Electronic Supplementary Material (ESI) for Green Chemistry.

Maximizing the sustainability of a macroalgae biorefinery: a superstructure optimization of a volatile fatty acid platform

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Table S.1. Nomenclature of the superstructure.

Notation	Description	Reference
1,1	Feed (SJ)	[1]
	Anaerobic digestion	
1,2	Anaerobic digestion of SJ	[2]
	Volatile fatty acids extraction	
1,3	Extraction followed by distillation	[3]
2,3	Membranes followed by extraction and distillation	[3,4]
	Mixed alcohols synthesis	
1,4	Bypass	
2,4	Hydrogenation	[5,6]
	Carbon dioxide utilization	
1,5	MA cultivation in open pond	[7,8]
2,5	MA cultivation in photobioreactor	[7,8]
3,5	Venting carbon dioxide to atmosphere	
	MA harvesting	
1,6	Gravity settler for MA harvesting	[9]
2,6	Hollow filter membranes for MA harvesting	[10,11]
3,6	Diffused air flocculation for MA harvesting	[12–14]
4,6	Electrocoagulation for MA harvesting	[15,16]
5,6	Centrifuge for MA harvesting	[17]
6,6	Belt filter press for MA harvesting	[18,19]
	Purification	
1,7	Hydrogen purification via PSA	[20]
2,7	Mixed acid purification via distillation	[21]
3,7	Mixed alcohol purification via pervaporation followed by distillation	[22]
4,7	Mixed alcohol purification via molecular sieves followed by distillation	[23–25]
5,7	DDS purification	[26]
	Wastewater treatment	
1,8	Wastewater treatment	[25,27]
	Products	
1,9	Hydrogen sold as a byproduct	-
2,9	Hydrogen utilized in the hydrogenation	-
3,9	Treated water recycle to process	-
4,9	Acetic acid	-
5,9	Propionic acid	-
6,9	Butyric acid	-
7,9	Ethanol	-
8,9	Propanol	-
9,9	Butanol	-
10,9	MA	-
11,9	DDS	-

Table S.2. Stoichiometric reactions used in anaerobic digestion.[2,3]

Component	**Reaction**
Glucose	$5C_6H_{12}O_6 + 4H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 12H_2$
Laminaran & cellulose	$5C_6H_{10}O_5 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 12H_2$
Mannitol	$5C_6H_{14}O_6 + 4H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$
Alginate	$5C_6H_{12}O_6 + 12H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 10H_2$
Fucose	$5C_6H_{12}O_6 + 9H_2O \rightarrow 6C_2H_4O_2 + 2C_3H_6O_2 + C_4H_8O_2 + 8CO_2 + 17H_2$
Protein	$23C_{13}H_{25}O_7N_3S + 99H_2O + 26H_2 \rightarrow 78C_2H_4O_2 + 26C_3H_6O_2 + 13C_4H_8O_2 + 13CO_2 + 69NH_3 + 23H_2S$
Lipid	$46C_{18}H_{34}O_2 + 238H_2O + 102H_2 + 13CO_2 \rightarrow 306C_2H_4O_2 + 02C_3H_6O_2 + 51C_4H_8O_2$

Table S.3. Design parameters for microalgae cultivation and harvesting.[8,16–18,28]

Process alternative	**Algae productivity**	**Lipid yield**	**Power consumption**	**Heat removed by chillers**	**Outlet concentration**	**Separation efficiency**
Open pond	25 g/m^2/day	25%	11 kW	-	-	-
PBR	1.25 kg/m^3/day	25%	3.9 kWh/acre	83.4 GJ/day	-	-
Gravity settler	-	-	Negligible		1%	90%
HFM	-	-	0.04 kWh/m^3		13%	99.5%
ECA	-	-	0.7 kWh/m^3		6%	95%
DAF	-	-	0.133 kWh/kg		6%	95%
Centrifuges	-	-	1.35 kWh/m^3		20%	99.7%
Belt filter press	-	-	0.3 kWh/m^3		20%	98%

1 Mathematical model

The mathematical model of the superstructure is formulated as an MINLP problem by considering the mass balance, energy balance, capital and operating cost constraints.

