

WASTES: Solutions, Treatments and Opportunities1st International Conference
September 12th – 14th 2011**BIODIESEL PRODUCTION BY MICROALGAE AND MACROALGAE FROM NORTH LITTORAL PORTUGUESE COAST**J. Carvalho¹, A. Ribeiro², J. Castro³, C. Vilarinho⁴ and F. Castro⁵

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ABSTRACT

Biodiesel, as an alternative fuel, has many benefits. It is biodegradable, non-toxic and compared to petroleum-based diesel, has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. In brief, these merits make biodiesel a good alternative to petroleum based fuel. Biodiesel feedstocks derived from microalgae and macroalgae have emerged as one of the most promising alternative sources of lipid for use in biodiesel production because of their high photosynthetic efficiency to produce biomass and their higher growth rates and productivity compared to conventional crops. In addition to their fast reproduction, they are easier to cultivate than many other types of plants and can produce a higher yield of oil for biodiesel production.

In this work biodiesel was produced using the species of microalgae *Chlorella emersonii* and *Botryococcus braunii* due to its high oil content. Biodiesel productions through macroalgae oil are in preliminary phase. Therefore, results and methodology will not be presented in this work. Technological assessment of process was carried out to evaluate their technical benefits, limitations and quality of final product. In this work biodiesel from microalgae oil was produced by an alkali-catalyzed transesterification and it was achieved 93% of mass conversion. The evaluation of quality from raw materials and final biodiesel was performed according to standard EN 14214. Results show that all parameters analyzed meet the standard and legislation requirements. This evidence proves that in those operational conditions the biodiesel produced from microalgae can substitute petroleum-based diesel.

Keywords: Biodiesel, Microalgae oil, Alkali-Catalyzed Transesterification**INTRODUCTION**

Energy is the most fundamental requirement for human existence and activities. As an effective fuel, petroleum has been serving the world to meet its need of energy consumption. But the dependence of mankind entirely on the fossil fuels could cause a major deficit in future. The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel [1, 2]. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide [1, 3]. Biodiesel reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel [4]. Puppen [5] have discussed the advantages of biofuels over fossil fuels to be: (a) availability of renewable sources; (b) representing CO₂ cycle in combustion; (c) environmentally friendly; and (d) biodegradable and sustainable. Other advantages of biodiesel are as follows: portability, ready availability, lower sulfur and aromatic content, and high combustion characteristics. Biodiesel, which is considered as a possible substitute of conventional diesel fuel is commonly, composed of fatty acid methyl esters that can be

prepared from triglycerides in vegetable oils by transesterification with methanol [6]. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics [7].

Transesterification is the process by which the glycerides present in fats or oils react with an alcohol in the presence of a catalyst to form esters and glycerol [8, 9, 10]. Catalyst increases the rate of the reaction and also the yield. This reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates [11]. Depending on the undesirable compounds (especially FFA and water), each catalyst has its advantages and disadvantages. Sodium hydroxide is very well accepted and widely used because of its low cost and high product yield [12]. The most common alcohols widely used are methyl alcohol and ethyl alcohol. Among these two, methanol found frequent application in the commercial uses because of its low cost [9].

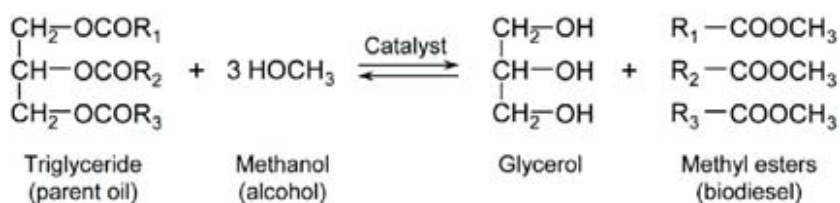


Figure 1 – Structure of triglycerides and principles of transesterification reaction

Vegetable oils are promising feedstocks for biodiesel production since they are renewable in nature, and can be produced on a large scale and environmentally friendly [11]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [13,14,15]. For instance, the mass plantation of monoculture plants could benefit the economy of rural population while negatively affecting the water resources and the biodiversity [14]. In order to overcome these disadvantages, many researchers are interested in others feedstocks as Algae oil [2,12,16,17].

The aim of this study was to evaluate biodiesel production through microalgae oil, testing different operating conditions and equipment designs for each stage of processing. Technological assessment of this process was carried out to evaluate their technical benefits, limitations and quality of final product.

MICROALGAE

Microalgae have high potentials in biodiesel production compared to other oil crops. First, the cultivation of microalgae does not need much land as compared to others plants [18]. Biodiesel produced from microalgae will not compromise the production of food and other products derived from crops. Second, microalgae grow extremely rapidly and many algal species are rich in oils. For instance, heterotrophic growth of *Chlorella* can accumulate lipids as high as 55% of the cell dry weight after 144 h of cultivation [19]. Oil levels of 20–50% are common in microalgae [18]. These technological advances suggest that the industrial production of biodiesel from microalgal oils may be feasible in the near future.

