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Design of Biodiesel and Bioethanol Production Process from Microalgae Biomass Using Exergy Analysis Methodology

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Microalgae are a promising source of energy and its principal advantage that does not compete with the feeding supply. Besides, microalgae have other benefits, such as the use of infertile land for its cultivation and seawater and flue gas as nutrients source. Exergy analysis is a useful tool for measure the quantity and quality of the energy sources and studies the sustainability process. This methodology requires analysing material and energy flows of each stage of the production process. In this study, exergy analysis was applied to one scenario taking a production capacity of 100 t/y of biodiesel from microalgae biomass. Chlorella sp was used as reference species. This strain has been widely studied, and their characteristics are known. The process designed have five stages: cultivation, harvesting, drying, oil transformation, and residual biomass transformation. The process was simulated using specialized software. The mass, energy and exergy balances were performed for each stream of the process. Finally, the exergy analysis was developed, and it was found that the residual biomass transformation stage with 32 % value present the lowest exergy efficiency of the process, followed by oil extraction stage with an efficiency of 52 %. The overall exergy efficiency of the process was 89 %, which indicates that designed process is adequate and have potential from the energy point of view.

1. Introduction

At present, the continued use of petroleum-based fuels is recognized as unsustainable, owing to their non-renewable origin which connects directly oil production with progressive decreasing of available reserves, this depletion creates consequences as the increase of fossil fuels prices worldwide, from the environmental point of view, growing consumption of fossil fuels for transport increases gas emissions after their combustion which contributes to environmental pollution by CO_2 release. These economic and environmental factors are favoured the development of new policies related to support of research, development and the use of alternative energy sources and renewable fuels, mainly those that can replace fossil fuels used in transportation.
Third-generation biofuels are derived from microorganisms, such as yeast, fungi and microalgae, some of these microbes can biosynthesize and accumulate large amounts of lipids and/or sugars, fungi like *Trichosporon fermentans* have been studied for microbial oil production and biodiesel preparation (Huang et al., 2009), however, the most attractive source for third generation biofuels production are microalgae. Microalgae are unicellular and simple multi-cellular microorganisms, including prokaryotic microalgae as cyanobacteria and eukaryotic microalgae as green algae, red algae and diatoms. The photosynthetic efficiency of microalgae is around of 50 times higher than terrestrial plants (Scragg et al., 2002). Microalgae have recently been rediscovered as promising candidates for biotechnological applications and efficient energy production systems. Depending on the strain, microalgae can grow in a wide range of temperatures, pH and nutrients availability. They have a growth rate between 20 and 30 times higher than other sources for biofuels, some microalgae species have the ability to produce up to 20 times more oil per unit area than palm, oil content of certain strains in some cases exceeds 80 % in dry weight biomass under appropriate conditions (Chisti, 2007).
Conversion of microalgae to biofuel can be classified in either a biochemical and thermochemical conversion process. The biochemical conversion processes of biofuel are transesterification and fermentation, which

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produce biodiesel and ethanol as main products, respectively. The thermochemical processes can be categorized as pyrolysis, liquefaction, gasification and hydrogenation. The biodiesel is one of the most well-known biofuel products from microalgae. Biodiesel is produced by transesterification with glycerol as co-product. Yields of more than 90 % of crude oil can be achieved with conversion conditions of 35 – 60 °C at atmospheric pressure, where the molar ratio of oil to alcohol is 3:1 – 6:1 (Peralta et al., 2010). In acid and basic transesterification, the methanol and catalyst are blended before being pumped into a reactor tank, the amounts of the methanol and the catalyst are controlled to avoid excess amounts, which reduces the quality of final product and increases the energy required to remove the excess alcohol.
Microalgae can be also potentially used for bioethanol production owing to the presence of carbohydrates within their composition and very low lignin percentage, cellulosic material must be removed from the cell wall before they can be used as a feedstock for fermentation. Acid hydrolysis of microalgae has been also used for reducing sugars release (Gonzalez-Delgado et al., 2013) such as a multifunctional process using methanol and ethanol. Ethanol yields of up to 0.26 g of ethanol per 1 g of microalgal biomass can be achieved (Harun et al., 2011). The ethanol production of microalgae can be improved by using yeast and an immobilized fermenter. The most preferable yeast for ethanol production is Saccharomyces cerevisiae, which has yields as high as 70 g/L. Engineered yeast can also produce up to 61.8 g of ethanol from 1 l of corn starch over a 72 h fermentation process (Shigechi et al., 2004).
Several methodologies based on thermodynamic principles have been used for the evaluation of industrial systems and thermal energy storage processes. The exergy analysis is presented as an alternative that allows overcoming the limitations of the first law of thermodynamics. Besides, shows the energy degradation sites in a process and it can help to improve a unit operation, a technology or a process. Also, the exergy analysis allows to choose different alternatives to enhance a process, and it is an appropriate tool for the new technologies evaluation for the production of biofuels. The need to find and to implement increasingly efficient alternative processes for energy production forces the human being to look for ways processes from non-conventional raw to produce biofuels.
For the above-mentioned reasons, biodiesel production process from microalgae and the use biomass residual for bioethanol production was proposed and then evaluated using exergy analysis methodology. The total exergy loss, the exergy of wastes, the exergy of utilities and exergy efficiency for each stage and the overall process was calculated. The results were analyzed and were evaluated the proposed process feasibility from the energy point of view compared concerning biofuels production from conventional others feedstock.

