MICROALGAE BIOMASS LIPID EXTRACTION – AN ENERGY AND COST ANALYSIS APPROACH OF PROCESS

Gustavo Strauch Wilin Finger, finger.gustavo@gmail.com
Lorena Panage Moura, lorena.panage.moura@gmail.com
UFPR - Federal University of Parana, CP 19011, 81531-980, PR, Brazil
Center for Reshearch in Self-Sustanable Energy (NPDEAS)
Post-Graduation Program in Material Science and Engineering (PIPE)

Gustavo Issamu Ogasawara, gusissamu@gmail.com
Isabela Caserta, casertaisabela@gmail.com
UFPR - Federal University of Parana, CP 19011, 81531-980, PR, Brazil
Center for Reshearch in Self-Sustanable Energy (NPDEAS).
Chemical Engineering College

Andre Bellin Mariano, andrebmariano@gmail.com
Jose Viriato Coelho Vargas, vargasjvcv@gmail.com
Wellington Balmant, wbalmant@gmail.com
UFPR - Federal University of Parana, CP 19011, 81531-980, PR, Brazil
Center for Reshearch in Self-Sustanable Energy (NPDEAS)
Post-Graduation Program in Material Science and Engineering (PIPE)

Abstract. *In order to produce biodiesel from microalgae biomass, the extraction of lipids from dry biomass is needed. The most used way is due to liquid extraction using organic solvents. In this process, lipids were extracted by 50% molar mixture of hexane and ethanol with a high effectiveness in lipids removal. The biomass used was produced by engineering scale photobioreactors (PBR) with 10 m*^{3} *capacity exposed to sunlight in Curitiba-Brazil. The process is carried out in an agitated batch reactor with a 20 L capacity, which processes 3 kg of algae biomass using 15 L of solvent mixture at 50ºC during 3.5 hours. Since the energy demand and the cost associated with the whole process are essential to any viability analysis, all equipment involved in such process was evaluated in terms of its electricity consumption in both transition state and steady state. The energy involved in the extraction was performed using thermodynamic energy balances and the subsequent solvent recuperation was evaluated and taken into account as well. The energy cost in all process of separation is the main problem to the industrial application of algae biomass and the study of its unit operation in pilot scale such as these are critical to determine if the process are viable or not. The total power demand of a batch was 11.73 kWh for a single process of oil extraction, which equals to R$ 8.9 of cost with electricity. The total power spent in each process of oil extraction were evalueted and presented as well.*

Keywords*: Thermal Analysis, Lipid Extraction, Algae Biomass, Cost Analysis*

1. NOMENCLATURE

Symbol	Definition
$\cos\varphi$	Power Factor
$\dot{m}$	Mass flow
$\dot{Q}$	Heat Flow
$\dot{W}$	Work flow
ANEEL	Brazilian Electrical Energy Agency
G8	Group of eight highly industrialized nations
h	Enthalpy of water flow
I	Electric Current
L	Liters
NPDEAS	Center for Self-Sustainable Energy
R$	Brazilian Currency Money - 'Reais'
U	Voltage
U$	USA Currency Money – 'Dollars'

Units	Definition
A	Ampere
h	hour
kJ	Kilo Joules
kWh	Kilo Watt Hour

Subscripts	Definition
in	Entering the Control Volume
out	Exiting the Control Volume

2. INTRODUCTION

The world energetic matrix is 79% dependent on fossil fuel (Pereira, 2012). Nowadays, the uses of diesel each year is about 1450 billion L, representing a direct CO_2 emission of 3886 billion kg, 12% of all CO_2 emissions; furthermore, it has been debated the fossil fuel environmental impact (Pereira, 2012) and its influence in global warming (Speranza, 2015). The renewable energy is an opportunity to minimize emissions (Pereira, 2012).

Another reason backing up renewable energy lays on the growing need of energy expected to increase 59% by 2035 (Viêgas, 2015). Also, the International Energy Outlook projects the oil price to reach U$ 133 per barrel. (Pereira, 2012).

