



Evaluation and optimization of the environmental performance of PHA downstream processing

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Appendix A. Supplementary data

The following are the Supplementary data to this article: Chemical Engineering Journal, 412 (2021), 127687. <https://doi.org/10.1016/j.cej.2020.127687>

Evaluation and optimization of the environmental performance of PHA downstream processing

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S1. Process H1

S1.1 Process design

Mass balance is presented in Table S1. Furthermore, process specifications and design outcomes are detailed in Table S2.

Table S1. Mass balance for P(4HB) downstream processing, expressed in tons per day.

Stream	Total	P(4HB)		NPCM	Water	Acetone	EtOH	Solids
		Recovered	Non-recovered					
1	3919.6	0.0	30.3	14.3	3875.1	0.0	0.0	44.6
2	3863.9	0.0	0.0	0.0	3863.9	0.0	0.0	0.0
3	55.7	0.0	30.3	14.3	11.1	0.0	0.0	44.6
4	10.7	0.0	0.0	0.0	10.7	0.0	0.0	0.0
5	45.0	0.0	30.3	14.3	0.5	0.0	0.0	44.6
6	187.6	0.0	0.0	0.0	9.4	0.0	178.3	0.0
7	232.7	0.0	30.3	14.3	9.8	0.0	178.3	44.6
8	177.0	0.0	0.0	0.0	8.8	0.0	168.1	0.0
9	55.7	0.0	30.3	14.3	1.0	0.0	10.1	44.6
10	10.7	0.0	0.0	0.0	0.5	0.0	10.2	0.0
11	45.0	0.0	30.3	14.3	0.5	0.0	0.0	44.6
12	891.3	0.0	0.0	0.0	0.0	891.3	0.0	0.0
13	936.3	28.5	1.8	14.3	0.5	891.3	0.0	16.1
14	909.5	28.2	0.0	0.0	0.5	880.9	0.0	0.0
15	26.8	0.3	1.8	14.3	0.0	10.4	0.0	16.1
16	927.2	0.0	0.0	0.0	46.4	0.0	880.9	0.0
17	1836.7	28.2	0.0	0.0	46.8	880.9	880.9	28.2
18	1789.8	0.0	0.0	0.0	46.3	871.7	871.7	0.0
19	46.9	28.2	0.0	0.0	0.5	9.1	9.1	28.2
20	18.5	0.0	0.0	0.0	0.5	9.0	9.0	0.0
21	28.4	28.2	0.0	0.0	0.0	0.1	0.1	28.2
22	867.2	0.0	0.0	0.0	1.0	859.2	6.9	0.0
23	922.6	0.0	0.0	0.0	45.3	12.5	864.8	0.0

Table S2. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [1], ^b [2], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
CE-101	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 19.3 kW ^b
S-101	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 601.6 kW ^c
R-101	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h ^a Ethanol-biomass ratio= 4:1 ^a	V = 9.7 m ³ Stirred power = 3.4 kW ^b
CE-102	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 19.3 kW ^b
S-102	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 601.6 kW ^c
R-201	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h ^a Acetone-biomass ratio= 20:1 ^a	V = 39.0 m ³ Stirred power = 13.7 kW ^b
FT-201	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b Solids output = 60 wt% ^a	A = 5.64 m ² Power = 6.5 kW ^b
SP-201	Distillation column Pressure = 101.325 kPa External reflux ratio = 2.119 Ethanol mole fraction in distillate = 0.01 Acetone mole fraction in bottoms = 0.01	D = 1 m Number of trays = 23 Heat duty = 18480 kW Cooling duty = 15870 kW
R-301	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h ^a Ethanol-acetone ratio= 1:1 ^a	V = 76.5 m ³ Stirred power = 26.8 kW ^b
FT-301	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b Solids output = 60 wt% ^a	A = 9.87 m ² Power = 12.8 kW ^b
S-301	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 1041.9 kW ^c

S1.2 LCA and LCC

S1.2.1 LCA

Results from life cycle impact assessment are addressed in Table S3.

Table S3. LCIA characterization of Process H1 for the production of P(4HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Acetone	0.321 kg	0.245	1.29·10 ⁻³	6.30·10 ⁻⁶	1.21·10 ⁻²	4.13·10 ⁻⁴	0.298
Ethanol	0.678 kg	0.735	1.95·10 ⁻³	2.44·10 ⁻⁴	5.99·10 ⁻³	9.99·10 ⁻⁵	0.642
Electricity	309 kJ	0.042	1.78·10 ⁻⁴	3.89·10 ⁻⁶	9.59·10 ⁻⁴	8.42·10 ⁻⁶	0.011
Heat duty	62972 kJ	5.100	1.62·10 ⁻²	6.89·10 ⁻⁵	1.30·10 ⁻¹	1.48·10 ⁻³	1.580
Cooling duty	48217 kJ	0.516	2.17·10 ⁻³	4.52·10 ⁻⁵	1.25·10 ⁻²	1.89·10 ⁻⁴	0.138
Wastewater	0.136 m ³	0.025	4.50·10 ⁻⁴	1.26·10 ⁻⁴	1.06·10 ⁻²	2.76·10 ⁻⁴	0.005
Biowaste	0.577 kg	0.116	8.40·10 ⁻⁴	2.65·10 ⁻⁷	7.31·10 ⁻⁵	2.70·10 ⁻⁶	0.002
Direct emissions	2.484 kg	2.484	0	0	0	0	0
PHA	1 kg	9.259	2.31·10⁻²	4.95·10⁻⁴	1.72·10⁻¹	2.47·10⁻³	2.675

S1.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S4. Also utilities and material costs are presented in Table S5. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6), distillation columns (4) and spray dryers (5) are detailed too in subsequent equations. Equations (1), (2), (3), (4) and (5) were taken from Seider et al. [4] and adapted to SI units and 2019 CEPCI index.

$$C_{pFT} = 256.6A [=] \text{€} \quad A = \text{Area} [=] \text{m}^2 \quad (1)$$

$$C_{pR} = 4416V^{0.513} + 3749P^{0.17} [=] \text{€} \quad (2)$$

$$V = \text{Volume} [=] \text{m}^3 \quad P = \text{Agitator power} [=] \text{kW}$$

$$C_{pCE} = 162202.5S^{0.3} [=] \text{€} \quad S = \text{Solids feed} [=] \text{t} \cdot \text{h}^{-1} \text{ solids} \quad (3)$$

$$C_{pSP} = F_M C_V + C_{pL} [=] \text{€}$$

$$C_{pL} = 1788(D_i)^{0.63316}(L)^{0.80161} \quad D_i = \text{Diameter} [=] \text{m} \quad L = \text{lenght} [=] \text{m}$$

$$C_V = 0.954 \exp\{7.2977 + 0.2189[\ln(W)] + 0.02297[\ln(W)]^2\} \quad (4)$$

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho [=] \text{kg}$$

$$t_s = \text{thickness} [=] \text{m} \quad \rho = \text{density} [=] \text{kg} \cdot \text{m}^{-3}$$

$$C_{pS} = 0.954 \exp(9.2567 + 0.8960[\ln(W)] - 0.0561[\ln(W)]^2) [=] \text{€} \quad (5)$$

$$W = \text{Evaporation rate} [=] \text{kg} \cdot \text{h}^{-1}$$

Table S4. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	CE-101	S-101	R-101	CE-102	S-102	R-201	FT-201	SP-201	R-301	FT-301	S-301
C _{pi} (\$)	219,431	328,837	21,096	219,431	328,946	32,503	1,626	77,044	53,290	2,847	363,205
C _{TCl} (€)	7,834,739										

Table S5. Utilities and materials annual costs summary. Costs adopted from: ^a [4], ^b [5], ^c [6]. Heat duty costs were estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers. Cooling duty costs were estimated considering the utilization of cooling water and a ΔT of 15K.

Item	Acetone ^a	EtOH ^b	Electricity ^a	Heat duty ^a	Cooling duty ^a	Wastewater ^a	Biowaste ^c
Cost (\$/y)	4,072,436	7,635,511	56,423	3,514,410	194,850	420,782	270,777
U+M (€/y)	14,575,746						

S1.3 Sensitivity analysis

Results from life cycle impact assessment considering oil (A) and natural gas (B) are addressed in Table S6 and Table S7 respectively.

Table S6. LCIA characterization of Process H1 for the production of P(4HB) considering oil (A) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP	TA	FE	HT	FEX	FD
		kg CO ₂ eq	kg SO ₂ eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Acetone	0.321 kg	0.245	$1.29 \cdot 10^{-3}$	$6.30 \cdot 10^{-6}$	$1.21 \cdot 10^{-2}$	$4.13 \cdot 10^{-4}$	0.298
Ethanol	0.678 kg	0.735	$1.95 \cdot 10^{-3}$	$2.44 \cdot 10^{-4}$	$5.99 \cdot 10^{-3}$	$9.99 \cdot 10^{-5}$	0.642
Electricity	309 kJ	0.042	$1.78 \cdot 10^{-4}$	$3.89 \cdot 10^{-6}$	$9.59 \cdot 10^{-4}$	$8.42 \cdot 10^{-6}$	0.011
Heat duty	62972 kJ	5.950	$3.69 \cdot 10^{-2}$	$8.99 \cdot 10^{-6}$	$5.24 \cdot 10^{-1}$	$2.88 \cdot 10^{-3}$	2.040
Cooling duty	48217 kJ	0.516	$2.17 \cdot 10^{-3}$	$4.52 \cdot 10^{-5}$	$1.25 \cdot 10^{-2}$	$1.89 \cdot 10^{-4}$	0.138
Wastewater	0.136 m ³	0.025	$4.50 \cdot 10^{-4}$	$1.26 \cdot 10^{-4}$	$1.06 \cdot 10^{-2}$	$2.76 \cdot 10^{-4}$	0.005
Biowaste	0.577 kg	0.116	$8.40 \cdot 10^{-4}$	$2.65 \cdot 10^{-7}$	$7.31 \cdot 10^{-5}$	$2.70 \cdot 10^{-6}$	0.002
Direct emissions	2.484 kg	2.484	0	0	0	0	0
PHA	1 kg	10.109	$4.38 \cdot 10^{-2}$	$4.35 \cdot 10^{-4}$	$5.66 \cdot 10^{-1}$	$3.87 \cdot 10^{-3}$	3.135

Table S7. LCIA characterization of Process H1 for the production of P(4HB) considering natural gas (B) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP	TA	FE	HT	FEX	FD	
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Acetone	0.321	kg	0.245	$1.29 \cdot 10^{-3}$	$6.30 \cdot 10^{-6}$	$1.21 \cdot 10^{-2}$	$4.13 \cdot 10^{-4}$	0.298
Ethanol	0.678	kg	0.735	$1.95 \cdot 10^{-3}$	$2.44 \cdot 10^{-4}$	$5.99 \cdot 10^{-3}$	$9.99 \cdot 10^{-5}$	0.642
Electricity	309	kJ	0.042	$1.78 \cdot 10^{-4}$	$3.89 \cdot 10^{-6}$	$9.59 \cdot 10^{-4}$	$8.42 \cdot 10^{-6}$	0.011
Heat duty	62972	kJ	4.540	$4.44 \cdot 10^{-3}$	$2.35 \cdot 10^{-5}$	$2.27 \cdot 10^{-2}$	$1.45 \cdot 10^{-3}$	1.670
Cooling duty	48217	kJ	0.516	$2.17 \cdot 10^{-3}$	$4.52 \cdot 10^{-5}$	$1.25 \cdot 10^{-2}$	$1.89 \cdot 10^{-4}$	0.138
Wastewater	0.136	m3	0.025	$4.50 \cdot 10^{-4}$	$1.26 \cdot 10^{-4}$	$1.06 \cdot 10^{-2}$	$2.76 \cdot 10^{-4}$	0.005
Biowaste	0.577	kg	0.116	$8.40 \cdot 10^{-4}$	$2.65 \cdot 10^{-7}$	$7.31 \cdot 10^{-5}$	$2.70 \cdot 10^{-6}$	0.002
Direct emissions	2.484	kg	2.484	0	0	0	0	0
PHA	1	kg	8.699	$1.13 \cdot 10^{-2}$	$4.49 \cdot 10^{-4}$	$6.99 \cdot 10^{-2}$	$2.44 \cdot 10^{-3}$	2.765

S2. Process H2

S2.1 Process design

A simplified process flow diagram for P(3HB) downstream processing is shown in Figure S1. Mass balance is presented in Table S8. Furthermore, process specifications and design outcomes are detailed in Table S9.

