



## Techno-economic risk assessment, life cycle analysis and life cycle costing for poly(butylene succinate) and poly(lactic acid) production using renewable resources



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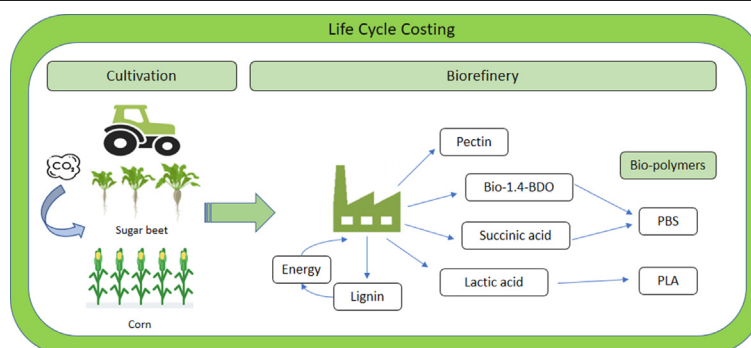
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### HIGHLIGHTS

- Biorefinery development using sugar beet pulp for sustainable PBS/PLA production
- Techno-economic and LCA impact indicators were estimated.
- Profitable biopolymer production at selling price equal to fossil counterparts
- The life cycle cost of biopolymers was compared with their fossil counterparts.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The sustainable production of poly(lactic acid) (PLA) or poly(butylene succinate) (PBS) from corn glucose syrup, corn stover and sugar beet pulp (SBP) have been assessed via process design, preliminary techno-economic evaluation, life cycle assessment and life cycle costing (LCC). Cost-competitive PLA and PBS production can be achieved in a SBP-based biorefinery, including separation of crude pectin-rich extract as co-product, leading to minimum selling prices of \$1.14/kg<sub>PLA</sub> and \$1.37/kg<sub>PBS</sub>. Acidification Potential, Eutrophication Potential and Human Toxicity Potential are lower when SBP is used. The LCC of PLA (\$1.42/kg<sub>PLA</sub>) and PBS (\$1.72/kg<sub>PBS</sub>) production from SBP are lower than biaxial oriented polypropylene (BOPP, \$1.66/kg) and general purpose polystyrene (GPPS, \$2.04/kg) at pectin-rich extract market prices of \$3/kg and \$4/kg, respectively. Techno-economic risk assessment via Monte-Carlo simulations showed that PLA and PBS could be produced from SBP at the market prices of BOPP (\$1.4/kg) and GPPS (\$1.72/kg) with 100% probability to achieve a positive Net Present Value at pectin-rich extract market prices of \$3/kg and \$4/kg, respectively. This study demonstrated that SBP-based biorefinery development ensures sustainable production of PLA and PBS as compared to fossil-derived counterparts and single product bioprocesses using glucose syrup and corn stover.

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## 1. Introduction

In 2019, global plastic production reached ca. 370 million t with an annual increase of 2.5% (Plastics Europe, 2019). Fossil resources are used for the production of the vast majority (99.4%) of plastics (European Bioplastics, 2019; Plastics Europe, 2019). The transition towards the bio-economy era necessitates the production of bio-based and biodegradable polymers. Poly(butylene succinate) (PBS) and poly(lactic acid) (PLA) are among the most widely used biopolymers with annual worldwide production capacities of 86,500 t and 394,500 t, respectively (European Bioplastics, 2019). PBS is a biodegradable polyester produced via polycondensation of succinic acid (SA) and 1,4-butanediol (BDO). Although bio-based SA is a versatile platform chemical, the expected industrial growth has not been achieved mainly due to competition with low petroleum prices. Bio-based BDO is a chemical intermediate with various applications (textiles, electronics, automotive, consumer goods, etc.). It has been produced by Novamont via fermentation since 2016 at an annual production capacity of 30,000 t (Genomatica, 2016). PBS has similar properties to polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET) (Moussa et al., 2012). PLA is a bio-based aliphatic polyester produced from lactic acid (LA) by various companies (e.g. NatureWorks, Corbion and Futerro) (E4tech et al., 2015). PLA has similar properties to biaxial oriented polypropylene (BOPP) and oriented polyethylene (Byun and Kim, 2013).

Conventional single-product bioprocesses using corn-derived glucose syrup as carbon source for the production of succinic acid, 1,4-butanediol and lactic acid lead to higher production costs than their fossil-derived counterparts. For instance, the market price of PLA (\$1.91–2.64/kg) is higher than BOPP (\$1.08–2.00/kg) (Plastic Insight, 2018). Agricultural residues ( $3.7 \times 10^9$  t) and food supply chain waste ( $1.3 \times 10^9$  t) produced in EU countries (Eurostat, 2019) could be used for biorefinery development leading to sustainable bio-economy business models including biopolymer production (Kachrimanidou et al., 2021). Novel biorefinery concepts should ensure both economic benefits and low environmental impact (Thomassen et al., 2019). Thus, the sustainable production of PBS or PLA within novel biorefineries should be demonstrated via techno-economic evaluation (TEA), life cycle assessment (LCA) and life cycle costing (LCC) as compared to conventional petroleum-derived benchmarks.

The main aim of this study is to demonstrate the sustainability potential of PBS or PLA production within a biorefinery using sugar beet pulp (SBP), which is a widely available industrial by-product in EU (10.35 million t/year) (Ioannidou et al., 2020). The wet SBP remaining after hot water sugar extraction from sugar beets is pressed, dehydrated and pelletized to facilitate its preservation and transportation. The dried SBP pellets are currently used as low nutritional value animal feed, while dehydration requirements contributing ca. 35% of the total energy requirements at the sugar mill (Mujumdar, 2014; Zheng et al., 2012). The biorefinery concept employed in this study utilizes the low-value wet SBP for the separation of a crude pectin-rich extract as co-product and the production of LA, SA and BDO via fermentation using the carbohydrate content of SBP.

TEA and LCA of lactic acid production and LCA of PLA production have been reported using various renewable feedstocks, such as corn-derived glucose, sugarcane-derived sucrose and food waste (Gironi and Piemonte, 2011; Vink and Davies, 2015; Kwan et al., 2018; Morão and de Bie, 2019). TEA and LCA of SA and BDO production as well as LCA of PBS production have also been reported using renewable feedstocks (Dickson et al., 2021; Forte et al., 2016; Patel et al., 2018; Tecchio et al., 2016). There are no LCC studies based on process design, TEA and LCA for the production of PLA or PBS employing either single-product processes or multi-product biorefinery concepts.

The main novelty of this study is to evaluate the sustainability potential of PBS or PLA production within the SBP-based biorefinery via TEA, LCA, LCC and techno-economic risk assessment using Monte-Carlo

simulations in comparison to single-product bioprocesses using corn glucose syrup and corn stover (CS) as well as GPPS and BOPP as fossil-derived counterparts. Corn-derived glucose syrup was used as the base case conventional scenario. Corn stover was selected as a representative agricultural residue that is widely studied in bioprocess development. This study has been divided into 5 different stages:

- Stage 1: Process design of PLA or PBS production using literature-cited experimental data to simulate pretreatment, fermentation, downstream separation and purification (DSP) and polymerization stages when glucose syrup, corn stover and SBP were used as feedstocks.
- Stage 2: TEA using the process design data (e.g. sizing of equipment, material and energy balances) for the estimation of PBS and PLA production costs at different plant capacities.
- Stage 3: LCA of PBS and PLA production using the CML 2001 methodology for comparison purposes with literature-cited environmental indicators.
- Stage 4: LCC of PBS and PLA production including manufacturing costs and environmental externality costs estimated with the ReCiPe 1.08 methodology according to De Bruyn et al. (2018).
- Stage 5: Techno-economic risk assessment via Monte-Carlo simulations of PBS and PLA production to assess process profitability at varying process and economic parameters.

## 2. Materials and methods

### 2.1. Stage 1 - Process design and description of process flow diagrams

The material and energy balances of PBS and PLA production processes from the three feedstocks were validated using UniSim (Honeywell). Every process flow diagram (Figs. S1-S3, ESI) operates 7920 h/y. Process design was carried out at various annual plant capacities (10–120 kt PLA or PBS). The functional unit employed is 1 kg (or 1 t) of PBS or PLA.

#### 2.1.1. Corn stover pre-treatment

The pre-treatment process (Area 100, Fig. S1, ESI) has been adopted from the 2011 NREL report on bioethanol production from corn stover (Humbird et al., 2011). The corn stover used in this study contains cellulose (35.1%, db), hemicellulose (28.9%, db) and lignin (15.8%, db). Initially, milled corn stover is fed into the receiving bins after its delivery in the factory. The pre-treatment reactor system includes a feedstock receiving system (S-101) followed by a vertical vessel with a long residence time for steam-heating. The vertical presteamer tank (M-101) is designed for a residence time of up to 10 min at a temperature of up to 165 °C, though in the current study it only operates at 100 °C such that no significant hydrolysis reactions occur in the presteamer. The remaining solids enter the horizontal pretreatment reactor (M-102), which operates at 5.5 atm, 158 °C and 5 min. Dilute sulfuric acid (22.1 mg acid/dry g of biomass) is added in this reactor using 30% (w/w) total solids. The temperature of the reactor is maintained constant by utilizing high-pressure steam. The reactor pressure is held at the bubble point for the mixture.

The pre-treatment reactor is discharged into a blowdown tank (V-101). The tank temperature is held at 130 °C via pressure control. The outflow enters the oligomer conversion tank (V-102), where it is held at 130 °C for 20–30 min. After this stage, the hydrolysate slurry containing 30 wt% total solids and 16.6 wt% insoluble solids at atmospheric pressure is added into the final tank of chemical pre-treatment (V-103). Here, the slurry is diluted with water to facilitate enzymatic hydrolysis using cellulase in the next stage. Ammonia gas is added into the dilution water to increase the hydrolysate pH to 5. The residence time is 30 min and the dilution cools the slurry to 75 °C.

