

Microalgae-based Oil for Biodiesel Production

Marc Veillette, Mostafa Chamoumi, Nathalie Faucheux and Michèle Heitz*

Abstract—Biodiesel is traditionally produced from oleaginous plants. On the other hand, increasing biodiesel production from these raw materials could create problems of food supply. Producing biodiesel from microalgae could help to overcome this difficulty, because microalgae are rich in lipids and do not compete for arable lands. However, no studies had compared vegetable and microalgae oil-based biodiesel in terms of yield, viscosity and heat of combustion. In the present study, commercial canola and microalgae oil were therefore transesterified with methanol under a homogenous alkali catalyst (potassium hydroxide) at 100°C for 1h. The result showed that microalgae-based oil has a higher yield in biodiesel with 89.7% (g biodiesel/g oil) and a lower kinematic viscosity (22°C) of 4.31 mm²/s than canola oil.

Keywords—Biodiesel, microalgae, canola, alkali-transesterification

I. INTRODUCTION

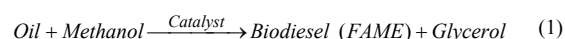
In Canada and the United States, most of 2005 energy need (70%) was supplied by non-renewable sources such as oil, natural gas and coal [1]. Among these energy sources, oil is a major source of energy mainly used in the transportation sector, which consumed 72% of the oil production in 2006 [2]. From 2000 to 2010, the world population increased from 6.1 to 6.9 billions [3]. Consequently, this rise, added to the industrialization of developing countries such as China and India, increased the world oil production from 74.9 to 81.4 barrels/day during the same period of time [4].

However, exploiting oil could have some other disastrous environmental, economic, political and social consequences such as the one created by the oil spill in the Atlantic Ocean. Consequently, the United States are planning to reduce by 1/3 their oil imports by 2022 [5]. Moreover, using non-renewable sources of energy could have major consequences on global warming, as they have a positive carbon balance related to carbon dioxide (CO₂) emissions.

Using biofuels, on the other hand, has many advantages over non-renewable fuels. Biofuels are generally carbon

neutral or carbon negative [6], [7]. Among biofuels, biodiesel is usually produced by transesterification of lipids (oil) of oleaginous plants such as soybean [8], corn [9], palm [10], [11], rapeseed [12], sunflower [13], Jatropha [14], cotton seed [15], etc.

For vegetable oil, transesterification reaction using methanol as an alcohol in the presence of catalyst to produce fatty acid methyl esters (FAME) can be resumed as follows:



In addition to reducing typical emissions of CO₂ by 15.5%, using, as an example, 20% (v/v) biodiesel in diesel fuel could reduce unburned hydrocarbons by 21%, carbon monoxide by 11%, particulate matter (PM) by 10% [16], [17].

Nevertheless, producing biodiesel could lead to food supply (world hunger) problems as the arable lands could be used to produce biodiesel [18]. In order to solve this problem, microalgae could be used to produce biodiesel without these down sides, because cultivating microalgae do not compete with food production [19]. Moreover, some microalgae species can contain up to 77% (dry weight) lipids [20]. However, as the biodiesel from microalgae biotechnology is relatively new, the production parameters remain to be optimized in order to decrease the production costs.

The main goal of this study is to produce biodiesel from canola and microalgae oils by homogenous alkali-catalyzed transesterification with methanol and to compare their physicochemical properties.

II. MATERIALS AND METHODS

A. Feedstock and chemical solvents

Commercial canola and microalgae-based oils (composed among others of *Schizochytrium sp.* and *Echium plantagineum*) were purchased from local Sherbrooke stores. Canadian microalgae mainly (*Nannochloropsis sp.*) were supplied by Nutrocéan Canada (Rimouski, Canada). Methanol, anhydrous sodium sulfate (Na₂SO₄) and the homogenous alkali catalyst, potassium hydroxide (KOH), were supplied by Fischer Scientific inc. (Canada) whereas the acid catalyst (acetyl chloride) for canadian microalgae transesterification was supplied by Fluka (Oakville, USA).