1.1 Mass balance constraints

The superstructure includes two types of splitters. The first is a fractional splitter that can take any value between 0 and 1, with several parallel pathways possible in this case. The second is a conditional splitter, which can take an integer value of either 0 or 1. These splitters must select one optimal technology from multiple alternatives. The first and second types of splitters are abbreviated as *spl1* and *spl2*, respectively.

The mass balance constraints of the splitters can be modeled as follows:

$$F_i^k = F_i^{in} \times \mu^k, \forall k \in K, \forall i \in I, \tag{1}$$

$$\sum_{k=1}^{n_k} \mu^k = 1, \tag{2}$$

$$F_{i,j}^{in} = \sum_{k=1}^{n_k} F_{i,j}^k, \forall i \in I, \forall j \in J, \tag{3}$$

and

$$F_{i,j}^k \leq y_{k,j} \times UB, \forall k \in K, \forall i \in I, \forall j \in J, \tag{4}$$

where F_i^k, F_i^{in}, μ^k, $F_{i,j}^{in}$, $F_{i,j}^k$, $y_{k,j}$, and UB represent the mass flow rate of component *i* in the outlet stream *k*, mass flow rate of component *i* in the inlet stream, split fraction of the stream *k*, mass flow rate of component *i* in the inlet stream *k* from stage *j*, mass flow rate of component *i* in the outlet stream *k* from stage *j*, binary variable used to select option *k* from stage *j*, and upper bound, respectively. The logical constraint that enforces the selection of only one technology is given by

$$\sum_{k=1}^{n_k} y_{k,j} \leq 1 \quad . \tag{5}$$

Eqs. (1) and (2) refer to *spl1*, while Eqs. (3)–(5) correspond to *spl2*.

The mass balance equation for reactors such as the anaerobic digester, open ponds, photobioreactors, and harvesting technologies where the reactant *r* is converted to the product *p* is given by

$$F_p^k = F_r^{in} \times \Phi_{p,r}^k + F_p^{in}, \forall k \in K, \forall p \in P, \forall r \in R \quad , \tag{6}$$

where F_p^k is the mass flow rate of product *p* in the outlet stream *k*, F_r^{in} is the mass flow rate of reactant *r* in the inlet stream, F_p^{in} is the mass flow rate of product *p* in the inlet stream, and $\Phi_{p,r}^k$ is the yield of product *p* from reactant *r* in the outlet stream *k*.

The mass balance of component *i* in the outlet stream *k* in the pressure swing adsorption (PSA), mechanical separator, dryer, and decanter is given by

$$F_i^k = F_i^{in} \times \zeta_i^k, \forall k \in K, \forall i \in I \quad , \tag{7}$$

and

$$\sum_{k=1}^{n_k} \zeta_i^k = 1 , \forall i \in I \quad , \tag{8}$$

where ζ_i^k represents the recovery of component *i* in the outlet stream *k.*

The mass composition (X_i^k) of component *i* in the stream *k* is given by

$$\sum_{k=1}^{n_k} X_i^k = \sum_{k=1}^{n_k} \frac{F_i^k}{F^k}, \forall i \in I \quad (9)$$

,

where F^k is the overall mass flow rate of the stream *k.*

In the flash column, the mass balance of component *i* in the outlet stream *k* can be determined by

overall mass balance: $$F_i^{in} = \sum_{k=1}^{n_k} F_i^k, \forall i \in I \quad (10)$$

,

Antoine relation: $$log_{10} VP_i^{in} = A_a^i - \frac{A_b^i}{T^{in} + A_c^i}, \forall i \in I \quad (11)$$

,

Henry relation: $$log VP_i^{in} = H_a^i + \frac{H_b^i}{T^{in}} + H_c^i \times log T^{in} + H_d^i \times T^{in}, \forall i \in I \quad (12)$$

,

equilibrium relation: $$K1_i^{in} = \frac{VP_i^{in}}{P^{in}}, \forall i \in I \quad (13)$$

