

D5.1. REPORT CONTAINING THE PROCESS MODELS FOR THE HYBRID SYSTEMS



***Artificial PHOTOSynthesis to produce FUELS and chemicals:
hybrid systems with microorganisms for improved light
harvesting and CO₂ reduction***

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EXECUTIVE SUMMARY

This document compiles the data of the hybrid systems into a mathematical model. This data includes information on the microorganisms (growth), photosensitisers (synthesis), medium (composition), reaction (conditions, conversion and selectivity), separation (energy and efficiency) and equipment (area of the photoreactor). The model is mainly based on the material and energy balances of the hybrid systems and consists of 946 equations with 826 variables.

Due to the early-stage state of current experiments, we based the results on published literature about hybrid photosynthesis systems. The model contains a number of parameters and scalars adjusted with this initial data. As the systems are developed experimentally, these values will be updated accordingly, and the model will predict the new behaviour of the system, always using the same set of proposed equations in this document.

1. INTRODUCTION

1.1 DESCRIPTION OF THE DOCUMENT AND PURSUE

The objective of this document is to propose an equation-based model to predict the behaviour of the studied systems for future sustainability assessment. This report outlines a mathematical model to describe hybrid systems. The model includes the material and energy balances of the processes and the design of the main equipment. It is formulated under the assumption that all phenomena occur ideally. However, a set of parameters is included to consider any deviation from said ideality.

1.2 WPS AND TASKS RELATED TO THE DELIVERABLE

This deliverable refers to “Task 5.1: Process models for the hybrid systems” included in WP5: Sustainability Assessment. This task focuses on the modelling of the hybrid systems to provide the necessary material and energy data required for the sustainability assessment.

2. HYBRID SYSTEMS

A hybrid system is defined as the synergistic combination of different technologies to achieve a specific goal. In the artificial photosynthesis context, microorganisms and photosensitisers act jointly to produce a useful chemical or fuel. The photosensitiser collects sunlight and transfers the energy to the microorganisms, which produces the fuels from CO₂ and a hydrogen donor.

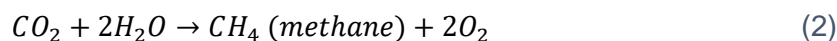
2.1 PROCESS DESCRIPTION

The hybrid systems consist of a mixture of raw materials, photosensitisers, microorganisms and medium that react in a sunlight photoreactor to produce fuel. In this project, we study two different systems:

- **The first system uses the *Moorella thermoacetica* (bacteria)** and the photosensitisers PDI and PFP to catalyse acetic acid production from CO₂ under solar radiation. The hydrogen donor in the system is cysteine (CyS) found in the reaction medium, while cysteine (CySS) is produced as a by-product (Eq.(1)):



- **In the second hybrid system, methane is produced from CO₂ and water using the *Methanosarcina barkeri* (archaea)** (Eq.(2)):



After the reaction, the resulting mixture from the reaction goes to the separation section, which may vary depending on the system. Here, the main product is recovered, and the rest is recycled back to the reactor after a small purge.

2.2 PHOTSENSITISERS

Photosensitisers are molecules that absorb light (photons) and transfer the energy to other molecules, increasing the efficiency, rate or selectivity of a chemical process. In essence, they act as photocatalysts. Currently, PDI and PFP are the chosen sensitisers for the hybrid systems. However, there are still ongoing experiments, and the final photosensitisers are likely to change.

2.2.1 PDI

The synthesis of PDI requires 3,4,9,10-perylenetetracarboxylic acid dianhydride and N,N-dimethylaminoethylamine [1]. A suspension of these chemicals (1:5 molar ratio) in water is stirred for 24 h at 100 °C and then cooled down to room temperature. PDI (77 wt.%) is obtained after three washes with a 1 % KOH aqueous solution and deionised water. The purification requires a 2:5 molar ratio mixture with 3-bromomethylphenylboronic acid in THF to be refluxed for an additional 24 h under a nitrogen atmosphere. The resulting crude is cooled down again and washed three times with acetonitrile and diethyl ether, affording 90 %wt. PDI after drying under vacuum.

