

Optimal Design of Poly (3-hydroxybutyrate) Production using alternative Carbon Sources

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Abstract

In this work, we propose a mixed integer nonlinear programming (MINLP) model to determine the optimal flowsheet and raw material for the production of poly (3-hydroxybutyrate) (PHB) from different carbon sources, namely, crude glycerol (with the possibility to be purified), cassava starch and sugarcane. The objective function is Net Present Value. Model equality constraints include mass and energy balances, and detailed capital cost for process equipment; while inequality constraints include product specifications and operating bounds on process units. The resulting MINLP model has 3167 continuous variables, 13 discrete variables and 3079 constraints. The proposed model constitutes a powerful tool to shortlist PHB production pathways with higher economic potential looking forward to the improvement of biopolymer production using alternative carbon sources and process schemes.

Keywords: PHB, modeling, optimization, MINLP

1. Introduction

PHB is a natural biopolymer that belongs to the polyesters family and is produced by microorganisms such as *Cupriavidus necator*, *Bacillus* sp. or *Alcaligenes latus* among others, as a carbon reserve in their cytoplasm. Due to its mechanical and thermal properties and biodegradability abilities, PHB constitutes an alternative to synthetic polymers. PHB has several applications in the biomedicine field, where it can be used for medical implants or as carrier for drug delivery. Food packaging is another application. However, the main difficulty limiting PHB production at industrial scale is the relative high cost of the carbon sources, as compared to usual petrochemical polymers (López et al., 2012). Even though there is a broad range of substrates that could be used as carbon sources for the fermentation process, current industrial production is based on substrates whose cost represents a large percentage of the total production cost (Moncada et al., 2013). A low cost extraction and purification step for PHB can also contribute to reduce the biopolymer production cost.

In this work, we propose a superstructure for the optimal design of a PHB biorefinery, including detailed equipment capital cost correlations. Net present value is the objective function. The model takes into account different carbon sources as raw materials and includes several alternatives for the fermentation, extraction and purification steps. The model is formulated and implemented in GAMS (Brooke et al., 2013) and numerical results show that PHB production can be economically attractive if appropriate technologies are considered.

2. Process description

The proposed superstructure, shown in Figure 1, involves three main processing stages with different technological alternatives: raw material feeding and purification, fermentation, biopolymer extraction and biopolymer purification.

