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Direct transesterification of microalgae biomass and biodiesel refining with vacuum distillation

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ABSTRACT

The objective of this study was the use of vacuum distillation to increase fatty acid methyl ester (FAME) content and quality of microalgae biodiesel produced through direct transesterification. Microalgae biodiesel obtained from direct transesterification of microalgae (crude biodiesel) has a FAME content of 64.98 ± 2.88%, viscosity of 17.7 ± 0.17 (mm^2/s), and a humidity level of 3.72%. As biodiesel's properties are related to FAME content, to increase FAME content and produce higher quality biodiesel two vacuum distillation experiments were conducted using different vacuum conditions. The best results were obtained in experiment 2 with two consecutive distillations, where FAME content increased from 64.98 ± 2.88% in crude biodiesel to 85.50 ± 2.60% in the D2.2 fraction, while viscosity decreased from 17.70 ± 0.17 (mm^2/s) in crude biodiesel to 3.76 ± 0.01 (mm^2/s) in the D2.2 fraction. Vacuum distillation, therefore, may represent an excellent alternative for the purification of microalgae-based biodiesel.

1. Introduction

Biodiesel is a mixture of fatty acid methyl esters (FAME) synthesized from vegetable fats, animal fat or frying oil [1]. The oil most frequently used to produce biodiesel globally is canola oil, followed by sunflower oil, palm oil, and soybean oil [2]. However, the need for fertile land to meet the demand for biodiesel production has resulted in environmental damage and deforestation in countries such as Malaysia, Indonesia, and Brazil. This situation has stimulated the search for alternative raw materials for biodiesel production, such as non-edible oils including *Jatropha curcas*, *Pongamia pinnata*, and *Madhuca indica* oil, among others. The advantage of these raw materials is that their cultivation doesn't require agricultural land [3–5]. Waste cooking oil is another alternative for biodiesel production, but it cannot be constantly supplied in adequate amounts to meet worldwide demand for biodiesel.

Numerous bibliographical reviews have been published in recent years related to biodiesel production from microalgae [6,7], including microalgae oil extraction methods for biodiesel production [8], microalgae's potential for biofuels production [9], the production process for obtaining biodiesel from microalgae biomass [10], and evaluation of microalgae biodiesel production in the laboratory and in pilot scale projects [11,12]. Microalgae are photosynthetic eukaryotic organisms capable of fixing CO_2 and transforming it into biomass with high lipid content. In addition, they grow rapidly, with varieties that can be cultivated in fresh, marine, and/or wastewater. Compared to biodiesel made from vegetable oils, microalgae do not require agricultural land for cultivation and are highly productive year-round. While crops such as canola, soybean, and Jatropha can produce 446–636 L lipids/ha, 1190 L lipids/ha and 1892 L lipids/ha, respectively, microalgae can generate up to 58,700 L lipids/ha, based on 30% lipid content [6]. Despite this high level of lipid productivity per hectare, microalgae biodiesel is still not commercially available and soybean is the most commonly used feedstock in biodiesel production today.

According to the literature, the lipid content of microalgae varies from 30 to 70% [6,13–14]. Recent studies of strains such as *Nannochloropsis gaditana* grown in large-scale systems have been found to have a lipid content of 20–25% [15–16]. The literature has also demonstrated that microalgae are comprised of a wide variety of lipids including saponifiable lipids (which can be converted into biodiesel) and non-saponifiable lipids. The chemical similarity of saponifiable and non-saponifiable lipids prevents selective extraction, resulting in a crude biodiesel that contains other lipid components such as carotenoids, chlorophylls, phospholipids and waxes, among others [10,8]. Only recently have some efforts been made to selectively extract

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esterifiable lipids from microalgae [17]. In that research, the authors found that a higher extraction yield of esterifiable lipids was obtained using both a chloroform–methanol mixture and a petroleum ether–-methanol mixture. At the laboratory scale, scientific research has focused on optimizing processes for producing biodiesel on the one hand by extracting lipids from microalgae, and on the other hand through direct transesterification of wet microalgal biomass.

According to the EN 14214 standard, biodiesel should have a 96.5% FAME percentage, which microalgae biodiesel does not achieve [10]. The objective of the study described in this paper is to apply a vacuum distillation process to refine biodiesel produced by direct transesterification of wet microalgal biomass. The difference in the boiling points of fatty acid methyl esters and other microalgae lipids such as waxes, carotenoids, and chlorophylls was used to refine biodiesel, increasing the methyl ester content of biodiesel and improving the quality of the final product.

