Chapter 9 Biofuels from Microalgae: Energy and Exergy Analysis for the Biodiesel Case

Daissy Lorena Restrepo-Serna, Mariana Ortiz-Sánchez and Carlos Ariel Cardona-Alzate

Abstract Nowadays, the microalgae have been gaining importance due to their different applications in the biofuel, food, and pharmaceutical industries. One of the applications that is commonly proposed for microalgae oil is the transformation into biodiesel through transesterification. This biodiesel is a biofuel that present energy yields similar to traditional diesel, generating an alternative to replace a fuel from petrochemical origin. The objective of this work is to analyze deeply a process for biodiesel production from microalgae oil. The process includes the cultivation, harvesting, and extraction stages for the oil. In this case, the software Aspen Plus is employed for simulation. From the results obtained (mass and energy balances), the energy, exergy, and economic and environmental analysis of the process are carried out through the development of different scenarios. Last allow to evaluate the energy, economic and environmental viability of this type of processes. As a result, this work shows the challenges to be overcome to make possible the real introduction of microalgae fuels.

Keywords Biodiesel · Biofuel · Microalgae · Exergy analysis Energy analysis

Overview

In the development of green processes, it is considered the biofuel synthesis as a representative example. Due to the growing energetic demand, in especial for the fossil fuels, the attention for generating new alternatives has increased (Quintero et al. 2012). In last years, biodiesel has received a great interest by the scientific community due that its use leads to the reduction in harmful emissions like carbon monoxide, carbon dioxide, and particles like SO_x that are responsible of greenhouse effect (Gouveia and Oliveira 2009). Additionally, biodiesel is the only one biofuel that can be used in a conventional diesel engine without needing great modifications.

D. L. Restrepo-Serna · M. Ortiz-Sánchez · C. A. Cardona-Alzate (⊠) Chemical Engineering Department, National University of Colombia, Manizales Campus, Km 07, Manizales, Colombia e-mail: ccardonaal@unal.edu.co

[©] Springer International Publishing AG 2018

E. Jacob-Lopes et al. (eds.), *Energy from Microalgae*, Green Energy and Technology, https://doi.org/10.1007/978-3-319-69093-3_9

Despite these characteristics, biodiesel presents certain disadvantages like a major consumption due to a less calorific power and less stability than diesel, making no possible to store it for a long time.

The biodiesel is obtained through the transesterification reaction between biological renewable sources such as vegetable oils, animal fats, and microalgae oil with an alcohol (Ma and Hanna 1999). The biodiesel production can be developed using different alkaline and organic catalysts as well as lipases obtained from animals, vegetables, or microorganism sources (Shahid and Jamal 2011). The microalgae are photosynthetic organisms that have the ability to grow very fast and live in adverse conditions. These microorganisms are present in all existent ecosystems, representing a great species variety (Shahid and Jamal 2011).

It is estimated that 50,000 microalgae species exist (Richmond 2004). Species like *Chlorella vulgaris* have aroused a major interest, due to its high protein, lipid (14–22% dry basis), and other products (Becker 1994). This specie has the ability to accumulate a great lipid quantity in absence of nitrogen, generating a fatty acid profile that can be used for biodiesel synthesis (Converti et al. 2009; Fradique et al. 2013). An advantage of microalgae is the capacity of growing in different conditions of cultivation due to its different types of growing: autotrophic, heterotrophic, and mixotrophic.

The microalgae growing includes the adaptation of its metabolism to different cultivation hostile mediums (Bumbak et al. 2011). *Desmodesmus* gene, for example has demonstrated an ordinated reproduction that exposes morphological changes in response to environmental changes like the nutrient availability, temperature an illumination (Trainor 2009).

In the present work, the use of *Chlorella protothecoides* in the biodiesel production was analyzed. For this, four steps were considered: culture and harvesting of microalgae, oil extraction and biodiesel production. To carry out the simulation of this process was used the Aspen Plus to obtain the mass and energy balances (Cerón-Salazar and Cardona-Alzate 2011), which was used in the energy, exergy, and economic and environmental analysis to understand the real viabilities of this process.

1 Microalgae Today: Applications and Uses

Microalgae have been used by indigenous populations to supply their food needing 2000 years ago. Microalgae species like *Nostoc, Arthrospira (Spirulina)*, and *Aphanizomenon* were used with that aim (Spolaore et al. 2006). An example is the Azteca culture, which used microalgae like a high important food source (Venkataraman 1997). Due to the high protein content of various microalgae species, they are a non-conventional source of these proteins that can be used in foods to increase its nutritional value (Guil-Guerrero et al. 2004).

One of the markets reason for microalgae is as a source of carotenoids, being used mainly as natural food colorants and as additives for animal feed. Although the

synthetic forms are less expensive than the naturals, microalgae carotenoids have the advantage of supplying natural isomers in their natural ratio (Guil-Guerrero et al. 2004; Waldenstedt et al. 2003). *D. Salina* is the microorganism most used for the production of β -carotene due to the possibilities of reaching 14% in dry weight, and its cultivation process is easy to implement (can be realized in raceway systems) (Spolaore et al. 2006). Due to the photosynthesis capacity, these microalgae are able to incorporate stable isotopes like ¹³C, ¹⁵N y ²H from inorganic chemical compounds such as ¹³CO₂, ¹⁵NO₃, ²H₂O that are used for protein quantification (Spolaore et al. 2006).

In recent years, due to oil crisis the studies are concentrated in the obtaining and use of microalgae lipids for energy generation, transforming it to biofuels, mainly to biodiesel (Chisti 2007). From this perspective, the microalgae cultivation has been focused on the biotechnological point of view, analyzing their implementation in biorefineries.

2 Process of Culture

2.1 Autotrophic Growth

Microalgae can implement oxygenic photosynthesis and carbon dioxide fixation through Calvin cycle. In other words, they can capture energy from light and use carbon dioxide like carbon source (Yang et al. 2000). Therefore, microalgae have the ability to mitigate carbon dioxide emissions that are produced by industry, generating high-value products (Chen et al. 2011).