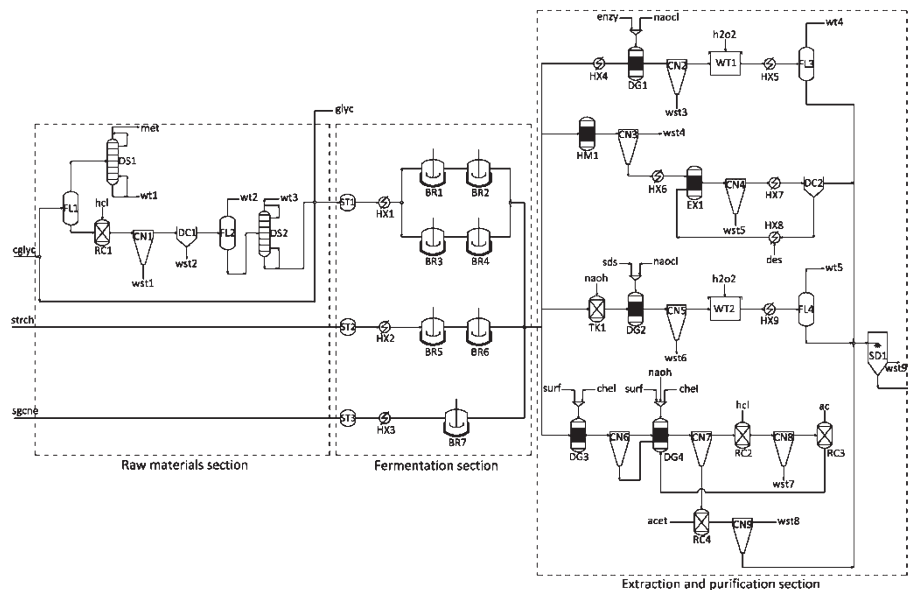


Figure 1: PHB biorefinery superstructure

Three different raw materials are considered as carbon source, namely, crude glycerol, cassava starch and sugarcane. Crude glycerol (glycerol 60.05 wt%, methanol 22.59 wt%, water 10.00 wt%, 2.80 wt% ashes, 2.62 wt% sodium methoxide, 1.94 wt% soaps) can be directly fed to the fermentation step after being sterilised, or it can be purified to improve downstream biomass growth. If glycerol purification step is selected, methanol can be sold as a co-product after recovery by the use of flash and distillation units. Furthermore, the methanol-free stream is neutralized with hydrochloric acid (HCl) in a reactor. Ashes and salts produced in the previous step are withdrawn by centrifugation. The resulting stream is washed with water in a decanter for soaps elimination. Finally, in an evaporation process, containing a flash and a distillation tower, water and other remaining volatiles compounds are evaporated resulting in a purified glycerol stream. It is worth mentioning that selling purified glycerol is set as a possible alternative instead of being use as carbon source for PHB production. In this work cassava starch and sugarcane are considered to be available with the required specifications for fermentation.

Biotechnological production of PHB takes place in the fermentation stage where bioreactors are used for microorganism's growth and biopolymer accumulation. For the case of crude glycerol, purified glycerol and cassava starch, two different bioreactors are used. The first one is intended for cell growth and the second one for intracellular PHB accumulation. Fermentative conditions are set depending on the selected carbon source. Bioreactor productivities depending on microorganisms strain can be found in the open literature (Tan et al., 2014).

After fermentation, a step where PHB is extracted from microorganism cytoplasm is required. We include four methods for the extraction and purification step in the proposed superstructure. The first one consists on an enzymatic digestion using *Burkholdeira* sp. PTU9 with sodium hypochlorite (NaOCl). In this process, enzymes complemented with NaOCl are used to degrade the cell membrane in a digester. Then, a centrifuge is used for the separation of the disrupted cell mass from the bioproduct. Finally, the PHB stream is washed with a hydrogen peroxide solution (H₂O₂) in a decanter and it is concentrated by a flash step followed, by a spray drier. The second option is solvent extraction with diethyl succinate (DES). Here, the solvent is used after a step of higher pressure homogenization for two purposes: modification of cell membrane permeability and dissolution of PHB. Residual biomass is eliminated by centrifugation, DES is recovered by a decantation step after cooling and concentrated PHB is obtained after flashing and spray drying. A third extraction method is chemical digestion, using anionic sodium dodecyl sulfate (SDS), which disrupts cells incorporating itself to the lipid bilayer membrane. In this alternative, an alkaline pretreatment using sodium hydroxide (NaOH) is carried out in an alkaline tank. Afterwards, cell digestion process is performed with SDS and NaOCl in a digester. Cell biomass is discarded in a centrifuge and the PHB stream is washed with H₂O₂ in a tank. Finally the bioproduct stream is concentrated in a flash unit and a spray drier. The last alternative corresponds to surfactant (betaine) and chelate (EDTA disodium salt) digestion. Chelate addition promotes surfactant cell disruption action through the destabilization of the outer membrane by forming complexes that also cause weakness in the inner membrane. At this point, the recycle wastewater process proposed by Chen et al. (2001) is formulated. It includes two digestion stages where surfactant and chelate diluted in water react with the biomass coming from fermentation. Also, it contains a centrifugation step where the polymer is separated from microorganism cytoplasm. Residual biomass is withdrawn using a centrifuge and the remaining water is treated using HCl and activated carbon prior recycling. PHB is rinsed with water and acetone and concentrated in a spray drying process.

