A cost-effective integrated process for PHA production from lignocellulosic waste: A new anaerobic biorefinery.

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Keywords: Purple phototrophic bacteria (PPB), polyhydroxyalkanoates, circular-economy, sustainability.
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Introduction

The biorefinery concept has gained interest in the last decades as a way to produce energy and high added-value products from different biomass feedstock while contributing to a reduction of the negative environmental impact of fossil-based products. However, in order to optimize their environmental and economic efficiency, robust multi-platform biorefineries must be developed, preferably from waste and integrating multiple conversion processes. One promising resource is lignocellulosic biomass, as it is the most abundant renewable resource around the world.

Some works described in literature, have faced the valorization of lignocellulosic wastes through anaerobic digestion but these materials have a complex structure and yield a relatively low digestibility (Kainthola et al., 2019). Hydrothermal pretreatments are known to break this recalcitrant structure, improving sugars biodegradability and producing a highly-organic loaded liquid stream that can be further processed for the synthesis of high added-value chemicals (Silva-Fernandes et al., 2015). In recent years, some studies have emerged trying to produce polyhydroxyalkanoates (PHA) from lignocellulosic wastes hydrolysates (Cesário et al., 2014), but the current high production costs make PHAs more expensive than conventional fossil plastics. In this context, the use of a mixed culture of phototrophic purple bacteria (PPB) in a photo-fermentation process can help to reduce production costs. PPB are highly metabolically diverse, allowing the assimilation of different carbon sources including sugars and organic acids in anaerobic conditions, which makes them perfect candidates for the treatment of heterogeneous materials as well as do not need equipment sterilization or aeration, two of the most expensive processes in the production of PHA (Allegue et al., 2020). Moreover, anaerobic digestion is an attractive, cost-effective process with high-energy recovery potential and limited environmental impact, which has been thoroughly studied for lignocellulosic biomass.

In this context, a new approach coupling a thermal pretreatment, anaerobic digestion on the solid phase and photofermentation on the liquid phase for an integrated production of PHA and biogas using lignocellulose biomass waste has been tested at lab-scale. A preliminary economic and energy balances are performed to serve as a proof-of-concept.

Materials and Methods

The lignocellulosic biomass samples were collected from an urban waste treatment facility located in Madrid (Spain), blended and homogenized with a blade mill. A thermal hydrolysis (TH) pretreatment was carried out at three different temperatures: 120ºC, 150ºC and 180ºC, fixing a 1/4 dried biomass/water mass ratio. Upon the reaction, the samples were centrifuged at 6000 rpm for 10 minutes and then separated into two phases: solid and liquid. The solid samples were characterized though infrared spectroscopic (FTIR) and X-ray diffraction (XRD) in order to determine the crystallinity indexes and amorphous states of the cellulose, hemicellulose and lignin before and after the TH. Biochemical methane potential (BMP) tests of the solid fraction and batch specific phototrophic activity test (SPA) using a mixed culture of PPB on the liquid fraction were performed (a control test fed with optimum growth media was used in comparison terms). Finally, an energy balance and an OPEX-CAPEX economic analysis were assessed in order to set the techno-economic viability of the current approach. All analytical determinations were carried out according to Standard Methods.

Results and Discussion

Upon TH pretreatment, the solid and liquid phases were studied. Crystallinity index increased after TH irrespective of the temperature, with high hemicellulose and cellulose solubilization and decreased surface lignin. High COD solubilization was achieved: 5.1, 5.8 and 11.6% for 120, 150 and 180ºC pretreatments, but with low N solubilization of 1.1, 1.6 and 2.0%, respectively. Despite TH at 180ºC yielded the highest COD solubilization, at this temperature transformation of sugars into low biodegradable by-products such as furfural or 5-HMF may compromise PPB photofermentation.