The advantages of culturing microalgae as a resource of biomass are:

- i. Algae are considered to be a very efficient biological system for harvesting solar energy for the production of organic compounds;
- ii. Algae are non-vascular plants, lacking (usually) complex reproductive organs;
- iii. Many species of algae can be induced to produce particularly high concentrations of chosen, commercially valuable compounds, such as proteins, carbohydrates, lipids and pigments;
- iv. Algae are microorganisms that undergo a simple cell division cycle;
- v. Microalgae can be grown using sea or brackish water;
- vi. Algal biomass production systems can easily be adapted to various levels of operational or technological skills [11,12,16,17,20]

BIODIESEL PRODUCTION WITH CATALYZED TRANSESTERIFICATION

Alkali-catalyzed transesterification

The use of alkali catalysts in transesterification reaction of microalgae oil is somewhat limited, because FFA content presents in this feedstock oil reacts with the most common alkaline catalysts (NaOH, KOH, and CH_3ONa) and forms soap [8]. This reaction is undesirable because soap lowers the yield of the biodiesel and inhibits the separation of esters from glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve a higher cost [9]. Feedstocks with high free fatty acid will react undesirably with the alkali catalyst thereby forming soap. Maximum amount of free fatty acids acceptable in an alkali-catalyzed system is below 3 wt. % FFA. If the oil feedstock has a FFA content over 3 wt.%, a pretreatment step is necessary before the transesterification process [14].

Process design

Fig. 1 shows a simplified flow chart of the alkali-catalyst process tested in this study for the transesterification of microalgae oil.

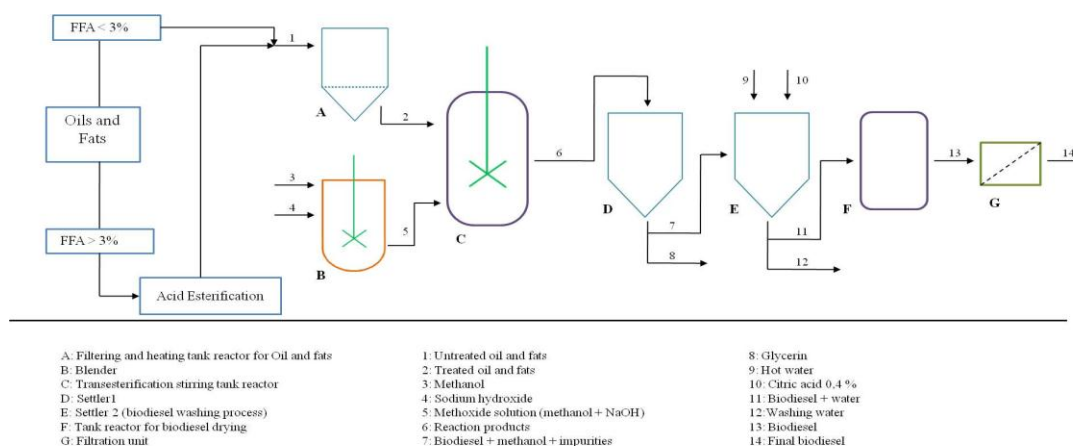


Figure 1 - Simplified process flow chart of alkali-catalyzed biodiesel production

Materials and experimental procedure

Materials

The fuel properties of microalgae methyl ester were determined at laboratory of CVR (Center for Waste Valorization) and FEUP (Engineering Faculty of Porto University). Microalgae species were chosen taking into account its content in oil. Therefore was selected the species of *Chlorella emersonii* and *Botryococcus braunii* which were purchased from ACOI - Coimbra Collection of Algae. Methanol (purity 99.7%) and sodium hydroxide with purity of 99% was purchased from Sigma-Aldrich, which were employed as the alkali catalysts in the reaction. Sulfuric acid was also purchased from Sigma-Aldrich, which were employed as the acid catalysts in the esterification reaction. Citric acid was also purchased from Sigma-Aldrich, which were employed in the washing process.

Microalgae oil

The microalgae cultures were development in semi-open flasks, to simulate the conditions of photobioreactors. The medium used, designated M7 medium was prepared according to seaweed collection provided by ACOI - Coimbra Collection of Algae. The recovery process for collecting algae biomass was realized trough flocculation by aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), iron chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). For the oil extraction were tested an ultrasound rupture system. Before transesterification, microalgae oil was filtered and heated among 65 - 70 °C for 30 min. Methanol (5:1 molar ratio methanol/oil) was mixed with sodium hydroxide (0.25% w/w), until all of the NaOH was dissolved in methanol. This mixture was then added to the

oil, and further heated to 60 °C, for 2 h. The ester was purified by washing with distilled water and citric acid and drying at 100 °C for 4 h. The final polishing process was realized by filtering the methyl ester in a filtering unit system.

Results and Discussion

Oil extraction

For collecting algae biomass it was tested three flocculants: aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), iron chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$). The results showed a similar behavior for the three flocculants tested. Oil extraction was accomplished by utilization of ultrasound to promote cellular rupture during 1 hour. Table 1 shows the oil extraction yield for both microalgae species tested.

