Microwave-assisted *in situ* transesterification of wet microalgae for the production of biodiesel: progress review

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Abstract. Continuous efforts are done by scientists in the quest of finding sustainable alternatives for fossil fuels. Various feedstock have been carefully selected to be utilized in the production of biodiesel. Microalgae has garnered a lot of attention as early as in the 80s and is regarded as one of the most promising feedstock to displace fossil fuel. However, the utilization of microalgae as feedstock in a mass production of biodiesel comes with considerable challenges. One of the main obstacles is the high cost involved in processes such as drying and the subsequent lipid extraction of the biomass. These two energy extensive processes created a bottleneck in the biodiesel production at a large scale. As a remedy, direct or *in situ* transesterification of the wet microalgae biomass can be applied to entirely circumvent the two processes; hence substantially reducing the production cost. However, the presence of water in the wet microalgae biomass posed a challenge in the transesterification process. This paper covers the specific techniques of utilizing microwave irradiation during the *in situ* transesterification of wet microalgae biomass.

1. Introduction
Fossil fuels are fuels are being extracted rigorously all over the world in order to quench the insatiable global thirst for power. The demand for fuel is so great, where it is estimated that 1.7 M barrels of crude oil is extracted on a daily basis, raising the concern of the depletion of the natural source in roughly 53.3 years [1]. To make the matter worse, the burning of fossil fuels has led to another alarming issue, which is the global warming phenomenon. From the transportation sector alone, 19% and 70% of the global carbon dioxide and carbon monoxide are being emitted, respectively [2].

Looking at both the issues of global warming and fossil fuel depletion, it is safe to say that biodiesel could be one of the most suitable solutions to tackle these two issues simultaneously. This is further supported by the fact that biodiesel can be directly used in the existing internal combustion engine without needing any or much modifications [3]. Hence, it is not surprising that biodiesel is the second most produced biofuels in the world, accounting about 6.9 billion gallons, and the most widely used biofuel in Europe [4]. The production of global biodiesel has also seen a significant growth in
countries such as Germany, Brazil, Argentina, France, and the United States, in the scale of 20% to 100% increment in the recent years [5].

However, the utilization of biodiesel comes with its own set of challenges. One of the most prominent challenges is the cost of the feedstock used for the production of biodiesel. The cost of feedstock alone could account to up to 70 – 95% of the total cost [6]. Hence, it is very important to carefully select the type of feedstock in order to make biodiesel to be at least competitive with fossil diesel. In addition to using cheaper feedstock, the utilization of better engineering devices and optimized processing techniques are among other ways to further reduce the price gap between biodiesel and petro diesel [7].

Microalgae is known as a cheap third generation feedstock for biodiesel, which has the capability to yield more oil per unit area in a relatively short time compared to other types of plants [8]. These prokaryotes and eukaryotes photosynthetic microorganisms thrive in all places and ecosystems around the world [9]. With a high energy content (approximately 80% of energy contained in petroleum), microalgae has become a serious candidate to totally replace petro diesel [10]. Its ability to grow in saline water without any usage of pesticides or herbicides also makes it a very desirable feedstock, without disturbing freshwater resources [11]. In addition, microalgae can also be utilized in treating wastewater or as an agent for carbon dioxide sequestration [12]. Intercellular lipid from microalgae is extracted by breaking down the cell walls. Transesterification is one of the processes involved in the production of algal biodiesel, where microalgae’s lipid with the addition of methanol and certain catalysts is converted biodiesel under certain conditions [13].

Even though it is widely accepted that microalgae is a relatively cheap feedstock, it is a known fact that the production cost of algal biodiesel has posed the most challenge in making it a feasible feedstock for commercial scale production [14]. The main bottleneck revolves around the drying and lipid extraction process, which are proven to consume tremendous amount of energy [15]. Even though there are some variations, most studies reported that the drying process alone would contribute up to 70% of the total biodiesel cost [16]. In addition, the high initial capital and the operation cost needed for the processing plant are among the main hindrances of having an industrialized algal biodiesel production [17,18].

Considering the cost to produce algal biodiesel is in the range of $2.00 and $2.59 through cultivations in photobioreactor and raceway, respectively, there is a pressing need to reduce the cost associated with the entire biodiesel production processes in order for it to at least compete with fossil fuel [19–21]. Among the ways to achieve this is by improving the production processes and utilizing better technologies. In fact, the usage of advanced technologies is generally considered as the most critical factor in the effort to produce biodiesel at a commercial scale [22]. So far, the production of biodiesel from microalgae is mainly restricted to lab-scale production, and no known proven technology has been applied for the commercialization purposes [23]. This paper looks into microwave-assisted in situ transesterification works done on wet microalgae with moisture content in the range of 60 - 80%, focusing on the progress and challenges involved.

