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Simulation and Energy Integration for a Biorefinery of Valuable Substances and Biofuel from Microalgae Biomass

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Traditional biofuels have been criticized, primarily, because there is not neutral CO2 balance and its production is based on raw materials used for human alimentation. Microalgae emerges as a promising renewable, not food, source for biofuels production, however, its principal obstacle are the high production costs. One alternative proposed by researchers to achieve a feasible production is the incorporation of the biorefinery concept, which is a framework for producing several products, including energy, from biomass giving economic competitiveness due to high value co-products. In this paper, a first approximation of a topology of microalgae biorefinery was analyzed. The analysis was based on process simulation with the software SuperPro Designer for modeling the topology through stages. The harvest stage consists of a chemical flocculation and a filter press; the lipid extraction stage was made first lysing the cells by means of acid and basic hydrolysis, then a pigment extraction with hexane, Polyunsaturated Fatty Acids (PUFAs) concentration forming urea complexes, and triglycerides (TGs) recovery from complexes formed; furthermore, the last stage where the transformation from lipids to biodiesel through homogeneous transesterification ocurred. Finally, taking into account the energy integration principle with Aspen Energy Analyzer was possible to reduce the external services of heating and cooling with the aim to improve the topology propoused.

1. Process description

The different flowsheet configurations were simulated using SuperPro Designer (Intelligent, Inc USA), suitable software, due to special models for bioprocess and its complete unit procedures databanks. However, in the pure compounds database was necessary to create seven molecules, thermodynamically the software was based on shortcuts because the system was considered moderately non ideal. Also, was used as solution algorithm for recycles the Wegstein method (with -5 parameter), and the operated tolerance was 0.001 in tears streams. On the other hand, from experimental data collected were defined the process strategies for each stage of a biorefinery capable of processing 100,000 tons of dry biomass. The involved processes are briefly described in the following sections and the Table 1 summarizes the operation conditions.

1.1 Harvest

In the Figure 1 is shown the first stage simulated, where was assumed as input biomass with moisture content of 99 %, the selected technology was chemical flocculation with hydraulic agitation characterised by its low energy requirements (Peralta et al 2012). For this process stage were selected as coagulant aluminum sulfate was used [$Al_2(SO_4)_3 \cdot 14H_2O$] because it has been widely employed with microalgae and even there are optimization models for the *Nannochloropsis* strain (Y. Shen et al 2013). Concentration efficiency was set at 90 % for dry biomass, in order to leave an initiation crop of microalgae. Finally, the later stages need biomass with moisture content of 84 %; therefore, filtration was added to be convenient as a concentration mechanism.

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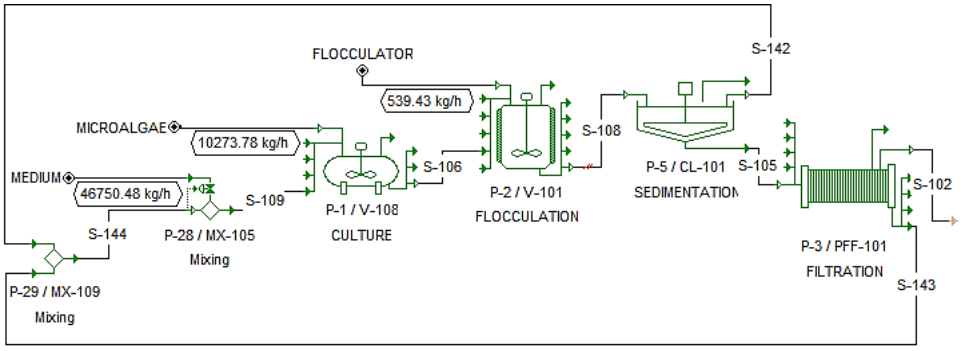

Figure 1: Harvest of biomass.