Chemical pre-treatment leads to low glucan conversion into glucose (9.9%), whereas xylan is almost completely converted into xylose. Enzymatic hydrolysis using cellulase leads to cellulose conversion into

glucose. The neutralized, diluted hydrolysate from chemical pre-treatment is firstly cooled and then mixed with cellulase at 48 °C. The total solids loading is 20 wt%. The first stage of enzymatic hydrolysis begins in a continuous, high-solids loading reactor (V-104). The residence time in this first stage is 24 h, thus low cellulose hydrolysis is achieved. The continuous high-solids loading hydrolysis reactor is considered as an empty tower, with the stream entering at the top and flowing down with gravity. The amount of enzyme which is purchased and used is determined by the amount of cellulose included in the hydrolysate and the specific activity of the enzyme. In the present study, the total cellulase loading is 20 mg enzyme protein per g cellulose to achieve 90% conversion into glucose.

Hydrolysis continues in the next reactor (V-105) where the main hydrolysis takes place at 48 °C. After 60 h, the glucose concentration is increased from 8.81 kg/m<sup>3</sup> to 73.66 kg/m<sup>3</sup>. The saccharified stream is centrifuged (CF-101) in order to isolate the remaining lignin and finally the sugar-rich hydrolysate stream is concentrated and cooled in order to enter the fermentation stage.

### 2.1.2. Sugar beet pulp pre-treatment

It has been assumed that SBP is used directly as side stream from sugar beet processing plants without drying. The SBP side stream is assumed to contain 30 g solids per 100 g SBP. The SBP used in this study contains free sugars (2.73%, db), cellulose (22.7%, db), hemicellulose (36.6%, db), pectin (22.8%, db), lignin (1.16%, db) and protein (11.4%, db).

The first stage in SBP pre-treatment (Area 100, Fig. S1, ESI) includes the extraction of pectin based on data provided by Zheng et al. (2013) and Dávila et al. (2015). SBP is fed into the mixing tank (V-106) along with dilute hydrochloric acid at 100 °C. The tank is designed for a residence time of 1 h. The outflow is centrifuged (CF-102) to separate the remaining solid fraction of SBP from the liquid fraction. Sodium hydroxide is used for neutralisation of the liquid stream, which is subsequently concentrated using a mechanical vapor recompression (MVR) - forced circulation evaporator system (EV-101). The concentrated pectin-rich liquid stream is, then, mixed with ethanol (93% v/v) to precipitate the pectins that are recovered via centrifugation. The amount of ethanol used is twice the volume of the pectin-rich liquid stream. The wet pectin stream recovered is dried (DR-101). The final step is the recycling of ethanol via distillation (T-101).

After the extraction of pectins, the remaining SBP solids are processed via chemical pre-treatment and enzymatic hydrolysis to convert cellulose and hemicellulose into C5 and C6 sugars using the process employed in the case of corn stover (Section 2.1.1). This process should be sufficient for complete cellulose and hemicellulose hydrolysis due to the significantly low lignin content in SBP.

### 2.1.3. PBS production via fermentation, DSP and polymerization

**2.1.3.1. Succinic acid production and purification.** Literature-cited studies reporting high SA production efficiencies (expressed as yield, productivity and final succinic acid concentration) during fermentation on glucose (Table S2, ESI) were initially selected. Techno-economic evaluation was subsequently carried out for all selected cases to identify the most profitable fermentation. This approach was followed in order to evaluate all parameters (e.g. nutrients used for fermentation media formulation, aerobic vs facultative anaerobic conditions) influencing bioprocess profitability. Case 2 exhibited the best techno-economic performance (Cost of Manufacture = \$2.18/kg) and thus the simulation of PBS production was carried out using the parameters presented by Ma et al. (2011) (final SA concentration: 101.0 g/L, yield: 0.78 g/g, productivity: 1.18 g/(L·h)). The techno-economic evaluation of the fermentation stage was carried out according to Dheskali et al. (2017).

The SA production plant consists of two main sections (Fig. S2, AREA 200, ESI), namely bioconversion and DSP. The bioconversion stage begins with mixing (V<sub>PBS-201</sub>) of process water with the carbon source

and nutrients (e.g. nitrogen sources, minerals) followed by continuous heat sterilization of fermentation media via two heat exchangers and a holding tube (E<sub>PBS-201</sub> to E<sub>PBS-203</sub>). Media are sterilized at 140 °C and then cooled to the fermentation temperature (37 °C) before addition into the bioreactors (F<sub>PBS-203</sub>). The inoculum used is 10% (v/v) of the fermentation broth per bioreactor. The pH is maintained at 6.7 with 10 M NaOH solution added during fermentation. MgCO<sub>3</sub> is added at the beginning of fermentation. CO<sub>2</sub> is used during fermentation due to metabolic requirements in the reductive TCA cycle to produce SA. The main metabolic by-product is acetic acid (1.67 g/L). The same fermentation efficiency has been assumed in the case of corn stover and SBP derived hydrolysates based on the existence of other *Escherichia coli* strains (e.g. *E. coli* AFP184) consuming efficiently C5/C6 sugars and potential strain engineering for fermentation efficiency improvements (Khunnonkwao et al., 2018; Sawisit et al., 2015).

The appropriate number of bioreactors depends on the desired production capacity and the maximum volume of bioreactors. Table S3 (ESI) presents the optimal parameters for the design of fermentation stage in various annual production capacities estimated according to Dheskali et al. (2017).

In the DSP stage, the fermented broth is centrifuged (CF<sub>PBS-201</sub>) to remove the bacterial biomass. The biomass free broth is then fed into the activated carbon columns (V<sub>PBS-202</sub>) for decolorisation and impurity removal. The decolorized effluent is fed into cation-exchange resin columns (V<sub>PBS-203</sub>) to transform organic acid salts into their corresponding organic acids. The acidified liquid stream is then mixed with the stream that comes from the crystallizers (CR<sub>PBS-201-202</sub>) before it is concentrated using the MVR-forced circulation evaporator system (EV<sub>PBS-201</sub>). The evaporation unit consists of a preheater that heats up the broth from 37 °C to 100 °C and an MVR-forced circulation evaporator system that concentrates the broth until the SA concentration reaches 214 kg/m<sup>3</sup>. The concentrated liquid is subsequently treated via crystallisation in continuous crystallizers (CR<sub>PBS-201-202</sub>) at 4 °C. Two crystallisation stages are carried out. The wet succinic acid crystals are dried in a spray dryer (DR<sub>PBS-201</sub>), while the remaining liquid is recycled at the evaporation stage. The SA crystal purity achieved is higher than 99.5%, while the overall succinic acid recovery yield in the DSP is ca. 95% (w/w). The DSP followed in this study has been presented by Alexandri et al. (2019).

**2.1.3.2. BDO production and purification.** Bioprocess design on BDO production (Fig. S2, AREA 200, ESI) has been based on the fermentation efficiency reported by Burgard et al. (2016) using a genetically engineered *E. coli* strain. The final concentration of BDO is 125 g/L with a yield of 0.4 g/g and a productivity of 3.5 g/(L·h). A similar BDO production efficiency is also feasible in crude hydrolysates rich in C5/C6 sugars (personal communication). The bioconversion section is designed and scheduled (e.g. optimal batch duration, number of bioreactors, total volume of each bioreactor) (Table S4, ESI) according to Dheskali et al. (2017). The pH is held at 7 during fermentation, while microaerobic conditions are used (0.02 vvm). Besides BDO, the main by-products produced at the end of fermentation are 4-hydroxybutyrate (4-HB, 5.71 g/L), acetic acid (3.82 g/L),  $\gamma$ -butyrolactone (GBL, 1.32 g/L) and ethanol (0.71 g/L).

In the DSP stage, BDO is purified to 99.7% purity with recovery yield of 92%. The microbial biomass is initially removed via centrifugation (CF<sub>PBS-202</sub>). The bacterial mass free liquid stream is processed through a series of cation- (V<sub>PBS-206</sub>) and anion-exchange (V<sub>PBS-207</sub>) resin columns to remove the minerals and organic acid salts that are present in the fermentation broth. The outlet liquid stream is subsequently concentrated using a MVR-forced circulation evaporator system (EV<sub>PBS-202</sub>) up to a BDO concentration of 632.6 g/L. BDO is purified via distillation (T<sub>PBS-201</sub>) at atmospheric pressure and 180 °C in order to separate the water and GBL.

**2.1.3.3. PBS polymerization.** The unit operations and the process conditions for the polymerization of PBS (Fig. S2, AREA 300, ESI) were taken from Kamikawa et al. (2013). This process is divided into three sections, the preparation of raw materials, esterification and polymerization. BDO and SA are initially mixed in a mixing tank ( $V_{\text{PBS-301}}$ ) at a molar ratio of 1.3:1 and 80 °C using low pressure steam (LPS). The liquid outflow enters the esterification reactor ( $R_{\text{PBS-301}}$ ), after it is heated to 180 °C. The esterification reaction is carried out for 3 h at 230 °C and 1 bar. The vapor stream is distilled ( $T_{\text{PBS-301}}$ ) to recycle the unreacted BDO. Ester polymerization is a polycondensation reaction in the presence of titanium tetrabutoxide as catalyst with a concentration of 2000 ppm (with respect to succinic acid) ( $R_{\text{PBS-302}}$ ). The temperature of the reaction is 240 °C and the vacuum applied is 2 Torr. After 16.5 h, the final product from the polycondensation reactor contains PBS with molecular weight of 70,000 Da. The vapor stream of the reactor is initially cooled and compressed and then distilled ( $T_{\text{PBS-302}}$ ) so as to recover the remaining BDO. The produced PBS is cooled, pelletized (not included in this study) and stored.

The simulation is performed in Honeywell UniSim considering the following assumptions. The first assumption is related to the thermodynamic data of the ester and PBS added in the software as hypothetical components. Their properties were determined using estimation methods, namely Joback for ester (Joback and Reid, 1987) and Van Krevelen for PBS (Van Krevelen and Te Nijenhuis, 2009). Another assumption is the use of an average molecular weight for PBS based on Kamikawa et al. (2013). Finally, owing to the lack of data about the specific reaction rate of polycondensation, a stoichiometric reaction for polymerization is assumed.

