.a. shows that the extraction rate using HCLE was higher compared to the conventional technique. This HCLE phenomenon was showing three different zones and it was agreed that the extraction curve was divided into two or three sections (Sovová, 2005) whereas the conventional extraction tends to change linearly in this time interval. The biggest difference between the two processes was at the initial process. It was shown that the HCLE rate was very fast at the beginning of the process compared to the conventional process. This indicates that the extraction process in this section is determined by lipid release from disruption of microalgae. While in the second section, from the second to the fifth-minute, the rate was decreased from the first section but it was still greater than the conventional technique. Whereas in the third section, after 5 minutes, the extraction rate was equal for both processes. This explained that the lipid mass transfer is determined by the mass transfer from the intact cell. Based on the phenomenon of HCLE process in the first section, lipid mass transfer is assumed to only occur from the disrupted microalgae to fluid. Lipid mass transfer from the intact microalgae was neglected because the rate was very small if compared with the disrupted microalgae. Lipid concentration in the disrupted microalgae after the extraction process was equal to the equilibrium value because lipid from the disrupted microalgae was effectively washed by methanol and hexane solvent (Gerde et al., 2012).

3.3. Evaluation of Microalgae Cell Disruption

Microalgae cell disruption can be assessed by measuring intracellular component such as the extracted lipids (Gerde et al., 2012). The portion of cell disruption in the HCLE can be predicted by lipid mass balance. Total lipids in the solvent are released from the disrupted and intact microalgae and it can be written in Equation (14).

$$y = rm_s(x_0 - x_e) + (1 - r)m_s y_c \quad (14)$$

where x_0 is the initial lipid concentration in the microalgae. The value is different for each repetition of extraction. x_e is lipid concentration in the disrupted microalgae and y_c is lipid concentration extracted by conventional extraction. The value of x_0 can be written as Equation (15).

$$x_{0,i+1} = x_{0,i} - y_{c,i} \quad (15)$$

where i is time dimension or number of repetition. y_c can be solved empirically using Ms. Excel based on the conventional extraction data in the Figure 4.a. and written as Equation (16).

$$y_c = -0.0031t^2 + 0.2154t \quad (16)$$

where t is extraction time. The fraction of disrupted microalgae (r) can be calculated based on data of y and y_c in the Figure 3 using Equation (14) by iteration methods. The result of r calculation for each time is shown in the Figure 4.b.

Figure 4.b. shows that the cell disruption trend was similar to the HCLE lipid yields as shown in Figure 4.a. It indicates that the amount of lipids released from the microalgae to the solvent in the HCLE is determined by microalgae cell disruption. Based on the fraction of cell disrupted, the amount of lipids released from the disrupted and intact microalgae can be determined as shown in Figure 4.c. It shows that the amount of lipids released from the disrupted microalgae are more than the intact microalgae, especially at the beginning of the process. Along the process, the fraction of lipids released from the intact microalgae tends to be increased due to the decreasing of microalgae disruption degree.

3.4. The HLCE Fitting Models

3.4.1. Total Lipid Mass Transfer Model (Model 1)

The HCLE total lipid mass transfer model (Model 1, Equation 4), was numerically solved using Runge-Kutta method. The value of the volumetric mass transfer coefficient ($k_T a_T$) was evaluated using Golden Section method for one variable minimization method, with the minimal target of sum of square of errors (SSE). The SSE can be formulated as shown in Equation (17).

$$SSE = \sum (y_{calc} - y_{data})^2 \quad (17)$$

where y_{calc} is the value of calculated result of y from Equation (4) and y_{data} is the value of y from the experiment. There are two estimations in the model solving. The first model was using one section of the extraction curve so that only one value of $k_T a_T$ for the whole time. While the second approximation was using three sections of extraction curves so there were three different values of $k_T a_T$ for each section. The calculation results of the model were described in Figure 5.a..