2.1.1 Open Ponds Systems

The open ponds systems is the most commonly used configuration for microalgae production, due that these cultivation methods are economically feasible for high-scale biomass production (Safi et al. 2014). The cells grow under sunlight and carbon dioxide supply (Slegers et al. 2013).

These systems have some limitations due to a strict environmental control with the aim to avoid biological contaminations like bacteria or not desired species, also neutralizing pollution in the systems and water evaporation (Safi et al. 2014).

2.1.2 Photobioreactors

Although the initial investment is the highest in comparison to open ponds systems, photobioreactors permit a better contamination control, as well as better use and control of light intensity, carbon dioxide, and nutrients supply (Sforza et al. 2012).

These systems are more appropriated for cells that cannot compete and grow in difficult environments and for the obtaining of pharmaceutical and food products (Safi et al. 2014). To increase lipid productivity in microalgae, growth conditions like nitrogen on nutrients limitation are applied (Mata et al. 2010).

2.1.3 Heterotrophic Growth

The heterotrophic culture of microalgae is interesting, due to the fact that it is expected that growth rates and productivity are major in comparison with autotrophic growth. Additionally, the biomass production using these systems allows a simple and low-cost harvesting (Chen 1996). Nevertheless, one of the main limitations of this type of cultures is the high-cost attached to carbon source (glucose or acetate), in comparison with another nutrients in the medium, added to the competition of these sources with food sector (Liang et al. 2009). Given this situation, it is of great interest to find a cheap carbon source, with the aim to make these cultures competitive when used on a commercial level (Abad and Turon 2012). For this reason, many studies have been focused on the analysis of microalgae growth in agroindustrial residues such as molasses, glycerol, and pig manure (Leesing and Kookkhunthod 2011). Almost it has been demonstrated that microalgae culture can be used for wastewater treatment with high organic and salt levels (Perez-Garcia et al. 2011).

2.1.4 Mixotrophic Growth

In this type of cultures, microorganisms as microalgae can be able to get metabolic energy from both, photosynthesis and carbon organics sources (Chen et al. 2011). It has been reported a high cellular density in mixotrophic cultures for *C. vulgaris*, demonstrating that these microalgae can grow in this type of cultures (Liang et al. 2009).

3 Process of Harvesting

To consider the lipids obtained from microalgae a viable raw material, it is necessary to have in mind the harvesting method to use. This stage can represent a 20–30% of the total cost for biomass obtaining (Rawat et al. 2011) that implies a cumulative high energetic demand for biodiesel production (Dassey and Theegala 2012). These difficulties are mainly associated to the small size of the microalgae and their suspension stability in aqueous media, as a result of negative charges. Additionally, the organic material and low concentration of the streams treated that come from diluted cultures makes difficult this stage (Liu et al. 2013). The harvesting process can be classified into physical, chemical, and biological methods. The selection of the best method depends on several factors like the final products' characteristics (Molina Grima et al. 2003), the deformation–destruction level of the algae after harvesting process thinking in posterior procedures and the economic and energetic costs (Barros et al. 2015).

3.1 Physical Methods

3.1.1 Filtration

Filtration is a dehydration method in which a pressure drop is required along the system with the object to force the fluid through a membrane (Barros et al. 2015). Certain types of filters have been used for the microalgae harvesting, depending on the cell or colonies size. Usually, a high recovery is reached if they are used in big cells, but it fails in the recovery of organisms near to bacterial size (Mohn 1980). Systems like microfiltration can be used for microalgae recovery of common microalgae with a size order of 5–6 μ m (Edzwald 1993). Process like macrofiltration can be used if a previous process of flocculation is performed (Milledge and Heaven 2013). In this type of process, microalgae have the tendency to deposit in the filtrate medium, growing its thickness and flux resistance (Show and Lee 2014). Micro- and ultra-filtration processes are possible alternatives to conventional filtration, but these methods are not usually used at large-scale (Molina Grima et al. 2003).

Methods like dead-end filtration have been evaluated giving as a result that this type of processes can be energetically competitive in comparison with other harvesting methods like flocculation or vacuum filtration (Bila et al. 2012).

Cross-flow filtration methods have demonstrated to be an alternative for microalgae concentration (being concentrated at about 150 times) using less energy that required for other methods like flocculation, centrifugation, or vacuum filtration (Drexler and Yeh 2014).

3.1.2 Centrifugation

In centrifugation, forces higher than gravity are generated with the aim of performing the cell separation, allowing the separation of almost all types of microalgae (Mohn 1980). Disk stack centrifuge are the most common centrifugation systems applied in the commercial plants for the production of high-cost derived products and in the production of pilot-scale biodiesel (Molina Grima et al. 2003). The centrifugation methods are very expensive and energetically no viable if used for low-cost products like biofuels due to the volume to be processed. An alternative for the energetic consumption diminution is the application of flocculation process before decreasing the volume to be treated for centrifugation in 65% (Barros et al. 2015, Wilson 2012).

3.1.3 Flotation

The flotation technique consists in making that the microalgae float up in the water surface through air bubbles. These bubbles catch the cells making they float up with the aim to be recollected in the surface (Sharma et al. 2013). This technology has the advantage to separate low-density microalgae cultures. In some cases, it is necessary the addition of a flocculating agent to perform an effective flotation (Edzwald 1993). It has been found that for a flotation system like dissolved air flotation, the energy demand is high due to the high pressure required for the bubbles' formation (Hanotu et al. 2012).

3.1.4 Ultrasound

This method consists in the cell concentration or flocculation due to acoustic forces, without generating shear strength in the microalgae, and then the cells are recollected by methods using gravity forces like centrifugation or sedimentation. As disadvantages, the low concentration factor in comparison with other methods, and operative costs make this method unsuitable yet (Bosma et al. 2003).