,

bottom composition: $$X1_i^{k1} = \left(\frac{LV + 1}{LV + K1_i^{in}}\right) \times X_i^k, \forall k1 \in K, \forall i \in I \quad (14)$$

,

top composition: $$Y1_i^{k2} = X1_i^{k1} \times K1_i^{in}, \forall i \in I, \forall k1, k2 \in K \quad (15)$$

,

top overall flowrate:

$$F^{k2} = \left(\frac{F^{in}}{LV + 1}\right), \forall i \in I, \forall k2 \in K, \tag{16}$$

top component flowrate:

$$F^{k2}_{i} = F^{k2} \times Y1^{k2}_{i}, \forall i \in I, \forall k2 \in K, \tag{17}$$

logical constraint 1:

$$\sum_{i}^{n_i} X1^{k1}_{i} = 1, \tag{18}$$

and logical constraint 2:

$$\sum_{i}^{n_i} Y1^{k2}_{i} = 1, \tag{19}$$

where VP^{in}_{i} is the vapor pressure of component *i* in the inlet stream, A^{i}_{a}, A^{i}_{b}, and A^{i}_{c} are the Antoine parameters of component *i*, H^{i}_{a}, H^{i}_{b}, H^{i}_{c}, and H^{i}_{d} are the Henry parameters of component *i*, T^{in} is the inlet temperature, $K1^{in}_{i}$ are the K-values of component *i* in the inlet stream, *LV* is the liquid to vapor ratio, $X1^{k1}_{i}$ is the bottom composition of component *i* in the stream *k1*, $Y1^{k2}_{i}$ is the top composition of component *i* in the stream *k2*, F^{k2} is the flowrate of the top stream, and F^{in} is the mass flowrate of the inlet stream.

In the extraction column, the mass balance of component *i* in the outlet stream *k* can be determined by

overall mass balance:

$$F^{in}_{i} + F^{in}_{MTBE} = \sum_{k=1}^{n_k} F^{k}_{i}, \forall i \in I, \tag{20}$$

extraction solvent:

$$F_{MTBE}^{in} = F^{in} \times \sum_{sf=1}^{sf_n} \lambda_{sf} \times b1_{sf} , \tag{21}$$

stages (*N*):

$$N = \sum_{st=1}^{st_n} \sum_{sf=1}^{sf_n} \nu_{st} \times b2_{sf}^{st} , \tag{22}$$

extract mass balance:

$$F_i^{k1} = F_i^{in} \times \sum_{st=1}^{st_n} \sum_{sf=1}^{sf_n} \xi_{i,sf}^{st} \times b2_{sf}^{st}, \forall k1 \in K, \forall i \in I , \tag{23}$$

raffinate mass balance:

$$F_i^{k2} = F_i^{in} - F_i^{k1}, \forall k2 \in K, \forall i \in I , \tag{24}$$

logical Constraint 1:

$$\sum_{sf=1}^{sf_n} b1_{sf} = 1 , \tag{25}$$

logical Constraint 2:

$$\sum_{st=1}^{st_n} \sum_{sf=1}^{sf_n} b2_{sf}^{st} = 1 , \tag{26}$$

and logical Constraint 3:

$$\sum_{sf=1}^{sf_n} b1_{sf} = \sum_{st=1}^{st_n} \sum_{sf=1}^{sf_n} b2_{sf}^{st} , \tag{27}$$

where F_{MTBE}^{in} is the mass flow rate of the extraction solvent in the inlet stream, λ_{sf} is the parameter corresponding to the solid to feed ratio, $b1_{sf}$ is the binary variable for selecting the optimal solid to feed ratio, ν_{st} is the parameter indicating the number of stages, $b2_{sf}^{st}$ is the binary variable for selecting the optimal number of stages, F_i^{k1} is the mass flow rate of component *i* in the extract stream, $\xi_{i,sf}^{st}$ is the split fraction of component *i* in the outlet stream *k*, and F_i^{k2} is the mass flow rate of component *i* in the raffinate stream.