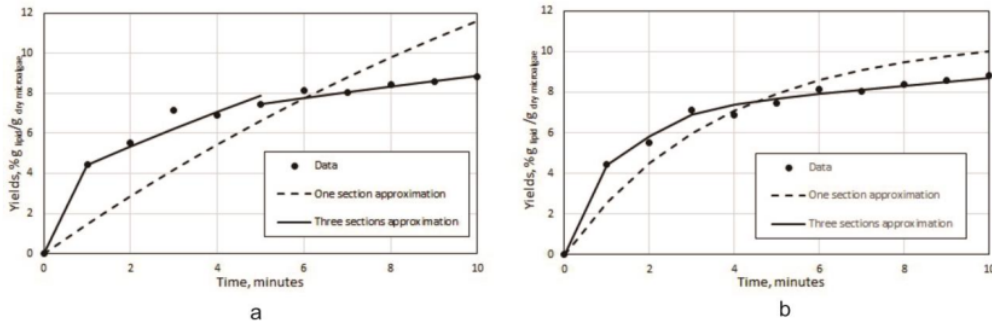


Figure 5.(a). Model plotting with assumption total flux mass (b). Model plotting with assumption from disrupted and intact microalgae flux mass.

3.4.1.1. Model Solution Using One Section

Figure 5.a. explains that the approximation using one section or one value of $k_T a_T$ gave the result of an almost linear simulation. Using the assumptions taken before, single value of $k_T a_T$ would give the linear relation between yield function time. This is because the amount of lipids released from the disrupted and intact microalgae for each step was calculated using the lipid concentration in the microalgae as the conventional extraction. Therefore, it resulted on the lipid concentration difference between in the microalgae and the solid as lipid mass transfer driving force was not significantly different for each step. The value of $k_T a_T$ was 0.596 1/minute with the coefficient of determination value was (-1.345). Overall, this approximation was very bad and could not describe well on the HLCE.

3.4.1.2. Model Solution Using Three Sections

Approximation of extraction curve using three sections could be done by dividing the extraction process based on the value of the curve slope (Sovová, 2005). The value of $k_T a_T$ using this approximation is tabulated in Table 1.

Table 1. Value of Volumetric Mass Transfer of HCLE

1 Section Approximation			3 Sections Approximation			
Time, minutes	$k_T a_T$, 1/minute	R ²	Time, minutes	Section	$k_T a_T$, 1/minute	R ²
1	0,596	-1,345	1	1	1.855	0.933
2			2	0.415		
3						
4						
5						
6			3	0.146		
7						
8						
9						
10						

Figure 5.a. show that the first section was the beginning of the extraction process which resulted the highest extraction rate, from minute-0 to 1. In this section, the curve slope value was 4.423 and at the highest slope. The second section was the middle extraction rate, this section from minute 1 to 5 with the slope value of 0.745. While the third section was at the constant extraction rate from minute 6 to the end of the process with the slope value of 0.239. Table 1 shows that the extraction using three sections approximation produced a better result than one section, with the value of R² was 0.933. Hence this approximation can describe the HCLE process very well. With this approximation, it was found that the three values of $k_T a_T$, with the differences on a_T values were caused by cell disruption.

3.4.1. Model Separated Lipid Mass Transfer from Disrupted and Intact Microalgae (Model 2)

In this model, the volumetric mass transfer from the disrupted microalgae ($k_f a_o$) and intact microalgae ($k_s a_s$) were separately evaluated. The evaluation uses two approximations; single section three sections. The results of the evaluation is presented in Figure 5.b.

3.4.2.1. Model Solution Using One Section

Figure 5.b. shows that the approximation using one section or one value of $k_f a_o$ and $k_s a_s$ resulted better simulation than Model 1. The value of $k_f a_o$ and $k_s a_s$ were 1.103 and 0.036 1/minutes with the coefficient of determination value was 0.367. This approximation gave a large deviation, so this approximation could not describe the HLCE process.

3.4.2.2. Model Solution Using Three Sections

In this approximation, the extraction curve was divided into three sections based on the difference between the value of the curve slopes. The first section, from minute 0 to 1, was the beginning extraction process which had the highest extraction rate. In this section, the curve slope value was 4.423 and this was the highest slope. The second section was the middle extraction rate, from minute 1 to 4, with the slope value of 0.824. While the third section, from minute 5 to the end of the process, had a constant extraction rate with the slope value of 0.318. The value of $k_f a_o$ and $k_s a_s$ using this approximation can be read in Table 2.

