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Optimal Design of an Integrated Microalgae Biorefinery for the Production of Biodiesel and PHBs

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In this work, we formulate a nonlinear programming model for the design of an integrated microalgae-based biorefinery for the production of biodiesel and value added co-products which depend on the particular microalgae species considered. The production of biogas by anaerobic digestion of the oil cake together with waste streams is included.
The process scheme includes the possibility to use glycerol, the main by-product in biodiesel production, as substrate for the production of poly(β-hydroxybutyrates), PHBs, which are polymers belonging to the polyesters class, bio-derived and biodegradable. In this case, we consider a three stage process: glycerol purification, fermentation and PHB extraction by cellular lysis.
The resulting model is a nonlinear programming problem and has been implemented in GAMS (Brooke et al., 2011). Numerical results provide useful insights on the design of integrated biorefineries that use carbon dioxide as carbon source.

1. Introduction

The increase of the worldwide energy consumption and the elevated consumption of crude based fuel (fossil fuels accounted 78.2 % of the primary energy consumption) in order to satisfy this demand has motivated the study of biofuels during the last years (REN21, 2013).First generation biofuels are extracted from food and oil crops including rapeseed oil, sugarcane, sugar beet, maize, vegetable oils and animal fats. The food-based biofuels seem to be mainly limited by the controversial discussions originated due to food competition and use of arable land. Second and third generation biofuels involve those based on lignocelluloses and algae biomass, respectively. The average annual growth rate over the period from the end of 2007 through 2012 was nearly 11 % for bioethanol and 17 % for biodiesel (REN21, 2013).
These statistics lead to focus the attention on the biodiesel world production and its main by-product, glycerol. Glycerol is mostly used for pharmaceutical products, but it can be employed as raw material for PHB production or even as carbon source for biogas producer microorganisms. These alternatives, offer the possibility of giving an added value to this important by-product in biodiesel production.
PHB production by microorganisms constitutes an alternative to the polymer production from fossil fuels. Furthermore, current PHB production is based on substrates that are expensive or compete with human diet such as sugar cane, sugar beet or maize. In these processes, the cost of the raw material can reach up to 50 % of the production cost. Consequently, the use of a less expensive carbon source, such as glycerol, would be an interesting approach in order to maximize the process profits (Cader, 2012).
On the other hand, due to several simple features for growth requirements such as light, carbon dioxide and inorganic nutrients, microalgae show a particular attraction to obtain products in pharmaceutical and biofuels industries (Laiglecia et al., 2013). The latter industry could be essential in order to design an integrated biorefinery including biodiesel production from algae, biodigestion and PHB production.

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2. Process description

The integrated biorefinery scheme for biodiesel and PHB production based on microalgae is presented in Figure 1. The biodiesel production process from algae under study consists of four main stages (Gebreslassie et al., 2013), namely: algae growth, harvesting and dewatering, lipid extraction and algal oil processing for obtaining biodiesel. The glycerol produced as a by-product in the biodiesel process is used as raw material in the PHB production process, which is composed of three main steps: glycerol purification, fermentation, and PHB extraction. Residues from the precedent processes, as well as glycerol, can be considered as an option to nourish to a power generation step. The produced energy is a significant alternative that can be used in the processing sections described before.

2.1 Algae based biodiesel production process

Algae growth takes place in a tubular photobioreactor where carbon dioxide, nitrogen and phosphorus are required (Iancu et al., 2012). Carbon dioxide can be provided from flue gases obtained from other industries such as a thermoelectrical plant. Depending on the flue gas composition, a scrubber is used to reduce the sulphur concentration, which is injurious for algae. During photosynthesis, carbon dioxide is fixed leading biomass production. *Haematococcus pluvialis* algae growth parameters are considered (Gebreslassie et al., 2013).Algal oil extraction requires an elevated concentration of algae. A primary harvesting step is used to concentrate the algae, and then a crucial step of dewatering is needed to increase the algae concentration concluding with a thermal drying process. Hexane is used as solvent to remove the algal oil from the recently dried algae biomass. The lipids are further refined and the solvent is recycled after a hexane recovery process. The oil cake, which is rich in proteins and carbohydrates, is also obtained in this step.

