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PRODUCTION AND ENERGETIC ANALYSIS OF MICROALGAE BIODIESEL THROUGH SAPONIFICATION PROCESS

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Abstract. *The economic and population growth and the consequent increase in energy demand today make the search for alternative energy sources becomes critical task for the scientific community. The microalgae are shown as a possible new source for the production of biofuels such as bioethanol and biodiesel. One of the major difficulties of microalgae biodiesel production is the oil extraction from the biomass. The cases reported in the literature are only analytical and in laboratory scale. This study aimed to evaluate the saponification process on a pilot scale for the extraction of oil and the consequent production of biodiesel. The energy consumption analysis of the process was also promoted. The best results demonstrated the extraction of 100 g of free fatty acids from 2 kg of microalgae dry biomass and the produce of 100 g of esters with 84% of purity. The energy analysis showed that the extraction of fatty acids from microalgae was feasible energy (energy yield 1.74) when compared to traditional methods which require the drying of the biomass. Assessing only the drying of biomass, the energy efficiency was 0.22.*

Keywords: *biodiesel, microalgae, saponification, energertic analysis*

1. INTRODUCTION

Microalgae are autotrophic micro-organisms present in aquatic systems. They exhibit great diversity of forms, features and ecological functions and can also be economically exploited in various fields (Campos *et al.,* 2010). The biochemical composition of microalgae, the total concentration of proteins, lipids and carbohydrates may vary with the species and growing conditions such as light intensity, temperature, nutrients, agitation, pH and growth phase (Brown *et al,*. 1997; Miao and Wu, 2004).

The interest in the use of microalgae to obtain biofuels has increased recently (Chisti, 2007). Biofuels that can be obtained from microalgae are the biogas from the anaerobic digestion of biomass microalgal; biodiesel from the oil of the microalgae, and the gaseous hydrogen produced bio-photobiologically.

The oil obtained from the microalgae is classified as a raw material of third generation biofuels. It's a potentially interesting economic alternative to fuels from other generations. Oil production by microalgae can be 20 times higher as compared to oil plant species (Chisti, 2007; Ahmad *et al,* 2011;. Feng *et al.,* 2011).

The lipid content of the cells of microalgae varies on average from 20% to 40% in terms of dry biomass, however, some studies report a lipid content of more than 85% for certain species of microalgae (Ma and Hanna, 1999; Luque *et al.,* 2010; Mairet *et al.,* 2011). These microorganisms can produce 25-220 times more than triacylglycerides terrestrial oil plants (Ahmad *et al.,* 2011).

After the cultivation of microalgae and the recovery of the biomass, oil extraction is performed. The extraction can be performed by physical methods, chemical, or both. These methods must be efficient, easy scaling, do not damage the oil and low energy consumption (Rawat, 2011).

There are several microalgae oil extraction methods described in the literature. One of these methods is the extraction through Soxhlet apparatus. However, this method consumes a lot of energy to heat large amounts of solvent

used for this process. Another problem is the possible thermal degradation of lipids due to the large amount of time that the system is heated (Luke and Garcia de Castro-Ayuso, 1998).

Other methods described in the literature and also used in order to extract lipids are Folch (Folch *et al.*, 1957) and Bligh & Dyer (Bligh and Dyer, 1959). These methods do not require heating, so there's no energy expenditure for that part of the process. However, both processes have other disadvantages as: are analytical methodologies, difficult scaling up; applicable only in dry or low moisture biomass and use toxic solvents and generate large amounts of toxic residues (Shin *et al.*, 2014).

The aim of this study was to evaluate the chemical and energy efficiency of the saponification process, on a pilot-scale, to extract fatty acids from microalgae biomass. Also the production of biodiesel was performed by enzyme method from the extracted fatty acids.

2. MATERIALS AND METHODS

2.1 Microalgae

The microalgae used in this study was *Scenedesmus* sp., obtained from cultivation in compact tubular photobioreactors of $10m^3$ in NPDEAS using as culture medium swine manure at a concentration of 2.5%. The figure 1 shows the photobioreactor of NPDEAS in which the microalgae was cultivated. The biomass was centrifuged in an industrial centrifuge at 3000 rpm and the final humidity achieved was 80%. The determination of the saponification mass yield was made by gravimetric analysis.

Figure 1. Photobioreactor where the microalgae *Scenedesmus* sp. was cultivated.