2.2.2 PFP

PFP is produced from 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene, 1,4-phenyldiboronic acid, 1,3-phenyldiboronic acid, Pd(dppf)Cl₂ and potassium carbonate (0.5:0.25:0.25:6 molar ratio, respectively) in a water/THF medium (1:2 molar) [2]. After a 24 h reflux at 85 °C, the mixture is precipitated in methanol, filtered and washed with more methanol and acetone. Solid PFP (78 %wt.) is obtained after vacuum drying for 24 h.

2.3 MICROORGANISMS

The microorganisms are in charge of transforming the light energy provided by the photosensitisers into chemical energy through the process of photosynthesis. The “hybrid systems” term was originated after this synergy. Each hybrid system works with different microorganisms. The *Moorella thermoacetica* (bacteria) is in charge of producing acetic acid in the first system, while *Methanosarcina barkeri* (archaea) produces methane in the second one.

2.3.1 *Moorella thermoacetica* (bacteria)

The *Moorella thermoacetica* ATCC 39073 samples were obtained from the Global Bioresource Centre ATCC and preserved at $-80\text{ }^{\circ}\text{C}$ with 30 % sterilised glycerine. The culture was incubated in anaerobic conditions ($52\text{ }^{\circ}\text{C}$, 150 kPag) in 50 mL heterotrophic medium with 0.1 wt.% cysteine with occasional agitation for 72 h. Then, it was reinoculated at $52\text{ }^{\circ}\text{C}$ for 24 h and harvested by centrifugation (7200 rpm, 3 min), finally being washed with phosphate-buffered saline (PBS) solution three times [3].

2.3.2 *Methanosarcina barkeri* (archaea)

The *Methanosarcina barkeri* ATCC 43241 samples were provided by the German Collection of Microorganisms and Cell Cultures (DSMZ). The incubation conditions were $37\text{ }^{\circ}\text{C}$ and 200 kPag. The culture was kept under these conditions in the absence of oxygen heterotrophic medium (Table 2.1) for seven days [4].

2.4 MEDIUM

The medium is a substance that supports the growth and nurturement of the microorganism (heterotrophic medium, HM) or serves as an artificial environment for the microorganism-photosensitiser interaction (defined photosynthesis medium, DPM). Their respective compositions are shown in Table 2.1 through

Table 2.4.

Table 2.1. Photosynthesis (DPM) and heterotrophic (HM) medium compositions.

Component	DPM [g/m³] [5]	HM <i>Thermoacetica</i> [g/m³] [5]	HM <i>Methanosarcina</i> [g/m³] [6]
NaCl	$4.00 \cdot 10^2$	$4.00 \cdot 10^{-1}$	$2.20 \cdot 10^3$
MgSO ₄	$3.30 \cdot 10^2$	$3.30 \cdot 10^{-1}$	$4.90 \cdot 10^2$
NH ₄ Cl	$4.00 \cdot 10^2$	$4.00 \cdot 10^{-1}$	$4.90 \cdot 10^2$
CaCl	$5.00 \cdot 10^1$	$5.00 \cdot 10^{-2}$	-
CaCl ₂	-	-	$2.45 \cdot 10^2$
KCl	$2.50 \cdot 10^2$	$2.50 \cdot 10^{-1}$	-
K ₂ HPO ₄	$6.40 \cdot 10^2$	$6.40 \cdot 10^{-1}$	$3.43 \cdot 10^2$
KH ₂ PO ₄	-	-	$2.25 \cdot 10^2$
NaHCO ₃	$2.50 \cdot 10^3$	$2.50 \cdot 10^0$	-
Yeast Extract	$2.00 \cdot 10^3$	-	$1.96 \cdot 10^2$
Tryptone	$2.00 \cdot 10^3$	-	-
Glucose	$9.00 \cdot 10^3$	-	-
Casitone (BD BBL)	-	-	$1.96 \cdot 10^2$
Na-acetate	-	-	$2.45 \cdot 10^2$
Sodium resazurin (0.1% w/v)	-	-	$4.90 \cdot 10^2$
NaHCO ₃	-	-	$1.96 \cdot 10^2$
Methanol	-	-	$7.75 \cdot 10^3$
L-Cysteine HCl x H ₂ O	-	-	$2.94 \cdot 10^2$
Na ₂ S x 9 H ₂ O	-	-	$2.94 \cdot 10^2$
Water	$9.80 \cdot 10^5$	$9.80 \cdot 10^5$	$9.79 \cdot 10^5$
Wolfe's vitamin mix*	10 m ³	10 m ³	10 m ³
Trace mineral mix*	10 m ³	10 m ³	-
Trace element solution*	-	-	1 m ³