2. Methodology

For to select the microalgae for the biofuels production process was taken into account a series of characteristics such as high oil content, high productivity, ease of production, resistance against contamination, low-cost production, among others. The production process of 100 t of biodiesel was simulated using the industrial process software Aspen Plus® version 8.1, which has been widely used for studies related to simulation of existing and emerging technologies for biofuels and co-products production in large scale using several feedstocks (Peralta et al., 2013). The Non-Random Two Liquid (NRTL) model was used to predict the activity coefficients of the components in the liquid phase, this model has been widely validated and used for the modelling of biodiesel production processes (Ofori-Boateng et al., 2012). It was considered the following stages: cultivation, harvesting, drying, oil extraction, oil transformation, residual biomass transformation. Then, it was performed the mass and energy balance for all process applying the Eq(1) and Eq(2). The energy balance was carried out using the Eq(3). Finally, for each stage of the process, the energy efficiency was determined using the Eq(4).

$$\sum_i (\dot{m}_i)_{in} = \sum_i (\dot{m}_i)_{out} \tag{1}$$

The energy balance is expressed as:

$$\sum_i (\dot{m}_i * h_i)_{in} - \sum_i (\dot{m}_i * h_i)_{out} + \dot{Q} - \dot{W} = 0 \tag{2}$$

where h_i is the enthalpy of the compounds i, $\dot{Q}$ is the heat transfer rate and $\dot{W}$ is the rate of work
The general exergy balance equation is defined in the rate form as:

$$\sum \dot{E}x_{mass,in} - \sum \dot{E}x_{mass,out} + \dot{E}x_{heat} - \dot{E}x_{work} = \sum \dot{E}x_{loss} \tag{3}$$

$\dot{E}x = \dot{m} * ex$ where ex is the specific exergy of the compound

The exergy efficiency is expressed as:

$$\eta = 1 - \left(\frac{\dot{E}x_{loss}}{\dot{E}x_{input}}\right) \quad (4)$$

3. Results

In this study Chlorella sp. it was taken as a representative genus, this strain has high growth rates and can produce in large amounts of lipids. For the simulation of the biomass composition, the microalgae were normalized taking into account information reported for (Peralta et al., 2013), the microalgae oil content was established in 30 % of this 5.11 % are free fatty acids and 94.89 % corresponding to triglycerides. In Table 1 some conditions for the designed process are shown.

Table 1: Some conditions for the designed biofuel production process

Characteristics of design	
Location	Guajira-Colombia
Superficial area	3,200 ha
Natural resources used	Seawater
Energy resources used	Solar light
Industrial waste used	Flue gas
Days worked per year	365

The technology selected for cultivation was an open pond. Open ponds have lower-cost construction and lower-cost operating, are easier to handle than photo bioreactors, and it is not necessary to have the equipment the oxygen release. For the harvesting stage the chemical flocculation was selected, it is a technique that has a lower operating time than filtration and sedimentation (Chun-Yen et al., 2011). It is easy to control compared to electrolyte techniques, the energy requirements and operating costs are lower compared to technologies such as centrifugation and flotation (Molina et al., 2003). The figure 1 shows the flocculation system proposed.