According to ANEEL, the production of biodiesel is growing [ANEEL]. Also, according to the Brazilian Agency of Natural Gas, Petroleum and Biofuel, in 2007 the country produced 402,154 m^3 to supply national and global market and, in 2008, the quota reached 784,832 m^3. This improvement was a consequence of a governmental program that stimulated production, the National Production and Use of Biodiesel (PNPB) [ANEEL].

The International Energy Agency (IEA) noticed that energy efficiency policies have a crucial participation in climate changes and economic objectives. Therefore, they suggested G8, 25 new efficiency policies in 2008. These suggestions have seven main areas including industry (Santana, 2015).

In recent study, there are three ways to improve energy efficiency: applying a more efficient technology, changing the behavior or converting the energy matrix to alternative fuels (Santana, 2015).

Renewable energy such as solar, wind and hydro can replace fossil fuels in several sectors. However, substitution of fossil fuels in transport can only be made by renewable fuel (Gnansounou and Raman, 2015). Biodiesel can be produced from several kinds of oil, such as soybean, corn oil, palm oil or algal oil. Difficulties in obtaining renewable fuel (e.g., biohydrogen, ethanol, biodiesel), in comparison to fossil fuel obtained directly by mineral extraction, are that renewable fuel requires energetically efficient systems to comply with the demand, so that the energy balance is compensatory. Cogeneration, tri-generation or multi-generation systems are possible alternatives to pursue, in order to reach that objective (Vargas et al., 2014). Microalgae has been considered an important third-generation feedstock, and its high lipid content is appreciated for biodiesel production (Lam and Lee, 2012). In addition, algae dry mass may have high amount of carbohydrates, which is ideal for bioethanol production (Hu et al., 2008).

The microalgae oil is environmentally interesting due to its ability to yield oil without requiring large areas of arable lands compared to traditional biodiesel production using vegetal biomass. Algae biomass is used to produce different and high value products such as dyes and biomedical products. To make biodiesel production viable it is important to connect biofuel production to these processes and reduce its total cost (Rizwan and Gani, 2015). Other advantages are faster growth and reduced need for water and other inputs (De Farias Silva and Bertucco, 2015).

Algal biodiesel production places in growth system that can be either photo bioreactors (PBR) or open raceways. Usually, the yields of PBR are higher but with considerable installation and operations cost (BrownBridge, 2014).

Drying algae is the costliest step. Next, the lipids need to be extracted and several methods were investigated. The extraction has already been made under supercritical condition, using microwave irradiation and ultrasound (Nautiyal, 2014) but those have very high cost when compared with solvent extraction that is a high efficiency and most used method. However, the extraction doesn't have a good selectivity, pulling out the polar and non-polar solvents. This leads to low extraction yields (Viêgas, 2015).

After the extraction, it comes the process of transesterification. This process also has been studied exhaustedly (Viêgas, 2015). The transesterification can be made using different catalysts, different oil sources, distinguish reagents or changing the solvent (Bharathiraja, 2014).

After lipid extraction for biodiesel production, the residual biomass can be used for bioethanol production due to the amount of carbohydrates, 40% of the dry mass (Hu et al., 2013). Most of the carbohydrates contained in microalgae are in form of starch and celulose (Lee et al., 2015).

Another method for biodiesel production is the use of wet algae. Furthermore, there are process that combine both extraction and transesterification in one stage (Nautiyal, 2014), leading to a less expensive process.

All industries have been investing in methods for cost reduction in their process. Therefore, to analyze the total energy process cost is relevant to measure and indicate where improvements can be made (Lam and Lee, 2012). With that concern, laboratory and pilot scale need to quantify costs to select where to innovate and improve.

The Center for Self-Sustainable Energy (NPDEAS), at Federal University of Parana, extracts algae oil using solvent extraction in a pilot scale, this work aims to measure the total energy cost and suggests improvement steps.

