Research Article

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Selection of oil extraction process from *Chlorella* species of microalgae by using multi-criteria decision analysis technique for biodiesel production

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Abstract: In the last few decades, the energy crisis has been one of the main concerns related to the lack of long-term petroleum-based reserves as primary energy resources. Biodiesel emerged as a promising alternative. Nowadays, it is produced from edible vegetable oil, thereby causing commodity prices and food security disruption. In this case, microalgae serve as a sustainable and renewable feedstock for their fast growth, high lipid content, and CO2 absorbing agent. Five processes are applied on the production of microalgae-based biodiesel, namely cultivation, harvesting, extraction, conversion, and refinement. There is currently limited study on technology selection on industrial-scale technology for oil extraction from *Chlorella* spp. of microalgae. Therefore, this study aims to review and select the most suitable technology using simple multi-attribute rating technique extended to ranking – multi-criteria decision analysis (SMARTER-MCDA). Preliminary studies showed that conventional organic solvent extraction (COE), ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), electric pulse extraction (EPE), supercritical fluid extraction (SFE), and hydrothermal liquefaction (HTL) were the most promising technologies. These technologies required a series of evaluations using SMARTER-MCDA with several criteria, including easy scalability, extraction productivity, energy input, additional compound, and environmental impact. The result ranking showed that MAE technology was selected as the most suitable technology for oil extraction from *Chlorella* spp.

Keywords: *Chlorella* spp., oil extraction, selection, multi-criteria decision analysis, simple multi-attribute rating technique extended to ranking

1 Introduction

The energy source crisis has become the primary world concern, given the lack of long-term petroleum-based reserves as primary energy resources [1]. Furthermore, the increase in fossil fuel usage associated with industrial activities contributes to a vast amount of CO2 released and causes severe issues like climate change and global warming [2]. To overcome these problems, world communities have been working on the development of renewable energy resources. In response to the issues, the Indonesian Government has assigned a new target, increasing the ratio of new and renewable energy use to overall energy use by 23% in 2025 [3].

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Biodiesel components are fatty acid methyl esters, which have properties similar to fossil-based diesel. Biodiesel has emerged as a promising alternative due to its advantages in renewability, less toxicity, not containing sulfur, and better lubricity properties [4]. Naylor and Higgins [5] reported that biodiesel could come from edible vegetable oil. Almost 69% of its global production comes from this source. In particular, in Indonesia, biodiesel is mainly produced from palm oil. With the high percentage of the edible resource used, this approach has threatening potential to cause food security and commodity prices disruption [6].

These have led to the interest in microalgae as synthetic cell factories and potential for biodiesel feedstock-based replacement. Microalgae are considered in this problem because of their fast growth and high lipid content. They can also grow in a harsh environment less appropriate for food crop plantation [7,8]. Besides, microalgae can absorb CO₂ from photosynthesis and produce oxygen as a by-product [9]. Different recent methods have been proposed to enhance biodiesel production economic viability from microalgae. For example, wastewater recycling to minimize consumption of freshwater and nutrient; integration with wastewater treatment; selective extraction so that other microalgae active components can be utilized; and utilization of waste (i.e., eggshell) for transesterification step catalyst.

Five steps are applied to produce microalgae-based biodiesel. They are cultivation, harvesting, extraction, conversion, and refinement. However, there is currently limited study on technology selection of industrial-scale microalgal oil extraction. Therefore, this study is aimed to review and select the most qualified technology for microalgal oil extraction using multi-criteria decision analysis (MCDA) method. This study chooses *Chlorella* spp. for large-scale oil extraction analysis because they have high lipid content (49–52%) and are easy to cultivate on a large-scale [6]. Also, a couple of research [23–48] has been conducted on this species and provided references comprehensively.

MCDA serves as the most popular method for the general class of operations research (OR) models. It deals with decision-making problems with several criteria [10]. Several variations in MCDA techniques include analytic network process (ANP), case-based reasoning (CBR), analytic hierarchy process (AHP), and simple multi-attribute rating technique (SMART) [11].

Simple multi-attribute rating technique extended to ranking (SMARTER), an improved SMART analysis, was chosen for this study since it could develop decision-making independently, allowing the alternative scoring to be irrelative. Furthermore, a new alternative rating does not impact the ratings of the original ones. The SMARTER method is a technique more flexible and superficial than ANP and AHP. CBR is irrelevant for this study because its model has similar past problems and experience-based judgment.

In SMART, the scores of each criterion are sorted based on scales. The most widely used value function method is the additive model or linearization scaling (ranging from 0 to 100) [12]. As an advanced method, SMARTER allows several ways of numerical weighting to overcome subjective weighting value. The weighting of criteria is applicable by determining a rank order from worst to best ranks. Several weight formulas based on the ranking have been proposed, including rank reciprocal (RR), rank sum (RS), and rank of centroid (ROC). ROC has proven to be better, at rank-based weighting, than RS and RR [11]. SMARTER was chosen in this study since the alternatives of oil extraction technologies had obtainable and measurable quantitative and qualitative attributes such as yield, time, operational condition, and technology maturity (TM).

