SUPPLEMENTARY INFORMATION

S1. TEA calculations for PHA or PHB production from well-defined carbon sources

For well-defined carbon sources analysis was performed based on Leong et al [62]. The PHB yield (Y_{PHB}, kg_{PHB}/kg_{carbon}) was calculated using the following equation:

$$Y_{PHB} = \frac{TP}{C_{raw} \times N_b} \tag{S1}$$

where TP is the target PHB production (ton/year), C_{raw} is the raw carbon source required for one batch (tons/run), and N_b is the number of batches (run/year).

PHB production (P_{PHB}, ton/year) was calculated as:

$$P_{PHB} = \frac{TP}{\left(\frac{RE}{100}\right)} \tag{S2}$$

where *RE* is the recovery efficiency (%).

Total time for each fermentation (T_{tf}, h), number of batches (N_b) and the required PHB production (P_{req}) for every batch (run) were calculated as:

$$T_{tf} = T_f + T_{ta} \tag{S3}$$

$$N_b = \frac{T_{op}}{T_{tf}} \tag{S4}$$

$$P_{req} = \frac{P_{PHB}}{N_b} \tag{S5}$$

where T_f is the fermentation time (h), T_{ta} is the turnaround time (h), T_{op} is the total operating time (h/year), N_b is the total number of batches (runs/year).

The required volume (V_{PHB}, L/run) and amount (C_{raw}, kg/run) of carbon source for each of the batches as well as the amount of carbon source required for the operation of the production plant for one year (TC_{raw}, kg/year) are calculated using the following equations:

$$V_{PHB} = \frac{P_{req}}{T_{tf} \times X_{PHB}} \tag{S6}$$

$$C_{raw} = \frac{P_{req}}{Y_{PHB}} \tag{S7}$$

$$TC_{raw} = C_{raw} \times N_b \tag{S8}$$

where P_{req} is the required PHB production in one run (kg/run), T_{tf} refers to the total time of each fermentation (h) and X_{PHB} is the PHB productivity value (kg/l h), Y_{PHB} is the PHB yield (kgPHB/kgcarbon), and Nb is the number of batches (run/year).

The economic analysis for calculating production costs was performed to estimate the capital costs of the process units and the operating costs. The total fixed capital cost (DFC, $) was calculated with the following equation:

$$DFC = TPDC + TPIC + OTC \tag{S9}$$

where TPDC term refers to the sum of total plant direct costs (equipment purchase, installation, process piping, instrumentation, etc.), TPIC refers to the total plant indirect costs (engineering and construction) and OTC refers to other costs (contractor's fee, contingency, etc.).

The fixed direct capital cost per ton of PHB produced (DFC_{PHB}, $/ton) and the unit cost of fixed direct capital per ton and per unit volume ($DFC_{V.PHB}$, $/ton m^3) required for each of the production batches were calculated as:

$$DFC_{PHB} = \frac{DFC}{TP} \tag{S10}$$

$$DFC_{V.PHB} = \frac{DFC_{PHB}}{V_{PHB}} \tag{S11}$$

where TP is the target PHB production (ton/year) and V_{PHB} is the volume needed for every batch (m^3).

The annual operating cost of the PHB production plant was also calculated based on the study of Leong et al [62]. Two terms related to the raw materials costs used in the PHB production process were considered, the raw carbon source and other raw materials costs. Therefore, the following equations were used to determine the annual operating costs of the plant, including total costs of raw materials (*RM*) and partial operational costs (without the raw carbon source costs, *POC*) :

$$RM = RM_{raw} + RM_o \tag{S12}$$

$$POC = RM_o + LD + FC + O + U + WTD \tag{S13}$$

where RM_{raw} is the cost of raw carbon source, RM_o refers to the costs of other materials, *LD* is the labor-dependent costs, *FD* is the facility-dependent costs, *O* refers to other consumable costs, *U* refers to utilities' costs and *WTD* refers to the waste treatment/disposal costs.

The partial operating cost of the plant per ton of PHB produced (POC_{PHB}, \$/ton) and the unit cost of the partial operating cost per ton and per unit volume ($POC_{V.PHB}$, \$/ton m^3) required for each of the production batches were calculated as:

$$POC_{PHB} = \frac{POC}{TP} \tag{S14}$$

$$POC_{V.PHB} = \frac{POC_{PHB}}{V_{PHB}} \tag{S15}$$

where TP is the target PHB production (ton/year) and V_{PHB} is the volume needed for every batch (m^3).