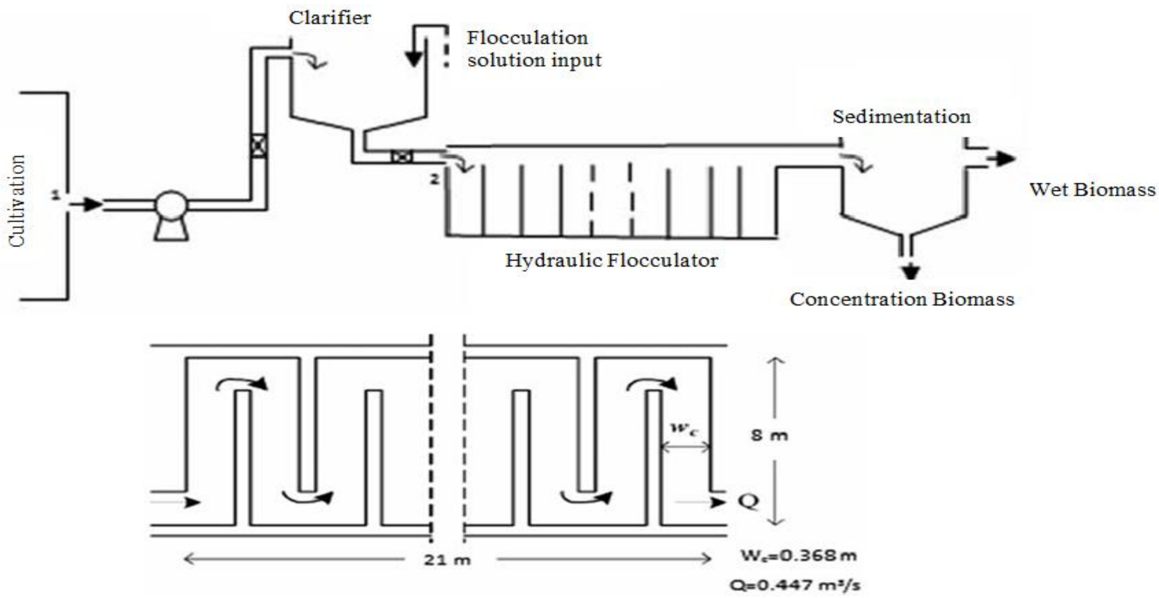

Figure 1: Chemical Flocculation system with hydraulic mixed

To the designed process, the main exergy inputs and outputs were calculated, and the results were shown in Table 2. For the oil extraction stage was selected the oil extraction with hexane method (HBE). In the HBE method, hexane was added to the microalgae biomass at ambient conditions (298 K, 101.325 kPa) with a solvent/biomass ratio of 20:1. After which the mixture is separated and filtered, obtaining a liquid stream rich in hexane and oil, and biomass stream rich in carbohydrates and proteins. The oil/hexane stream is distilled, and the hexane is recirculated to the process, the liquid components present in the biomass stream are separated and purified to increase extraction efficiency, this method was chosen because of its ease implementation and its similarity to processes used for the soybean oil solvent-based extraction. The main exergy inputs and outputs of the stage were calculated, and the results were shown in table 3.

Table 2: Main exergy inputs and outputs for the cultivation-harvesting (CH) stages

Input	Exergy MJ	Output	Exergy MJ
See Water	30,046.22	Evaporated Water	4.56
Flue gas	$3.3x10^{17}$	Biomass+ Culture Media	$9.61x10^{10}$
Walne's Medium	7,325,114.28	Oxygen	1,500,542.04
Flocculant	13,528,406.25	Flue gas poor	$2.98X10^{17}$
Utilities	30,046.22	Evaporated Water	4.56
Days worked per year	365		

Table 3: Main exergy inputs and outputs for the oil extraction with hexane (HBE) stage

Input	Exergy MJ	Output	Exergy MJ
Dry Biomass	$1.04x10^6$	Oil	$4.94x10^5$
Hexane	1,727.94	Residual Biomass	27.62
Utilities	$9.85x10^5$	Residual Water	30,041.67

The oil obtained was pre-treated with an esterification process for to transform to biodiesel the free fatty acids (FFA) of the oil. The esterification reaction was simulated based on the stoichiometry and assuming fractional conversion of 0.97 mol based on the FFA. Sulfuric acid was used as the acid catalyst in an amount of 2.26 % catalyst/oil mass ratio and methanol as alcohol in a molar ratio of 6.13:1 alcohol/oil and the reaction were carried out at 55°C (Marchetti and Errazu, 2008). The transesterification stage was carried out under the same conditions mentioned for (Peralta et al., 2009). The microalgae biodiesel obtained satisfies most of the specifications of the ASTM. The main exergy inputs and outputs of the stage were calculated, and the results were shown in Table 4.