### 2 Methodology

Previous work conducted by Kigozi and Aboyade [13] presented several steps that work during decision-making: (1) problem determination; (2) finding possible solutions; (3) criteria definition; (4) selection by decision-preferred analysis technique; (5) solution evaluation in respect to each selection criteria; and (6) consensual solution searching. In this study, the framework was modified with certain steps illustrated in Figure 1. The first step was a literature study of the lipid extraction by alternative technologies. The second step was preliminary technologies review and selection. The third step was MCDA selection using the SMARTER method, which involves criteria determination and weighting score determination. The weighting scores for all criteria were calculated based on the ranking by following the equation of ROC method [11] as shown in equation (1). Let *n* be the number of criteria and *k* be the rank criteria,

\[
w_i = \frac{1}{n} \sum_{k=1}^{n} \frac{1}{k},
\]

The fourth step was the score calculation of each technology for each criterion based on which the total weighted score was calculated. Thereby, the most
suitable microalgal oil extraction technology based on the MCDA method was obtained.

3 Results

3.1 Preliminary technology selection

Many technologies have been explored for microalgal oil extraction on the laboratory scale, yet no well-established industrial methods have been selected [6]. However, many pieces of research have been finished to optimize extraction residence time, enhance extraction yield, and improve free fatty acids in the extracted product. In addition, solvents play a crucial role in this process to be used directly or assisted by chemical, biological, or mechanical cell disruption for improving extraction efficiency [14].

Chemical-microalgal oil extraction technology includes several solvents: organic solvent, acid-based solvent, nanoparticle, supercritical fluids, and ionic fluids. The organic solvent used in microalgal oil extraction is a well-matured technology in other industrial sectors (i.e., pharmaceuticals).

Many publications revealed it with several combinations and other variables optimization. The supercritical fluid model has advantages over organic solvent extraction techniques. It does not need to use polluting solvents or uses polluting solvents but only at the minimum level. Besides, it can extract lipid easily [15]. Based on preliminary studies, organic solvent and supercritical fluid solvent have been selected for further detailed studies. Acid-base, nanoparticle, and ionic solvents are advantageous due to their higher lipid recovery than conventional organic solvents. However, using these technologies in large-scale processes is still further away as it is still in recent development or optimization in the laboratory scale.

Methods using mechanical-assisted solvents for microalgal oil extraction include conventional mechanical pressing, microwave-assisted oil extraction (MAE), ultrasound-assisted oil extraction (UAE), electric pulse-assisted oil extraction (EPE), and cell homogenization. Conventional mechanical pressing causes high biomass losses and low lipid selectivity, thus not feasible for industrial application [16]. On the other hand, cell homogenization can reduce cost intensive in the drying process and can be scaled up in large volumes [17]. However, for Chlorella vulgaris, Santos et al. [18] found that the yield in the homogenization process was more insufficient than, and even similar to, the conventional extraction under similar solvent conditions. Thus, it could be concluded that cell homogenization is not suitable for Chlorella vulgaris. Therefore, mechanical pressing and cell homogenization were not chosen in this preliminary selection step.

The biological-assisted oil extraction method, which is generally enzyme-based cell lysis, is more efficient in energy use and environmentally friendly. But considering its high operational cost, longer reaction time, and enzymes specificity, its implementation on an industrial scale needs to be addressed [15].

The recent development in microalgal oil extraction is thermochemical-assisted technology, namely hydrothermal liquefaction (HTL) technology. It is a potential method for converting wet algal biomass into a crude biooil [19]. Hot compressed water at around 325°C is used to break down the bio-macromolecules in algae [20]. As a result, biomass is converted into high-water contents, thus minimizing the high cost and energy consumption in the drying steps. Hence, HTL is selected to be one of the technologies considered in this study.

Thus, the technologies selected from the preliminary study were conventional organic solvent extraction (COE), UAE, MAE, EPE, supercritical fluid extraction (SFE), and HTL.
Table 1: Reports of conventional oil extraction from *Chlorella* spp.