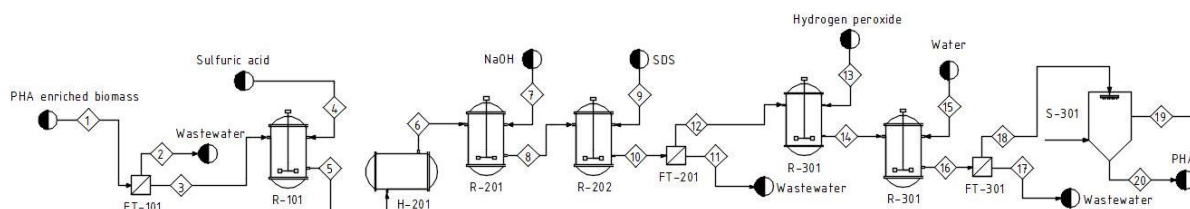


Figure S1. Scheme of H2 process.

Table S8. Mass balance for P(3HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB)		NPCM	Water	H ₂ SO ₄	NaOH	SDS	H ₂ O ₂	Solids
		Recovered	Non-recovered							
1	584.4	0.0	30.3	13.0	541.1	0.0	0.0	0.0	0.0	43.3
2	295.8	0.0	0.0	0.0	295.8	0.0	0.0	0.0	0.0	0.0
3	288.6	0.0	30.3	13.0	245.3	0.0	0.0	0.0	0.0	43.3
4	3.7	0.0	0.0	0.0	3.3	0.4	0.0	0.0	0.0	0.0
5	292.3	0.0	30.3	13.0	248.6	0.4	0.0	0.0	0.0	43.3
6	292.3	25.2	5.2	13.0	248.6	0.4	0.0	0.0	0.0	43.3
7	1.8	0.0	0.0	0.0	0.3	0	0.3	1.2	0.0	0.0
8	294.1	25.2	5.2	13.0	248.9	0.4	0.3	1.2	0.0	43.3
9	1176.3	0.0	0.0	0.0	1176.3	0.0	0.0	0.0	0.0	0.0
10	1470.3	25.2	5.2	13.0	1425.2	0.4	0.3	1.2	0.0	43.3
11	1292.2	0.0	4.6	11.7	1274.2	0.3	0.3	1.0	0.0	16.3
12	178.1	25.2	0.5	1.3	151.0	0.0	0.0	0.1	0.0	27.0
13	22.3	0.0	0.0	0.0	15.6	0.0	0.0	0.0	6.7	0.0
14	200.4	23.6	2.0	1.3	166.5	0.0	0.0	0.1	6.7	27.0
15	607.3	0.0	0.0	0.0	607.3	0.0	0.0	0.0	0.0	0.0
16	807.7	23.6	2.0	1.3	773.8	0.0	0.0	0.1	6.7	27.0
17	772.9	0.0	2.0	1.3	762.8	0.0	0.0	0.1	6.6	3.3
18	34.8	23.6	0.0	0.0	11.1	0.0	0.0	0.0	0.0	23.7
19	10.9	0.0	0.0	0.0	10.9	0.0	0.0	0.0	0.0	0.0
20	23.8	23.6	0.0	0.0	0.2	0.0	0.0	0.0	0.0	23.6

Table S9. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [7], ^b [2], ^c [8], ^d [3], ^e [9].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
FT-101	Microfiltration ^a $\Delta P = 80 \text{ kPa}^b$ Membrane permeate flux (q_0/A) = $55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2b}$ Solids output = $15 \text{ wt}\%^a$	$A = 60.73 \text{ m}^2$ Power = 1.1 kW^b
R-101	Continuous stirred tank Mild agitation ^b Residence time = 0.25 h^b $\text{pH} = 4.5^a$	$V = 3 \text{ m}^3$ Stirred power = 0.4 kW^b
H-201	High pressure homogenizer ^a $\Delta P_H = 100000 \text{ kPa}^{ac}$ $\eta_{Hm} = 0.9^c$ $\eta_{he} = 0.9^c$ Recovery yield = $83\%^a$	Power = 418 kW^c
R-201	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h^e $\text{pH} = 10^a$ SDS concentration in R-201 = $4 \text{ g}\cdot\text{L}^{-1}^a$	$V = 12.3 \text{ m}^3$ Stirred power = 4.3 kW^b
R-202	Continuous stirred tank Mild agitation ^b Residence time = 0.25 h^b Stream/water dilution ratio = $1:4^a$	$V = 12.3 \text{ m}^3$ Stirred power = 1.4 kW^b
FT-201	Microfiltration ^a $\Delta P = 80 \text{ kPa}^b$ $q_0/A = 55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2b}$ Solids output = $15 \text{ wt}\%^a$	$A = 37.49 \text{ m}^2$ Power = 2.7 kW^b
R-301	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h^e $\text{H}_2\text{O}_2:\text{stream} = 1:8^a$	$V = 8.4 \text{ m}^3$ Stirred power = 2.9 kW^b
R-302	Continuous stirred tank Mild agitation ^b Residence time = 0.25 h^b Stream/water dilution ratio = $1:3^a$	$V = 8.4 \text{ m}^3$ Stirred power = 1 kW^b
FT-301	Microfiltration ^a $\Delta P = 300 \text{ kPa}^b$ $q_0/A = 55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2b}$ Solids output = $60 \text{ wt}\%^a$	$A = 7.32 \text{ m}^2$ Power = 5.6 kW^b
S-301	Spray dryer ^a Solids output = $99 \text{ wt}\%^a$ Heat duty consumption = $4.87 \text{ GJ}\cdot\text{t}^{-1}$ water evaporated ^d	Heat duty = 876.5 kW^d

S2.2 LCA and LCC

S2.2.1 LCA

Results from life cycle impact assessment are addressed in Table S10.

Table S10. LCIA characterization of Process H2 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI		Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.028	kg	0	0	0	0	0	0
SDS	0.049	kg	0.071	3.71·10 ⁻⁴	2.37·10 ⁻⁶	1.11·10 ⁻²	3.39·10 ⁻⁵	0.060
NaOH	0.013	kg	0.010	4.41·10 ⁻⁵	8.35·10 ⁻⁷	4.35·10 ⁻⁴	3.09·10 ⁻⁶	0.003
H ₂ O ₂	0.280	kg	0.249	8.50·10 ⁻⁴	1.14·10 ⁻⁵	1.01·10 ⁻²	2.18·10 ⁻⁴	0.089
H ₂ SO ₄	0.015	kg	0.001	1.00·10 ⁻⁴	1.78·10 ⁻⁸	5.50·10 ⁻⁵	2.28·10 ⁻⁶	0.002
Electricity	1581	kJ	0.212	9.12·10 ⁻⁴	1.99·10 ⁻⁵	4.91·10 ⁻³	4.31·10 ⁻⁵	0.056
Heat duty	3171	kJ	0.257	8.13·10 ⁻⁴	3.47·10 ⁻⁶	6.53·10 ⁻³	7.48·10 ⁻⁵	0.080
Wastewater _r	0.032	m ³	0.006	1.06·10 ⁻⁴	2.97·10 ⁻⁵	2.49·10 ⁻³	6.49·10 ⁻⁵	0.001
PHA	1	kg	0.806	3.20·10⁻³	6.77·10⁻⁵	3.56·10⁻²	4.40·10⁻⁴	0.290

S2.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S11. Also utilities and material costs are presented in Table S12. Cost correlations for microfiltration (1), vessels and stirrers (2), high pressure homogenizers (6) and spray dryers (5) were employed. Equation (6) was taken from Gurieff et al. [10].

$$C_{pH} = 10^{4.85} \cdot Q^{0.43} [=] \$ \quad Q [=] m^3 h^{-1} \quad CEPCI = 346 \quad (6)$$

Table S11. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	FT-101	R-101	H-201	R-201	R-202	FT-201	R-301	R-302	FT-301	S-301
C_{pi} (\$)	17,510	12,307	364,144	23,338	22,408	10,808	19,794	18,985	2,392	353,295
C_{TCI} (€)	4,016,495									

Table S12. Utilities and materials annual costs summary. Costs adopted from: ^a [4], ^b [5]. Heat duty costs were estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers.

Item	Water ^a	SDS ^b	NaOH ^b	H2SO4 ^b	H2O2 ^b	Electricity ^a	Heat duty ^a	Wastewater ^a
Cost (\$/y)	60,519	281,422	10,078	9,714	881,782	242,267	135,476	82,909
U+M (€/y)	1,533,752							

S2.3 Sensitivity analysis

Results from life cycle impact assessment considering the Polish electricity mix (A) and the Swedish mix (B) as electricity sources are addressed in Table S13 and Table S14 respectively.

Table S13. LCIA characterization of Process H2 for the production of P(3HB) considering the Polish electricity mix (A) as electricity source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP	TA	FE	HT	FEX	FD	
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Water	0.028	kg	0	0	0	0	0	
SDS	0.049	kg	0.071	3.71·10 ⁻⁴	2.37·10 ⁻⁶	1.11·10 ⁻²	3.39·10 ⁻⁵	0.060
NaOH	0.013	kg	0.010	4.41·10 ⁻⁵	8.35·10 ⁻⁷	4.35·10 ⁻⁴	3.09·10 ⁻⁶	0.003
H ₂ O ₂	0.280	kg	0.249	8.50·10 ⁻⁴	1.14·10 ⁻⁵	1.01·10 ⁻²	2.18·10 ⁻⁴	0.089
H ₂ SO ₄	0.015	kg	0.001	1.00·10 ⁻⁴	1.78·10 ⁻⁸	5.50·10 ⁻⁵	2.28·10 ⁻⁶	0.002
Electricity	1581	kJ	0.439	2.34·10 ⁻³	5.34·10 ⁻⁵	1.03·10 ⁻²	3.93·10 ⁻⁵	0.116
Heat duty	3171	kJ	0.257	8.13·10 ⁻⁴	3.47·10 ⁻⁶	6.53·10 ⁻³	7.48·10 ⁻⁵	0.080
Wastewater _r	0.032	m ³	0.006	1.06·10 ⁻⁴	2.97·10 ⁻⁵	2.49·10 ⁻³	6.49·10 ⁻⁵	1.00·10 ⁻³
PHA	1	kg	1.033	4.62·10⁻³	1.01·10⁻⁴	4.10·10⁻²	4.36·10⁻⁴	0.350

Table S14. LCIA characterization of Process H2 for the production of P(3HB) considering the Swedish electricity mix (B) as electricity source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP kg CO2 eq	TA kg SO2 eq	FE kg P eq	HT kg 1,4-DB eq	FEX kg 1,4-DB eq	FD kg oil eq	
Water	0.028	kg	0	0	0	0	0	
SDS	0.049	kg	0.071	$3.71 \cdot 10^{-4}$	$2.37 \cdot 10^{-6}$	$1.11 \cdot 10^{-2}$	$3.39 \cdot 10^{-5}$	0.060
NaOH	0.013	kg	0.010	$4.41 \cdot 10^{-5}$	$8.35 \cdot 10^{-7}$	$4.35 \cdot 10^{-4}$	$3.09 \cdot 10^{-6}$	0.003
H ₂ O ₂	0.280	kg	0.249	$8.50 \cdot 10^{-4}$	$1.14 \cdot 10^{-5}$	$1.01 \cdot 10^{-2}$	$2.18 \cdot 10^{-4}$	0.089
H ₂ SO ₄	0.015	kg	0.001	$1.00 \cdot 10^{-4}$	$1.78 \cdot 10^{-8}$	$5.50 \cdot 10^{-5}$	$2.28 \cdot 10^{-6}$	0.002
Electricity	1581	kJ	0.020	$1.08 \cdot 10^{-4}$	$1.40 \cdot 10^{-6}$	$2.07 \cdot 10^{-3}$	$1.04 \cdot 10^{-5}$	0.005
Heat duty	3171	kJ	0.257	$8.13 \cdot 10^{-4}$	$3.47 \cdot 10^{-6}$	$6.53 \cdot 10^{-3}$	$7.48 \cdot 10^{-5}$	0.080
Wastewater	0.032	m ³	0.006	$1.06 \cdot 10^{-4}$	$2.97 \cdot 10^{-5}$	$2.49 \cdot 10^{-3}$	$6.49 \cdot 10^{-5}$	0.001
PHA	1	kg	0.614	$2.390 \cdot 10^{-3}$	$4.92 \cdot 10^{-5}$	$3.28 \cdot 10^{-2}$	$4.07 \cdot 10^{-4}$	0.239

S3. Process H3

S3.1 Process design

A simplified process flow diagram for P(3HB-co-4HB) downstream processing is shown in Figure S2. Mass balance is presented in

Table S15. Furthermore, process specifications and design outcomes are detailed in Table S16.

