



Techno-economic and carbon footprint assessment of methyl crotonate and methyl acrylate production from wastewater-based polyhydroxybutyrate (PHB)



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ABSTRACT

This paper assesses whether a cleaner and more sustainable production of the chemical building blocks methyl crotonate (MC) and methyl acrylate (MA) can be obtained in an innovative process in which resource consumption, waste generation and environmental impacts are minimized by using polyhydroxybutyrate (PHB) produced from wastewater as feedstock. For this purpose, conceptual process design, process modelling, economic and carbon footprint assessments of five conversion alternatives for wastewater-based PHB to MC or MA are performed. The PHB conversion step is modelled based on experimental data for both intracellular and extracellular feedstock. Results show that, despite the lower reaction selectivity of the direct conversion of intracellular PHB to MC or MA, this route is economically and environmentally preferred because no intensive downstream process is required for cell release after wastewater fermentation. The lowest total production costs are achieved when dry intracellular PHB is used as feedstock: 1.31 €/kg MC and 2.89 €/kg MA. However, the use of aqueous PHB as starting material leads to minimal carbon footprint due to lower energy demand: 3.25 kg CO₂-eq/kg MC and 8.78 kg CO₂-eq/kg MA, respectively. A sensitivity analysis is conducted to evaluate the eco-efficiency of the PHB conversion routes when the co-products methyl 3-hydroxybutyrate, crotonic acid and propylene are sold.

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1. Introduction

Sustainable production of chemicals and materials is attaining widespread interest due to concerns associated with depletion and environmental impacts of using fossil resources. The exploration of alternative pathways and products is essential in the transition towards a sustainable economy. As a consequence, much research has focused on the production of renewable chemicals, materials and polymers. A particular product of interest is polyhydroxybutyrate (PHB), a naturally synthesized and biodegradable polymer belonging to the family of polyhydroxyalkanoates (PHAs) (Verlinden et al., 2007). PHAs market is expected to grow from 10 kt/a in 2013 to about 34 kt/a by 2018 (Markets and markets, 2013)

as they are suitable for use in the medical/biological fields (GoodFellow, 2016) and their biodegradability brings added value in packaging applications (SmithersRapra, 2016).

However, despite technological advances that have been made on PHB production, its market penetration has been limited by the use of expensive pure carbon sources for intracellular bacterial fermentation (Reis et al., 2003) and large energy requirements during the cell release process (Gurieff and Lant, 2007). Industrial wastewater has been considered an alternative raw material as it poses several advantages, e.g., it reduces waste streams, it leads to costs savings on feedstock production, and it may potentially lower the PHB production costs because non-sterile conditions can be used (Khardenavis et al., 2007).

Pilot plant studies (Tamis et al., 2014) and commercial scale plants (Veolia, 2013) have already demonstrated the technical feasibility of PHB production from industrial wastewater. In a previous study (Fernández-Dacosta et al., 2015), we investigated the techno-economic and environmental performance of large-scale production of PHB via bacterial fermentation of wastewater. In spite of the promising results obtained when compared to

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traditional pure-culture PHB production, the developed processes still need further optimization before becoming competitive with petrochemicals, and concerns have been raised on whether the quality of the final product would be acceptable for thermo-plastic polymer application. Anticipating these issues, PHB applications could be expanded by including those with high added value, *i.e.* medical implants, drug delivery carriers, printing and photographic materials, nutritional supplements, fine chemicals, and biofuels (Chen, 2009).

This article aims to provide a preliminary assessment of alternative uses of PHB as a platform chemical and to identify potential economic and environmental bottlenecks of PHB conversion. Intracellular PHB obtained by fermentation of industrial wastewater is used as feedstock for the production of two different final products, the chemical building blocks methyl crotonate (MC) and methyl acrylate (MA). Since PHB is converted to MC or MA, quality standards for PHB polymer application are no longer an issue. After fermentation, the extracellular PHB can be released following different downstream processing (DSP) routes. Our previous study (Fernández-Dacosta et al., 2015) showed that DSP has the largest share in the production costs and the environmental impacts of the waste-to-PHB technologies. Therefore, in addition to investigate the conversion of extracellular PHB, the conversion of intracellular PHB is also explored in this article. Besides MC or MA production, the co-products obtained are also identified, to potentially maximize the economic profitability and minimize the carbon footprint of the complete value chain.

2. Methods

The feasibility of large-scale wastewater-based PHB conversion to MC or MA is investigated combining conceptual process design, modelling, techno-economic analysis and carbon footprint assessment.

2.1. Process design

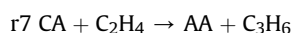
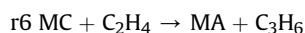
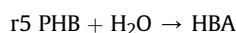
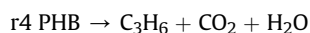
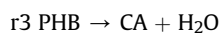
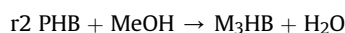
A conceptual process design is developed based on literature (Spekreijse et al., 2012, 2015, 2016; Schweitzer and Snell, 2015) and on additional selectivity values achieved in the laboratory of Bio-based Chemistry and Technology of the department of Agro-technology & Food Sciences of Wageningen University (WUR) in the Netherlands (personal communication with Spekreijse, WUR, November 2014–April 2015). Process modelling in ASPEN Plus software is used for scaling-up the plant.

Three cases for wastewater-based PHB conversion to MC, and two cases for PHB conversion to MA are designed based on different starting raw material conditions (Fig. 1):

- (i) Case I: Conversion of extracellular PHB to MC. Cell release via alkali DSP (for DSP details see Fernández-Dacosta et al., 2015).
- (ii) Case II: Conversion of intracellular PHB to MC.
- (iii) Case III: Conversion of aqueous PHB to MC. Aqueous PHB is intracellular which still contains 11 wt% water from the fermentation (for fermentation details see Fernández-Dacosta et al., 2015).
- (iv) Case IV: Conversion of intracellular PHB to MA via MC as intermediate product.
- (v) Case V: Conversion of aqueous PHB to MA via MC as intermediate product.

In the five cases investigated, all PHB is esterified with methanol to MC (r1). The potential co-products are methyl 3-hydroxybutyrate (M₃HB), crotonic acid (CA), propylene, carbon

dioxide and hydroxybutyric acid (HBA) (r2–r5). MC is the final product in Cases I to III. However, in Cases IV and V, MC is an intermediate in the production of MA. In these cases, following the esterification reaction, 81% of MC reacts with ethylene in a metathesis reaction yielding MA (r6). Acrylic acid (AA) is formed from the conversion of 81% of crotonic acid (r7):



Specific reaction selectivities and conversions to the co-products were assumed depending on the starting raw material and based on laboratory work (Schweitzer and Snell, 2015; Spekreijse et al., 2012, 2015, 2016; personal communication with Spekreijse, WUR, November 2014–April 2015), Table 1.