B. Transesterification of oils

Commercial canola and microalgae-based oils were transesterified with methanol and an alkali-catalyst by a modified procedure of Dmytryshyn et al. [21]. Twenty-five g of oil was combined in a glass batch reactor with 5.65 g of methanol containing 0.25 g of KOH. The solution was heated for 4 different times (0.5, 1, 1.5, 2h) at 60°C (with continuous stirring) under a reflux. For the transesterification of

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microalgae-based oil, 2 reaction times were tested (1 and 1.5h). The transesterification of Canadian microalgae with methanol and an acid catalyst has been described elsewhere [22].

C. Biodiesel recovery

The solution (biodiesel and glycerol) was cooled off and transferred into a separation funnel for 1h. Glycerol (bottom dark brown phase) was separated and recovered. Biodiesel was washed with distilled water (60°C) to neutralize the catalyst (KOH) and the excess of methanol. The blend was allowed to settle overnight for a phase separation and then the biodiesel phase was recovered. The biodiesel was dried using Na_2SO_4 and the methanol was evaporated by using a rotoevaporator at 65°C under a vacuum.

D. Specific gravity, kinematic viscosity, and heat of combustion

Specific gravity of canola oil at room temperature (22°C) was measured using a Anton Paar DMA 3000 portable density meter (Graz, Austria). Viscosity was measured at room temperature (22°C) using a Brookfield DV-III Ultra rheological instrument (Brookfield Engineering Laboratories, Inc., Middleboro, Massachusetts, USA) while the heat of combustion was determined using a 1341 Calorimeter with a 6775 digital thermometer and a 2901 ignition unit (Parr instrument Company, Moline, Illinois, USA).

A specific gravity of 0.89 (for oil and biodiesel) was assumed (based on a previous study by Ehimen et al. [23]) to transform viscosities into kinematic viscosities for microalgae-based oil. Table I presents the measured properties of both oils in terms of specific gravity, kinematic viscosity, and heat of combustion.

TABLE I
OILS PROPERTIES

| Oil | Specific gravity (22°C) | Kinematic viscosity (22°C) (mm^2/s) | Heat of combustion (MJ/kg) |
|------------------|-------------------------|---|----------------------------|
| Canola | 0.92 | 33.8 | 39.5 |
| Microalgae-based | 0.89* | 20.3 | 36.4 |

*assumed

E. Biodiesel qualitative composition

The biodiesel qualitative composition in terms of FAME was analyzed using a Hewlett-Packard G1800A GCD Serie II gas chromatograph equipped with an electron ionization detector (Avondale, Pennsylvania, USA). The capillary column was a HP-Innowax polyethylene glycol (PEG) (30m x 0.25mm I.D., 0.50 μm film thickness). An external standard of 37 FAMES (Supelco, 18919-1AMP) was used to identify the different FAMES.

The biodiesel chromatographic analysis was performed with a similar procedure used by Lisa et al. [24]. Using a constant injector temperature of 250°C and helium (carrier gas) at a flow rate of 0.7 mL/min, the oven was maintained at 160°C for 6 min, heated from 160 to 200°C at 20°C/min, heated from 200 to 240°C at 5°C/min and maintained at 240°C for 28 min.

III. RESULTS AND DISCUSSION

A. Effect of reaction time

Fig. 1 presents the biodiesel yield and viscosity (22°C) for homogenous alkali-catalyzed transesterification of canola oil as a function of the reaction time at 60°C. As seen in Fig. 1, for reaction times between 0.5 and 1.5h, the biodiesel yield varied from 77 to 88% (g biodiesel/g oil) while the kinematic viscosity remains relatively stable ($6.64 \pm 0.1 \text{ mm}^2/\text{s}$). For transesterification reaction time ranging from 1.5 to 2h, the biodiesel yield decreased from 88 to 81% (g biodiesel/g oil) while the kinematic viscosity increased from 5.55 to 6.55 mm^2/s .