3.2 Chemical Methods

3.2.1 Chemical Flocculation

Due to the negative charge present in microalgae, it does not permit the aggregation of suspended cells. These superficial charges can be neutralized adding flocculating agents, allowing the increment in particle size due to cell aggregation, increasing the sedimentation or flotation rate (Mata et al. 2010). The ideal flocculating agent must have some characteristics like non-toxic, inexpensive, and effective in low concentration compound (Molina Grima et al. 2003). For this reason, inorganic flocculating agents like FeCl₃ and $Al_2(SO_4)_3$ that are very effective are not ideal for an environmental suitable process (Lee et al. 2014). Another disadvantage for chemical flocculation is the possibility of cell alterations generated by flocculating agents that can interfere in the final processing of biomass like lipid extraction (Uduman et al. 2010).

4 **Process of Oil Extraction**

Lipid extraction from microalgae and its efficiency are an important factor in the biodiesel production process (Adam et al. 2012). Two options for lipid recovery are available, dry algal biomass and wet algal biomass extractions. In the dry algal

biomass extraction, the yield is higher, but the associated cost due to biomass drying is considerable (Taher et al. 2014). On the other hand, if wet biomass is used, the cell rupture is realized in the solution where the microalgae were cultivated (Ghasemi Naghdi et al. 2016) and better energy efficient is achieved, but lipid extraction yield is low (Taher et al. 2014).

4.1 Organic Solvent Extraction

Lipid extraction with organic solvents is based on the interaction between long hydrophobic chains of fatty acids and neutral lipids through van der Waals forces, forming globules in the cytoplasm (Medina et al. 1998), which in presence of a nonpolar solvent form a solvent–lipid complex, that leave the cell due to a concentration gradient (Halim et al. 2012). Similar mechanism is applied for the extraction of polar lipids when polar solvents like alcohols are used, due to the interruption of hydrogen bonds (Pragya et al. 2013). An ideal solvent must have certain characteristics like non-toxic, cheap, volatile, and selective compound (Rawat et al. 2011).

4.2 Soxhlet Extraction

This method has the advantage that the cells are in constant contact with fresh organic solvent, avoiding the equilibrium limitation present in batch processes with solvents (Mubarak et al. 2015). It has been demonstrated that using this method, it is possible to recover almost all the microalgae lipids, been the reference method to compare with another extraction methods (Prommuak et al. 2012).

4.3 Bligh and Dyer's Method

The Bligh and Dyer's method is one of the most common methods for lipid extraction, using 1:2 chloroform/methanol (v/v); the lipids in the chloroform phase are separated (Ranjith Kumar et al. 2015). To upgrade this method, many modifications have been proposed, one of those is the addition of 1 M NaCl to avoid denatured lipids. With this method, extraction yields upon 95% from total lipid content had been obtained, with the possibility for using it in both dry and wet algal biomass (Pragya et al. 2013).

4.4 Microwave Extraction

Due to the heat generated by the interaction between water (a polar fluid) and the electric field produced by microwaves, vapor is generated next to the cell. This action breaks the cell wall and releases the compounds that are inside the microalgae (Ghasemi Naghdi et al. 2016). The heating with microwaves is very fast allowing short times for the lipid extraction (Dai et al. 2014).

4.5 Ultrasound Extraction

This method is based on the rupture of the cell through the cavitation produced from the collapse of microbubbles generated by the ultrasound waves. These bubbles are near of the cell wall and when they collapse, a shock wave is created, breaking the cell wall, releasing the internal compounds of the microalgae (Ghasemi Naghdi et al. 2016). The study of the ultrasound method has been combined with the use of organic solvents or solvent-free with the aim of has a clean and environmental process (Adam et al. 2012).

4.6 Supercritical Fluids

The extraction using supercritical fluids is a new green technology with the potential to substitute other types of extraction like the extraction with organic solvents. The use of supercritical fluids has a series of advantages due to the fluid properties like favorable mass transfer that facilities the input to the cell inside, their property variability with operational conditions and that the extracted lipids do not require a posterior stage of purification because are solvent-free (Halim et al. 2012).

4.7 Ionic Liquids Extraction

Ionic liquids are salts that have a melting point under 100 °C that due to unique properties like their thermal stability, high selectivity, solubility, and non-volatile characteristics, which are called to be an alternative for the use of organic solvents (Kim et al. 2012). It has been found that the ionic liquids with a high hydrophobicity and high acidity have better extraction yields (Yu et al. 2016).

4.8 Electroporation

Electroporation is a process in which microalgae cell wall is exposed to high intensities generated by electric fields during certain periods, destabilizing the cell wall with the object to extract the intern compounds of microalgae (Joannes et al. 2015). Electroporation is one of the most used transfection methods due to high efficiency and convenience in comparison with other transfection methods (Kang et al. 2015). This technology is called to be a promising method for cell lipid extraction due to low energy consumption, economic and possibility to be scaled-up (Toepfl et al. 2006).

5 Process of Biodiesel Production

Biodiesel production is developed using vegetable oils, animal fats, and short-chain alcohols. Methanol is the most common used alcohol and presents the best conversions, although ethanol is also used (Demirbas 2005). For the transesterification reaction advance, the use of a catalyst is needed. In last years, the biodiesel production has been investigated from the use of chemical homogeneous catalyst like acids (sulfuric acid) or basics (sodium hydroxide, sodium methoxide, potassium hydroxide, etc.); chemical heterogeneous catalyst, acids (Amberlyst 15, $SO_4^{2^-}$), and basics (KNO₃, Al₂O₃, MgO); lipases from animal, vegetables, or microorganism sources (*Chromobacterium Viscosum*, *Candida Rugosa*, and pork pancreas) (Shahid and Jamal 2011).

6 Exergetic Analysis in Process

From the analysis of energy and especially of the exergy, it is possible to identify the zones of the process in which the main energy changes occur. In this way, it is possible to take measures in order to obtain maximum yields in terms of conversion or separation processes and above all the energy yield involved in each stage (Emets et al. 2006; Ruiz-Mercado et al. 2012; Young and Cabezas 1999).