* the new concentration after mixing is calculated multiplying the solution concentrations (g/m³) by the amount of solution in the media (m³) and dividing by the total new volume (m³)

Table 2.2. Wolfe's vitamin mix composition [6]

Component	Concentration [g/m³]
Pyridoxine·HCl	$1.00 \cdot 10^1$
Thiamine·HCl	$5.00 \cdot 10^0$
Riboflavin	$5.00 \cdot 10^0$
Nicotinic acid	$5.00 \cdot 10^0$
Calcium D-(+)-pantothenate	$5.00 \cdot 10^0$
Thioctic acid	$5.00 \cdot 10^0$
p-Aminobenzoic acid	$5.00 \cdot 10^0$
Biotin	$2.00 \cdot 10^0$
Folic acid	$2.00 \cdot 10^0$
Vitamin B12	$1.00 \cdot 10^{-1}$
Water	$1.00 \cdot 10^6$

Table 2.3. Trace mineral mix composition

Component	Concentration [g/m³]
Nitriloacetic acid	$2.00 \cdot 10^3$
MnSO ₄ ·H ₂ O	$1.00 \cdot 10^3$
Fe(SO ₄) ₂ (NH ₄) ₂ ·6H ₂ O	$8.00 \cdot 10^2$
CoCl ₂ ·6H ₂ O	$2.00 \cdot 10^2$
ZnSO ₄ ·7H ₂ O	$2.00 \cdot 10^{-1}$
CuCl ₂ ·2H ₂ O	$2.00 \cdot 10^1$
NiCl ₂ ·6H ₂ O	$2.00 \cdot 10^1$
Na ₂ MoO ₄ ·2H ₂ O	$2.00 \cdot 10^1$
Na ₂ SeO ₄	$2.00 \cdot 10^1$
Na ₂ WO ₄	$2.00 \cdot 10^1$
Water	$1.00 \cdot 10^6$

Table 2.4. Trace element solution composition

Component	Concentration [g/m³]
HCl	$2.50 \cdot 10^3$
FeCl ₂ ·4H ₂ O	$1.50 \cdot 10^3$
ZnCl ₂	$7.00 \cdot 10^1$
MnCl ₂ ·4H ₂ O	$1.00 \cdot 10^2$
H ₃ BO ₃	$6.00 \cdot 10^0$
CoCl ₂ ·6H ₂ O	$1.90 \cdot 10^2$
CuCl ₂ ·2H ₂ O	$2.00 \cdot 10^0$
NiCl ₂ ·6H ₂ O	$2.40 \cdot 10^1$
Na ₂ MoO ₄ ·2H ₂ O	$3.60 \cdot 10^1$
Water	$1.00 \cdot 10^6$

3. PROCESS MODEL FOR THE HYBRID SYSTEMS

The proposed generalised model for the hybrid systems considers material and energy balances for the reactions and separation of the main product. A set of data (raw material and medium composition, chemical reaction coefficients, ideal separation energy, etc.) defines the specific system at hand. Regardless of the degree of development of each process, the model estimates the performance based on a set of parameters (reaction conversions, separation recoveries, energy efficiencies, etc.). These parameters can also be calculated with external models (reaction kinetics, separation model, etc.) to produce results under specific conditions or optimise the process conditions. Although the microorganisms and photosensitisers are described, and their respective scalars and variables are included in the model, the values will be calculated in the following works since they are bound to change due to the early stage of the experiments.