1.2 Cellular Lysis

The Figure 2 was simulated from the work reported by Sathish A. and Sims R. (2012), where was possible to separate lipids from microalgae biomass, first, by cell hydrolysis with acid solutions during 30 min at 90 °C. Once made the disruption, a basic solution was added during 30 min at 90 °C for neutralizing the mixture, producing salts and saponifying the complex lipids. When temperature drop to normal conditions was split the supernatant with the interested substances of the residual biomass through centrifugation. That waste could be converted into acetone, buthanol and ethanol by fermentation. To improve lipid recovery was washed the sediment with clean water, followed of centrifugtion procedure. To the previous supernant stream was bubbled waste CO_2 to lower pH below 7 and thus return the formed salts for freeing the fatty acids and precipitating the unsaponifiable lipids, which are rich in pigments.

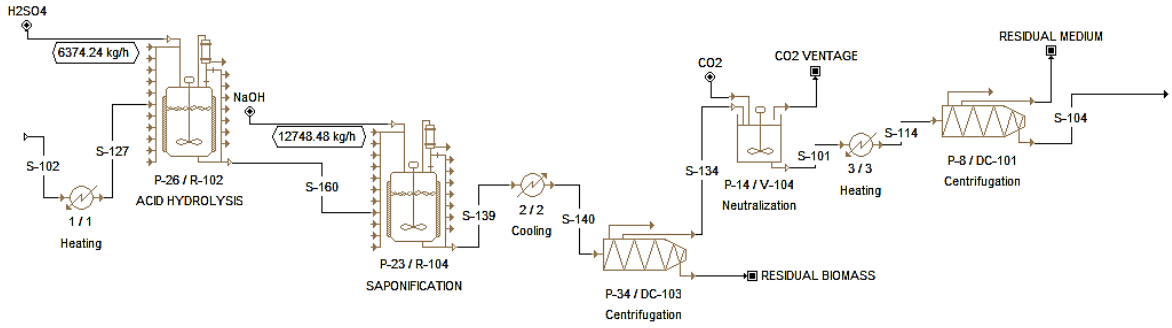

Figure 2: Cellular lysis of the microalgae.

1.3 Pigment extraction

The photosyntethic pigments are lipids wich bind to proteins present in some plasma membranes; they are characterized by their variety between single and double bonds. This is related to its ability to harness light to initiate chemical reactions and have own color. In the Figure 3 the previous solid-liquid suspension was centrifuged; the aqueous supernatant primarily composed by soluble water components like sugars, proteins, and organic matter was removed. On the other hand, the recovered lipids were exposed to hexane extraction during 15 min at 90 °C, then the mixture was cooled and centrifugated to separate a rich pigments extract.

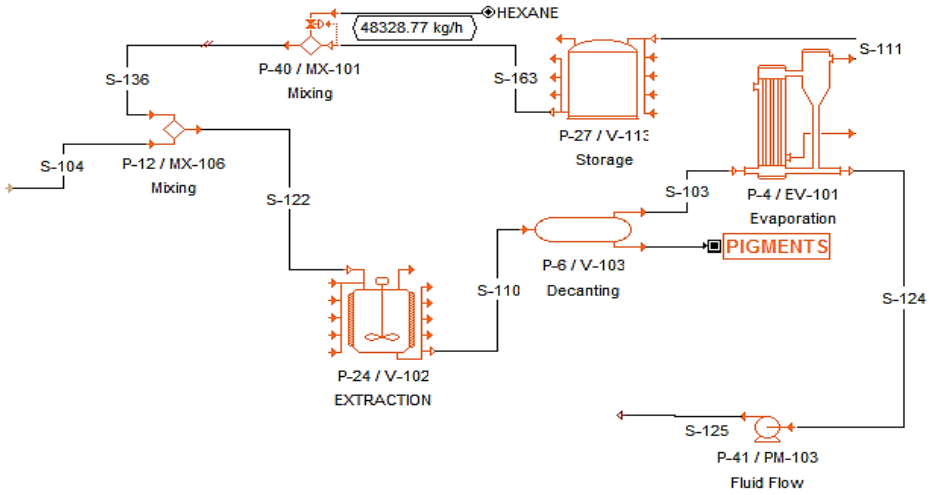

Figure 3: Pigment extraction of microalgae lipids.