| Microalgae species | Solvent                      | Yield (mg/g cell) | Time (min) | Extraction condition                                                                                                                                 | Ref.  |
|--------------------|------------------------------|-------------------|------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| *Chlorella vulgaris* | Hexane (solvent can be reused) | 184.5             | 360        | $P = 1$ atm; $T =$ room temp.; 20 g solvent/g cell; 1,000 rpm stirring speed; batch reactor                                                                 | [23]  |
| *Chlorella vulgaris* | Hexane–methanol (7:3 v/v) (solvent can be reused) | 185.4             | 360        | $P = 1$ atm; $T =$ room temp.; 20 g solvent/g cell; 1,000 rpm stirring speed; batch reactor                                                                 | [23]  |
| *Chlorella vulgaris* | Chloroform–methanol (2:1 v/v) (solvent can be reused) | 378.0             | 360        | $P = 1$ atm; $T =$ room temp.; 20 g solvent/g cell; 1,000 rpm stirring speed; batch reactor                                                                 | [23]  |
| *Chlorella vulgaris* | Chloroform–methanol (1:2 v/v) (solvent can be reused) | 327.0             | 1,440      | $P = 1$ atm; $T =$ room temp.; 200 mL solvent/g cell; 400 rpm stirring speed; conical flask                                                                 | [24]  |
| *Chlorella vulgaris* | Dichloromethane–methanol (1:1 v/v) (solvent can be reused) | 8.44              | 60         | $P = 1$ atm; $T = 37^\circ C$; 0.9 mL solvent/50 mg cell; centrifuge tube                                                                               | [25]  |
| *Chlorella vulgaris* | Methanol–ethyl acetate (2:1 v/v) (solvent can be used) | 18.1              | 120        | $P = 1$ atm; $T =$ n.a.; 20 mL solvent/20 mg cell; centrifuge tube                                                                                     | [27]  |
| *Chlorella vulgaris* | Chloroform–methanol–water (2:2:1 v/v/v) (solvent can be reused) | 246.0             | n.a.       | $P = 1$ atm; $T = 22–26^\circ C$; 25 mL solvent/5 g cell; Bligh and Dyer method                                                                         | [28]  |

3.2 COE

Conventional extraction of lipid using an organic solvent is done based on the “like dissolves like” chemical concept. The polar solvent dissolves the polar lipid, and, at the same time, the non-polar solvent dissolves the non-polar lipid [21]. Commercially, this process is well-established as studies have been conducted to obtain the most suitable solvent. Ideally, the solvent must have high selectivity to lipid fraction and low boiling point to ensure the minimum distillation energy and the simplicity of product separation [22]. However, organic solvents have a significant drawback in the environmental aspect due to their adverse effects and toxicity [6].

Chloroform, hexane, and methanol have been considered the most potential solvents [14]. Choi et al. [23] discovered the effect of different solvents; chloroform–methanol solvent (1:1 v/v) achieved the most excellent yield with 378 mg/g of cells of lipid extracted. As for hexane and hexane methanol solvents (7:3 v/v), the extracted lipid amounts were 184.5 and 185.4 mg/g, respectively. Thus, solvents, including their ratios, are the main factor in organic solvent technology. For detailed information, the summary of several studies is presented in Table 1.

Table 2: Reports of UAE from *Chlorella* spp.

| Microalgae species | Solvent                  | Yield (mg/g cell) | Time (min) | Extraction condition                                                                                     | Ref.  |
|--------------------|--------------------------|-------------------|------------|----------------------------------------------------------------------------------------------------------|-------|
| *Chlorella vulgaris* | Chloroform–water (1:1 v/v) (solvent can be reused) | 311               | 41         | $P = 1$ atm; $T = 22–26^\circ C$; Ultrasonification 20 kHz, 500 W; Bligh and Dyer extraction method for 20 mL solvent/5 g cell | [28]  |
| *Chlorella sp.*     | n.a.                     | 215               | n.a.       | $P = 1$ atm; $T =$ n.a.; Ultrasonification 20 kHz, 700–1,000 W; Bligh and Dyer extraction method for 10 g cell | [30]  |
| *Chlorella vulgaris* | Chloroform–methanol (1:1 v/v) (solvent can be reused) | 80                | 5 (sonication process) | $P = 1$ atm; $T =$ n.a.; Ultrasonification 10 kHz; Bligh and Dyer extraction method for 0.5 g cell | [32]  |
| *Chlorella vulgaris* | Chloroform–methanol (2:1 v/v) (solvent can be reused) | 2.4               | 30         | $P = 1$ atm; $T = 40^\circ C$; Ultrasonification 10 kHz; Bligh and Dyer extraction method for 0.5 g cell | [33]  |
3.3 UAE

Mechanical pretreatment approach of algal biomass aids in releasing intracellular lipids into the solvent, followed by enhancement of its recovery [15]. One of the most promising mechanical-assisted extraction is ultrasonic extraction that utilizes a sound wave frequency of >20 kHz to propagate the pressure fluctuations that induce cavitation [22,29], which will disrupt the cytoplasm and open the cell bodies, leading the solvent extraction yield to increase. Studies [28,30] on microalgae *Chlorella* sp. reported that ultrasonic pretreatment can increase the yield of extraction and reduce the extraction time up to more than 15 times, compared to conventional organic extraction.

Additionally, Natarajan et al. [30] concluded that rigid walled microalgae such as *Chlorella* sp. is suitable to be processed with UAE. However, it is inapplicable on microalgae with flexible walls such as *Nannochloropsis* sp. and *T. suecica*. However, the ultrasonic pretreatment process may lead to intracellular denaturation and escalate the energy cost due to its high temperature [31]. For detailed information, the summary of several studies is shown in Table 2.

3.4 MAE

Microwave-assisted technology utilizing frequencies of electromagnetic radiation ranging from 0.3 to 300 GHz has been used widely for intracellular components’ drying and extraction in food and pharmaceutical industries [15]. Microwaves interact with polar compounds and damage the cell membrane by inducing localized heat and pressure, leading to intracellular lipid extraction. Like ultrasonic-assisted technology, the microwave-assisted method offers a minimal amount of solvents and shorter extraction residence time.

