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# Mathematical Modeling of Hydrodynamic Cavitation as Low Energy Extraction Technique to Remove Lipid from Nannochloropsis sp.

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#### ABSTRACT

Lipid extraction through hydrodynamic cavitation (HCLE) is one of the promising processes with low energy requirements. Therefore, this study focuses on reducing energy requirements using a discrete flow system as well as evaluating two models to be used in calculating volumetric mass transfer coefficient. It was discovered that the variations in the number of repetitions, cavitation number, microalgae concentration, and temperature affected the energy requirement value and the lowest energy requirement was recorded to be 10 kJ/gram lipid. Moreover, the first model was designed using total lipid mass transfer approximation (Model 1) while the second was through separated lipid mass transfer approximation (Model 2). It was found that the extraction curve consists of three sections and the values of total volumetric mass transfer coefficient  $(k_T a_T)$  for sections 1, 2, and 3 based on Model 1 were 1.166 x 10<sup>-2</sup>, 3.113 x 10<sup>-3</sup>, and 1.285 x 10<sup>-3</sup> min<sup>-1</sup> with a coefficient of determination (R<sup>2</sup>) of 0.9797, respectively. Meanwhile, the values of volumetric mass transfer coefficient from disrupted microalgae  $(k_f a_o)$ for sections 1, 2, and 3 based on Model 2 were 1.131 x 10<sup>-2</sup>, 2.925 x 10<sup>-</sup> <sup>3</sup>, and 1.260 x 10<sup>-3</sup> min<sup>-1</sup> respectively, and from the intact microalgae  $(k_s a_s)$  was 0.051, 0.030 and 0.011 1/min with R<sup>2</sup> of 0.9766. This means the two models showed similar results and the lipid released from the disrupted microalgae was observed to be dominant compared to the intact microalgae. Therefore, the discrete flow system of HCLE is a promising technique to be developed and scaled up to extract lipids from microalgae.

## I INTRODUCTION

The increasing human population and modern human lifestyle have increased energy demand and

this is currently mostly fulfilled through the reliance on petroleum resources. This has created some global energy problems due to the contradiction between the demand and supply [1], [2] as indicated

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by the continuous increase in demand with a reduction in the stocks of petroleum resources considered to be non-renewable. Another important problem is the occurrence of global warming due to greenhouse gas emissions such as carbon dioxide. This led to the proposition of some solutions such as the application of new and renewable energy resources such as biomass and vegetable oil to fulfill energy demands in the future. This is expected to solve energy and environmental problems because of the need to grow carbon dioxide to produce these energy resources, thereby, forming a closed chain of carbon [3], [4].

Some potential problems have, however, been observed in relation to the use of biomass and vegetable oil as energy resources and these include threats against food and land security. This is the reason it is preferable to select either a non-edible vegetable oil or biomass waste to serve as energy resources [5]. Previous studies have investigated some fuels produced from non-edible and waste renewable resources such as bio-oil from palm empty fruit branch (EFB) [6], biodiesel from palm fatty acid distillate [7], biodiesel from cooking oil waste [8], gas from sugarcane bagasse [9], bio-oil from woods, vegetables, and fruits waste [10], biooil from microalgae waste [11] and biodiesel from non-edible seeds such as jatropha and papaya seed [12]. In recent times, the production of the third generation of biodiesel from microalgae lipid has also been investigated [5].

Microalgae have been proved to be a potential feedstock to produce future energy due to their numerous attractive features such as higher productivity and oil content than other energy crops. Moreover, the lower consumption of freshwater and utilization of arable land to obtain microalgal biomass ignite research interest to exploit them for product development such as biofuel [13]. Most importantly, these microalgae use carbon dioxide for photosynthesis, thereby, leading to the reduction of global warming effects. They also have other added value in the form of biomass waste that can be used to produce bio-oil in addition to their oil content which can be used to produce energy [11].

Previous studies on biodiesel production from microalgae concluded that microalgal biodiesel is not profitable at an industrial scale [14], [15] due to the higher extraction energy required compared to the potential energy from biodiesel. This highenergy input accounts for more than 30% of the total cost of extracting lipids and this makes the current commercial microalgal biofuel production economically unfeasible. It has also been reported that the energy required to extract microalgal lipid mechanically is approximately 529 kJ.g<sup>-1</sup> dry microalgae [16] and the lowest is 3 kJ.g<sup>-1</sup> dry microalgae while the High Heating Value (HHV) of the biodiesel is only 42 kJ.g<sup>-1</sup> [17]. This means the lowest energy needed to achieve a 10% g/g yield is 30 kJ.g<sup>-1</sup>. This comparison shows that extraction energy requirement plays is very important in providing enough gap to obtain both positive and large net energy to be consumed for further processing.