Finally, the algal oil is converted to biodiesel. This processing subsection is composed of a reactor where thetransesterification reaction takes place using methanol and sodium methoxide as catalyst to form methyl esters and glycerol from the oil triglycerides. The remaining free fatty acids (FFA) in the algal oil react with sodium methoxide to produce soap and methanol. Glycerol and impurities are separated from the methyl ester stream by a decanter and a washing column. These streams are sent to a further purification process where glycerol is purified and methanol is recovered to reuse.

2.2 PHB production process

Three main stages can be highlighted in the PHB production process from crude glycerol.

In the first stage, a glycerol purification step is required because of the impurities (methanol, fats, soaps, catalyst, ash and water) that could contain the stream obtained from the biodiesel production process. For this purpose, the methanol contained in the crude glycerol stream is stripped using superheated steam. The saturated methanol vapour could meet afterwards the necessary conditions to be reused in the biodiesel process. The resulting glycerol solution from the bottom of the stripper is sent to a reactor where a neutralization reaction with an acid solution takes place. The existing catalyst in the stream reacts with the acid to form methanol and salt, and the soaps present in this stream react to form FFA and salt as well. Using a decanter, the FFA and the other impurities such as ash or salts are removed from main stream. Finally, water is evaporated in a flash evaporator and a stream of glycerol-rich product is obtained.

In the second stage, the biotechnological production of PHB is developed in a fermentation stage. A bacterial strain is induced to produce PHB by a limitation of an essential nutrient, such as nitrogen or phosphorus, and an excess of a carbon source. Before the glycerol stream (carbon source) entrance to the biodigesters, a dilution is made. In a first biodigester, cell growth is maintained without nutrient limitation, while in a second biodigester, an essential nutrient is limited to allow an efficient PHB synthesis.

Finally, PHB is extracted from the cytoplasm. In order to do so, a reactor is used to separate the polymer from the cell residual material by solvent extraction. Isovalerate is used in a 1/6 ratio of biomass/solvent. Then, the disrupted mass cell is discarded by a centrifugation process and the solvent used in the modification of the membrane permeability is recovered after a decantation step. Purified PHB is obtained by spray drying (Posada et al., 2011).

2.3 Energy production by anaerobic digestion process

Purified glycerol, waste paper and the residues generated in the lipid extraction (oil cake) are sent to an anaerobic digester where a biogas mixture with nearly 60 % methane and 40 % carbon dioxide is produced.

An amount of purified glycerol is fed to the digester mainly because it increases methane production (Ehimen et al., 2011). At this point, a consideration is made: the methane yield does not depend on the biodigester feed composition. Waste paper is used to feed the digester in order to obtain a C/N ratio between 20 and 25 (Morken et al.,2013), which is the optimal operation point for the biodigester (Yen and Brune, 2007).One product of the digestion is liquor (rich in nutrients. such as nitrogen and phosphorus)

which is re-circulated to the biodiesel process. Solid wastes are generated in this step, as well. These residues can be used as fertilizers to give an added value to the process. Finally, the biogas product is enhanced in a biogas upgrading unit where water, rich in carbon dioxide, is eliminated from the process stream and sent to the tubular photobioreactor in the algae growth step. Finally, the purified biogas is sent to a combined heat and power cycle to generate electric and thermal power.