To determine the change of exergy in the streams of a system can be used, the mathematical model presented in (Zhang et al. 2012):

$$Ex = Ex^{ph} + Ex^{ch} + Ex^{ki} + Ex^{po}$$
⁽¹⁾

where Ex^{ph} , Ex^{ch} , Ex^{ki} and Ex^{po} denote the physical, chemical, kinetic, and potential exegetical flows of each stream, respectively. Usually, the kinetic ($Ex^{ki} = mV^2/2$) and potential (E = mhZ) exergy not present significant values for which Eq. 1 is:

$$Ex = Ex^{ph} + Ex^{ch} \tag{2}$$

Physical exergy is defined as:

$$Ex^{ph} = \sum_{i} n_i ex_i^{ph} \tag{3}$$

$$ex_i^{ph} = (h_j - h_o) - T_o(s_j - s_o)$$
⁽⁴⁾

The differences $(h_j - h_o)$ and $(s_j - s_o)$ can be calculated from Eqs. 5 and 6:

$$(h_j - h_o) = \int_{T_o}^{T_j} Cp dT$$
(5)

$$\left(s_{j}-s_{o}\right)=\int_{T_{o}}^{T_{j}}\frac{Cp}{T}dT-RLn\left(\frac{P}{P_{o}}\right)$$
(6)

The chemical exergy is calculated to take into account the standard exergy of each component (ex_i^{ch})

$$Ex^{ch} = \sum_{i} n_i \left(ex_i^{ch} + RT_o Ln\left(\frac{n_i}{\sum n_i}\right) \right)$$
(7)

For the equipment which presents the need to supply power from an external source, it considered another source of exergy to analyze. This is calculated by Eq. 8.

$$Ex = \int_{T_1}^{T_2} \left(1 - \frac{T_o}{T} \right) \delta Q \tag{8}$$

7 Study Case: Biodiesel from Microalgae: Chlorella Protothecoides Case

7.1 Process Design

7.1.1 Culture of Microalgae

In this work, it was considered a feed flow of 100,000 kg/h as calculation basis. The microalgae culture was considered (for simulation purpose) using the conditions reported by Yoo et al. (2014). The substrate employed was glucose at a

concentration of 40 g/L. Before to carry out the culture, the medium was autoclaved at 121 °C for 15 min. Then the inoculum was added.

Cultivation was performed in such a way that an average residence time of 15 days was generated. Then to carry out a concentration of the biomass obtained, the mixture from the culture step was passed by a centrifugation process (Luangpipat and Chisti 2016). At this point, a cell disruption stage is carried out, in which autoclaving was used at 125 °C with 1.5 MPa for 5 min. To carry out the removal of the lipids from the previous step, a mixture of chloroform–methanol (1:1 v/v) was added in a ratio of 1:1 (Lee et al. 2010).

For the production of biodiesel, a mixture of ethanol and sodium hydroxide was realized (Bambase et al. 2007). The resulting mixture is added to the lipids previously obtained. Heating was carried out to 60 °C and passed to the transesterification reactor. This reactor is designed based on kinetics reported by Mussatto et al. (2014). In order to recover the ethanol which not reacts, a distillation step was carried out. The bottom product is mixed with hot water in a 1:3 v/v ratio. The mixture was decanted allowing the separation of the unreacted oil and a mixture of biodiesel and glycerol. This mixture was brought to a separation train in which a purity of 95% biodiesel was achieved. The obtained glycerol was mixed with the catalyst, which was sulfuric acid, which allows the precipitation of the salt generated obtaining a glycerol with a purity of 80%.

7.2 Energy and Exergy Analysis

The energy and exergetic analyses are performed from the data obtained in the simulated Aspen Plus. For the energy analysis, a quantification of the energy required by each equipment involved in each processing step was performed. Similarly for the exergetic analysis, the exergy consumed in each stage is quantified and additionally the calculation of the exergy of the currents involved in each stage of processing was carried out in order to determine the energy efficiency of the process as mentioned above. To carry out the energy and exergetic analyses of biodiesel production from microalga oil, three stages of processing are considered: culture and harvesting of microalgae, oil extraction, and biodiesel production (see Fig. 1). From this, the following results can be obtained for the analyzed case.

7.3 Economic Analysis

Using the mass and energy balances obtained by simulating the process of obtaining biodiesel, an economic analysis was carried out. For this purpose, Aspen Process Economic Analyzer software was used. In this analysis, the method of depreciation of straight line is considered. This allows to determine the economic

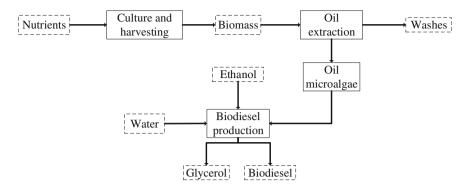


Fig. 1 Stages considered in the analysis of this work

viability of this type of processes. In Table 1 can be found economic parameters and costs of raw materials used in performing the analysis under Colombian context.

7.4 Environmental Analysis

By the determination of the environmental impact caused by the proposed process, the software developed by the Environmental Protection Agency (EPA): Waste Algorithm Reduction (WAR) was used. It allows to evaluate the environmental impact through eight categories: Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential Exposure (HTPE), Terrestrial Toxicity Potential (TTP), Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Smog Formation Potential (PCOP), and Acidification Potential (AP) (Young et al. 2000).

7.5 Results and Discussion

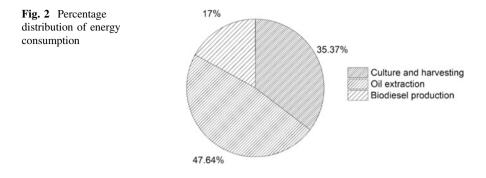
For the production of biodiesel from microalgae, there is an energy requirement of 1,003,967 MJ/h (taken into account a calculation base for feed flow of 100,000 kg/h). Here the percentage distribution of this energy is presented in Fig. 2. In this figure, it is possible to observe how the extraction of the oil of the microalgae has the highest energy consumption. One of the causes for this situation is due to the energy required for solvent evaporation once the oil extraction has been performed. On the other hand, there is the energetic requirement of the bioreactor where microalgae cultivation is carried out. Under the conditions analyzed, it is necessary that the culture and