Studies [28,32,34] on microalgae *Chlorella* sp. reported that microwave-based pretreatment increases the yield of extraction and reduces the extraction time by more...
Chlorella vulgaris CO$_2$ (solvent can be reused)

than 15 times, compared to conventional organic extraction. Microwaves offer various advantages related to their suitability for the large-scale process. However, there are significant concerns related to energy requirements [15], polar solvents issues for volatile compounds [36], and microwave radiation effect on carbon chain bonds [35]. For detailed information, the summary of several studies is presented in Table 3.

### 3.5 EPE

Electric pulse can affect the properties of a biological cellular membrane by producing about 36 kV/cm of pulsed electric fields. An increase in trans-membrane voltage will increase both the membrane conductivity and permeability [37]. Garoma and Janda [28] reported lower lipid yields in EPE than ultrasonic and microwave-assisted technology. However, the ratio of energy gain per energy input in this technology was highest, compared to that using microwave and ultrasonic methods.

Considering the simplicity and lower energy consumption, this method is suitable for large-scale applications [15]. Furthermore, selective extraction of lipids, carbohydrates, pigments, and protein compounds in microalgae can be done in this technology, making it more suitable for biorefinery applications [38]. However, the electric pulse sensitivity to the salty medium becomes a significant drawback for seawater algae without prior washing [39]. For detailed information, the summary of several studies is presented in Table 4.

### 3.6 SFE

Supercritical fluids (SCFs) are alternative solvents for oil extraction. Their characteristics are high diffusivity, high dissolving power, low viscosity, and ease of separation [40]. A fluid presenting above the critical point at which different liquid and gaseous phases do not exist is supercritical. The most widely used SCF for the extraction of bio-compounds is supercritical CO$_2$ [41].

Several studies [42–44] have reported the yield of supercritical CO$_2$-based extraction as at par with conventional organic extraction, but it took a shorter time, thus increasing extraction productivity. However, this technology has more advantages than the COE techniques, including having better yield without using any polluting solvent or using polluting solvent but only at the minimum level. It, moreover, offers more flexibility in controlling criteria and easiness in lipid separation [6].

Unfortunately, studies on Chlorella sp. based microalgae are still fewer than those on the COE method. Therefore, the effect of such variables in supercritical oil extraction from Chlorella sp. must be optimized more. Furthermore, the high temperature and pressure

### Table 5: Reports of SFE of oil from Chlorella spp.

| Microalga species | Solvent | Yield (mg/g cell) | Time (min) | Extraction condition | Ref. |
|-------------------|---------|-------------------|------------|----------------------|------|
| Chlorella vulgaris| CO$_2$-ethanol (10:1 v/v) (solvent can be reused) | 40.3 ± 1.1% of total 244 ± 10 mg/g cell | 240 | $P = 246.7$ atm; $T = 50^\circ$C; autoclave | 42 |
| Chlorella protothecoides | CO$_2$-ethanol (20:1 v/v) (solvent can be reused) | 181.5 | 90 | $P = 148–296$ atm; $T = 65^\circ$C; steel vessel extractor; 0.40 ± 0.05 kg solvent/h | 43 |
| Chlorella vulgaris | CO$_2$ (solvent can be reused) | 1.81% of 150 g total cell | 540 | $P = 1$ atm; $T = 22–26^\circ$C; thermostatic extractor; 150 g cell; CO$_2$ 10 kg/h | 44 |

### Table 6: Reports of HTL application for oil extraction from Chlorella spp.

| Microalga species | Solvent | Yield (mg/g cell) | Time (min) | Extraction condition | Ref. |
|-------------------|---------|-------------------|------------|----------------------|------|
| Chlorella sp. | Water (solvent can be reused) | 320 | 60 | $P = 59.22$ atm; $T = 350^\circ$C; Parr reactor (induction heated 250 mL) | 20 |
| Chlorella vulgaris | Water; 1 M solution of Na$_2$CO$_3$; 1 M of formic acid solution | 20–40 | 60 | $P = 197.39$ atm; $T = 350^\circ$C; Parr reactor (induction heated 75 mL) | 45 |
| Chlorella Vulgaris | Water (solvent can be reused) | 82.9 ± 1.7 of dry cell | 60 | $P = 345.42$ atm; $T = 350^\circ$C; Parr reactor (induction heated 100 mL) | 47 |
requirement will be a significant concern in industrial applications. For detailed information, the summary of several studies is displayed in Table 5.

3.7 HTL

HTL is considered one of the promising alternative methods in converting wet algal biomass into a crude bio-oil [19]. HTL involves the reaction between biomasses in the water at high temperature and pressure with or without any catalyst. With this process, HTL bypasses the drying process, thus eliminating significant cost and energy consumption [45]. HTL is applied in a closed reactor at 200–350°C and 5–15 MPa, usually assisted by water [46]. Studies [20,45,47] reported that HTL shows the highest bio-oil yield compared to the other five technologies. However, the reaction time is still longer than that of mechanical-assisted oil extraction. The major disadvantages of this technology are high temperature and pressure. For detailed information, the summary of several studies can be seen in Table 6.