3.1 MATERIAL BALANCE

The overall material balance of the systems is based on the process scheme shown in Figure 3.1. The scheme shows the fresh feed entering the process, which composition is the sum of the components contained in the reaction and heterotrophic medium and CO₂. This feed is mixed with the recycle coming from the separation section, and the resulting stream enters the photoreactor. After the reaction, the products enter the separation section. Here, the final product is purified, and the rest is recycled after a small purge to avoid the build-up of by-products in the system. The global reactions of each hybrid system are represented by Eq.(1) and Eq.(2). Hence, the reaction coefficients ($coefficient_{ij}$) of the main reacting species j for each reaction i (Table 3.1) can be defined and used to calculate the overall material balance in the reactor for each system i .

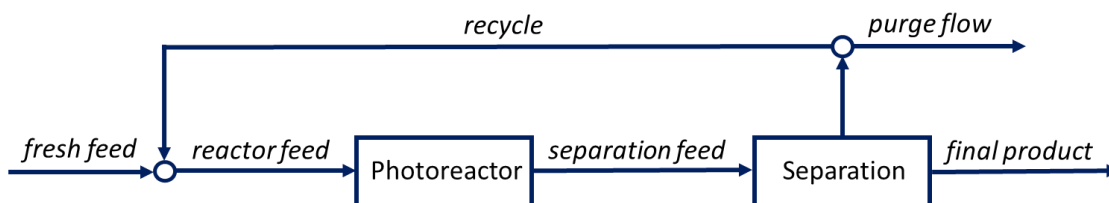


Figure 3.1. Simplified process scheme of the hybrid systems.

Table 3.1. Global reaction coefficients ($coefficient_{ij}$) for both systems. The coefficients of missing components are accounted as zero in both systems.

Component j	$i = \text{acetic acid}$	$i = \text{methane}$
CO ₂	-1	-1
H ₂ O	0	-2
CH ₄	0	1
O ₂	0	2
CH ₃ COOH	1	0
Cysteine	-2	0
Cystine	1	0

The products obtained in the process are computed using Eq.(3)-(5):

$$reaction\ product_{ij} = reactor\ feed_{i,CO_2} \cdot conversion_i \cdot coefficient_{ij} \quad \forall i, j \in I, J \quad (3)$$

$$separation\ feed_{ij} = reactor\ feed_{ij} + reaction\ product_{ij} \quad \forall i, j \in I, J \quad (4)$$

$$final\ product_{ij} = separation\ feed_{ij} \cdot recovery_{ij} \quad \forall i, j \in I, J \quad (5)$$

where J and I denote the sets of components and the hybrid systems, respectively; $reaction\ product_{ij}$ is the change of molar flow (kmol/s) of component j in the photoreactor of system i (positive for the products and negative for the reactants); $reactor\ feed_j$ is the molar flow (kmol/s) of component j fed to the photoreactor of system i ; $conversion_i$ is the fractional conversion of CO₂ in the reaction of system i ; $separation\ feed_{ij}$ is the molar flow of component j that enters the separation section in system i ; $recovery_{ij}$ is the recovery of component j after the separation in system i and $final\ product_{ij}$ is the molar flow (kmol/s) of component j in the final product of system i .

After the separation, the molar flow (kmol/s) of component j in system i that is recycled back to the reaction section ($recycle_{ij}$) is defined as (Eq.(6)):

$$recycle_{ij} = separation\ feed_{ij} \cdot (1 - recovery_{ij}) \cdot (1 - purge_i) \quad \forall i, j \in I, J \quad (6)$$

where $purge_i$ is the fraction of the unrecovered flow after the separation that leaves the process as a waste/off-gas. The purged flow ($purge\ flow_{ij}$) of component j in system i is calculated using Eq.(7):

$$purge\ flow_{ij} = separation\ feed_{ij} \cdot (1 - recovery_{ij}) \cdot purge_i \quad \forall i, j \in I, J \quad (7)$$

The reactor feed is computed as the sum of the fresh feed ($fresh\ feed_{ij}$) and the recycled material stream of each component j in system i (Eq.(8)):

$$reactor\ feed_{ij} = fresh\ feed_{ij} + recycle_{ij} \quad \forall i, j \in I, J \quad (8)$$

