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# Conceptual Framework for the Production of Bioethanol and Byproducts from Microalgae Biomass

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Biofuel production from biomass is a promising alternative to fossil fuels. Biodiesel and bioethanol can be produced from lipids and carbohydrates of microalgae biomass, respectively. In this paper, a processing pathway from conceptual design process is proposed for liquid biofuels, to extract value-added products such as pigments and proteins from microalgae (Chlorella vulgaris). The process diagram consists of six main stages: vinasse anaerobic digestion, algae culture, biomass recovery, both bioethanol and biodiesel production. Simulations in ASPEN PLUS® software were performed in order to evaluate the mass and energy balances; heat integration using the Pinch Method was applied in order to minimize utilities consumption. 30 Ton/ h of vinasse were considered for treatment. Acid hydrolysis of cellulose to glucose was considered with a 96% performance and bioethanol production was carried out through a simultaneous saccharification and fermentation process, with a yield of 92.3% on the stage, 112 kg/h of ethanol, 28.5 kg/h of biodiesel, 126.5 kg/h of protein and 3 kg/h of glycerol were obtained by the process simulation.

## 1. Introduction

Several products in commercial scale such as nutritional supplements for humans and animals, and feedstock for pharmaceutical and cosmetic products are produced from microalgae. This source of biomass constitutes a market of 5kt/year (Acién et al 2014). Recently the microalgae biomass has been considered as a third generation feedstock for bioethanol production, because some microalgae species accumulate a large amount of carbohydrates (40% w/w of the dry weight) in terms of starch and cellulose. These microalgae have advantages over traditional feedstock as follows: high growth rate and productivity; short harvesting cycle (10 days), absence of lignin, requiring less pretreatment, and easy saccharification. Recent studies indicated that the production of only one product from microalgae biomass is not economically feasible due to the current market condition and production technology; for this reason the biorefinery concept has been identified as the most promising way for the creation of an industry based on biomass (Ribiero, 2015). The concept of biorefinery can be applied to microalgae biomass for the production of biofuels and high added value products based on the composition of promising microalgae species. A microalgae based biorefinery must take into account several issues for its sustainability such as water requirements, production costs, environmental impacts and process efficiency.

## 2. Economic gross potential (EGP)

Economic gross potential (EGP) was used to determine the potential economic viability as shown in Ec (1), it expresses mathematically the difference between the annual production flow by selling price and the annual flow of raw material per unit cost. Table 1 shows the unit cost for the raw material used and the selling price for the selected products presented. A result greater than zero indicates the process might be considered for a more detailed analysis (El-Halwagi, 2012).

$$\boldsymbol{EGP} = \sum_{P=1}^{Nproduct} Annual\ production\ rate\ of\ product\ p * Selling\ price\ of\ product\ p - \sum_{r=1}^{N\ reactants} Annual\ feed\ rate\ of\ reactant\ r * Purchased\ price\ of\ reactant\ r \quad (1)$$

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*Table 1. Unit cost for raw and selling price for the selected material*

| Component | Amount (kg) | Selling Price ($/kg) | Reference |
|---|---|---|---|
| Biomass | 1000 | 38 | Fedebiocombustibles (2015) |
| Bioethanol | 255.5 | 0.1 | |
| Biodiesel | 120.5 | 0.1 | |
| Proteins | 200 | 120 | Koller et al 2014 Acién et al 2014) |
| Pigments | 50 | 300 | |

## 3. Process description

This paper proposes a conceptual design for the production of biofuels (bioethanol and biodiesel) and value-added products as pigments and proteins from microalgae biomass grown in cane vinasse. The process consists of six main stages: biodigestion, cultivation, harvesting, pigments and lipid extraction and production of bioethanol and biodiesel. The simulation flowsheet is shown in Figure 1 where were considered six hierarchies, one for each stage and it was carried out in ASPEN Plus$^{TM}$ software using a NRTL thermodynamic model (Non-Liquid Two Ramdom) due the system being defined as biphasic, with low operating pressures (> 5 atm) and non-electrolyte polar components . The simulation was performed in steady state.

