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Direct supercritical methanolysis of wet and dry unwashed marine microalgae (*Nannochloropsis gaditana*) to biodiesel

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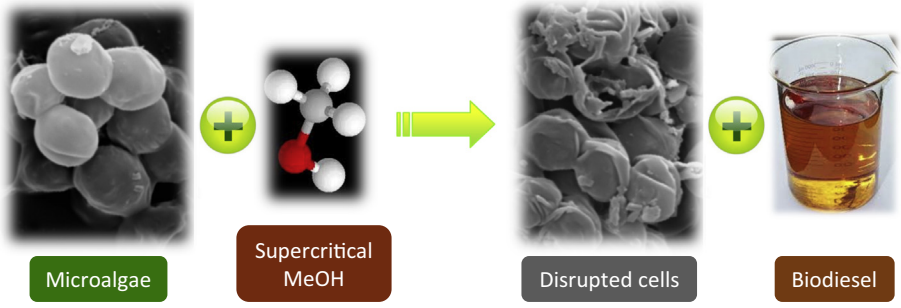
HIGHLIGHTS

- Biodiesel fuel from wet and dry algae was synthesized using supercritical methanol.
- Water content of unwashed algae did not significantly affect the yield of biodiesel.
- Influence of methanol to dry algae ratio, reaction time and temperature was studied.
- A significant interaction effect between reaction time and temperature was not observed.
- Scanning electron micrographs showed disruption of algal cell walls during the process.

GRAPHICAL ABSTRACT



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ABSTRACT

Microalgae, which are promising candidates for biodiesel production, possess a robust cell wall which prevents the release of intracellular lipids in the medium. The breaking of the algal cell wall for lipid releasing can be energy-intensive. The direct or *in situ* supercritical transesterification method is considered to have the potential to disrupt the rigid algal cell wall and convert the extracted lipids into biodiesel in only one step, thus reducing significantly the process energy consumption. In this work, wet (~80 wt.% moisture) and dry unwashed marine microalgae *Nannochloropsis gaditana* were used directly to synthesize biodiesel in a single-step process by direct transesterification with no added catalysts using supercritical methanol. The effect of main process parameters (methanol to dry algae ratio, reaction time and temperature) was studied. Initially, the methanol to dry algae ratio (6:1–12:1 vol./wt.) was investigated and then the synergic effect between reaction time (10–50 min) and temperature (245–290 °C) was studied using a factorial experimental design. In addition, the effect of the supercritical process on the structure of the algal cell walls was studied by scanning electron microscopy observations. Maximum biodiesel yields of ~0.46 and ~0.48 g/g of lipids were reached from wet and dry unwashed algal biomass, respectively, at 255–265 °C, 50 min reaction time, and using a methanol to dry algae ratio of 10:1

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(vol./wt.). The highest biodiesel yields obtained from dry microalgae were only between 2% and 9% higher than those reached from wet microalgae, indicating that a high content of water in the unwashed algal biomass did not significantly affect the supercritical process.

1. Introduction

With the exhaustion of fossil fuels and the alarming environmental deterioration, the search for renewable and clean energies is becoming necessary for the global energy demand. Currently, biodiesel has attracted public attention as one of the best renewable, sustainable and environmental friendly energy for replacing petroleum diesel [1,2]. Traditionally, biodiesel is produced from first generation edible oils (rapeseed, soybean, palm, peanut, etc.) and second generation non-edible oils (animal fats, used vegetable oils, jatropha and karanja oils, etc.) [3,4]. However, the major bottlenecks of these conventional feedstocks are their high price and unsustainable supply [5].

Among third generation biofuel feedstocks, microalgae-based biodiesel has been suggested as one of the most promising alternatives to fossil fuels [6] because of the overall potential advantages of microalgae [7–9]: (1) Comparing with terrestrial oilseed crops, microalgae present higher biomass productivity, faster growth rate and higher lipid accumulation levels; (2) Microalgae can grow successfully on degraded land unsuitable for food production in open ponds and photobioreactors; (3) Microalgae have environmental benefits due to their photosynthetic activity, such as mitigation of CO_2 and bioremediation of wastewater.