#### 2.1.4. PLA production via fermentation, DSP and polymerization

**2.1.4.1. Lactic acid production process.** Literature-cited publications were initially selected reporting high LA production efficiency (i.e., yield, productivity, LA concentration) using glucose as carbon source (Table S6, ESI). Cases 3, 5, 7, 8 and 11 were rejected due to the lack of necessary data to perform the simulation. Cases 1, 5 and 11 were rejected due to the use of raw materials that resulted in high processing costs. Other cases were rejected due to the low purity of L-lactic acid (cases 4 and 6) or the neutralizing agents used (e.g. NaOH,  $\text{NH}_4\text{OH}$ ) that did not fit with the selected DSP (case 2, 5 and 11). The remaining cases 9, 10 and 12 were compared by estimating the cost of manufacture for the fermentation stage with case 10 leading to the lowest COM (\$1.46/kg). The same fermentation efficiency has been also assumed for C5/C6-rich hydrolysates as in the case of SA and BDO.

The unit operations used in the bioconversion stage (Fig. S3, AREA 200, ESI) are the same as the ones described in the cases of SA and BDO. Calcium carbonate is used during fermentation as a neutralizing agent leading to calcium lactate formation. The bioconversion section is designed and scheduled (e.g. optimal batch duration, number of bioreactors, total volume of each bioreactor) (Table S7, ESI) according to Dheskali et al. (2017). The DSP to recover pure L-lactic acid with optical purity higher than 99.4% is based on the following three stages as presented by Bapat et al. (2014). In the first stage, bacterial biomass is initially separated from the fermentation broth via centrifugation ( $\text{CF}_{\text{PLA-201}}$ ). Then, calcium lactate is treated with 50% sulfuric acid at 30 °C for 1 h ( $R_{\text{PLA-201}}$ ) to produce dilute lactic acid and solid calcium sulphate. Calcium sulphate is then separated from the product stream via centrifugation ( $\text{CF}_{\text{PLA-202}}$ ). The lactic acid concentration in the liquid stream is increased to ca. 50% (w/w) via evaporation ( $\text{EV}_{\text{PLA-201}}$ ). Inevitably, a small amount of lactic acid is evaporated, so the vapor effluent is recycled. The second stage involves the esterification of the LA-rich liquid stream with methanol (99.6%) in a CSTR ( $R_{\text{PLA-202}}$ ) to produce methyl lactate and water. The product stream of the reactor is heated to 105 °C (E-206). In the third stage, polymer grade L-lactic acid is obtained via hydrolysis of methyl lactate in a reactive distillation column ( $T_{\text{PLA-201}}$ ). Methanol and excess water outflow as

distillate followed by methanol recycling to the second stage via distillation ( $T_{\text{PLA-202}}$ ). The overall process yield of the DSP is 97.7%.

**2.1.4.2. PLA polymerization.** Process design for PLA production is based on Gruber et al. (1993). This process could be divided into three sections, prepolymer production, lactide production and PLA production.

The lactic acid from AREA 200 (Fig. S3, ESI) is fed into the prepolymer reactor ( $R_{\text{PLA-301}}$ ), where it is condensed continuously by removing water at 120 °C for 1 h. When lactic acid undergoes a condensation reaction, low molecular weight poly(lactic acid) (prepolymer) is formed. The vapor stream contains vaporized lactic acid and trace amounts of low molecular weight oligomers. A column ( $T_{\text{PLA-301}}$ ) is used to separate them from water and return them to the process.

The prepolymer stream is added into the lactide reactor ( $R_{\text{PLA-302}}$ ) with stannous octoate as catalyst where the oligomers form lactide rings, which are the cyclic dimers of lactic acid. Heat is added to vaporize the lactide which is continuously removed as vapor. The liquid outflow contains unreacted oligomers; thus, it is recycled back into the reactor. Other than lactide, the vapor stream contains unreacted lactic acid, lactic acid oligomers and water. The purification of lactide takes place in a series of two distillation columns ( $T_{\text{PLA-302-303}}$ ) under vacuum. In the first column, water is removed from the lactide stream, while the second column separates the residual lactic acid. It should be noted that the overhead product of all three distillation columns contains a significant amount of lactic acid, thus it is collected and recycled back to the lactic acid recovery stage.

The purified lactide stream is mixed with catalyst (stannous octoate) and fed into the polymerization reactor ( $R_{\text{PLA-303}}$ ) where high molecular weight PLA is produced via ring-opening polymerization of lactide. The resulting product stream contains a substantial amount of unreacted lactide. The residual lactide is removed under vacuum in a devolatilizer ( $\text{DV}_{\text{PLA-301}}$ ) and recycled back to the reactor. The refined PLA stream is pelletized (not included in this study) and stored.

In order to calculate the mass and energy balances of the PLA production process, several simplifications were implemented due to the lack of crucial data and the complexity of the unit operations employed. The simulation was performed in Honeywell UniSim that has limited capability regarding polymerization reactions. The first challenge was the nature of polymerization reactions. To be more specific, it is known that the products of polymerization reactions are diverse and only an average molecular weight can be estimated. The first reaction was the prepolymerization of lactic acid to oligomers. This reaction belongs to the category of step growth polymerization and it is known that the prepolymers reach an average degree of polymerization (DP) of 7–20. A total reaction was assumed yielding a prepolymer with a DP of 10. The second reaction was the production of lactide. Lactide is formed by backbiting and end biting reactions. The first type yields lactide and lactic acid oligomers, while the second type yields lactide and water. Owing to the lack of data about the oligomer in the backbiting reaction, it was assumed that lactide is formed mainly from the end biting reaction. Furthermore, it is known that lactide exists in three stereoisomeric forms L, D and *meso*. Due to the high optical purity of the produced lactic acid (higher than 97% L-isomer content), it is safe to assume that D-lactide will exist in a negligible amount and the final product will contain only L- and *meso*-isomers. Unfortunately, there are insufficient data about the exact ratio of the two isomers and this is usually a complex parameter to control. For the preliminary design of the process, *meso* content was also considered negligible. Finally, for the ring opening polymerization, which is a form of chain-growth polymerization, the final polymer molecular weight was considered to be around 55,000 Da. Another obstacle was the lack of essential information about reaction rates as well as thermodynamic and general data about the intermediate products that had to be inserted as hypothetical components in the simulation.

## 2.2. Stage 2 – Preliminary techno-economic evaluation

### 2.2.1. Estimation of total capital investment

Process design data were used for the estimation of fixed capital investment (FCI). Equipment sizing was based on established methodologies (Clark and Blanch, 1997; Peters et al., 2003; Turton et al., 2018; Ulrich and Vasudevan, 2004), while the estimation of free-on-board purchased equipment costs (Ce<sub>q.fob</sub>) was based on established textbooks and literature-cited reports (Couper et al., 2012; Dheshkali et al., 2017; Humbird et al., 2011; Peters et al., 2003). Tables S1, S5 and S8 present the characteristic size and the Ce<sub>q.fob</sub> related to the stages of pectin extraction, PBS production and PLA production, respectively, while the cost of corn stover pretreatment and SBP pretreatment after pectins' extraction has been estimated based on the techno-economic results presented by Humbird et al. (2011). The FCI has been estimated by multiplying the sum of all Ce<sub>q.fob</sub> with 5 (Dheshkali et al., 2017). The working capital (WC) has been estimated as 5% of the FCI as recommended by Humbird et al. (2011). The total capital investment is the sum of FCI and WC.

### 2.2.2. Estimation of cost of manufacture (COM)

The equation proposed by Turton et al. (2018) has been used for the estimation of COM.

$$\text{COM} = 0.18 \times \text{FCI} + 2.73 \times C_{\text{OL}} + 1.23 \times (C_{\text{UT}} + C_{\text{RM}})$$

where  $C_{\text{OL}}$ ,  $C_{\text{UT}}$ , and  $C_{\text{RM}}$  stand for the cost of operating labour, utilities and raw materials, respectively.

The unitary cost of utilities, supplied by off-sites, has been taken from Turton et al. (2018) (Table S9, ESI), while  $C_{\text{UT}}$  is estimated by multiplying the unitary costs with the utility requirements presented in Tables S1, S5 and S8. The unitary cost of raw materials (Table S10, ESI) has been divided into the cost of the main renewable resources used as feedstocks and the cost of miscellaneous materials used in plant operation.  $C_{\text{RM}}$  is estimated by multiplying the unitary raw material costs with the mass balances of each case, presented in the developed inventories (Tables S15–S20). The methodology reported by Ulrich and Vasudevan (2004) has been employed to estimate the operating labour cost considering the number of workers per shift ( $N_{\text{OL}}$ ) necessary to operate each plant (Table S11, ESI), the total number of workers required in the industrial plant based on the annual plant operation, the working time of each worker and the average labour cost.

### 2.2.3. Economic analysis and TEA indicators

The IRS-MACRS methodology (Internal Revenue Service) has been employed for the calculation of depreciation. Discounted cash flow (DCF) analysis has been carried out for the estimation of the Minimum Selling Price (MSP) in all alternative processing scenarios using the parameters presented in Table S12 (ESI) (Kookos, 2018; Koutinas et al., 2016). The MSP per kg product is estimated by determining the market price of the product where the Net Present Value is zero at the end of plant life time.

The TEA indicators used in this study were FCI, COM, MSP, Optimum Plant Capacity (OPC) leading to minimum COM, Minimum Feedstock Requirements (MFR) and Discounted Payback Period (DPP). The selection of these indicators was based on their wide utilization in TEA of bioprocesses and biopolymer production studies (Ioannidou et al., 2020; Briassoulis et al., 2020). The OPC defines the capacity at which the COM or MSP reach a plateau and thereafter remain constant. The MFR represents the amount of feedstock required to satisfy the OPC. The DPP is the time required, after the initiation of plant operation, to recover the capital investment. Table S13 presents an example of the summary of the individual costs of each stage (feedstock pretreatment, monomer production and polymerization) for the production of PBS and PLA in the OPC. These costs have been estimated at different plant

capacities for both biopolymers in order to perform the DCF analysis and estimate the proposed indicators.