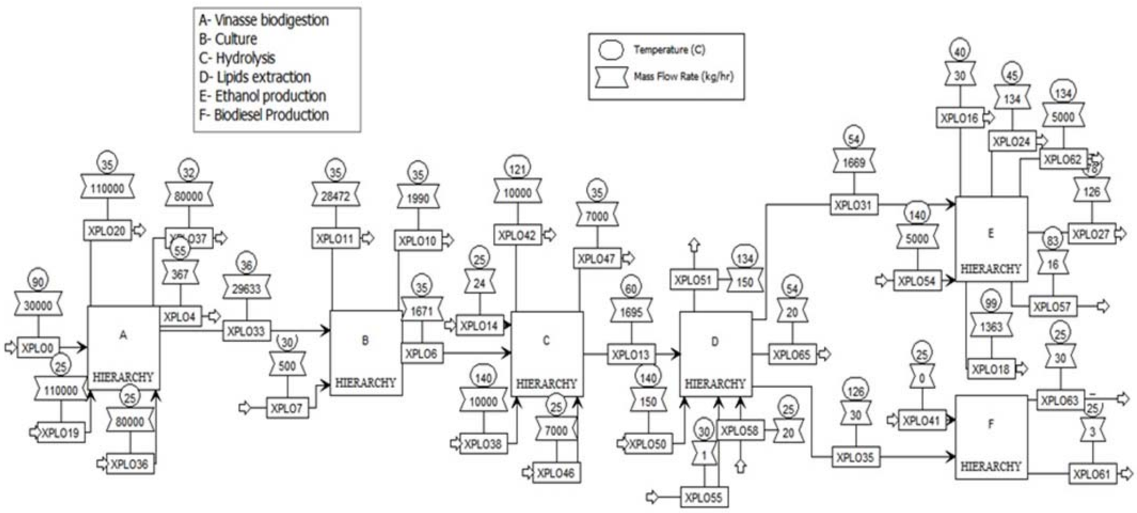


*Figure 1. Flowsheet of simulation*

### 3.1 Biodigestion

The effluent from the sugar fermentation is called vinasse, in this case, cane juice was assumed as the source of sugars which composition is described in Table 2 (modified AC Wilkie et al 2000). The used of this effluent as a culture is favorable because of its adequate levels of micro and macro-nutrients such as nitrogen, potassium and phosphorus (Moraes et al. 2014) and its high water content. Nevertheless with the aim of removing the organic load between 85 and 95% of COD (chemical oxygen demand) anaerobic biodigestion in thermophilic conditions (55 ° C) was considered. One advantage of the biodigestion is that it also can produce biogas whit a 70 -80% of methane and 15-30% of $CO_2$ (Kardos et al. 2011).
The physicochemical parameters considered for vinasse are shown in table 2. Biodigestion was simulated with 4 yield reactors at each stage and was taken as priority to a reaction step, for the separation of biogas we used a flash tank, before digestion the vinasse was cooled to 55 ° C.

*Table 2: Vinasse composition*

| Parameter | Vinasse (before biodigestion) |
|---|---|
| pH | 4 |
| COD | 25,912.19 |
| $NH_3$ mg/L | 1,040 |
| $P_2O_5$ mg/L | 62.35 |
| $SO_4$ mg/L | 1,557.85 |
| $K_2O$ mg/L | 2,076.42 |
| CaO mg/L | 519.32 |

### 3.2 Microalgae

Chlorella vulgaris was chosen as the microalgae to be grown in the vinasse culture because it has been one of the most used on an industrial scale due its ease of raise and high rate of growth (Lev et al 2010), as well as high resistance to contamination (Huntley et al 2007). Table 3 shows the composition of these microalgae.

*Table 3: Chlorella vulgaris composition (Shih-Hsin Ho 2013)*

| **Component** | % |
|---|---|
| Lipids | 12 |
| Protein | 20 |
| Carbohydrates | 51 |
| Pigments | 5 |
| Ash | 12 |

### 3.3 Culture and harvest

An open pond was proposed for the culturing step because it has more preference in industry (Kumar et al 2015). A rate of 1,325 $CO_2$ / kg of biomass was considered, and for its simulation a performance reactor was used, the growth model was adjusted to a reaction according to Eq (2), the vinasse feeding and $CO_2$ were mixed in a mixer before the gases are extracted through a flash after the reactor. To harvest microfiltration technology was chosen assuming a Disc Centrifuge, with ideal separation, yielding 0.7 and considering the particle size of the biomass (2 to 10 microns).

$$CO_2 + 1{,}014\ H_2O + 0{,}151\ NH_3 \rightarrow Biomass + 0{,}988\ O_2 \quad Yield = 0{,}9 \tag{2}$$

### 3.4 Pretreatment

In this stage acid hydrolysis was chosen as pretreatment because it benefits the lipid extraction and sugars fermentation. The acid used is $H_2SO_4$ with a concentration of 2% (Shih-Hsin Ho 2013). Acid stream is mixed with the main stream in the mixer and heated to 110°C by a heat exchanger and then this mix is sent to the hydrolysis reactor where cell lysis and hydrolysis of cellulose occurs.