Item	Unit	Value	Ref.
Investment Parameters			
Tax rate	%	25	Dávila et al. (2014)
Interest rate	%	17	
Raw materials			
Potassium dihydrogen phosphate	USD/kg	161	Sigma-Aldrich (n.d.)
Dibasic potassium phosphate	USD/kg	199.5	
Magnesium sulfate heptahydrate	USD/kg	127.9	
Iron (II) sulfate heptahydrate	USD/kg	117.9	
Boric acid	USD/kg	92.4	
Calcium chloride dihydrate	USD/kg	149.5	
Manganese (II) chloride tetrahydrate	USD/kg	198.4	
Zinc sulfate heptahydrate	USD/kg	142.4	
Cupric sulfate pentahydrate	USD/kg	144	
Molybdenum trioxide	USD/kg	581.9	
Thiamine hydrochloride	USD/kg	426.5	
Glucose	USD/kg	165	
Glycine	USD/kg	94.3	
Sodium hydroxide	USD/kg	111.6	
Chloroform	USD/L	87.1	
Methanol	USD/L	65.4	
Ethanol	USD/L	0.55	ICIS (n.d.)
Utilities			
LP steam	USD/tonne	1.57	Moncada et al. (2015)
MP steam	USD/tonne	8.18	
HP steam	USD/tonne	9.86	
Potable water	USD/m ³	1.25	Dávila et al. (2014)
Fuel	USD/MMBTU	7.21	
Electricity	USD/kWh	0.1	
Operation			· ·
Operator	USD/h	2.14	Dávila et al. (2014)
Supervisor	USD/h	4.29	

 Table 1 Investment parameters and prices used in the economic analysis

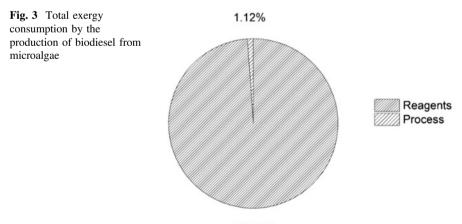
harvesting stage presents a consumption of 35.37% of the total energy required for the process. Finally, it is observed that the production of biodiesel presents the lowest energy consumption for this case. Thus, in energy terms, the production of microalgae oil presents a high energy consumption, due to the low yields obtained in the production of microalgae oil.

Similarly, as observed in the energy analysis, in the exergy analysis, an exergetic consumption of 19,601,822.14 MJ/h (taken into account a feed flow of

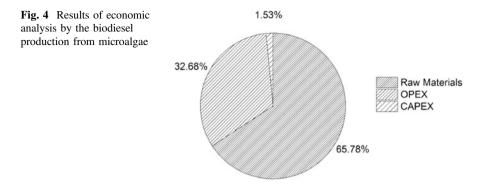


100,000 kg/h) was evidenced, where the exergy present in the form of energy contained inside of reagents used throughout the process represents 98.88% of this percentage (see Fig. 3). On the other hand, the stage of the process that presents a greater exergetic consumption is the culture and harvesting of the microalgae. This factor is presented by the high duration of microalgae cultivation, which is why an exergetic consumption of 39.53% is present at this stage. The extraction of oil and the production of biodiesel present a percentage of 43.77 and 16.7%, respectively. Thus, the most inefficient stage of the process is the cultivation and harvesting of the microalgae. Under the process conditions analyzed, an exergetic efficiency of 37.08% was presented.

In production processes, different sources of expenses are presented, such as operating expenses, operating expenses, or operational expenses (OPEX) together with the costs of equipments (CAPEX). Similarly, another expense is the acquisition of the raw materials needed to obtain a final product such as biodiesel. Figure 4 shows the percentage distribution of expenses. In this figure, it can be

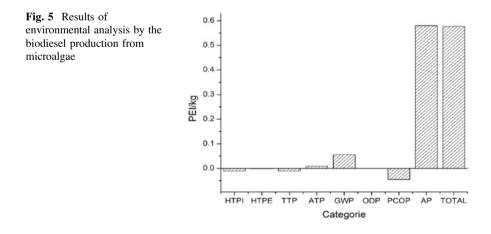


98.88%



observed that the greatest expense presented in this productive process is associated with raw materials. This is because it was necessary to use a high feed flow in the growing stage to obtain an amount of oil such that it could be used for the production of biodiesel. But even with this consideration, only the production of biodiesel does not provide a profit so that it can meet the expenses incurred throughout the process allowing a positive a profit margin. In this sense, other processes can be implemented which allow the production of other value-added products from the waste generated within the process. This alternative may lead to a decrease in OPEX, which is mainly represented by 76.14% of the cost of utilities required in the process. For this, it is necessary to carry out an energy integration of the different stages of the process, thus allowing a higher use in the energy and exergetic resources.

As for the environmental analysis, it is obtained that given the amount of waste generated in this process, a negative impact on the environment was presented. That is, the waste generated presents a higher index of contamination than the reagents used. The above can be seen in Fig. 5. Among the wastes generated are those



obtained from the extraction of the oil, which still have a potential for its use in obtaining other products through fermentation processes or chemical synthesis. On the other hand, these types of processes present a high acidification potential, which is mainly due to the high energy demand that is presented. For this, it is necessary to use a large amount of fuel to supply it. During the combustion process to obtain the required energy, there is a high release of carbon dioxide, which has a negative impact on the environment by altering the acidity of the air. As a consequence of this process can cause acid rain among other phenomena caused by the high concentration of this type of gases in the atmosphere.

8 Energy Production from Microalgae *Chlorella Protothecoides* Through the Biorefinery Concept: A New Proposal

Microalgae present a high potential to be used to obtain different value-added products, which can lead to a more sustainable production of bioenergy. For this, it is necessary to apply concepts such as biorefinery (Moncada et al. 2013; Mussatto et al. 2013). From this concept, it is possible to use the different residues that are presented in a stand-alone case of biodiesel production in other processes. Among the products with great potential to be obtained under this concept is energy from the biomass resulting from the process of lysis. In this same process, it is possible to obtain both glucose and lipids. The glucose obtained can be used in ethanol production (Quintero and Cardona 2009). Where it can be used in conjunction with lipids for the biodiesel production. Figure 6 presented this idea.