The calculation basis for all cases is 2.04 kt/a of intracellular PHB obtained from wastewater fermentation, based on 6.8 kt COD (chemical oxygen demand)/a, available from the wastewater of the primary industry and specific fermentation yields (Fernández-Dacosta et al., 2015). In Case I, extracellular PHB obtained from intracellular PHB after DSP for cell release is used in the esterification. Accounting for losses during DSP, the total amount of extracellular PHB available for esterification is 1.5 kt/a (Fernández-Dacosta et al., 2015). In Cases II to V, intracellular PHB obtained after the wastewater fermentation is directly esterified, thus avoiding losses of PHB in the DSP. A total amount of 2.04 kt/a of intracellular PHB is fed to the esterification reactor in Cases II and III (Table 2).

2.2. PHB to MC. Cases I–III

2.2.1. Case I: extracellular PHB to MC

Methanol and extracellular waste-based PHB released via alkali treatment are fed into the esterification packed bed reactor (R-101) in Fig. 2a. At 200 °C, 16 bars and with a residence time of 5 h, all PHB and half of the methanol fed into the reactor are converted to the reaction products. MC is the main product with 60% of reaction selectivity (Table 1). Following the esterification reaction, the co-products propylene and carbon dioxide are separated at 45 °C in a flash unit (V-101 in Fig. 2a) together with 14 wt% of the excess of methanol after the reaction. The gases leaving the process are burned for heat recovery. In a second flash (V-102), methanol is recovered at 20 °C and recycled back to the esterification reactor R-101.

After the removal of propylene and carbon dioxide, the remaining methanol and M₃HB are separated at the top of a distillation column (C-101), while MC and water are recovered at the bottom. The distillation is carried out at 2 bars to avoid condensation temperatures below 18 °C, which would require the use of very cold utilities in the condenser and thus result on extra energy costs. M₃HB and methanol are separated in a second distillation column (C-102). Prior to the distillation, off-gas is flashed out at 50 °C in V-103 to keep the condensation temperature of the distillation no lower than 17 °C. Methanol has enough purity (86 wt%) to be directly recycled to the esterification reactor and the

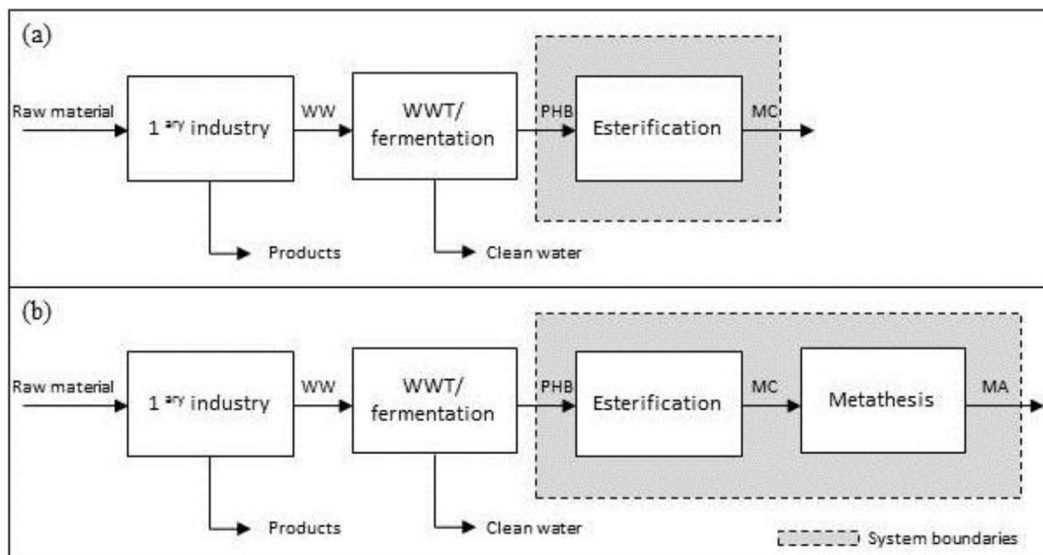


Fig. 1. Value chain. (a) Methyl crotonate (MC) production via esterification of wastewater-based PHB. (b) Methyl acrylate (MA) production via esterification of wastewater-based PHB to MC and subsequent metathesis.

Table 1
Reaction selectivity and conversion (mol%)^a.

Reaction	Selectivity (%)					Conversion (%)
	Case I	Case II	Case III	Case IV	Case V	
r1	60	54	41	54	41	100
r2	8	8	31	8	31	100
r3	6	12	7	12	7	100
r4	26	26	13	26	13	100
r5	–	–	8	–	8	100
r6	–	–	–	100	100	81
r7	–	–	–	100	100	81

^a Based on Spekreijse et al., 2012, 2015, 2016; Schweitzer and Snell, 2015; with additional personal communication with Spekreijse, WUR, November 2014–April 2015.

M₃HB stream (69 wt%) is burned for heat recovery. Alternatively, M₃HB can be sold as a co-product but this would require an additional distillation unit to further purify M₃HB to 90 wt% purity (Table 5).

After distillation in C-101, MC and water are separated via decantation (D-101) at 95 °C. MC is obtained at 90 wt% purity.

2.2.2. Case II: intracellular PHB to MC

Laboratory experiments have shown that intracellular PHB can successfully be converted into MC (Spekreijse et al., 2015). Following wastewater fermentation, no DSP is required for cell

release. Water is simply removed via centrifugation, filtration and evaporation. Intracellular PHB is fed to the esterification fluidised bed reactor (R-101 in Fig. 2b). HBA is produced through reaction five (r5) only when the volume ratio of water to methanol is at least 20:1 (Spekreijse et al., 2016). In this case study, the water to methanol ratio is 5.6. Reaction five (r5) does not occur and thus, there is no HBA in the system.

However, selectivity towards MC drops to 54%, compared to 60% in the conversion of extracellular PHB (Table 1). The process design is similar to Case I, but contrary to the extracellular conversion, cell material is present during the reaction. Based on laboratory data, it is assumed that after the reaction, 10 wt% of the cell material ends as soot and the rest is released in gas form. The soot is separated via filtration and undergoes solid treatment before disposal.

Another difference with respect to Case I is the introduction of an additional separation step because the amount of CA produced in the esterification reactor is about two times larger. Therefore, after water is removed in the decanter D-101, the MC stream still contains 14 wt% of CA. An additional distillation unit (C-103) is required to separate CA as the bottoms and obtain MC at 94 wt% purity in the top product.

2.2.3. Case III: aqueous PHB to MC

A volume ratio of water to methanol higher than 20 negatively affects the selectivity towards MC (from 60% in Case I and 54% in Case II, to 41% in Case III, Table 1) because HBA, which is not present

Table 2a
Process design results. PHB to MC.

PHB to MC			Case I	Case II	Case III
Intracellular PHB from WWT		amount (kt/a)	2.0	2.0	2.0
Feed esterification	PHB	amount (kt/a)	1.5	2.0	2.0
Final product	MC	amount (kt/a)	1.1	1.3	1.0
		purity (wt%)	89.5	94.3	93.8
Co-product streams burned for heat recovery	M ₃ HB	amount (kt/a)	0.2	0.2	0.8
		purity (wt%)	69.4	70.8	89.8
	CA	amount (kt/a)	–	0.2	–
		purity (wt%)	–	100	–
Heat from burning co-products		(kW)	89.8	188.6	239.7
Yield		(kg MC/kg PHB)	0.5	0.6	0.4

Table 2b
Process design results. PHB to MA.