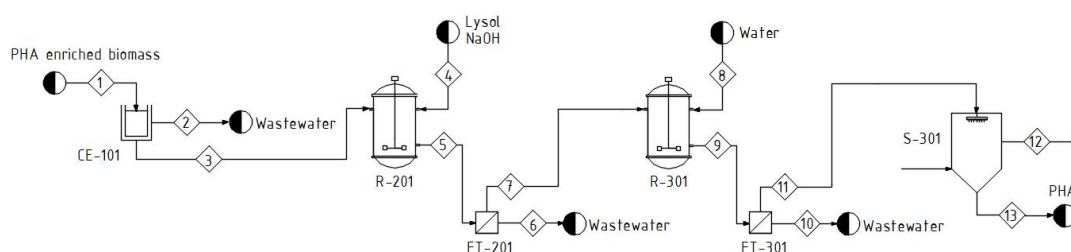


Figure S2. Scheme of H3 process.

Table S15. Mass balance for P(3HB-co-4HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB-co-4HB)		NPCM	Water	Lysol	NaOH	Solids
		Recovered	Non-recovered					
1	3807.6	0.0	30.3	13.0	3764.4	0.0	0.0	43.3
2	3753.5	0.0	0.0	0.0	3753.5	0.0	0.0	0.0
3	54.1	0.0	30.3	13.0	10.8	0.0	0.0	43.3
4	807.7	0.0	0.0	0.0	791.1	11.8	4.7	0.0
5	861.8	27.3	3.0	13.0	801.9	11.8	4.7	43.3
6	815.8	0.0	3.0	12.7	783.9	11.6	4.6	15.7
7	46.1	27.3	0.1	0.3	18.0	0.3	0.1	27.6
8	139.6	0.0	0.0	0.0	139.6	0.0	0.0	0.0
9	185.6	27.3	0.1	0.3	157.6	0.3	0.1	27.6
10	140.1	0.0	0.1	0.3	139.4	0.2	0.1	0.3
11	45.5	27.3	0.0	0.0	18.2	0.0	0.0	27.3
12	17.9	0.0	0.0	0.0	17.9	0.0	0.0	0.0
13	27.6	27.3	0.0	0.0	0.2	0.0	0.0	27.3

Table S16. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [2], ^b [11], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
CE-101	Basket centrifuge Solids output = 80 wt% ^a	Power = 18.8 kW ^a
R-201	Continuous stirred tank Vigorous agitation ^a Residence time = 1.14 h ^b Lysol concentration in R-201 = 2 v/v% ^b NaOH concentration in R-201 = 0.15 M ^b	V = 40.9 m ³ Stirred power = 14.3 kW ^a
FT-201	Microfiltration $\Delta P = 80$ kPa ^a $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^a Solids output = 60 wt% ^a	A = 9.69 m ² Power = 6 kW ^a
R-302	Continuous stirred tank Mild agitation ^a Residence time = 0.5 h ^b Stream/water dilution ratio = 1:3	V = 9.58 m ³ Stirred power = 1.3 kW ^a
S-301	Spray dryer	Heat duty = 1010.8 kW ^c

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
	Solids output = 99 wt%	
	Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	

S3.2 LCA and LCC

S3.2.1 LCA

Results from life cycle impact assessment are addressed in Table S17.

Table S17. LCIA characterization of Process H3 for the production of P(3HB-co-4HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.005	kg	0	0	0	0	0	0
Lysol	0.429	kg	1.960	6.81·10 ⁻³	6.28·10 ⁻⁵	4.22·10 ⁻²	2.45·10 ⁻³	1.100
NaOH	0.172	kg	0.129	5.84·10 ⁻⁴	1.10·10 ⁻⁵	5.75·10 ⁻³	4.09·10 ⁻⁵	0.034
Electricity	128	kJ	0.017	7.19·10 ⁻⁵	1.60·10 ⁻⁶	3.45·10 ⁻⁴	3.22·10 ⁻⁶	0.004
Heat duty	3166	kJ	0.256	8.12·10 ⁻⁴	3.46·10 ⁻⁶	6.52·10 ⁻³	7.46·10 ⁻⁵	0.079
Wastewater _r	0.171	m ³	0.032	5.66·10 ⁻⁴	1.58·10 ⁻⁴	1.33·10 ⁻²	3.47·10 ⁻⁴	0.006
PHA	1	kg	2.394	8.84·10⁻³	2.37·10⁻⁴	6.81·10⁻²	2.92·10⁻³	1.223

S3.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S18. Also utilities and material costs are presented in Table S19. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6) and spray dryers (5) were employed.

Table S18. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	CE-101	R-201	FT-201	R-301	FT-201	S-301
C _{pi} (\$)	217,531	39,939	2,794	13,600	2,762	361,532
C_{TCI} (€)	3,033,387					

Table S19. Utilities and materials annual costs summary. Costs adopted from: ^a [5], ^b [9]. Heat duty costs was estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers.

Item	Water ^a	Lysol ^b	NaOH ^b	Electricity ^a	Heat duty ^a	Wastewater ^a
Cost (\$/y)	60,519	281,422	10,078	242,267	135,476	82,909
U+M (€/y)	6,047,320					

S3.3 Sensitivity analysis

Mass balances and process specifications and design outcomes resulting of substituting Lysol by SDS with a recovery unit by crystallization are collected in Table S20 and Table S21 respectively.

Table S20. Mass balance for P(3HB-co-4HB) downstream processing substituting Lysol by SDS with a recovery unit by crystallization, expressed in tons per day.

Stream	Total	P(3HB-co-4HB)		NPCM	Water	SDS	NaOH	Solids
		Recovered	Non-recovered					
14	815.8	0.0	3.0	12.7	783.9	11.6	4.6	15.7
15	815.8	0.0	3.0	12.7	783.9	11.6	4.6	15.7
16	800.3	0.0	2.9	12.6	777.9	2.3	4.6	0.0
17	15.4	0.0	0.0	0.1	6.0	9.3	0.0	9.3

Table S21. Process specifications and design outcomes considering Lysol substitution by SDS with a recovery unit by crystallization, expressed in tons per day.. Specifications and estimations adopted from: ^a [2], ^b [12].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
E-201	Shell and tube exchanger Discharge temperature = 9 °C ^b	A = 2.21 m ² Cooling duty = 323 kW
R-203	Continuous stirred tank Mild agitation ^a Residence time = 1 h ^b	V = 34 m ³ Stirred power = 3.9 kW ^a
FT-202	Microfiltration $\Delta P = 80 \text{ kPa}$ ^a $q_0/A = 55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ ^a Solids output = 60 wt% ^a	A = 168.4 m ² Power = 5.6 kW ^a

Results from life cycle impact assessment where base case scenario Lysol is substituted by SDS with a recovery unit by crystallization are showed in Table S22.

Table S22. LCIA characterization of Process H3 for the production of P(3HB-co-4HB) considering Lysol is substituted by SDS with a recovery unit by crystallization, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI		Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.005	kg	0	0	0	0	0	0
SDS	0.084	kg	0.119	$6.36 \cdot 10^{-4}$	$4.06 \cdot 10^{-6}$	$1.90 \cdot 10^{-2}$	$5.82 \cdot 10^{-5}$	0.103
NaOH	0.172	kg	0.129	$5.84 \cdot 10^{-4}$	$1.10 \cdot 10^{-5}$	$5.75 \cdot 10^{-3}$	$4.09 \cdot 10^{-5}$	0.034
Electricity	157	kJ	0.017	$7.19 \cdot 10^{-5}$	$1.60 \cdot 10^{-6}$	$3.45 \cdot 10^{-4}$	$3.22 \cdot 10^{-6}$	0.004
Heat duty	3166	kJ	0.256	$8.12 \cdot 10^{-4}$	$3.46 \cdot 10^{-6}$	$6.52 \cdot 10^{-3}$	$7.46 \cdot 10^{-5}$	0.079
Cooling duty	1011	kJ	0.011	$4.55 \cdot 10^{-5}$	$9.48 \cdot 10^{-7}$	$2.61 \cdot 10^{-4}$	$3.96 \cdot 10^{-6}$	0.003
Wastewater	0.171	m ³	0.032	$5.66 \cdot 10^{-4}$	$1.58 \cdot 10^{-4}$	$1.33 \cdot 10^{-2}$	$3.47 \cdot 10^{-4}$	0.006
PHA	1	kg	0.568	$2.73 \cdot 10^{-3}$	$1.79 \cdot 10^{-4}$	$4.53 \cdot 10^{-2}$	$5.29 \cdot 10^{-4}$	0.230

S4. Process H4

S4.1 Process design

A simplified process flow diagram for P(3HB-co-3Hxx) downstream processing is shown in Figure S3. Mass balance is presented in

Table S23. Furthermore, process specifications and design outcomes are detailed in

Table S24.

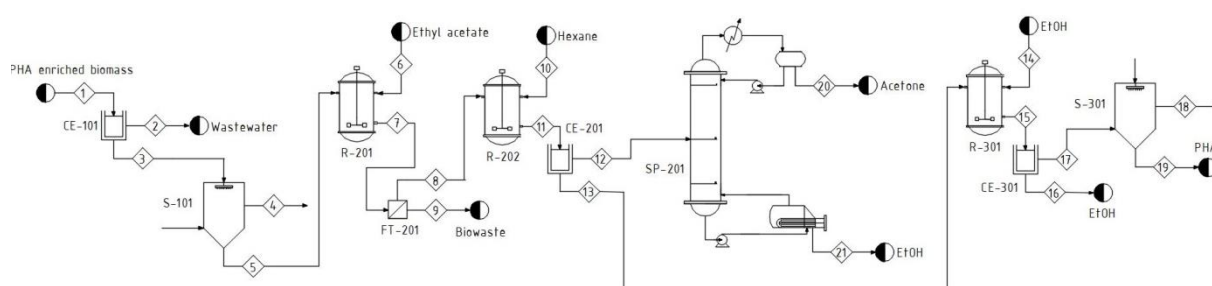


Figure S3. Scheme of H4 process.

Table S23. Mass balance for P(3HB-co-3Hxx) downstream processing, expressed in tons per day.

