COBEM 2021 Florianópolis - Brasil

ABCM Associação Brasileira de Engenharia e Ciências Mecânicas
26th ABCM International Congress of Mechanical Engineering
November 22-26, 2021. Florianópolis, SC, Brazil

COB-2021-0204

ENERGY ANALYSIS OF BIODIESEL PRODUCTION FROM MICROALGAE

Eduardo J. C. Cavalcanti
Mariane L. Cattaneo
Federal University of Rio Grande do Norte, Department of Mechanical Engineering, 59072-970, Natal/RN, Brazil
educanti@gmail.com, marianecattaneo@gmail.com

Monica Carvalho
Federal University of Paraíba (UFPB), Department of Renewable Energy Engineering, João Pessoa/Paraíba, Brazil
monica@cear.ufpb.br

Abstract. *The utilization of renewable fuels to substitute fossil fuels has been attracting attention due to the mitigation of environmental issues, especially those associated with climate change and global warning. Microalgae are able to produce biodiesel and sequestrate carbon dioxide from atmosphere. This work evaluates the five phases of biodiesel production from Chrorella sp: algae cultivation, oil extraction, transesterification, biodiesel purification, and glycerin separation/methanol recovery. The first law of thermodynamics is applied to establish energy balances, and the analysis includes the distillation columns as well. The results obtained herein are compared with literature data. The high energy demands of the dryers and distillation process are disadvantageous. Understanding the degradation of energy can help improve the biodiesel production process.*

Keywords: *microalgae, renewable fuel, biodiesel, Chrolella sp, thermodynamics.*

1. INTRODUCTION

Life quality standards have been rising worldwide, leading to an increase in energy demands along with the blossoming of environmental conscience, which searches for ways to compensate for the higher consumption of fossil fuels and its consequences. A transition to alternative or renewable energy systems has been in the spotlight, motivated by environmental concerns (especially regarding climate change) and depletion of traditional energy resources. Meeting future energy demands, as mentioned by Carvalho, Lozano and Serra (2012) will certainly have to consider stricter requirements to reduce the environmental impact of energy systems, which could play a major role in reducing the threat of climate change. Biofuels should be part of this energy transition, and a solution to the issue of dependence on fossil fuels. Sustainable energy development has been in the spotlight of research concerning the production of biofuels, due to its energy-intensive characteristics. The consumption of energy resources is the main cost associated with many energy-intensive chemical processes such as biodiesel production.

The social, economic, and environmental importance of biofuels in the future has been reported by Demirbas (2017), where the advantages of biofuels include sustainability, reduction of greenhouse gas (GHG) emissions, regional development, social structure and agriculture, and security of supply. One of the most common biofuels is biodiesel, an alternative to diesel fuel, which can be blended with petroleum-based diesel. According to Bockey (2019), biodiesel has gained global overall acceptance as an admixture component in the countries where the corresponding resource production also takes place (USA, Argentina, Brazil, EU, Indonesia, and Malaysia).

The production of biodiesel has been advancing over the years, and started from the conventional base-catalyzed transesterification process with virgin vegetable oils, advancing to strategies that employ non-edible (microalgae, oleaginous seeds, microorganisms) and waste raw materials (waste oils and fats) (Ali et al., 2017).

Focusing on microalgae, these present significantly higher area productivity and large-scale microalgae growth in saline media or in photobioreactors does not compete with agriculture (which is an issue regarding land use and consumption of fresh water resources) (Ofori-Boateng et al., 2012a). Regarding the depletion of fresh water resources, Raghuvanshi et al. (2018) mentioned that the use of wastewater for biodiesel production is a viable sustainable solution Advances in current biodiesel conversion technologies will help accelerate microalgae biodiesel production, especially in terms of energy and cost savings (Tan et al., 2018).

Algae is considered a promising biodiesel feedstock due to its fast grow rate (Uludamar, 2018), and microalgae-biodiesel can replace conventional diesel in a diesel gen-set without any modifications. Blended fuels with small proportions of microalgae-biodiesel (such as 20% by volume) can be considered to be viable alternative fuels (Yaşar and Altun, 2018).

Biodiesel production still suffers from challenges in terms of cost, cold performance, storage stability, engine warranty, post production issues, boundary setting in life cycle assessments, and public perception (Manaf et al., 2019). Besides, according to Avramović, Veličković & Veljković (2018), the influence of biofuels on energy and food markets must be addressed, along with working conditions and workers' rights regarding occupational health, the inconsistency of biofuel policies, and land change.

Although biodiesel has been contributing with a greener portion of the emissions associated with the use of diesel engines, it is energy- and water-intensive and requires many chemicals, to the point that Luque and Melero (2012) affirmed that although biodiesel is a green product, it is not manufactured by a green process. Sustainable biodiesel production must take into account low-cost feedstock (as it is the major cost involved in biodiesel production - Srivastava et al., 2018), energy-efficient non-conventional heating and mixing technologies (Xu et al., 2018), and renewable raw materials and energy sources (or waste materials, as Hajjari et al. (2017) suggested waste-oil biodiesel utilization as a strategy). The identification and implementation of sustainable biofuel production is paramount: price competitiveness, affordability, and reliability in comparison to fossil fuels are essential, according to Correa et al. (2019), and systems that are able to meet biofuel production targets and socioeconomic targets should be preferred.