3.8 Criteria and weighting factor

The criteria ranking and weighting factor using the ROC method are presented in Table 7.

3.9 Reference selection

The selected technologies from the preliminary study were COE, UAE, MAE, EPE, SFE, and HTL. The detailed information of the selected references is shown in Table 8.

3.10 Technology scoring

The scoring result of the selected technology for each criterion is presented in Tables 9–13. The score summary of each parameter in all technologies is shown in Table 14.

4 Discussion

4.1 Criteria and weighting factor

Extraction efficiency, reactivity with lipids, duration, process safety, capital, operational costs, and waste generated are categorized as crucial variables for implementing microalgal oil extraction technology on an extensive scale application [48]. In this study, the criteria to evaluate the six most promising technologies in industrial-scale oil extraction are easy scalability, extraction productivity, energy input, additional compound, and environmental impact. These criteria need to be weighted based on their importance using equation (1).

Easy scalability is the measure of the easiness of the technology to be implemented on an industrial-scale. This criterion considers TM, difficulty in OM, and safety impact considering the use of the hazardous compound or extreme operational condition. Scalability is an essential criterion since the objective is to select microalgae extraction technology in industries. Extraction productivity represents the amount of obtained lipid per time. Since those technologies have different yields and times of extraction, this criterion provides an objective comparison. Extraction productivity is the second important factor because the high productivity will lead to cost reduction due to the minimum additional compound or energy input requirement.

Table 7: Criteria, criteria ranking, and weighting factor

| Rank | Criteria                     | Definition                                                                 | Weighting factor |
|------|------------------------------|---------------------------------------------------------------------------|------------------|
| 1    | Easy scalability             | The measurement of the ease of technology development into an industrial-scale technology | 0.53             |
|      | This criterion considers TM, difficulty in operation, maintenance, and safety |                               |                  |
| 2    | Extraction productivity      | The amount of extracted oil per time                                       | 0.17             |
| 2    | Energy input                 | The required energy per mass of extracted oil                              | 0.17             |
| 3    | Additional compound          | The price of the added compound per mass of extracted oil                  | 0.07             |
| 3    | Environmental impact         | The impact of added compounds to the environment                           | 0.07             |
Table 8: Selected references of six most promising extraction technologies

| Microalgae species       | Technology | Solvent                          | Yield (mg/g cell) | Time (min) | Extraction condition                                                                 |
|-------------------------|------------|----------------------------------|-------------------|------------|-------------------------------------------------------------------------------------|
| *Chlorella vulgaris*    | COE        | Chloroform–methanol (2:1 v/v) (solvent can be reused) | 378.0             | 360        | • $P = 1$ atm<br>• $T =$ room temp.<br>• Chloroform–methanol solvent (1:1 v/v)<br>• 20 g solvent/g cell<br>• 1,000 rpm stirring speed in batch reactor |
| *Chlorella vulgaris*    | UAE        | Chloroform–water (1:1 v/v) (solvent can be reused) | 311               | 41         | • $P = 1$ atm<br>• $T = 22–26^\circ C$
• Ultrasonification 20 kHz, 500 W<br>• Bligh and Dyer extraction method for 20 mL solvent/5 g cell |
| *Chlorella vulgaris*    | MAE        | Chloroform–water (1:1 v/v) (solvent can be reused) | 317.0             | 21.83      | • $P = 1$ atm<br>• $T = 22–26^\circ C$
• Microwave oven 700 W<br>• Bligh and Dyer extraction method for 20 mL solvent/5 g cell |
| *Chlorella vulgaris*    | EPE        | Chloroform–water (1:1 v/v) (solvent can be reused) | 259               | 29.3       | • $P = 1$ atm<br>• $T = 22–26^\circ C$
• Electric pulse: 1.15 kV, 100 Hz, 10 µs of pulse width, 10.2 cm² of electrode area, 0.284 of electrolyte distance, 55 A of applied current<br>• Bligh and Dyer extraction method for 20 mL solvent/5 g cell |
| *Chlorella protothecoides* | SFE       | CO₂–ethanol (20:1 v/v) (solvent can be reused) | 181.5             | 90         | • $P = 148–296$ atm<br>• $T = 65^\circ C$
• Conducted in steel vessel<br>• 0.40 ± 0.05 kg solvent/h |
| *Chlorella vulgaris*    | HTL        | Water (solvent can be reused) | 207.3             | 60         | • $P = 345.42$ atm<br>• $T = 350^\circ C$
• 4 g water/g cell<br>• Parr reactor (induction heated 100 mL) 100 rpm stirring speed |
Energy input corroborates the required energy per mass lipid extracted from microalgae. This criterion is placed in the same rank as extraction productivity due to its impact on production cost. On the other hand, the additional compound is considered the least important criterion. It depicts the price of the added compound to the extraction system. Although it impacts production cost, most solvents used in selected technology can be reused. Hence, this criterion will not affect production cost as high as the energy input. Environmental impact is placed in the same rank as an additional compound because, with the proper treatment, environmental impact can be minimized. Although it leads to increased production cost, the effect will not be as high as the energy input. The criteria ranking and its weighting using the ROC method can be checked in Table 7.