3. MATERIALS AND METHODS

The process of extracting oil from microalgae biomass involves a reactor batch where 3 kg of algae biomass is put together with 15 liters of inorganic solvents (70% hexane and 30% ethanol) (Taher, 2013). Figure 1 brings a schematic diagram of how the whole process is performed at NPDEAS, at UFPR. A boiler provides hot water at 50°C that flows to the reactor's jacket. The water flow does not get in contact with the biomass and the solvents. Therefore, it is responsible only for transferring the necessary heat to the reactor, returning to the heater after circulating the batch. An electric engine is attached over the reactor to mix the biomass and the solvents during the extraction, obtaining a homogeneous contact among them. The biomass is kept in the batch for approximately 3.5 hours until a valve is open on the bottom of reactor to collect the oil and the solvents. The extracted content is then put in the solvent extraction where it will be separated. The microalgae oil is finally removed and distillated to obtain the final biofuel.

To characterize the physical process involved in the analyses, it was used a control volume that contains the reactor and its mixer. It is important to notice that in the process showed in Figure 1, energy is consumed in the reactor, in the hexane separator and in the distillation process. For the analysis, it had been considered the three stages separately.

3.1 Oil Extraction

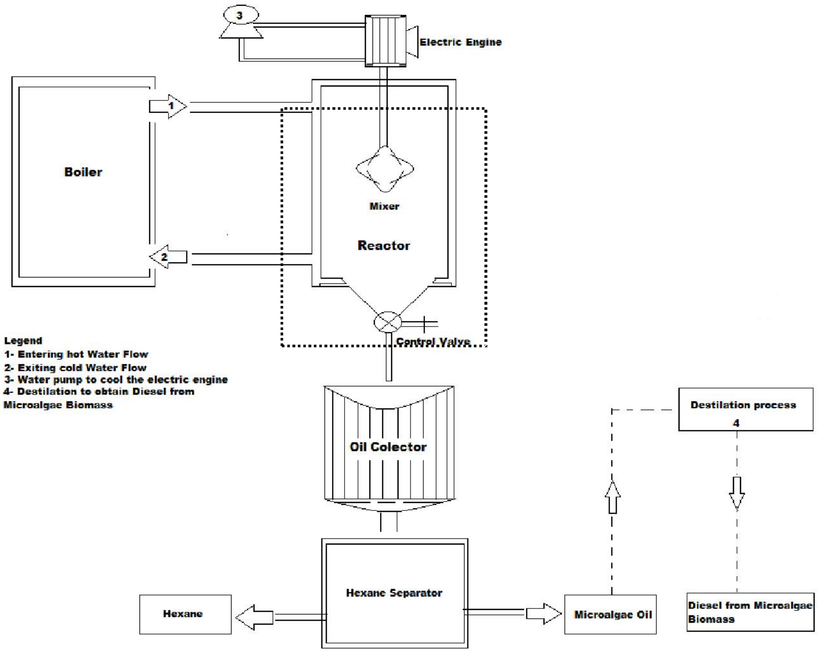

Figure 1. Diagram of process

An entrance and an exit of hot water responsible for the heat load compose the reactor. The mixer is an electric engine with nominal power (true power) of 519.45 W (watts). The engine true power was calculated using Eq. (1):

$$True\ Power\ [W] = \sqrt{3}\,.\,U\,.\,I\,.\,cos\,\varphi \tag{1}$$

Where the voltage (U) is equals to 220 V, the electrical current (I) is 1.92 A and the power factor (cos φ) is 0.71. Resulting value is similar to nominal power given by the manufacturer. Figure 2 shows the reactor with its mixer attached.

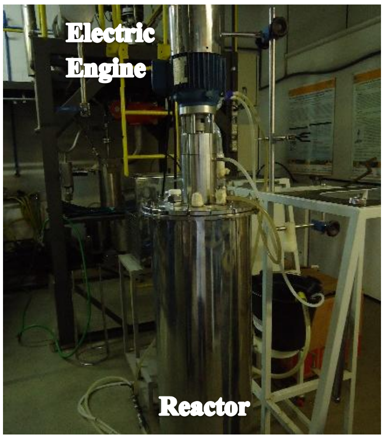

Figure 2. Reactor batch and the electric engine attached.

