

Biodiesel production from used frying oil and microalgae: a preliminary study

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Abstract

In order to replace 1st generation biodiesel, used frying oil (UFO) and microalgae lipids (*Tetraselmis sp.*) were tested as feedstocks for biodiesel production. The following conditions were tested for UFO homogenous alkali transesterification: temperature – 60°C; methanol to UFO molar ratio – 6:1; catalyst (potassium hydroxide) to UFO mass ratio – 1%; reaction time – 10 min. A biodiesel yield of 80% (g biodiesel/g UFO) was obtained with a fatty acid methyl ester (FAME) content of 87% (g FAME/g biodiesel). For microalgae lipids homogenous acid transesterification (catalyst: sulphuric acid), a reaction time of 10 min and a temperature of 68°C led to a biodiesel yield of 50% (g biodiesel/g lipid). This study showed the potential of *Tetraselmis sp.* microalgae as feedstock for biodiesel production even if UFO resulted in a higher biodiesel yield.

Keywords: used frying oil (UFO), microalgae, transesterification, biodiesel, Tetraselmis sp.

1 Introduction

As a consequence of the increase of oil consumption, the disappearance of non-renewable sources of energy will create a problem of fuel depletion. As an example, the Energy Information Administration (EIA) estimates the oil stock to 1690 billion oil barrels [1], which would correspond to a complete depletion in 2050 [2]. This could be attributable to the increase of emerging countries industrialization such as China (second oil consumer with 10.3 million barrels per day) [3]. Consequently, in 2012, the world oil consumption was 90 million barrels per day [1] and it will reach 107 million barrels per day in 2030 (80% of this increase would be attributable to the transportation sector) [4].



In order to solve this problem, some countries have the objective to increase their biofuels (bioethanol, biodiesel, etc.) production. As an example, the United States of America will increase their biofuels production to 160 billion L by 2022 [5]. Consequently, this higher amount biofuel production could lead to several difficulties such as the availability of raw materials required to produce biodiesel and could increase the food prices. In parallel, high volumes of used frying oil (UFO) are produced from cooking industry, which represents an interesting avenue to produce biodiesel instead of using virgin oil. In the United States of America, 11.4 billion L of waste oil are produced annually by hotels and restaurants [6], which could be a part to fulfill the need in raw material for biodiesel production. Microalgae are also interesting to produce biodiesel, as these photosynthetic microorganisms can consume carbon dioxide (CO_2) and synthesize a biomass with lipid contents up to 75% dry weight [7]. Moreover, as this biomass is cultivated in water, this type of raw material for biodiesel production does not compete with food crops in opposition to oleaginous plants [8, 9]. Moreover, microalgae have growth rates and culture yields 30 times higher than other oleaginous species [7].

Fatty acid methyl esters (FAME) are produced by a transesterification reaction between 1 molecule of triglyceride, contained in oleaginous seeds or in microalgae, and 3 molecules of an alcohol (usually methanol because it is cheaper) in presence of a homogenous or heterogeneous catalyst (acid, alkali or enzymatic). Homogenous alkali transesterification is often preferred for 1st generation biodiesel production because it is faster than homogenous acid reaction [10].

On the other hand, for microalgae lipids, alkali homogenous transesterification is less effective than homogenous acid transesterification. As an example, using heterotrophic microalgae, Nagle and Lemke [11] showed that the FAME yield obtained by homogenous acid transesterification (using hydrochloric acid (HCl)) at 70°C for 30 min was 50 times higher than homogenous alkali transesterification (using sodium hydroxide (NaOH)) by employing the same operating conditions (68 vs. 1.3% g FAME/g lipid).

Among the microalgae, *Tetraselmis sp.* is a green phytoplankton [12] extensively studied for aquaculture [13], pharmacological purposes (due to antioxidant content) [14, 15] and to evaluate the marine ecotoxicity [16]. Moreover, this microalgae could be interesting for biodiesel production because its lipids content can reach up to 23% (g lipid/g dry biomass) [9].