BMP tests show 155 LCH_4 gVS^{-1} for the raw lignocellulosic biomass with no statistical relevant differences between the raw waste and the solid phase of the 120ºC and 150ºC pre-treated biomass. For the 180ºC pretreatment a 21% increase in methane production is observed, yielding 207 LCH_4 gVS^{-1}. This result is prominent considering the removal of the liquid fraction, which is likely the most biodegradable fraction. Kinetic parameters of the anaerobic digestion demonstrate that TH increases the anaerobic biodegradability of the less biodegradable fraction, thus it increases the total profitability of the proposed strategy.

The energy balance of the TH was assessed by extrapolating the BMP results from laboratory tests to pilot plant. A TH requires a large amount of thermal energy to be carried out being one of the main limitations for the process to be economically feasible (Passos and Ferrer, 2015). Energy balance results are summarized in Table 1. These results prove the positive energetic balance of the process, expected for the 150ºC pretreatment, in which the increase in the pretreatment temperature was not matched by an increase in biogas production.

Table 1. Energy integration balance. Results simulated for a CHP system for electricity and thermal energy.

Substrate	Electrical balance kWh ton^{-1}	Thermal energy balance kWh ton^{-1}
Raw AD	83.19	163.09
TH- 120ºC	70.31	43.42
TH- 150ºC	57.32	-3.84
TH- 180ºC	84.73	12.78

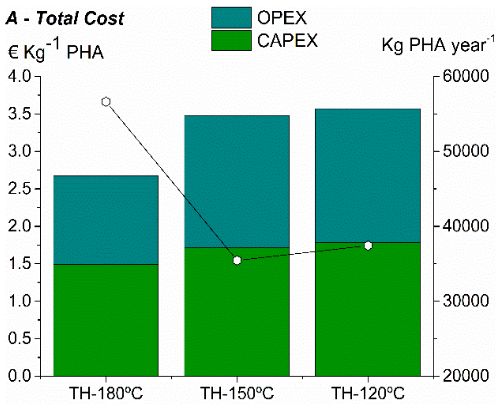

Figure 1. Cost comparison for an open raceway reactor. Results show capital and operational expenditure.

Standard SPA tests were performed on the liquid fraction upon pretreatment. PPB biomass assimilated between 40-60% of SCOD, as well as >99% of the nutrients (P and N). Photoheterotrophic metabolism was assessed by calculating the specific phototrophic activity (k_M) and the biomass yield ($Y_{X/S}$). SPA test yielded a 55-60% efficiency on k_M and 82-93% efficiency on $Y_{X/S}$ compared to the control test. Lower performance on the 180ºC pretreatment was evidenced, probably due to the solubilization of less biodegradable compounds.

PHA content was measured at 25 h of the experiment (70% SCOD consumed). Data shows that PHA production is slightly depending on the TH temperatures, but with no clear statistical trends. PHA yields are 19%, 17% and 16% for 120ºC, 150º and 180ºC respectively. These results are outstanding for a non-adapted culture, as falls within the higher range found in literature for adapted phototrophic consortia (3 to 30%) (Fradinho et al., 2019).

Currently, the industrial PHA production uses sterilized pure cultivation conditions with refined feedstock, which implies high-energy requirements that strongly increases the PHA production costs (Kourmentza et al., 2017). Our preliminary results showed in Figure 1 estimates 2.6 Euros /kg PHA for the photo-fermentation with a 180ºC pretreatment. This result falls into the expected range of scaled up industrial biotechnology-based process (2-4 Euros/kg PHB), but for much more mature processes than the one proposed in this study. PET current market price is 1.3 Euros/kg, which still is 50% less expensive, but with higher environmental impact due to its fossil-fuel origin.

Summarizing, these results are promising and encourage future research to maximize the production of PHA in a continuous process using lignocellulosic biomass waste as a low-cost feedstock, in an integrated PPB based biorefinery that can reduce production costs and diversify their product portfolio in easily up-scalable and sustainable processes.

Acknowledgements

Financial support from the Regional Government of Madrid through the project S2018/EMT-4344 BIOTRES-CM is gratefully acknowledged. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 754382, GOT ENERGY TALENT. The content of this abstract does not reflect the official opinion of the European Union. Responsibility for the information and views expressed herein lies entirely with the authors.

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