The concept of sustainability is complex, as it can encompass environmental, economic, and social variables - currently, the quantitative assessment of sustainability comprehends the calculation of different indicators, separately (Venturini et al., 2020). Therefore, assessment of the sustainability of biofuel/biodiesel systems can be carried out from different viewpoints. Energy analysis employs energy and mass balances (First Law of Thermodynamics, FLT), exergy-based analysis takes into account the quality of energy (Second Law of Thermodynamics, SLT), Life Cycle Assessment (LCA) quantifies the potential environmental impacts throughout the life cycle of the process, accounts for the exploitation of natural resources and direct and indirect solar energy requirements for biofuel production, and exergoenvironmental analysis combines the exergy-based and environmental aspects, to name a few.

The objective of this study is to carry out an energy assessment for biodiesel production from microalgae, detailing the mass and energy balances developed, and comparing results with scientific literature data.

2. MATERIAL AND METHODS

Figure 1 depicts the microalgae biodiesel production plant studied herein, based on Ofari-Boateng et al. (2012a).

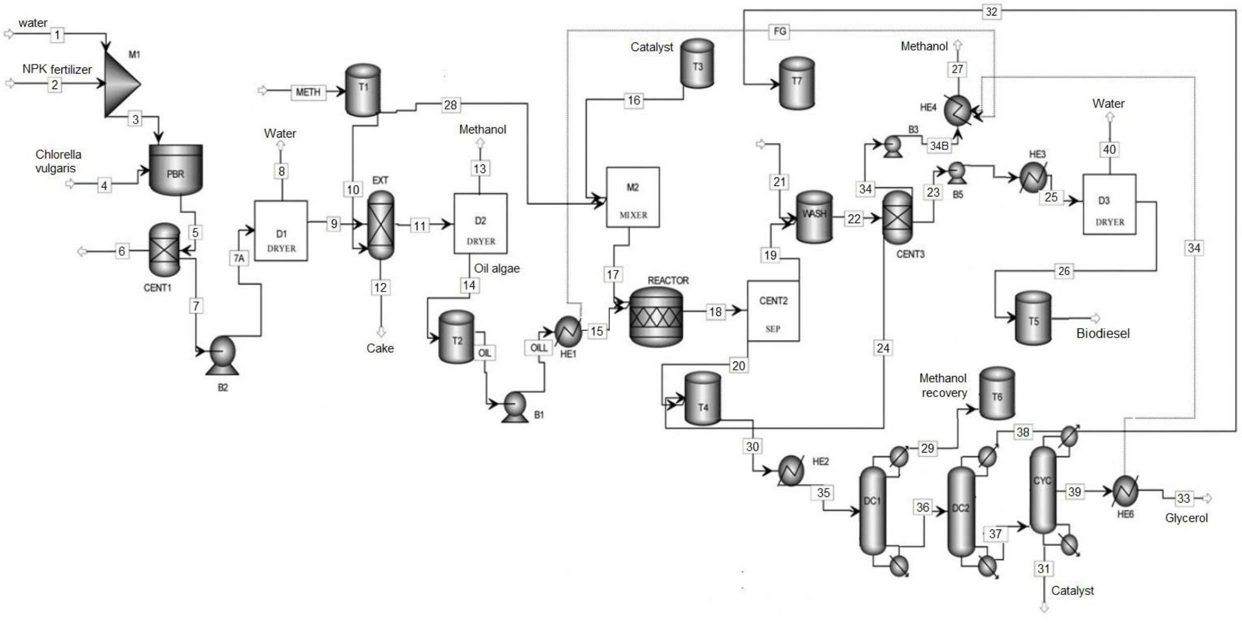

Figure 1. Schematic diagram of microalgal biodiesel production.

The processes include five stages: microalgae cultivation, algae oil extraction, algae oil transesterification, biodiesel purification, and the methanol recovery processes using a rectification column. The functional unit is the production of one tonne of biodiesel.

In the algae cultivation system, there are three unit operations: algae cultivation, separation of algae medium, and drying of algae biomass. Solvent extraction employed methanol, and acid-catalyzed transesterification used the solid sulfated zirconia catalyst $Zr(SO_4)_2$. For oils with a high content of Free Fatty Acids, sulfated zirconia enables the simultaneous esterification and transesterification of triglycerides under appropriate reaction conditions. This behavior eliminated the complicated two-stage process for the production of acid methyl ester (FAME), which includes an acid-catalyzed esterification process and an alkaline-catalyzed transesterification process (Ofari-Boateng et al., 2012b).

The catalyst was mixed with methanol and loaded into a reactor containing the algae oil. The reaction was carried out at 150 °C to obtain biodiesel. Of the triglycerides that entered the reactor, 98.7% were transformed into biodiesel. The methyl ester phase contained glycerides, methyl esters and methanol. This mixture was fed into a washer, where water at 55ºC was added, and then flowed to distillation where methanol was recovered and biodiesel was obtained.

The biodiesel obtained was then dried. Approximately 95% of the methanol from the biodiesel phase was recovered in a distillation column, which counted with ten column stages and a reflux ratio of 2.5 (Ofari-Boateng et al., 2012b). The glycerin phase, which contains glycerin, water and methanol, was fed into a distillation tank. A small amount of catalyst and methanol was present in the biodiesel and glycerol products. The glycerol-water system is an important industrial system that presents a nonlinear equilibrium relationship. Glycerol can be obtained from fat, oil, or from the soap industry. Because of its high boiling point (290 °C at 760 mmHg) and heat sensitivity, glycerol is separated from water by vacuum distillation (5-10 mmHg abs) using packed-bed distillation columns containing structured packings. The equilibrium curve of the glycerol-water system is highly nonlinear, and glycerin is commercially required at purities higher than 99.5%. (Attarakih et al., 2001). The glycerol phase, which contained some methanol, was then sent to a flash separator, from where most of the methanol was removed, obtaining 97% glycerol. The catalyst and the glycerol were finally separated. Eight column stages and a reflux ratio of 1.5 were used to separate methanol and water from the glycerin phase. The catalyst was then separated with the help of a cyclone (Ofari-Boateng et al., 2012b).