2.2 Saponification

Fatty acids were extracted from the biomass by saponification. The biomass (10 kg) containing about 80% moisture was directly saponified in the presence of NaOH (0.1 $g.g^{-1}$ biomass) and ethanol (96.5% v / v - 1 $mL.g\ biomass^{-1}$) and stirred at inox reactor of 30 liters for one hour at 500 rpm and 60 ° C using methodology enhanced by Schroeder *et al.* (2011).

Thereafter, protonation is carried out with the addition of concentrated HCl to the alcoholic solution until the pH decreased to 1.0, releasing free fatty acids. The free fatty acids were extracted from alcoholic solution through a liquid-

liquid extraction using hexane. The phase separation was made in separatory funnel, the organic phase containing hexane was evaporated, leaving just the free fatty acids extracted. Figure 2 shows the experimental apparatus used to perform the saponification reaction:

Figure 2. Reactor utilized for the extraction of fatty acids by saponification process.

2.3 Biodiesel by enzimatic esterification

The enzymatic esterification of free fatty acids from microalgae was performed with the immobilized enzyme Novozym® CAL B 435 (Novozymes). The reaction proceeded for 24 hours at 40 ° C. The reaction medium contained 1.5 liters of hexane, 100 g of free fatty acids and 10 grams of the enzyme. The next step was the filtration of the reaction medium with cellulose filter to recover the enzyme imibilizada. Thereafter, the hexane was evaporated, leaving only the esters produced during the reaction and unreacted compounds. The percentage of esters contained in enzymatic biodiesel was evaluated by ANP standard (EN 14103). The Figure 3 shows the complete flowchart of the process developed in this study.

