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Optimization of Microalgae Composition for Development of a Topology of Biorefinery based on Profitability Analysis

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Microalgae are considered promising candidates for the development of biorefineries due to the variety of metabolites such as carbohydrates, lipids, pigments, proteins and other special substances that are produced in different proportions, which can be extracted and/or transformed to obtain marketable products and energy. In this work, an analysis of the potentially obtainable products in a biorefinery from microalgae was performed, based on the optimization of the percentage of metabolites, taking into account techno-economic issues in order to rank obtainable products according to the minimum feedstock composition required; considering biofuels as main products, production capacity and raw material cost were set in 100,000 ton of biomass/year and \$500/ton respectively. Results confirms the economic unsustainability of exclusive production of a biofuel from microalgae under feedstock and production costs evaluated, being the minimum attractive oil composition over 100%; but the valuable substances generates positive income as pigments and polyunsaturated fatty acids (PUFAs) with minimum profitable composition of 4.87% and 9.67% respectively.

1. Introduction

Microalgae are increasingly seen as an alternative to the traditional biofuels feedstock such as edible vegetable oils (Mata, et al., 2010a), animal fats and other residual products like spent coffee grounds (Caetano, et al., 2012). Furthermore, they can produce substances at commercial scale such as nutritional supplements for humans or animals and in the cosmetics industry as extracts of valuable pigments, however with the current level of development of the technologies, the production of biofuels from microalgae does not compete favorably with fuels from fossil resources. According to the authors Slade and Bauen (2013) the costs of microalgal biomass production in the best of scenarios is between 0.4-0.7 € / kg (1\$=0.73€) that are high costs for exclusive energy use, therefore, there arises a need to include the integral use of biomass, it means, defining several routes for obtaining both of biofuels as high added value products (González-Delgado & Kafarov, 2012). Microalgae are generally composed of carbohydrates, lipids, proteins and pigments that can be converted into biofuels and valuable products. In principle it is necessary to determine the products that generate the highest annual profits, taking into account the Total Annualized Cost of production (TAC) and its retail price in the current market; Finally with a hierarchical classification of potential products can be set a strain of microalgae that will fit the highest profitability, determining a minimum composition of metabolite/dry biomass where profits are equal to the costs being the point where it begins generate positive dividends for the plant.

2. Analysis of potentially obtainable products in a biorefinery

Microalgae are unicellular organisms composed primarily of carbohydrates, lipids, proteins and pigments in different proportions depending on both genus and species of the culture conditions applied during cell growth. The components of microalgae can be transformed into valuable products through various processing routes.

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CARBOHYDRATES: The microalgae strains as *Chlorella, Dunaliella, Chlamydomonas, Scenedesmus* and *Spirulina* have relatively high efficiency of photosynthesis and are able to accumulate more than 46% of carbohydrates in dry weight biomass (Ho, et al., 2012). Carbohydrates in algae are composed mostly of starch, glucose, cellulose and hemicellulose that can be potentially used in the production of biofuels, such as bioethanol, biogas and hydrogen.

LIPIDS: Microalgae accumulate lipids under specific culture conditions, such as low carbon and nitrogen concentration in culture media which also leads to low cell reproducibility, it means, low productivity of biomass and lipids; hence to determine a promising strain is preferable considering lipid productivity. The lipids in the microalgae are classified into two groups depending on the number of carbons, which can be transformed into biodiesel (14-20 carbons) and food supplements (more than 20 carbons). Lipids with more than 20 carbons and several unsaturations are defined as PolyUnsaturated Fatty Acids PUFAs.

PROTEINS: can be used in human or animal nutrition, biofertilizers industry and proteins as amino acids and peptides are desired in the field of health products. However, some microalgae contain proteins that are not digested. Proteins can be divided into a water-soluble fraction that is valuable for human consumption, but is not sold due to the consistency of the powdered dry biomass, its dark green color and smell, which limits the incorporation of microalgae in conventional food as preparations of bread or noodles. The other fraction is insoluble in water and is used mostly as fertilizer and animal feed. In this work the contribution of protein as valuable product is not taken into account.