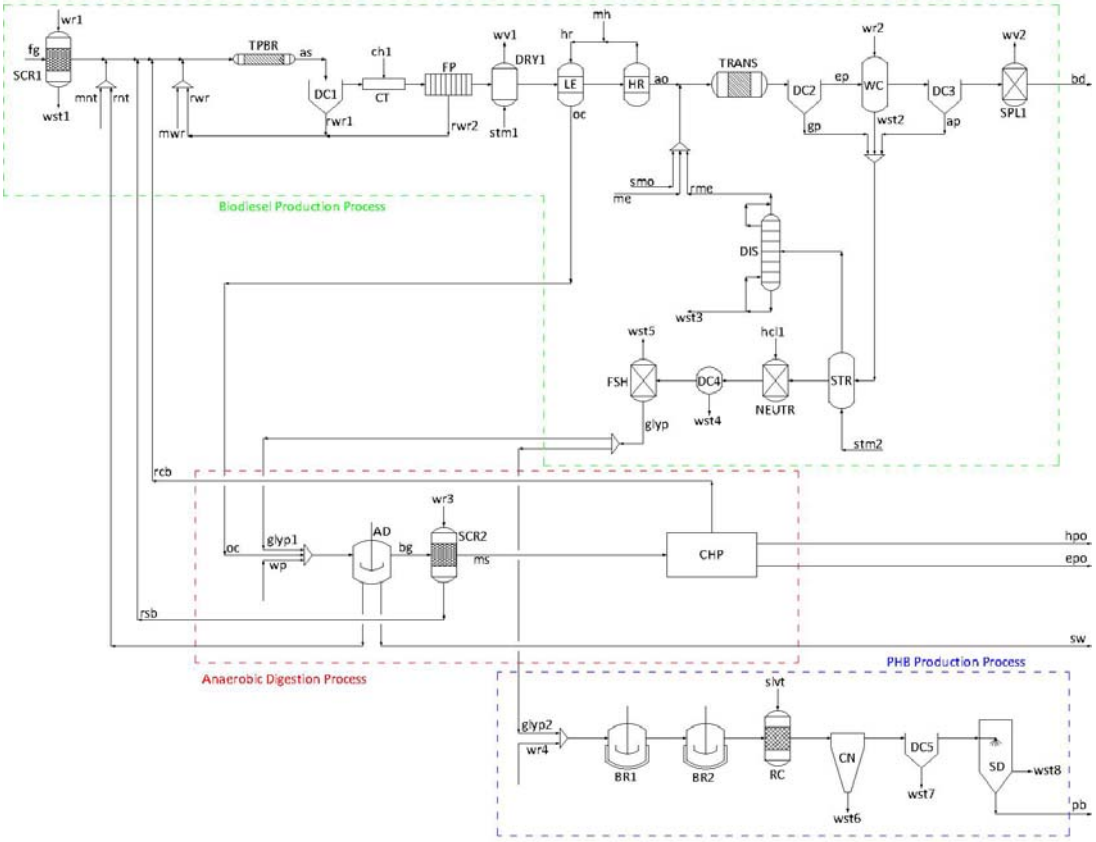

Figure 1: Microalgae based biorefinery flowsheet

3. Flowsheet notation

3.1 Process components and streams

The components involved in the integrated biorefinery are shown in Table 1, while the streams involved in the integrated biorefinery shown in Fig. 1 are presented in Table 2.

Table 1: Process components

Nomenclature	Component	Nomenclature	Component	Nomenclature	Component
Al	Algae	Hex	Hexane	Phb	PHB
Bd	Biodiesel	Lip	Lipids	Pot	Phosphorus
carb	Carbohydrates	Merc	Mercaptans	Prot	Proteins
cdo	Carbon dioxide	Met	Methanol	Smo	Sodium methoxide
ch1	Coagulant	Micr	Microorganisms	Sox	Sulphur oxides
ch4	Methane	Nacl	Sodium chloride	Sp	Soaps
Ffa	Free fatty acids	Nit	Nitrogen	Wp	Waste paper
glyc	Glycerol	Nox	Nitrogen oxides	Tg	Triglycerides
Hcl	Chloride acid	Oxy	Oxygen	Wr	Water

Table 2: Process streams

Streams	Components	Streams	Components	Streams	Components
Ao	Algae oil	Hpo	Heat power	Rme	Recycled methanol
Ap	Aqueous phase	Stm	Steam	Rnt	Recycled nutrients
As	Algae sludge	Oc	Oil cake	rsb	CO_2 enriched water
Bd	Biodiesel	Hr	Recycled hexane	rwr	Recycled water
Bg	Biogas	Me	methanol	slvt	Solvent
Ch	Conditioner	Mh	Hexane makeup	smo	Sodium methoxide
Ep	Ester phase	Mnt	Nutrients makeup	stm	Steam
Epo	Electric power	Ms	Methane	sw	Solid waste
Fg	Flue gas	Mwr	Water makeup	wp	Waste paper
Glyp	Purified glycerol	Oc	Oil cake	Wr	Water
Gp	Glycerol phase	Pb	PHB	Wst	Waste stream
Hcl	Chloride acid	Rcb	Recycled flue gas	Wv	Water vapour

3.2 Process units

The non-reactive units k and the reactive units l involved in the integrated biorefinery shown in Fig. 1 are referenced in Table 3 and Table 4, respectively.