The main objective of this project was therefore to evaluate the potential of using UFO and microalgae lipids as raw materials to produce biodiesel.

2 Materials and methods

2.1 Feedstock

Hexane, methanol and chloroform ACS grade solvents and potassium hydroxide (KOH) were purchased from Fischer Scientific inc. (Whitby, On., Canada), while sulfuric acid (H_2SO_4) (95–98 wt%) and anhydrous sodium sulfate (Na_2SO_4) (99 wt%) were provided by Anachemia (Lachine, Qc, Canada).



Raw UFO was supplied by the Université de Sherbrooke cafeteria (Université de Sherbrooke, Sherbrooke, Canada). In order to remove solids, the raw UFO was centrifugated at 4000 rpm for 30 min at room temperature. The upper phase was filtered under vacuum and dried overnight at 105°C in order to remove water traces.

Wet microalgae (*Tetraselmis sp.*) were supplied by Aquamerik Inc. (Saint-Nicolas, Qc, Canada). The microalgae size ranged from 10 to 12 micrometers with a solid content of 18 wt% (supplier data).

2.2 Microalgae lipid extraction

Frozen microalgae were lyophilized for 24 h at -50°C under reduced pressure (< 100 mbar) using a Virtis freeze dryer (model 24D824, Gardiner, New York, USA) for 1–2 days. Microalgae lipids were extracted with a 2-steps extraction using a Soxhlet apparatus: 1st and 2nd step (both for 2 h) used hexane and chloroform, respectively. The organic solvents were evaporated under vacuum (65°C) and the lipids were weighted. Following both extractions, the lipid yield obtained was $12.4 \pm 0.4\%$ (g lipid/g dry biomass) with no significant effect of the chloroform extraction. This lipid yield was slightly lower than that mentioned by Chisti [9] (15 to 23% g lipid/g dry weight) using the microalgae *Tetraselmis sp.*

2.3 Transesterification and biodiesel separation

2.3.1 Used frying oil

Into a 100 mL 3-necks round bottom flask equipped with a reflux column, 12.5 g of UFO were heated at the required temperature with magnetic stirring. Then, 2.9 g of a 4 wt% KOH-methanol solution were added to the UFO (corresponding to a methanol to UFO molar ratio of 6:1 and a KOH to UFO ratio of 1 wt%). At the end of reaction time, the flask was cooled down and the product was transferred into a separation funnel. Then, glycerol (dark brown bottom phase) was recovered and distilled water was added in order to neutralize the organic phase (biodiesel) and to wash methanol. The blend was allowed to settle for 20h, the biodiesel was recovered and dried using Na₂SO₄. Then, methanol was evaporated at 65°C under vacuum.

2.3.2 Microalgae lipids

Into a 15 mL round bottom flask equipped with a reflux column, between 0.2 and 0.3 g of the extracted lipids from *Tetraselmis sp.* were transesterified using 4 mL of a 4% (v/v) H₂SO₄/methanol solution and 1 mL hexane. The blend was heated (water bath) to 3 temperatures (24, 40 and 68°C) for 4 reaction times (10, 30, 60 and 180 min). The blend was cooled down and transferred into a separation funnel with 20 mL hexane. The organic phase (biodiesel and hexane) was recovered and washed with 20 mL distilled water. The blend was allowed to settle overnight prior to the separation. Then, Na₂SO₄ was used to dry the organic phase (biodiesel and hexane) and the organic solvent (hexane) was evaporated at 65°C under vacuum.



2.4 Biodiesel analysis

2.4.1 Physicochemical analysis

Biodiesel viscosity was measured at 40°C using a Brookfield DV-III Ultra rheological instrument (Brookfield Engineering Laboratories, Inc., Middleboro, Massachusetts, USA).