## 2.3. Stage 3 - Life cycle assessment

LCA was performed according to the stages outlined in the ISO 14040 and 14044 standards (ISO, 2006). This framework includes four discrete phases: the goal and scope definition, the inventory analysis, the impact assessment and the interpretation of results.

### 2.3.1. Goal and scope

The aim of the LCA is to assess the environmental performance of PBS and PLA production using corn-derived glucose syrup, corn stover and SBP. A “cradle-to-gate” LCA approach has been followed for PBS and PLA production considering 1 kg of final product as functional unit. The system boundaries for the LCA include the cultivation, pretreatment and fractionation of feedstocks, fermentation and purification stages, and polymerization for biopolymer production.

### 2.3.2. Life cycle inventory (LCI)

Material and energy related data for agricultural cultivation of corn grain, stover and sugar beet are presented in Table S14 (ESI). On-field emissions from corn and sugar beet cultivation, due to the application of agrochemicals and field management, were estimated using various literature-cited methods. In particular,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  (Nemecek et al., 2014),  $\text{NH}_3$ ,  $\text{NO}_2$  (EEA, 2013) and pesticides (European Commission, 2018) were considered to account for air emissions.  $\text{NO}_3^-$  and P leaching, P runoff (Emmenegger et al., 2009), pesticides (European Commission, 2018) and heavy metals (Durlinger et al., 2017) were considered to account for emissions to waterbodies. Heavy metals (Durlinger et al., 2017) and pesticides (European Commission, 2018) were considered in relation to soil emissions.

Process design was employed to generate mass and energy inputs and outputs (inventories) for all processes presented in Section 2.1. Tables S15–S17 and Tables S18–S20 present the PBS and PLA production inventories from the three different feedstocks, respectively.

**2.3.2.1. Cultivation of corn grain and stover.** This process was adapted from the AgriFootprint® LCA database (Durlinger et al., 2017). The corn cultivation process is a conventional agricultural system that makes use of both chemical and organic fertilizers, in addition to pesticides and soil additives, such as lime and sulphur. It has been assumed that corn is cultivated in France with an annual yield of 9.3 t/ha. France was chosen due to the high availability in corn stover (Wietschel et al., 2019). It was assumed that only 30% (2.79 t/ha) of the corn stover is harvested and baled each year. Stover is an important soil conditioner and agent against soil erosion. Therefore, care must be taken to not compromise the quality of the soil (Murphy and Kendall, 2013). The baling process is included in the system boundaries. As this process delivers two products (corn grain and stover), economic allocation was chosen to assign the environmental burdens for each product. Corn grain and stover market prices were taken as \$174.5/t (FAO, 2018) and \$58.5/t (Humbird et al., 2011).

**2.3.2.2. Corn grain refining and starch hydrolysis.** Inventory data for corn grain processing has been taken from Renouf et al. (2008). The wet milling process is employed involving enzymatic starch hydrolysis. Impurities are initially removed from the corn grains. The wet milling process separates the germ from the kernel and the starch from the gluten, leading to the production of various co-products such as corn oil, corn gluten feed and corn gluten meal (Ramirez et al., 2008). Enzymatic hydrolysis converts the starch into glucose at 95% conversion yield. As this process generates many co-products, economic allocation was applied to allocate the environmental impacts of each product. The market prices for glucose syrup, corn oil, gluten feed and gluten meal were considered

as \$230/t, \$624/t, \$123/t and \$518/t, respectively (United States Department of Agriculture and Economic Research Service, 2018).

**2.3.2.3. Cultivation of sugar beet.** The sugar beet cultivation process was adapted from Muñoz et al. (2014). The farming stage is a conventional agricultural system that makes use of chemical fertilizers, pesticides and the soil additive lime. It is considered that sugar beet is cultivated in France with an annual yield of 84 t/ha. France was chosen because it is one of the main producers of sugar beet in Europe (Eurostat, 2019). During the harvesting process, the leaves are separated from the beet. In this study, it was assumed that 100% of the beet leaves are left in the field for soil conditioning. Therefore, no allocation is necessary in this process, as it only delivers sugar beet as a product. The harvested sugar beet goes to a sugar processing plant.

**2.3.2.4. Sugar beet pulp production.** Inventory data concerning the production of SBP was adapted from Renouf et al. (2008). The beet root is washed to remove impurities (e.g. sand and stones) and subsequently cut into small “cosettes” that are diluted in hot water in a process called diffusion. SBP is the by-product of the diffusion process. The raw juice goes through a purification process with the addition of lime and carbon dioxide to remove impurities from the beet juice, producing lime fertilizer as a by-product. In a traditional sugar mill, the purified raw juice undergoes a crystallisation process that produces sucrose and molasses as by-product. However, this process does not consider the recovery of molasses. The SBP by-product is mainly used as animal feed in the form of dry pellets. However, industrial fermentation processes may rely on wet beet pulp that has a very low market value. The market prices considered in this study for the economic allocation were \$370/t (United States Department of Agriculture and Economic Research Service, 2018), \$116/t (Durlinger et al., 2017) and \$5/t (www.thebeefsite.com) for sugar beet juice, lime fertilizer and wet SBP, respectively. The market price of beet juice was considered the same as sucrose (Tomaszewska et al., 2018).

### 2.3.3. Life cycle impact assessment

LCA was carried out using two different methodologies, CML 2001 (Jan. 2016) and ReCiPe 1.08 (Guinée et al., 2002). The CML methodology was used as the most cited methodology for environmental assessment (Ioannidou et al., 2020) to compare the environmental impact of PBS and PLA production estimated in this study using the three feedstocks with literature-cited data. The LCA software GaBi was employed for the estimation of the environmental indicators Global Warming Potential (GWP 100 years), Abiotic Depletion (ADP fossil), Acidification Potential (AP), Eutrophication Potential (EP) and Human Toxicity Potential (HTP).

The ReCiPe methodology was employed for the estimation of environmental externality costs because this method is used in the LCC methodology reported by De Bruyn et al. (2018) (see next section). The system boundaries, the functional unit and the assumptions are the same to those considered in the CML methodology.

### 2.4. Stage 4 – Life cycle costing

LCC was based on the ReCiPe Mid/Endpoint method, version 1.08 (December 2012) methodology (Goedkoop et al., 2013) involving the estimation of twelve different environmental categories followed by their conversion into monetized environmental externalities. The external costs are estimated considering an economic parameter representing the accounting price per unit of impact and a physical parameter representing the unit of the impact. The principal stages for the implementation of the methodology are described by Bickel and Friedrich (2005). The monetization of the estimated impacts is based on the environmental prices reported by De Bruyn et al. (2018) for EU28 countries using a dollar to euro exchange rate of 0.856 (Table S21, ESI).

### 2.5. Stage 5 – Sensitivity analysis

Sensitivity analysis has been carried out in each case study to assess the sensitivity to process (e.g. conversion yields in feedstock pretreatment/fractionation, hydrolysis, fermentation and chemical conversions) and economic (e.g. utility costs, market prices) parameters. A single-point sensitivity was initially carried out using MATLAB by changing one variable at a time with case-specific limits (i.e. reasonable minima and maxima that were selected for each variable). Subsequently, Monte Carlo sensitivity analysis was carried out on the most important variables to compute the cumulative probability function of the Net Present Value (NPV) of a specific process using the methodology of Khazen and Dubi (1999). A Monte Carlo simulation is a model used to predict the probability of different outcomes which are affected by distinct parameters. It is one of the well-developed stochastic approaches to quantify risk/uncertainty in economic assessments, by investigating the ranges and probability distributions of values for economic performance (Mandegari et al., 2018; Pavan et al., 2019). Uniform distribution was assumed for the conversion yield and power consumption for bioreactor agitation, while exponential distribution was assumed for fermentation duration. Each model is iterated 10 million times by changing in each iteration the combination of the selected parameters.

## 3. Results and discussion

### 3.1. Stage 2 - Preliminary techno-economic evaluation

#### 3.1.1. Fixed capital investment

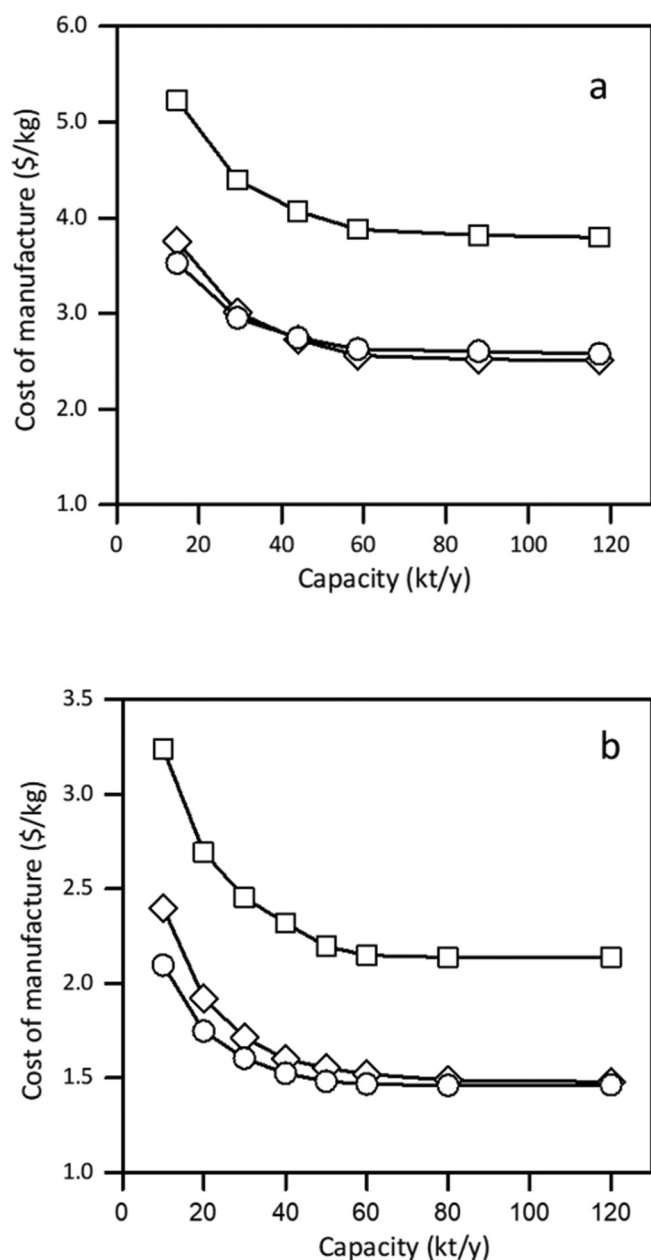
The stages of feedstock pretreatment (including pectin extraction in the case of SBP), fermentation, DSP and polymerization have been included in the estimation of FCI per kg PBS or PLA at different plant capacities (10–120 kt/y) (Fig. S4a and S4b, ESI). Different plant capacities were evaluated to identify the one where a constant value of FCI per kg is reached (58.63 kt/year for PBS and 50 kt/year for PLA). The lowest FCI per kg is estimated in the case of glucose, while the highest FCI per kg is estimated when SBP is employed. The estimation of equipment size, purchase equipment cost and FCI for the OPC for either PBS or PLA production are presented in Tables S1, S5, S8 and S13 (ESI).