The mass balance for a closed system is expressed by Equation 1:

$$\boldsymbol{m_{in}} = \boldsymbol{m_{out}} \tag{1}$$

$\boldsymbol{m_{in}}$ and $\boldsymbol{m_{out}}$ are the input and output mass flows, respectively.

The First Law of Thermodynamics for closed systems (Moran et al., 2007) is used to carry out the energy balance, as shown in Eq. (2).

$$\mathbf{Q - W = (U_2 - U_1)} \tag{2}$$

where $\boldsymbol{Q}$, $\boldsymbol{W}$ and $\boldsymbol{U}$ refer to heat, work and internal energy, respectively. Changes in kinetic and gravitational potential energy values are negligible

The internal energy was evaluated by Equation 3, when there is no change of chemical composition for each substance (i).

$$\mathbf{(U_2 - U_1)} = \sum [\boldsymbol{m_i . cp_i . (T_2 - T_1)}] \tag{3}$$

$\boldsymbol{m}$, $\boldsymbol{cp}$, and $\boldsymbol{T}$ refer to mass, specific heat and temperature, respectively.

In the reactor, a change of chemical composition occurs, and the energy balance should consider the energy involved in the formation of each chemical substance (through the enthalpy of formation, $\bar{h}_f^0$). The First Law of Thermodynamics for systems and reagents for a closed system (Moran et al., 2007) is shown by Eq. (4).

$$\mathbf{Q} + \sum_{R} \boldsymbol{n_{in}} \left(\boldsymbol{\bar{h}_f^0} + \Delta\boldsymbol{\bar{h}}\right)_{\boldsymbol{in}} = \sum_{P} \boldsymbol{n_{out}} \left(\boldsymbol{\bar{h}_f^0} + \Delta\boldsymbol{\bar{h}}\right)_{\boldsymbol{out}} + \mathbf{W} \tag{4}$$

$\boldsymbol{n}$ is the number of moles of reactants and products in the combustion reaction, $\boldsymbol{\bar{h}_f^0}$ is the enthalpy of formation of each substance, and $\Delta\boldsymbol{\bar{h}}$ is the variation of the formation enthalpy concerning the dead state. Subscripts **R** and **P** correspond to the reagent and product, respectively. There is no difference between enthalpy and internal energy for liquids.

The formation enthalpy is a function of chemical composition, and the values for algae ($C_{24}H_{44}O_6$), biodiesel ($C_{19}H_{34}O_2$) and algae oil ($C_{52}H_{96}O_6$) considered its combustion with pure oxygen at environmental conditions and produced CO_2 and H_2O, according to Equation (5):

$$\mathbf{PM.HHV} + \bar{h}_f^0 = n_{CO2}.\left(\bar{h}_{f\,CO2}^0\right) + n_{H2O}.\left(\bar{h}_{f\,H2O}^0\right)_{liq} \tag{5}$$

HHV is the higher heating value, and PM is the molar weight.

The formation enthalpy of Glycerin ($C_3H_8O_3$) and Methanol (CH_3OH) were obtained from Ofori-Boateng et al. (2012b), as -7283 kJ/kg and -7466 kJ/kg, respectively. Other substances required the calculation of HHV (Miao, 2019) (Eq. 6) and LHV (lower heating value, Eq. 7):

$$HHV = 0.3383\, Porc_C + 1.422\, (Porc_H - \frac{Porc_O}{8}), \tag{6}$$

$$HHV - LHV = 2450(9\,h + moist), \tag{7}$$

h and $moist$ refer to the mass ratio of hydrogen and moisture, respectively. $Porc_C$, $Porc_H$ and $Porc_O$ are the mass percentage of carbon, hydrogen and oxygen, respectively.

The mass and energy balances for reactor are shown in Equations (8) and (9):

$$m_{15} + m_{17} = m_{18}, \tag{8}$$

$$m_{28}\left(\frac{hf_m}{PM_m} + cp_m\,(T_{17} - T_1)\right) + m_{16}\,cp_{cat}(T_{17} - T_{18}) + m_{15}\left(\frac{hf_{oil}}{PM_{oil}} + cp_{oil}(T_{15} - T_1)\right) + \\ Q_{reator}1000 = m_{met_{18}}\left(\frac{hf_m}{PM_m} + cp_m\,(T_{18} - T_1)\right) + m_{bio_{18}}\left(\frac{hf_{bio}}{PM_{bio}} + cp_{bio}\,(T_{18} - T_1)\right) + \\ m_{gly_{18}}\left(\frac{hf_{gly}}{PM_{gly}} + cp_{gly}\,(T_{18} - T_1)\right), \tag{9}$$

m, cat, oil, bio and gly are methanol, catalyst, algae oil, biodiesel and glycerol, respectively.

Components are considered adiabatic, except for mixer 2 and centrifuge 2, which present 30% energy losses to the environmental.

Table 1 summarizes the specific molecular weights and heats. The specific heat capacity of algae was considered equal to the specific heat capacity of water, which is a good approximation as the algae solution is over 98% water in weight (Barkan et al., 2018).

Table 1. Properties of substances.