2.4.2 Gas chromatography

Qualitative biodiesel FAME composition was analysed using a Varian-3800 gas chromatograph equipped with a mass spectrometer (Varian Inc, Canada). One μL of a biodiesel-hexane solution was injected in a DB-225 cyanopropylphenyl-dimethylpolysiloxane (30 m x 0.25 mm I.D., 0.25 μm film thickness) capillary column (Agilent, Canada). The column oven was heated at 70°C for 1 min, from 70 to 180°C at 20°C/min, from 180 to 220°C at 3°C/min and maintained at 220°C for 15 min. Helium (Praxair, Canada) was used as a gas carrier at a flow rate of 2.2 mL/min (100:1 split ratio).

A commercial standard of 37 FAMES (Supelco, 18919-1AMP, USA) was used.

3 Results and discussion

3.1 Used frying oil transesterification

Figure 1 presents the biodiesel yield and the FAME content as a function of the reaction temperature for UFO transesterification. For both reaction times (10 and 60 min), the reaction temperature had a limited effect of FAME content, as the FAME contents varied respectively from 83.4 to 87.3% (g FAME/g biodiesel) and from 91.6 to 93.6 (g FAME/g biodiesel), for 10 and 60 min reaction time, respectively. The reaction temperature (for a reaction time of 60 min) has also a limited effect on the biodiesel yield with values ranging from 79.4 to 80.5% (g biodiesel/g UFO). For a 10 min reaction time, an increase of the reaction temperature from 24 to 60°C increased biodiesel yield from 64.1 to 81.0% (g biodiesel/g UFO). Over a temperature of 60°C, the biodiesel yield remained relatively stable at about 81% (g FAME/g UFO).

The fact that the temperature has no great effect on the FAME content means that the reaction of transesterification using KOH as a catalyst is a fast reaction. Despite the fact that biodiesel yields were similar for reaction times of 10 and 60 min at a temperature superior or equal to 60°C, a reaction time of 60 min is preferable in order to obtain a higher FAME content. In fact, a lower FAME content would mean that the content of unconverted UFO was higher, creating problems during the biodiesel combustion [17] and increasing the cost linked to the biodiesel purification. Furthermore, the values of viscosity obtained were significantly lower for a reaction time of 60 min ($3.47 \pm 0.50 \text{ mm}^2/\text{s}$) than for a reaction time of 10 min ($5.00 \pm 0.77 \text{ mm}^2/\text{s}$) (data not shown). It is to be noted that most of vegetable oil transesterification is performed at a temperature of 60°C for at least 60 min reaction time [18, 19].

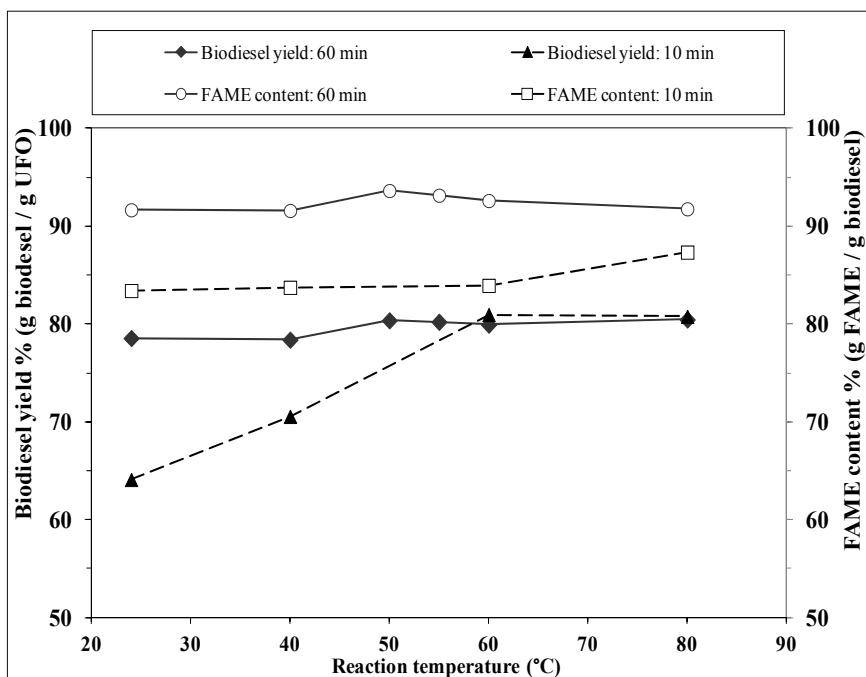


Figure 1: Biodiesel yield and FAME content for UFO transesterification for 10 min and 60 min reaction times as a function of reaction temperature (methanol to UFO molar ratio: 6:1; catalyst (KOH) concentration: 1 wt% relative to UFO).