Table 3: Process units

Non-reactive units nomenclature	Units names	Non-reactive units nomenclature	Units names	Non-reactive units nomenclature	Units names
AD	Anaerobic digester	DRY	Dryer	SCR	Scrubber
CHP	Combined heat power unit	FP	Filter press	SD	Spray dryer
CN	Centrifuge	FSH	Flash	SPL	Splitter
CT	Conditioner tank	HR	Hexane recovery	STR	Stripper
DC	Decanter	LE	Lipid extractor	WC	Washing column
DIS	Distillation column	RC	Digester		

Table 4: Process units

Reactive units nomenclature	Units names	Reactive units nomenclature	Units names
BR	Fermenter	TPBR	Tubular photobioreactor
NEUTR	Neutralization reactor	TRANS	Reactor

4. Modeling and optimization

A nonlinear optimization problem is formulated describing an integrated biorefinery for biodiesel and PHB production, as well as a combined-cycle for energy production. The model is implemented in GAMS (Brooke et al., 2011) with the following general formulation:

$$Max\ Z = f(x) \tag{1}$$

$$s.t.$$

$$h(x) = 0 \tag{2}$$

$$g(x) \leq 0 \tag{3}$$

$$x^L \leq x \leq x^u \tag{4}$$

Eq (1) represents the objective function to be maximized (Z). In this case, Z comprises PHB production for a given biodiesel demand. Eq (2) corresponds to the model equality constraints such as mass balances, while Eq (3) include process constraints, such as the requirement that the carbon dioxide produced by the

integrated biorefinery must be less than the required amount for biomass generation in the photobioreactor. In this way, a global reduction of the carbon dioxide emissions to the biosphere is ensured. The upper bound of carbon dioxide, from flue gas stream, is limited by the carbon dioxide that is produce in a thermoelectrical industry, located in the city of Bahía Blanca. Furthermore, the C/N ratio in the photobioreactor must be between specific values with the purpose of an optimal operation. An upper bound for the waste paper amount fed to the anaerobic digester is needed. The constraint of this stream, which ensures the substrate requirements in the digester, is assumed to be the total amount of the domestic recycled paper in Bahia Blanca's city. A lower bound constraint on the glycerol flowrate stream to the biodigester is required to ensure the amount of carbon necessary for biogas production.

4.1 Mass Balances

Mass balances for the integrated biorefinery are implemented in GAMS (Brooke et al., 2013) for each component. Considering domain S between j,k,l where j is a source/sink stream, l is a reactive unit and k is a non-reactive unit; r and t have the same domain as s, while C_{rt} could be 0 if r and t are units/streams which are not connected, or 1 if r and t are connected. Mass balances for component i in a non-reactive unit k*, where k* belongs to k if s is different from k*, can be formulated as follow:

$$\sum_{h} \dot{m}_{i,s,k^*} = \sum_{g} \dot{m}_{i,k^*,s} \tag{5}$$

where, h represents the unit where C_{sk^*}=1, g represents the unit where C_{k^*s}=1, $\dot{m}_{i,s,k^*}$ is the flowrate for component i which is leaving source s and leading to unit k*, $\dot{m}_{i,k^*,s}$ is the flowrate for component i which is leaving unit k* and leading to s.

Mass balances for component i in a reactive unit l*, where l* belongs to k if s is different from l*, are formulated as follows:

$$\sum_{w} \dot{m}_{i,s,l^*} + \xi_{l^*} \cdot STC_i = \sum_{p} \dot{m}_{i,l^*,s} \tag{6}$$

$$\xi_{l^*} \cdot STC_i = \chi_{i,l^*} \cdot \dot{m}_{i,s,l^*} \tag{7}$$

where w represents the unit where C_{sl^*}=1, p represents the unit where C_{l^*s}=1; ξ_{l^*} is the extent of reaction in reactive unit l*; STC_i is the stoichiometric number of the component i for the reaction in l*; χ_{i,l^*} is the conversion of the reactant i in the reactive unit l*; $\dot{m}_{i,s,l^*}$ is component i flowrate coming from s and entering l*; $\dot{m}_{i,l^*,s}$ is component i flowrate coming from l* and entering s.