The most conventional extraction techniques of microalgal lipids involve longer processing steps, time, and sometimes high energy consumption and this hinders the full commercialization of lipids products [18]. Therefore, there is a need for an economical, fast, and robust approach to extracting lipids from microalgae. It is important to note that microalgae cell disruption is a major factor in maximizing extraction yields [19] and one of the extraction methods with much lower energy and the ability to produce a considerably high amount of lipid is hydrodynamic cavitation [20]. This technique provides a fast extraction rate [21] and low energy cell disruption using cavitation generated by dropping flow pressure through an increment in flow velocity [16] [22], thereby, making it easy to scale up this method [23]. It is also important to reiterate that hydrodynamic cavitation follows a solid-liquid mass transfer principle due to the cell disruption process and the initial concentration of microalgae is observed to be a crucial factor in improving the efficiency of the lipid recovery process. Moreover, higher microalgal concentration also affects the rate of solid-liquid mass transfer [24] and this led to the recommendation of distribution between 5% to 10% gram microalgae per gram of feed mixture [23]. This present study focuses on investigating the

correlation between the initial concentration and convective mass transfer parameters during the extraction of microalgal biomass via a discrete flow system of hydrodynamic cavitation. The energy required was measured and mathematical modeling was subsequently developed to understand the overall extraction process.

## II MATERIALS AND METHODS 2.1 Microalgae

The microalgae used in this experiment is Nannochloropsis sp which was purchased from Balai Budidaya Air Payau in Situbondo East Java Indonesia and delivered in green powder which was stored in a desiccator and used as received for further analysis.

#### 2.2 Solvents

The solvents used in this experiment include n-hexane (PT. Brataco Chemica, Indonesia, MW 86.18, 99.5%), and methanol (CV. Multi Kimia, Indonesia, MW 32.04, 99.5%) selected based on their non-ideal properties in terms of the boiling point when mixed. The mixture of 95 ml hexane and 41 ml methanol has a boiling point lower than their respective separate boiling points as indicated by 52, 64.96, and 68.73 °C for the mixture, methanol, and hexane respectively.

#### 2.3 Equipment

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



Figure 1. The Scheme of Hydrodynamic Cavitation Equipment.
2.4 Experimental Procedures

The HCLE discrete flow system experiments were conducted by varying the microalgae concentration, cavitation number, and temperature. The Nannochloropsis sp. biomass was varied at 5, 7.5, 10, and 12.5 grams, the cavitation number at different pressure boosters of 3.125, 4.167, 5, and 6.25 atm, the temperature at 30, 34, 38, 42, 46, and 50 °C. It is important to restate that a mixture of methanol and hexane was used as the extraction solvent. The biomass and solvents were loaded into the sample chamber, flowed through the venturi with a pressure booster, and the mixtures were re-flowed at 2, 3, 4, and 5 cycles to study the degree of cell disruption and lipid yields. The completion of the extraction process was followed by the separation of the extracts and solid phase using the centrifugation process. Moreover, the solids were washed with an equal amount of methanol and hexane to ensure all the lipids extracted from the microalgae were retrieved and weighed and those dissolved in the mixture solvent were recovered as a residue by vaporizing the solvent. This residue was weighed and recorded as w<sub>1</sub>, washed with 5 ml hexane three times to obtain the mass of lipids that are free of solids, while the remaining solids were dried until the weight remained constant and recorded as w2. The lipid-free solids

weight  $(w_p)$  obtained from the biomass was calculated using the following Equation 1.

$$\mathbf{w}_{\mathbf{p}} = \mathbf{w}_1 \cdot \mathbf{w}_2 \tag{1}$$

The extraction yield is the weight of extracted lipids compared to the weight of dry microalgae as indicated in Equation (2).

$$y = \frac{w_p}{w_{mi}} \tag{2}$$

Where, y is extraction yield and  $w_{mi}$  is the weight of dry microalgae used as the sample.

#### 2.5 Experimental Procedures

# 2.5.1. The Extraction Energy Requirement Calculation

The discrete flow system of the HCLE process requires energy to drive the microalgae and solvent to flow through the cavitator in order to generate the cavitation. This energy was calculated by multiplying the air pressure booster with the cross-sectional area of the sample chamber and sample depth using the relationship in Equation (3).

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

Where, E is the extraction energy required (Joule), P is the pressure of the sample chamber (kg/cm<sup>2</sup>), D is the diameter of the sample chamber (cm), L is the distance of the sample surface to the cavitator (cm) and, 9.8 is the conversion factor from kgf to Newton.

## 2.5.2. Mathematical Model

The HCLE is the process of transferring lipid from the solid (microalgae) to the liquid (solvent) phase using hydrodynamic cavitation and to aid the disruption of the microalgae wall. The inception cavitation number used to generate the cavitation for this system is 0.45 [25] while the Reynold number was more than 32,000, thereby, indicating fully turbulent flow. These values were used because the microalgae have a very small particle size, ranging from 1 to 10  $\mu$ m [26]. The other assumptions made to govern the model include the following:

a. Diffusion mass transfer in the microalgae body is neglected because of the small size of microalgae cells.