3. Mathematical modelling

The proposed superstructure is formulated as an MINLP problem and implemented in GAMS. The model includes mass balance constraints, energy balance and correlation constraints, detailed equipment design and cost capital correlations, integer constraints and an economic objective function.

3.1. Mass balance constraints

Mass balances are formulated for each non-reactive unit (θ) in the superstructure shown in Figure 1 as follows:

$$\sum_{k \in K} f_{\theta,j}^k = \sum_{r \in R} f_{r,j}^{\theta} \quad \forall j \in J \quad (1)$$

where:

$f_{\theta,j}^k$: Mass flowrate of component j from inlet stream k to unit θ [kg j/day]

$f_{r,j}^{\theta}$: Mass flowrate of component j from θ to outlet stream r [kg j/day]

Similarly, mass balances for each reactive unit (θ') are described by Eq. (2) considering stoichiometric coefficient (ξ_{j,s_h}) between component j and limiting reactant for reaction h (s_h), molecular weight of component j and h (M_j , M_{s_h} , respectively), and limiting reactant conversion (C_{s_h}).

$$f_{r,j}^{\theta'} = \sum_{k \in K} f_{\theta',j}^k + \sum_{h \in H} \xi_{j,s_h} \cdot M_j / M_{s_h} \cdot C_{s_h} \cdot \sum_{k \in K} f_{\theta',s_h}^k \quad \forall j \in J \quad (2)$$

3.2. Energy balance constraints

Energy balances include energy consumed by the equipment involved in the selected technology. For heat exchangers, the assumption of saturated streams, allows knowing the specifications of temperatures and pressures for the streams involved in the analysis. Applying overall energy balances to the hot and cold streams and considering negligible heat transfer between the heat exchanger and its surroundings, negligible potential and kinetic energy changes, and steady state, it is possible to use Eq. (3) to calculate the heat duty (q_{ϑ}) for all exchangers knowing the outlet and inlet fluid enthalpy (h_o and h_i , respectively).

$$q_{\vartheta} = f_{\vartheta,j}^k \cdot (h_o - h_i) \quad (3)$$

Energy requirements by centrifuges, reactors, digesters and homogenizers are considered in their design, based on the mass flows. Linear relations are assumed for energy consumption (EC_{ϑ}) considering an energy consumption ratio (ECR_{ϑ}) per unit of mass flowrate (m_{ϑ}) relative to unit ϑ (it includes θ and θ' units)

$$EC_{\vartheta} = ECR_{\vartheta} \cdot m_{\vartheta} \quad (4)$$

3.3. Equipment design correlations and cost capital constraints

Detailed equipment design and cost equations have been used following the methodology presented by Ulrich and Vasudevan (2004) for each unit. Considering a general case (e.g. process vessels), it mainly consists of defining the vessel diameter (D) in the first place, Eq. (5), using the maximum vapor flowrate ($f_{\theta,j}^k$), vapor flow velocity based on total tower cross section (u_{sg}) and gas density (ρ_g); secondly, to calculate shell (C_{shell}) and accessories (C_{access}) costs, Eq. (6) and Eq. (7), respectively, with the equipment size information previously obtained and material (f_m) and thickness (f_e) correction factor, and the amount of material used for each equipment (m_{mat}); and thirdly, to obtain the equipment purchase cost (C_{eq}), Eq. (8), using a correction factor for pressure (f_p), a tank factor (f_t) and the chemical engineering plant cost index (I_{CE}).

$$D^2 = \frac{4 f_{\theta,j}^k}{\pi \cdot u_{sg} \cdot \rho_g \cdot 86400} \quad (5)$$

$$C_{shell} = (98.04098 - 95.99045 \cdot D^{0.00436}) \cdot f_m \cdot f_e \cdot m_{mat} \quad (6)$$

$$C_{access} = 1861.42108 + 199.90278(m_{mat}^{0.42652}) \quad (7)$$

$$C_{eq} = f_t \cdot f_p \cdot \frac{I_{CE}}{182.1} (C_{shell} + C_{access}) \quad (8)$$