The molar flow (kmol/s) of the different components that enter the process are defined by Eq.(9):

$$fresh\ feed_{ij} = \frac{volumetric\ flow_i \cdot concentration_{ij}}{molar\ mass_j} \cdot 10^{-3} \quad \forall i, j \in I, J \quad (9)$$

where $volumetric\ flow_i$, $concentration_{ij}$ and $molar\ mass_j$ represent the total initial volumetric flow (m^3/s) of the feed in system i , the molecular weight (kg/kmol) of component j and the initial feed concentration (g/m^3) of component j in system i , respectively. Finally, the overall material balance of the system i is calculated using Eq.(9):

$$fresh\ feed_{ij} = final\ product_{ij} + purge\ flow_{ij} \quad \forall i, j \in I, J \quad (10)$$

The next Section 3.2 will present the energy balance of the system.

3.2 ENERGY BALANCE

The energy requirements of the systems can be satisfied by providing artificial sunlight to the photoreactor when the sun is not available and electricity, together with heating and cooling to the separation system. Additionally, the energy required to cultivate the microorganisms and synthesise the photosensitisers can be considered, although its impact is likely to be negligible in comparison to other contributors to the total impact. Hence, the overall energy balance is based on the scheme shown in Figure 3.2.

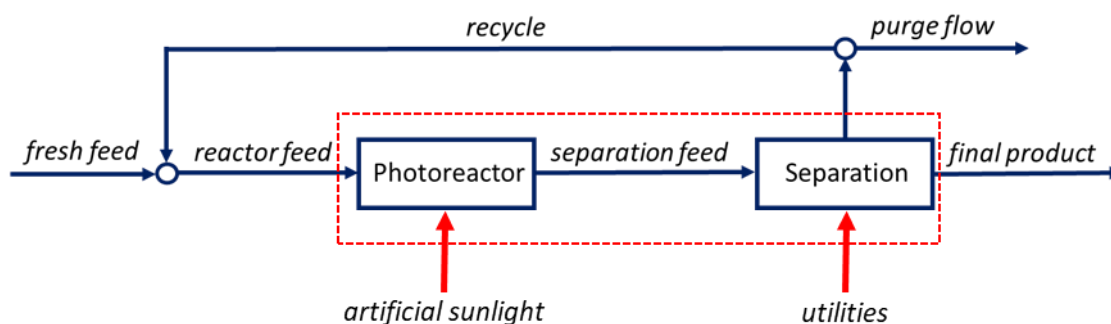


Figure 3.2. Simplified process scheme of the hybrid systems with process energy streams

The energy required in each process associated with the separation section is estimated using Aspen HYSYS v12 process simulations. The electricity (MJ/kmol of main component) needed to compress the reactor effluent is calculated assuming an initial pressure and temperature of 1 bar and 25 °C. For the acetic acid system (Figure 3.3), a shortcut distillation column is used to approximate the energy of the separation for a 1:4 molar mixture of acetic acid and water at atmospheric pressure entering the column at its bubble point. The energy required to operate the separation system is based on the reboiler and condenser duties (MJ/kmol acetic acid) of the column. Regarding the methane system (Figure 3.4), a mixture (0.01 molar fraction of methane in CO₂) mixture is compressed to 30 bar and cooled down to 40°C. Then, it enters the separation system, simulated as a component splitter, considering that the methane is recovered at 40 °C and 1 bar. Here, the ideal energy of the separation (MJ/kmol of methane) is calculated. The values of these parameters are shown in Table 3.2.

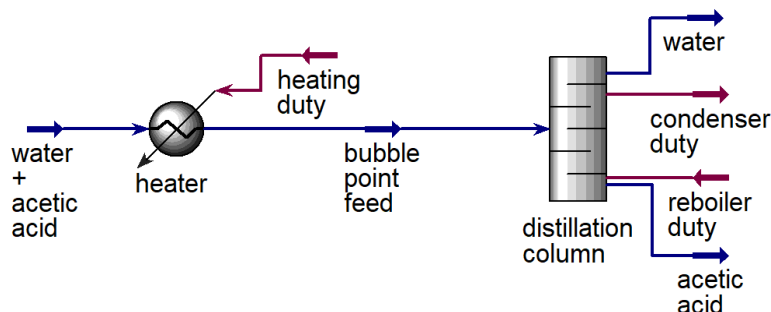


Figure 3.3. Simplified Aspen HYSYS v12 simulation of the acetic acid/water separation system