Substance	Molecular Weight (kg/kmol)	Specific Heat (kJ/kg.K)
Algae ($C_{24}H_{44}O_6$)	428.00	2.550$^{(d)}$
Biodiesel ($C_{19}H_{34}O_2$)	294.00	3.197$^{(b)}$
Algae Oil ($C_{18}H_3O_2$)	280.00	9.732$^{(b)}$
Glycerin ($C_3H_8O_3$)	92.00	2.391$^{(b)}$
Water (H_2O)	18.02	4.184$^{(a)}$
Catalyst ($Zr(SO_4)_2$)	283.34	0.607$^{(c)}$
Methanol (CH_3OH)	32.04	2.550$^{(a)}$
NPK (N-P-K)	66.46	1.572$^{(c)}$

$^{(a)}$ (Sonntag et al., 2003), $^{(b)}$ (Sogurven; Ozilgen,, 2010), $^{(c)}$ (Wolfran Research, 2021), $^{(d)}$ (Barkan et al., 2018)

The distillation column presents three sections: feed, rectification and stripping sections. The rectification section is located at the top of the column, followed by the feeding section, with the stripping section located at the lower part of the column. The mixture enters through the feeding section; the vapors of the more volatile components flow to the upper section and condensed liquid flows to the rectification section. Thus, the distilled product is obtained at the upper section of the column, while the product is obtained at the last plate of the stripping section and can be recycled (Fig. 2).

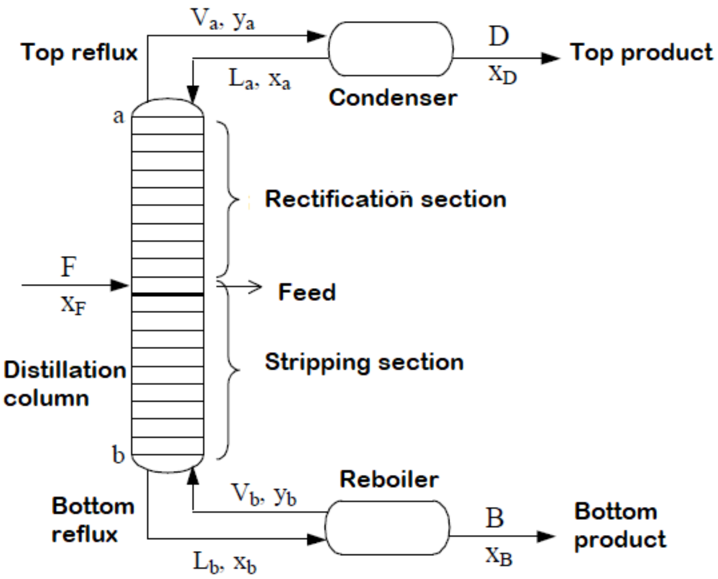

Figure 2. Schematic diagram of the distillation column.

Considering the basic concepts of liquid-vapor equilibrium for ideal binary mixtures with two components, ‘a’ and ‘b’ in a closed reservoir, the laws of Dalton and Raoult are used (Eq. 10 – 16). These equations are necessary to describe the distillation processes.

$$P = P_a + P_b \,, \tag{10}$$

$$P_a = P_a^0\, x_a \,, \tag{11}$$

$$P_b = P_b^0\, x_b \,, \tag{12}$$

$$x_a + x_b = 1 \,, \tag{13}$$

$$y_a + y_b = 1 \,, \tag{14}$$

$$x_a = (P - P_b^0)/(P_a^0 - P_b^0) \,, \tag{15}$$

$$y_a = (P_a^0\, x_a)/P \,, \tag{16}$$

where P, P^0, P_a, x and y are the total, partial, saturation pressure of each substance, mole fraction of the solvent in the liquid phase and mole fraction in the gas phase, respectively.

The methanol glycerin recovery operates at steady conditions. Partial and global control volumes were considered in the distillation column (DC) (Eq. 17 – 19), as shown in Equations (17)-(19):

$$m_{35} = m_{29} + m_{36} \,, \tag{17}$$

$$m_{Va}\, h_{Va} + Q_{cond}\, 1000 = m_D\, h_D + m_L\, h_L \,, \tag{18}$$

$$m_F\, h_F + (Q_{cond} + Q_{reb})1000 = m_D\, h_D + m_B\, h_B \,, \tag{19}$$

Glycerol was recovered in a flash distiller. Appendix 1 shows all thermodynamic balances developed.

3. RESULTS

The fertilizer is a mixture of salts, and there it is essential to evaluate its properties. Table 2 shows the detailed calculations of the molecular weight and specific heat of NPK fertilizer.

Table 2. Molecular weight and specific heat calculations for NPK.

Substance	**Molar mass (M) (kg/kmol)**	**Mass (kg)**	**Cp (kJ/kg.K)**	**x_i**	**y_i**	**Cp.x_i (kJ/kg. kmol)**	**M.yi (kg/kmol)**
$Ca(OH)_2$	74.092	2.0	1.1810	0.0651	0.0584	0.0769	4.3294
KCl	74.550	6.0	0.4896	0.1954	0.1742	0.0957	12.9882
$MgSO_4$	120.374	1.0	0.8018	0.0326	0.0180	0.0261	2.1647
NaH_2PO_4	119.980	4.7	0.8000	0.1531	0.0848	0.1225	10.1741
$FeCl_2$	126.753	1.0	0.6052	0.0326	0.0171	0.0197	2.1647
NH_4Cl	53.491	26.0	1.5720	0.5212	0.6475	0.8193	34.6352
NPK						**1.1602**	**66.4563**

For NPK fertilizer, the specific heat of mixture is 1.1602 (kJ/kg.K). Some components as NH_4Cl was collected data from (Wolfram Research, 2021).

