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Direct supercritical methanol transesterification of lyophilized unwashed marine microalgae *nannochloropsis gaditana* to biodiesel

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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. Traditionally, biodiesel is produced from first generation edible oils (rapeseed, soybean, palm, etc.) and second generation non-edible oils (animal fats, used vegetable oils, jatropha and karanja oils, etc.). However, the major bottlenecks of these conventional feedstocks are their high price and unsustainable supply. Among third generation biofuel feedstocks, microalgae-based biodiesel has been suggested as one of the most promising alternatives to fossil fuels because of the overall potential advantages of microalgae: (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 CO₂ and bioremediation of wastewater. In the present study, the direct supercritical methanol transesterification of lyophilized unwashed marine microalgae *Nannochloropsis gaditana* Lubián CCMP 527, cultivated in outdoor open raceways, was carried out. The process was conducted in only one step and without the use of catalysts. These microalgae, which have a lipid content of 22 wt% on dry and ash free basis, were directly used after cultivation, centrifugation and lyophilization, and any washing step was performed to remove residual salts. Experiments were conducted with 4 g of lyophilized powder (3.2 g of dry algal biomass) in a batch shaken tank reactor (a stainless steel cylindrical autoclave of 83 ml capacity) to investigate the influence of reaction temperature (245, 255, 265 and 275 °C) and reaction time (10, 20, 35 and 50 min) on the yield of biodiesel (FAME yield) at a methanol to dry algae ratio of 10:1 (vol./wt.) (optimal ratio, internal communication). The analysis of fatty acid methyl esters (FAME) was performed according to the pressures reached inside the reactor at 245, 255, 265 and 275 °C were 9, 11, 13 and 15 MPa, respectively. Results showed that the FAME yield increased continuously with the reaction time for practically all the temperatures tested. The only exception to this behavior was evidenced at 275 °C, temperature at which the FAME yield increased up to 35 min reaction time and then decreased slightly for a longer reaction time (50 min). Likewise, the FAME yield increased gradually with the temperature for all the reaction times used, the only exception being at 50 min. At this reaction time, the maximum FAME yield was reached at 255 °C and the yield gradually decreased at higher temperatures. The decrease observed in yield for long reaction times and temperatures higher than 255 °C was probably due to the thermal degradation of the unsaturated fatty acid methyl esters generated. Accordingly, the maximum FAME yield (47.8 wt. %) was reached at 255°C after 50 min reaction time.

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