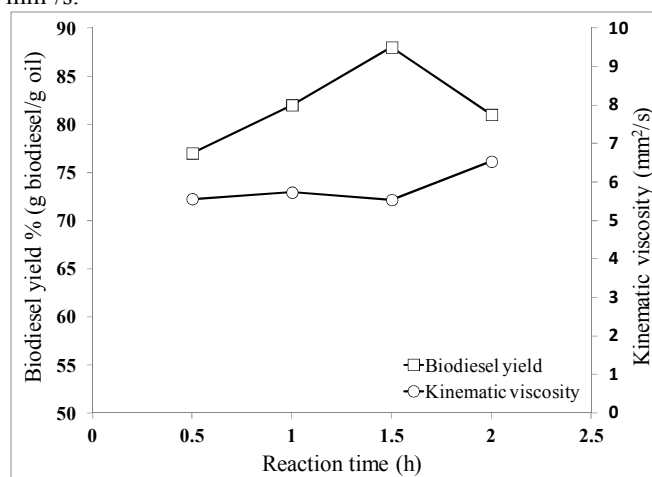


Fig. 1 Biodiesel yield and viscosity (22°C) as a function of the time for canola oil biodiesel

From Table I and Fig. 1, the kinematic viscosity of canola oil decreased from 33.8 to less than 6.5 mm^2/s , which indicates that the transesterification of the lipids was effective. The first goal of transesterifying an oil is to reduce its viscosity and to increase its volatility in order to avoid deposits in the combustion chamber [25]. The fact that the biodiesel yield increases with the reaction time for canola oil was also observed in the literature. As an example, using canola oil in methanol, with a homogenous alkali catalyst (KOH) at a temperature of 65°C, an agitation speed of 600 rpm and other similar operating conditions than the ones used in the present study, Rashid and Anwar [26] observed an increase of FAME yield from 88 to 96% (g FAME/g oil) for reaction times from 0.42 to 1.5h. However, they did not observe a decrease of biodiesel yield for a higher reaction time as observed in the present study. The fact that the biodiesel yield was lower for 2h than 1.5h could be explained by the higher viscosity of the biodiesel obtained at 2h compared to the one at 1h of reaction. In fact, the viscosity of the biodiesel reduces the contact between the fatty acids and methanol, reducing the yield of biodiesel production. A less effective separation of glycerol and biodiesel could also lead to increasing the viscosity of the biodiesel produced (the viscosity of glycerol is more than 3 times higher than biodiesel at 12 cSt) [27].

B. Comparison between canola and microalgae-based oils

Table II presents the biodiesel yield, the kinematic viscosity and the heat of combustion for both canola and microalgae-based oil for 1 h of transesterification at 60°C. For canola and microalgae oils, the biodiesel yield, kinematic viscosity (22°C) and heat of combustion obtained were respectively 82.0% (g biodiesel/g oil), 6.51 mm²/s and 39.9 MJ/kg. Under the same operating conditions, microalgae-based oil biodiesel had a higher yield (89.7% (g biodiesel/g oil)), a lower kinematic viscosity (4.27 mm²/s), and a lower heat of combustion (37.1 MJ/kg).

TABLE II
BIODIESEL YIELD AND PROPERTIES AS A FUNCTION OF OIL

| | Biodiesel yield % (g biodiesel/g oil) | Kinematic viscosity (22°C) (mm ² /s) | Heat of combustion (MJ/kg) |
|----------------------|--|--|-------------------------------|
| Canola oil | 82.0 | 6.51 | 39.6 |
| Microalgae-based oil | 89.7 | 4.27 | 37.1 |

The fact that viscosity of microalgae oil-based biodiesel was lower than canola oil could be explained by the fact that microalgae and echium oil lipids had a higher content of polyunsaturated (more than 2 double bounds) with respective content up to 56% (w/w) [28] and 55% [29], which reduces the biodiesel viscosity [28]. A biodiesel with lower viscosity has the advantage of producing less friction and lower deposits in the engine [30]. However, the high polyunsaturated microalgae-oil based biodiesel tend to have lower oxidation stability and a lower cetane number (usually between 39 and 54) than vegetable oil biodiesel (45 to 70) [28, 31]. Even at a lower temperature (20 vs 40°C), the value of viscosity for microalgae biodiesel was lower than the minimum value required by the ASTM standard between 2.8 to 5.7 mm²/s [32], [33].

Producing biodiesel from the transesterification of heterotrophic microalgae lipids (*Chlorella protothecoides*) with methanol and an acid catalyst (sulfuric acid) (methanol/oil molar ratio of 56:1), Miao and Wu [34] obtained a respective maximum biodiesel yield, kinematic viscosity (40°C) and heat of combustion of 68% (g biodiesel/g oil), 5.2 mm²/s and 41 MJ/kg. Consequently, the higher yield in biodiesel obtained from the microalgae oil in the present study could be interesting even if the heat of combustion obtained was slightly lower at 37 MJ/kg.