The enthalpies of formation (hf) and lower heating values (LHV) of algae, biodiesel and algae are represented at table 3.

Table 3. Enthalpies of formation and lower heating values of algae, biodiesel and algae oil.

Substance	**hf (MJ/kmol)**	**LHV (MJ/kg)**
Algae ($C_{24}H_{44}O_6$)	-1439.00	31.138
Biodiesel ($C_{19}H_{34}O_2$)	-356.75	38.206
Algae Oil ($C_{52}H_{96}O_6$)	-1128.00	37.925

Tables 4 and 5 show the mass and molar fractions for the sections of the distillation column, considering methanol and water, and glycerol and water, respectively. Considering that the distillation column recovered 95% of methanol from the biodiesel phase, the design parameters included nine column stages and a reflux ratio of 18.

Table 4. Mass and molar fractions of the distillation column, for methanol and water.

Sections	**Mass Fraction**	**Molar Fraction**
Feed	0.0958	0.0562
Rectification	0.9534	0.9200
Stripping	0.0049	0.0028

The methanol is the most volatile substance of the mixture, which is removed from the distillation column at the upper part. The water and glycerol are removed at the lower sections. The high water content reduces the feed fraction. This low value requires a high reflux ratio of 18 at the rectification section.

Figure 3 depicts a McCabe-Thiele diagram, where ‘LA’ refers to the feed line, ‘LO’ is the operation line, ‘Equilibrium’ is the equilibrium line, ‘LOR’ is the rectification line and ‘YLOE’ is the stripping line.

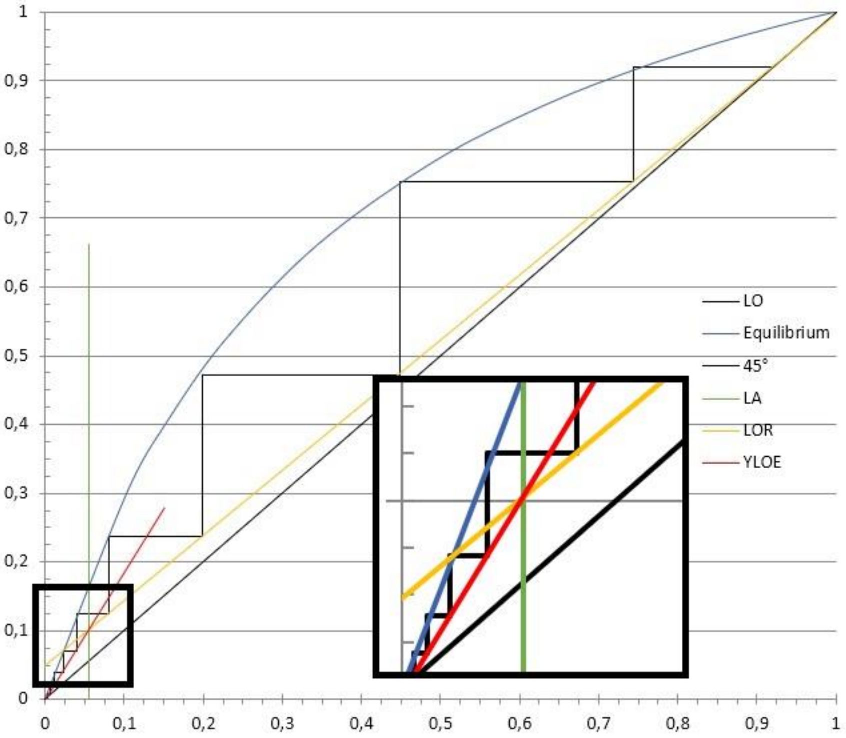

Figure 3. Methanol recovery distillation column steps.

The feed is saturated liquid with vertical line in diagram. The rectification section has 5 stages plus condenser at top. In relation to the distillation columns, due to the large amount of water in relation to methanol in the mixture, a high value of the reflux ratio of 18 was obtained, which is much higher than the reference values of 2.5. Also, the feed line was placed too low, and therefore the rectification line included many stages (as shown in Figure 3). The reflux ratio of 2.5 from Ofari–Boateng et al. (2012b) becomes the rectification line more horizontal and has a limitation for methanol recovery. This reflux ratio value should be higher for better recovery stage.

The second recuperation is glycerol. The glycerol-water separation system has a low pressure drop, small liquid holdup, and large surface area per unit volume of packing. Glycerol and water were separated at pressure of 10 mmHg. 99% glycerol was obtained from flash distillation. The fractions at sections are shown in table 5.

Table 5. Mass and molar fractions of the distillation column, for glycerol and water.

Sections	**Mass Fraction**	**Molar Fraction**
Feed	0.9234	0.9840
Rectification	0.9949	0.9990
Stripping	0.0614	0.2505

Within the mixture, water is most volatile substance. Glycerol is removed at the bottom. The high water content increases the feed fraction, and this high value does not allow any reflux ratio at rectification section. For higher purity of water, column separation can be used instead of flash distillation. The high purity of glycerol is easily obtained due to the good equilibrium curve water-glycerol. There is a high change of water concentration at vapor and liquid phase at same temperature.

Energy balances were developed for each component of the biodiesel production process, yielding the energy values displayed in Table 6. Results are compared with scientific literature data (Ofori-Boateng et al., 2012b).

Table 6. Results of energy balances, per component.