PHB to MA			Case IV	Case V
Feed	PHB	amount (kt/a)	2.0	2.0
Final product	MA	amount (kt/a)	1.0	0.76
		purity (wt%)	99.6	99.6
Co-product streams burned for heat recovery	C ₃ H ₆	amount (kt/a)	0.5	0.4
		purity (wt%)	99.5	92.5
	M ₃ HB	amount (kt/a)	0.2	0.8
		purity (wt%)	70.8	89.8
	CA	amount (kt/a)	0.20	–
		purity (wt%)	100	–
Heat from burning co-products		(kW)	7.9	6.8
Yield		(kg MA/kg PHB)	0.5	0.4

in Cases I and II, is produced following reaction five (r5). Compared to Case II, and due to the presence of HBA, the process design includes an additional distillation step to separate CA and HBA as the bottoms and recover additional amount of MC in the top product (C-104 in Fig. 2c). The purity of the final product MC is 94 wt%, the same as in Case II.

2.3. PHB to MA. Cases IV–V

Following the esterification of PHB to MC, MA can be obtained via the metathesis of MC with ethylene (r6). The first part of the process (PHB conversion to MC) is the same as described in section 2.1.1. The conversion of extracellular PHB to MA is not investigated due to the high production costs and related environmental impacts associated to the production of the intermediate product MC with lower purity (90 wt% in Case I, against 94 wt% in Cases II and III). The second part of the process is the metathesis of MC to MA. The same processing steps are required regardless whether the MC is produced from intracellular PHB (Case II) or aqueous PHB (Case III).

The metathesis is carried out in reactor R-101 (Fig. 2d), at 40 °C, 1 bar and with a residence time of 22 h (Schweitzer and Snell, 2015; personal communication with Spekrijse, WUR, November 2014–April 2015). Dichloromethane (DCM) is used as solvent, with a mass ratio of 3:1 (DCM:MC). A catalyst is required for the metathesis of MC. A homogeneous ruthenium based catalyst (Hoveyda-Grubbs 2nd generation) is used and recycled with a turnover number (TON) of 322 (Schweitzer and Snell, 2015; personal communication with Spekrijse, WUR, November 2014–April 2015).

A rather complex DSP is required after the reaction in order to: (i) minimize DCM solvent losses and fresh material requirements because DMC poses potential human health risks (EPA, 2014); (ii) maximize the overall conversion of the process by recovering the non-reacted MC and recycling it to the metathesis reactor R-101; and (iii) obtain a final product with >99 wt% MA.

The first step of the DSP after the metathesis reaction is a flash separation (V-101 in Fig. 2d), at 20 °C. The gas stream contains the majority of the propylene produced in the reaction between MC and ethylene and 11 wt% of DCM flowing out of the metathesis reactor. The remaining DCM, MA, and the unreacted MC mainly form the liquid stream. The DCM in the gas stream is purified via distillation of the propylene (C-101) and decantation of the water at 5 °C (D-101). The DCM in the liquid stream is recovered at the top of the distillation tower (C-102) together with some propylene and water. A DCM stream with 98 wt% is recycled to the metathesis reactor after distillation (C-103) and decantation (D-102), in which propylene and water are separated, respectively.

Due to the presence of propylene gas and the low boiling point of DCM (40 °C), pressure distillation (8–10 bar) is implemented in the columns C-101, C-102 and C-103 to avoid temperatures lower

than 10 °C in the condensers and therefore the use of expensive refrigerant.

Unreacted MC is recovered as the bottoms of the distillation column C-104 and recycled back to the reactor. The final product MA is obtained at the top of the column C-104 at a purity of 99.6 wt%.

2.4. Economic evaluation

The economic evaluation provides total production costs, covering capital investment, energy, material, labour and maintenance costs.

Bare equipment costs are estimated from independent cost data for the process industry (DACE, 2014). The total investment is calculated applying typical factors for capital cost based on delivered equipment costs (Smith, 2005). Annual depreciation is calculated assuming an interest rate of 5% and a depreciation schedule of 20 years. Maintenance is assumed 3% of the total fixed capital costs, and labour 10% of the total annual costs (Peters et al., 2003). Utilities costs are based on the amounts consumed and prices calculated following Ulrich and Vasudevan (2006) correlations. Catalyst costs are based on the ruthenium content in the Hoveyda-Grubbs 2nd generation catalyst, a ruthenium market price of 1.42 €/kg (Johnson Matthey, 2015), and assuming that the catalyst is reused with a TON of 322 (Schweitzer and Snell, 2015). Material costs include methanol and PHB used as raw materials in the esterification as well as ethylene and DCM used in the metathesis.

Intracellular PHB is obtained as part of the bacterial fermentative wastewater treatment of the primary industry (Fig. 1). Assuming that the water effluent after wastewater fermentation has the same quality as the one obtained with the traditional wastewater treatment process, the wastewater fermentation costs are associated to the primary industry. In the conversion of intracellular PHB (Cases II to V), the PHB inside the bacterial cells is directly used after fermentation and thus, it is a free of costs feedstock. Extracellular PHB (Case I) is obtained after DSP for cell release and thus, the production costs of extracellular PHB are the ones of the DSP (1.40 €/kg PHB, Fernández-Dacosta et al., 2015).

2.5. Carbon footprint assessment

The carbon footprint of each process alternative is estimated using a life cycle perspective following the guidelines of ISO 14040–14044 (ISO, 2006a and ISO, 2006b). An inventory of all the input and output flows of materials and energy for each case study is derived from the mass and energy balances obtained in ASPEN Plus. The global warming potential (GWP) of individual material and energy carriers is taken from the database Ecolnvent v2.2. Two different bases for comparison are considered in this paper. For Cases I to III, the basis for comparison is 1 kg of MC. For Cases IV and V, the basis for comparison is 1 kg of MA. As this work is a