Table 2. Value of $k_f a_o$ and $k_s a_s$ and R^2 from Model 2

1 Section				3 Sections			
Time, minutes	$k_f a_o$	$k_s a_s$	R^2	Time, minutes	$k_f a_o$	$k_s a_s$	R^2
1	1.103	0.036	0.367	1	2.137	0.051	0.971
2				0.997	0.039		
3							
4				0.277	0.026		
5							
6							
7							
8							
9							
10				10			

Table 2 shows that the approximation using 3 sections of extraction gave the best result for the two models, with Model 2 gave better results than Model 1. Therefore, Model 2 can describe the HCLE process better than the Model 1.

3.5. Comparison between Model 1 and Model 2

Based on the separated calculation between the disrupted and intact microalgae approximation, Model 2 gave better result than the total approximation, with the R^2 value of 0.971 for Model 2 and 0.933 for Model 1. This is due to the disruption factor was involved in the calculation in the model 2, hence this model described the real process of HCLE. However, Model 1 could also use to describe the HCLE process because the percentage of lipid released from the intact microalgae is too small if compared with the amount of lipids released from the disrupted microalgae. The smallest comparison was in the beginning of the process. At minute-1 (1 pass) extraction, the percentage of lipid released from the intact microalgae is 2.95% whereas the disrupted microalgae was 97.05%. Both values tend to change as a function of time. The value of the intact microalgae tends to increase while the value of the disrupted microalgae tends to decrease. At time 10 minutes (10 passes), the percentage of lipid released from the intact microalgae was 8.36% and 91.64% for the disrupted cells. The HCLE process was determined in the early 5 minutes, which at this time 85% of total lipids had been extracted. With the reason of the small percentage of lipid released from intact microalgae, the approximation using total lipid released can describe the process with more simple calculation.

4. Conclusion

The extraction energy requirement for HCLE is affected by the number of repetitions, cavitation number, microalgae concentration, and temperature process. The value of extraction energy requirement (E) can be adjusted to set those variables with the intention of the value of E lower than the HHV of biodiesel. It was found that the lowest value of E was 10 kJ/ gram lipid, therefore this process is promising to be developed and scaled up for commercial applications.

The HCLE was modeled using different mass transfer model; the total mass transfer from intact and disrupted microalgae (Model 1), separated mass transfer (Model 2) and through sections of extraction curve. The calculation results show that the Model 2 gave better result than Model 1, and the value of the volumetric mass transfer coefficient decreased from section 1 to 3. In the case of HCLE using Model 1, the value of $k_T a_T$ for section 1, 2, and 3 were 1.855, 0.415 and 0.146 1/min respectively with the coefficient of determination (R^2) was 0.933. On the other hand, the result of Model 2 shows that $k_f a_o$ for section 1, 2, and 3 were 2.137, 0.997 and 0.277 1/min respectively, and $k_s a_s$ are 0.051, 0.039 and 0.026 1/min respectively with R^2 was 0.971.

Acknowledgments

2 We would like to thank Process System Engineering Research Group, Chemical Engineering Department, Gadjah Mada University, Yogyakarta, Indonesia which has provided research facilities and Ahmad Dahlan University, Yogyakarta, Indonesia which has provided research fund.