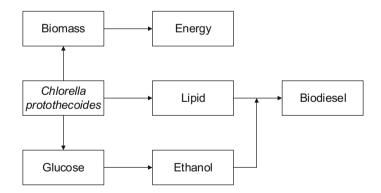


Fig. 6 Application of the Chlorella protothecoides under biorefinery concept

9 Conclusion

Given the high energy requirements presented by this type of processes, it is necessary to look others alternatives that allow the reduction of energy consumption in the culture and harvesting of microalgae and oil extraction stages. This can be achieved through the implementation of other technologies that allow carrying out the same process, but which require low energy consumption. In this way, a reduction in the energy requirements of the process and thus in the costs of profits can be achieved, which is reflected directly in the cost of production.

The application of energy and exergetic analysis was presented as a powerful tool for the determination of inefficiencies in this type of processes. Here the major irreversibilities are presented in the extraction of the oil due to the cellular lysis that must be made for the obtaining of the same, which makes this stage of the process present the greatest irreversibilities.

References

- Abad, S., & Turon, X. (2012). Valorization of biodiesel derived glycerol as a carbon source to obtain added-value metabolites: Focus on polyunsaturated fatty acids. *Biotechnology Advances*, 30(3), 733–741.
- Adam, F., Abert-Vian, M., Peltier, G., & Chemat, F. (2012). "Solvent-free" ultrasound-assisted extraction of lipids from fresh microalgae cells: A green, clean and scalable process. *Bioresource Technology*, 114, 457–465.
- Bambase, M. E., Nakamura, N., Tanaka, J., & Matsumura, M. (2007). Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. *Journal of Chemical Technology and Biotechnology*, 82(3), 273–280.
- Barros, A. I., Gonçalves, A. L., Simões, M., & Pires, J. C. M. (2015). Harvesting techniques applied to microalgae: A review. *Renewable and Sustainable Energy Reviews*, 41, 1489–1500.
- Becker, E. (1994). Microalgae—biotechnology and microbiology. *Journal of Experimental Marine Biology and Ecology*, 183, 300–301.
- Bilad, M. R., Vandamme, D., Foubert, I., Muylaert, K., & Vankelecom, I. F. J. (2012). Harvesting microalgal biomass using submerged microfiltration membranes. *Bioresource Technology*, 111, 343–352.
- Bosma, R., Van Spronsen, W. A., Tramper, J., & Wijffels, R. H. (2003). Ultrasound, a new separation technique to harvest microalgae. *Journal of Applied Phycology*, 15(2–3), 143–153.
- Bumbak, F., Cook, S., Zachleder, V., Hauser, S., & Kovar, K. (2011). Best practices in heterotrophic high-cell-density microalgal processes: Achievements, potential and possible limitations. *Applied Microbiology and Biotechnology*. https://doi.org/10.1007/s00253-011-3311-6.
- Cerón-Salazar, I., & Cardona-Alzate, C. (2011). Integral evaluation process for obtaining pectin and essential oil from orange peel. *Inginería y Ciencia*, 7(13), 1794–9165.
- Chen, C. Y., Yeh, K. L., Aisyah, R., Lee, D. J., & Chang, J. S. (2011). Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: A critical review. *Bioresource Technology*, 102(1), 71–81.
- Chen, F. (1996). High cell density culture of microalgae in heterotrophic growth. *Trends in Biotechnology*, 14(11), 421-426.
- Chisti, Y. (2007). Biodiesel from microalgae. Biotechnology Advances, 25(3), 294-306.

- Converti, A., Casazza, A. A., Ortiz, E. Y., Perego, P., & Del Borghi, M. (2009). Effect of temperature and nitrogen concentration on the growth and lipid content of Nannochloropsis oculata and Chlorella vulgaris for biodiesel production. *Chemical Engineering and Processing: Process Intensification*, 48(6), 1146–1151.
- Dai, Y. M., Chen, K. T., & Chen, C. C. (2014). Study of the microwave lipid extraction from microalgae for biodiesel production. *Chemical Engineering Journal*, 250, 267–273.
- Dassey, A.J., Theegala, C.S. (2012). Cost Analysis of Microalgal Harvesting for Biofuel Production. 2012 Dallas, Texas, July 29 - August 1, 2012. St. Joseph, Mich.: ASABE. https:// doi.org/10.13031/2013.41701.
- Dávila, J. A., Hernández, V., Castro, E., & Cardona, C. A. (2014). Economic and environmental assessment of syrup production. *Colombian case. Bioresource Technology*, 161, 84–90.
- Demirbas, A. (2005). Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. *Progress in Energy and Combustion Science*.
- Drexler, I. L. C., & Yeh, D. H. (2014). Membrane applications for microalgae cultivation and harvesting: A review. *Reviews in Environmental Science & Biotechnology*, 13(4), 487–504.
- Edzwald, J. K. (1993). Algae, bubbles, coagulants, and dissolved air flotation. *Water Science and Technology*, 27, 67–81.
- Emets, S. V., Hoo, K. A., & Mann, U. (2006). A modified hierarchy for designing chemical processes. *Industrial and Engineering Chemistry Research*, 45, 5037–5043.
- Fradique, M., Batista, A. P., Nunes, M. C., Gouveia, L., Bandarra, N. M., & Raymundo, A. (2013). Isochrysis galbana and Diacronema vlkianum biomass incorporation in pasta products as PUFA's source. *LWT - Food Science and Technology*, 50(1), 312–319.
- Ghasemi Naghdi, F., González González, L. M., Chan, W., & Schenk, P. M. (2016). Progress on lipid extraction from wet algal biomass for biodiesel production. *Microbial Biotechnology*, 9 (6), 718–726.
- Gouveia, L., & Oliveira, A. C. (2009). Microalgae as a raw material for biofuels production. Journal of Industrial Microbiology and Biotechnology, 36(2), 269–274.
- Guil-Guerrero, J.L., Navarro-Juárez, R., López-Martínez, J.C., Campra-Madrid, P., Rebolloso-Fuentes, M.M. (2004). Functional properties of the biomass of three microalgal species. *Journal of Food Engineering*, 65(4), 511–517.
- Halim, R., Danquah, M. K., & Webley, P. A. (2012). Extraction of oil from microalgae for biodiesel production: A review. *Biotechnology Advances*, 30(3), 709–732.
- Hanotu, J., Bandulasena, H. C. H., & Zimmerman, W. B. (2012). Microflotation performance for algal separation. *Biotechnology and Bioengineering*, 109(7), 1663–1673.
- ICIS. (n.d.). Retrieved July 13, 2017, from http://www.icis.com/chemicals/channel-infochemicals-a-z/.
- Joannes, C., Sipaut, C.S., Dayou, J., Yasir, S.M., Mansa, R.F. (2015). Review Paper on Cell Membrane Electroporation of Microalgae using Electric Field Treatment Method for Microalgae Lipid Extraction. *IOP Conference Series: Materials Science and Engineering*, 78, 12034. https://doi.org/10.1088/1757-899X/78/1/012034.
- Kang, S., Kim, K. H., & Kim, Y. C. (2015). A novel electroporation system for efficient molecular delivery into Chlamydomonas reinhardtii with a 3-dimensional microelectrode. *Scientific Reports*, 5, 15835.
- Kim, Y. H., Choi, Y. K., Park, J., Lee, S., Yang, Y. H., Kim, H. J., et al. (2012). Ionic liquid-mediated extraction of lipids from algal biomass. *Bioresource Technology*, 109, 312–315.
- Lee, C. S., Robinson, J., & Chong, M. F. (2014). A review on application of floculants in wastewater treatment. *Process Safety and Environmental Protection*, 92, 489–508.
- Lee, J. Y., Yoo, C., Jun, S. Y., Ahn, C. Y., & Oh, H. M. (2010). Comparison of several methods for effective lipid extraction from microalgae. *Bioresource Technology*, 101(1), S75–S77.
- Leesing, R., & Kookkhunthod, S. (2011). Heterotrophic Growth of Chlorella sp. KKU-S2 for Lipid Production using Molasses as a Carbon Substrate, *9*, 87–91.
- Liang, Y., Sarkany, N., & Cui, Y. (2009). Biomass and lipid productivities of Chlorella vulgaris under autotrophic, heterotrophic and mixotrophic growth conditions. *Biotechnology Letters*, 31 (7), 1043–1049.