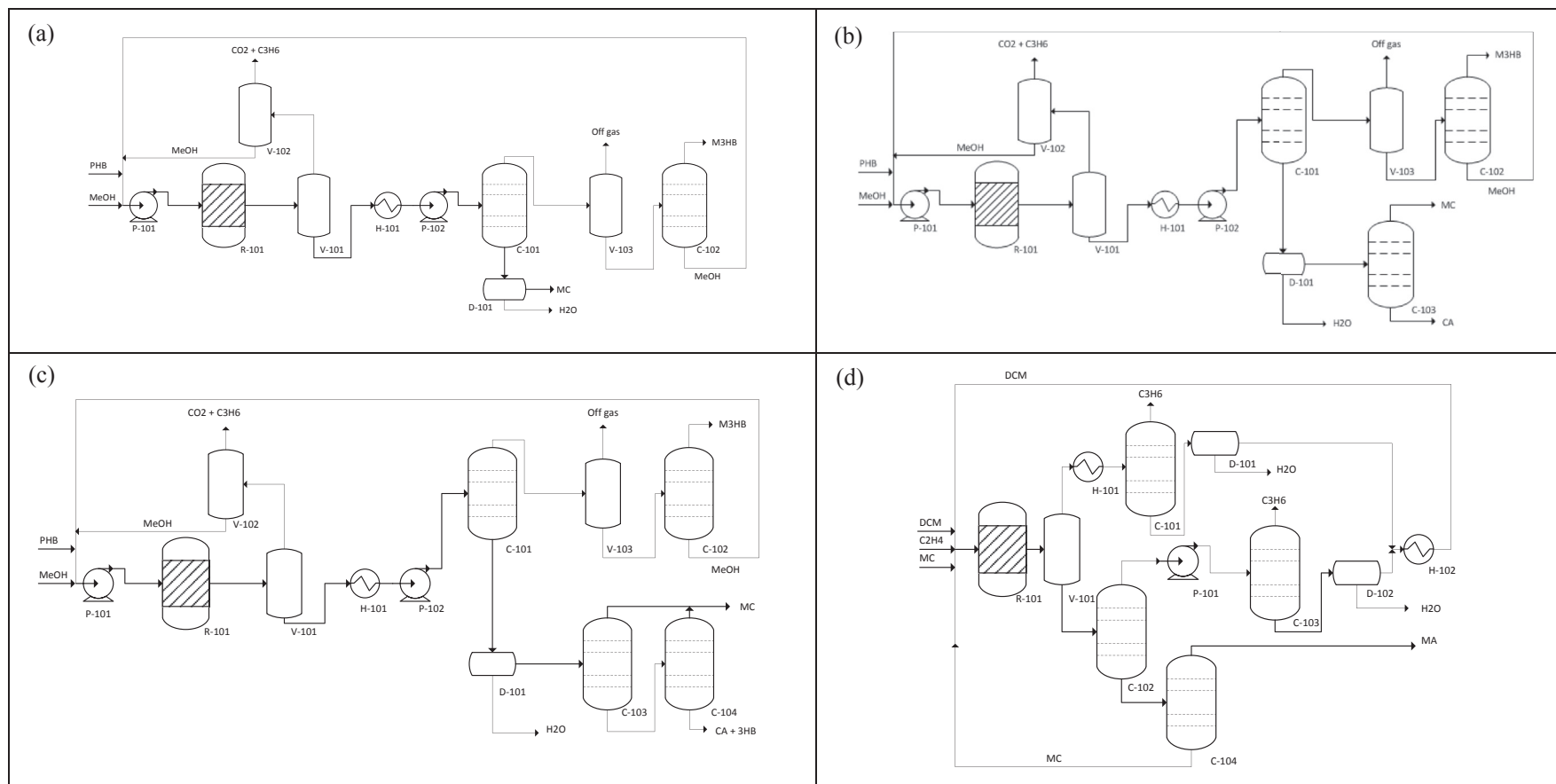


Fig. 2. Process flow diagrams. (a) Extracellular PHB conversion to MC. P-101: pump, R-101: esterification reactor, V-101: flash, V-102: flash, H-101: cooler, P-102: pump, C-101: distillation, D-101: decanter, V-103: flash, C-102: distillation. (b) Intracellular PHB conversion to MC. P-101: pump, R-101: esterification reactor, V-101: flash, V-102: flash, H-101: cooler, P-102: pump, C-101: distillation, V-103: flash, C-102: distillation, D-101: decanter, C-103: distillation. (c) Aqueous PHB conversion to MC. P-101: pump, R-101: esterification reactor, V-101: flash, V-102: flash, H-101: cooler, P-102: pump, C-101: distillation, V-103: flash, C-102: distillation, D-101: decanter, C-103: distillation, C-104: distillation. (d) MC conversion to MA. R-101: metathesis reactor, V-101: flash, H-101: cooler, C-101: distillation, D-101: decanter, C-102: distillation, P-101: pump, C-103: distillation, D-102: decanter, H-102: heater, C-104: distillation.

comparative study of PHB conversion routes, a cradle-to-gate approach is applied. The system boundaries are shown in Fig. 1. Note that in Cases I to III they include wastewater-based PHB esterification to MC. In Cases IV and V the system boundaries also include MC metathesis to MA.

Following life cycle practices, intracellular PHB is considered free of any environmental burden because it is generated as a product waste of the primary industry. However, extracellular PHB cannot be treated as a feedstock free of environmental burden because intensive DSP is needed for cell release after fermentation (Case I). Thus, the carbon footprint associated to extracellular PHB is that of the DSP for cell release (2.99 kg CO₂-eq/kg PHB, Fernández-Dacosta et al., 2015).

2.6. Sensitivity analysis

In the base scenarios (section 2.1.), the streams coming out of the processes were treated as waste or burned for heat recovery. However, some of these streams can be sold as co-products. A sensitivity analysis was performed to investigate the effect of selling co-products on economics and on the carbon footprinting.

Depending on the raw material conditions, different amounts of M₃HB are produced in the esterification of PHB to MC (Table 1). Furthermore, during the intracellular conversion of PHB to MC (Case II), a substantial quantity of CA is produced. Propylene, also obtained as co-product in the metathesis of MC to MA, can potentially be sold (Cases IV and V). To allow consistent and fair comparisons, additional separation steps were included in the process models to ensure the same purity of the co-products sold in the sensitivity analysis (Table 5).

Due to the many uncertainties related to the application and market value of the co-products, a range of selling prices is considered. The market price for M₃HB is estimated at 1 €/kg for a fuel use, in line with global ethanol price (Scott et al., 2013) and 1.1 €/kg when used as fuel additive (Chen, 2009). However, M₃HB could also be used in high added value applications such as optically active starting material (Santa Cruz Biotechnology, 2015) or for pharmaceutical purposes (Zhang et al., 2013). For these types of applications only laboratory prices are found (Sigma Aldrich, 2015a). These values are most likely on the high side as the price of any material is lower at industrial scale due to economies of scale and impurities (Kuppens et al., 2010). Rough scaling factors relating large-scale market prices to lab-scale prices for lactic acid (technical grade, 88%, ICIS, 2015; highly pure, 98%, Sigma Aldrich, 2015a) are used to convert the laboratory prices found for M₃HB into market values (Santa Cruz Biotechnology, 2015; Sigma Aldrich, 2015b). Following this approach, M₃HB market price can reach a value of 3 €/kg for specific applications.

Crotonic acid is mainly used in the synthesis of copolymers (Mamat et al., 2014). Monomer market prices range from 2 to 5 €/kg (Scott et al., 2013). Used in cosmetic, resin, coating or plasticizer applications, the CA market price is about 4–5 €/kg (Alibaba, 2015). Also rough scaling factors are used to convert the laboratory price for CA (Sigma Aldrich, 2015c) to market price. In this case the laboratory price of acetic acid (Sigma Aldrich, 2015d) is divided by the industrial price of acetic acid (ICIS, 2015). Applying these rough scaling factors the values obtained for the CA price decrease to 0.7–0.8 €/kg.