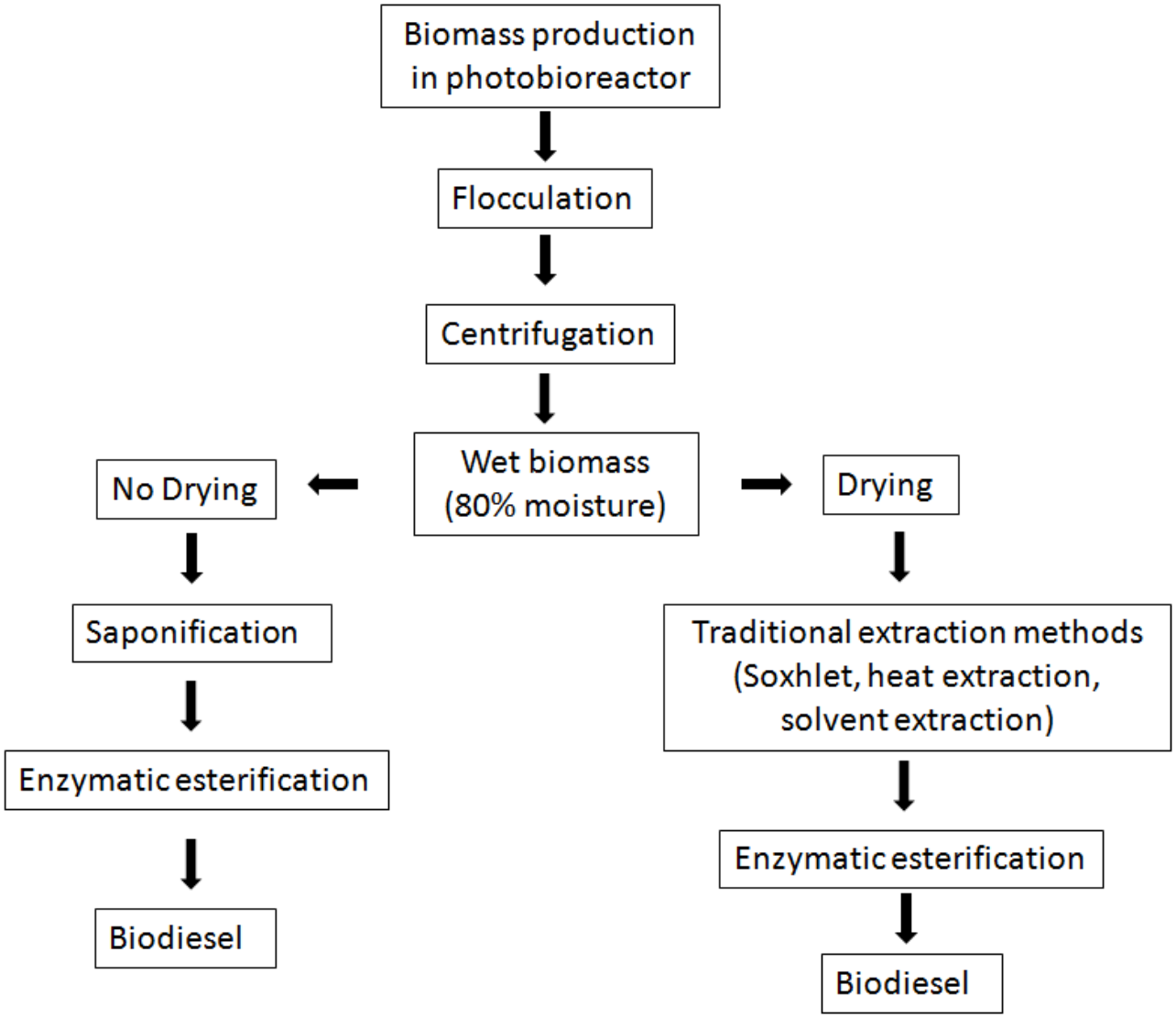

Figure 3. Flowchart of the process of biodiesel production from microalgae.

2.4 Energetic analysis comparisson

For energetic analysis, two paths of biodiesel production was analyzed, the wet path and the dry path. For the wet path, the energetic analysis was stipulated, for calculation basis, 10 kg of wet biomass with 80% humidity. In calculating of the energetic analysis, the saponification was considered the stage that consumes more energy. The energy expenditure was considered for heating the reactor from 20° C to 60° C. With this amount of wet biomass are needed 10 kg of ethanol as reaction medium. It was found that the reaction mixture is compound of ethanol and water in the biomass. The dried biomass and sodium hydroxide for they are in very small amounts compared to ethanol and water were disregarded for the calculation of energy balance.

To the dry path, the stage that consumes more energy is the drying. To calculate the drying was found that a reduction of biomass humidity from 80% to 10% is required. It was considered that the energy expended in drying taking into account the enthalpy of evaporation of water at 60 ° C.

3. RESULTS AND DISCUSSION

3.1 Saponification and biodiesel production through enzimatic esterification

Throuh the saponification process, it was obtained 100 grams of free fatty acids from 10 kg of wet biomass with 80% humidity. The enzymatic reaction produced 100 grams of biodiesel with a percentage of 84% of esters.

3.2 Energetic analysis

To calculate the wet path, in the reaction medium, there is 10 kg of ethanol and 8 kg of water (10 kg of biomass with 80% humidity equals to 8 kg of adsorbed water in the biomass). The amount of heat for heating the reaction medium from 20 ° C to 60 ° C can be estimated by using the sensible heat of the equations:

$$Q_{Eth} = M_{Eth}.cp_{Eth}.(60-20) \quad (1)$$

$$Q_{Wat} = M_{Wat}.cp_{wat}.(60-20) \quad (2)$$

The specific heat of ethanol and water are 2443.47 J.kg^{-1} and 4180 J.kg^{-1} respectively. Thereby it is obtained that:

$$Q_{Eth} = 977\,\mathrm{k}J \quad (3)$$

$$Q_{Wat} = 1337\,\mathrm{k}J \quad (4)$$

$$Q_{Tot} = 2314\,kJ \quad (5)$$

The enthalpy of the reaction was disregarded in this calculation, considering that in 10 kg of wet biomass there is approximately 100 grams of fatty acid, equivalent to 0,4 mole of fatty acid about (based on palmitic acid). The enthalpy for saponification of 1 mol of fatty acid release only 11 heat kJ, negligible as compared to total 2314 kJ spent on heating the reactor.

To the dry path, with respect to drying the biomass, for the moisture reduction from 80% to 10% in 10 kg of wet biomass, is necessary to evaporate 7.7 kg of water. Therefore the final amount of water adsorbed onto the biomass is 0.3 kilograms. The enthalpy of vaporization of water is 2360.47 kJ.kg^{-1}, there has then:

$$Q_{evap} = M_{Wat}.H_{Wat} \quad (6)$$

$$Q_{evap} = 18172\ kJ \quad (7)$$

The heat released in the combustion of 1 mol of hexadecanoate methyl (based on the calculation that all fatty acid sample was palmitic acid) is 10107 kJ/mol. The energy efficiency of the two processes can be calculated as follows:

$$Ef_{sap} = \frac{Q_{gen}}{Q_{con}} \quad (8)$$

$$Ef_{sap} = 1.74 \quad (9)$$

$$Ef_{dry} = \frac{Q_{gen}}{Q_{con}} \quad (10)$$

$$Ef_{dry} = 0.22 \quad (11)$$

Therefore, the traditional oil extraction process that requires biomass drying demands more energy than it is contained in the biodiesel.