Stream	Total	P(3HB-co-3Hxx)		NPCM	Water	Ethyl acetate	Heptane	EtOH	Solids
		Recovered	Non-recovered						
1	1272.7	0.0	30.3	30.3	1212.1	0.0	0.0	0.0	60.6
2	1197.0	0.0	0.0	0.0	1197.0	0.0	0.0	0.0	0.0
3	75.8	0.0	30.3	30.3	15.2	0.0	0.0	0.0	60.6
4	14.5	0.0	0.0	0.0	14.5	0.0	0.0	0.0	0.0
5	61.2	0.0	30.3	30.3	0.6	0.0	0.0	0.0	60.6
6	1224.4	0.0	0.0	0.0	0.0	1224.4	0.0	0.0	0.0
7	1285.6	28.5	1.8	30.3	0.6	1224.4	0.0	0.0	60.6
14	1232.1	28.5	0.0	0.0	0.6	1203.0	0.0	0.0	0.0
15	53.5	0.0	1.8	30.3	0.0	21.4	0.0	0.0	32.1
10	3608.9	0.0	0.0	0.0	0.0	0.0	3608.9	0.0	0.0

Stream	Total	P(3HB-co-3Hxx)		NPCM	Water	Ethyl acetate	Heptane	EtOH	Solids
		Recovered	Non-recovered						
11	4841.0	28.5	0.0	0.0	0.6	1203.0	3608.9	0.0	28.5
12	4805.4	0.0	0.0	0.0	0.6	1201.2	3603.6	0.0	0.0
13	35.6	28.5	0.0	0.0	0.0	1.8	5.3	0.0	28.5
14	120.0	0.0	0.0	0.0	6.0	0.0	0.0	114.0	0.0
15	155.6	28.5	0.0	0.0	6.0	1.8	5.3	114.0	28.5
16	119.9	0.0	0.0	0.0	5.7	1.7	5.0	107.6	0.0
17	35.7	28.5	0.0	0.0	0.3	0.1	0.3	6.4	28.5
18	6.8	0.0	0.0	0.0	0.3	0.1	0.3	6.1	0.0
19	28.9	28.5	0.0	0.0	0.0	0.0	0.0	0.3	28.5
20	1136.6	0.0	0.0	0.0	0.6	1123.1	12.9	0.0	0.0
21	3478.9	0.0	0.0	0.0	0.0	30.6	3448.3	0.0	0.0

Table S24. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [9], ^b [2], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
CE-101	Basket centrifuge ^a Solids output = 80 wt% ^b	Power = 26.3 kW ^b
S-101	Spray dryer ^a Solids output = 99 wt% Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 819.5 kW ^c
G-101	Grinder ^a Reduction ratio = 15 ^b	Power = 3.2 kW ^b
R-201	Continuous stirred tank Vigorous agitation ^b Residence time = 2 h ^a Ethyl acetate-biomass ratio= 20:1 ^a	V = 107.1 m ³ Stirred power = 37.5 kW ^b

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
FT-201	Microfiltration $\Delta P = 300 \text{ kPa}^b$ $q_0/A = 55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2b}$ Solids output = 60 wt% ^b	$A = 5.64 \text{ m}^2$ Power = 6.5 kW ^b
R-301	Continuous stirred tank Mild agitation ^b Residence time = 1 h ^a Heptane-ethyl acetate ratio= 3:1 ^a	$V = 201.7 \text{ m}^3$ Stirred power = 27.2 kW ^b
CE-301	Basket centrifuge ^a Solids output = 80 wt% ^b	Power = 12.4 kW ^b
R-302	Continuous stirred tank Vigorous agitation ^b Residence time = 1 h ^a Ethanol-biomass ratio= 4:1 ^a	$V = 6.5 \text{ m}^3$ Stirred power = 2.3 kW ^b
CE-302	Basket centrifuge ^a Solids output = 80 wt% ^b	Power = 12.4 kW ^b
S-301	Spray dryer Solids output = 99 wt% Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 385.2 kW ^c
SP-201	Distillation column Pressure = 101.325 kPa External reflux ratio = 5.500 Heptane mole fraction in distillate = 0.01 Ethyl acetate mole fraction in bottoms = 0.01	Number of trays = 24 Heat duty = 35560 kW Cooling duty = 31390 kW

S4.2 LCA and LCC

S4.2.1 LCA

Results from life cycle impact assessment are addressed in Table S25.

Table S25. LCIA characterization of Process H4 for the production of P(3HB-co-3Hxx), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Ethyl acetate	0.803 kg	1.87	$8.09\cdot 10^{-3}$	$2.28\cdot 10^{-4}$	$6.99\cdot 10^{-2}$	$2.68\cdot 10^{-3}$	1.150

Heptane	0.185	kg	0.046	$3.63 \cdot 10^{-4}$	$7.40 \cdot 10^{-7}$	$3.18 \cdot 10^{-3}$	$1.15 \cdot 10^{-4}$	0.094
Ethanol	0.223	kg	0.242	$6.40 \cdot 10^{-4}$	$8.03 \cdot 10^{-5}$	$1.97 \cdot 10^{-3}$	$3.28 \cdot 10^{-5}$	0.211
Electricity	382	kJ	0.051	$2.21 \cdot 10^{-4}$	$4.81 \cdot 10^{-6}$	$1.19 \cdot 10^{-3}$	$1.04 \cdot 10^{-5}$	0.014
Heat duty	110082	kJ	8.910	$2.82 \cdot 10^{-2}$	$1.20 \cdot 10^{-4}$	$2.27 \cdot 10^{-1}$	$2.60 \cdot 10^{-3}$	2.760
Cooling duty	93989	kJ	1.010	$4.23 \cdot 10^{-3}$	$8.81 \cdot 10^{-5}$	$2.43 \cdot 10^{-2}$	$3.68 \cdot 10^{-4}$	0.270
Wastewater	0.041	m ³	0.008	$1.36 \cdot 10^{-4}$	$3.80 \cdot 10^{-5}$	$3.19 \cdot 10^{-3}$	$8.32 \cdot 10^{-5}$	0.003
Biowaste	1.113	kg	0.224	$1.62 \cdot 10^{-3}$	$5.11 \cdot 10^{-7}$	$1.41 \cdot 10^{-4}$	$5.36 \cdot 10^{-6}$	0.001
Direct emissions	0.595	kg	0.595	0	0	0	0	0
PHA	1	kg	12.956	$4.35 \cdot 10^{-2}$	$5.60 \cdot 10^{-4}$	$3.31 \cdot 10^{-1}$	$5.89 \cdot 10^{-3}$	4.503

S4.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S26. Also utilities and material costs are presented in Table S27. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6) and spray dryers (5) were employed.

Table S26. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	CE-101	S-101	GR-101	R-201	FT-201	R-301	CE-301	R-302	CE-302	S-301	SP-201
C_{pi} (\$)	240,635	349,210	5,845	62,374	1,626	82,889	191,892	17,787	191,892	295,873	79,055
C_{TCI} (€)											

Table S27. Utilities and materials annual costs summary. Costs adopted from: ^a [5], ^b [6], ^c [6]. Heat duty costs were estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers. Cooling duty costs were estimated considering the utilization of cooling water and a ΔT of 15K.

Item	Acetone ^a	EtOH ^b	Electricity ^a	Heat duty ^a	Cooling duty ^a	Wastewater ^a	Biowaste ^c
Cost (\$/y)	4,072,436	7,635,511	56,423	479,148	194,850	420,782	270,777
U+M (€/y)							
				7,220,015			

S4.3 Sensitivity analysis

Results from life cycle impact assessment considering oil (A) and natural gas (B) are addressed in Table S28 and Table S29 respectively.

Table S28. LCIA characterization of Process H4 for the production of P(3HB-co-3Hxx) considering oil (A) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP	TA	FE	HT	FEX	FD	
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Ethyl acetate	0.803	kg	1.87	$8.09 \cdot 10^{-3}$	$2.28 \cdot 10^{-4}$	$6.99 \cdot 10^{-2}$	$2.68 \cdot 10^{-3}$	1.150
Heptane	0.185	kg	0.046	$3.63 \cdot 10^{-4}$	$7.40 \cdot 10^{-7}$	$3.18 \cdot 10^{-3}$	$1.15 \cdot 10^{-4}$	0.094
Ethanol	0.223	kg	0.242	$6.40 \cdot 10^{-4}$	$8.03 \cdot 10^{-5}$	$1.97 \cdot 10^{-3}$	$3.28 \cdot 10^{-5}$	0.211
Electricity	382	kJ	0.051	$2.21 \cdot 10^{-4}$	$4.81 \cdot 10^{-6}$	$1.19 \cdot 10^{-3}$	$1.04 \cdot 10^{-5}$	0.014
Heat duty	110082	kJ	9.930	$2.14 \cdot 10^{-2}$	$1.45 \cdot 10^{-5}$	$1.82 \cdot 10^{-1}$	$4.62 \cdot 10^{-3}$	3.440
Cooling duty	93989	kJ	1.010	$4.23 \cdot 10^{-3}$	$8.81 \cdot 10^{-5}$	$2.43 \cdot 10^{-2}$	$3.68 \cdot 10^{-4}$	0.270
Wastewater	0.041	m ³	0.008	$1.36 \cdot 10^{-4}$	$3.80 \cdot 10^{-5}$	$3.19 \cdot 10^{-3}$	$8.32 \cdot 10^{-5}$	0.003
Biowaste	1.113	kg	0.224	$1.62 \cdot 10^{-3}$	$5.11 \cdot 10^{-7}$	$1.41 \cdot 10^{-4}$	$5.36 \cdot 10^{-6}$	0.001
Direct emissions	0.595	kg	0.595	0	0	0	0	0
PHA	1	kg	13.976	$3.67 \cdot 10^{-2}$	$4.55 \cdot 10^{-4}$	$2.68 \cdot 10^{-1}$	$7.91 \cdot 10^{-3}$	5.183

Table S29. LCIA characterization of Process H4 for the production of P(3HB-co-3Hxx) considering natural gas (B) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category.

LCI	Unit	GWP	TA	FE	HT	FEX	FD	
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Ethyl acetate	0.803	kg	1.87	$8.09 \cdot 10^{-3}$	$2.28 \cdot 10^{-4}$	$6.99 \cdot 10^{-2}$	$2.68 \cdot 10^{-3}$	1.150
Heptane	0.185	kg	0.046	$3.63 \cdot 10^{-4}$	$7.40 \cdot 10^{-7}$	$3.18 \cdot 10^{-3}$	$1.15 \cdot 10^{-4}$	0.094
Ethanol	0.223	kg	0.242	$6.40 \cdot 10^{-4}$	$8.03 \cdot 10^{-5}$	$1.97 \cdot 10^{-3}$	$3.28 \cdot 10^{-5}$	0.211
Electricity	382	kJ	0.051	$2.21 \cdot 10^{-4}$	$4.81 \cdot 10^{-6}$	$1.19 \cdot 10^{-3}$	$1.04 \cdot 10^{-5}$	0.014
Heat duty	110082	kJ	3.53	$4.28 \cdot 10^{-3}$	$1.74 \cdot 10^{-5}$	$2.48 \cdot 10^{-2}$	$1.39 \cdot 10^{-3}$	1.360
Cooling duty	93989	kJ	1.010	$4.23 \cdot 10^{-3}$	$8.81 \cdot 10^{-5}$	$2.43 \cdot 10^{-2}$	$3.68 \cdot 10^{-4}$	0.270

Wastewater	0.041	m ³	0.008	$1.36 \cdot 10^{-4}$	$3.80 \cdot 10^{-5}$	$3.19 \cdot 10^{-3}$	$8.32 \cdot 10^{-5}$	0.003
Biowaste	1.113	kg	0.224	$1.62 \cdot 10^{-3}$	$5.11 \cdot 10^{-7}$	$1.41 \cdot 10^{-4}$	$5.36 \cdot 10^{-6}$	0.001
Direct emissions	0.595	kg	0.595	0	0	0	0	0
PHA	1	kg	7.576	$1.96 \cdot 10^{-2}$	$4.58 \cdot 10^{-4}$	$1.29 \cdot 10^{-1}$	$4.68 \cdot 10^{-3}$	3.103

S5. Process L1

S5.1 Process design

A simplified process flow diagram for P(3HB-co-4HB) downstream processing is shown in

Table **S30**. Furthermore, process specifications and design outcomes are detailed in

Table S31.

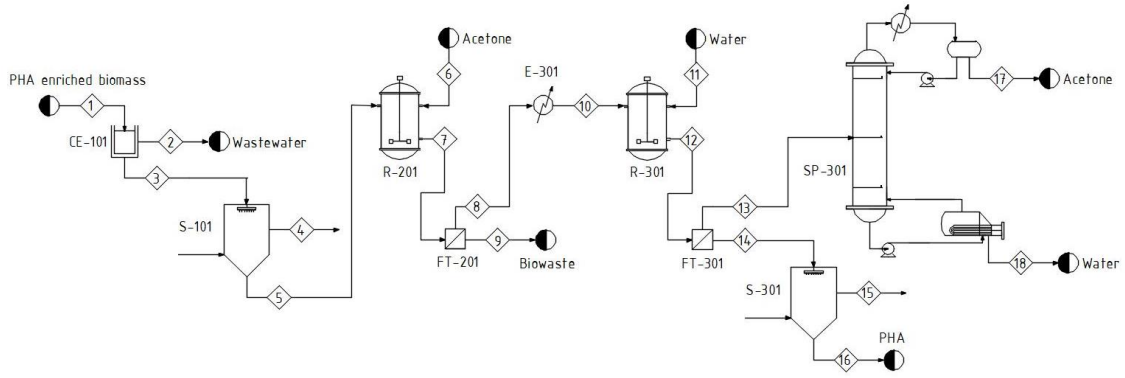


Figure S4. Scheme of L1 process.