2. Conventional, dry in situ, and wet in situ transesterification of microalgae

Various methods to produce biodiesel from harvested microalgae are presented in Figure 1 [24–26]. As seen in Figure 1, the stages involved in producing biodiesel through conventional transesterification method are quite lengthy compared to in situ transesterifications [27]. Via this method, the harvested microalgae could be dried using several ways such as freeze drying, solar drying, oven drying, and spray drying [28]. As described above, the main challenge for this method is the energy extensive drying stage. Combined with the energy requirement to rupture the robust cell wall in order to release the intercellular lipid, the conventional process is a less favorable way to produce biodiesel from microalgae. Therefore, alternative production method is needed in order to simplify the overall process.
Dry in situ transesterification of algal biomass is performed when the individual lipid extraction stage is combined with transesterification process. By having this integrated procedure, the labor extensive lipid extraction process can be circumvented, resulting in cheaper production cost of biodiesel [29]. Even though lipid extraction and transesterification processes are done in a single step, this type of in situ transesterification still utilizes dried microalgae [30,31]. Hence, the overall cost can only be reduced up to a certain extend.

In situ transesterification can be further expended by using wet microalgae biomass as the feedstock. Referring to Figure 1, wet in situ transesterification would entirely skip two individual stages, namely drying and lipid extraction processes during the production of biodiesel [32]. Hence, as described above, energy and time required to obtain the biodiesel can be cut tremendously. However, the utilization of wet microalgae in the transesterification process is still considered a challenge, mainly due to the negative effect of the water, where the formed biodiesel could be hydrolyzed back into methanol and free fatty acid [33]. Most of the in situ transesterification for wet algal biomass are proven to be energy consuming, mainly due to the high temperature needed for the reaction to take place [34]. Hence, the usage of physical aids such as ultrasound and microwave are advisable to assist in the breakdown of the rigid cell wall and enhance the biodiesel yield without needing excessive energy for heating [35]. Regardless of the vast potential of microalgae, there is still lack of technology to produce biodiesel at a commercial scale from wet microalgae [36].

3. Microwave-assisted in situ transesterification for wet microalgae biomass

The usage of technologies such as ultrasound and microwave is very important in order to facilitate the in situ transesterification process, especially in the low temperature reaction region of less than 100°C [37]. By having the reaction to take place in low temperature region, the energy required to rupture the
cell wall and to facilitate the mass transfer between lipid and the reactant can be reduced significantly. Even though it is not yet economical for commercial purposes, numerous lab-scale microwave-assisted in situ transesterification have been conducted for microalgae, mostly using dried microalgae in their study [13,38].

However, the presence of water in the undried microalgae works in favor for the microwave-assisted wet in situ transesterification process, since water helps in heating substances using microwave irradiation [39]. Via this process, the localized heating process occurs from the inside of the microalgae cell; hence resulting in a more effective heating of the overall cell compared to the conventional heating process where heat is transferred via conduction and convection [40]. Due to the intermolecular fraction, pressure and temperature rapidly build up inside the microalgae cell which lead to its rupture, releasing the lipid contained inside the cell.

Contrary to the conventional heating, microwave-assisted process reduces the time and energy taken for the in situ transesterification process. From the perspective of energy consumption, the amount of energy used in the microwave-assisted transesterification process is only about a third of the total energy used in the conventional process [32]. Normally, a microwave-assisted transesterification process would take only a few minutes compared to the conventional transesterification process; which may takes hours to reach completion [41]. A higher biodiesel yield can also be achieved via microwave-assisted reaction compared to the conventional transesterification. In a study, 78.1% and 96.2% lipid conversion for Chlorella sp. are obtained using the conventional Bligh and Dyer and the microwave-assisted transesterification, respectively [42]. The usage of physical aided technology such as microwave is very important during the wet in situ transesterification in order to assist the process.

In an innovative way of utilizing microwave irradiation, wet microalgae biomass (20% moisture content) was processed using a method called simultaneous cooling and microwave heating (SCMH) and the result was found to be very encouraging, where five times biodiesel yield managed to be obtained when benchmarked against the conventional water bath method [43]. Using this method, the cooling action managed to prevent non-uniform heat concentration in the reaction mixture. In other words, this allows for a more uniform microwave irradiation throughout the mixture. This illustrates the versatility of microwave irradiation method in the in situ transesterification of wet microalgae.

Generally, low biodiesel yield is obtained when conducting wet in situ transesterification without the presence of any physical aided devices. In one of the early works done to investigate the feasibility to perform in situ transesterification of wet Schizochytrium limacinum microalgae without the usage of any physical aided devices, it was found that the biodiesel yield from wet biomass was about 20% lower compared to the one obtained using dried microalgae [34].

In a study conducted by Patil et. al., wet microalgae from the Nannochloropsis salina species was used in a catalyst-free microwave-assisted in situ transesterification utilizing supercritical ethanol [44]. In this study, ethanol is heated inside the microwave up to its supercritical stage (245 - 285°C at 65 – 80 bar) for several minutes. As a result, a maximum biodiesel yield of 30.9% (per dried biomass) was obtained by using this green solvent at an optimized conditions. In addition to being a catalyst-free in situ transesterification, this is considered as a cleaner production of biodiesel compared to using methanol, since ethanol is a renewable resource. Several works related to microwave-assisted in situ transesterification of wet microalgae are presented in Table 1.