18 different scenarios for PHB conversion to MC and 15 scenarios for PHB conversion to MA are developed changing the co-products market price. Given the reasons discussed above, and to cover a wide spectrum of potential large-scale market prices, the market price selected for M₃HB is in the range of 1–3 €/kg, and 0.7 to 5 €/kg for CA. Propylene market is quite established and prices are well known, thus a fixed value of 0.75 €/kg is assumed based on

real suppliers data (ICIS, 2015).

Sensitivity analysis for the carbon footprint results is also performed to evaluate the robustness of the GWP of MC and MA value chains with respect to changes in the co-products (M₃HB, CA, propylene). The ISO 14040-14044 series (ISO, 2006a and ISO, 2006b) recommend applying substitution (system expansion) to evaluate these types of multifunctional systems. In this particular case, it is also interesting to get insights of the impacts associated to the individual products. The ISO guidelines (ISO, 2006a and ISO, 2006b) recommend using relevant variables that reflect the physical relationship, such as the mass content. Therefore, mass allocation is applied in the sensitivity analysis to obtain consistent results uniformly applied across the co-products (Tsiropoulos et al., 2014). Economic allocation is not applied due to many uncertainties in the co-products market prices.

The results of both sensitivity analyses are combined in a graph of eco-efficiency (Fig. 4). The carbon footprint is shown on the x-axis, whereas the total production costs are shown in the y-axis. The most promising alternatives are those located in the lower left side quadrant (low production costs and carbon footprint) and the least preferred options are those located in the upper right quadrant of the eco-efficiency figure (high total production costs and carbon footprint).

3. Results and discussion

3.1. Process design

3.1.1. PHB to MC. Cases I–III

For the Cases I to III, approximately 1 kt/a of MC, at ≥ 90 wt% of purity, was obtained based on 2 kt/a of intracellular PHB. However in Case I, only 1.5 kt/a of extracellular PHB enters the esterification reactor due to losses during the DSP for cell release (Table 2a). The overall process yield and product amounts obtained in each process option vary subject to the reaction selectivities (Table 1). The material and energy flows based on the process designs modelled in ASPEN Plus (Fig. 2) are summarised in Table 3a.

The process scheme of Case I is the simplest because of a higher reaction selectivity towards MC. Less separation steps are needed after the reaction to obtain 1.12 kt/a of MC. However, fewer purification steps also imply that the maximum purity attained for the final product is 90 wt%. Additional separation steps to obtain higher purity would increase the costs and environmental burdens of Case I. Thus, Case I is discarded for further analysis and no extra processing units are included since this route already shows higher production costs and environmental impacts at a low purity of 90 wt%, when compared to Cases II and III (Sections 3.2 and 3.3).

In Case II, an additional separation step is required because a

Table 3a
Process inputs and outputs. PHB to MC.

PHB to MC	Case I	Case II	Case III
Process input			
PHB (kg/kg MC)	2.0	1.7	2.3
MeOH (kg/kg MC)	0.4	0.5	1.1
Steam (kg/kg MC)	0.2	1.3	2.4
Cooling water (kg/kg MC)	126.0	176.4	206.7
Chilled water (kg/kg MC)	164.2	185.6	0.0
Electricity (MJ/kg MC)	0.01	2.6	3.6
Process output			
Water treatment (m ³ /kg MC)	0.0	0.0	0.0
Solid treatment (kg/kg MC)	–	0.1	0.9
Gases (kg/kg MC)	0.4	0.5	0.4
M ₃ HB (kg/kg MC)	0.2	0.2	0.9
CA (kg/kg MC)	–	0.1	–

Table 3b
Process inputs and outputs. PHB to MA.

PHB to MA	Case IV	Case V
Process input		
PHB (kg/kg MA)	1.9	2.6
MeOH (kg/kg MA)	0.5	0.9
MC (kg/kg MA)	1.2	1.2
DCM (kg/kg MA)	0.01	0.01
C ₂ H ₄ (kg/kg MA)	0.3	0.4
Steam (kg/kg MA)	3.0	2.8
Cooling water (kg/kg MA)	57.9	57.8
Chilled water (kg/kg MA)	119.2	115.8
Electricity (MJ/kg MA)	0.01	0.01
Refrigerant (kg/kg MA)	26.6	37.9
Process output		
Water treatment (m ³ /kgMA)	0.0	0.0
Propylene (kg/kg MA)	0.5	0.5
M ₃ HB (kg/kg MA)	0.2	1.1
CA (kg/kg MA)	0.2	–

larger quantity of the co-product CA is produced in the esterification reaction. Consequently, more amount of MC is recovered at a higher purity (1.28 kt/a, 94 wt%). The overall yield of the process is 0.49 kg MC/kg intracellular PHB (before DSP) in Case I and 0.59 kg MC/kg intracellular PHB in Case II. The lower yield reached in Case I is a consequence of losing part of the intracellular PHB during the DSP after the wastewater fermentation, whereas in Case II intracellular PHB is directly converted to MC after the fermentation.

The formation of the co-product HBA only occurs in Case III and thus this alternative incorporates an additional separation step compared to Case II. In order to reach the same purity of the final product (94 wt% MC), lower yield and lower amount of MC (0.44 kg MC/kg intracellular PHB, 0.96 kt/a) are obtained due to reduced reaction selectivity towards MC.

3.1.2. PHB to MA. Cases IV–V

The entire value chain from wastewater-based PHB to MA is investigated only using intracellular PHB as starting material due to the lower performance of the extracellular conversion of PHB to MC (Case I). Analogous process schemes are designed for the metathesis of MC to MA regardless whether intracellular or aqueous PHB is used as starting material (Cases IV and V, respectively, Fig. 2d). Due to a lower reaction selectivity in the PHB esterification to MC when using aqueous PHB, almost 30% less amount of final product MA is obtained in Case V: 0.76 kt MA/a vs. 1.05 kt MA/a in Case IV. The overall yield of intracellular PHB conversion to MA (at 99.6 wt%, see Table 2b) is 0.5 and 0.4 kg MA/kg PHB, for Cases IV and V, respectively.

3.2. Economic evaluation

3.2.1. PHB to MC. Cases I–III

Table 4a depicts the results of the economic evaluation. Lower Capex and utilities in Case I originate from its simplest process design. Due to lower reaction selectivities towards MC and the production of larger amount of co-products, Case II incorporates one additional separation step, while Case III requires two additional separation steps, resulting on a Capex of 0.15 €/kg MC in Case I, 0.20 €/kg MC in Case II and 0.26 €/kg MC in Case III. However, extra separation steps led to a final product purity of 94 wt% MC in Cases II and III, whereas in Case I it was only 90 wt%. Due to these differences in purity, the MC produced in Case I might be considered for different final use.