Table S30. Mass balance for P(3HB-co-4HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB-co-4HB)		NPCM	Water	Acetone	Solids
		Recovered	Non-recovered				
1	10590.6	0.0	303.0	303.0	9984.5	0.0	606.1
2	9833.0	0.0	0.0	0.0	9833.0	0.0	0.0
3	757.6	0.0	303.0	303.0	151.5	0.0	606.1
4	145.4	0.0	0.0	0.0	145.4	0.0	0.0
5	612.2	0.0	303.0	303.0	6.1	0.0	606.1
6	5454.5	0.0	0.0	0.0	0.0	5454.5	0.0
7	6066.7	277.6	25.5	303.0	6.1	5454.5	606.1
8	5656.1	277.6	0.0	0.0	6.0	5372.5	0.0
9	410.6	0.0	25.5	303.0	0.1	82.0	328.5
10	5656.1	277.6	0.0	0.0	6.0	5372.5	277.6
11	1790.8	0.0	0.0	0.0	1790.8	0.0	0.0
12	7447.0	277.6	0.0	0.0	1796.9	5372.5	277.6
13	6984.3	0.0	0.0	0.0	1750.5	5233.8	0.0
14	462.6	277.6	0.0	0.0	46.4	138.7	277.6
15	182.2	0.0	0.0	0.0	45.7	136.6	0.0
16	927.2	0.0	0.0	0.0	46.4	0.0	880.9
17	1836.7	28.2	0.0	0.0	46.8	880.9	880.9
18	1789.8	0.0	0.0	0.0	46.3	871.7	871.7

Table S31. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [13], ^b [2], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
CE-101	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 263 kW ^b
S-101	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 8195.2 kW ^c
E-101	Shell and tube exchanger Discharge temperature = 90 °C ^a	A = 85.6 m ² Heat duty = 5134 kW ^b
R-201	Continuous stirred tank Vigorous agitation ^b Residence time = 2 h ^a Acetone-biomass ratio = 9:1 ^a T = 90 °C ^a P = 3 bar ^a	V = 505.6 m ³ Stirred power = 176.9 kW ^b
CE-201	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 142.6 kW ^b
SP-201	Distillation column Pressure = 101.325 kPa External reflux ratio = 0.572 Ethanol mole fraction in distillate = 0.01 Acetone mole fraction in bottoms = 0	D = 1 m Number of trays = 21 Heat duty = 56500 kW Cooling duty = 49250 kW
E-301	Shell and tube exchanger Discharge temperature = 40 °C ^a	A = 148.9 m ² Cooling duty = 7443 kW ^b
FT-301	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b Solids output = 60 wt% ^a	A = 97.35 m ² Power = 51.7 kW ^b
S-301	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 10272.5 kW ^c

S5.2 LCA and LCC

S5.2.1 LCA

Results from life cycle impact assessment are addressed in Table S32.

Table S32. LCIA characterization of Process L1 for the production of P(3HB-co-4HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.0002 m ³	0	0	0	0	0	0
Acetone	0.487 kg	0.371	1.96·10 ⁻³	9.57·10 ⁻⁶	1.84·10 ⁻²	6.26·10 ⁻⁴	4.52·10 ⁻¹
Electricity	206 kJ	0.028	1.19·10 ⁻⁴	2.60·10 ⁻⁶	6.41·10 ⁻⁴	5.26·10 ⁻⁶	7.31·10 ⁻³
Heat duty	24684 kJ	2.000	6.33·10 ⁻³	2.70·10 ⁻⁵	5.08·10 ⁻²	5.82·10 ⁻⁴	6.19·10 ⁻¹
Cooling duty	17470 kJ	0.187	7.86·10 ⁻⁴	1.64·10 ⁻⁵	4.52·10 ⁻³	6.84·10 ⁻⁵	5.02·10 ⁻²
Wastewater	0.006 m ³	0.001	1.99·10 ⁻⁵	5.56·10 ⁻⁶	4.67·10 ⁻⁴	1.22·10 ⁻⁵	2.05·10 ⁻⁴
Biowaste	1.172 kg	0.236	1.71·10 ⁻³	5.38·10 ⁻⁷	1.48·10 ⁻⁴	5.64·10 ⁻⁶	3.59·10 ⁻³
Direct emissions	1.109 kg	1.109	0	0	0	0	0
PHA	1 kg	3.931	1.09·10⁻²	6.17·10⁻⁵	7.50·10⁻²	1.30·10⁻³	1.132

S5.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S33. Also utilities and material costs are presented in Table S34. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6), distillation columns (4),

spray dryers (5) and heat exchangers (7) were employed. Equation (7) was taken from Seider et al. [4] and adapted to SI units and 2019 CEPCI index.

$$C_{pE} = 18186A^{0.42} [=] \text{€} \quad A = \text{Area} [=] \text{m}^2 \quad (7)$$

Table S33. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	CE-101	S-101	E-101	R-201	CE-201	SP-201	E-301	FT-301	S-301
C _{pi} (\$)	479,147	364,010	45,554	122,381	398,721	42,140	57,481	26,198	356,372
C_{Tci} (€)	10,083,358								

Table S34. Utilities and materials annual costs summary. Costs adopted from: ^a [4], ^b [5], ^c [6]. Heat duty costs were estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers. Cooling duty costs were estimated considering the utilization of cooling water and a ΔT of 15K.

Item	Water ^a	Acetone ^b	Electricity ^a	Heat duty ^a	Cooling duty ^a	Wastewater ^a	Biowaste ^c
Cost (\$/y)	4,070	60,842,099	371,428	55,297,782	696,071	188,831	5,420,000
U+M (€/y)	111,076,589						

S5.3 Sensitivity analysis

Results from life cycle impact assessment considering oil (A) and natural gas (B) are addressed in Table S35 and Table S36 respectively.

Table S35. LCIA characterization of Process L1 for the production of P(3HB-co-4HB), considering oil (A) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f	
		kg CO ₂ eq	kg SO ₂ eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Water	0.0002	m ³	0	0	0	0	0	
Acetone	0.487	kg	0.371	1.96·10 ⁻³	9.57·10 ⁻⁶	1.84·10 ⁻²	6.26·10 ⁻⁴	0.452
Electricity	206	kJ	0.028	1.19·10 ⁻⁴	2.60·10 ⁻⁶	6.41·10 ⁻⁴	5.26·10 ⁻⁶	0.007
Heat duty	24684	kJ	2,25	4,56·10 ⁻³	4,29·10 ⁻⁶	3,10·10 ⁻²	9,64·10 ⁻⁴	0.781
Cooling duty	17470	kJ	0.187	7.86·10 ⁻⁴	1.64·10 ⁻⁵	4.52·10 ⁻³	6.84·10 ⁻⁵	0.050
Wastewater	0.006	m ³	0.001	1.99·10 ⁻⁵	5.56·10 ⁻⁶	4.67·10 ⁻⁴	1.22·10 ⁻⁵	0
Biowaste	1.172	kg	0.236	1.71·10 ⁻³	5.38·10 ⁻⁷	1.48·10 ⁻⁴	5.64·10 ⁻⁶	0.004
Direct emissions	1.109	kg	1.109	0	0	0	0	0
PHA	1	kg	4,181	9,15·10⁻³	3,90·10⁻⁵	5,52·10⁻²	1,68·10⁻³	1,294

Table S36. LCIA characterization of Process L1 for the production of P(3HB-co-4HB), considering natural gas (B) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f	
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq	
Water	0.0002	m ³	0	0	0	0	0	
Acetone	0.487	kg	0.371	1.96·10 ⁻³	9.57·10 ⁻⁶	1.84·10 ⁻²	6.26·10 ⁻⁴	0.452
Electricity	206	kJ	0.028	1.19·10 ⁻⁴	2.60·10 ⁻⁶	6.41·10 ⁻⁴	5.26·10 ⁻⁶	0.007
Heat duty	24684	kJ	0,805	9,61·10 ⁻⁴	3,91·10 ⁻⁶	5,56·10 ⁻³	3,11·10 ⁻⁴	0.304
Cooling duty	17470	kJ	0.187	7.86·10 ⁻⁴	1.64·10 ⁻⁵	4.52·10 ⁻³	6.84·10 ⁻⁵	0.050
Wastewater	0.006	m ³	0.001	1.99·10 ⁻⁵	5.56·10 ⁻⁶	4.67·10 ⁻⁴	1.22·10 ⁻⁵	0
Biowaste	1.172	kg	0.236	1.71·10 ⁻³	5.38·10 ⁻⁷	1.48·10 ⁻⁴	5.64·10 ⁻⁶	0.004
Direct emissions	1.109	kg	1.109	0	0	0	0	0
PHA	1	kg	2,736	5,56·10⁻³	3,86·10⁻⁵	2,97·10⁻²	1,03·10⁻³	0,817

S6. Process L2

S6.1 Process design

Mass balance is presented in Table S37. Furthermore, process specifications and design outcomes are detailed in Table S38.

Table S37. Mass balance for P(3HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB)		NPCM	Water	Salts	SDS	Solids
		Recovered	Non-recovered					
1	1196.6	0.0	4.5	4.5	1136.4	51.1	0.0	9.1
2	1181.4	0.0	0.0	0.0	1130.6	50.9	0.0	0.0
3	15.2	0.0	4.5	4.5	5.8	0.3	0.0	9.1
4	15.2	0.0	4.5	4.5	5.8	0.3	0.0	9.1
5	1137.5	0.0	0.0	0.0	1136.4	0.0	1.1	0.0

Stream	Total	P(3HB)		NPCM	Water	Salts	SDS	Solids
		Recovered	Non-recovered					
6	1152.7	4.5	0.1	4.5	1142.2	0.3	1.1	9.1
7	1147.1	0.0	0.1	4.5	1141.0	0.3	1.1	4.6
8	5.6	4.5	0.0	0.0	1.1	0.0	0.0	4.5
9	557.4	0.0	0.0	0.0	557.4	0.0	0.0	0.0
10	563.0	4.5	0.0	0.0	558.5	0.0	0.0	4.5
11	279.3	0.0	0.0	0.0	279.3	0.0	0.0	0.0
12	283.7	4.5	0.0	0.0	279.2	0.0	0.0	4.5
13	278.2	0.0	0.0	0.0	278.2	0.0	0.0	0.0
14	561.9	4.5	0.0	0.0	557.4	0.0	0.0	4.5
15	556.3	0.0	0.0	0.0	556.3	0.0	0.0	0.0
16	5.6	4.5	0.0	0.0	1.1	0.0	0.0	4.5
19	1.1	0.0	0.0	0.0	1.1	0.0	0.0	0.0
20	4.5	4.5	0.0	0.0	0.0	0.0	0.0	4.5

Table S38. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [2], ^b [14], ^c [15], ^d [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
FT-101	Microfiltration $\Delta P = 3000 \text{ kPa}^a$ $q_0/A = 55 \text{ mL}\cdot\text{s}^{-1}\cdot\text{m}^{-2a}$ Solids output = 60 wt% ^a	$A = 3.19 \text{ m}^2$ Power = 8.3 kW ^a
E-101	Shell and tube exchanger Discharge temperature = 60 °C ^b	$A = 15.83 \text{ m}^2$ Heat duty = 1900 kW ^b
E-102	Shell and tube exchanger Discharge temperature = 60 °C ^b	$A = 1188.69 \text{ m}^2$ Heat duty = 190190 kW ^b
R-201	Continuous stirred tank Vigorous agitation ^a Residence time = 2 h ^b SDS concentration in R-201 = 0.1 wt% ^{bc} $T = 60 \text{ °C}^b$	$V = 96.1 \text{ m}^3$ Stirred power = 33.6 kW ^a
CE-201	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 1.9 kW ^b
R-301	Continuous stirred tank Mild agitation ^a Residence time = 0.5 h ^b	$V = 11.6 \text{ m}^3$ Stirred power = 1.3 kW ^a
CE-201	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 23 kW ^b
R-302	Continuous stirred tank Mild agitation ^a Residence time = 0.5 h ^b Solids content = 1 wt%	$V = 11.7 \text{ m}^3$ Stirred power = 1.3 kW ^a
CE-201	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 1.9 kW ^b
S-301	Spray dryer Solids output = 99 wt% Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 60.2 kW ^c

S6.2 LCA and LCC

S6.2.1 LCA

Results from life cycle impact assessment are addressed in Table S39.