### Table 9: Score justification of easy scalability criteria for evaluated technologies

| Technology | TM | S  | OM | Justification                                                                                                                                                                                                 | Score |
|------------|----|----|----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| COE        | 8.0| 8.0| 8.0| Organic solvent use in microalgae oil extraction is well-established technology as it has many publications with several combinations of organic solvent and other variable optimization. Furthermore, this technology is safest among others due to atmospheric pressure and ambient temperature. Hence, it already has user-friendly operation and maintenance (OM). Therefore, a total score of 8.00 was given to conventional extraction technology. | 8.00  |
| UAE        | 6.5| 7.5| 7.0| UAE technology integrates ultrasound pretreatment with existing extraction technology. In the safety aspect, this technology uses atmospheric pressure and high temperature in the 20 min of the sonification process. Therefore, a total score of 6.95 was given to UAE | 6.95  |
| MAE        | 6.5| 7.0| 7.5| MAE technology integrates microwave pretreatment with existing extraction technology. In the safety aspect, this technology uses atmospheric pressure and high temperature. Therefore, a total score of 6.95 was given to MAE | 6.95  |
| EPE        | 5.5| 5.0| 6.0| EPE technology is having the same basis as conventional extraction technology. The main challenge is to integrate electric pulse pretreatment with existing extraction technology. For the safety aspect, this technology uses atmospheric pressure and slightly high temperature. However, the use of a direct electric pulse should be considered in this process. Furthermore, the electric pulse is sensitive to the conductivity of the medium and cannot be directly applied to seawater algae without prior washing. Therefore, a total score of 6.50 was given to EPE | 5.50  |
| SFE        | 5.0| 5.0| 5.5| SFE requires high temperature and pressure above the critical point of the fluid. Thus, a total score of 5.15 was given to SFE | 5.15  |
| HTL        | 5.5| 5.0| 6.0| HTL technology is a recently developed technology for microalgal oil extraction and is still developing for the industrial process. The major disadvantages of this technology are high temperature and pressure. Thus, a total score of 5.50 was given for HTL | 5.50  |

### Table 10: Score justification of extraction productivity criteria for evaluated technologies

| Technology | Yield (mg/g) | Time (h) | Extraction productivity (mg/g/h) | Score |
|------------|--------------|----------|----------------------------------|-------|
| COE [23]   | 378.0        | 6.00     | 63                               | 1.19  |
| UAE [28]   | 311.0        | 0.68     | 455                              | 5.47  |
| MAE [28]   | 317.0        | 0.36     | 871                              | 10.00 |
| EPE [28]   | 259.0        | 0.49     | 530                              | 6.28  |
| SFE [43]   | 181.5        | 4.00     | 45                               | 1.00  |
| HTL [47]   | 207.3        | 1.50     | 138                              | 2.01  |

### Table 11: Score justification of energy input criteria for evaluated technologies

| Technology | Energy input (kW h/kg) | Score |
|------------|------------------------|-------|
| COE*       | 0.00                   | 10.00 |
| UAE [28]   | 4.50                   | 9.62  |
| MAE [28]   | 2.39                   | 9.80  |
| EPE [28]   | 0.15                   | 9.99  |
| SFE**      | 106.44                 | 1.00  |
| HTL**      | 90.74                  | 2.33  |

* Energy input calculation has not evaluated the stirring process due to lack of stirring information in the article.
** Energy input calculated the heating process using Aspen Simulation.

### 4.2 Reference selection

Several pieces of research have been conducted and reported for each kind of technology. Therefore, a preliminary selection of those references is needed. In this step, the main concern in the criterion extraction productivity due to yield and extraction time data is mainly provided by the reference quantitatively. For example, in extraction technology, Choi et al. [23] reported that several different solvents such as hexane, hexane–methanol (7:3 v/v),...
and chloroform–methanol (2:1 v/v), with a 1 h extraction time, show yields of 184.5, 185.4, and 378 mg/g, respectively. Lam et al. [24] reported a yield of lipid of 327 mg/g in a 12 h extraction time with a solvent of chloroform and methanol (1:2 v/v). Garoma and Janda [28] reported a lipid yield of 0.246 mg/g using chloroform, water, and methanol (2:2:1 v/v). The comparative study showed that the solvent mixture of chloroform and methanol (2:1 v/v) gave the highest oil extraction productivity [23].