1.4 PUFAs concentration

In the Figure 4 the saponificable lipids obtained in the previous phase were mixed with hexane, for recovering this solvent the solution was evaporated. A PUFAs concentration technique widely used is the fractionation with urea, this procedure consist in to separate PUFAs of the TGs, starting from a hot urea saturated solution with all the fatty acids. The solution was cooled for inducing the TGs crystallisation with urea, due to its long straight chains structure that catchs the transesterificable lipids, while PUFAs stay in the mixture.

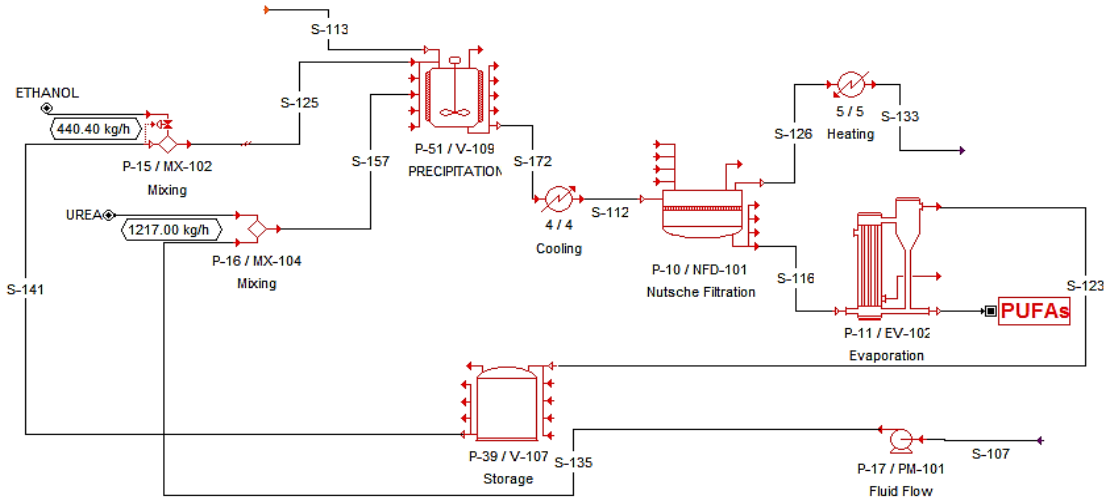

Figure 4: PUFAs concentration with urea.

1.5 TGs recovery

Given that long chain PUFAs have low tendency to form inclusion compounds of urea at temperatures above 0 °C the solution was kept at 4 °C. Subsequently, the mixture was filtered twice for 3 h at 4 °C. Considering that after this stage was desired to have TGs availables, was adding twice the weight of hot acid water to the urea complex for feeing the transesterificable, the flowsheet is shown in the Figure 5.