#### 3.1.2. Cost of manufacture

Fig. 1a and b present the COM for all case studies at various plant production capacities (10–120 kt/y). When SBP is employed, the highest COM is estimated due to the incorporation of pectin extraction. In the case of glucose and corn stover, the calculated COM is similar for either PLA or PBS. For example, in the case of PBS, the estimated COM is \$2.63/kg for glucose and \$2.56/kg for corn stover at 58.63 kt annual PBS production capacity (Fig. 1a).

#### 3.1.3. Minimum selling price

The MSP for PBS or PLA at various plant capacities is presented in Fig. 2a and b. For comparison purposes, the market prices for PBS and PLA were considered as \$4/kg<sub>PBS</sub> and \$2.22/kg<sub>PLA</sub> (E4tech et al., 2015). Although further processing of the crude pectin extract may be needed, depending on the final market application, no further processing has been considered. The selling prices of the crude pectin extract were assumed at \$3/kg in the case of PLA production and \$4/kg in the case of PBS production. These market prices are significantly lower than the current pectin market prices for conventional food applications, such as low methoxy pectin (\$11–12/kg) (Ciriminna et al., 2016). The production cost of orange peel derived pectin is \$3.76/kg (Dávila et al., 2015). Thus, conservative market prices (\$3–4/kg) have been assumed in this study that are lower than pectin market prices for conventional food applications. Future studies should evaluate further processing requirements of crude pectin extracts for the production of marketable products.

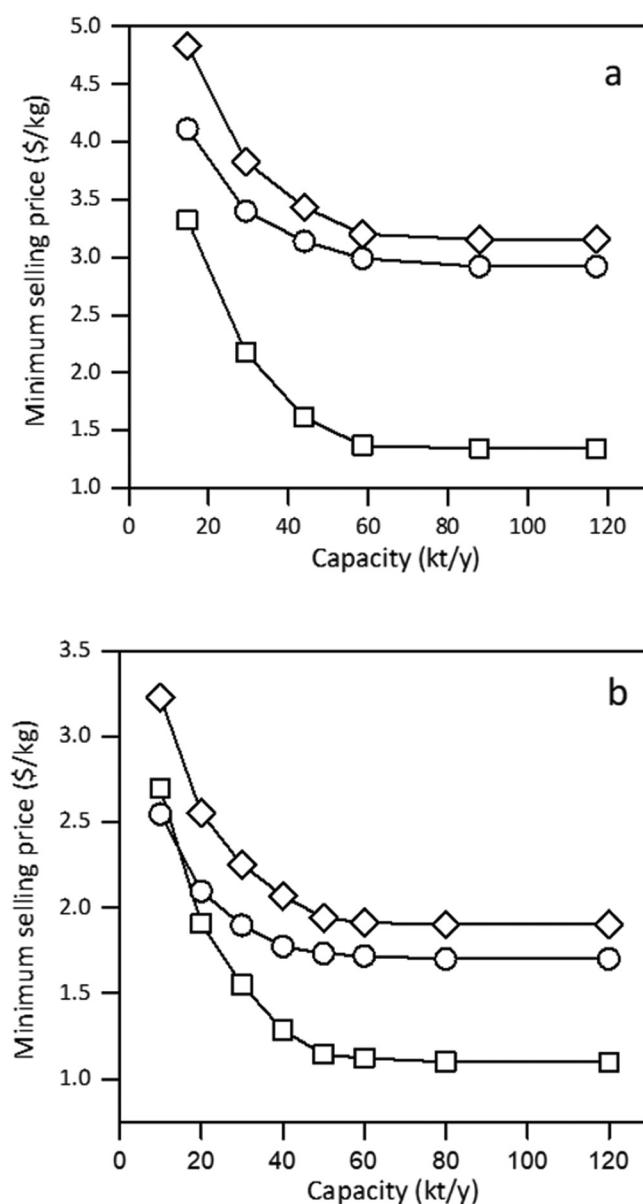


**Fig. 1.** Cost of manufacture for PBS (a) and PLA (b) as a function of annual production capacity using glucose syrup (o), corn stover (◇) and SBP (□) as feedstocks.

When SBP was used, the revenue from crude pectin extract sales as co-product is also considered leading to lower MSP than glucose syrup and corn stover for both biopolymers (Fig. 2a and b). More specifically, the MSP of PBS and PLA production from SBP is 54.3% and 33.8% lower than the respective MSP values estimated in glucose-based processes at the plant capacity where the lowest MSP is reached. At a crude pectin extract market price of \$4/kg<sub>pectin</sub>, the MSP<sub>PBS</sub> is lower than the current market price of PBS (\$4.0/kg<sub>PBS</sub>) at all production capacities evaluated (Fig. 2a). When a crude pectin extract market price of \$3/kg<sub>pectin</sub> was considered, the MSP<sub>PBS</sub> calculated in this study is higher than the current market price of PBS (data not shown). At a crude pectin extract market price of \$3/kg, the MSP<sub>PLA</sub> was lower than the current market price of PLA (\$2.22/kg) at all plant capacities evaluated (Fig. 2b).

### 3.1.4. TEA indicators at the optimum plant capacity

Table 1 presents OPC, COM, MSP, DPP and MFR values for all case studies. The lowest MSP and DPP values were estimated when SBP



**Fig. 2.** Minimum selling price for PBS (a) and PLA (b) as a function of annual production capacity using glucose syrup (o), corn stover (◇) and SBP (□) as feedstocks. In the case of SBP, crude pectin extract market prices of \$4/kg and \$3/kg have been considered for PBS and PLA, respectively.

was used for either PBS or PLA production. The lowest MSP values of PBS (\$1.37/kg) and PLA (\$1.14/kg) production from SBP are lower than the market prices of GPPS (\$1.72/kg) and BOPP (\$1.4/kg) (taken

**Table 1**

TEA indicators for PBS and PLA production at the optimum plant capacity considering pectin-rich extract market prices of \$4/kg in the case of PBS and \$3/kg in the case of PLA. A 70% water content has been assumed for SBP.

	OPC (kt/year)	COM (\$/kg)	MSP (\$/kg)	DPP (year)	MFR (kt/year)
PBS					
Glucose	58.63	2.63	2.99	7	151.28
Corn stover	58.53	2.56	3.20	9	314.67
Sugar beet pulp	58.63	3.88	1.37	6	865.18
PLA					
Glucose	50.00	1.48	1.73	7	64.84
Corn stover	50.00	1.55	1.94	12	134.88
Sugar beet pulp	50.00	2.20	1.14	6	370.85

from [www.alibaba.com](http://www.alibaba.com)), while the lowest MSP values estimated when glucose syrup and corn stover were used are higher than the market prices of GPPS and BOPP. The MFR can be associated with the availability of SBP or corn stover in different geographic regions. The MFR presented in Table 1 in the case of SBP utilization for PBS (0.86 million t) and PLA (0.37 million t) production corresponds to wet SBP with 70% water content, indicating that drying and pelletisation have not been considered. Based on FAOSTAT data for 2018, France, Germany and Poland produced annually 2.34 million t, 1.55 million t and 0.85 million t of SBP pellets with 7% moisture content (FAO, 2018). If the MFR presented in Table 1 is expressed as dried SBP pellets with 7% moisture content, then the MFR for SBP would be 0.28 million t for PBS and 0.12 million t for PLA production. Therefore, the utilization of PBS for PBS and PLA production is feasible in these three countries as the required SBP quantities are available.

France, Romania and Hungary are the main countries producing corn in EU-28. The ratio of corn stover to corn grain production is 1 kg/kg (Murphy and Kendall, 2013). However, around 0.3 kg corn stover per kg corn grain is assumed to be available for biopolymer production in order to use the remaining corn stover in the agricultural field to minimize soil erosion. Thus, the corn stover that is available annually for biopolymer production is 3.8 million t, 5.6 million t and 2.4 million t in France, Romania and Hungary, respectively (FAO, 2018). Table 1 shows that the MFR for corn stover is 0.314 million t for PBS and 0.134 million t for PLA production. These quantities are also available in the specific three countries.

### 3.2. Stage 3 - Life cycle assessment

Fig. 3 presents the LCA indicators (GWP 100 years, ADP fossil, AP, EP and HTP) for PBS and PLA production using the three feedstocks. These indicators were estimated by the CML 2001 (Jan. 2016) methodology using the GaBi software. In the case of corn stover, combustion of lignin for energy production has been considered. The environmental performance of GPPS and BOPP has been also presented as the fossil counterparts of PBS and PLA, respectively.