In the stripping column, the mass balance of component *i* in the outlet stream *k* can be determined by

overall mass balance:

$$F_i^{in} + F_{LP}^{in} = \sum_{k=1}^{n_k} F_i^k, \forall i \in I \quad , \tag{28}$$

LP-steam balance (F_{LP}^{in}):

$$F_{LP}^{in} = \frac{F^{in} \times \varphi}{\sum_{i=1}^{n_i} K1_i^{in}} \quad , \tag{29}$$

stages (*N*):

$$\frac{\varphi - 1}{\varphi^{N+1} - 1} = 1 - \square \quad , \tag{30}$$

absorption factor (A_i):

$$A_i = \frac{F_i^{in}}{K1_i^{in} \times F_{LP}^{in}}, \forall i \in I \quad , \tag{31}$$

stripping factor (S_i):

$$S_i = \frac{K1_i^{in} \times F_{LP}^{in}}{F_i^{in}}, \forall i \in I \quad , \tag{32}$$

fraction of components not absorbed ($\gamma 1_i$):

$$\gamma 1_i = \frac{A_i - 1}{A_i^{N+1} - 1}, \forall i \in I \quad , \tag{33}$$

fraction of components not stripped ($\gamma 2_i$):

$$\gamma 2_i = \frac{S_i - 1}{S_i^{N+1} - 1}, \forall i \in I \, , \tag{34}$$

bottom mass balance (F_i^{k1}):

$$F_i^{k1} = F_i^{in} \times \gamma 2_i + F_{LP}^{in} \times \left(1 - \gamma 1_i\right), \forall k1 \in K, \forall i \in I \, , \tag{35}$$

and top mass balance (F_i^{k2}):

$$F_i^{k2} = F_i^{in} - F_i^{k1}, \forall k2 \in K, \forall i \in I \, , \tag{36}$$

where φ is the stripping factor and ⍰ is the recovery of the key component.

In the distillation model, it is assumed that all components heavier than the heavy key component would accumulate in the bottom stream. Similarly, all components lighter than the light key component will accumulate in the distillate. The mass balance equations of the light key (*lk*) and heavy key (*hk*) components in the distillate **(***d***)** and bottom (*b*) stream can be modeled as

$$F_{lk}^{d} \geq F_{lk}^{in} \times \omega_{lk}^{D}, \ \forall d \in K, \forall lk \in I \, , \tag{37}$$

$$F_{lk}^{b} \leq F_{lk}^{in} \times (1 - \omega_{lk}^{D}), \ \forall b \in K, \forall lk \in I \, , \tag{38}$$

$$F_{hk}^{d} \leq F_{hk}^{in} \times \omega_{hk}^{D}, \ \forall d \in K, \forall hk \in I \, , \tag{39}$$

$$F_{hk}^{b} \geq F_{hk}^{in} \times (1 - \omega_{hk}^{D}), \ \forall b \in K, \forall hk \in I \, , \tag{40}$$

where ω_{lk}^{D} and ω_{hk}^{D} are the split fractions of the light key and heavy key components in the distillate, which can be estimated by modeling the rigorous distillation column (Radfrac) in the Aspen Plus ® V10 software.

The mass balance constraint for the mixers, pumps, compressors, and heat exchangers is

$$F_{i}^{out} = \sum_{k=1}^{n_k} F_{i}^{k}, \forall i \in I \quad , \tag{41}$$

where F_{i}^{k} is the mass flowrate of component *i* in the inlet steam *k*.

The amount of solids at any stage *j* is controlled by

$$F_{i,j}^{k} \leq \alpha_{i,j}^{k} \times F_{j}^{k}, \forall k \in K, \forall i \in I, \forall j \in J \, , \tag{42}$$

and

$$F_{j}^{k} = \sum_{i=1}^{n_i} F_{i,j}^{k}, \forall k \in K, \forall j \in J \quad , \tag{43}$$

where $F_{i,j}^{k}$ is the mass flowrate of component *i* in the stream *k* of stage *j*, F_{j}^{k} is the total mass flowrate in stream *k* of stage *j*, and $\alpha_{i,j}^{k}$ is the mass fraction of component *i* in the stream *k* of stage *j*.