The cost of raw carbon source, (RM_{raw}, \$) was calculated by multiplying the total amount of carbon source required in the annual PHB production process and the unit cost of the carbon source:

$$RM_{raw} = TC_{raw} \times CC_{raw} \tag{S16}$$

where TC_{raw} is the raw carbon source required per year (kg/year) and CC_{raw} is the unit cost of raw carbon source required (\$/kg).

Furthermore, the total annual operating cost (OC, \$/year) was calculated considering the total cost of the carbon source (RM_{raw}, \$) and the partial operating cost (POC, \$) as:

$$OC = POC + RM_{raw} \tag{S17}$$

The PHB production cost can be calculated using this total annual operating value (OC, \$/year) and the target PHB production value (TP, ton/year):

$$PC_{PHB} = \frac{OC}{TP} \tag{S18}$$

To scale an initial production capacity to a target value and obtain the direct fixed capital costs and operational costs, the energy cost of the production plant and the capacity were considered [71]:

$$\left(\frac{PC_1}{PC_2}\right)^{0.8} = \frac{DFC_1}{DFC_2} \tag{S19}$$

$$\left(\frac{PC_1}{PC_2}\right)^{0.8} = \frac{OC_1}{OC_2} \tag{S20}$$

where PC_1 and PC_2 refer to the initial and target capacity of the production plant, respectively. DFC_1 and DFC_2 refer to the total fixed capital cost (DFC, \$) of the corresponding production capacity. OC_1 and OC_2 refer to the total annual operating value (OC, \$) of the corresponding production capacity. When using complex carbon sources that are considered waste, such as wastewater, residual biomass, or carbon dioxide, relevant credits were considered in some cases that could affect the annual operating cost. In addition, the costs shown in the comparative table have been adjusted to 2020 U.S. dollars using the producer price index (PPI) for total manufacturing industries [63]. All other inputs are specified for each case.

S2. TEA calculations for PHA or PHB production from complex carbon sources in a two-step process

The two-step process includes a fermentation step to transform carbohydrates into volatile fatty acids and other carboxylic acids, followed by the step of PHB production. For the two-step process, the calculations were based on the work of Fernandez-Dacosta [12]. The equations used for the calculations are given for PHB production through the process of accumulation (Ac), selection, feast/famine (SFF) regime and finally the acidogenic fermentation (AF) process to calculate the flow rate of organic wastes required for PHB production. The total operating hours were assumed to be 7920 h per year.

The amount of PHB to be produced is calculated using equation (S2), considering the target PHB production and the efficiency of recovery. The total time required to carry out a production batch of PHB (T_t, h) is calculated using the following equation:

$$T_t = T_{AF} + T_{SFF} + Tcl_{SFF} + Tcl_{Ac} + T_{ta} \quad \text{(S21)}$$

where T_{AF} is the solid residence time required in the anaerobic fermentation time (h), T_{SFF} is the solid residence time required in the selection, feast/famine regime (h), Tcl_{SFF} is the cycle length time in the selection, feast/famine regime (h), Tcl_{Ac} is the cycle length time in the accumulation stage (h) and T_{ta} is the turnaround time (h).

The total number of batches (runs/year) and the required PHB production in one run (ton/run) are calculated using equations (S4) and (S5). PHB produced per batch (B_{req}, ton/run) was calculated as

$$B_{req} = \frac{P_{req}}{IC} \tag{S22}$$

where P_{req} is the required PHB production in one batch (ton/run) and *IC* is the PHB intracellular content (%).

For the PHB production stage, the required volume (V_{Ac}, m^3/run) and the COD concentration (C_{AC}, kg/run) are calculated using the following equations:

$$V_{Ac} = \frac{B_{req}}{TSS} \tag{S23}$$

$$C_{Ac} = \frac{B_{req}}{Y_{Ac}} \tag{S24}$$

where *TSS* is the total suspended solid concentration (kg/m^3) and Y_{Ac} is the conversion yield from COD to PHB (kg $_{\mathrm{PHB}}$/ kg $_{\mathrm{COD}}$).