#### 3.2.1. Environmental performance of PBS production

The greenhouse gas (GHG) emissions of PBS production from glucose syrup, corn stover and SBP are  $-0.24$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>,  $0.25$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub> and  $2.35$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>, respectively. The GHG emissions of the bioprocess producing PBS is  $2.31$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub> considering only fermentation, DSP and polymerization stages, excluding the impact of the raw material. The negative environmental impact of GWP in the case of glucose syrup occurs because the biogenic CO<sub>2</sub> of corn cultivation ( $-2.55$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>) is taken into consideration. The same assumption has also been considered for corn stover as agricultural residue of corn cultivation. However, the pretreatment of corn stover and the lower economic allocation owing to the lower price of corn stover than corn grain, increases the environmental impact to  $1.54$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>. The combustion of lignin for energy generation plays a vital role in the final impact, as the lower consumption of utilities in the bioprocess decreases the final impact to  $0.25$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>. SBP has the highest environmental impact among the three feedstocks. Biogenic CO<sub>2</sub> is also taken into account due to sugar beet cultivation. However, the high utility requirements in SBP pre-treatment contributes to a high environmental impact of the whole process ( $2.35$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>). It should be stressed though that allocation of GHG emissions and other environmental impacts to pectin should be carried out when marketable products are developed.

Patel et al. (2018) reported a GWP of approximately  $2.2$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub> for PBS production from corn grain, while a GWP of approximately  $0.77$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub> was reported when corn stover was used (without considering the conversion of PBS into a specific end-product in both cases). The results reported by Patel et al. (2018) have been estimated

without taking into account the biogenic CO<sub>2</sub> associated with corn cultivation. If the results of this study are expressed without taking into consideration biogenic CO<sub>2</sub> from corn cultivation, the GHG emissions are  $2.31$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>, which is similar to the value reported by Patel et al. (2018) for PBS production from corn grain. Tecchio et al. (2016) reported that GHG emissions of PBS production range from  $4.17$  to  $6.34$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>. The reported environmental impacts are higher than the results estimated in this study. The difference is mainly attributed to the fact that the PBS considered by Tecchio et al. (2016) is partly bio-based, i.e. it is obtained only from bio-based succinic acid while the BDO is produced from fossil resources. The GWP of the bio-based PBS produced from the three feedstocks is lower than its petroleum-based counterpart GPPS ( $2.78$  kg CO<sub>2</sub>-eq/kg<sub>GPPS</sub> according to PlasticsEurope). Moreover, the GWP of the fossil-derived PBS ( $6.6$  kg CO<sub>2</sub>-eq/kg<sub>PBS</sub>) is significantly higher than the bio-based PBS (Moussa et al., 2012).

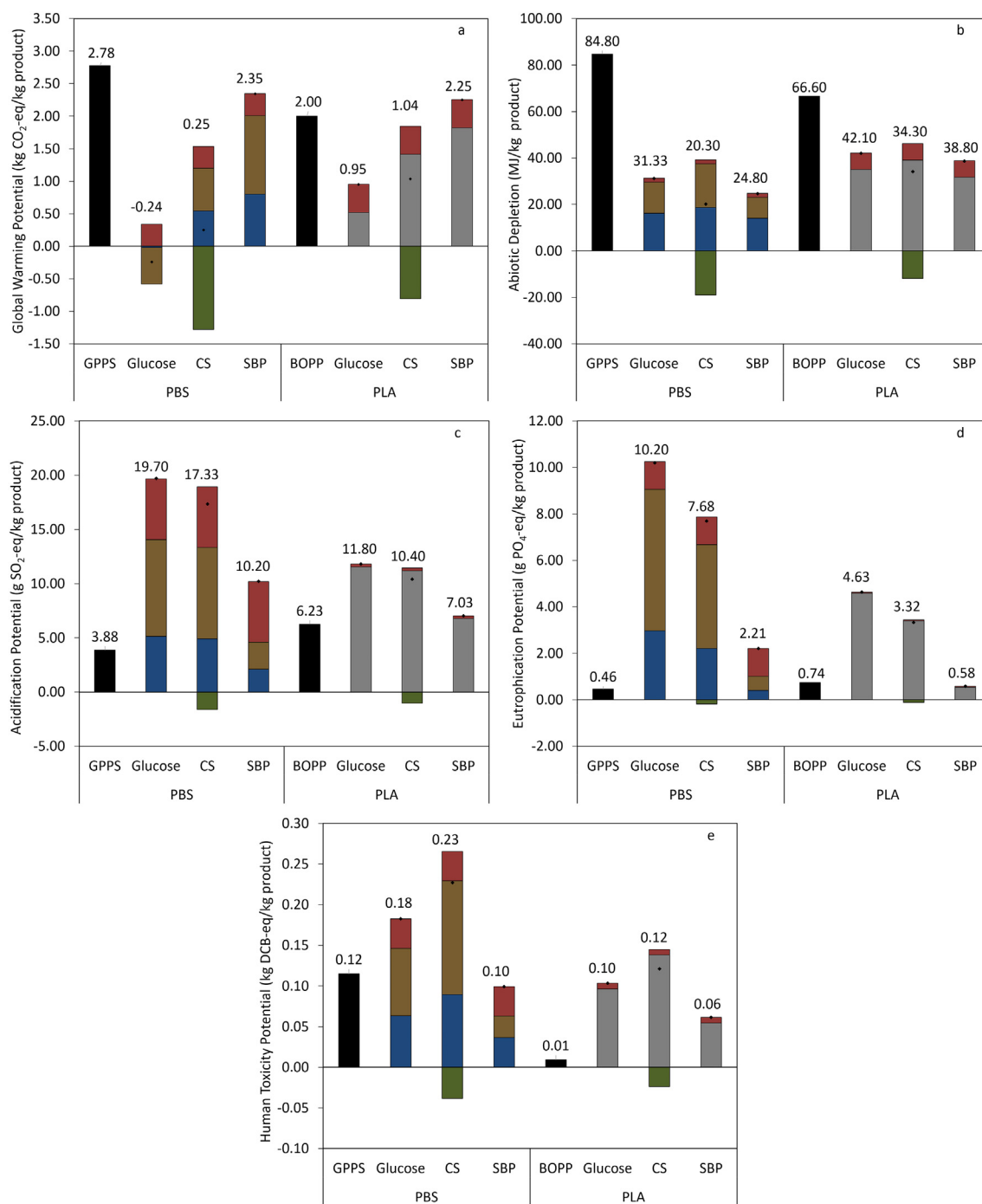
The ADP fossil varies between  $20.3$  and  $31.33$  MJ/kg<sub>PBS</sub> (Fig. 3b). The fossil-energy requirements of the PBS production process are  $15.8$  MJ/kg<sub>PBS</sub>. The lowest ADP fossil occurs when corn stover is employed, as lignin combustion reduces fossil-energy requirements. The ADP fossil of GPPS is  $84.80$  MJ/kg<sub>GPPS</sub> (PlasticsEurope), 2.7-fold higher than the ADP fossil of PBS production from glucose syrup. Patel et al. (2018) reported ADP fossil values for PBS production of  $75$  MJ/kg<sub>PBS</sub> for corn grain and  $50$  MJ/kg<sub>PBS</sub> for corn stover. Tecchio et al. (2016) reported an ADP fossil value for PBS production of  $140$  MJ/kg<sub>PBS</sub>, a value equal to the fossil-based PBS (Moussa et al., 2012).

AP (Fig. 3c) corresponds to  $19.7$  g SO<sub>2</sub>-eq/kg<sub>PBS</sub>,  $17.33$  g SO<sub>2</sub>-eq/kg<sub>PBS</sub> and  $10.2$  g SO<sub>2</sub>-eq/kg<sub>PBS</sub> for glucose syrup, CS and SBP, respectively. EP (Fig. 3d) corresponds to  $10.2$  g PO<sub>4</sub>-eq/kg<sub>PBS</sub>,  $7.68$  g PO<sub>4</sub>-eq/kg<sub>PBS</sub> and  $2.21$  g PO<sub>4</sub>-eq/kg<sub>PBS</sub> for glucose, CS and SBP, respectively. PBS production from glucose syrup exhibits the worst AP and EP performance. The AP and EP values of GPPS are  $3.88$  g SO<sub>2</sub>-eq/kg<sub>GPPS</sub> and  $0.46$  g PO<sub>4</sub>-eq/kg<sub>GPPS</sub>, which are significantly lower than PBS production. The cultivation of the agricultural crops has a significant contribution in these two impact categories and therefore the AP and EP values of the fossil-based polymer are lower. HTP (Fig. 3e) corresponds to  $0.18$  kg DCB eq./kg<sub>PBS</sub>,  $0.23$  kg DCB eq./kg<sub>PBS</sub> and  $0.10$  kg DCB eq./kg<sub>PBS</sub> for glucose syrup, CS and SBP, respectively. The HTP of GPPS is  $0.12$  kg DCB eq./kg<sub>GPPS</sub>. SBP presents the lowest HTP value among the three feedstocks and GPPS, as sugar beet depicts better environmental performance than corn. It should be mentioned that to the best of our knowledge, there are no literature-cited data on AP, EP and HPT for bio-based PBS production.