Table 4: Main exergy inputs and outputs for the oil esterification-transesterification (ET) stage

Input	Exergy MJ	Output	Exergy MJ
Oil	$4.92x10^5$	Biodiesel	$4.72x10^5$
Methanol	$1.02x10^5$	Glycerol	$5.15x10^4$
Sulfuric Acid	$4.12x10^4$	Coproduct	$1.13x10^5$
Sodium Hydroxide	$2.97x10^5$	Wastes	$7.06x10^4$
Utilities	$4.45x10^4$		

The biomass residual of the oil extraction process was treated with diluted acid as pre-treatment for to remove the lignin, then Saccharification and Simultaneous Co-Fermentation SSCF technology, the hydrolysis of cellulose and the fermentation of hexoses and pentoses are carried out simultaneously in a single stage using cellulase and *Zymomonas mobilis* recombinant according to the process presented by (Bautista and Sierra, 2012) followed by distillation and molecular sieves technology for concentration and purification of the bioethanol. The main exergy inputs and outputs of the stage were calculated, and the results were shown in Table 5.

Table 5: Main exergy inputs and outputs for the residual biomass transformation (RBT) stage

Input	Exergy MJ	Output	Exergy MJ
Biomass Residual	$2.06 x10^5$	Ethanol	$1.08x10^5$
Water	$5.05 x10^5$	Vinasse	$4.95x10^5$
Sulfuric Acid	$1.35 x10^4$		
Calcium Hydroxide	$3.91 x10^4$		
Ammonia	$3.29 x10^2$		
Enzyme	$2,3 x10^3$		
Utilities	98.1		

For each stage of the designed process and taking into account the information of the tables 2 to 5, the total exergy of the inlets, outlets, wastes and, utilities were calculated. The exergy efficiency for each sub-process was determined using the Eq(4). In Figure 2 shows the comparative results for each stage. The CH stage shows highest exergy efficiency of the process with a value of 91 % and, non-significant exergy of waste. The CH stage shows that from the energetic point of view is very efficient; this is due to the presence of streams with high exergy and low cost or free as in the case of the flue gas and solar energy.