- Liu, J., Zhu, Y., Tao, Y., Zhang, Y., Li, A., Li, T., et al. (2013). Freshwater microalgae harvested via flocculation induced by pH decrease. *Biotechnology for Biofuels*, *6*(1), 98.
- Luangpipat, T., & Chisti, Y. (2016). Biomass and oil production by Chlorella vulgaris and four other microalgae - Effects of salinity and other factors. *Journal of Biotechnology*, 257, 47–57.
- Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource Technology*, 70(1), 1–15.
- Mata, T. M., Martins, A. A., & Caetano, N. S. (2010). Microalgae for biodiesel production and other applications: A review. *Renewable and Sustainable Energy Reviews*, 14(1), 217–232.
- Medina, A. R., Grima, E. M., Gimenez, A. G., & Gonzalez, M. J. I. (1998). Downstream processing of algal polyunsaturated fatty acids. *Biotechnology Advances*, 16(3), 517–580.
- Milledge, J. J., & Heaven, S. (2013). A review of the harvesting of micro-algae for biofuel production. *Reviews in Environmental Science and Biotechnology*, 12(2), 165–178.
- Mohn, F.H. (1980). Experiences and strategies in the recovery of biomass from mass cultures of microalgae. Algal Biomass, 471–547.
- Molina Grima, E., Belarbi, E. H., Acién Fernández, F. G., Robles Medina, A., & Chisti, Y. (2003). Recovery of microalgal biomass and metabolites: Process options and economics. *Biotechnology Advances*, 20(7–8), 491–515.
- Moncada, J., Hernández, V., Chacón, Y., Betancourt, R., & Cardona, C. A. (2015). Citrus Based Biorefineries. In D. Simmons (Ed.), *Citrus Fruits. Production, Consumption and Health Benefits* (pp. 1–26). Nova Publishers.
- Moncada, J., Matallana, L. G., & Cardona, C. A. (2013). Selection of Process Pathways for Biorefinery Design Using Optimization Tools: A Colombian Case for Conversion of Sugarcane Bagasse to Ethanol, Poly-3-hydroxybutyrate (PHB), and Energy. *Industrial and Engineering Chemistry Research*, 52(11), 4132–4145.
- Mubarak, M., Shaija, A., & Suchithra, T. V. (2015). A review on the extraction of lipid from microalgae for biodiesel production. *Algal Research*, 7, 117–123.
- Mussatto, S. I., Moncada, J., Roberto, I. C., & Cardona, C. A. (2013). Techno-economic analysis for brewer's spent grains use on a biorefinery concept: The Brazilian case. *Bioresource Technology*, 148, 302–310.
- Mussatto, S. I., Santos, J. C., Filho, W. C. R., & Silva, S. S. (2014). Purification of xylitol from fermented hemicellulosic hydrolyzate using liquid–liquid extraction and precipitation techniques. *Applied Energy*, 123, 108–120.
- Perez-Garcia, O., Escalante, F.M.E., de-Bashan, L.E., & Bashan, Y. (2011). Heterotrophic cultures of microalgae: Metabolism and potential products. *Water Research*, 45, 11–36.
- Pragya, N., Pandey, K. K., & Sahoo, P. K. (2013). A review on harvesting, oil extraction and biofuels production technologies from microalgae. *Renewable and Sustainable Energy Reviews*, 24, 159–171.
- Prommuak, C., Pavasant, P., Quitain, A. T., Goto, M., & Shotipruk, A. (2012). Microalgal lipid extraction and evaluation of single-step biodiesel production. *Engineering Journal*, 16(5), 157– 166.
- Quintero, J. A., & Cardona, C. A. (2009). Ethanol dehydration by adsorption with starchy and cellulosic materials. *Industrial and Engineering Chemistry Research*, 48(14), 6783–6788.
- Quintero, J. A., Felix, E. R., Rincón, L. E., Crisspín, M., Fernandez Baca, J., Khwaja, Y., et al. (2012). Social and techno-economical analysis of biodiesel production in Peru. *Energy Policy*, 43, 427–435.
- Ranjith Kumar, R., Hanumantha Rao, P., & Arumugam, M. (2015). Lipid extraction methods from microalgae: A comprehensive review. *Frontiers in Energy Research*, 2, 1–9.
- Rawat, I., Ranjith Kumar, R., Mutanda, T., & Bux, F. (2011). Dual role of microalgae: Phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. *Applied Energy*, 88(10), 3411–3424.
- Richmond, A. (2004). Handbook of microalgal culture: biotechnology and applied phycology/ edited by Amos Richmond. Orton. Catie. Ac. Cr, 472. https://doi.org/10.1002/9780470995280.
- Ruiz-Mercado, G. J., Smith, R. L., & Gonzalez, M. A. (2012). Sustainability indicator for chemical processes: I. taxonomy. *Industrial & Engineering Chemistry Research*, 51, 2309–2328.