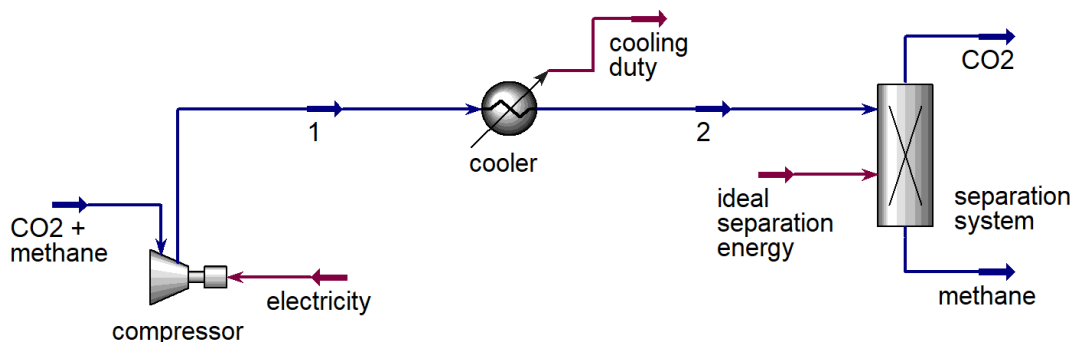


Figure 3.4. Simplified Aspen HYSYS v12 simulation of the methane/CO₂ separation system

Table 3.2 below shows the values of the energy balance for the utility parameters for the two target products (acetic acid and methane).

Table 3.2. Energy balance utility parameter values.

System <i>i</i>	electricity _{<i>i</i>} [MJ/kmol]	heating _{<i>i</i>} [MJ/kmol]	cooling _{<i>i</i>} [MJ/kmol]
Acetic acid	0	1.23·10 ²	8.77·10 ²
Methane	1.61·10 ³	1.76·10 ⁴	1.78·10 ⁴

The microorganisms (*microorganism_{ik}*) and photosensitizer (*photosensitizer_{ik}*) contribution in system *i* of utility *k* can be calculated as (Eq.(11)-(13)):

$$microorganism_{ik} = microorganism\ energy_{ik} \sum_{j \in BCT} fresh\ feed_{ij} \quad \forall i, k \in I, K \quad (11)$$

$$photosensitizer_{ik} = photosensitizer\ energy_{ik} \sum_{j \in PTZ} fresh\ feed_{ij} \quad \forall i, k \in I, K \quad (12)$$

$$feed\ energy_{ik} = microorganism\ energy_{ik} + photosensitizer\ energy_{ik} \quad \forall i, k \in I, K \quad (13)$$

where $microorganism\ energy_{ik}$ and $photosensitizer\ energy_{ik}$ are the energy consumptions of microorganisms and photosensitiser production [MJ/kmol] per kmol of the microorganism medium and photosensitiser in the process feed, respectively; and $feed\ energy_{ik}$ is the total utility k energy consumption associated with the feed stream in system i .

From these parameters, the electricity consumption ($electricity_i$), heating ($heating\ utilities_i$) and cooling utilities ($cooling\ utilities_i$) of system i are computed using Eqs.(14)-(16):

$$electricity_i = feed\ energy_{i,elec} + \left(light_i \cdot (1 - capacity) + \frac{compression_i}{efficiency_{i,elec}} \right) \cdot \sum_j separation\ feed_{ij} \quad \forall i, j \in RSC \quad (14)$$

$$heating\ utilities_i = feed\ energy_{i,heat} + \frac{heating_i}{efficiency_{i,heat}} \cdot \sum_j separation\ feed_{ij} \quad \forall i, j \in RSC \quad (15)$$

$$cooling\ utilities_i = feed\ energy_{i,cool} + \frac{cooling_i}{efficiency_{i,cool}} \cdot \sum_j separation\ feed_{ij} \quad \forall i, j \in RSC \quad (16)$$

where RSC is a set that relates the systems with their respective representative component (acetic acid system with acetic acid (CH_3COOH) and methane system with methane (CH_4)). Moreover, $compression_i$, $heating_i$ and $cooling_i$ define the ideal compression electricity, separation heating and cooling requirements for each system i , while $efficiency_{ik}$ is a parameter that measures the efficiency of heat transfer using utility k in system i . The constant $light_i$ [MJ/kmol] measures the electricity consumption related to artificial light input in system i , and $capacity$ is a parameter that evaluates the fraction of the time that natural sunlight can be used to power the reaction.