Table 1 – Oil extraction yield for *Chlorella emersonii* and *Botryococcus braunii*

	Algae biomass (g/l)	Dry weight (g/l)	%	Extracted Oil (g/l) (dry weight)	%
<i>Chlorella emersonii</i>	115.2	37.4	32.2	14.8	39.7
<i>Botryococcus braunii</i>	86.0	36.1	42.0	18.3	50.7

Results showed that *Chlorella emersonii* achieved $14.8 \text{ g}_{\text{oil}}/\text{l}_{\text{algae culture}}$ and *Botryococcus braunii* obtained $18.3 \text{ g}_{\text{oil}}/\text{l}_{\text{algae culture}}$. Considering the culture time and total algae biomass produced it was reached an extraction coefficient of $3.7 \text{ g}_{\text{oil}} \text{ d}^{-1}$ for *Chlorella emersonii* and $4.6 \text{ g}_{\text{oil}} \text{ d}^{-1}$ for the *Botryococcus braunii*. Campbell *et al.* [21] realized a technical-economic study for biodiesel production through *Chlorella* microalgae. In that study, they concluded that it was necessary an extraction yield of $30 \text{ g}_{\text{oil}} \text{ m}^{-2} \text{ d}^{-1}$ to economic ensure the process. The lower growth rate and extraction coefficient obtained in this work can be explained by the utilization of semi-open flasks to simulate an open batch photobioreactor. According to Brennan and Owende [16] this type of reactor presents the lowest biomass growth rate.

Mass conversion

One of the most important dependent variables in this experiment is the mass conversion, which is given by the mass ratio of biodiesel (product) to the total initial mass of the raw material and the additives [1]. Table 2 shows the mass conversion from transesterification reaction on microalgae oil.

Table 2– Mass conversion (%) of biodiesel from microalgae oil

	FFA content [%]	Mass conversion [%]
Microalgae oil	<1	93

Mass conversion depends on several parameters like, reaction temperature and pressure, reaction time, rate of agitation, type of alcohol used and molar ratio of alcohol to oil, type and concentration of catalyst used and principle concentration of free fatty acids (FFA) in the feed oil [8,9,22]. In this case previous FFA determination revealed that microalgae oil has less than 1%. Therefore it was realized an alkali-catalyzed transesterification. The results demonstrated that microalgae biodiesel was the maximum mass conversion of 93%.

Quality of Biodiesel

The major focal point for biodiesel high quality is the adherence to biodiesel standard specifications. These standard specifications in European Union are established by EN 14214 for biodiesel fuel [1,8,23]. The results of the analyses in the different types of biodiesel produced (Table 3) showed that in generally the quality parameters of standard EN 14214 was accomplished

Table 3 – Results of biodiesel produced from algae oil according to standard EN 14214

Property	Unit	Microalgae biodiesel result	Limits		Test Method
			Minimum	Maximum	
Ester content	% (m/m)	97,5 ± 0,2	96,5		EN 14103
Density at 15 °C	kg/m ³	862 ± 5	860	900	EN ISO 3675
Viscosity at 40 °C	mm ² /s	4,21 ± 0,05	3,00	5,00	EN ISO 3104
Flash point	°C	160 ± 1,5	120	-	EN ISO 3679
Carbon residue	% (m/m)	0,05 ± 0,01	-	0,30	EN ISO 10370
Water content	mg/kg	472 ± 5	-	500	EN ISO 3679
Acid value	mg KOH/g	0,36 ± 0,05	-	0,50	EN 14104
Iodine value	g iodine/100 g	110 ± 1,50	-	120	EN 14111
Linolenic acid methyl ester	% (m/m)	4,6 ± 0,20	-	12,0	EN 14103
Methanol content	% (m/m)	0,1 ± 0,01	-	0,20	EN 14110
Group I metals (Na + K)	mg/kg	4,02 ± 0,15	-	5	EN14108 EN 14109

Conclusions

Biodiesel is gradually gaining acceptance in the market as an environmentally friendly alternative diesel fuel. However, for biodiesel to established and continue to mature in the market, various aspects must be examined and overcome. Some of the key issues such as improving efficiency of the production process and using low cost feedstock have been reviewed and analyzed in this work. Biodiesel production from microalgae oil presents various advantages compared to other low cost feedstocks. However in other to compete with petroleum-based fuels cost, biodiesel production from microalgae needs to be cheaper.

On this work it was possible to conclude the technically feasibility of the process. Microalgae oil had a high yield of conversion and analyses on final biodiesel showed that all quality parameters of the standard 14214 have been respected. According to these results, it is possible to conclude that the biodiesel produced with these feedstock was liable to be used in diesel car engines, in a unique way (B100) or blending with fuel diesel (B20, B30 and B50), without decrease of engine efficiency. Nonetheless is important to note that in this work microalgae growth rate and extraction coefficient had low yields which increased cost-production. The solution for this problem requires improvements in algal biology, and in photobioreactor engineering, as the usage of tubular photobioreactors.

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