The assumptions to analyse the energy balance were:

i. Steady State
ii. Neglect potential and kinetic energy variation

$$0 = \dot{Q} - \dot{W} + \sum_{in} \dot{m}_{in} \left(h_{in} + 0\right) - \sum_{out} \dot{m}_{out} \left(h_{out} + 0\right) \quad (2)$$

$$\dot{Q} = \dot{W} + \dot{m}(h_{out-} h_{in}) \quad (3)$$

Since liquid water is entering in the reactor's cooling jacket at 50°C and leaving at 49°C (steady state), the enthalpy is 209.330 kJ/kg and 205.135 kJ/kg, respectively. The mass flow (ṁ) measured was 0.113 kg.s^{-1}. The work done by the mixer was shown on Eq. (1). It has a negative value because the work is realized over the system and the heat flow being dissipated to environment is also negative.

$$\dot{Q} = (-566)[J.s^{-1}] + 0.113\ [kg.s^{-1}] * (205.135 - 209.33)[kJ.Kg^{-1}] = -1040.04\ [J.s^{-1}] \quad (4)$$

According to the power distribution company (Copel) the price charged per kWh consumed is 0.76 R$, taxes and fees included. Since the whole process to extract oil takes 3.5 hours, the price of the process can be obtained by Eq (5).

$$Cost\ with\ Proces\ [R\$] = Q\ [kW] * 3.5\ [h] * 0.76\ [R\$.kWh^{-1}] = 2.77\ R\$ \quad (5)$$

The costs involved with other machinery, such as those to heat the water and to refrigerate the mixer shall be take in account as well. The hot water is provided by a thermostatic bath, which takes 30 minutes to heat water from environment temperature to 50 ºC. This equipment is manufactured by Marconi® and is composed by an 18 L water tank, a water pump, an electrical resistance and a control panel.

Figure 3. Thermostatic bath used to heat the water

The heating process to achieve the operational temperature of 50 ºC uses the maximum power provided by a thermostatic bath which is, by the manufacturer's datasheet, 1500 W during 30 min. To calculated the cost with the heating process, a similar approach used in Eq. (5) can lead to

$$Cost\ with\ thermostatic\ bath\ [R\$] = 1.5\ [kW] * 0.5\ [h] * 0.76[R\$.kWh^{-1}] = 0.57\ R\$ \quad (6)$$

Still according to the manufacturer, the water pump used in the process to circulate hot water into the reactor's cooling jacket consumes 40 W of power. The cost with water circulation is obtained as follow

$$Cost\ with\ water\ circulation\ [R\$] = 0.04\ [kW] * 3.5\ [h] * 0.76[R\$.kWh^{-1}] = 0.11\ R\$ \quad (7)$$

Since the power spent by the thermostatic bath to maintain the heating during the process is shorter than that to achieve the operational temperature of 50°C, the re-heating process in steady state was neglected in this analysis. Furthermore, the heating entering the reactor has been calculated in Eq. (4).

A small 27 W water pump, similar to those found in fish tanks, refrigerates the mixer's electric engine. This refrigeration is needy to avoid overheat. The cost is obtained by Eq. (8).

$$Cost\ mixer\ refrigeration\ [R\$] = 0.027\ [kW] * 3.5\ [h] * 0.76[R\$.kWh^{-1}] = 0.07\ R\$ \tag{8}$$

Finalizing the cost analyses with the process of extracting oil from microalgae, it must calculate the total cost summing the thermostatic bath, water circulation, mixer refrigeration and heating costs. This can be easily done summing Eq. (5), (6), (7) and (8), leading to the total cost in Eq. (9).

$$Total\ Cost\ of\ oil\ extraction\ [R\$]\ = 2.77 + 0.57 + 0.11 + 0.07 = 3.52\text{ R\$} \tag{9}$$

3.2 Solvent Recovery

The hexane and the ethanol used as solvents were recovered by one stage distillation process in a solvent recovering showed in Figure 4. The temperature was set to 95 ºC so ethanol could be recovered as well as the hexane.