Utilities costs account for 18% of total production costs in Case I, 62% in Case II and 61% in Case III. Compared to Case I, utilities costs

Table 4a
Economic evaluation results. PHB to MC.

PHB to MC		Case I	Case II	Case III
Total costs (€/kg MC)				
CAPEX	Depreciation	0.15	0.20	0.26
OPEX	Utilities	0.54	0.81	1.06
	Materials	2.02	0.16	0.24
	Maintenance	0.00	0.01	0.01
	Labour	0.30	0.13	0.17
TOTAL	(€/kg MC)	3.02	1.31	1.74

are larger in Cases II and III because they consume extra steam in the reboilers of the additional distillation columns and they include solid treatment due to the presence of cell material (0.01 €/kg MC). Steam costs are 0.18 €/kg MC in Case I, 0.37 €/kg MC in Case II and 0.46 €/kg MC in Case III.

While Case I presents lower Capex and utilities costs, the use of extracellular PHB has a large impact in the material costs. In Case I, PHB is released from the cell material in a cost-intensive DSP after wastewater fermentation. Thus, the costs of extracellular PHB increased to 1.40 €/kg (Fernández-Dacosta et al., 2015), which are 62% of the overall MC production costs in Case I. Eventually, total production costs in Case I are 3.02 €/kg MC for a final product which can not reach a purity higher than 90 wt%. In Cases II and III, intracellular PHB is directly converted to MC after wastewater fermentation, avoiding any DSP. Hence, the share of the material costs decrease to 12% and 14% of the total production costs (1.31 €/kg MC in Case II and 1.74 €/kg MC in Case III). The final product has a purity of 94 wt% in both cases, which was not possible not achieve following the scheme of Case I. No additional separation steps were considered in Case I to increase the purity of the final product MC because at already 90 wt% purity the total production costs were the highest among the three cases.

3.2.2. PHB to MA. Cases IV–V

As in the Case of MC, the production costs of MA are driven by the material costs. Case V has 30% higher material costs with respect to Case IV because of the higher production costs of MC from aqueous PHB (Case III) than from intracellular PHB (Case II). The amount of utilities used are comparable in both cases because similar processing steps are included in the designs (Table 3b, Fig. 2d). The contribution of the utilities on the total costs is 23% in both processes. However, due to larger amounts of MA produced in Case IV, the costs of utilities per kg of final product are lower, 0.65 €/kg MA, whereas in Case V utilities costs are 0.86 €/kg MA (Table 4b). MA production costs are 2.89 €/kg MA employing dry intracellular PHB (Case IV) and 3.80 €/kg MA using aqueous PHB as starting material (Case V).

3.3. Carbon footprint assessment

3.3.1. PHB to MC. Cases I–III

Likewise to the economic evaluation, the overall results of Case II and Case III show lower carbon footprint than Case I because intracellular PHB is immediately converted after fermentation, avoiding any energy-intensive and polluting DSP. The overall GWP of the esterification of extracellular PHB to MC (Case I) is 6.83 kg CO₂-eq/kg MC (Fig. 3). Case II shows a GWP of 4.12 kg CO₂-eq/kg MC. The GWP in Case III is 3.25 kg CO₂-eq/kg MC (Fig. 3a).

Whereas the intracellular PHB used in Cases II and III is burden-free, the extracellular PHB used in Case I includes the carbon emissions associated with the DSP for cell release. Extracellular PHB accounts for 59% of the total GWP in Case I (2.99 kg CO₂-eq/kg PHB,

Table 4b

Economic evaluation results. PHB to MA.

PHB to MA		Case IV	Case V
Total costs (€/kg MA)			
CAPEX	Depreciation	0.10	0.10
OPEX	Utilities	0.65	0.86
	Materials	1.85	2.46
	Maintenance	0.00	0.00
	Labour	0.29	0.38
TOTAL	(€/kg MA)	2.89	3.80

Fernández-Dacosta et al., 2015).

Methanol is the other raw material used in the esterification of PHB towards MC. The GWP associated with the use of methanol is similar for Cases I and II, 0.28 and 0.30 kg CO₂-eq/kg MC, respectively. However, in Case III 0.72 kg CO₂-eq/kg MC are emitted due to lower reaction selectivity towards MC, thereby requiring more raw material per kg of final product obtained.

The carbon footprint of the utilities is lower in Case I because fewer separation steps are required. Nonetheless, the amount of chilled water used in Case III is greatly reduced due to the presence of the co-product HBA. Since HBA has a boiling point of 269 °C, the temperatures in the condensers in the distillation towers (where chilled water is mainly required) increase and thus cooling water instead of chilled water can be used as condensing utility. Consequently, the GWP of chilled water accounts for 1.69 and 1.91 kg CO₂-

eq/kg MC in Case I and Case II, respectively, but only 0.02 kg CO₂-eq/kg MC in Case III.

3.3.2. PHB to MA. Cases IV–V

The carbon footprint of PHB conversion to MA by MC metathesis is primarily driven by the impacts associated with the production of the intermediate material, MC (Fig. 3b). The shares of producing MC account for 52% of the overall emissions in Case IV and 46% in Case V (5.03 and 4.06 kg CO₂-eq/kg MA, respectively).

After the intermediate material MC, chilled water appears as the input with the highest impacts. The GWP share of chilled water is rather similar for both cases: 23–24% of the total CO₂ emissions (2.18–2.12 kg CO₂-eq/kg MA for Cases IV and V, respectively). The rest of the process inputs present similar contributions to the overall impacts. However, the gross impacts in absolute terms