#### 3.2.2. Environmental performance of PLA production

The GWP of PLA production is estimated at  $0.95$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub>,  $1.04$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub> and  $2.25$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub> for glucose, corn stover and SBP, respectively (Fig. 3a). The GHG emissions of the bioprocess producing PLA is  $2.23$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub> considering only fermentation, DSP and polymerization stages, excluding the impact of the raw material. The lowest GWP occurs when glucose syrup is used because the biogenic CO<sub>2</sub> of corn cultivation ( $-1.28$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub>) is taken into consideration. Corn stover presents the second best GWP performance considering both the CO<sub>2</sub> uptake from corn cultivation ( $-0.39$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub>) and the utility savings due to lignin combustion ( $-0.8$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub>). Higher GWP for PLA production ( $1.5$  and  $1.9$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub>) has been reported using corn-derived glucose (Gironi and Piemonte, 2011; Vink et al., 2003). When corn stover is used as feedstock combined with utilization of wind power, the GHG emissions are reduced to  $-1.7$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub> (Vink et al., 2003). NatureWorks reported that the GWP of Ingeo PLA production is  $0.62$  kg CO<sub>2</sub>-eq/kg<sub>PLA</sub> (Vink and Davies, 2015) having taken into account the biogenic CO<sub>2</sub> from corn cultivation, result that is lower than the GWP value estimated in this study. The GWP of PLA production from glucose and corn stover is lower than its fossil counterpart BOPP ( $2$  kg CO<sub>2</sub>-eq/kg<sub>BOPP</sub> according to PlasticsEurope). In the case of SBP, the GWP is slightly





**Fig. 3.** LCA for PBS and PLA production from glucose, corn stover and SBP. The environmental impacts of their fossil counterparts are also presented. Bars have been color-coded based on the contribution of each production stage: diamond – net total impact, black – fossil-based counterpart, blue – succinic acid, brown – BDO, grey – lactic acid, red – polymerization, green – savings from lignin combustion. Monomer production includes the environmental impacts of pretreatment, fermentation and DSP stages. Labels indicate the net total impact of each process.

higher than BOPP due to the high utility requirements during the pretreatment stage.

The ADP fossil of PLA production was estimated at 42.1 MJ/kg<sub>PLA</sub>, 34.3 MJ/kg<sub>PLA</sub> and 38.8 MJ/kg<sub>PLA</sub> for glucose, corn stover and SBP, respectively (Fig. 3b). The lowest ADP fossil impact occurs when corn stover is employed as lignin combustion contributes 11.81 MJ/kg<sub>PLA</sub>. The ADP fossil of the conventional polymer is 66.6 MJ/kg<sub>BOPP</sub> (PlasticsEurope), 1.6-fold higher than the ADP fossil of PLA production from glucose syrup. Vink et al. (2003) reported 54.1 MJ/kg<sub>PLA</sub>, while Gironi and Piemonte (2011) estimated 53.7 MJ/kg<sub>PLA</sub>. NatureWorks reported 33.5 MJ/kg<sub>PLA</sub> for Ingeo PLA (Vink and

Davies, 2015). The ADP fossil estimated in this study is within the range of literature-cited values.

AP (Fig. 3c) corresponds to 11.8 g SO<sub>2</sub>-eq/kg<sub>PLA</sub>, 10.4 g SO<sub>2</sub>-eq/kg<sub>PLA</sub> and 7.03 g SO<sub>2</sub>-eq/kg<sub>PLA</sub> for glucose syrup, corn stover and SBP, respectively. The EP (Fig. 3d) corresponds to 4.63 g PO<sub>4</sub>-eq/kg<sub>PLA</sub>, 3.32 g PO<sub>4</sub>-eq/kg<sub>PLA</sub> and 0.58 g PO<sub>4</sub>-eq/kg<sub>PLA</sub> for glucose syrup, corn stover and SBP, respectively. PLA production from glucose exhibits higher AP and EP values than the other two feedstocks. Ingeo PLA production resulted in 7.26 g SO<sub>2</sub>-eq/kg<sub>PLA</sub> for AP and 1.44 g PO<sub>4</sub>-eq/kg<sub>PLA</sub> when corn-derived glucose is used (Vink and Davies, 2015). BOPP production corresponds to 6.23 g SO<sub>2</sub>-eq/kg<sub>BOPP</sub> and 0.74 g PO<sub>4</sub>-eq/kg<sub>BOPP</sub>, which are

**Table 2**  
Cost of externalities expressed as \$/kg for GPPS and PBS production from glucose syrup, corn stover and SBP.

Impact category	GPPS	PBS (glucose)	PBS (CS)	PBS (SBP)
Climate change	0.184	-0.015	0.050	0.155
Freshwater ecotoxicity	$2.51 \times 10^{-5}$	$2.41 \times 10^{-4}$	$1.61 \times 10^{-4}$	$3.08 \times 10^{-5}$
Freshwater eutrophication	$6.54 \times 10^{-6}$	$1.56 \times 10^{-4}$	$-9.99 \times 10^{-6}$	$1.51 \times 10^{-4}$
Human toxicity	0.008	0.019	0.014	0.012
Ionising radiation	0.005	0.018	0.020	0.021
Marine ecotoxicity	$1.04 \times 10^{-5}$	$2.23 \times 10^{-5}$	$1.52 \times 10^{-5}$	$6.39 \times 10^{-6}$
Marine eutrophication	0.001	0.056	0.033	0.009
Ozone depletion	$1.93 \times 10^{-13}$	$3.06 \times 10^{-12}$	$2.49 \times 10^{-8}$	$1.56 \times 10^{-8}$
Particulate matter formation	0.060	0.194	0.118	0.097
Photochemical oxidant formation	0.041	0.013	0.008	0.008
Terrestrial acidification	0.024	0.099	0.058	0.042
Terrestrial ecotoxicity	$1.30 \times 10^{-4}$	0.079	0.055	0.003
Total	0.322	0.463	0.356	0.346

lower than the values estimated in this study and those reported for Ingeo PLA production. As in the PBS case study, the crop cultivation stage contributes a high impact to AP and EP. However, the EP of PLA production from SBP is 0.58 g PO<sub>4</sub>-eq/kg<sub>PLA</sub>, which is 27% lower than the BOPP performance due to the low economic allocation employed.

HTP (Fig. 3e) corresponds to 0.1 kg DCB eq./kg<sub>PLA</sub>, 0.12 kg DCB eq./kg<sub>PLA</sub> and 0.06 kg DCB eq./kg<sub>PLA</sub> for glucose syrup, corn stover and SBP, respectively. The HTP of BOPP is 0.01 kg DCB eq./kg<sub>BOPP</sub>. SBP illustrates the lowest HTP among the three feedstocks, but the HTP of PLA production is higher than BOPP for all three feedstocks. The HTP of Ingeo PLA production (0.08 kg DCB eq./kg<sub>PLA</sub>) is close to the one estimated in this study (Vink and Davies, 2015).

### 3.3. Stage 4 – Life cycle costing

Based on the LCC methodology of De Bruyn et al. (2018), the ReCiPe 1.08 methodology was used for the estimation of environmental assessment indicators (Tables S22 and S23) that were subsequently converted into monetized values (Tables 2 and 3) (Goedkoop et al., 2013). The total cost of externalities for GPPS is lower than the cost of externalities for PBS production from all three feedstocks. The indicators that predominantly contribute to the cost of externalities for GPPS are climate change, particulate matter formation, photochemical oxidant formation and terrestrial acidification. In the case of PBS, the most influential indicators are climate change (mainly when SBP is used), particulate matter formation, terrestrial acidification and terrestrial ecotoxicity. Among

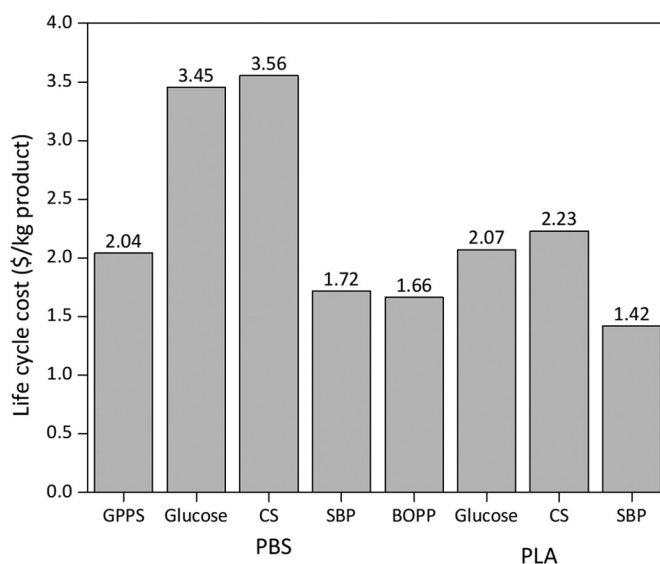
**Table 3**  
Cost of externalities expressed as \$/kg for BOPP and PLA production from glucose, corn stover and SBP.

Impact category	BOPP	PLA (glucose)	PLA (CS)	PLA (SBP)
Climate change	0.130	0.063	0.094	0.148
Freshwater ecotoxicity	$9.06 \times 10^{-8}$	$1.19 \times 10^{-4}$	$7.91 \times 10^{-5}$	$1.29 \times 10^{-5}$
Freshwater eutrophication	$2.10 \times 10^{-4}$	$1.03 \times 10^{-5}$	$-6.46 \times 10^{-5}$	$7.78 \times 10^{-6}$
Human toxicity	0.0	0.008	0.006	0.005
Ionising radiation	0.0	0.009	0.009	0.011
Marine ecotoxicity	$2.61 \times 10^{-8}$	$1.13 \times 10^{-5}$	$7.95 \times 10^{-6}$	$3.30 \times 10^{-6}$
Marine eutrophication	0.001	0.025	0.015	0.002
Ozone depletion	0.0	$1.5 \times 10^{-12}$	$1.25 \times 10^{-8}$	$7.84 \times 10^{-9}$
Particulate matter formation	0.095	0.123	0.089	0.074
Photochemical oxidant formation	0.005	0.007	0.004	0.004
Terrestrial acidification	0.033	0.064	0.046	0.035
Terrestrial ecotoxicity	$1.87 \times 10^{-6}$	0.040	0.028	0.002
Total	0.264	0.339	0.290	0.281