3.4. Integer constraints

Potential units in the proposed superstructure are associated to binary variables y_i

3.5. Objective function

Net present value (NPV) is the objective function. It includes total capital investment (I), which involves fixed capital (capital basic costs from equipment correlations affected by a 1.18 factor to account for contingencies and fee and an additional 0.3 factor for new plants) and working capital (10% of fixed capital). Net cash income (NCI) is considered in the objective function in order to take into account revenues from sales, manufacturing and general expenses, and income taxes. Working capital shut down ($WCSD$) is an income received after shutting down the plant. In order to take into account time value of money, each cash flow is discounted back to its present value considering a project lifetime of 15 years and a discount rate of 10% (Ulrich and Vasudevan, 2004).

$$NPV = -I + a^{-1} \cdot NCI + f^{-1} \cdot WCSD \quad (9)$$

4. Numerical Results

The MINLP model has 3167 continuous variables and 13 binary variables, with 3079 constraints. It was solved with DICOPT (CONOPT and CPLEX) in three major iterations and 0.82 s. The optimal flowsheet corresponding to NPV maximization includes the use of sugarcane as carbon source (1,000 kg/d) for the production of 281.62 kg_{PHB}/d using an enzymatic extraction. Optimization results are shown in Table 1 for the optimal configuration. In order to compare with total capital investment cost, present value is considered for manufacturing and general expenses, income taxes, revenue from sales and working capital income. The NPV for this processing pathway is \$ 67.3952 MM, proving to be a promising alternative for a PHB production project.

Table 1. Summary of economics results for optimal configuration.

Economic variables	Present value (\$ MM)
Total capital investment	1.7909
Manufacturing expenses	10.4709
General expenses	2.2191
Income taxes	36.2709
Revenue from sales	117.5648
Working capital income	0.5822
NPV	67.3952

Considering Almendra and Martin (2016) research contribution, PHB production cost was estimated, resulting in a unit production cost of nearly 0.7 \$/kg_{PHB}. Figure 2 shows the contribution of different costs to the total PHB production cost. Main percentages are associated to raw materials (sugarcane, NaOCl, H₂O₂ and enzymes) and operating labor, 35 % and 27 %, respectively. The project profitability is due to the high PHB production rate. This can be achieved because of the sugarcane influence on PHB high productivity compared to other carbon source.

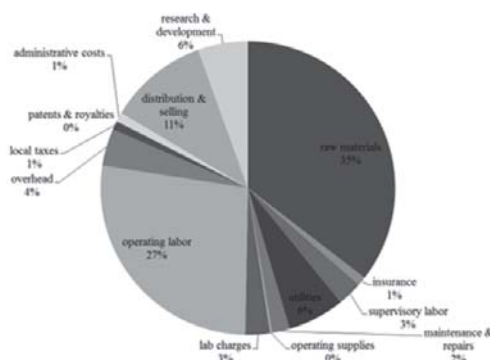


Figure 2: PHB production cost breakdown.

5. Conclusions

In this work, a detailed MINLP model is formulated to determine the optimal process configuration for PHB production, based on NPV maximization. Optimization results present the sugarcane-*Cupriavidus necator*-enzyme option as a promising alternative for a PHB biorefinery with a production cost of 0.7 \$/kg_{PHB}. High revenues allow obtaining a NPV of nearly \$ 67 MM. This could be due to sugarcane choice, with better nutrients bioavailability for biomass growth and biopolymer intracellular accumulation. Furthermore, this model can contribute on guiding future research work looking for promising economic alternatives for PHB production. Our future work includes sensitivity analysis and a detailed pre-processing section for cassava starch and sugarcane raw materials will be incorporated to the mathematical model.

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