- Safi, C., Zebib, B., Merah, O., Pontalier, P. Y., & Vaca-Garcia, C. (2014). Morphology, composition, production, processing and applications of Chlorella vulgaris: A review. *Renewable and Sustainable Energy Reviews*, 35, 265–278.
- Sforza, E., Bertucco, A., Morosinotto, T., & Giacometti, G. M. (2012). Photobioreactors for microalgal growth and oil production with Nannochloropsis salina: From lab-scale experiments to large-scale design. *Chemical Engineering Research and Design*, 90(9), 1151–1158.
- Shahid, E. M., & Jamal, Y. (2011). Production of biodiesel: A technical review. *Renewable and Sustainable Energy Reviews*, 15(9), 4732–4745.
- Sharma, K. K., Garg, S., Li, Y., Malekizadeh, A., & Schenk, P. M. (2013). Critical analysis of current microalgae dewatering techniques. *Biofuels*, 4, 397–407.
- Show, K.Y., Lee, D.J. (2014). Chapter 5 Algal Biomass Harvesting BT Biofuels from Algae (pp. 85–110). Amsterdam: Elsevier. https://doi.org/10.1016/B978-0-444-59558-4.00005-X.
- Sigma-Aldrich. (n.d.). Retrieved July 13, 2017, from https://www.sigmaaldrich.com/us-export. html.
- Slegers, P. M., Lösing, M. B., Wijffels, R. H., van Straten, G., & van Boxtel, A. J. B. (2013). Scenario evaluation of open pond microalgae production. *Algal Research*, 2(4), 358–368.
- Spolaore, P., Joannis-Cassan, C., Duran, E., & Isambert, A. (2006). Commercial applications of microalgae. *Journal of Bioscience and Bioengineering*, 101(2), 87–96.
- Taher, H., Al-Zuhair, S., Al-Marzouqi, A. H., Haik, Y., & Farid, M. (2014). Effective extraction of microalgae lipids from wet biomass for biodiesel production. *Biomass and Bioenergy*, 66, 159– 167.
- Toepfl, S., Mathys, A., Heinz, V., & Knorr, D. (2006). Review: Potential of High Hydrostatic Pressure and Pulsed Electric Fields for Energy Efficient and Environmentally Friendly Food Processing. *Food Reviews International*, 22(4), 405–423.
- Trainor, F. R. (2009). Perspective: Breaking the habit. Integrating plasticity into taxonomy. Systematics and Biodiversity, 7(2), 95–100.
- Uduman, N., Qi, Y., Danquah, M. K., Forde, G. M., & Hoadley, A. (2010). Dewatering of microalgal cultures: A major bottleneck to algae-based fuels. *Journal of Renewable and Sustainable Energy*, 2, 1–15.
- Venkataraman, L. V. (1997). Spirulina platensis (Arthrospira): Physiology, Cell Biology and Biotechnologym, edited by Avigad Vonshak. *Journal of Applied Phycology*, 9(3), 295–296.
- Waldenstedt, L., Inborr, J., Hansson, I., & Elwinger, K. (2003). Effects of astaxanthin-rich algal meal (Haematococcus pluvalis) on growth performance, caecal campylobacter and clostridial counts and tissue astaxanthin concentration of broiler chickens. *Animal Feed Science and Technology*, 108(1), 119–132.
- Wilson, M. (2012). Cross flow filtration for mixed-culture algae harvesting for municipal wastewater lagoons. Master of Science Thesis, Utah State University.
- Yang, C., Hua, Q., & Shimizu, K. (2000). Energetics and carbon metabolism during growth of microalgal cells under photoautotrophic, mixotrophic and cyclic light-autotrophic/ dark-heterotrophic conditions. *Biochemical Engineering Journal*, 6(2), 87–102.
- Yoo, S. J., Kim, J. H., & Lee, J. M. (2014). Dynamic modelling of mixotrophic microalgal photobioreactor systems with time-varying yield coefficient for the lipid consumption. *Bioresource Technology*, 162, 228–235.
- Young, D. M., & Cabezas, H. (1999). Designing sustaibanle processes with simulation: The waste reduction (WAR) algorithm. *Engineering, Computers and Chemical*, 23, 1477–1491.
- Young, D., Scharp, R., & Cabezas, H. (2000). The waste reduction (WAR) algorithm: Environmental impacts, energy consumption, and engineering economics. *Waste Management*, 20(8), 605–615.
- Yu, Z., Chen, X., & Xia, S. (2016). The mechanism of lipids extraction from wet microalgae Scenedesmus sp. by ionic liquid assisted subcritical water. *Journal of Ocean University of China*, 15(3), 549–552.
- Zhang, Y., Li, B., Li, H., & Zhang, B. (2012). Exergy analysis of biomass utilization via steam gasification and partial oxidation. *Thermochimica Acta*, 538, 21–28.