- b. Diffusion mass transfer in the fluid film is neglected because there is a turbulent flow in the fluid.
- c. The convective mass transfer mechanism is the main process of mass transfer.

It is important to note that two others assumptions were made based on the disrupted and intact types of microalgae cells. The first assumption is that the lipid mass transfer from the disrupted and intact microalgae is taken as the total lipid mass transfer from the microalgae to the solvent and this means only one value of the volumetric mass transfer coefficient represents the lipid mass transfer as illustrated in Figure 2a. The second assumption is that the lipid mass transfer from the disrupted and intact microalgae was obtained separately which led to two different values of volumetric mass transfer coefficient as indicated in Figure 2b. This, therefore, led to the development of two different models based on these assumptions.



Figure 2. Illustration of Lipid Mass Transfer: a) Total Lipid Mass Transfer and 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 2a with total lipid flux  $(j_T)$ . It was discovered at the initial condition of the solid-fluid extraction that the concentration of lipid in the solvent (y) is zero while the changing value of y as a function of the time is equal to the amount of lipids released from the solid  $(j_T)$ , and this is presented as Equation (4):

$$m_f \frac{\partial y}{\partial t} = j_T \tag{4}$$

Where,  $m_f$  represents the mass of the fluid phase and t represents time. It is also important to note that the amount of lipid released is equal to the mass transfer coefficient multiplied by the concentration gradient

between the microalgae surface and the bulk of liquid which is represented in the following Equation (5):

$$j_T = k_T a_T m_f (y^* - y) \tag{5}$$

Where,  $k_T a_T$  is the total volumetric mass transfer coefficient and  $y^*$  is lipids concentration on microalgae surface. The value of  $y^*$  can be predicted using Equation (6):

$$y^* = K x \tag{6}$$

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

The lipid mass transfer from the disrupted and intact microalgae was obtained separately in this model and the changing lipid concentration in the solvent is presented as Equation (7):

$$m_f \frac{\partial y}{\partial t} = j_f + j_s \tag{7}$$

Where,  $j_f$  is the lipid mass flux from the disrupted microalgae and  $j_s$  is the lipid mass flux from the intact microalgae. Moreover, the lipid mass flux from disrupted microalgae is a function of disrupted microalgae fraction and changing lipid concentration in the microalgae which are represented by the following Equation (8):

$$rm_s \frac{dx_1}{dt} = -j_f \tag{8}$$

Where, r is the fraction of disrupted microalgae,  $x_1$  is the lipid concentration in the disrupted microalgae, and  $m_s$  is the mass of dry microalgae. The lipid mass flux from disrupted microalgae can also be written as the mass transfer equation in Equation (9):

$$j_f = k_f a_o m_f (y_1^* - y)$$
 (9)

Where,  $k_f a_o$  represents the volumetric mass transfer coefficient from disrupted microalgae and  $y_1^*$  is the lipid concentration at the surface of disrupted microalgae. Meanwhile, the lipid mass transfer from intact microalgae is presented as indicated in Equation (10):

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

Where,  $x_2$  represents lipid concentration in the intact microalgae. The lipid mass flux from intact microalgae can also be written as a mass transfer equation as indicated in the following Equation (11):

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$$j_s = k_s a_s m_f (y_2^* - y)$$
 (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.

## **III RESULTS AND DISCUSSION**

## 3.1. The Extraction Energy Requirement

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



**Figure 3a.** Extraction energy requirement (E) as a function of the number of repetitions at the pressure of 6.8 kg/cm<sup>2</sup>, a temperature of 30°C, and cavitation number of 0.068



**Figure 3b.** Extraction energy requirement (E) as a function of the cavitation number at the pressure of 6.8 kg/cm<sup>2</sup> and temperature of 30 °C



**Figure 3c.** Extraction energy requirement (E) as a function of the microalgae concentration at the pressure booster of 6.8 kg/cm<sup>2</sup> and the temperature of 30°C



**Figure 3d.** Extraction energy requirement (E) as a function of the temperature at the pressure booster of 6.8 kg/cm<sup>2</sup> and cavitation number of 0.068

Figure 3a shows that the value of E increased linearly as the number of repetitions increased because the energy used for each extraction step was the same as the constant pressure booster. It was also discovered that this E value was one-third of the HHV of biodiesel which is as high as 42 kJ/g [27] at the condition. Moreover, the influence of the pressure booster on the E value was represented by the effect of cavitation number ( $\sigma$ ) on the value and this was calculated using Equation (12) [25].

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

Where,  $P_2$  is the pressure booster,  $P_v$  is the vapor pressure of the fluid, and v is the fluid linear velocity. <u>The E</u> value was subsequently calculated as a function of  $\sigma$  as described in Figure 3b.