For UAE, Lee et al. [32] reported a yield of lipid of 80 mg/g using chloroform and methanol solvent. Drira et al. [33] reported a yield of lipid of 2.4 mg/g after

Table 12: Score justification of additional compound criteria for evaluated technologies

| Technology | Solvent | Price per kg cells (USD) | Score |
|------------|---------|--------------------------|-------|
| COE [23]   | Chloroform–methanol (2:1 v/v); 20 g solvent/g cell | 2.70  | 0.59 |
| UAE [28]   | Chloroform–water (1:1 v/v); 20 mL solvent/5 g cell | 0.64  | 2.52 |
| MAE [28]   | Chloroform–water (1:1 v/v); 20 mL solvent/5 g cell | 0.64  | 2.52 |
| EPE [28]   | Chloroform–water (1:1 v/v); 20 mL solvent/5 g cell | 0.64  | 2.52 |
| SFE [43]   | Solvent rate 0.45 g/g cell CO₂ | 0.90  | 1.78 |
| HTL [47]   | 4 g water/g cell | 0.16  | 10.00 |

Table 13: Score justification of environmental impact criteria for evaluated technologies

| Technology | Justification | Score |
|------------|---------------|-------|
| COE        | Conventional organic solvent technology uses non-eco-friendly solvents, chloroform and methanol. Based on Material Safety Data Sheet (MSDS) data by National Fire Protection Association (NFPA), the total toxicity rating of two solvents is 3. Considering the high amount of the solvent, a score of 5 was given for COE technology | 5.00 |
| UAE        | UAE uses chloroform and water mixture as solvent. Based on MSDS data by NFPA, the total toxicity rating of the solvent is 2. Thus, a score of 6 was given for UAE technology | 6.00 |
| MAE        | MAE uses chloroform and water mixture as solvent. Based on MSDS data by NFPA, the total toxicity rating of the solvent is 2. Thus, a score of 6 was given for MAE technology | 6.00 |
| EPE        | EPE uses chloroform and water mixture as solvent. Based on MSDS data by NFPA, the total toxicity rating of the solvent is 2. Thus, a score of 6 was given for EPE technology | 6.00 |
| SFE        | SFE uses CO₂ as the primary solvent and ethanol as a co-solvent. Based on MSDS data by NFPA, the total toxicity rating of solvent is 2. The use of ethanol is minimal. The use of CO₂ solvent is eco-friendlier compared with chloroform. Thus, a score of 8 was given for SFE technology | 8.00 |
| HTL        | HTL uses water as solvent and reactant. Based on MSDS data by NFPA, the total toxicity rating of solvent is 0. In addition, the materials used in this process are non-hazardous. Thus, a score of 10 was given for HTL technology | 10.00 |

Table 14: Summary of SMARTER-MCDA score for evaluated technologies

| Criteria            | COE   | UAE   | MAE   | EPE   | SFE   | HTL   |
|---------------------|-------|-------|-------|-------|-------|-------|
| Easy scalability    | 8.00  | 6.95  | 6.95  | 5.50  | 5.15  | 5.50  |
| Extraction productivity | 1.19  | 5.47  | 10.00 | 6.28  | 1.00  | 2.01  |
| Energy input        | 10.00 | 9.62  | 9.80  | 9.99  | 1.00  | 2.33  |
| Additional compound | 0.59  | 2.52  | 2.52  | 2.52  | 1.78  | 10.00 |
| Environmental impact| 5.00  | 6.00  | 6.00  | 6.00  | 8.00  | 10.00 |

Table 15: Final result of weighted SMARTER-MCDA score for evaluated technologies

| Criteria            | Weighted factor | COE   | UAE   | MAE   | EPE   | SFE   | HTL   |
|---------------------|-----------------|-------|-------|-------|-------|-------|-------|
| Easy scalability    | 0.53            | 4.27  | 3.71  | 3.71  | 2.93  | 2.75  | 2.93  |
| Extraction productivity | 0.17            | 0.20  | 0.91  | 1.67  | 1.05  | 0.17  | 0.34  |
| Energy input        | 0.17            | 1.67  | 1.60  | 1.63  | 1.66  | 0.17  | 0.39  |
| Additional compound | 0.07            | 0.04  | 0.17  | 0.17  | 0.17  | 0.12  | 0.67  |
| Environmental impact| 0.07            | 0.33  | 0.40  | 0.40  | 0.40  | 0.53  | 0.67  |
| Total score         | 1.00            | 6.50  | 6.79  | 7.57  | 6.21  | 3.73  | 4.99  |
30 min of total sonification and extraction process using chloroform and methanol solvent. Natarajan et al. [30] reported that fatty acid yield was 215 mg/g. Unfortunately, the extraction time and solvent were not directly stated. Garoma and Janda [28] published that the oil yield was 311 mg/g after 21 min of residence time using chloroform and water solvent in the ultrasound-assisted extractor. Based on the highest result, the study by Garoma and Janda [28] was used as a reference for MAE technology.

Lee et al. [30] reported a yield of lipid of 10 mg/g using chloroform and methanol solvent and microwave pretreatment. Cheng et al. [34] reported a yield of lipid of 251.92 mg/g for 20 min of the whole process with chloroform and methanol solvent. Garoma and Janda [28] reported an oil yield of 317 mg/g after 21 min extraction and 50 s microwave pretreatment using chloroform and water solvent. Garoma and Janda [28] reported the highest extraction productivity. Therefore, the study by Garoma and Janda [28] was referred to MAE technology.