The feedstock purchase is bounded by its availability (*Θ)* and minimum purchase amount (*Y*):

$$\Theta \geq Feed \geq Y. \tag{44}$$

1.2 Energy balance constraints

The following energy balance constraint was used for each unit operation:

$$\sum_{i=1}^{n_i} F_i^{in} \times cp_i^{in} \times T^{in} + Q_{GEN} + Q_{EXT} = \sum_{i=1}^{n_i} F_i^{out} \times cp_i^{out} \times T^{out}, \tag{45}$$

where cp_i^{in} and cp_i^{out} are the specific heat values of component *i* corresponding to the inlet and outlet conditions, respectively, T^{in} and T^{out} are the temperatures with respect to the inlet and outlet conditions, respectively, F_i^{in} and F_i^{out} are the flows corresponding to the inlet and outlet conditions, respectively, and Q_{GEN} and Q_{EXT} are the heat power values generated during the process and external heat duty, respectively.

Heat balance in the reboiler and condenser is determined by a simple relation and can be rearranged as

$$Q_{EXT} = (1 + R)\sum_{i=1}^{n_i} f_{b,i}\lambda_i, \tag{46}$$

and

$$Q_{EXT} =- (1 + R)\sum_{i=1}^{n_i} f_{d,i}\lambda_i, \tag{47}$$

where $f_{d,i}$, $f_{b,i}$, R, and λ_i are the component molar flowrate in the distillate, component molar flowrate at the bottom, reflux ratio, and latent heat of the component *i,* respectively.

The temperature and pressure of the outlet stream of the flash, distillation, and stripping columns and membranes can be determined using Eqs. (11) and (12), and the bubble point and due point equations.

The power (kW) required for the pumps and compressors can be determined by

$$Power = \frac{\sum_{i=1}^{n_i} \rho_i \times \left(P^{out} - P^{in}\right)}{\eta_{pump}}, \tag{48}$$

and $$Power = \sum_{k=1}^{n_k} \sum_{i}^{n_i} \frac{F_i^k}{MW_i^k} \times T^k \times r \times \left(\frac{\gamma}{\gamma - 1}\right) \times PR^{\left(\frac{\gamma}{\gamma - 1} - 1\right)} \times \frac{1}{\eta_{comp}} \times n_{comp}, \tag{49}$$

where ρ_i is the volumetric density of component *i*, P^{out} is the outlet pressure, P^{in} is the inlet pressure, η_{pump} is the pump efficiency, MW_i^k is the molecular weight of component *i* in the stream *k*, *r* is the general gas constant, γ is the heat capacity ratio, η_{comp} is the compressor efficiency, n_{comp} is the number of stages in the compressor, and *PR* is the pressure ratio. PR can be determined by

$$(PR)^{n_{comp}} = \frac{P^{out}}{P^{in}}. \tag{50}$$

The inter-stage cooling load (kW) between the stages of a multi-stage compressor can be determined using Eq. (45)

1.3 Economic analysis constraints

A techno-economic model was formulated to conduct multiperiod economic analysis, which includes constraints for estimating the total capital investment (TCI) and total cost of manufacturing (TCOM).

1.3.1 Total capital investment

The TCI consists of the total direct costs (TDC), total indirect costs (TIDC), working capital costs, and land costs. The TDC includes the costs related to the equipment, site development, and warehouse, along with additional expenses for the piping and instrumentation. Similarly, the TIDC includes the portable and field expenses, project contingency costs, and home and office construction costs. The equipment cost was determined using the relevant economic data from literature, which are summarized in Table S.1.