### 3.5 Lipids and pigment extraction

**Wet extraction:** The process was proposed by Sathish and Sims (2012) and up to 80% of lipids can be extracted. It requires prior acid hydrolysis and is divided into a basic hydrolysis, centrifugation, pigment precipitation, hexane addition, centrifugation, and finally lipid extraction. The hydrolyzed stream is mixed with a base (NaOH) in order to neutralize acid and fatty acids present. The stream is mixed with hexane, and for the extraction of pigments and lipids simulation, once centrifuged a splitter is used, the hexane stream rich in lipids is subjected to distillation to recover and recirculate hexane.

### 3.6 Bioethanol production

After lipid extraction the supernatant obtained is subjected to fermentation. According to Shin-Hsin Ho (2013) a simultaneous saccharification and fermentation (SSF) process is chosen to make sure a faster process and that the reaction occurs in a single reactor due to starch hydrolysis and fermentation of glucose happening in the same step. Z. mobilis bacteria was used in fermentation and endoglucanase enzyme (0.65 U mL 1), b-glucosidase (0.30 U mL 1), and amylases (0.75 mL U 1) for hydrolysis. Distillation was used for purification and subsequently molecular sieves.

After the fermentation step a separation by centrifugation was proposed to obtain proteins which can be used as animal feed.

### 3.7 Biodiesel production

The lipids obtained from the extraction step are converted into biodiesel. According to a process established by Hideki Fukuda (2001), it is proposed to perform a trans-esterification in the presence of a basic catalyst (KOH) because it is 4000 times faster than when it uses an acid catalyst; also it was used a molar ratio of 6: 1 methanol: lipid allowing a conversion of 98%. The methanol in excess was recovered by distillation and then recycled to the process. Biodiesel and glycerol are insoluble reason which, they could be separated by decanting and subsequently purified. Ec (3) shown the trans -esterification reaction (King 2012).

$$C_{57}H_{104}O_6 + 3(CH_4O) \rightarrow 3\,(C_{19}H_{36}O_2) + C_3H_8O_3 \qquad (3)$$

## 4. Energy integration

Pinch analysis was chosen for energy integration as El-Hawalgi (2012) proposed. The mainstream processes were considered for calculating the minimum cooling and heating utilities. The hot and cold streams are reorganized in such a way to maximize its heat. Initially, utilities were 19,700 kg / h of steam and 15,150 kg / h of cooling water.

The steps to carry out energy integration are described below:

1. Pinch point identification. After the identification of process hot (H) and cold (C) streams, a cascade diagram was performed to find the minimum utilities, which correspond to 127.64 MJ / h for heating and 6617.15 MJ / h for cooling, and it was found the pinch point 90°C for heating and 80°C to cooling. Table 4 shows the description of the hot and cold streams.

*Table 4. Hot and cold streams*

| | H1 | H2 | H3 | C1 | C2 | C3 |
|---|---|---|---|---|---|---|
| Stream | Vinasse | Digestate | Hydrolyzed | To hidrolyzed | Extraction | To distill |
| Flow(kg/h) | 30000 | 29630 | 1695 | 1695 | 595 | 1632 |
| Cp (KJ/kg °C) | 4 | 4.2 | 3.43 | 3 | 2 | 4.695 |
| $T_i$ ( °C ) | 90 | 55 | 110 | 35 | 30 | 45 |
| $T_f$ (°C) | 55 | 35 | 60 | 110 | 65 | 90 |
| Duty(MJ/h) | 4523.9 | 2488.9 | 290.7 | 418.2 | 51.2 | 344.8 |

2. For the synthesis of heat exchanger network, taking into account the minimum requirements of heating and cooling and the pinch point, the loads above and below the pinch for each stream were determined. With these loads, stream pairing (matching) is possible to assess the minimum number of heat exchangers. The code used for this purpose was a modified version of the one proposed by El-Hawagi (2012) and resolved using Lingo optimization tool, resulting in nine heat interchangers.

Table 5 shown the heat before and after energy integration, total consumption was 2,254.947 KW before the integration, mainly due to the cooling requirements of vinasse in the pretreatment step of the medium, the consumption after integration was 1,873.55 KW which represents energy savings of 17%. Energy integration requires minimum 9 exchangers, which is 3 less than when compared to the system without integration.