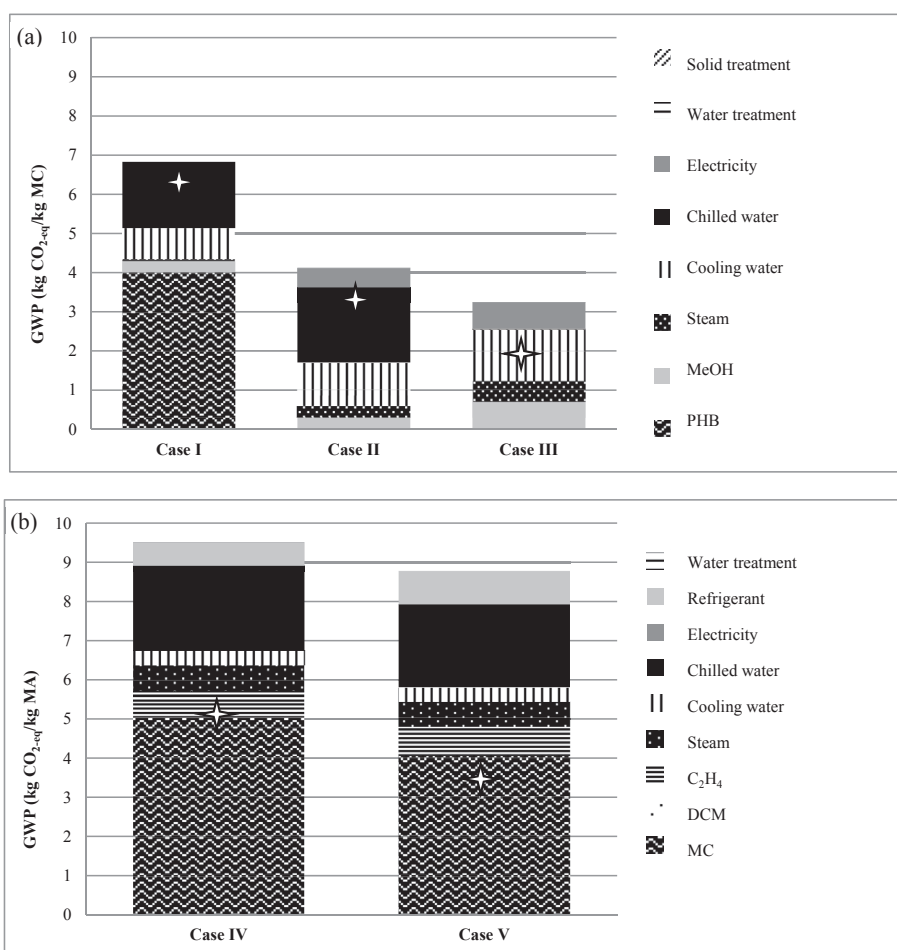


Fig. 3. Carbon footprint assessment. (a) PHB to MC. (b) PHB to MA. Sensitivity analysis results. GWP estimation applying mass allocation under the assumption that all products and co-products (MC, MA, M₃HB, CA and propylene) are recovered and sold, instead of being burned for heat recovery as in the base case.

differ. Case IV presents a GWP of 9.52 kg CO₂-eq/kg MA whereas for Case V the GWP decreases to 8.78 kg CO₂-eq/kg MA due to the lower carbon footprint of the intermediate material MC.

3.4. Sensitivity analysis

3.4.1. Economic evaluation

M₃HB and CA are produced during the PHB esterification to MC and propylene is a co-product in the metathesis of MC to MA. In the base cases no co-products were sold and thus they were burned for heat recovery. When M₃HB and CA are sold, these streams are no longer available for burning and thus the steam demand and costs increase with respect to the base case. Steam costs rise to 0.23 €/kg MC in Case I, 0.42 €/kg MC in Case II and 0.55 €/kg MC in Case III.

Moreover, under the assumption that M₃HB can be sold, an extra distillation step is required in Cases I, II and IV to obtain M₃HB at 90 wt% (Table 5). In the base Cases III and V, M₃HB is already available at this level of purity, and thus no additional purification equipment are needed for the base case. The amount of M₃HB obtained at 90 wt% varies according to the reaction selectivities of each case (Table 1), so that 0.11 kg M₃HB/kg MC, 0.14 kg M₃HB/kg MC and 0.89 kg M₃HB/kg MC are produced in Cases I, II and III, respectively and 0.16 kg M₃HB/kg MA and 1.11 kg M₃HB/kg MA in Cases IV and V. Cases III and V are most affected by changes in the market price of M₃HB. CA, another co-product of the system, is only produced at a reasonable quantity and purity in Cases II and IV (0.15 kg CA/kg MC in Case II and 0.19 kg CA/kg MA in Case IV, 100 wt% purity). In the metathesis of MC to MA propylene is produced and sold at 0.75 €/kg (ICIS, 2015). To obtain the same propylene purity in Cases IV and V (99.5 wt%, Table 5), additional separation steps were included in the process models of Case V. In the base Case IV, propylene has already a purity of 99.5 wt% and thus no changes were done to the model.

Whereas in the base scenarios Case II is the preferred option, Case III presents lower production costs when the co-products are sold. When the most optimistic market prices are implemented (3 €/kg M₃HB and 5 €/kg CA), the total production costs decrease to -1.21 €/kg MC in Case III. MC production combined with high-value sellable co-products can lead to negative values for the total production costs of MC because of: (i) integrating of wastewater treatment process with material production, thus using a free of costs feedstock and (ii) multi-product systems in which the co-products have higher price than the main product. In this case, the revenues from selling a basket of different products surpass the costs of their production. The main product is selected based on its market value, a combination of the product price and market volume. Future process optimization focusing only on the co-products with high price could be very attractive but with a very limited market potential due to lower volume of production and little option to grow in the short term.

In the production of MA, Case IV is preferred when no co-

Table 5b

Sensitivity analysis. Process design results. PHB to MA.

PHB to MA			Case IV	Case V
Feed	PHB	amount (kt/a)	2.0	2.0
Final product	MA	amount (kt/a)	1.0	0.8
		purity (wt%)	99.6	99.6
Co-products	C ₃ H ₆	amount (kt/a)	0.5	0.4
		purity (wt%)	99.5	99.5
	M ₃ HB	amount (kt/a)	0.2	0.8
		purity (wt%)	90.4	89.8
	CA	amount (kt/a)	0.2	–
		purity (wt%)	100	–
Yield		(kg MA/kg PHB)	0.5	0.4

products are sold but Case V would be preferred when the co-products are sold. The results of the economic sensitivity analysis are summarised in Table S3 and Fig. S1 of the supplementary material.

3.4.2. Carbon footprint assessment

Mass allocation is applied to estimate the carbon footprint of each case study, under the assumption that all products and co-products (MC, MA, M₃HB, CA and propylene) are recovered at enough amount and purity.

In the sensitivity analysis no co-products are burned for heat recovery in any case study, and therefore almost double the amount of steam as compared to the base cases is required to fulfil the heating demand. Moreover, an extra distillation column is needed in Cases I and II to further purify M₃HB to 90 wt% (Table 5), increasing the amount of cooling water and steam required. The use of mass allocation affects the GWP the most in the cases in which higher amounts of co-products are obtained. In the production of MC, the carbon footprint of Case III decreases 40% respect to the base case, to 1.94 kg CO₂-eq/kg MC (Fig. 3a).

In the production of MA, the GWP of Case V is 3.57 kg CO₂-eq/kg MA when all co-products are recovered, which is 59% lower than for the base case in which co-products are burned (Fig. 3b). Further details of the sensitivity analysis of the carbon footprint are summarised in Table S4 of the supplementary material.

3.4.3. Eco-efficiency

The results of the sensitivity analysis of the total production costs and the carbon footprint of MC and MA production are combined in a graph of eco-efficiency (Fig. 4a for MC routes and Fig. 4b for MA routes). The base cases and all the scenarios evaluated in the sensitivity analysis are compared to identify additional opportunities and challenges. The most promising alternatives are those located in the left-low side quadrant of Fig. 4. Case II is the option with lowest production costs in the base scenarios of the conversion of PHB to MC, but Case III shows lower GWP. When co-products are recovered, Case III becomes the most preferred alternative, with the lowest costs and carbon footprint. In the base scenarios of the conversion of PHB to MA, the total production costs of MA are lower in Case IV than in Case V, but at the expenses of higher GWP. When co-products are sold, the total production costs and GWP of Case V are more affected and thus it is the most interesting alternative for PHB conversion to chemical building blocks.