Figure 3b shows that the E value tends to decrease as the  $\sigma$  increase and this means the energy requirement is lower at higher  $\sigma$  because the pressure is low. In this case, the HCLE found the limit or maximum value of  $\sigma$ 

during the process of cavitation and this is called an inception cavitation number ( $\sigma_i$ ) with the value observed to depend on the type of the channel such that the  $\sigma_i$  was recorded to be 0.45 when elliptical form with an axis ratio of <sup>1</sup>/<sub>4</sub> was used. Beside this limitation, a higher  $\sigma$  value tends to produce a constant E value and this means the amount of energy input is decreased at higher  $\sigma$  while the constant E value indicates lower yield extraction. This shows the conduct of HCLE at a high  $\sigma$  value is not economical and the best value was obtained at approximately 0.13 when the E value started to become constant.

The microalgae and solvent formed a solid-liquid system with fast settling slurries. It is important to note that the solid concentration slips the velocity in the system [28] and Figure 3c shows that the extraction energy requirement tends to decrease as the microalgae concentration increases. This means the amount of energy input is equal for each concentration with the constant pressure booster. The decreasing E value indicates an increase in the amount of lipid extracted. Meanwhile, the E value tends to be constant at the concentration above 0.073 g microalgae/g feed and this also means the amount of lipid extracted remains constant and this shows a reduction in the yield at high concentration compared to the microalgae feed. Therefore, the optimal concentration in this condition was found to be 0.073 g microalgae/g feed.

The extraction process is affected by temperature [29] as indicated by the decrease in the extraction efficiency when the solid concentration was reduced during the process of extracting Jatropha oil using a mixture of methanol and hexane solvent [30]. Moreover, temperature shows a significant contribution to the distribution coefficient, and this relationship was determined according to the Van't Hoff Equation as follows [31].

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

Where, K is the distribution coefficient,  $\Delta H^o$  is the enthalpy change in the standard condition (kJ/mole),  $\Delta S^o$  is the entropy change in the standard condition (J/mole/K), and R is the universal gas constant (J/mole/K), and the value of  $\Delta H^o$  and  $\Delta S^o$  in the common extraction process are both positive [31].

A previous study conducted by the authors showed that the value of K was influenced by temperature such that an increase in the temperature lead to an increase in the K values [21]. Meanwhile, the effect of temperature on extraction energy requirement in the HCLE process is described in Figure 3d which shows that the E value slightly increased from 30 to 37°C followed by a decrease to 42°C and a later increase. Moreover, the minimum energy requirement was found to be 21.464 kJ/kg lipid for 1 pass extraction at 30°C and this means this is the optimum temperature for the process.

#### 3.2. Lipid Release Mechanism

Microalgae lipids are entrapped and protected by cell walls which need to be disrupted to ensure an efficient lipid extraction from the matrix using a solvent. The understanding of the mechanism of lipids released from microalgae in the HCLE is an important step to making the right assumptions in the mass transfer model evaluation. The difference between the lipids release rate from the disrupted and intact microalgae needs to determined to understand this mechanism. be Therefore, this study compared the HCLE and conventional extraction techniques, and the results presented in Figure 2 showed that the yield of the HCLE was higher than the conventional process, thereby, indicating the lipid release in the HCLE was not only from the intact but also from the disrupted microalgae [32]. This is possible because the method is assumed to involve a simultaneous extraction of lipid from disruption and intact microalgae while the conventional method is only from the intact microalgae [23].



Figure 4a. Comparison of extraction curve between HCLE and conventional extraction



Figure 4b. Fraction of disrupted microalgae as a function of time



Figure 4c. Comparison of lipids released from disrupted and intact microalgae

Figure 4a shows that the extraction rate using HCLE was higher compared to the conventional technique. It was also discovered that the HCLE showed three different zones with the extraction curve divided into two or three sections [33] while the conventional extraction tends to change linearly during the time interval. The biggest difference between the two processes was observed at the initial process with the HCLE rate found to be faster and this indicates the extraction at the section was determined by the lipid released by disrupting microalgae. In the second section which was from the second to the fifth minute, the rate decreased but was also higher than the conventional technique while after 5 minutes, which is the third section, the rate was equal for both processes. This simply shows that the lipid mass transfer is determined by the intact cell while the transfer in the first section of the HCLE was assumed to be only from the disrupted microalgae to fluid with the intact microalgae neglected because its rate was very small compared to the disrupted. Moreover, the lipid concentration in the disrupted microalgae after the extraction process was equal to the equilibrium value because it was effectively washed with methanol and hexane solvent [34].

#### 3.3. Evaluation of Microalgae Cell Disruption

Microalgae cell disruption can be assessed by measuring intracellular components such as the extracted lipids [34] while the portion of cell disruption in the HCLE can be predicted using lipid mass balance. This is possible because the total lipids in the solvent are released from the disrupted and intact microalgae as indicated in Equation (14).