Table S.4. Data for calculating the capital cost.[3,8,18,25,29,30]

Equipments	**Baseline Purchased Cost USD**	**Year of quote**	**Scaling Exponents**	**Installation factor**
Pump	22,500	2009	0.8	2.3
Heater	92,000	2010	0.7	2.2
Digester	2,700,000	2010	0.6	1
Cooler	85,000	2010	0.7	2.2
Flash tank	511,000	2009	0.7	2
Compressor	870,000	2009	0.68	1.6
Pressure swing adsorption	4,855,471	2002	0.6	2.47
Mechanical separator	3,294,700	2009	0.8	1.7
Dryer	10,500,000	1990	0.6	1
Condenser	34,000	2009	0.7	2.2
Membrane	1,000	2010	-	-
Heat exchanger	85,000	2010	0.7	2.2
Extraction column	1,210,000	2012	-	5
Stripping column	114,000	2018	0.6	3
Decanter	569,000	2015	0.6	2
Hydrogenation	2,026,515	2002	0.56	2.47

reactor				
Molecular sieves	901,362	1998	0.7	2.47
Distillation column	3,300,000	2018	0.6	1
Open ponds	158,506,910	2011	1	1
Photobioreactors	109,000	2011	1	1
Inoculum system	18.22/m2	2011	1	1
Covered pond	233,000	2011	1	1
Open lined pond	87,000	2011	1	1
Lining for covered inoculum pond	3,097,827	2014	1	1
Air supported greenhouse for covered inoculum ponds	3/ft2	2014	1	1
Lining for open inoculum pond	3,097,827	2014	1	1
CO_2 piping	1,400,800	2014	0.6	1.25
Storage tank immersion	70,500	2014	1	1.76
Trunk line	1,661,900	2014	1	1.76
Branch line	912,300	2014	1	1.76
Within plot piping	2,210,000	2014	1	1
Makeup delivery section	5,421,935	2014	1	1.37
Primary settler	1,715,000	2014	1	1
Hollow filter membranes	12,864,000	2014	0.75	1
Centrifuge for dewatering microalgae	560,000	2013	1	1

The power law was used to estimate the capacity-adjusted capital cost C_n as follows:

$$C_n = (I_n)(C_{n,o})\left(\frac{Q_n}{Q_{n,o}}\right)^{a_n}, \forall n \in N \quad (51)$$

,

where I_n is the installation factor, $C_{n,o}$ is the cost of the baseline equipment *n*, Q_n and $Q_{n,o}$ are the adjusted and baseline capacities of equipment *n*, and a_n is a scaling exponent, which varies depending on the type of equipment *n*. Once the capacity-adjusted equipment cost has been determined, the capital cost of the equipment is then updated to the year of analysis using the chemical engineering plant cost index (CEPCI):

$$UC_n = C_n\left(\frac{CEPCI_{2019}}{CEPCI_{ref}}\right), \forall n \in N \quad (52)$$

,

where UC_n is the updated equipment cost in the year of interest, and $CEPCI_{2019}$ and $CEPCI_{ref}$ are the index values corresponding to the year 2019 and baseline year, respectively.

The factor approach is used to calculate the TDC and TIDC after the equipment cost has been determined in the year of interest. Tables S.2. and S.3. present the cost factors used to estimate the direct and indirect costs of the volatile fatty acid (VFA) and microalgae sections, respectively.

Table S.5. Cost factors used to estimate the direct and indirect costs of the VFA section.[3,25]

Direct cost	**% of installed costs**
Installed costs	100%
Warehouse	4%
Site development	9%
Additional piping	4.5%
Indirect costs	**% of total direct costs**

Portable costs	10%
Field expenses	10%
Home office and construction	20%
Project contingency	10%
Other costs	10%

Table S.6. Cost factors used to estimate the direct and indirect costs of the microalgae section.[8]

Direct cost	**% of dewatering installed cost**	**% of cultivation installed cost[a]**	**% of OSBL installed cost[b]**
Warehouse	4%	1.2%	-
Site development	9%	-	\$1,534/acre
Additional piping	4.5%	-	-
Indirect costs	**% of dewatering TDC**	**% of cultivation and inoculum pond TDC**	**% of OSBL TDC**
Portable costs	10%	4%	1%
Field expenses	10%	4.5%	1%
Home office and construction	20%	10.3%	1%
Project contingency	10%	10%	10%
Other costs	10%	2.6%	1%

[a] cultivation includes open ponds or photobioreactors and the inoculum system installed cost
[b] Outside battery limit (OSBL) includes the CO_2 delivery installed cost

After all the TDC and TIDC sections have been estimated, the above-mentioned costs are then summed to yield the fixed capital investment (FCI). The working capital, at 5% of the total installed cost, and land costs are subsequently added to obtain the TCI.