4. Conclusions

Wastewater-based PHB conversion to building blocks is a potential alternative to its traditional biopolymer use. Economic and carbon intensive DSP for cell release after wastewater fermentation for PHB bacterial growth and quality issues can be avoided by

Table 5a

Sensitivity analysis. Process design results. PHB to MC.

PHB to MC			Case I	Case II	Case III
Intracellular PHB from WWT		amount (kt/a)	2.0	2.0	2.0
Feed esterification	PHB	amount (kt/a)	1.5	2.0	2.0
		amount (kt/a)	1.1	1.3	1.0
Final product	MC	purity (wt%)	89.5	94.3	93.8
		amount (kt/a)	0.1	0.2	0.8
Co-products	M ₃ HB	amount (kt/a)	0.1	0.2	0.8
		purity (wt%)	90.2	90.4	89.8
	CA	amount (kt/a)	–	0.2	–
		purity (wt%)	–	100	–
Yield		(kg MC/kg PHB)	0.5	0.6	0.4

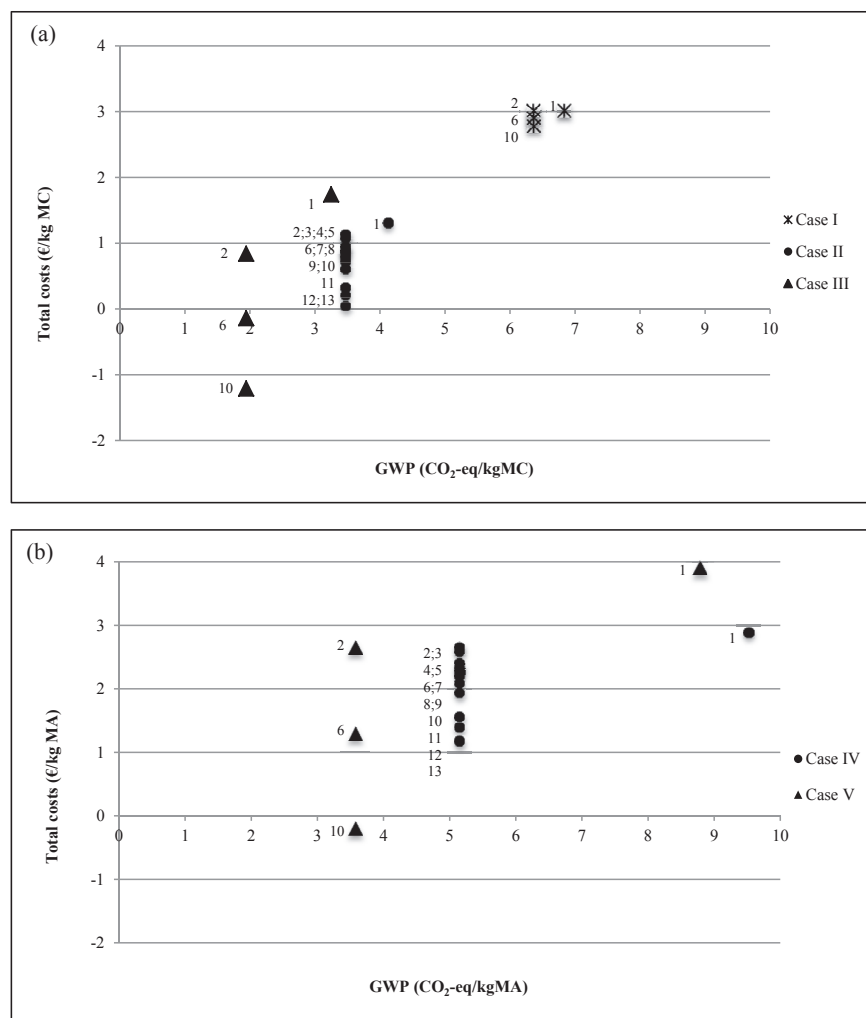


Fig. 4. Sensitivity analysis. Eco-efficiency comparison of alternative scenarios. (a) PHB to MC. (b) PHB to MA. 1. Base case; 2. Sell M₃HB at 1 €/kg and CA at 0.7 €/kg; 3. Sell M₃HB at 1 €/kg and CA at 1 €/kg; 4. Sell M₃HB at 1 €/kg and CA at 2 €/kg; 5. Sell M₃HB at 1 €/kg and CA at 5 €/kg; 6. Sell M₃HB at 2 €/kg and CA at 0.7 €/kg; 7. Sell M₃HB at 2 €/kg and CA at 1 €/kg; 8. Sell M₃HB at 2 €/kg and CA at 2 €/kg; 9. Sell M₃HB at 2 €/kg and CA at 5 €/kg; 10. Sell M₃HB at 3 €/kg and CA at 0.7 €/kg; 11. Sell M₃HB at 3 €/kg and CA at 1 €/kg; 12. Sell M₃HB at 3 €/kg and CA at 2 €/kg; 13. Sell M₃HB at 3 €/kg and CA at 5 €/kg.

directly converting dry intracellular PHB into MC or MA instead of using extracellular PHB, thus reducing the production costs of MC from 3.02 €/kg MC to 1.31 €/kg MC. Production costs of MA from dry intracellular PHB are 2.89 €/kg MA, and 3.80 €/kg MA from aqueous intracellular PHB. The direct conversion of aqueous PHB after wastewater fermentation reduces the carbon footprint of the processes from 6.83 kg CO₂-eq/kg MC to 3.25 kg CO₂-eq/kg MC. The carbon footprint of dry intracellular PHB is 9.52 kg CO₂-eq/kg MA, and the carbon footprint of aqueous PHB conversion to MA is 8.78 kg CO₂-eq/kg MA. In the reaction of PHB with water, HBA is produced. Due to the high boiling point of HBA, no chilled water is used in the aqueous conversion of PHB, thus reducing the carbon footprint with respect to the routes that use dry intracellular PHB.

Co-products valorisation can largely decrease the total production costs because of the integration of wastewater treatment process (thus using a free of costs feedstock) and having multi-product systems in which the co-products have high market price. When applying mass allocation, the carbon footprint of the PHB conversion routes also decreases if co-products are sold. When no co-products are sold, the use of dry PHB is economically preferred but aqueous PHB presents lower carbon footprint. When co-products are sold, aqueous PHB is the preferred feedstock for utilisation in the manufacture of the chemical building blocks MC

and MA, both in economic and carbon footprint terms.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jclepro.2016.07.152>.

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Abbreviations

- AA: acrylic acid
 CA: crotonic acid
 DCM: dichloromethane
 DSP: downstream processing
 GWP: global warming potential
 HBA: hydroxybutyric acid
 MA: methyl acrylate
 MC: methyl crotonate
 M₃HB: methyl 3-hydroxybutyrate
 PHB: polyhydroxybutyrate
 TON: turnover number
 UU: Utrecht University in the Netherlands
 WUR: Wageningen University in the Netherlands
 WWT: wastewater treatment