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

Where,  $x_0$  is the initial lipid concentration in the microalgae and 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 using the conventional method. The value of  $x_0$  can be written as Equation (15).

$$x_{0,i+1} = x_{0,i} - y_{c,i} \tag{15}$$

Where, *i* is the time dimension or number of repetitions. Meanwhile,  $y_c$  can be solved empirically using Ms. Excel based on the conventional extraction data in Figure 4a as indicated in the following Equation (16).

$$y_c = -0.0031t^2 + 0.2154t \tag{16}$$

Where, t is the extraction time. The fraction of disrupted microalgae (r) can also be calculated based on y data and  $y_c$  in Figure 3 using Equation (14) by iteration methods. The *r* calculated for each time is presented in Figure 4b.

Figure 4b shows that the cell disruption trend was similar to the HCLE lipid yields presented in Figure 4a and this means the amount of lipids released from the microalgae to the solvent in the HCLE was determined by the microalgae cell disruption. Moreover, the fraction of cell disrupted was used to determine the amount of lipids released from the disrupted and intact microalgae as shown in Figure 4c. It was discovered that the amount of lipids released from the disrupted microalgae is more than for intact microalgae, especially at the beginning of the process, while the fraction released from the intact microalgae tends to increase along the process due to the reduction in the degree of disruption.

#### **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 the Runge-Kutta method while the value of the volumetric mass transfer coefficient  $(k_T a_T)$  was evaluated using the Golden Section method for one variable minimization with the minimum target of the sum of square of errors (SSE) which was formulated as shown in Equation (17).

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

Where,  $y_{calc}$  is the value of y calculated from Equation (4) and  $y_{data}$  is the value of y from the experiment. There are two estimations in solving this model and the first involves using one section of the extraction curve to have only one value of  $k_T a_T$  for the whole time while the second focuses on using three sections of extraction curves to have three different values of  $k_T a_T$  for each section. The results for the model are described in Figure 5a.



Figure 5a. Model plotting with an assumption of total flux mass



Figure 5b. Model plotting with the assumption from disrupted and intact microalgae flux mass.

#### 3.4.1.1. Model Solution Using One Section

Figure 5a shows that the approximation using one section or one value of  $k_T a_T$  provided an almost linear simulation result. The application of the assumptions of a single value of  $k_T a_T$  was observed to provide a linear relationship between yield function and time 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. This led to the lipid concentration difference in the microalgae and the solid because the lipid mass transfer driving force was not significantly different for each step.

The value of  $k_T a_T$  was 0.6087 1/minute while the coefficient of determination value was 0.4347 and this generally means the approximation was very bad and unable to be effectively used to describe the HLCE.

## 3.4.1.2. Model Solution Using Three Sections

The approximation of the extraction curve using three sections was conducted by dividing the extraction process based on the value of the curve slope [33]. The value of  $k_T a_T$  in this method is tabulated in Table 1.

| Tał | ole 1. | Va | lue | of | V | olumetri | c M | fass [ | Fransf | er c | of | Η | C | LI | Ξ |
|-----|--------|----|-----|----|---|----------|-----|--------|--------|------|----|---|---|----|---|
|-----|--------|----|-----|----|---|----------|-----|--------|--------|------|----|---|---|----|---|

| One Section |  |     | Three Sections Approximation |      |             |                |  |  |
|-------------|--|-----|------------------------------|------|-------------|----------------|--|--|
| Ti          | $\frac{10\pi}{k_T a_T}$ R <sup>2</sup> |     | Time,                        | Sec  | $k_T a_T$ , | R <sup>2</sup> |  |  |
| me,         | ,                                      |     | minutes                      | tion | 1/minut     |                |  |  |
| min         | 1/mi                                   |     |                              |      | e           |                |  |  |
| utes        | nute                                   |     |                              |      |             |                |  |  |
| 1           |  |     | 1                            | 1    | 1.7579      |                |  |  |
| 2           |  |     | 2                            |      |             | -              |  |  |
| 3           |  |     | 3                            | 2    | 0.4652      |                |  |  |
| 4           |  |     | 4                            |      |             |                |  |  |
| 5           | 0,60                                   | 0.4 | 5                            |      |             | 0.9            |  |  |
| 6           | 87                                     | 347 | 6                            |      |             | 783            |  |  |
| 7           |  |     | 7                            |      |             |                |  |  |
| 8           |  |     | 8                            | 3    | 0.1925      |                |  |  |
| 9           |  |     | 9                            |      |             |                |  |  |
| 10          |  |     | 10                           |      |             |                |  |  |

Figure 5a shows that the first section, which is the beginning of the extraction process from 0 to 1 minute, produced the highest extraction rate as indicated by the highest curve slope value of 0.04423. The second section was the middle extraction rate from 1st to 5th minute with a slope value of 0.00745 and the third

section was at the constant extraction rate from the 6th minute to the end of the process with a slope value of 0.00239. Table 1 shows that the extraction using this three-section approximation produced a better result than one section with the R<sup>2</sup> value of 0.9783 and this means it has the ability to describe the HCLE process effectively. This indicates the existence of three values of  $k_T a_T$  differentiated by the  $a_T$  values associated with the cell disruption.