1.3.2 Total cost of manufacturing

The TCOM consists of the total direct manufacturing cost (TDMC), total fixed manufacturing cost (TFMC), and general manufacturing cost (GMC). The TDMC includes the costs of the raw materials

(C_{RM}), utilities (C_{UT}), operating labor (C_{OL}), waste treatment (C_{WT}), maintenance and repairs, and patents and royalties. Fixed manufacturing costs include depreciation, local taxes, insurance, and plant overhead. General costs are related to the administration, distribution, and selling expenses in addition to the research and development costs. The cost of the raw materials and utilities can be estimated using the mass and energy balance constraints detailed in Sections 1.1 and 1.2. The cost of operating labor is determined by estimating the labor require for the plant (N_{OL}) based on the following constraints [29]:

$$N_{OL} = C_0 + C_1 N_{np}, \tag{53}$$

and

$$N_{np} = \sum Equipment, \tag{54}$$

where C_0 and C_1 are constants and N_{np} represents the number of nonparticulate processing steps including compression, heating, cooling, mixing, and reaction. The updated wages for the operating labor were retrieved from the U.S. Bureau of Labor and Statistics and subsequently multiplied by N_{OL} to determine C_{OL} [31]. A C_{WT} of \$2.5 per 1000 gal was applied. T_{COM} can be estimated as follows:

$$T_{COM} = f_1 C_{OL} + f_2 F_{CI} + f_3 (C_{UT} + C_{RM} + C_{WT}), \tag{55}$$

where f_1, f_2, and f_3 are multipliers, and F_{CI} is the fixed capital investment.

The total process revenues (*Rev*) from the sale of mixed acids, mixed alcohols, microalgae, hydrogen, and DDS are given by

$$Rev = \sum_{p=1}^{n_p} f_p P_p \quad (56)$$

where n_p is the number of products, f_p is the mass flow rate of product p, and P_p is the wholesale price of product p.