*Table 5. Requirements before and after integration*

| Area | steam | Before integration KW | | After integration KW | % |
|---|---|---|---|---|---|
| 1 | Vinasse | 1256.65 | 1098.21 | 12.6 | |
| | digestate | 691.37 | 691.37 | 0 | |
| | Subtotal | 1948.01 | 1789.58 | 8.13 | |
| 3 | To hydrolyze | 116.18 | 14.17 | 87.8 | |
| | Hydrolyzed | 80.75 | 48.45 | 40 | |
| | Subtotal | 196.93 | 62.62 | 68.2 | |
| 4 | Extraction | 14.23 | 0.00 | 0 | |
| | Subtotal | 14.23 | 0.00 | 0 | |
| 5 | To distill | 95.78 | 21.28 | 77.78 | |
| | Subtotal | 95.78 | 21.28 | 77.78 | |
| | Total | 2254.95 | | 1873.56 | 16.94 |

## 5. Economic analysis

The economic analysis took into account the cost of purchase of equipment, the cost of labor, the cost of utilities and cost of raw materials; according to the methodology proposed by Turton et al (2009), which is based on the cost of bare module (CBM). This technique is a mathematical relationship of all purchases, costs of equipment for some base conditions: units made of common materials (Carbon Steel), all operating at ambient conditions. Table 6 summarizes the cost of equipment for the biodigestion stage; the cost of 1 biodigester was calculated with a volume of 50 $m^3$ for 30 Ton of vinasse; for the culture stage, it was calculated as the cost of 32 open ponds of 16000 $m^3$, each one for a residence time of eight days. For the filtration step, the cost of a Filter Cartridge type was calculated, which are most commonly used in such processes (Gerardo et al 2015) and the value was taken as reported on the website which provides costs of process equipment for chemical industry and metallurgical engineering. The cost of the distillation towers was obtained using the power rule 0.6 based on costs reported by El-Galad et al (2015).

*Table 6: Cost of mayor equipment in the process.*

| Stage | Equipment | Cost US$ | Total Cost US$ |
|---|---|---|---|
| **Biodigestion** | Biodigester | 251,155 | 251,155 |
| **Culture** | Openpond | 763,912 | 763,912 |
| **Hydrolysis and fermentation** | Hydrolysis and fermentation reactor | 47,259 | 47,259 |
| **Filter** | Cartridge Filter | 128,600 | 1,286,000 |
| **Biodiesel production** | Transesterification reactor | 19,303 | 19,303 |
| | Distillation tower | 12,102 | 12,102 |
| **Bioethanol production** | Distillation tower 1 | 73,296 | 73,296 |
| | Distillation tower 2 | 19,887 | 19,887 |
| | | TOTALUS$ | 2472914 |

*This cost is taken into account 1 bio digesters.
**This cost is taken into account total hectares: 32.

To calculate the cost of labor work, also was used the methodology proposed by Turton et al (2009), for which the equipment listed in Table 5 were taken into account, and a total annual cost of US $ 67.150 was obtained. The utilities cost: water, energy and steam is based on calculations made by the simulation in Aspen Plus before and after the integration, multiplied by the cost of each of them in Colombia; as it is shown in Table 7, the cost of steam, cooling water and energy after integration was decreased by 35.3%, 9.4% and 17% respectively.

*Table 7: Utilities costs*

| | Before integration | | After integration | |
|---|---|---|---|---|
| | Requirements | Cost US$ | Requirements | Cost US$ |
| **Steam Kg/h** | 19700 | 179.22 | 3087.5 | 28.10 |
| **Cooling water Kg/h** | 15150 | 0.17 | 13725.6 | 0.16 |
| **Energy KWh** | 2254.95 | 77.42 | 1873.55 | 64.33 |

## 6. Conclusions

Energy integration proposed allowed an 85% reduction in heating requirements and 10% in the cooling, reducing the utilities costs in a 35.3% for heating and 9.4% for cooling respectively, for energy the reduction cost was 17%. And using the methodology proposed by El-Halwagi shows that the process requires minimum 9 exchangers, 3 more without integration increasing the fixed costs. Nevertheless, it was calculated a net present value (NPV) to ten years including equipment costs sale and services, in which the recovery of investment was at the third year without energy integration and first year with energy integration; then, energy integration shows an inversion recovery in a less period of time that without it. It is important to note that in this calculate was not taking into account maintenance costs, labor and taxes.
The total cost of mayor equipment was US$14,219,207 were the open ponds, the biodigester and the filter represents the 69%, 21% and the 8.9% respectively of the total cost.

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