Equipment	**This study (MJ) Heat**	**This study (MJ) Work**	**Exergy (MJ)** (Ofori-Boateng et al., 2012b)
Algae Cultivation			
Mixer 1		12	12
Centrifuge 1		61	61
Dryer 1	3463		167/(1-298/372.6)=834
Algal Oil Extraction			
Oil extractor	96		32/(1-298/328)=350
Dryer 2	6228		98/(1-298/337.7)=833
Transesterification			
Reactor	933		41/(1-298/423)=139
Mixer 2		22	22
Centrifuge 2		48	48
Washer	-126	16	16
Centrifuge 3		44	44
Dryer 3	349		96/(1-298/373)=477
Methanol Recovery			
Distillation column 1 – Condenser	3016		-
Distillation column 1 – Boiler	3022		245/(1-298/373)=1218
Distillation column 2 – Boiler	2474		221/(1-298/358)=1319
Cyclone		21	21

The work of Ofori-Boateng et al. (2012b) evaluated exergy. Although work has the same exergy value, heat must must be corrected by Carnot‘s efficiency to evaluate its energy.

The work consumed for mixers 1 and 2; centrifuges 1, 2 and 3; washer and the cyclone, were used similar to (Ofori-Boateng et al., 2012b) and the output temperature of process was calculated.

In dryers 1 and 2, the thermal energy supplied has high difference of work (Ofori-Boateng et al., 2012b). The required energy was not sufficient to guarantee completion of the drying process: 3463 MJ is much higher than the reference value of 834 MJ. Considering only the enthalpy of water vaporization multiplied by the mass in dryer 1 yields 2615 MJ, an order of magnitude higher than 834 MJ. In dryer 2, the same situation occurs: methanol data yielded 6228 MJ, also much higher than the reference value of 833 MJ (of the 6228 MJ, 6197 MJ accounts for the enthalpy of water vaporization multiplied by the mass in dryer 2). In dryer 3, the value of thermal energy is slightly better in relation to the others dryers.

In the oil extractor, the difference of value is still high. Similar to dryers, the reactor needs more energy than the reference values (as calculated by Equations 8 and 9). It is important to know that when there is a chemical reaction as occurs in the reactor, the enthalpy of formation must be taken into account. In the washer, the hot flow from reactor at 150°C is centrifuged and enters the washer, mixing with water. The solution should be cooled to avoid reaching the methanol saturation temperature of 64.7 °C. The distillation columns are energy-intensive, as the vaporization of methanol and water needs high energy for the distillation process. Few details were provided by Ofori-Boateng et al. (2012b) on distillation columns, such as condensers, number of stages and position of feed stages. The high amount of water introduced into the washer harms the destillation process, due to the high energy demand required. A reduction of supply water can improve the process, reducing the energy consumption. The dryers and distillation collums have the highest energy demands, which can be reduced to optimize the global process. The thermodynamic assessment presented herein has highlighted some inconsistencies in data presented by Ofori-Boateng et al. (2012b).

Finally, as mentioned by Klein et al. (2018), microalgae have the potential to help support biorefineries, which is promising regarding the transition to a bio-based economy. In the near- to medium-term, microalgae can be used to produce biofuels and other bioproducts, and it is suggested to couple microalgae production with large-scale facilities to better explore the benefits of process integration. There are still margins for the improvement of microalgae cultivation, requiring further research at laboratory scale and through the deployment of pilot plants (Klein et al., 2018). This field of research is relevant, and economic viability can be achieved by exploring processing techniques and culture parameters, followed by thermodynamic assessments.

4. CONCLUSION

This study investigated the potential of microalgae as an alternative medium for the production of a renewable fuel. It was verified that the dryers present insufficient energy for the drying process. For a more efficient distillation process, it is necessary to reduce the water supply to the distillation columns due to the pronounced change in enthalpy that occurs on the condenser side. This means that the water supply is introduced too low in the column and should be moved to the top in the case of methanol recovery, and moved downwards in the case of glycerol recovery. Appropriate placement of the supply removes distortions observed and can reduce the energy required by the condenser or reboiler.

A case is made herein for the complete analysis of biodiesel production from microalgae, which should encompass all production units within the plant: microalgae cultivation, algae oil extraction, algae oil transesterification, biodiesel purification, and distillation processes. Such a detailed assessment can help establish the margins for improvement of each process (e.g., product recycling, use of microalgae cake, glycerin, water, and improvements in equipment). Mass and energy assessments were carried out, which should be complemented by an exergy assessment that can identify the hotspots and thermodynamic efficiency of biodiesel production.

5. ACKNOWLEGMENTS

The authors wish to acknowledge the support of the National Council for Scientific and Technological Development (CNPq, Brazil) Research Productivity grant nº 307394/2018-2.

6. REFERENCES

Ali, O. M., Mamat, R., Rasul, M. G., & Najafi, G., 2017. “Potential of Biodiesel as Fuel for Diesel Engine”. In: Clean Energy for Sustainable Development (pp. 557-590). Academic Press.

Attarakih, M, Fara, D.A. and Sayed, S., 2001. “Dynamic Modeling of a Packed-Bed Glycerol-Water Distillation Column”. *Ind. Eng. Chem. Res.*, Vol. 40, pp. 4857-4865.

Avramović, J., Veličković, A., & Veljković, V. (2018). Challenges in biodiesel industry: Socio-economic, occupational health, and policy issues. Safety Engineering, 8(2), 79-83.

Barkan, C.M., DeLuca, K.A. and Preston, M.R., 2018. “Design of A Flexible, High-volume Direct Flue Gas-to-Algae Conversion Process for Value-added Bioproducts”. Senior Design Reports (CBE), No. 102.

Bockey, D., 2019. “The significance and perspective of biodiesel production–A European and global view”. *OCL*, 26, 40.