PIGMENTS: There are three major classes of photosynthetic pigments in microalgae: chlorophylls, phycobilins and carotenoids. Some potential chlorophylls sources are the microalgae *Porphyridium cruentum*, *Synechococcus sp.* and *Chlorella* which are used for food and cosmetics as well. *Dunalliella salina* microalgae is promising for the production of carotenoids with a composition up to 16% (García-González, et al., 2003) under stress culture and a high light intensity. Phycobilins are tied to polypeptides to form phycobiliproteins that are water soluble, when are purified, these substances are highly fluorescent.

3. Methodology

3.1 Techno-economic criteria

To determine the overall cost of production it is important to take into account investment costs (direct and indirect) and operational (fixed and direct) process costs. The Fixed Capital Investment (FCI) includes both direct and indirect costs. Direct costs are directly associated with the production, Indirect costs include values that are not directly related to production. To estimate the FCI of a "B" production capacity from FCI production capacity known "A" in biomass transformation processes, can be used the seven tenths rule factor.

$$FCI_B = FCI_A * \left(\frac{capacity_B}{capacity_A}\right)^{0.7} \qquad (1)$$

The FCI are paid at the beginning of the investment regularly through financing; therefore, to annualize this value should be taken into account the depreciation which is an equivalent distributed in the lifetime of the plant. The Annualized Fixed Costs (AFC) are calculated by the following equation:

$$AFC = \frac{FCI_0 - FCI_S}{N} \qquad (2)$$

Where FCI_0 is the initial value investment without the land cost, FCIs is the salvage value of the investment and N is the lifetime of the investment. For this work is considered a straight-line depreciation and not salvage value with a useful life period of 10 years. The operational costs can be also divided into Fixed Operational Costs (FOC), which does not depend on the production capacity of the plant, such as labor, equipment maintenance, insurance and taxes, and Variable Operational Costs (VOC) which are costs varying with respect to the production capacity of the plant such as raw material, solvents, reagents, catalysts, energy services and waste arrangement. The Annual Operating Costs (AOC), can be calculated as follows.

$$AOC = FAOC + VAOC \tag{3}$$

To determine the Total Annualized Cost of production (TAC) must be add the deferred investment costs in the lifetime of the plant (10 years in this case) with annual operating costs.

$$TAC = AFC + AOC \tag{4}$$

3.2 Techno-economic evaluation and TAC of each potentially obtainable product from microalgae

For each product an economic evaluation reported in the literature was selected, where the following values were taken: the Delivered Purchased processing Equipment in the plant (DPE),the Annual Cost of Materials needed for production without raw material (ACM), the Annual Cost of Energy services, heating and cooling (ACE) and the Annual Cost of the Wages earned by the operators of the plant (ACW). All data were adjusted to the same production capacity and raw material cost (100,000 tons of biomass/year 500$/ton biomass (Slade and Bauen, 2013)) in order to compare the TAC of each product, also taking into account the parameters that contribute to this cost and value over time assume the following assumptions:

- To standardize the parameters contributing to the TAC is determined the ratio factors for the specification of each cost, both investment (Table 1) as operational (Table 2) that are evaluated with data reported in the techno-economic analysis of each product. This factors have been estimated using standard process engineering data (Humphreys, 1991) (Peters & Timmerhaus, 1991)
- Economic evaluations of products or services that are in different years and places are equal in time to the following equations:

$$FCI_{t2} = FCI_{t1}\left(\frac{CPI_{t2}}{CPI_{t1}}\right) \tag{5}$$

$$Price_{t2} = Price_{t1}\left(\frac{CPI_{t2}}{CPI_{t1}}\right) \tag{6}$$

Where CPI is the Consumer Price Index that is set for each year, in this case was determined for October 2013.

- For the case of the costs of services (ACE and ACW) the average annual increase, which in this case is 3.5% and 3% respectively.

Table 1: Factors for the specification of each cost of Total Capital Investment (TCI).