4. CONCLUSIONS

Microalgae are a promising alternative for the production of alternative biofuels. Improve the parameters of cultivation, maximize productivity and reduce costs and energy consumption is fundamental for establishing this new technology. This study investigated the saponification process as an alternative method for extracting fatty acids from microalgae. It was demonstrated the lower energy consumption of the process when compared to steps of traditional methods of lipid extraction. Furthermore, through the experimental process, it was possible to extract the fatty acids and biodiesel was produced by enzymatic method.

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6. REFERENCES

Ahmad, A.L., Yasin, N.H.M., Derek, C.J.C. and Lim, J.K., 2011. Microalgae as a sustainable energy source for biodiesel production: a review. *Renewable and Sustainable Energy Reviews*. Vol. 15, p. 584-593.

Bligh, E. G., and Dyer, J. W., 1959. A Rapid Method of Total Lipid Extraction and Purification. *Canadian Journal of Biochemistry and Physiology*. Vol. 37, p. 911-917.

Brown, M.R., Jeffrey, S.W., Volkman, J.K. and Dunstan, G.A., 1997. Nutritional properties of microalgae for mariculture. *Aquaculture*. Vol. 151 p. 315-331.

Campos, V. B., Barbarino, E. and Lourenço, S. O., 2010. Crescimento e composição química de dez espécies de microalgas marinhas em cultivos estanques. *Ciência Rural*. Vol.40, n.2, p. 339-347.

Chisti, Y., 2007. Biodiesel from microalgae. *Biotechnology Advances*. Vol. 25, p. 249-306.

Feng, Y., Li, C. and Zhang, D., 2011. Lipid production of Chlorella vulgaris cultured in artificial wastewater medium. *Bioresource Technology*. Vol. 102, p. 101-105.

Folch, J., Lees, M., and Stanley, G. H. S.,1957. A Simple Method for the Isolation and Purification of Total Lipids from Animal Tissues, *Journal of Biological Chemistry*. Vol. 497, p. 497-509.

Luke de Castro, M. D., and Garcìa-Ayuso, L. E., 1998. Soxhlet Extraction of Solid Materials: as Outdated Technique with a Promising Innovative Culture, *Analytica Chimica Acta*. Vol. 369, p. 1-10.

Luque, R., Lovett, J.C., Datta, B., Clancy, J., Campelo, J.M. and Romero, A.A., 2010. Biodiesel as feasible petrol fuel replacement: a multidisciplinary overview. *Energy Environmental Science*. Vol. 3, p. 1706–1721.

Ma, F. and Hanna, M.A., 1999. Biodiesel production: a review. *Bioresource Technolony*. Vol. 70, p. 1-15.

Mairet, F., Bernard, O., Masci, P., Lacour, T. and Sciandra, A., 2011. Modelling neutral lipid production by the microalga Isochrysis aff. galbana under nitrogen limitation. *Bioresource Technology*. Vol. 102, p. 142-149.

Miao, X. and Wu, Q., 2004. High yield bio-oil production from fast pyrolysis by metabolic controlling of Chlorella protothecoides. *Journal of Biotechnology*. Vol. 110, p. 85-93.

Rawat I., Kumar R.R, Mutanda T. and Bux F., 2011. Dual role of microalgae:phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. *Applied Energy*. Vol. 88, p. 3411-3424

Rawat, I., Ranjith Kumar, R., Mutanda, T., and Bux, F., 2013. Biodiesel from microalgae: a critical evaluation from laboratory to large scale production, *Applied Energy*, Vol. 103. p. 444-467.

Schroeder, L., Schafranski, A. S., Mello, T. C., Barbosa, F. T., Mariano, A. B., Vargas, J. V. C., 2011. "Methodology for Fatty Acid Extraction from *Scenedesmus* spp. Biomass for Production of Biodiesel. In *Proceedings of the 21st International Congress of Mechanical Engineering -COBEM 2011*. Natal, Brazil.

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