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

The volumetric mass transfer from the disrupted microalgae  $(k_f a_o)$  and intact microalgae  $(k_s a_s)$  was separately evaluated in this model using two approximations of single and three sections. The results are presented in Figure 5b.

## 3.4.2.1. Model Solution Using One Section

Figure 5b shows that the approximation using one section or one value of  $k_f a_o$  and  $k_s a_s$  produced a better simulation than Model 1 as indicated by 0.5835 and 0.030 1/minutes respectively with the coefficient of determination value recorded to be 0.4415. This approximation has a large deviation and this means it cannot be used to describe the HLCE process.

## 3.4.2.2. Model Solution Using Three Sections

The extraction curve was divided into three sections based on the difference in the value of the slopes. The first section, from minute 0 to 1, was the beginning extraction process and had the highest extraction rate as indicated by the highest curve slope value of 0.04423. The second section was the middle extraction rate, from minute 1 to 4, with a slope value of 0.00824 and the third section, from minute 5 to the end of the process, had a constant extraction rate with a slope value of 0.00318. The values of  $k_f a_o$  and  $k_s a_s$  using this approximation are presented in Table 2.

**Table 2.** Value of  $k_f a_o$  and  $k_s a_s$  and  $\mathbb{R}^2$  from Model 2

| 1                    | Sectio                        | on                            |                | 3 Sections           |                   |                               |                |  |  |
|----------------------|-------------------------------|-------------------------------|----------------|----------------------|-------------------|-------------------------------|----------------|--|--|
| Time,<br>minute<br>s | k <sub>f</sub> a <sub>o</sub> | k <sub>s</sub> a <sub>s</sub> | R <sup>2</sup> | Time,<br>minute<br>s | k <sub>f</sub> ao | k <sub>s</sub> a <sub>s</sub> | R <sup>2</sup> |  |  |
| 1                    |                               |                               |                | 1                    | 1.7<br>08         | 0.<br>05<br>1                 |                |  |  |
| 2                    |                               |                               |                | 2                    | 0.4               | 0.                            |                |  |  |
| 3                    |                               |                               |                | 3                    | 36                | 03                            |                |  |  |
| 4                    | 0.5                           | 0.                            | 0.4            | 4                    | 5                 | 0                             | 0.9            |  |  |
| 5                    | 83                            | 03                            | 41             | 5                    |                   |                               | 77             |  |  |
| 6                    | 5                             | 0                             | 5              | 6                    |                   |                               | 8              |  |  |
| 7                    |                               |                               |                | 7                    | 0.1               | 0.                            |                |  |  |
| 8                    |                               |                               |                | 8                    | 82                | 01                            |                |  |  |
| 9                    |                               |                               |                | 9                    | 9                 | 1                             |                |  |  |
| 10                   |                               |                               |                | 10                   |                   |                               |                |  |  |

Table 2 shows that the approximation using 3 sections of extraction provided the best result for the two models with Model 2 observed to be better than Model 1 and this means it has the ability to describe the HCLE process better.

#### 3.5. Comparison between Model 1 and Model 2

The calculation of the disrupted and intact microalgae approximation separately showed that Model 1 and 2 have equal results with R<sup>2</sup> values of 0.9783 and 0.9778 respectively and this means they can both be used to describe the HCLE process because the percentage of lipid released from the intact microalgae is too small compared to the disrupted. The most significant difference was found at the beginning of the process such that the percentage of lipid released from the intact microalgae at minute-1 (1 pass) extraction was 2.95% while the disrupted microalgae had 97.05%. These values changed with time as observed with an increase in the intact microalgae while disrupted microalgae decreased such that the percentage of lipid released at the 10th minute (10 passes) was 8.36% and 91.64% respectively. It is important to note that the HCLE process was determined early at the 5th minute when 85% of total lipids had been extracted. This means a simpler approximation involving total lipid released can be used to describe the process considering the fact that the intact microalgae only produced a small percentage of lipid.

## **IV CONCLUSION**

The extraction energy requirement (E) for HCLE using a discrete flow system was observed to be influenced by the number of repetitions, cavitation number, microalgae concentration, and temperature process. The value can be adjusted to ensure it is lower than the HHV of biodiesel by setting these variables. It was also discovered that the lowest E value was 10 kJ/ gram lipid and this means the process is promising to be developed and scaled up for commercial applications.