Carvalho, M., Lozano, M. A., & Serra, L. M. ,2012. “Multicriteria synthesis of trigeneration systems considering economic and environmental aspects”. *Applied Energy*, 91(1), pp.245-254.

Correa, D. F., Beyer, H. L., Fargione, J. E., Hill, J. D., Possingham, H. P., Thomas-Hall, S. R., & Schenk, P. M., 2019. “Towards the implementation of sustainable biofuel production systems”. *Renewable and Sustainable Energy Reviews*, 107, pp. 250-263.

Demırbas, A., 2017.” The social, economic, and environmental importance of biofuels in the future”. *Energy Sources, Part B: Economics, Planning, and Policy*, 12(1), pp. 47-55.

Hajjari, M., Tabatabaei, M., Aghbashlo, M., & Ghanavati, H., 2017. “A review on the prospects of sustainable biodiesel production: A global scenario with an emphasis on waste-oil biodiesel utilization”. *Renewable and Sustainable Energy Reviews*, 72, pp. 445-464.

Luque, R., & Melero, J. A., 2012. “Introduction to advanced biodiesel production”. In: Advances in biodiesel production (pp. 1-9). Woodhead Publishing.

Klein, B. C., Bonomi, A., & Maciel Filho, R. (2018). Integration of microalgae production with industrial biofuel facilities: A critical review. Renewable and Sustainable Energy Reviews, 82, 1376-1392.

Manaf, I. S. A., Embong, N. H., Khazaai, S. N. M., Rahim, M. H. A., Yusoff, M. M., Lee, K. T., & Maniam, G. P., 2019. “A review for key challenges of the development of biodiesel industry”. *Energy conversion and management*, 185, pp. 508-517.

Miao, C., Chakraborty, M. and Chen, S., 2012. “Impact of reaction conditions on the simultaneous production of polysaccharides and bio-oil from heterotrophically grown Chlorella sorokiniana by a unique sequential hydrothermal liquefaction process”. Bioresource Technology, Vol. 110, pp. 617–627.

Moran, M. J. and Shapiro, H. N. 2007. Fundamentals of Engineering Thermodynamics. 6th. John Wiley & Sons, Inc. New York.

Ofori-Boateng, C., Keat, T. L., & JitKang, L., 2012a. “Feasibility study of microalgal and jatropha biodiesel production plants: Exergy analysis approach” *Applied Thermal Engineering*, Vol. 36, pp. 141-151.

Ofari–Boateng, C., Keat, T. L., & JitKang, L., 2012b. “Sustainability assessment of microalgal biodiesel production processes: an exergetic analysis approach with Aspen Plus”. *Int. J. Exergy*, Vol. 10, No. 4, pp. 400-416.

Raghuvanshi, S., Bhakar, V., Chava, R., Sangwan, K. S., 2018. “Comparative study using life cycle approach for the biodiesel production from microalgae grown in wastewater and fresh water”. *Procedia CIRP*, 69, pp. 568-572.

Sonntag, R.E., Borgnakke, C., Wylen, G.J.V., 2003. “Fundamentals of Thermodynamics”. Sixth edition, U.S.A., John Wiley & Sons, Inc.

Sorguven, E. and Ozilgen, M., 2010. “Thermodynamic assessment of algal biodiesel utilization”. Renewable Energy, Vol. 35, pp. 1956–1966.

Srivastava, N., Srivastava, M., Gupta, V. K., Manikanta, A., Mishra, K., Singh, S., ... & Mishra, P. K., 2018. “Recent development on sustainable biodiesel production using sewage sludge”. *3 Biotech*, 8(5), pp. 245.

Tan, X. B., Lam, M. K., Uemura, Y., Lim, J. W., Wong, C. Y., & Lee, K. T., 2018. “Cultivation of microalgae for biodiesel production: A review on upstream and downstream processing”. *Chinese Journal of Chemical Engineering*, Vol. 26, pp. 17-30.

Uludamar, E., 2018. “Effect of hydroxy and hydrogen gas addition on diesel engine fuelled with microalgae biodiesel” *Int. J. of Hydrogen Energy*, Vol. 43, pp. 18028-18036.

Venturini, O. J., Júnior, J. C. F., Palacio, J. C. E., Batlle, E. A. O., Carvalho, M., & Lora, E. E. S., 2020. “Indicators for sustainability assessment of biofuels: Economic, environmental, social, and technological dimensions”. In: Biofuels for a More Sustainable Future (pp. 73-113). Elsevier.

Xu, K., Lv, B., Huo, Y. X., & Li, C., 2018. “Toward the lowest energy consumption and emission in biofuel production: combination of ideal reactors and robust hosts”. *Current opinion in biotechnology*, 50, pp. 19-24.

Yaşar, F., Altun, Ş., 2018. “The Effect of Microalgae Biodiesel on Combustion, Performance and Emission Characteristics of a Diesel Power Generator”. *Thermal Science*, Vol. 22, No. 3, pp. 1481-1492.

Wolfram Research, Inc., 2021. *Wolfram Alpha LLC,* Champaign, IL, https://www.wolframalpha.com. Accessed 20 January 2021.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.