Table S39. LCIA characterization of Process L2 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.314 m ³	0	0	0	0	0	0
SDS	0.252 kg	0.366	1.91·10 ⁻³	1.22·10 ⁻⁵	5.71·10 ⁻²	1.74·10 ⁻⁴	0.308
Electricity	1372 kJ	0.184	7.91·10 ⁻⁴	1.73·10 ⁻⁵	4.26·10 ⁻³	3.74·10 ⁻⁵	0.049
Heat duty	43847 kJ	3.550	1.12·10 ⁻²	4.80·10 ⁻⁵	9.03·10 ⁻²	1.03·10 ⁻³	1.100
Wastewater _r	0.316 m ³	0.059	1.05·10 ⁻³	2.93·10 ⁻⁴	2.46·10 ⁻²	6.41·10 ⁻⁴	0.011
PHA	1 kg	4.159	1.50·10⁻²	3.71·10⁻⁴	1.76·10⁻¹	1.88·10⁻³	1.467

S6.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S40. Also utilities and material costs are presented in Table S41. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6), spray dryers (5) and heat exchangers (7) were employed.

Table S40. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	FT-201	E-101	E-102	R-201	CE-201	R-301	CE-301	R-302	CE-302	S-301
C _{pi} (\$)	858	3,447	21,142	55,308	266,365	20,421	266,285	20,494	266,285	140,025

Unit	FT-201	E-101	E-102	R-201	CE-201	R-301	CE-301	R-302	CE-302	S-301
C_{TCI} (€)	5,401,665									

Table S41. Utilities and materials annual costs summary. Costs adopted from: ^a [5], ^b [9]. Heat duty costs was estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers.

Item	Water ^a	SDS ^b	Electricity ^a	Heat duty ^a	Wastewater ^a
Cost (\$/y)	126,037	271,610	39,620	606,577	154,671
U+M (€/y)	1,078,663				

S6.3 Sensitivity analysis

Mass balances and process specifications and design outcomes resulting of introducing a SDS recovery unit by crystallization are collected in Table S42 and Table S43 respectively.

Table S42. Mass balance for P(3HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB)		NPCM	Water	Salts	SDS	Solids
		Recovered	Non-recovered					
21	1147.1	0.0	0.1	4.5	1141.0	0.3	1.1	4.6
22	1147.1	0.0	0.1	4.5	1141.0	0.3	1.1	4.6
23	1.5	0.0	0.0	0.0	0.6	0.1	0.9	0.9
24	1145.6	0.0	0.1	4.5	1140.5	0.2	0.2	0.2

Table S43. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [2], ^b [12].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
E-401	Shell and tube exchanger Discharge temperature = 9 °C ^b	A = 7.57 m ² Cooling duty = 1514 kW ^b
R-401	Continuous stirred tank Mild agitation ^a Residence time = 1 h ^b SDS recovery yield = 80% ^b	V = 47.8 m ³ Stirred power = 5.5 kW ^a
FT-401	Microfiltration $\Delta P = 3000$ kPa ^a $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^a Solids output = 60 wt% ^a	A = 241 m ² Power = 8.0 kW ^a

Results from life cycle impact assessment are addressed in Table S44.

Table S44. LCIA characterization of Process L2 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit		GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.314	m3	0	0	0	0	0	0
SDS	0.252	kg	0.073	3.82·10 ⁻⁴	2.44·10 ⁻⁶	1.14·10 ⁻²	3.48·10 ⁻⁵	0.062
Electricity	1372	kJ	0.219	9.40·10 ⁻⁴	2.06·10 ⁻⁵	5.06·10 ⁻³	4.44·10 ⁻⁵	0.058
Heat duty	43847	kJ	3.550	1.12·10 ⁻²	4.80·10 ⁻⁵	9.03·10 ⁻²	1.03·10 ⁻³	1.100
Cooling duty	29062	kJ	0.310	1.31·10 ⁻³	2.72·10 ⁻⁵	7.52·10 ⁻³	1.14·10 ⁻⁴	0.083
Wastewater	0.316	m3	0.059	1.05·10 ⁻³	2.93·10 ⁻⁴	2.46·10 ⁻²	6.41·10 ⁻⁴	0.011
PHA	1	kg	4,184	1,44·10⁻²	2,58·10⁻⁴	0,128	1,57·10⁻³	1,309

S6.4 Improvement actions

S6.4.1 Residual heat integration

E-101 and E-102 were simulated in Aspen HYSYS (Aspen Technology, Inc., US) considering as hot stream a vapor at atmospheric pressure and 115°C, which is produced within canning food processing.

Table S45. Process specification and design outcomes of E-101 and E-102

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
E-101	Shell and tube exchanger 1:2 Hot stream flow = 45 kg·h ⁻¹ Hot stream inlet temperature = 115 °C Cold stream flow = 631.3 kg·h ⁻¹ Cold stream inlet temperature = 20 °C Cold stream outlet temperature = 60 °C Pressure = 101.3 kPa	Hot stream outlet temperature = 80 °C A = 60.32 m ² Heat duty = 30 kW
E-102	Shell and tube exchanger 1:2 Hot stream flow = 3375 kg·h ⁻¹ Hot stream inlet temperature = 115 °C Cold stream flow = 47396 kg·h ⁻¹ Cold stream inlet temperature = 20 °C Cold stream outlet temperature = 60 °C Pressure = 101.3 kPa	Hot stream outlet temperature = 80 °C A = 60.32 m ² Heat duty = 2223 kW

Results from life cycle impact assessment considering the residual vapor stream integration are addressed in Table S46.

Table S46. LCIA characterization of Process L2 for the production of P(3HB), considering heat integration including each life cycle inventory item (LCI) item contribution to each impact

category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.314 m ³	0	0	0	0	0	0
SDS	0.252 kg	0.366	1.91·10 ⁻³	1.22·10 ⁻⁵	5.71·10 ⁻²	1.74·10 ⁻⁴	0.308
Electricity	1372 kJ	0.184	7.91·10 ⁻⁴	1.73·10 ⁻⁵	4.26·10 ⁻³	3.74·10 ⁻⁵	0.049
Heat duty	1157 kJ	0.094	2.95·10 ⁻⁴	1.27·10 ⁻⁶	2.38·10 ⁻³	2.72·10 ⁻⁵	0.029
Wastewater	0.316 m ³	0.059	1.05·10 ⁻³	2.93·10 ⁻⁴	2.46·10 ⁻²	6.41·10 ⁻⁴	0.011
PHA	1 kg	0,702	4,05·10⁻³	3,24·10⁻⁴	0,088	8,80·10⁻⁴	0,396

S7. Process L3

S7.1 Process design

A simplified process flow diagram for P(3HB) downstream processing is shown in Figure S5. Mass balance is presented in Table S47. Furthermore, process specifications and design outcomes are detailed in Table S48.

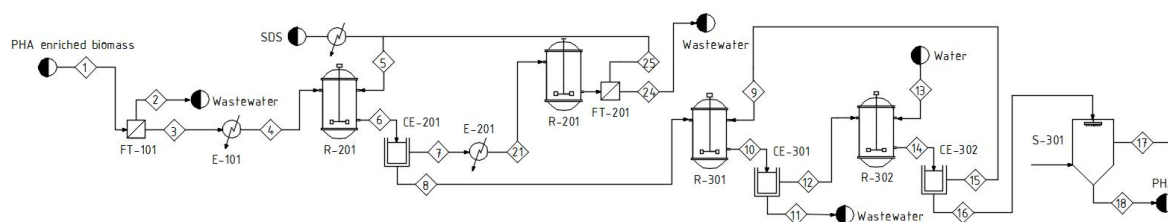


Figure S5. Scheme of L3 process.

Table S47. Mass balance for P(3HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB)		NPCM	Water	Salts	SDS	Solids
		Recovered	Non-recovered					
1	113.3	0.0	4.5	1.9	106.8	0.0	0.0	6.5
2	113.3	0.0	4.5	1.9	106.8	0.0	0.0	6.5
3	5.8	0.0	0.0	0.0	0.0	5.8	0.0	0.0
4	119.1	4.0	0.5	1.9	106.8	5.8	0.0	6.5
5	109.6	0.0	0.0	1.7	102.3	5.6	0.0	1.7
6	9.6	4.0	0.5	0.2	4.5	0.2	0.0	4.8
7	86.0	0.0	0.0	0.0	84.2	0.0	1.9	0.0
8	95.6	4.5	0.0	0.2	88.7	0.2	1.9	4.8
9	89.6	0.0	0.0	0.0	87.5	0.2	1.8	0.0
10	6.0	4.5	0.0	0.2	1.2	0.0	0.0	4.8
11	100.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
12	106.0	4.5	0.0	0.2	101.2	0.0	0.0	4.8

Stream	Total	P(3HB)		NPCM	Water	Salts	SDS	Solids
		Recovered	Non-recovered					
13	100.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
14	6.0	4.5	0.0	0.2	1.2	0.0	0.0	4.8
15	100.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
16	106.0	4.5	0.0	0.2	101.2	0.0	0.0	4.8
17	100.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0
18	6.0	4.5	0.0	0.2	1.2	0.0	0.0	4.8
19	1.1	0.0	0.0	0.0	1.1	0.0	0.0	0.0
20	4.8	4.5	0.0	0.2	0.0	0.0	0.0	4.8
21	109.6	0.0	0.0	1.7	102.3	5.6	0.0	1.7
23	109.6	0.0	0.0	1.7	102.3	5.6	0.0	1.7
24	102.1	0.0	0.0	1.7	99.3	1.1	0	0.0
25	7.5	0.0	0.0	0.0	2.9	4.5	0.0	4.5

Table S48. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [2], ^b [12,16], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
E-101	Shell and tube exchanger Discharge temperature = 55 °C ^b	A = 0.91 m ² Heat duty = 164 kW ^b
R-201	Continuous stirred tank Vigorous agitation ^a Residence time = 0.25 h ^b SDS:NCPM ratio = 3:1 ^b T = 55 °C ^b	V = 1.2 m ³ Stirred power = 0.4 kW ^a
CE-201	Basket centrifuge ^a Solids output = 50 wt% ^a	Power = 3.3 kW ^b
R-202	Continuous stirred tank Vigorous agitation ^a Residence time = 0.5 h ^b NaClO:NCPM ratio = 8:1 ^b T = 55 °C ^b	V = 2 m ³ Stirred power = 0.7 kW ^a
CE-202	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 3.3 kW ^b
E-201	Shell and tube exchanger Discharge temperature = 9 °C ^b	A = 0.56 m ² Cooling duty = 87 kW ^b
R-203	Continuous stirred tank Mild agitation ^a Residence time = 1 h ^b SDS recovery yield = 80% ^b	V = 4.6 m ³ Stirred power = 0.5 kW ^a
FT-201	Microfiltration $\Delta P = 3000$ kPa ^a $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^a Solids output = 60 wt% ^a	A = 1.57 m ² Power = 0.7 kW ^a
R-301	Continuous stirred tank Mild agitation ^a Residence time = 0.5 h ^a	V = 2.2 m ³ Stirred power = 0.3 kW ^a
CE-301	Basket centrifuge ^a	Power = 2.1 kW ^b

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
	Solids output = 80 wt% ^a	
R-302	Continuous stirred tank Mild agitation ^a Residence time = 0.5 h ^a Solids content = 5 wt% ^a	V = 2.2 m ³ Stirred power = 0.3 kW ^a
CE-302	Basket centrifuge ^a Solids output = 80 wt% ^a	Power = 2.1 kW ^b
S-301	Spray dryer Solids output = 99 wt% Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 64.6 kW ^c

S7.2 LCA and LCC

S7.2.1 LCA

Results from life cycle impact assessment are addressed in

Table **S49**.