5. Results and discussion

The 43,200 t/y biodiesel production plant shown in Figure 1 is modelled and optimized. The NLP model has 2,602 variables and 2,608 constraints and it has been implemented in GAMS (Brooke et al., 2013). CPU time is 0.047 seconds. The optimal value for PHB production is 738 t/y, which is a commercial scale plant for PHB. Current PHB plants in Brazil and Japon produce 50 t/y and 1,000 t/y respectively (Chanprateep, 2010). At the same time, anaerobic biodigestion of the residue streams, as well as waste paper, which is externally supply, provide a contribution of thermal and electric energy to the biorefinery process by the production of biogas. Biogas is scrubbed to obtain clean methane which is supply to a combined heat and power cycle (CHP) where electricity and useful thermal energy in a single, integrated system are generated. Heat that is normally wasted in conventional power generation is recovered as useful energy, which avoids the losses that would otherwise be incurred from separate generation of heat and power. While the conventional method of producing usable heat and power separately has a typical combined efficiency of 45 %, CHP systems can operate at levels as high as 80 %. The biodigestion of the mentioned substrates leads to the generation of $1.57 \cdot 10^6$ GJ/y of thermal energy and $8.82 \cdot 10^5$ GJ/y of electrical energy. On the other hand, solid residues obtained in the anaerobic digestion step can be used as fertilizers. The amount of PHB obtained in this process can be used as raw material for bag production. This allows the manufacture of $1.03 \cdot 10^8$ bag/year, taking into consideration that 7 kg of plastics is required to produce 1,000 bags. Due to domestic reutilization of these bags for dumping garbage and a strategic separation, the use of this biopolymer could be an attractive option. For instance, feeding the biodigester with the domestic rubbish and the used PHB bags is an interesting alternative. The possibility of an integrated biorefinery and the incorporation of an anaerobic digestion stage, increase the added value of the biopolymer and allow the reduction of the environmental impact due to minimization of the consumption of non-renewable resources. Figure 2 shows main streams after optimization.

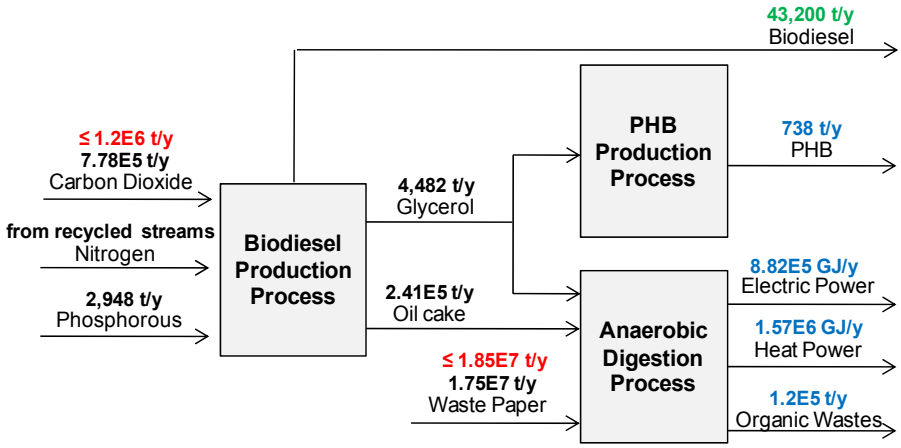

Figure 2: Microalgae based biorefinery model results

6. Conclusions

In this work, an integrated scheme to produce biodiesel and PHB from algae was analyzed. Numerical results show that it is possible to maximize the production of PHB biopolymer, taking advantage of the by-product obtained in the biodiesel production and using algae and carbon dioxide as microorganisms and substrate, respectively. Minimizing net carbon dioxide emissions by other industries was taken into consideration for algae growth. Moreover, the oil cake generated in the biodiesel process was used together with urban waste paper to feed a biodigester in order to generate fertilizers and energy that could be used to supply the integrated biorefinery. As future work, a further analysis on the energy balance will be carried out to determine the amount of energy that the biodigestion stage could provide to the system in order to reduce the external supply of it, as well as an economical analyse of the proposed scheme.

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