The production of volatile fatty acids (P_{VFA}, kg/run) and the volume required (V_{SFF}, m^3/run) in the selection and feast/famine stage are calculated using the following equations:

$$V_{SFF} = \frac{C_{Ac}}{MC_S} \tag{S25}$$

$$P_{VFA} = \frac{C_{Ac}}{Y_{SFF}} \tag{S26}$$

where MC_{S} is the maximum biomass concentration in the selector (kg/m^3) and Y_{SFF} is the biomass yield on a substrate (kg $_{\mathrm{PHB}}$/ kg $_{\mathrm{COD}}$).

For the acidogenic fermentation stage, the following equations were used to obtain the productivity of volatile fatty acid (X_{VFA}, kg/m^3 h), the target concentration of CODs in the effluent (C_{AF}, kg/run), as well as the required volume of effluent (V_e, m^3/run) to satisfy the target PHB production.

$$X_{VFA} = \frac{CC_{AF}}{T_{AF}} \tag{S27}$$

$$C_{AF} = \frac{P_{VFA}}{Y_{AF}} \tag{S28}$$

$$V_e = \frac{C_{AF}}{C_e} \tag{S29}$$

$$TV_e = V_e \times N_b \tag{S30}$$

where T_{AF} is the residence time required in the anaerobic fermentation (h), CC_{AF} is the conversion capacity of organic wastes into soluble CODs per day (kg/m^3), P_{VFA} is the production of volatile fatty acids (kg/run), Y_{AF} is the yield in the acidogenic fermentation stage (kg COD/ kg COD), C_e is the concentration of CODs in the effluent after the fermentation step (kg/m^3), TV_e is the required volume of the effluent (m^3/year) and N_b is the number of batches (run/year).

When the initial volume of the organic materials is known, the equations can be used as follows. During the acidogenic fermentation stage, the following equations are applied:

$$V_e = \frac{TV_e}{N_b} \tag{S31}$$

$$C_{AF} = V_e \times C_e \tag{S32}$$

$$V_{AF} = \frac{C_{AF}}{X_{VFA} \times T_{AF}} \tag{S33}$$

$$P_{VFA} = C_{AF} \times Y_{AF} \tag{S34}$$

In the selection feast/famine stage, the following equations are applied:

$$C_{Ac} = P_{VFA} \times Y_{SFF} \tag{S35}$$

$$V_{SFF} = \frac{C_{Ac}}{MC_S} \tag{S36}$$

In the accumulation stage, the following equations are applied:

$$B_{req} = C_{Ac} \times Y_{Ac} \tag{S37}$$

$$P_x = B_{req} \times IC \tag{S38}$$

$$P_{req} = P_x \times \left(\frac{RE}{100}\right) \tag{S39}$$

$$P_{PHB} = P_{req} \times N_b \tag{S40}$$

Finally, to obtain the value of overall yield of PHB production per unit volume of wastewater (*GY*, kg PHB/m3) and to obtain the value of overall yield per unit of chemical oxygen demand in wastewater (*CY*, kg PHB/kg COD effluent), the following equations are used:

$$GY = \frac{P_{req}}{V_e} \tag{S41}$$

$$CY = \frac{P_{req}}{C_{AF}} \tag{S42}$$

where V_e is the required volume of effluent per batch (m^3/run), TV_e is the total required volume of effluent (m^3/year), N_b is the number of batches (run/year), C_{AF} is the required amount of CODs in the effluent (kg/run), C_e is the concentration of COD in the effluent (kg/m^3), V_{AF} is the volume required in the acidogenic fermentation stage (m^3/run), X_{VFA} is the productivity of volatile fatty acid (kg (m^3 h)$^{-1}$) from organic wastes, T_{AF} is the residence time required in the anaerobic fermentation (h), is the production of volatile fatty acids (kg/run), Y_{AF} is the yield in the acidogenic fermentation stage (kg COD/ kg COD), V_{Ac} is the required volume at the accumulation stage (m^3/run), C_{AC} is the COD amount at the accumulation stage (kg/run), *TSS* is the total suspended solid concentration (kg/m^3), Y_{Ac} is the conversion yield from COD to PHB (kg PHB/ kg COD), *MCS* is the maximum biomass concentration in the selector (kg/m^3), Y_{SFF} is the biomass yield on CODse (kg PHB/ kg COD), V_{SFF} is the volume required in the selection and feast/famine stage (m^3/run), CC_{AF} is the daily conversion capacity of organic wastes into CODs (kg/m^3), B_{req} refers to the PHB producing bacteria per batch (ton/run), P_{req} is the required PHB production in one batch (ton/run), *IC* is the PHB intracellular content (%).