References

- Beacham, T.A., Bradley, C., White, D.A., Bond, P., Ali, S.T., 2014. Lipid productivity and cell wall ultrastructure of six strains of *Nannochloropsis*: Implications for biofuel production and downstream processing. *Algal Res.* 6, 64–69. <https://doi.org/10.1016/j.algal.2014.09.003>
- Chatsungnoen, T., Chisti, Y., 2016. Oil production by six microalgae: impact of flocculants and drying on oil recovery from the biomass. *J. Appl. Phycol.* 28, 2697–2705. <https://doi.org/10.1007/s10811-016-0823-6>
- Collet, P., Lardon, L., Hélias, A., Bricout, S., Lombaert-Valot, I., Perrier, B., Lépine, O., Steyer, J.-P., Bernard, O., 2014. Biodiesel from microalgae—Life cycle assessment and recommendations for potential improvements. *Renew. Energy* 71, 525–533. <https://doi.org/http://dx.doi.org/10.1016/j.renene.2014.06.009>
- Dagostin, J.L.A., Carpiné, D., Corazza, M.L., 2015. Extraction of soybean oil using ethanol and mixtures with alkyl esters (biodiesel) as co-solvent: Kinetics and thermodynamics. *Ind. Crops Prod.* 74, 69–75. <https://doi.org/10.1016/j.indcrop.2015.04.054>
- Daniyanto, Sutijan, Deendarlianto, Budiman, A., 2016. Reaction kinetic of pyrolysis in mechanism of pyrolysis gasification process of dry torrefied sugarcane bagasse. *ARPN J. Eng. Appl. Sci.* 11, 9974–9980.
- de Boer, K., Moheimani, N.R., Borowitzka, M.A., Bahri, P.A., 2012. Extraction and conversion pathways for microalgae to biodiesel: A review focused on energy consumption. *J. Appl. Phycol.* 24, 1681–1698. <https://doi.org/10.1007/s10811-012-9835-z>
- Franc, J.-P., Michel, J.-M., 2005. *Fundamentals of Cavitation*. Kluwer Academic Publishers, New York.
- Gerde, J.A., Montalbo-Lomboy, M., Yao, L., Grewell, D., Wang, T., 2012. Evaluation of microalgae cell disruption by ultrasonic treatment. *Bioresour. Technol.* 125, 175–181. <https://doi.org/10.1016/j.biortech.2012.08.110>
- He, Y., Peng, T., Guo, Y., Li, S., Guo, Y., Tang, L., Chen, F., 2017. Nontoxic oil preparation from *Jatropha curcas* L. seeds by an optimized methanol/n-hexane sequential extraction method. *Ind. Crops Prod.* 97, 308–315. <https://doi.org/10.1016/j.indcrop.2016.12.034>
- Islam, M.A., Brown, R.J., O'Hara, I., Kent, M., Heimann, K., 2014. Effect of temperature and moisture on high pressure lipid/oil extraction from microalgae. *Energy Convers. Manag.* 88, 307–316. <https://doi.org/10.1016/j.enconman.2014.08.038>
- Jamilatun, S., Budiman, A., Budhijanto, Rochmadi, 2017. Non-catalytic slow pyrolysis of *Spirulina Platensis* residue for production of liquid biofuel. *Int. J. Renew. ENERGY Res. S. Jamilatun* al 7.
- Kusumaningtyas, R.D., Aji, I.N., Hadiyanto, H., Budiman, A., 2016. Application of Tin (II) Chloride Catalyst for High FFA *Jatropha* Oil Esterification in Continuous Reactive Distillation Column. *Bull. Chem. React. Eng. Catal.* 11, 66.
- Lee, A.K., Lewis, D.M., Ashman, P.J., 2015. Microalgal cell disruption by hydrodynamic cavitation for the production of biofuels. *J. Appl. Phycol.* 27, 1881–1889. <https://doi.org/10.1007/s10811-014-0483-3>
- Lee, A.K., Lewis, D.M., Ashman, P.J., 2013. Force and energy requirement for microalgal cell disruption: An atomic force microscope evaluation. *Bioresour. Technol.* 128, 199–206. <https://doi.org/10.1016/j.biortech.2012.10.032>
- Lee, I., Han, J.I., 2015. Simultaneous treatment (cell disruption and lipid extraction) of wet microalgae using hydrodynamic cavitation for enhancing the lipid yield. *Bioresour. Technol.* 186, 246–251. <https://doi.org/10.1016/j.biortech.2015.03.045>
- Maity, J.P., Bundschuh, J., Chen, C.Y., Bhattacharya, P., 2014. Microalgae for third generation biofuel production, mitigation of greenhouse gas emissions and wastewater treatment: Present and future perspectives - A mini review. *Energy* 78, 104–113. <https://doi.org/10.1016/j.energy.2014.04.003>