For electric pulse oil extraction technology, Lee et al. [32] reported a yield of lipid of 128 mg/g after 30 h of the complete process, using chloroform and methanol solvent. Luengo et al. [38] reported that the oil yield was 0.4 pigment/g cell using ethanol solvent. Garoma and Janda [28] reported that the oil yield was 259 mg/g after 21 min extraction and 500 s electric pulse treatment using chloroform and water solvent. The article by Garoma and Janda [28] was referred to EPE technology.

Obeid et al. [42] reported a yield of lipid of 40.3% from a total lipid of 244 mg/g using supercritical CO₂ and ethanol as co-solvent in a 4 h extraction time. Solana et al. [43] reported a yield of lipid of 181.5 mg/g using a similar solvent mixture after a 1 h 30 min extraction time. Dejoye et al. [44] reported a lipid yield of 1.81% after a 9 h extraction time from 150 g cell using supercritical carbon solvent. Thus, the study by Solana et al. [43] was referred to SFE technology.

Yang et al. [20] reported a bio-oil yield of 320 mg/g after a 1 h HTL process. Biller and Ross [45] reported a 20-40% bio-oil yield after a 1 h HTL process. Li et al. [47] reported a bio-oil yield of 82.9% after 90 min HTL treatment. Finally, Li et al. [47] showed the highest extraction productivity and was then referred to HTL technology. For detailed information, the summary of several studies is shown in Table 8.

4.3 Technology scoring: easy scalability

Easy scalability is the measure of the easiness of the technology to be implemented on an industrial-scale. This criterion considers TM, difficulty in OM, and safety (S) aspects considering the use of hazardous compounds or extreme operational conditions. TM, OM, and S were weighted by 40, 30, and 30% for the easy scalability score. The justification of each technology is shown in Table 9.

4.4 Technology scoring: extraction productivity

Extraction productivity defines the amount of extracted oil per time. The highest extraction productivity was obtained by MAE technology. Therefore, a score of 10 was given for this technology. The lowest extraction productivity was reported in SFE process. It was then scored by 1. The other technologies were scored by linearization. Detailed data and justification are shown in Table 10.

4.5 Technology scoring: energy input

Energy input defines the required energy per mass of extracted oil. The lowest energy input was achieved by the conventional organic extraction with a score of 10. The highest energy input was required by SFE with a score of 1. The other technologies were scored by linearization. Detailed data and justification are shown in Table 11.

4.6 Technology scoring: additional compound

Additional compound defines the price of compound added to the extraction system. Although it impacts production costs, most of the solvents used in selected technology can be reused. Therefore, this criterion will not affect production cost as high as the energy input. The score of this criterion was measured by the price of solvent per extraction cycle. The lowest additional compound price was HTL technology, so it was given a score of 10. The other technologies are scored by linearization. Detailed data and justification are shown in Table 12.

4.7 Technology scoring: environmental impact

Environmental impact is placed in the same rank as an additional compound because, with the proper treatment, environmental impact can be minimized. Although it will increase production costs, the effect will not be as high as
energy input. This aspect was evaluated by comparing the toxicity of each solvent used in the particular technology. Toxicity was scaled based on MSDS provided by the NFPA. The lowest toxicity was obtained by HTL technology, so it was given a score of 10. The other technologies are scored by linearization and several justification adjustments. Detailed data and justification are shown in Table 13.

4.8 SMARTER selection

The score summary of each criterion in all technologies is shown in Table 14. The obtained scores were then multiplied by the weighting factor of each measure. The results of the weighted scores are shown in Table 15. The final scores of the evaluation based on SMARTER-MCDA are shown in Table 15.

4.9 Economic feasibility and future prospect

The study mainly focused on reviewing and selecting microalgal oil extraction technology using the SMARTER-MCDA technique. The criteria involved in the evaluation are: (1) easy scalability, (2) extraction productivity, (3) energy input, (4) additional compound, and (5) environmental impact. The preliminary economic feasibility in this study is measured indirectly by criteria numbers 1–4, which will affect the capital investment cost and operational cost. Therefore, further study on capital investment and the operating cost of selected extraction technology is required on the biodiesel production feasibility study.

With many potential prospects, the development of microalgal-based biodiesel faces numerous challenges. They are a wide variation in optimum culture growth, high capital investment, and operational cost [50]. Based on the study by Kovacevic and Wesseler [51], microalgal-based biofuel could cost 51.60 euros/GJ by 2020, compared to crude oil which is around $10–20/GJ. It indicates that microalgal-based biodiesel requires further development to select the optimum conditions of each stage from cultivation, harvesting, extraction, conversion, and refinery.

5 Conclusion

Based on preliminary studies, there were six most promising technologies of oil extraction from Chlorella spp. They were COE, UAE, MAE, EPE, SFE, and HTL. Criteria used to evaluate the promising technologies for industrial-scale application were easy scalability, extraction productivity, energy input, additional compound, and environmental impact. Based on SMARTER-MCDA method, the most suitable technology for industrial-scale oil extraction from Chlorella spp. was MAE.

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