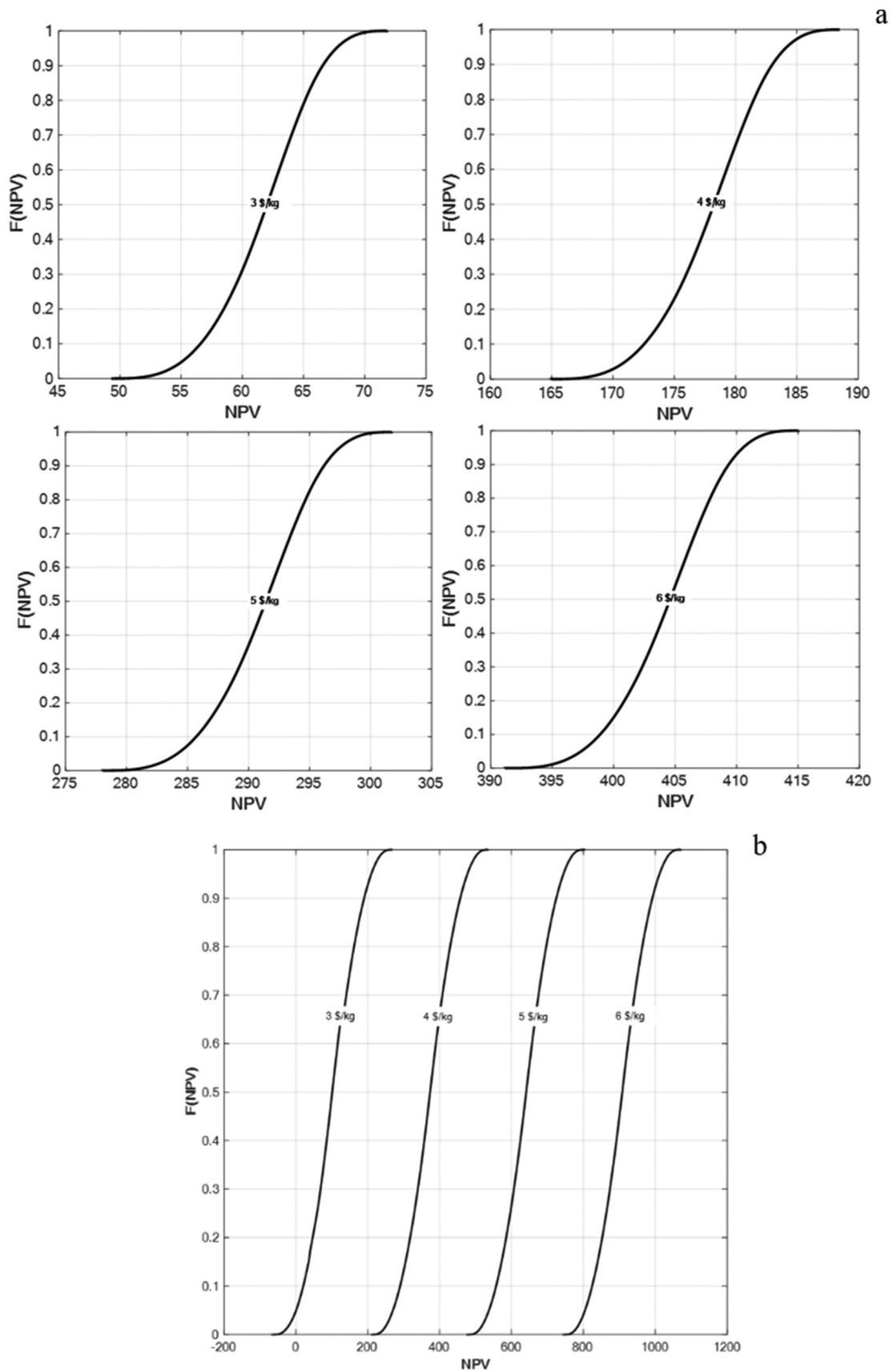
the three renewable feedstocks, the use of SBP led to the lowest total environmental externality costs (\$0.346/kg<sub>PBS</sub>).

The total cost of externalities for BOPP is lower than PLA production from all three feedstocks (Table 3). The indicators that predominantly contribute to the cost of externalities for BOPP and PLA production are climate change, particulate matter formation and terrestrial acidification. Among the three renewable feedstocks, the use of SBP led to the lowest external cost (\$0.281/kg<sub>PLA</sub>).

Fig. 4 presents the life cycle costs of PBS and PLA and their fossil counterparts. The MSP presented in Table 1 and the total externality costs presented in Tables 2 and 3 have been used for the estimation of life cycle costs for PBS and PLA. The MSP was used in order to incorporate the effect of biorefinery development in the overall assessment where the revenue from crude pectin-rich extract sales has been considered. The market prices of GPPS (\$1.72/kg) and BOPP (\$1.4/kg) and the total externality costs presented in Tables 2 and 3 have been used for the estimation of the life cycle costs of GPPS and BOPP. Fig. 4 illustrates that the life cycle costs of PBS and PLA are lower than GPPS and BOPP, only in the case of SBP where the crude pectin-rich extract has been considered as co-product at market prices of \$3/kg and \$4/kg for PLA and PBS, respectively. The life cycle cost of SBP-derived PBS is 13% lower than the life cycle cost of GPPS, while the life cycle cost of SBP-derived PLA is 9.7% lower than the life cycle cost of BOPP. These results do not include the End-of-Life phase and thus could be further improved considering



**Fig. 4.** Life cycle costing of PBS and PLA production considering the sum of the MSP estimated when each biopolymer is derived from glucose syrup, corn stover or SBP (Table 1) and the total externality costs presented in Tables 2 and 3. The life cycle costs of fossil-derived counterparts have been estimated considering the sum of their market price and the total external costs presented in Tables 2 and 3.



**Fig. 5.** Probability to achieve positive NPV (million \$) in the case of PLA production (a) and PBS production (b) from SBP at different market prices of crude pectin extracts (\$3–6/kg pectin). The Monte-Carlo simulations have been carried out considering a low sugar to BDO conversion yield of 0.32  $g_{BDO}/g_{TS}$  and a low sugar to PLA conversion yield of 0.85  $g_{LA}/g_{TS}$ . The market prices of GPPS (\$1.72/kg) and BOPP (\$1.40/kg) have been considered for PBS and PLA, respectively.

that the fossil-derived products have a higher environmental impact than bio-based products in the EoL stage. In any case, it is illustrated that only biorefinery concepts can lead to sustainable production of PBS and PLA provided that marketable applications are developed for pectin-rich extracts.

### 3.4. Stage 5 – Sensitivity analysis

The analysis is carried out by developing a techno-economic model (based on the results of process design and TEA) that evaluates the sensitivity to varying process and economic parameters considering that the biopolymers are sold at the current market price of their fossil counterparts (\$1.72/kg<sub>GPPS</sub> and \$1.4/kg<sub>BOPP</sub>). A single-point sensitivity was initially carried out using MATLAB by changing one variable at a time with case-specific limits. The most important variables (i.e., fermentation duration, unitary cost of steam, electricity cost, succinic acid market price, sugar to BDO or lactic acid conversion yield) identified via single-point sensitivity are presented in Table S24 (ESI). Monte Carlo simulations were subsequently carried out to identify the probability to develop a profitable process for PBS or PLA production by estimating the NPV using the most important variables and their corresponding value ranges presented in Table S24 (ESI). The design parameters used in the techno-economic model are the ones presented in the process design section, while case-specific design parameters are presented in Table S24 (ESI). It should be pointed out that the total sugar to BDO (0.32, 0.40, 0.48 g/g) or lactic acid (0.85, 0.90, 0.97 g/g) conversion yields have been varied at these three distinct values.

The Monte Carlo simulations carried out in the case of PBS and PLA production from SBP considered four different market prices for crude pectin extracts (\$3, 4, 5 and 6/kg<sub>pectin</sub>). Fig. 5b presents the probability of NPV to be positive, and thus the process to be profitable, in the case of PBS production considering the market price of GPPS and the lowest sugar to BDO conversion yield (0.32 g<sub>BDO</sub>/g<sub>TS</sub>). The probability for positive NPV is 100% when the pectin selling price is higher than \$4/kg, while the probability to achieve positive NPV is 98% when the pectin selling price is \$3/kg. In the case of PLA, the probability to achieve positive NPV is 100% at all pectin market prices even when the lowest sugar to lactic acid conversion yield (0.85 g<sub>LA</sub>/g<sub>TS</sub>) is considered (Fig. 5a).

Figs. S5 and S6 (ESI) show that the probability of NPV to be positive is zero when PBS and PLA are produced from corn stover considering three different fermentation yields. Figs. S7 and S8 (ESI) show that the probability to achieve positive NPV is zero when PBS and PLA are produced from glucose syrup considering three different glucose syrup market prices (170, 230 and 290 \$/t). Thus, PBS or PLA production from corn stover and glucose syrup will not be profitable if they are sold at the market prices of their fossil counterparts.

The main conclusion of the risk assessment study is that only the potential development of a biorefinery concept using SBP could lead to a profitable process when the biopolymers are sold at prices equal to those of their fossil counterparts. This would be feasible though as long as marketable products from crude pectin-rich extracts are developed.

## 4. Conclusions

Sustainability and profitability assessment of bioprocesses and biorefineries producing bio-based products is usually presented via separate process design, TEA and LCA studies. This study presents a novel approach for sustainability and profitability assessment of fermentation products produced within biorefinery concepts combining process design, TEA, LCA, LCC and techno-economic risk assessment via Monte-Carlo simulations. LCC, a methodology that combines techno-economic costs with environmental externality costs, constitutes a useful tool for sustainability assessment. This study has shown the high sustainability potential of biorefineries using food industry side

streams for the production of bio-based chemicals and biopolymers as long as co-products with several market outlets are also developed.

## CRedit authorship contribution statement

**Sofia Maria Ioannidou:** Conceptualization, Investigation, Software, Writing – original draft, Writing – review & editing. **Dimitrios Ladakis:** Conceptualization, Software, Data curation, Supervision. **Eleni Moutousidi:** Investigation, Writing – original draft. **Endrit Dheskali:** Software. **Ioannis K. Kookos:** Conceptualization, Data curation, Supervision. **Iana Cãmara-Salim:** Investigation, Writing – original draft. **María Teresa Moreira:** Data curation, Supervision. **Apostolis Koutinas:** Conceptualization, Resources, Data curation, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.150594>.

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