C. Biodiesel composition

Fig. 2 presents the qualitative FAME composition of the canola oil, microalgae-based oil and canadian microalgae biodiesel produced in terms of peak area. As seen in Fig. 2, the more important FAMES in terms of peak area for respective canola oil and microalgae-based oil were oleate (C18:1) with 60.9%, linolenate (C18:3) with 32.3% and palmitate (C16:0) with 25.8%. Some FAMES were present in the microalgae-based oil that were not present in canola oil such as methyl stearidonate (C18:4) and myristate (C14:0) with peak area of respectively of 10.1 and 1.5%. The eicosapentanoate (C20:5) (EPA) FAME was present in the canadian microalgae lipids

biodiesel (almost 10%) while their peak area in canola and microalgae-based oils were negligible with 0.3 %. Moreover, the canadian microalgae lipids had more other FAME compounds than the oils with 12.7% versus less than 4.4%.

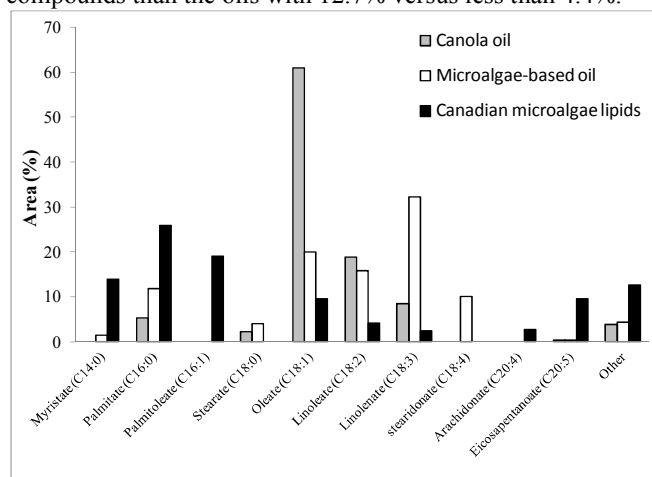


Fig. 2 Chromatographic area (%) for each FAME as a function of the type of raw material

The fact that oleate (C18:1) FAME was the most important compound for canola oil derived biodiesel was expected as it is often seen in some studies [35], [36] with up to 63% (w/w) [35]. Oleate FAME is suitable to produce biodiesel as it has a high cetane number, better resistance to oxidation and better cold properties such as cold filter plugging point (CFPP) [37].

For microalgae-based oil, linolenate (C18:3) FAME has the highest peak area, which indicates that the echium oil used in the production of the oil probably has a high content in linolenate (C18:3). In fact, echium oil (*Echium plantagineum*) used to produce the oil has a high peak area of methyl linoleate up to 43% and 13% of methyl stearidonate (C18:4) [29] while microalgal oil (*Schizochytrium sp.*) has no linolenate (C18:3) FAME [38]. A high linoleate (C18:3) content is less interesting for biodiesel production in terms of oxidation stability, but antioxidants can be added to the biodiesel in order to increase its oxidation stability [38].

IV. CONCLUSION

As many countries are looking for alternate fuel sources, biodiesel from microalgae could replace 1st generation biofuels that use arable lands. In this paper, commercial canola and microalgae-based oils were compared in order to produce biodiesel. The results of this study show that a maximum biodiesel yield of 89.7% (g biodiesel/g oil) was obtained with a homogenous alkali-transesterification (1% w/w of KOH) of microalgae-based oil with a methanol/oil molar ratio of 6:1 for a reaction time of 1h at a temperature of 60°C. The results also showed that the kinematic viscosity (22°C) of microalgae-based biodiesel was lower at 4.31 mm²/s than canola-based biodiesel while the heat of combustion obtained for microalgae-based oil was lower at 37.1 MJ/kg.

The results of qualitative FAME composition of biodiesel also showed that the biodiesel produced from microalgae-based oil had a more abundant ratio of unsaturated FAME compounds, which explained the lower viscosity and heat of combustion observed.

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