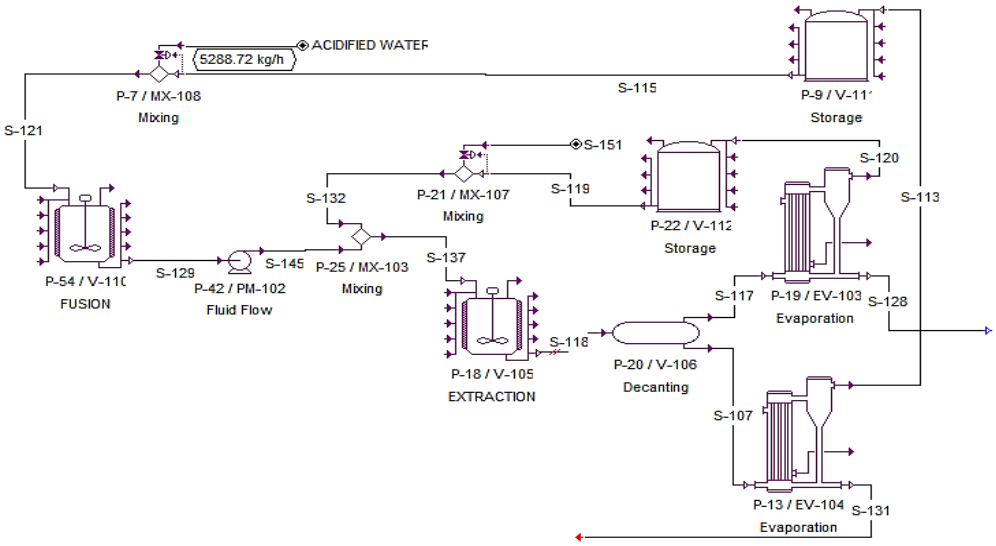

Figure 5: TGs recuperation from inclusion compounds of urea.

1.6 TGs transesterification

In the first instance, triglicerydes are dehydrated by a rotary dryer afterward to transform microalgae oil into biodiesel was selected a transesterification reaction with basic catalyst because requires low temperature and presion. Its conversión yields reach to 98 % and do not need special building materials to carry out the reaction. Besides, as excess reactant was chosen methanol because it leads to increase methyl esters production, moreover, compared to ethanol is cheaper and easier to recover. According to the authors, Plata et al. (2010) the optimal conditions to the transesterification of microalgae oil are: methanol molar ratio 14:1 (methanol:TGs), NaOH catalyst weight 0.42 % and operation temperatura at 43 °C. The Figure 6 shows the simulated stage.

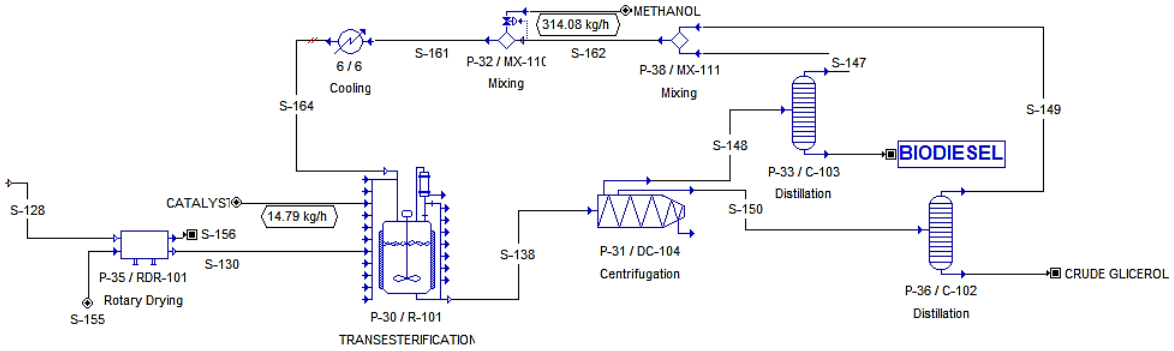

Figure 6: TGs transesterification to obtain biodiesel.

In this development, as well as, in the previous stages were considered as products, the streams composed mainly of desired compound, howerver, further stages may be needed to ensure the purity required in the market.

Table 1: Operation conditions summary of the proposed biorefinery from microalgae.

Operating conditions	Value	Source
	Harvest	
Initial solid concentration (%w/w)	1	
Flocculator dose (weight)	1biomass:0,05$Al_2(SO_4)_3$	Peralta et al. (2012)
Final solid concentration (%w/w)	4	
	Cellular lysis	
Solvent dose (weight)	[1biomass:1H_2SO_4][1biomass:2NaOH]	Sathish A. and Sims R. (2012)
Temperature (°C)	90	
Final pH, neutralized solution	6-5	
	Pigment extraction	
Solvent dose (weight)	[1TGs:98C_6H_{14}]	Sathish A. and Sims R. (2012)
Temperature (°C)	90	
	PUFAs concentration	
Solvent dose (weight)	[1TGs:3urea][1TGs:3.75ethanol] [1TGs:0.25H_2O]	Guil-Guerrero J. and Belarbi E. (2001); Seanayake S.N. and Shahidi F. (2000)
Temperatures (°C)	60 and 4	
Recovery efficiency (%)	PUFAs 65 and TGs 98	
	TGs recovery	
Solvents dose (weight)	[1TGs:3urea][1TGs:3.75ethanol] [1TGs:0.25H_2O]	Seanayake S.N. and Shahidi F. (2000) and Helmut T.; Hans-Juergen W. (1988).
Temperature (°C)	40	
	TGs transesterification	
Reagent and catalyst dose (weight)	[1TGs:93methanol][1TGs:0.0042NaOH]	
Temperature (°C)	43	Plata V. et al. (2010)
Reaction efficiency (%)	97	