Total Capital Investment (TCI)		
	%FCI	Values
Working capital	7%	5-12%
Star up	10%	10-20%
CALCULATION OF FCI		
Total direct plant cost		
Purchased equipment (installation)	20%	20-90%
Instrumentation (Installed)	8%	6-40%
Piping (Installed)	20%	10-70%
Electrical (installed)	13%	10-15%
Total indirect plant cost		
Engineering and supervision	32%	25-75%
Construction expenses	34%	15% of total direct cost
Legal expenses	1%	
Contractors'fee	7%	
Contingency	8% of above cost	8-25% of above cost

Table 2: Factors for the specification of each Operational Cost (OP).

Operational Costs (OC)	
General expenses	20% OC
Direct production costs	
Maintenance and repairs	5% FCI
Operating supplies	5% ACM
Supervision and clerical labor	15% ACW
Laboratory charges	10% ACW
Fixed charges	
Depreciation	10% FCI
Local taxes	2% FCI
Insurance	0,4% FCI
Interest	1% TCI

3.3 Profitability analysis

Assuming that all production is sold, the selection criterion to determine the profitability of each product is the highest gain evaluated by the following equation:

$$Revenue\left[\frac{\$}{yr}\right] = (selling\ price * capacity * efficiency * X')\left[\frac{\$}{yr}\right] - TAC\left[\frac{\$}{yr}\right] \quad (7)$$

Where X' is the product composition of the dry biomass for the extraction stage, if there is a chemical transformation is evaluated the following relationship:

$$X\left[\frac{Tonm}{Tonb}\right] = \frac{X'\left[\frac{Tonp}{Tonb}\right]}{Y\left[\frac{Tonp}{Tonm}\right]} \quad (8)$$

As the objective function is the microalgae composition, first step is to find the specific metabolite composition per 100% of biomass useful to generate a minimum income (0.001), this assessment is called analysis of Break Even Point (BEP) fixed the conditions for that the total cost of production be equal to the revenue generated products. For the profitability analysis were used representative sale prices of extracts (not pure) of valuable substances.

4. Results

4.1 Evaluated products

A biorefinery is analogous to an oil refinery among other things because they have a main line of energy production but also obtain during processing chemical byproducts, taking into account this concept is selected as the main products the biofuels that can be from lipids (biodiesel) or carbohydrates (bioethanol, biogas and hydrogen). As the aim of the plant is to produce biofuel but also generate incomes are limited the ranges of metabolite for valuable products to avoid a only production fine substances and pigments, thus the maximum amount of lipids (with carbons > 20) and pigments and are 10% and 5 % (metabolite/ dry biomass) respectively. In the case of proteins is identifies a possible use of waste products in the processing in the field of fertilizers but this development was not taken into account for the analysis of profitability.

4.2 Techno-economic data

Tables 3 and 4 shows information about the maximum theoretical yield (Y[Tonp/Tonm]) for each potential product evaluated, in the case of chemical transformations and the total amount of the product for metabolite extractions (in this case Y=1). Process efficiency (EF[%]) which depends on the processing technology and annual production costs (fixed and operational) TAC is necessary for some technologies also consider methods of harvesting and drying. It is considered that the harvesting and drying of the biomass assume a maximum humidity of 20% and 80% respectively.

The technologies evaluated are Simultaneous Sacharification and Co-Fermentation (SSCF), Anaerobic Digestion (AD), Supercritical Water Gasification (SCWG), homogeneous transesterification (TRANS. HO), esterification (ESTERIF), Supercritical Fluid Extraction (SFE) and homogenous extraction with solvents (EXT. HO.).

Table 3: of the evaluated products.

Metabolite	Product	Technology	Harvesting	Drying	Y	EF
Carbohydrates	Bioethanol	SSCF	Yes	Yes	0.51	0.8
	Biogas	AD	Yes	No	0.22	0.75
	Hydrogen	SCWG	Yes	No	0.11	0.76
Lipids C<20	Biodiesel	trans. ho.	Yes	Yes	1	0.94
Lipids C>20	PUFAs	sterif.	Yes	Yes	1	0.7
Pigments	Carotenoids	SFE	Yes	Yes	1	0.94
	Chlorophyll	SFE	Yes	Yes	1	0.94
	Phycobiliproteins	ext. ho.	Yes	No	1	0.33

Table 4: Technical data of the evaluated products.