2. Material and methods

2.1. Microalgae biodiesel production

Microalgae biomass of *Nannochloropsis gaditana* was provided by Almería University in Spain. It was produced in continuous mode at a 0.3 day^{-1} dilution rate in closed tubular outdoor photobioreactors of 3.0 m^3, using seawater enriched with fertilizers as culture medium. The microalgae biomass was subject to direct transesterification in a 300 L pilot scale reactor build-up at Almería University. For this, 20 kg of wet microalgae (4.0 kg of dry biomass and 16 L of water), then 36.4 L of MeOH were inserted into the reactor and 18.2 L H_2SO_4 98% were slowly added. The reactor was closed and purged with N_2 for 5 min to create a nitrogenous atmosphere (0.5 bars). Agitation and steam heating were applied and a 2-hour reaction time was started once the reactor reached 95–100 °C. After two hours, the water entry valve in the sleeve was opened and the reactor was cooled to 30–34 °C. The reactor was depressurized and opened, and 36.4 L of hexane was added. It was purged again and the N_2 atmosphere was created, and it was then agitated for 30 min. The phases were separated by centrifugation. Then the hexane was cleaned with water to eliminate the acid catalyzer and the phases were separated by centrifugation again. To obtain the biodiesel, the hexane was subsequently eliminated using vacuum evaporation and then the biodiesel obtained was characterized with gas chromatography to determine the fatty acid content, viscosity, and humidity.

2.2. Microalgae biodiesel refining with vacuum distillation

Vacuum distillation was used to refine crude microalgae biodiesel. Fig. 1 shows the distillation equipment used.

2.2.1. Experiment 1

Vacuum distillation was performed using 50 g of biodiesel. The system pressure was maintained at 150 mbar, the temperature was increased from room temperature to 300 °C. Fractions of the distillate (D1.1) and residue (R1.1) (see Fig. 2) were collected, and the mass of both products was recorded to compare the yield with the initial mass of the distilled biodiesel. Both the distillate and residue samples were stored for subsequent characterization. The biodiesel distillate (D1.1) fraction obtained in the previous distillation was distilled again, with a system vacuum of 15 mbar (10 times less vacuum in the system). From this second distillation, fractions of distillate (D1.2) and distillation residue (R1.2) were collected. As in the first distillation, the mass of the fraction (D1.2) and the residue (R1.2) obtained in the second distillation was recorded to compare the yield to the distillate mass. Both the distillate and residue samples were stored for subsequent characterization.

2.2.2. Experiment 2

As in experiment 1, 50 g of biodiesel were vacuum distilled, applying 15 mbar of pressure, the temperature was increased from room temperature to 300 °C. Fractions of distillate (D2.1) and residue (R2.1) were collected (see Fig. 2) and the mass of the distillate fraction was recorded to compare the yield with the initial mass of distilled biodiesel (D2.1). Then, a second distillation was performed on the distilled fraction of biodiesel (D2.1) obtained in the previous step, applying a vacuum of 15 mbar to the system. From this second distillation, a fraction of distillate (D2.2) and a distillation residue (R2.2) were collected. The distillate and residue samples were stored for subsequent characterization.

2.3. Physicochemical characterization of biodiesel and refined biodiesel

Kinematic viscosity of the samples was determined according to ASTM Standard D445 using a Koehler KV 1000 viscosity bath. Acidity and iodine values were determined through titration, according to standards EN 14104 and EN 14111, respectively. Humidity was determined according to the EN 12937 standard using a Titroline KF Shott triturator, with chloroform, anhydrous methanol, and standard trituration solution. Carbon residue was determined using an ALCOR MCRT 160 micro carbon residue tester, in accordance with ASTM D 4530. Density was determined according to ASTM Biodiesel standard D6751.

2.4. Chemical characterization of biodiesel and refined biodiesel

Fatty acid methyl ester (FAME) composition was determined through gas chromatography (GC) (Agilent Technologies 6890N Series Gas Chromatograph, Santa Clara, CA, USA). Samples (i.e., crude biodiesel and vacuum distillation fractions) with 10 mL (0.125 mg) of

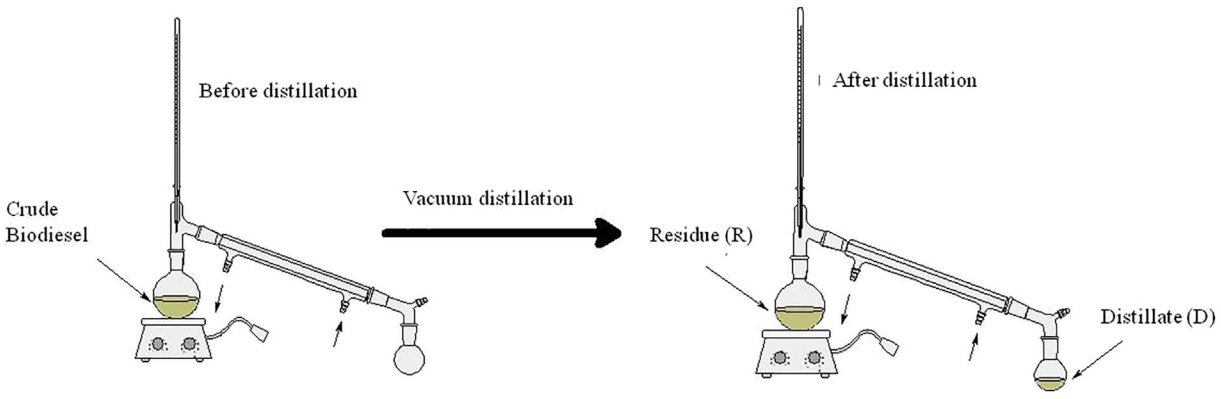

Fig. 1. Distillation equipment of microalgae biodiesel refining.