Figure 4. Solvent Recovering

The total process may be divided as: (i) heating curve and (ii) stationary evaporation. The electrical current dispend in the process was measured during several moments and result constant 19.4 ± 0.8 A. During the heating curve, the resistance was on until the temperature of 95 ºC was achieved, after 30 min (Figure 5). Then, it was in and out resulting in 45 % of the time on. As the solvent was being evaporated, the total volume in the equipment was decreasing, so, the needy for heat to maintain the temperature and evaporate the solvent left. The process was stopped when the electric resistance was on for only 14% of the time. It means there were no solvents left, so the oil didn't need heat to evaporate any more solvent, only to maintain its temperature.

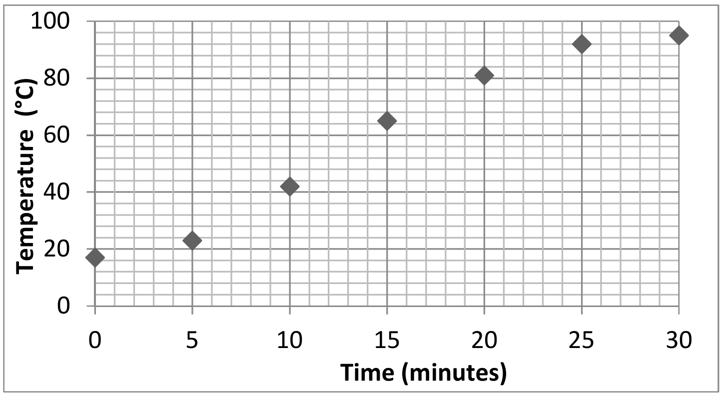

Figure 5 heating curve for Solvent Extraction

The total duration of the extraction was 2 hours and 52 minutes. The first 30 minutes of heating curve and 1 hour and 22 minutes of separation. Since the resistance was on only for 45% of the time, the total time on is:

$$Total\ Time\ On = 0.5 +\ 1.367 * (0.45) = 1.57\text{ h} \tag{10}$$

The power used during the process was calculated using the network tension of 220 V and the current (I) measured of 19.4 A resulting in 4.268 kW. The total energy dispends and the cost of the process were obtained by the power times the time of the process, the result were 6.69 kWh. Finally, the total cost of this process is obtained by Eq. (11).

$$Total\ Cost\ [R\$]\ of\ Solvent\ Extraction = 6{,}69\ [kWh] * 0.76[R\$.kWh^{-1}] = 5.08\ [R\$] \tag{11}$$

3.3 Second Solvent Recovery: Rotary Evaporation

Unfortunately, it is hard to remove the oil from the Solvent Recovery. To make it easier, some solvent was used to help the process. To purify the oil, it passed through a rotary evaporation process (Figure 6) that consisted in hot bath that warms up the oil in a flask that turns by an electrical motor force. The system is connected to a vacuum pump that makes the solvent more susceptible to evaporate and also has a condenser with cold water to recovery all solvent.

Figure 6. Rotary Evaporation

The cold water circulation, the rotary evaporator and the vacuum pump have nominal power so their energy consumption was calculated by the total time of the process, 1 hour and 5 minutes.

Table 1. Energy Consumed at Rotary Evaporation

Equipment	Power [W]	Energy [kWh]
Vacuum Pump	85	0.092
Rot evaporator	70	0.076
Cold water pump	40	0.043

The hot bath was set to 35 ºC and it took 10.5 minutes to achieve the temperature. As the ambient temperature was 21 ºC, there was low heat lost to the environment, meaning the resistant would be on, only, to maintain the bath temperature and it represents only 4% of the extraction time. The electrical current to the hot bath was 4,37 ± 0,03 A.

$$Total\ time\ [h]\ for\ Hot\ Bath = 10.5\,min + 65\ min * 0.04 = 13.1\ minutes = 0.22\ h \tag{12}$$

The total power of this equipment was calculated and resulted in:

$$P[W] = U[V].I[A] = 220\ [V] * 4.37[A] = 960\ [W] \tag{13}$$

$$Energy\ spent\ on\ hot\ bath\ [KWh] = P[W] * t[h] = 960[W] * 0.22[h] = 210\ [Wh] = 0.21\ kWh \tag{14}$$