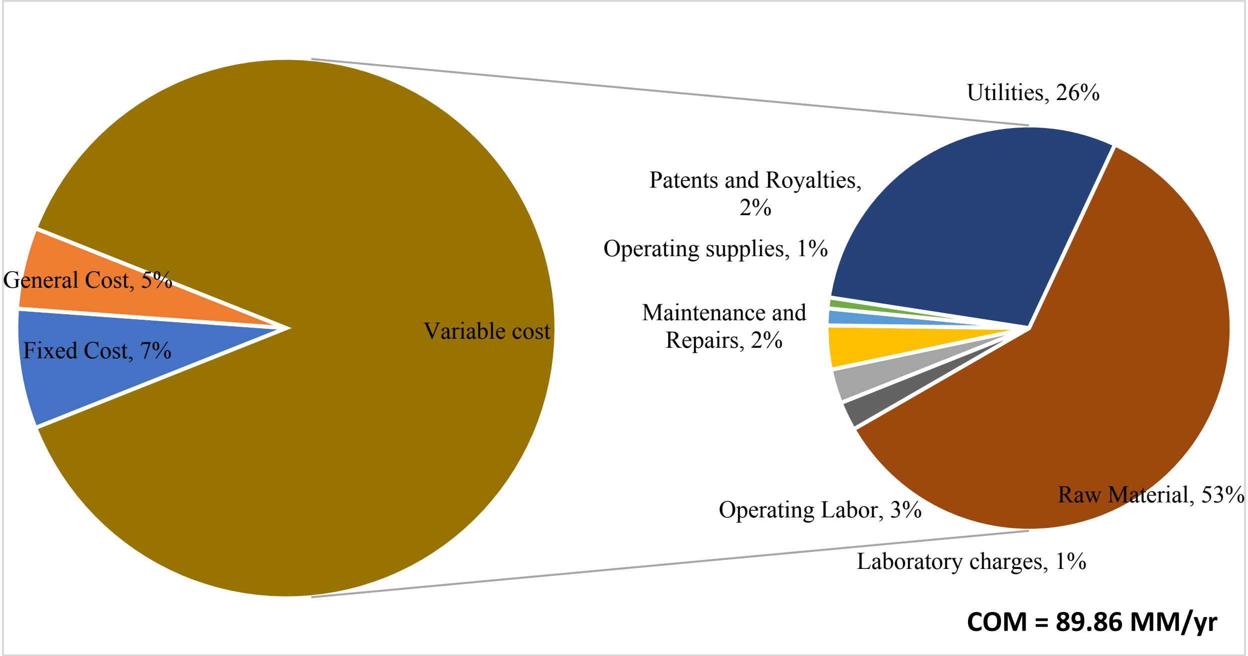

Fig. S.1. Breakdown of the manufacturing costs of the VFA section.

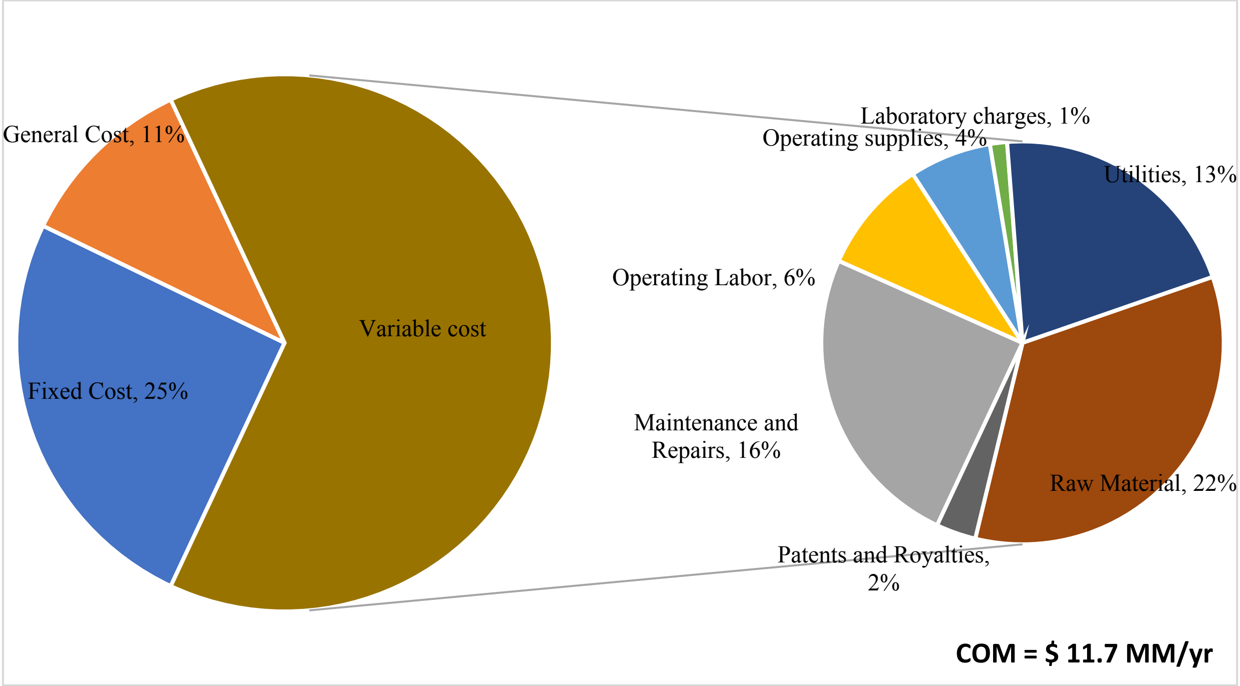

Fig. S.2. Breakdown of the manufacturing costs of the microalgae section.

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