Table S49. LCIA characterization of Process L3 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO ₂ eq	kg SO ₂ eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Water	0.039 m ³	0	0	0	0	0	0
SDS	0.303 kg	0.440	2.29·10 ⁻³	1.46·10 ⁻⁵	6.87·10 ⁻²	2.10·10 ⁻⁴	0.370
NaClO	0.414 kg	0.320	1.49·10 ⁻³	1.74·10 ⁻⁵	3.06·10 ⁻²	1.77·10 ⁻⁴	0.082
Electricity	237 kJ	0.032	1.37·10 ⁻⁴	2.99·10 ⁻⁶	7.37·10 ⁻⁴	6.47·10 ⁻⁶	0.008
Heat duty	4380 kJ	0.355	1.12·10 ⁻³	4.79·10 ⁻⁶	9.02·10 ⁻³	1.03·10 ⁻⁴	0.110
Cooling duty	1659 kJ	0.018	7.47·10 ⁻⁵	1.55·10 ⁻⁶	4.29·10 ⁻⁴	6.50·10 ⁻⁶	0.005
Wastewater	0.065 m ³	0.012	2.15·10 ⁻⁴	6.02·10 ⁻⁵	5.06·10 ⁻³	1.32·10 ⁻⁴	0.002
PHA	1 kg	1.177	5.33·10⁻³	1.02·10⁻⁴	1.15·10⁻¹	6.35·10⁻⁴	0.577

S7.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S50. Also utilities and material costs are presented in Table S51. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6), spray dryers (5) and heat exchangers (7) were employed.

Table S50. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	E-101	R-201	CE-201	R-202	CE-202	E-201	R-203	FT-201	R-301	CE-301	R-302	CE-302	S-301
C _{pi} (\$)	7,251	9,198	319,456	11,026	291,390	5,887	14,589	453	10,785	291,390	10,066	291,390	144,693
C_{Tci} (€)	6,743,242												

Table S51. Utilities and materials annual costs summary. Costs adopted from: ^a [5], ^b [9]. Heat duty costs was estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers.

Item	Water ^a	SDS ^b	NaClO ^b	Electricity ^a	Heat duty ^a	Cooling duty ^a	Wastewater ^a
Cost (\$/y)	15,500	327,101	709,714	6,883	258,962	12,367	31,769
U+M (€/y)	1,214,936						

S7.3 Sensitivity analysis

Results from life cycle impact assessment without SDS recovery unit are addressed in Table S52.

Table S52. LCIA characterization of Process L3 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a kg CO ₂ eq	TA ^b kg SO ₂ eq	FE ^c kg P eq	HT ^d kg 1,4-DB eq	FEX ^e kg 1,4-DB eq	FD ^f kg oil eq
Water	0.039 m ³	0	0	0	0	0	0
SDS	1.293 kg	1.881	9.79·10 ⁻³	6.24·10 ⁻⁵	2.94·10 ⁻¹	8.98·10 ⁻⁴	1.582
NaClO	0.414 kg	0.320	1.49·10 ⁻³	1.74·10 ⁻⁵	3.06·10 ⁻²	1.77·10 ⁻⁴	0.082
Electricity	214 kJ	0.029	1.23·10 ⁻⁴	2.69·10 ⁻⁶	6.64·10 ⁻⁴	5.83·10 ⁻⁶	0.008
Heat duty	4380 kJ	0.355	1.12·10 ⁻³	4.79·10 ⁻⁶	9.02·10 ⁻³	1.03·10 ⁻⁴	0.110
Wastewater _r	0.065 m ³	0.012	2.15·10 ⁻⁴	6.02·10 ⁻⁵	5.06·10 ⁻³	1.32·10 ⁻⁴	0.002
PHA	1 kg	2.597	1.27·10⁻²	1.47·10⁻⁴	3.39·10⁻¹	1.32·10⁻³	1.783

S8. Process L4

S8.1 Process design

A simplified process flow diagram for P(3HB) downstream processing is shown in Figure S6. Mass balance is presented in

Table S53. Furthermore, process specifications and design outcomes are detailed in

Table S54.

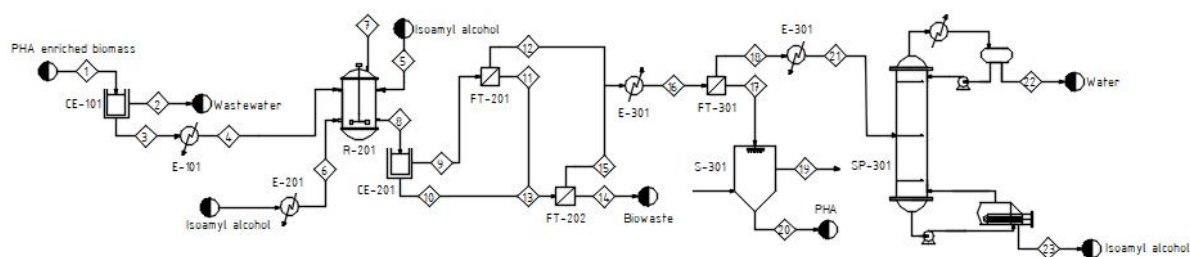


Figure S6. Scheme of L4 process.

Table S53. Mass balance for P(3HB) downstream processing, expressed in tons per day.

Stream	Total	P(3HB)		NPCM	Water	Isoamyl alcohol	Solids
		Recovered	Non-recovered				
1	3318.9	0.0	303.0	129.9	2886.0	0.0	432.9

Stream	Total	P(3HB)		NPCM	Water	Isoamyl alcohol	Solids
		Recovered	Non-recovered				
2	1587.3	0.0	0.0	0.0	1587.3	0.0	0.0
3	1731.6	0.0	303.0	129.9	1298.7	0.0	432.9
4	1731.6	0.0	303.0	129.9	1298.7	0.0	432.9
5	26181.8	0.0	0.0	0.0	0.0	26181.8	0.0
6	5423.1	0.0	0.0	0.0	0.0	5423.1	0.0
7	2450.8	0.0	0.0	0.0	370.2	2080.6	0.0
8	30885.7	0.0	303.0	129.9	928.5	29524.3	432.9
9	23099.3	0.0	227.3	32.5	696.4	22143.2	259.7
10	7786.4	0.0	75.8	97.4	232.1	7381.1	173.2
11	5799.2	0.0	56.8	32.5	174.1	5535.8	89.3
12	17300.2	0.0	170.5	0.0	522.3	16607.4	170.5
13	13585.6	0.0	132.6	129.9	406.2	12916.9	262.4
14	217.0	0.0	0.4	129.9	52.2	34.6	130.2
15	13368.5	0.0	132.2	0.0	354.0	12882.3	132.2
16	30668.7	0.0	302.7	0.0	876.3	29489.7	302.7
17	504.5	0.0	302.7	0.0	5.8	196.0	302.7
18	30164.2	0.0	0.0	0.0	870.4	29293.8	0.0
19	198.7	0.0	0.0	0.0	5.7	193.0	0.0
20	305.7	0.0	302.7	0.0	0.1	3.0	302.7
21	30164.2	0.0	0.0	0.0	870.4	29293.8	0.0
22	1239.4	0.0	0.0	0.0	1176.0	63.4	0.0
23	31375.6	0.0	0.0	0.0	64.6	31311.0	0.0

Table S54. Process specifications and design outcomes. Specifications and estimations adopted from: ^a [17], ^b [2], ^c [3].

Unit	Operating Conditions/Design Basis	Outcomes/Process Design
CE-101	Basket centrifuge ^a Solids output = 25 wt% ^a	Power = 601.3 kW ^b
E-101	Shell and tube exchanger Discharge temperature = 90 °C ^a	A = 84.39 m ² Heat duty = 5907 kW ^b
R-201	Continuous stirred tank Vigorous agitation ^b Residence time = 10 min ^a Solvent-biomass ratio = 75:1 ^a T = 115 °C ^a	V = 214.5 m ³ Stirred power = 75.1 kW ^b
CE-201	Hydrocyclone ^a Upper stream (75% of the feed stream) contains 25% solids of feed stream ^a	Power = 142.6 kW ^b
FT-201	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b	A = 1120 m ² Power = 160.4 kW ^b
FT-202	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b Solids output = 60 wt% ^a	A = 46 m ² Power = 120.1 kW ^b
E-201	Shell and tube exchanger Discharge temperature = 90 °C ^a	A = 908 m ² Heat duty = 40893.2 kW ^b
SP-201	Distillation column Pressure = 101.325 kPa External reflux ratio = 1.710 Isoamyl alcohol mole fraction in distillate = 0.0109 Water mole fraction in bottoms = 0.01	D = 1 m Number of trays = 6 Heat duty = 102768.4 kW Cooling duty = 103245.4 kW
E-202	Shell and tube exchanger Discharge temperature = 135 °C ^a	A = 718 m ² Heat duty = 32329.3 kW ^b
E-301	Shell and tube exchanger Discharge temperature = 40 °C ^a	A = 934 m ² Cooling duty = 67277 kW ^b
FT-301	Microfiltration ^a $\Delta P = 300$ kPa ^b $q_0/A = 55$ mL·s ⁻¹ ·m ⁻² ^b Solids output = 60 wt% ^a	A = 97.35 m ² Power = 51.7 kW ^b
E-302	Shell and tube exchanger Discharge temperature = 90 °C ^a	A = 718 m ² Heat duty = 40893 kW ^b
S-301	Spray dryer ^a Solids output = 99 wt% ^a Heat duty consumption = 4.87 GJ·t ⁻¹ water evaporated ^c	Heat duty = 11201.4 kW ^c

S8.2 LCA and LCC

S8.2.1 LCA

Results from life cycle impact assessment are addressed in Table S55.

Table S55. LCIA characterization of Process L4 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b

Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit		GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Isoamyl alcohol	0.962	kg	3.6	1.43·10 ⁻²	1.06·10 ⁻⁴	1.08·10 ⁻¹	9.17·10 ⁻⁴	1.890
Electricity	353	kJ	0.0469	2.01·10 ⁻⁴	4.45·10 ⁻⁶	1.04·10 ⁻³	9.15·10 ⁻⁶	0.012
Heat duty	73582	kJ	5.96	1.89·10 ⁻²	8.05·10 ⁻⁵	1.51·10 ⁻¹	1.73·10 ⁻³	1.84
Cooling duty	29177	kJ	0.312	1.31·10 ⁻³	2.73·10 ⁻⁵	7.54·10 ⁻³	1.14·10 ⁻⁴	0.084
Wastewater	0.009	m3	0.00167	2.98·10 ⁻⁵	8.34·10 ⁻⁶	7.01·10 ⁻⁴	1.83·10 ⁻⁵	0
Biowaste	0.710	kg	0.143	1.03·10 ⁻³	3.26·10 ⁻⁷	8.99·10 ⁻⁵	3.42·10 ⁻⁶	0.002
Direct emissions	1.578	kg	1.578	0	0	0	0	0
PHA	1	kg	10.064	0.036	2.27·10⁻⁴	0.268	2.79·10⁻³	3.829

S8.2.2 LCC

The total capital investment (C_{TCI}), including each unit price, is summarized in Table S56. Also utilities and material costs are presented in Table S57. Cost correlations for microfiltration (1), vessels and stirrers (2), basket centrifuges (6), distillation columns (4), spray dryers (5) and heat exchangers (7) were employed. Equation (7) was taken from Seider et al. [4].

$$C_{pE} = 7,030A^{0.42} [=] \$ A [=] ft^2 \quad CEPCI = 567 \quad (8)$$

Table S56. Process total capital investment summary, applying a recommended Lang Factor of 5.03, characteristic from a solids-fluids processing plant [4], and 2019 CEPCI index of 607.5.

Unit	CE-101	E-101	R-201	CE-201	FT-201	FT-202	E-201	SP-201	E-202	E-301	FT-301	S-301
C_{pi} (\$)	434,030	48,523	86,695	434,031	51,858	13,169	131,663	36,670	36,700	133,211	30,607	378,163
C_{TCI} (€)	10,446,584											

Table S57. Utilities and materials annual costs summary. Costs adopted from: ^a [4], ^b [5], ^c [6], ^d Isoamyl alcohol is a byproduct of ethanol biorefinery and its cost is assumed as 0.

Heat duty costs were estimated considering the utilization of low pressure vapor and 2 kg of vapor per kg of water evaporated in spray dryers. Cooling duty costs were estimated considering the utilization of cooling water and a ΔT of 15K.

Item	Isoamyl alcohol ^d	Electricity ^a	Heat duty ^a	Cooling duty ^a	Wastewater ^a	Biowaste ^c
Cost (\$/y)	0	693,030	31,579,137	1,267,646	307,831	3,581,192
U+M (€/y)			34,044,072			

S8.3 Sensitivity analysis

Results from life cycle impact assessment considering oil (A) and natural gas (B) are addressed in Table S58 and Table S59 respectively.