- Mata, T.M., Martins, A.A., Caetano, N.S., 2010. Microalgae for biodiesel production and other applications: A review. *Renew. Sustain. Energy Rev.* 14, 217–232. <https://doi.org/10.1016/j.rser.2009.07.020>
- Paulo, L., Silva, S., Martínez, J., 2014. Mathematical modeling of mass transfer in supercritical fluid extraction of oleoresin from red pepper. *J. Food Eng.* 133, 30–39. <https://doi.org/10.1016/j.jfoodeng.2014.02.013>
- Perry, R.H., Green, D.W., 2008. 10. Transport and storage of fluids, in: *Perry's Chemical Engineers' Handbook*. p. 2400. <https://doi.org/10.1036/0071511334>
- Pradana, Y.S., Sudiby, H., Suyono, E.A., Indarto, Budiman, A., 2017. Oil Algae Extraction of Selected Microalgae Species Grown in Monoculture and Mixed Cultures for Biodiesel Production. *Energy Procedia* 105, 277–282.
- Sawitri, D.R., Sutijan, Budiman, A., 2016. Kinetics study of free fatty acids esterification for biodiesel production from palm fatty acid distillate catalysed by sulphated zirconia. *ARPN J. Eng. Appl. Sci.* 11, 9951–9957.
- Setyawan, M., Mulyono, P., Sutijan, Budiman, A., 2018. Comparison of *Nannochloropsis* sp. cells disruption between hydrodynamic cavitation and conventional extraction, in: *MATEC Web of Conferences*. pp. 1–5. <https://doi.org/https://doi.org/10.1051/mateconf/201815401023>
- Sivaramakrishnan, K., Ravikumar, P., 2011. Determination of Higher Heating Value of Biodiesels. *Int. J. Eng. Sci. Technol.* 3, 7981–7987.
- Sovová, H., 2005. Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation. *J. Supercrit. Fluids* 33, 35–52. <https://doi.org/10.1016/j.supflu.2004.03.005>
- Suali, E., Sarbatly, R., 2012. Conversion of microalgae to biofuel. *Renew. Sustain. Energy Rev.* 16, 4316–4342. <https://doi.org/10.1016/j.rser.2012.03.047>
- Sudiby, H., Pradana, Y.S., Samudra, T.T., Budiman, A., Indarto, Suyono, E.A., 2017. Study of cultivation under different colors of light and growth kinetic study of *Chlorella zofingiensis* Dönn for biofuel production. *Energy Procedia* 105, 270–276.
- Suganya, T., Varman, M., Masjuki, H.H., Renganathan, S., 2016. Macroalgae and microalgae as a potential source for commercial applications along with biofuels production: A biorefinery approach. *Renew. Sustain. Energy Rev.* 55, 909–941. <https://doi.org/10.1016/j.rser.2015.11.026>
- Sunarno, Rochmadi, Mulyono, P., Aziz, M., Budiman, A., 2018. Kinetic study of catalytic cracking of bio-oil over silica-alumina catalyst. *BioResources* 13, 1917–1929. <https://doi.org/10.15376/biores.13.1.1917-1929>
- Wicakso, D.R., Sutijan, Rochmadi, Budiman, A., 2017. Study of Catalytic Upgrading of Biomass Tars using Indonesian Iron Ore, in: *AIP Conference Proceedings*. pp. 1–8. <https://doi.org/10.1063/1.4978167>
- Yamamoto, K., King, P.M., Wu, X., Mason, T.J., Joyce, E.M., 2015. Effect of ultrasonic frequency and power on the disruption of algal cells. *Ultrason. Sonochem.* 24, 165–171. <https://doi.org/10.1016/j.ultsonch.2014.11.002>
- Yen, H., Hu, I., Chen, C., Ho, S., Lee, D., Chang, J., 2013. Biore source Technology Microalgae-based biorefinery – From biofuels to natural products. *Bioresour. Technol.* 135, 166–174. <https://doi.org/10.1016/j.biortech.2012.10.099>

Paper

ORIGINALITY REPORT

15%

SIMILARITY INDEX

15%

INTERNET SOURCES

5%

PUBLICATIONS

0%

STUDENT PAPERS

PRIMARY SOURCES

1

ejournal.undip.ac.id

Internet Source

9%

2

www.matec-conferences.org

Internet Source

2%

3

ijrer.com

Internet Source

1%

4

pdffox.com

Internet Source

1%

5

idoc.pub

Internet Source

1%

Exclude quotes On

Exclude matches < 1%

Exclude bibliography On