8. APPENDIX A

Mixer 1:

$$m_1 + m_2 = m_3 \, , \tag{A1}$$

$$m_1 \, cp_w \, (T_1 - T_3) + \mathrm{Q}_{\mathrm{m}_1} 1000 = m_2 \, cp_{NPK} (T_3 - T_2), \tag{A2}$$

Centrifuge 1:

$$m_5 = m_6 + m_7 \, , \tag{A3}$$

$$m_6 \, (x_6 \, cp_a + (1 - x_6) \, cp_w)(T_5 - T_6) + m_7 \, (x_7 \, cp_a + (1 - x_7) \, cp_w)(T_5 - T_7) + \mathrm{Q}_{c_1} 1000 = 0, \tag{A4}$$

Dryer 1:

$$m_7 = m_8 + m_9 \, , \tag{A5}$$

$$m_8 \, (u_7 - u_8) + m_9 \, cp_a (T_7 - T_9) + \mathrm{Q}_{\mathrm{D1}} 1000 = 0, \tag{A6}$$

Extractor 1:

$$m_9 + m_{10} = m_{11} + m_{12} \, , \tag{A7}$$

$$m_9 \, cp_a (T_9 - T_{11}) + m_{10} \, cp_m (T_{10} - T_{11}) + \mathrm{Q}_{\mathrm{E1}} 1000 = 0, \tag{A8}$$

Dryer 2:

$$m_{11} = m_{13} + m_{14} \, , \tag{A9}$$

$$m_{13} \, (u_{11} - u_{13}) + m_{14} \, cp_{oil} (T_{11} - T_{14}) + \mathrm{Q}_{\mathrm{D2}} 1000 = 0, \tag{A10}$$

Mixer 2:

$$m_{28} + m_{16} = m_{17} \, , \tag{a11}$$

$$m_{28} \, cp_m (T_{28} - T_{17}) + m_{16} \, cp_{cat} (T_{16} - T_{17}) + Q_{\mathrm{m2}} \; 0.7 \; 1000 = 0, \tag{A12}$$

Reactor:

$$m_{15} + m_{17} = m_{18}\ , \tag{A13}$$

$$m_{28}\left(\frac{hf_m}{PM_m} + cp_m\,(T_{17} - T_1)\right) + m_{16}\,cp_{cat}(T_{17} - T_{18}) + m_{15}\left(\frac{hf_{oil}}{PM_{oil}} + cp_{oil}(T_{15} - T_1)\right) + Q_{reator}1000 = m_{met_{18}}\left(\frac{hf_m}{PM_m} + cp_m\,(T_{18} - T_1)\right) + m_{bio_{18}}\left(\frac{hf_{bio}}{PM_{bio}} + cp_{bio}\,(T_{18} - T_1)\right) + m_{gly_{18}}\left(\frac{hf_{gly}}{PM_{gly}} + cp_{gly}\,(T_{18} - T_1)\right), \tag{A14}$$

Centrifuge 2:

$$m_{18} = m_{19} + m_{20}\ , \tag{A15}$$

$$m_{19}\left(x_{bio_{19}}\,cp_{bio} + x_{gly_{19}}\,cp_{gly} + x_{m_{19}}\,cp_m\right)(T_{18} - T_{19}) + \left(m_{20}\left(x_{gly_{20}}\,cp_{gly} + x_{m_{20}}\,cp_m + x_{cat_{20}}\,cp_{cat}\right)(T_{18} - T_{20})\right) + Q_{cent_2}\,0.7\,1000 = 0\ , \tag{A16}$$

Washer:

$$m_{19} + m_{21} = m_{22}\ , \tag{A17}$$

$$m_{19}\left(x_{bio_{19}}\,cp_{bio} + x_{gly_{19}}\,cp_{gly} + x_{m_{19}}\,cp_m\right)(T_{19} - T_{22}) + m_{21}\,cp_w\,(T_{21} - T_{22}) + (Q_{w_1} - W_{w_1})\,1000 = 0\ , \tag{A18}$$

Centrifuge 3:

$$m_{22} = m_{23} + m_{24} + m_{34}\ , \tag{A19}$$

$$m_{23}\,(x_{bio_{23}}\,cp_{bio} + x_{w_{23}}\,cp_w)(T_{23} - T_{22}) + m_{24}\left(x_{gly_{24}}\,cp_{gly} + x_{m_{24}}\,cp_m + x_{w_{24}}\,cp_w\right)(T_{24} - T_{22}) + m_{34}(u_{34} - u_{22}) - Q_{cent_3}\,1000 = 0\ , \tag{A20}$$

Dryer 3:

$$m_{25} = m_{40} + m_{26}\ , \tag{A21}$$

$$m_{40}\,(u_{25} - u_{40}) + m_{26}\,cp_a(T_{25} - T_{26}) + Q_{d_3}\,1000 = 0\ , \tag{A22}$$

DC1:

$$m_{35} = m_{29} + m_{36}\ , \tag{A23}$$

$$m_{Va}\,h_{Va} + Q_{cond}\,1000 = m_D\,h_D + m_L\,h_L\ , \tag{A24}$$

$$m_F\,h_F + (Q_{cond} + Q_{reb})1000 = m_D\,h_D + m_B\,h_B\ , \tag{A25}$$

DC2:

$$m_{36} = m_{37} + m_{38}\ , \tag{A26}$$

$$m_V\,h_{Va} + Q_{cond}\,1000 = m_D\,h_D\ , \tag{A27}$$

$$m_F\,h_F + (Q_{cond} + Q_{reb})1000 = m_D\,h_D + m_B\,h_B\ , \tag{A28}$$

where $\boldsymbol{m}$, $\boldsymbol{cp}$, $\boldsymbol{T}$, $\boldsymbol{x}$, $\boldsymbol{u}$, $\boldsymbol{Q}$,**W**, $\boldsymbol{h}$, $\boldsymbol{PM}$ are the mass, specific heat, temperature, mass fraction, internal energy, heat, work, enthalpy, and molar weight, respectively.