There are two types of microalgae strains: freshwater and seawater microalgae. However, it is known that freshwater is becoming a scarce natural source, making the selection of marine microalgae for the production of renewable energy a better solution to preserve freshwater for food production and human consumption [10,11]. Among the wide variety of marine microalgae, only few of them can be exploited for biodiesel production, *Nannochloropsis* being one of them. *Nannochloropsis* species are an appealing alternative for biodiesel production since they grow rapidly, doubling their biomass once a day, and possess high lipid productivities ranging from 12 wt.% to 53 wt.% [12,13]. Among the most referenced *Nannochloropsis* species, *Nannochloropsis gaditana* (*N. gaditana*) has attracted the interest for biodiesel production. López-González et al. [14] studied thermal characteristics of microalgae under oxidizing atmosphere and found that *N. gaditana* showed the highest heat of combustion.

Many studies have explored biodiesel production from microalgae via a conventional approach consisting of: (i) algae cultivation; (ii) cell harvesting and drying; (iii) lipid extraction with chemical solvent; (iv) oil to biodiesel conversion using catalysts; and (v) separation and purification of biodiesel fraction [3,15,16]. It should be noted that marine microalgae are usually cultured in seawater supplemented with nutrient salts, which must be removed by washing at the end of the culture. This conventional approach is limited by some techno-economical drawbacks that increase considerably the cost of the process and prevent the algal biodiesel commercialization. One of the major hurdles is lipid recovery since microalgae have a rigid protective cell wall that confers them a high resistance and makes lipid extraction difficult [17]. Another drawback is the drying of the wet harvested microalgae before lipid extraction, which is responsible for up to 59% of the total energy consumed during biodiesel production [18]. A more interesting approach is the direct extraction of lipids from wet algal biomass, but it remains a great challenge since water around algal cells generates a hydrated shell that acts as a barrier severely decreasing the lipid recovery [19].

A concurrent and interesting approach is the use of a technique permitting at the same time the breakage of the resistant algal cell walls and the diffusion of the solvent into the cells to reach the lipids [20]. Among the different techniques that can be used for this purpose, the direct (or *in situ*) supercritical transesterification has many environmental and economical advantages. Indeed, this technique is carried out at high pressure and temperature disrupting successfully the cell walls of microalgae, thus allowing lipids to be extracted and converted to fatty acid methyl esters (FAMEs) in only one step [16]. Moreover, supercritical biodiesel synthesis is normally carried out without any catalyst added, so that the final product should not be washed and, therefore, pollutant effluents are not generated [21]. In addition, water and free fatty acids, which can be present in large amounts in the algal biomass, do not disturb the efficiency of the supercritical reaction, but on the contrary they improve it [22,23]. However, although the direct supercritical methanol treatment of algae eliminates the need to use a solvent for extracting the oil before transesterification, it requires a unit operation after the supercritical process to separate the produced biodiesel from the non transesterifiable material, thus reducing the profitability of the global process.

The synthesis of biodiesel using supercritical alcohols (methanol and ethanol) has shown an increasing interest in the last few years from various vegetable oils, such as camelina oil [24], jatropha oil [25], rapeseed oil [26] and soybean oil [27]. However, very few studies have been published until now on the direct or *in situ* supercritical synthesis of biodiesel from microalgae [3,4,16,28–31]. All these studies were focused on the use of microalgae *Chlorella* (*C. pyrenoidosa*, *C. vulgaris* and *C. protothecoides*) [4,29,30] and *Nannochloropsis* (*N. sp.* and *N. salina*) [3,16,28,31]. However, the potential of *N. gaditana* species was not yet studied to date.

Most of the above mentioned investigations from microalgae were carried out using supercritical ethanol [4,28–31], while supercritical methanol has received very little attention [3,16]. In fact, methanol is the most used alcohol in the world for biodiesel production because it is cheaper and more reactive than ethanol. Furthermore, most of the aforementioned researches used a pretreatment step (microwave, hydrothermal carbonization or lipid hydrolysis) before the supercritical process or a catalyst during the process, which involve the consumption of a large amount of energy. Conversely, the direct and non-catalytic supercritical methanolysis of microalgae to biodiesel, which is carried out in only one stage, results in lower energy consumption.

In the present study, the direct supercritical methanol transesterification of *N. gaditana* was carried out with no added catalysts. This marine algal biomass was directly used after cultivation and any washing step was performed to remove residual salts. Experiments were conducted on wet (concentrated paste) and dry (lyophilized powder) algal biomass to study the influence of reaction temperature (245–290 °C), reaction time (10–50 min), and methanol to dry algae ratio (6:1–12:1 vol./wt.). The reaction was monitored by gas chromatography to analyze fatty acid methyl esters. Moreover, the effect of the supercritical transesterification process on the structure of algal cell walls was studied by scanning electron microscopy (SEM).