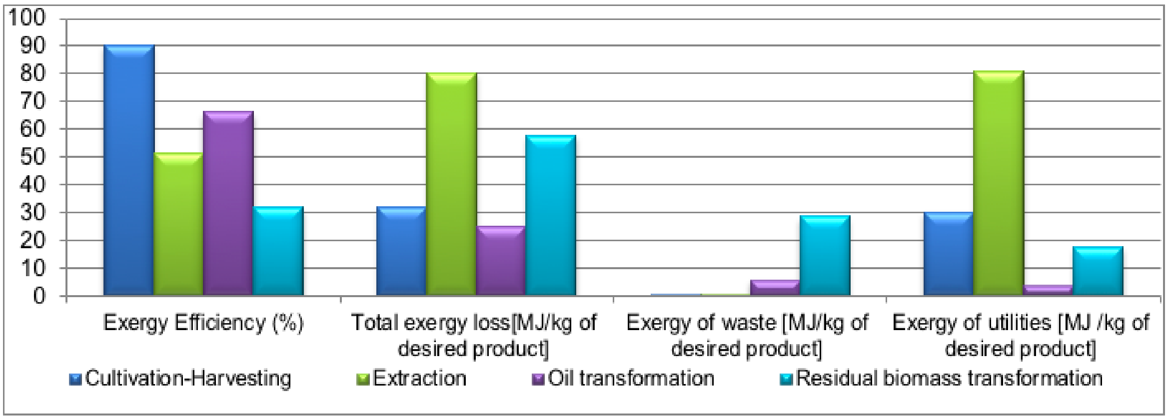

Figure 2: Exergy analysis of each stage of the process

HBE stage presents the second lower exergy efficiency of the process with a 51 % value; this is mainly due to the material inputs are more valuable from the exergetic point of view than the products obtained in this stage. Also, the HBE stage has a high consumption the utilities this influenced by the separations processes required for biomass treatment. For the ET stage, the exergy efficiency was calculated in 64 %; the exergy loss is caused by the consideration of only to recycle the methanol in the process. The exergy losses can be reduced increasing the number of recycles in the process, some waste streams by its composition can be used as fertilizer, which would provide other value-added product decreasing exergy losses for waste streams. Finally, the RBT stage presents the lowest exergy efficiency of the process and show the same behaviour that the HBE stage, ethanol exergy is lower than residual biomass and other exergies of the stage as observed in Table 5. It is necessary to value waste such as vinasse and thus increase the energetic efficiency of the process.

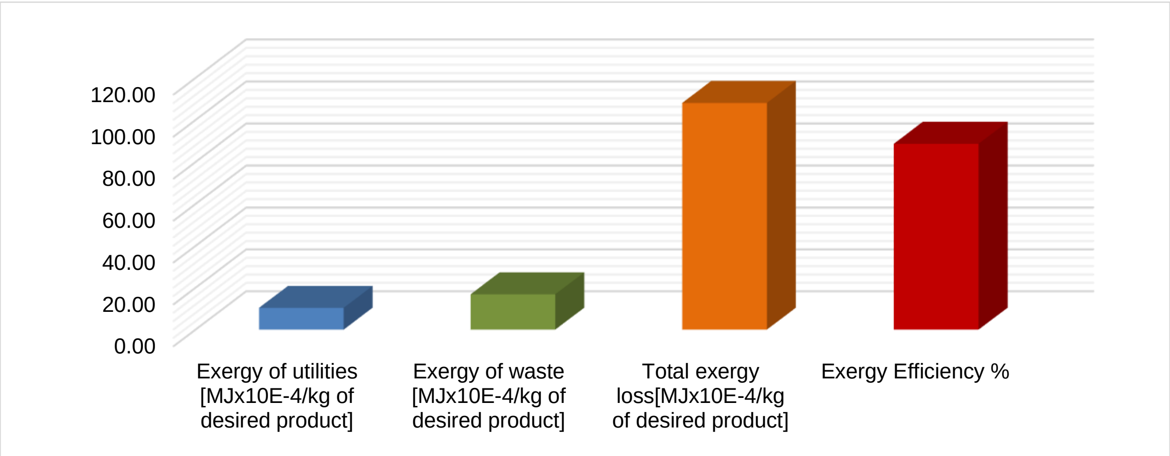

Figure 7: Exergy Analysis of the biofuels production process from microalgae biomass

Figure 7 shows the third-generation biofuels production proposed design. This process produced biodiesel and bioethanol and had an overall exergy efficiency of 88.6 %. Wastes streams and utilities required mainly cause the high exergy losses; it is necessary the use of energy integration methodology in the process for to identify what streams have potential to be used in heating and cooling processes of the proposed design. The results obtained are promissory with respect of other processes of biofuels production from different biomasses evaluated using exergy analysis methodology. Jaimes et al. (2012) assessed two scenarios of palm oil biodiesel production, the first was with homogeneous transesterification and second with heterogeneous esterification, obtaining 14.2 % and 18 % of the overall exergy efficiency of the process respectively. Ofori-Boateng et al. (2012) achieved an overall energy efficiency of 44% in the Jatropha biodiesel production process and Blanco-Marigorta et al. (2013) efficiency of 63 % for the same feedstock. The previous data shows that microalgae biofuels production process is a possible alternative of solution for to decrease the fossil fuel use and the obtained results are an important initial stage of the research, but it is necessary to perform an economic and environmental evaluation of the process and thereby to validate this alternative the biofuels production.

4. Conclusions

A design was proposed for third generation biofuels production, obtaining biodiesel and bioethanol, the process presented a high exergy efficiency with a value of 89 %, the residual biomass transformation stage present 31 % of exergy efficiency is the lowest of the process, these results confirm the necessity to use the residual streams for to produce value-added products. The proposed process shows potential from the energy point of view compared with biofuels of other feedstocks and can be a viable alternative to take account as an alternative solution for the problem of the fossil fuels use and the global warming. It is recommended to perform an economic and environmental study of the process, to evaluate the sustainability. Also, the use of wastewater as microalgae culture medium.

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