The total energy demand was obtained by:

$$Total\ Energy\ spent\ on\ Rot\ Evaporation = 0.21 + 0.092 + 0.043 + 0.076 = 0.421\ kWh \tag{15}$$

Therefore, the total energy cost of rot evaporation was:

$$Total\ Cost\ [R\$]\ of\ Rot\ Evaporation = 0.421\ [KWh] * 0.76\ [R\$.kWh^{-1}] = 0.32\ [R\$] \tag{16}$$

4. RESULTS AND DISCUSSION

It is possible to get oil from algal biomass using solvent extraction. For this purpose, a mixture of a non-polar organic solvent and a polar solvent facilitates the extraction of lipids from algae (Malekzadeh, 2016). Even thow a mixture of chloroform/methanol gets a higher yield when compared with hexane/ethanol, the toxitity of those components turns preferable the use of hexane/ethanol and still with polarity-non polarity behave maintained.

The extraction was conducted over a molar rate 1:1 for hexane and ethanol that ensure the best recovery for fatty acid. Also, considering this molar ratio, the increase of temperature might modify the total crude lipids and fatty acids recovered. A high temperature induced a better extraction recovery from wet algae. (Malekzadeh, 2016).

The price of the energy through the process of extraction was expected to be high due the intensive electric and thermal energy input (Skorupskaite, 2016). The total consumption of electricity in this study is shown at Tab. (2).

Table 2. Total Electricity and Cost required

Process	Cost [R$]	Energy [kWh]
Oil Extraction	3.52	4.62
Solvent Recovery	5.08	6.69
Rot Evaporation	0.32	0.421
	8.92	11.73

When compared to the total energy cost of the entire process (R$8.90), the solvent recovery value is equivalent approximately 57%. However, there are a few paths to optimize the process. Considering the size of the reactor, it had been noticed that the equipment was over dimensioned, once it is capable to process more reagent, using the same energy. Another action that may improve the viability of this process is reducing the time to warm up. If the reactor works in a continuous process, the energy to start would be absent. At the same time, there is a price for maintaining this reactor working, so it is recommended a case study to determine which is the cheapest mode of producing.

The use of the hexane as the non-polar solvent should be analyzed. Like it was expected, the effectiveness of corroborated with the data in literature, proving that hexane shows a high yields lipids extraction for algae (Shin, 2014) (Malekzadeh, 2016). However, the quantities lost in a process was very considerable. Similar losses occurs for the process of extraction oil of soybeans, which the manufacture loses 3800L of hexane for 300 tons of raw material per day (Skorupskaite, 2016). Therewith, a recovery of the solvent must be object of study in order to minimize costs.

The solvent recovery is important and in this process was performed twice. Besides saving resources with solvent, the uptake of the solvents would guarantee a cleaner environment, in as much as the wasted hexane or ethanol might go the atmosphere. With that in mind, once that the ethanol and hexane have different boiling point, a recovery in two distinct temperatures may be considered. The first one for hexane boiling point and the second one for ethanol's. Also, this reactor`s size can already be considered as a step of a scale up, whereas lots of this experiment are made in laboratory scale.

5. CONCLUSION

Several alternatives have been proposed to obtain cleaner fuels, such as biofuels derived from different kinds of biomass. When derived from alga oil, fuels are known as third generation feedstock and are gaining attention as they have high lipid content. During the extraction of algal biodiesel in this study, three main steps were taken: the oil extraction, the solvent recovery and the final rot evaporation. In total, for one batch extraction, it was consumed 11.7 kWh of electricity, resulting in R$ 8.9 spent. The economic aspects of biodiesel extraction are important concerns for industry feasibility in larger scales. Almost 60 % of all energy involved was spent during the solvent recovery step. From 3 kg of microalgae biomass and 15 liters of solvents, it was obtained 0.2 liters of algal lipids. The viability of commercial biodiesel derived from a microalgae still seems to be very small; however, the reduction of energy spent and the maximization of oil extracted are factors that may help the biodiesel derived from microalgae became commercially viable in a near future.

6. ACKNOWLEDGEMENTS

The authors thank the Federal University of Parana for its help and support. The authors would like to acknowledge CAPES financial support.

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