3.2 Microalgae lipids transesterification

Figure 2 presents the biodiesel yield as a function of the temperature for microalgae lipid transesterification. For temperatures ranging from 24 to 68°C, the biodiesel yield increased from 31.1 to 50.2% (g biodiesel/g lipid) and from 41.0 to 51.0% (g biodiesel/g lipid) for respective reaction times of 10 and 60 min.

As seen in Figure 2, in opposition to homogenous alkali catalysis (Figure 1), temperature had a more important effect on the biodiesel yield, as homogenous acid catalysis is 4000 times slower than homogenous alkali catalysis [10]. Moreover, a temperature of 24°C and a reaction time of 10 min resulted in a lower biodiesel yield (~24%) compared to a reaction time of 60 min. The results indicate that the conversion of lipids contained in the microalgae is influenced by the reaction temperature [20].

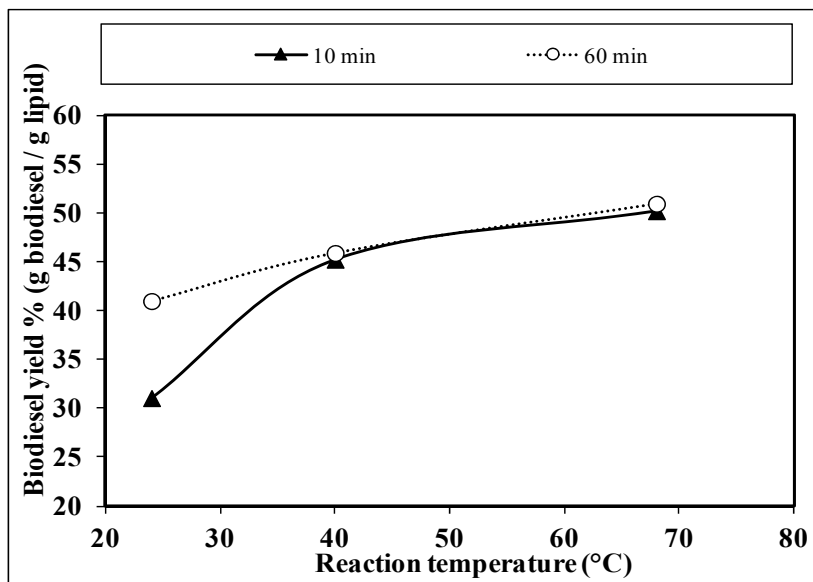


Figure 2: Biodiesel yield as a function of the reaction temperature for microalgae lipid transesterification for 10 and 60 min reaction times (methanol to lipid ratio: 13 mL/g; catalyst concentration: 4% v/v H₂SO₄/methanol solution).

3.3 Comparison of biodiesel FAME compositions

Figure 3 presents the chromatographic area for each FAME issued from UFO and microalgae biodiesel. As seen in Figure 3, the UFO biodiesel presents a very different composition compared to the microalgae biodiesel. The first difference is the number of different FAMES: Microalgae biodiesel contained 14 FAMES (from C14 to C20) while UFO biodiesel contained only 6 FAME (from C16 to C18). For UFO, the main compounds were methyl elaidate (C18:1-trans, 63.9%), methyl linoleate (C18:2, 18.7%) and methyl linoate (C18:3, 7.9%). For microalgae, the main components were methyl palmitate, (C16:0, 20.1%) methyl palmitoleate (C16:1, 17.3%) and methyl 4, 7, 10, 13 hexadecatetraenoate (C16:4, 15.0%).