However, the usage of microwave for in situ transesterification process also comes with some challenges. Microwave irradiation is known to create localized hot spots in the heated biomass [49]. Hence, stirring action is needed during the transesterification process, especially if the reaction takes place at an extended period of time. Another concern is the scalability of the apparatus when considering mass production of biodiesel via microwave-assisted transesterification. This concern is mainly due to the ability of microwave irradiation to effectively penetrate the biomass at a depth of only 10 to 20 mm [50].
Table 1. In situ transesterification of wet microalgae biomass using microwave irradiation.

| Species and moisture content (w/w %) | Catalyst | Maximum biodiesel yield conditions | Biodiesel yield (w/w %) | Reference |
|-------------------------------------|----------|------------------------------------|-------------------------|-----------|
| Nannochloropsis sp., 20 %           | NaOH     | 800W microwave irradiation at 65°C for 10 mins, using SCMH method | 75 %                   | [43]      |
| Nannochloropsis sp., 80%            | [EMIM][MeSO₄] | 700W microwave irradiation at 65°C, [EMIM][MeSO₄] as solvent for 15 mins at 350rpm | 36.79% per dried biomass | [45]      |
| Chlorella pyrenoidosa, 77%          | Sulfonated graphene oxide, SGO | 40 minutes of 600W microwave irradiation at 90 ºC | 84.6%       | [46]      |
| Nannochloropsis sp. 80%             | [EMIM][MeSO₄] | 700W microwave irradiation, [EMIM][MeSO₄] as solvent at 25min, methanol:IL ratio 1:0.5, algae:methanol ratio 1:4 | 40.9% per dried biomass | [47]      |
| Nannochloropsis salina              | None     | Supercritical ethanol as both catalyst and solvent. Microwave irradiation of 1400W to reach supercritical phase of ethanol, then 800W holding at 25min and 260°C with wet algae:ethanol ratio of 1:9 | 30.9%       | [44]      |
| Chlorella pyrenoidosa, 75%          | Graphene oxide, GO | Microwave output of 600W during the heating and 500W during the holding process, reaction at 90°C for 40 mins, 0.2g | 95.1%       | [48]      |
| Nannochloropsis salina              | NaOH     | 700W microwave irradiation for lipid extraction with methanol:hexane ratio of 1:2,65°C for 5 min. For transesterification, 0.2g NaOH was added and stirred for 15mins before heated for 10mins with methanol:hexane ratio 1:1 | 86.41%      | [32]      |

4. Future prospects for microwave-assisted in situ transesterification of wet microalgae

With the aim of further reduce the overall cost to produce algal biodiesel, it is advisable to recycle the used solvent, catalyst and methanol after the microwave-assisted in situ transesterification process. Hence, the usage of heterogeneous catalysts is recommended since these types of catalysts can be reused for several times before losing the efficiencies. The utilization of high cost catalysts such as expensive biocatalysts are not recommended when producing biodiesel with the intention to reduce of overall costs. In addition to recycling the used solvents, it is recommended to have an optimized usage of solvent, since this will help in reducing the overall production cost. Coupled with the energy saving from using microwave instead of the conventional heating, cheaper algal biodiesel could be produced for commercial purposes.
The usage of green solvents such as ionic liquids and deep eutectic solvents is seen as an advancement to further simplify the biodiesel production utilizing wet microalgae biomass. Apart from promoting a cleaner production process, these solvents would also increase the overall biodiesel yield. It is already been proven that green solvents are compatible to be used with microwave irradiation.

To further increase the feasibility of producing algal biodiesel at a commercial scale, the industry must be integrated with other industrial needs such as wastewater treatment, carbon dioxide sequestration and specific valuable by-products production such as pigments and glycerol. When combined with industrial scale physical aided devices such as microwave and ultrasound, biorefinery concept is a very convincing way to push forward the idea of having a large scale production of algal biodiesel. By using this concept, auxiliary strengths of microalgae can be put to use, especially in controlling the air and water pollution while having a mass production of algal biodiesel.

5. Conclusion
A lot of work have been conducted to show the potential of microalgae to be used as feedstock for the production of biodiesel. Due to the negative effect of water to the transesterification process, most of the works utilize dried microalgae in the biodiesel production. When combined with the cost involved in the lipid extraction process, this resulted in the high production cost of algal biodiesel; making it undesirable for commercialization purposes. Hence, some researchers opted to skip the drying process by using wet microalgae biomass for the transesterification process. When wet microalgae is utilized in the in situ transesterification, two of the most costly processes in the biodiesel production, which are drying and lipid extraction can be circumvented entirely. Physical aided devices such as microwave can be used to further improve the wet in situ transesterification process. Even though the obtained results for the microwave-assisted in situ transesterification using wet microalgae biomass seem to be very promising at the lab-scale, there are still plenty of rooms for improvement, especially in the catalysts and solvents used in the process. From the review, more extensive works need to be conducted before scaling-up for commercial purposes.

Acknowledgement
Funding: This work was supported by the Ministry of Energy, Science, Technology, Environment, And Climate Change (MESTECC) [AAIBE Chair for Renewable Energy grant number 201801KETTHA].

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