2. Energetic integration procedure

In order to identify the stages with higher energy consumption were determined balances through the simulated topology with SuperPro Designer, thus, the stage which requires greater external services is celular lysis. The reason was reflected mostly by heating and cooling services necessary to meet 1,318.52 kW. With Aspen Energy Analyzer was developed an Heat Exchange Network (HEN), which aim is to use own process streams to supply external heating and cooling services. The suitable biorefinery streams are shown in Table 2, with that information and considering a minimum difference temperature approximation between heat exchangers (ΔTmin) of 8 °C was calculated the pinch point and the energy targets.

The pinch point mínimum approximation was selected given that, it is a biochemical process at low temperatures, nevertheless, according to the total annualized cost variation with respect to possible target HENs the ΔTmin should be 18 °C. But taking into account only this criterion, one possible configuration would fulfill the analysis conditions and would carry to higher energy expenditure than the selected design at ΔTmin = 8 °C.

Table 2: Features of suitable biorefinery stream.

Stream	Inlet T(°C)	Outlet T(°C)	MCp (kJ/°C-h)	Enthalpy (kJ/h)	Flowrate (kg/h)	Cp (kJ/kg-°C)
1	80.3	10	247,054.6	17,367,942.2	76,685.1	3.2
2	25	90	207,127.7	13,463,302.4	57,563.7	3.6
3	16.57	40	216,947.9	5,083,089.9	74,074.1	2.9
4	41.16	4	175,272.7	6,513,132.2	73,493.4	2.4
5	4.07	40	9,452.5	339,628.3	6,846.1	1.4
6	54.4	43	3,056.7	34,846.5	1,197.7	2.5

3. Results

The purpose of developing a conceptual topology of a biorefinery from microalgae, given a schema for using the whole biomass to become in biofuels and valuable substances; is grounded on making contributions to the principal obstacle of renewable energy production, high production costs.

In the case of the proposed biorefinery, was identified as the highest external energy requirement contributing 49 % of the total consumed by the process. Total external energy for services of heating and cooling reach to 42,801.9kW without a HEN. Through energy integration was generated the composite curve and two pinch points 33 y 25 °C with ΔT min at 8 °C. For the process streams was calculated the mínimum services for heating and cooling 3.709E+06 kJ/h and 8.738E+06 kJ/h. Subsequently, by using the pinch analysis rules and recommended design alternatives were obtained the HEN, the selection criterion for the optimization was the minimum total annualized cost.

In short, the biorefinery can be improved using energy integration with HEN. The proposed network will allow a reduction of 39% for heating and 51% for cooling (Table 3). However, network needs more heat exchanges (2 new equipments, 8 total), wich may lead to an increase of the capital cost.

Table 3: Comparision of base case and selected design.

Requirements	Without HEN	With HEN
Heating services (kJ/h)	18,882,600	7,269,000
Cooling services (kJ/h)	23,917,850	12,300,000
Units	6	8
Extra services cost ($/s)	0.0282	0.0132
Saving (%)		47

4. Conclusions

A topology biorefinery from microalgae was proposed for producing biodiesel and valuable susbtances such pigments and PUFAs through SuperPro Designer. From energy balances of each stage process, celular lysis was identified with greater energy requirements (1,318.52 kW) mostly due to external heating and cooling services. When designing the HEN external services costs decreased about 47 % but heat exchangers units increased about 2 with ΔTmin at 8 °C.

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