The HCLE was also modeled using different mass transfer models including the total mass transfer from intact and disrupted microalgae (Model 1) and separated mass transfer (Model 2) using both one and three sections of the extraction curve. The results showed that both models provided the same result due to the very small amount of lipid released from the intact microalgae compared to the disrupted microalgae. Moreover, the volumetric mass transfer coefficient value decreased from sections 1 to 3. In the case of HCLE with Model 1, the  $k_T a_T$  value for sections 1, 2, and 3 were 1.7579, 0.4652, and 0.1925 1/min respectively with a coefficient of determination (R<sup>2</sup>) of 0.9783 while the  $k_f a_o$  values for Model 2 were 1.708, 0.4365, and 0.1829 1/min and k<sub>s</sub>a<sub>s</sub> were 0.051, 0.030 and 0.011 1/min respectively with an R<sup>2</sup> value of 0.9778.

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#### References

- [1] Y. S. Pradana, H. Sudibyo, E. A. Suyono, Indarto, and <u>A. Budiman</u>, "Oil algae extraction of selected microalgae species grown in monoculture and mixed cultures for biodiesel production," *Energy Procedia*, vol. 105, pp. 277–282, 2017.
- [2] <u>H. Sudibyo, Y. S. Pradana, T. T. Samudra, A. Budiman, Indarto, and E. A. Suyono</u>, "Study of cultivation under different colors of light and growth kinetic study of Chlorella zofingiensis Dönz for biofuel production," *Energy Procedia*, vol. 105, pp. 270–276, 2017.
- [3] T. M. Mata, A. A. Martins, and N. S. Caetano,

"Microalgae for biodiesel production and other applications: A review," *Renew. Sustain. Energy Rev.*, vol. 14, no. 1, pp. 217–232, 2010.

- [4] J. P. Maity, J. Bundschuh, C. Y. Chen, and P. <u>Bhattacharya</u>, "Microalgae for third generation biofuel production, mitigation ofgreenhouse gas emissions and wastewater treatment: Present andfuture perspectives - A mini review," *Energy*, vol. 78, pp. 104–113, 2014.
- [5] T. Suganya, M. Varman, H. H. Masjuki, and S. <u>Renganathan</u>, "Macroalgae and microalgae as a potential source for commercial applications along with biofuels production: A biorefinery approach," *Renew. Sustain. Energy Rev.*, vol. 55, pp. 909–941, 2016.
- [6] Sunarno, Rochmadi, P. Mulyono, M. Aziz, and A. Budiman, "Kinetic study of catalytic cracking of biooil over silica-alumina catalyst," *BioResources*, vol. 13, no. 1, pp. 1917–1929, 2018.
- [7] D. R. Sawitri, Sutijan, and A. Budiman, "Kinetics study of free fatty acids esterification for biodiesel production from palm fatty acid distillate catalysed by sulphated zirconia," ARPN J. Eng. Appl. Sci., vol. 11, no. 16, pp. 9951–9957, 2016.
- [8] S. Kathirvel, A. Layek, and S. Muthuraman, "Engineering Science and Technology, an International Journal Exploration of waste cooking oil methyl esters (WCOME) as fuel in compression ignition engines : A critical review," Eng. Sci. Technol. an Int. J., vol. 19, no. 2, pp. 1018–1026, 2016.
- [9] Daniyanto, Sutijan, Deendarlianto, and A. Budiman, "Reaction kinetic of pyrolysis in mechanism of pyrolysis gasification process of dry torrified sugarcane bagasse," ARPN J. Eng. Appl. Sci., vol. 11, no. 16, pp. 9974–9980, 2016.
- [10] D. R. Wicakso, Sutijan, Rochmadi, and A. Budiman, "Study of Catalytic Upgrading of Biomass Tars using Indonesian Iron Ore," in AIP Conference Proceedings, 2017, vol. 20094, pp. 1–8.
- [11] <u>S. Jamilatun, A. Budiman, Budhijanto, and Rochmadi</u>, "Non-catalytic slow pyrolysis of Spirulina Platensis residue for production of liquid biofuel," *Int. J. Renew. ENERGY Res. S. Jamilatun al*, vol. 7, no. 4, 2017.
- [12] R. D. Kusumaningtyas, I. N. Aji, H. Hadiyanto, and A. <u>Budiman</u>, "Application of tin (II) chloride catalyst for high FFA Jatropha oil esterification in continuous reactive distillation column," *Bull. Chem. React. Eng. Catal.*, vol. 11, no. 1, p. 66, 2016.
- [13] <u>T. Chatsungnoen and Y. Chisti</u>, "Oil production by six microalgae: impact of flocculants and drying on oil recovery from the biomass," *J. Appl. Phycol.*, vol. 28, no. 5, pp. 2697–2705, 2016.
- [14] <u>P. Collet *et al.*</u>, "Biodiesel from microalgae–Life cycle assessment and recommendations for potential improvements," *Renew. Energy*, vol. 71, pp. 525– 533, 2014.