The calculation of costs of PHB production from a complex carbon source are performed using the following methodology. The fixed capital cost (DFC, \$), the fixed direct capital cost per ton of PHB produced ($\mathrm{DFC_{PHB}}$, \$/ton) and the unit cost of fixed direct capital per ton and per unit volume ($\mathrm{DFC_{V.PHB}}$, \$/ton m^3) are calculated in the same way as in the case of PHB production from well-defined carbon sources using the equations (S9), (S10) and (S11).

Similarly, the annual operating cost of the PHB production plant is obtained according to the partial operating cost (*POC*, \$) which consider the raw materials (RM-carbon source and RM-other), labor-dependent elements (LD), facility-dependent elements (FD), other consumables (O), utilities (U) and waste treatment/disposal (WTD) calculated using the equation (13). For PHB production from organic wastes disposal credits are taken into account. Therefore, the calculation of the PHB production is provided considering (OC_{C}, \$), or disregarding (OC_{NC}, \$) the credits associated with waste disposal.

$$OC_{NC} = POC \tag{S43}$$

$$OC_{C} = POC - (Cd \times TP) \tag{S44}$$

where *POC* is the partial operating cost ($), *Cd* refer to the credits associated to the use of waste carbon sources ($/ton) and *TP* refers to the target of PHB production (ton/year).

PHB production costs are calculated using equation (S18). Similarly, the process of calculating the scaling of a production plant to a specified target is performed using equations (19) and (20) to obtain the total fixed capital cost and the total annual operating value for the target production capacity. Finally, the costs are also adjusted to 2020 U.S. dollars using the producer price index (PPI) for total manufacturing industries [63].

S3. TEA calculations for PHA and PHB production from CO_2

For the two-stage process of PHB production from CO_2 in a MES, acetate production from CO_2 (first stage) was evaluated by calculating the daily production of acetate (P_{AC}, kg/day) :

$$P_{Ac} = X_{Ac} \times T_{o} \tag{S45}$$

where X_{AC} is the productivity of acetate formation from CO_2 (kg/h) and T_o is the operating time during one day (h/day).

The amount of CO_2 required to achieve the target production of acetate (C_{CO2}, kg/day) the following equation was used:

$$C_{C02} = \frac{P_{Ac}}{MY_{Ac}} \tag{S46}$$

where MY_{Ac} is the yield in the MES to produce acetate from CO_2.

The calculation of the costs of production of acetate with CO_2 as raw material was made considering Eq. S9 for fixed capital cost (DFC, \$) calculation, which is the sum of total plant direct costs (equipment purchase, installation, process piping, instrumentation, etc.). Equipment cost analysis for MES included the electrode.

The calculation of operating costs for acetate production (OC_{AC}, \$/year) was carried out considering fixed costs and variable costs:

$$OC_{Ac} = FC_{Ac} + VC_{Ac} \tag{S47}$$

where FC_{AC} (\$) is the fixed costs including maintenance (labor and materials), operating labor, laboratory costs, supervision, plant overheads, capital charges, rates (taxes) and insurance. FC_{AC} (\$) refers to the variable costs, which are mainly raw materials, utilities, and biocatalysts. As the MES was considered to operate continuously, biocatalysts were included as a single cost in the raw materials. However, their storability and reproducibility at minimal cost were considered.

The acetate production cost (PC_{Ac}, \$/kg) can be calculated using this total annual operating value (OC_{Ac}, \$/year) and the target acetate production (TP, kg/year):

$$PC_{Ac} = \frac{OC_{Ac}}{TP} \tag{S48}$$

Finally, to scale the production capacity to a target capacity, the equations (S19) and (S20) were used to obtain the direct fixed capital costs and operational costs.

For the stage of PHB production from acetate, the methodology for well-defined carbon sources was followed.