Table S58. LCIA characterization of Process L4 for the production of P(3HB), considering oil (A) as heat source, including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Isoamyl alcohol	0.962 kg	3.600	1.43·10 ⁻²	1.06·10 ⁻⁴	1.08·10 ⁻¹	9.17·10 ⁻⁴	1.890
Electricity	353 kJ	0.047	2.01·10 ⁻⁴	4.45·10 ⁻⁶	1.04·10 ⁻³	9.15·10 ⁻⁶	0.012
Heat duty	73582 kJ	4.980	1.01·10 ⁻²	9.49·10 ⁻⁶	6.85·10 ⁻²	2.13·10 ⁻³	1.730
Cooling duty	29177 kJ	0.509	2.17·10 ⁻³	4.52·10 ⁻⁵	1.25·10 ⁻²	1.89·10 ⁻⁴	0.138
Wastewater	0.009 m3	0.002	2.98·10 ⁻⁵	8.34·10 ⁻⁶	7.01·10 ⁻⁴	1.83·10 ⁻⁵	0
Biowaste	0.710 kg	0.143	1.03·10 ⁻³	3.26·10 ⁻⁷	8.99·10 ⁻⁵	3.42·10 ⁻⁶	0.002
Direct emissions	1.578 kg	1.578	0	0	0	0	0
PHA	1 kg	10.064	0.036	2.27·10⁻⁴	0.268	2.79·10⁻³	3.829

Table S59. LCIA characterization of Process L4 for the production of P(3HB), considering natural gas (B) as heat source, including each life cycle inventory item (LCI) item

contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit		GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
			kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Isoamyl alcohol	0.962	kg	3.600	1.43·10 ⁻²	1.06·10 ⁻⁴	1.08·10 ⁻¹	9.17·10 ⁻⁴	1.890
Electricity	353	kJ	0.047	2.01·10 ⁻⁴	4.45·10 ⁻⁶	1.04·10 ⁻³	9.15·10 ⁻⁶	0.012
Heat duty	73582	kJ	3.880	3.85·10 ⁻³	2.04·10 ⁻⁵	2.40·10 ⁻²	2.63·10 ⁻⁵	1.450
Cooling duty	29177	kJ	0.312	1.31·10 ⁻³	2.73·10 ⁻⁵	7.54·10 ⁻³	1.14·10 ⁻⁴	0.084
Wastewater	0.009	m3	0.002	2.98·10 ⁻⁵	8.34·10 ⁻⁶	7.01·10 ⁻⁴	1.83·10 ⁻⁵	0
Biowaste	0.710	kg	0.143	1.03·10 ⁻³	3.26·10 ⁻⁷	8.99·10 ⁻⁵	3.42·10 ⁻⁶	0.002
Direct emissions	1.578	kg	1.578	0	0	0	0	0
PHA	1	kg	10.064	0.036	2.27·10⁻⁴	0.268	2.79·10⁻³	3.829

S8.4 Improvement actions

S8.4.1 Heat integration

Hot and cold streams summary as well as PTA calculation are showed in Table S60 and Table S61 respectively.

Table S60. Hot and cold streams summary including their temperature, heat capacity and enthalpy.

Stream (Flow diagram)	T _{in} (K)	T _{out} (K)	MCp (kW/K)	Q (kW)
H1 (15)	388	318	961	67,277
C1 (3)	298	368	84	-5,907
C2 (20)	318	363	909	-40,893
C3 (23)	403	408	6466	-32,329

Table S61. PTA calculation of Process L4 hot and cold streams considering a ΔT_{\min} of 10K..

i	H1	C1	C2	C3	Col. A	T _{int} (K)	MCp _{int} (kW/K)	Q _{int} (kW)	Q _{cas} (kW)	R _{cas} (kW)
0						413	0	0	0	32,329
1						408	6,466	32,329	-32,329	0
2						383	-961	-24,028	-8,302	24,028
3						373	-877	-8,767	465	32,795
4						368	32	160	305	32,635
5						323	32	1441	-1,136	31,193
6						313	-877	-8,767	7,631	39,961
7						303	84	844	6,787	39,117

Proposed heat exchanges are summarized in Table S62.

Table S62. Process L4 heat integration.

Heat exchange	T _{out} (K)	Q (kW)
C3-Utilities	Stream completed (408 K)	32,329
C2-H1	Cold stream completed Hot stream = 382 K	40,893
C1-H1	Cold stream completed Hot stream = 345 K	5,907
Utilities-H1	Hot stream completed	20,477

Results from life cycle impact assessment considering heat integration are addressed in Table S63.

Table S63. LCIA characterization of Process L3 for the production of P(3HB), including each life cycle inventory item (LCI) item contribution to each impact category. ^a IPCC GWP 100a, ^b Terrestrial acidification, ^c Freshwater eutrophication, ^d Human toxicity, ^e Freshwater ecotoxicity, ^f Fossil depletion.

LCI	Unit	GWP ^a	TA ^b	FE ^c	HT ^d	FEX ^e	FD ^f
		kg CO2 eq	kg SO2 eq	kg P eq	kg 1,4-DB eq	kg 1,4-DB eq	kg oil eq
Isoamyl alcohol	0.962 kg	1.800	7.15·10 ⁻³	5.30·10 ⁻⁵	5.40·10 ⁻²	4.59·10 ⁻⁴	0,945
Electricity	353 kJ	0.047	2.01·10 ⁻⁴	4.45·10 ⁻⁶	1.04·10 ⁻³	9.15·10 ⁻⁶	0,012
Heat duty	4134 kJ	3.311	1.06·10 ⁻²	4.52·10 ⁻⁵	8.49·10 ⁻²	9.77·10 ⁻⁴	1,038
Cooling duty	36633 kJ	0.387	1.65·10 ⁻³	3.44·10 ⁻⁵	9.50·10 ⁻³	1.44·10 ⁻⁴	0,105
Wastewater	0.009 m ³	0.002	2.98·10 ⁻⁵	8.34·10 ⁻⁶	7.01·10 ⁻⁴	1.83·10 ⁻⁵	3,07·10 ⁻⁴
Biowaste	0.710 kg	0.143	1.03·10 ⁻³	3.26·10 ⁻⁷	8.99·10 ⁻⁵	3.42·10 ⁻⁶	2,17·10 ⁻³
Direct emissions	1.578 kg	1.578	0	0	0	0	0
PHA	1 kg	10.064	0.036	2.27·10⁻⁴	0.268	2.79·10⁻³	3.829

S9. Sensitivity analysis

Results of sensitivity analysis to recovery yield uncertainty are displayed on Table S63, Figure S7 and Figure S8.

Table S64. Results of uncertainty analysis to extraction yield in each scenario sensitivity analysis (TRL<6), considering a variation ±5% in recovery yield.

GWP	TA	FE	HT	FEX	FD
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Yield	-5%	5%	-5%	5%	-5%	5%	-5%	5%	-5%	5%	-5%	5%
H3	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
H4 A	7%	-2%	6%	-5%	6%	-6%	6%	-5%	7%	-6%	6%	-5%
H4 B	7%	-1%	7%	-6%	6%	-6%	7%	-6%	8%	-6%	6%	-5%
L1 A	3%	-3%	5%	-4%	4%	-4%	3%	-3%	3%	-3%	3%	-3%
L1 B	3%	-2%	5%	-4%	4%	-4%	2%	-2%	2%	-2%	2%	-2%
L2	5%	-2%	5%	-2%	5%	-2%	5%	-2%	5%	-2%	5%	-2%
L3	5%	-5%	5%	-5%	2%	-9%	4%	-4%	2%	-9%	3%	-2%

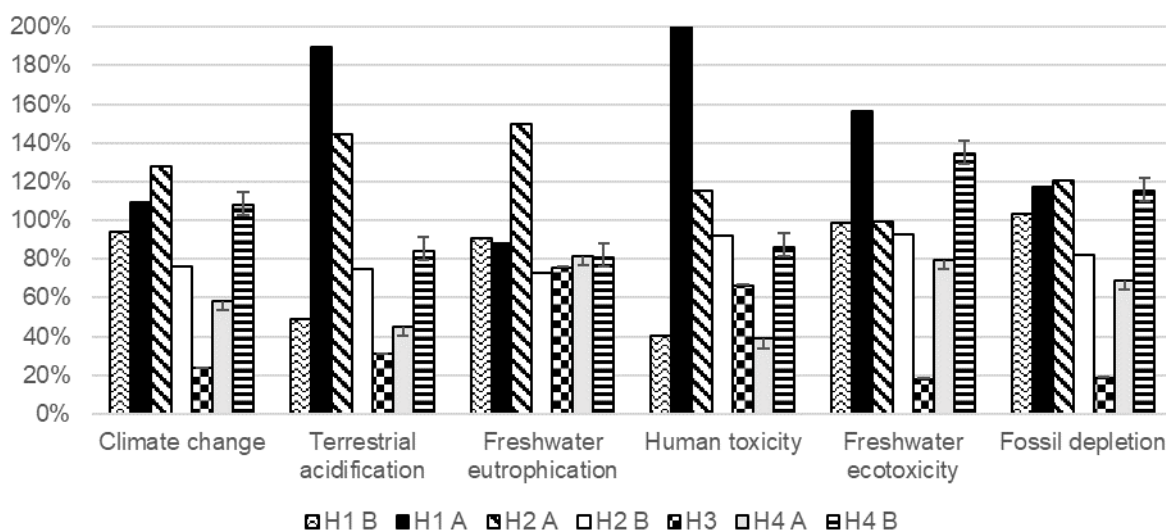


Figure S7. Variation of LCIA on sensitivity analysis to high-grade PHA processes, being 100% each baseline process. H1 A, H4 A employ oil as source for heat production while option B employ natural gas. H2 A and H2 B employ Polish and Swedish electricity mix respectively. H3 uses SDS as surfactant and includes a crystallization unit. Error bars represent each scenario sensitivity to the recovery yield uncertainty.

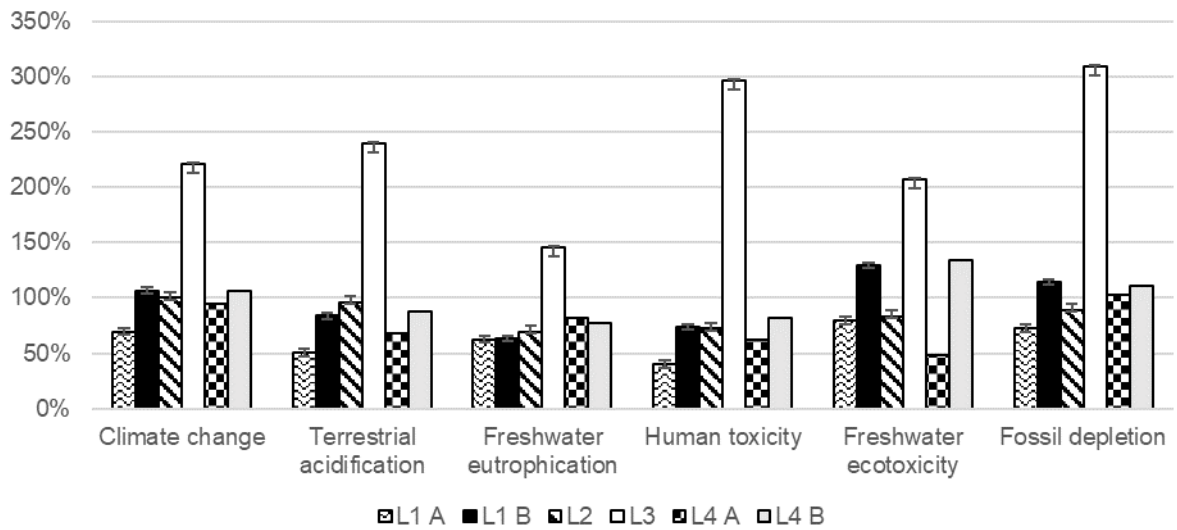


Figure S8. Variation of LCIA on sensitivity analysis to low-grade PHA processes including recovery yield uncertainty, being 100% each baseline process. L1 A and L4 A employ oil as source for heat production while option B employ natural gas. L2 add a crystallization unit for SDS recovery while L3 do not consider a crystallization unit. Error bars represent each scenario sensitivity to the recovery yield uncertainty.