Metabolite	Product	Technology	Price [$/ton]	TAC [$/yr]	Modified from
Carbohydrates	Bioethanol	SSCF	827.8	9.21E+7	(Aden, et al., 2002)
	Biogas	AD	1124.6	8.05E+7	(Ryan, et al., 2011)
	Hydrogen	SCWG	4000	2.47E+8	(Gasafi, et al., 2008)
Lipids C<20	Biodiesel	Trans. Ho.	1023.6	1.23E+8	(Apostolakou, et al., 2009)
Lipids C>20	PUFAs	Esterif.	728000	4.96E+9	(Molina Grima, et al., 2003)
Pigments	Carotenoids	SFE	7000	8.23E+7	(Rosa, 2005)
	Chlorophyll	SFE	8000	8.23E+7	(Rosa, 2005)
	Phycobiliproteins	Ext. Ho.	148000	2.41E+8	(Bermejo, et al., 2002)

Once the individual costs that make up the TAC of each product for a year are determined, capacity and raw material cost, the minimum Break Even Point (BEP analysis) where production generates no earnings or economic losses is established. The graph of BEP, where the gain is zero, is generated depending on the capacity of the plant, which in this case is constant for all the products, thus the only variable in the equation (7) is X'.

4.3 Value pyramid of products and minimum composition of metabolites according its economic profitability

Figure 1 represents the valorization of microalgal biomass as function of the general potential products, regardless of special substances of each strain. Since it is an economically viable biorefinery on biofuel production emphasis that could generate negative profits are counteracted with profits left by the marketing of fine chemicals. The order of the pyramid is based on the minimal cost composition of the metabolite in the dried microalgal biomass. The composition largely depends on the environmental microalgae, such as intensity of light, temperature and nutrient availability factors. The ranges reported in the literature for each metabolite varies but generally found high concentrations of lipids 2% -90%, must take into account that high percentages are under specific nutrient limitation condition that causes a decrease in the productivity of the microalgae, besides all the lipid content is not suitable for transforming into biodiesel. Biofuels from carbohydrates are not profitable under any possible composition. However, hydrogen can be a promising candidate as a biofuel but it is necessary to develop technologies that have a higher conversion of the metabolite, considering that carbohydrates in the microalgae are present in concentrations from 5% to 50%. There are wide opportunities and incentives regarding biofuels due to the need to partially replace fossil fuels, so there are different policies that offer incentives to producers and farmers. Given these economic improvements the minimum composition of metabolites to generate biofuels without taxes and legal fees is: 124.6% Biodiesel, Bioethanol 256.9%, biogas 385.6%.

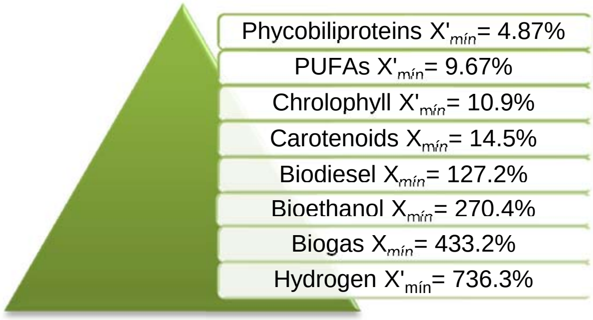

Figure 1: Value pyramid of microalgae products and minimum profitable composition of metabolites

5. Conclusion

The production of biofuels from microalgae does not present positive incomes because is need a minimum profitable oil or carbohydrates composition over 100%;, however, these economic losses could be countered with the integral use of biomass generating positive profits with marketing valuable substances such as pigments or PUFAs with minimum profitable composition of 4.87% and 9.67% respectively.

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