One of the usual problems with microalgae lipids is the presence of polyunsaturated FAMES (> 3 double bounds) which could create problems of oxidation during biodiesel storage [21, 22]. In case of *Tetraselmis sp.* microalgae, the polyunsaturated FAMES content (such as C16:4 and C18:4) of the biodiesel (based on chromatographic relative area) was lower than 29%.

Based on these results, UFO biodiesel would be more suitable for biodiesel production than microalgae lipids because the latter would require further purification steps but polyunsaturated lipids contained in *Tetraselmis sp.* microalgae lipids could have interesting properties for other purposes than biodiesel production [23].

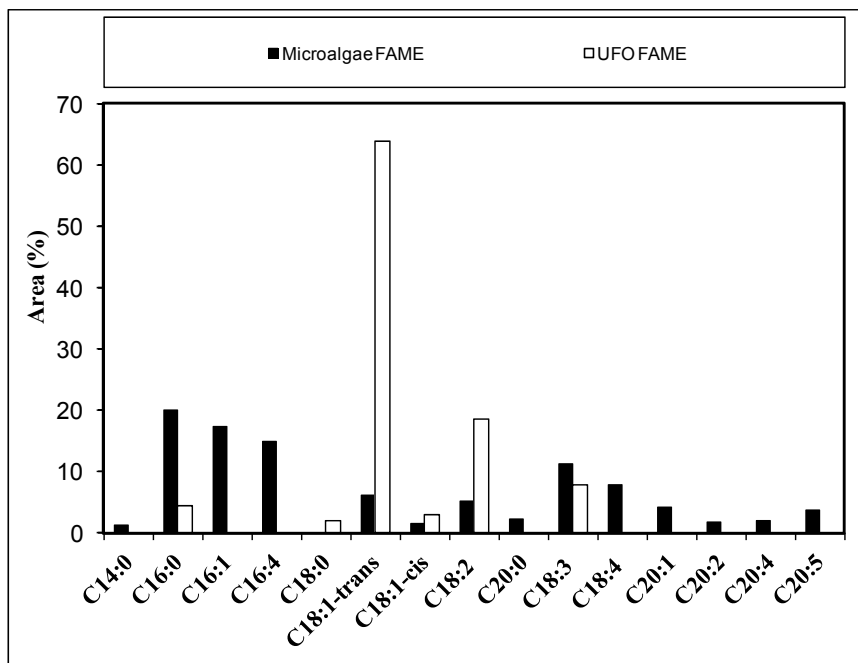


Figure 3: Qualitative FAME composition (chromatographic relative area) for UFO transesterification (temperature: 60°C; methanol to UFO molar ratio: 6:1; KOH to UFO mass ratio: 1%) and microalgae lipids transesterification (temperature: 68°C; 4% v/v H₂SO₄/methanol solution; methanol to lipid ratio: 13 mL/g) for a reaction time of 60 min.

4 Conclusion

In order to reduce oil consumption, new feedstocks should be considered to produce biofuels such as biodiesel. The main objective of this study was to test UFO and microalgae lipids (*Tetraselmis sp.*) as feedstocks for biodiesel production. For UFO homogenous alkali transesterification (KOH) at a temperature of 60°C (methanol to UFO ratio: 6:1 and catalyst (KOH) to UFO ratio: 1 wt%), the reaction time had no effect on the FAME contents (91.6–93.6 % g FAME/g biodiesel) and the biodiesel yields (79.4 to 80.5% (g biodiesel/g UFO)) which indicates that the reaction of transesterification (in these operating conditions) is not sensitive to the temperature.

For microalgae lipid homogenous acid transesterification (H₂SO₄), for a reaction time of 60 min, an increase of the reaction temperature from 24 to 68°C seems to have a significant effect on the biodiesel yield with an increase from 41.0 to 51.0% (g biodiesel/g lipid). These results showed that UFO is adapted to replace 1st generation biodiesel but *Tetraselmis sp.* microalgae biodiesel should be further investigated.

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