- [15] <u>E. Suali and R. Sarbatly</u>, "Conversion of microalgae to biofuel," *Renew. Sustain. Energy Rev.*, vol. 16, no. 6, pp. 4316–4342, 2012.
- [16] <u>A. K. Lee, D. M. Lewis, and P. J. Ashman</u>, "Force and energy requirement for microalgal cell disruption: An atomic force microscope evaluation," *Bioresour. Technol.*, vol. 128, pp. 199–206, 2013.
- [17] A. K. Lee, D. M. Lewis, and P. J. Ashman, "Microalgal cell disruption by hydrodynamic cavitation for the production of biofuels," *J. Appl. Phycol.*, vol. 27, no. 5, pp. 1881–1889, 2015.
- [18] K. de Boer, N. R. Moheimani, M. A. Borowitzka, and P. A. Bahri, "Extraction and conversion pathways for microalgae to biodiesel: A review focused on energy consumption," J. Appl. Phycol., vol. 24, no. 6, pp. 1681–1698, 2012.
- [19] <u>B. Momin, S. Chakraborty, and U. Annapure</u>, "Investigation of the cell disruption methods for maximizing the extraction of arginase from mutant Bacillus licheniformis (M09) using statistical approach," *Korean J. Chem. Eng.*, vol. 35, no. 3, pp. 1–12, 2018.
- [20] H. Yen, I. Hu, C. Chen, S. Ho, D. Lee, and J. Chang, "Microalgae-based biorefinery – From biofuels to natural products," *Bioresour. Technol.*, vol. 135, pp. 166–174, 2013.
- [21] M. Setyawan, P. Mulyono, Sutijan, and A. Budiman, "Comparison of Nannochloropsis sp. cells disruption between hydrodynamic cavitation and conventional extraction," in *MATEC Web of Conferences*, 2018, vol. 1023, pp. 1–5.
- [22] S. I. Choi, J. P. Feng, H. S. Seo, Y. M. Jo, and H. C. Lee, "Evaluation of the cavitation effect on liquid fuel atomization by numerical simulation," *Korean J. Chem. Eng.*, vol. 35, no. 11, pp. 2164–2171, 2018.
- [23] I. Lee and J. I. Han, "Simultaneous treatment (cell disruption and lipid extraction) of wet microalgae using hydrodynamic cavitation for enhancing the lipid yield," *Bioresour. Technol.*, vol. 186, pp. 246– 251, 2015.
- [24] L. Paulo, S. Silva, and J. Martínez, "Mathematical modeling of mass transfer in supercritical fluid extraction of oleoresin from red pepper," J. Food Eng., vol. 133, pp. 30–39, 2014.
- [25] J.-P. Franc and J.-M. Michel, Fundamentals of Cavitation. New York: Kluwer Academic Publishers, 2005.
- [26] T. A. Beacham, C. Bradley, D. A. White, P. Bond, and <u>S. T. Ali</u>, "Lipid productivity and cell wall ultrastructure of six strains of Nannochloropsis: Implications for biofuel production and downstream processing," *Algal Res.*, vol. 6, no. PA, pp. 64–69, 2014.
- [27] K. Sivaramakrishnan and P. Ravikumar, "Determination of Higher Heating Value of Biodiesels," Int. J. Eng. Sci. Technol., vol. 3, no. 11, pp. 7981–7987, 2011.

- [28] <u>R. H. Perry and D. W. Green</u>, "10. Transport and storage of fluids," in *Perry's Chemical Engineers' Handbook*, 2008, p. 2400.
- [29] M. A. Islam, R. J. Brown, I. O'Hara, M. Kent, and K. <u>Heimann</u>, "Effect of temperature and moisture on high pressure lipid/oil extraction from microalgae," *Energy Convers. Manag.*, vol. 88, pp. 307–316, 2014.
- [30] Y. He et al., "Nontoxic oil preparation from Jatropha curcas L. seeds by an optimized methanol/n-hexane sequential extraction method," *Ind. Crops Prod.*, vol. 97, pp. 308–315, 2017.
- [31] J. L. A. Dagostin, D. Carpiné, and M. L. Corazza, "Extraction of soybean oil using ethanol and mixtures with alkyl esters (biodiesel) as co-solvent: Kinetics and thermodynamics," *Ind. Crops Prod.*, vol. 74, pp. 69–75, 2015.
- [32] K. Yamamoto, P. M. King, X. Wu, T. J. Mason, and E. M. Joyce, "Effect of ultrasonic frequency and power on the disruption of algal cells," *Ultrason. Sonochem.*, vol. 24, pp. 165–171, 2015.
- [33] <u>H. Sovová</u>, "Mathematical model for supercritical fluid extraction of natural products and extraction curve evaluation," *J. Supercrit. Fluids*, vol. 33, no. 1, pp. 35–52, 2005.
- [34] J. A. Gerde, M. Montalbo-Lomboy, L. Yao, D. Grewell, and T. Wang, "Evaluation of microalgae cell disruption by ultrasonic treatment," *Bioresour. Technol.*, vol. 125, pp. 175–181, 2012.