3.3 REACTOR DESIGN

The ideal surface area of the photoreactor ($area_i$) (m^2) can be calculated from the radiant flux density (kW/m^2), also known as irradiance, of light received by the photoreactor (*irradiance*) and the power required to carry out the reaction ($power_i$) (kW), which is a function of the enthalpy of reaction (*reaction enthalpy_i*) ($kJ/kmol$) (Eqs.(17)-(18)):

$$area_i = \frac{power_i}{irradiance} \quad \forall i \in I \quad (17)$$

$$power_i = \frac{reaction\ enthalpy_i}{-coefficient_{i,CO_2}} \cdot reactor\ feed_{i,CO_2} \quad \forall i \in I \quad (18)$$

On the other hand, the irradiance can be estimated as the minimum value of the irradiance provided by the sun (around $1\ kW/m^2$ on a sunny day) and the irradiance provided by an artificial sunlight lamp. This choice results in the most restrictive value of the ideal area (Eq.(19)):

$$irradiance = \min(solar\ irradiance, artificial\ irradiance) \quad (19)$$

Since other factors, such as the number of photons absorbed by the photosensitisers or the volume/geometry of the photoreactor, can affect the value of the area, Eq.(17) can be rewritten as:

$$area_i = \frac{power_i}{irradiance \cdot ideality_i} \quad \forall i \in I \quad (20)$$

where $ideality_i$ is a parameter that considers the deviation from ideality in the photoreactor area calculation in system i .

4. CONCLUSION

In this document, we developed a general mathematical model to estimate the mass and energy balances of the hybrid systems from experimental data. The model is based on general process simulations that can be easily adjusted depending on the experimental yields observed in practice, which are, at this early stage of the project, still unavailable. The model shall be refined as more experimental results become available by adjusting the values of its parameters, providing estimates that will be used to compare the emerging technologies developed in the project with the business-as-usual ones.

Future work will hence focus on adapting the model as experimental results are generated and using its outputs to evaluate the environmental, economic, and social impacts of the hybrid systems.

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A ANNEX: NOMENCLATURE

A.1 SETS

$BCT := \{\text{Table 2.1} - \text{Table 2.4}\}$	Relation set of microorganism medium components and hybrid systems
$I := \{\text{acetic acid, methane}\}$	Hybrid systems
$J := \{\text{set of components}\}$	Components
$K := \{\text{elec, heat, cool}\}$	Utilities
$PTZ := \{(\text{acetic acid, PDI}), (\text{acetic acid, PFP}), (\text{methane, PDI}), (\text{methane, PFP})\}$	Relation set of photosensitiser components and hybrid systems
$RSC := \{(\text{acetic acid, CH}_3\text{COOH}), (\text{methane, CH}_4)\}$	Relation set of main components and hybrid systems

A.2 COMPONENTS

Table A.1. List of components and their respective molecular weights.

Component <i>j</i>	Molar mass [kg/kmol]
CO ₂	44.0
H ₂ O	18.0
CH ₄	16.0
O ₂	32.0
CH ₃ COOH	60.0
Cysteine	121.2
Cystine	240.3
PDI	874.7
PFP*	1.88·10 ⁴
NaCl	58.4
MgSO ₄	120.0
NH ₄ Cl	53.5
CaCl	75.0
CaCl ₂	111.0
KCl	74.5
K ₂ HPO ₄	174.2
KH ₂ PO ₄	136.1
NaHCO ₃	84.0
Yeast Extract	274.3
Tryptone	71.1
Glucose	180.2
Casitone (BD BBL)**	1000.0
Na-acetate	82.0
Sodium resazurin (0.1% w/v)	251.2
NaHCO ₃	84.0
Methanol	32.0
L-Cysteine-HCl·H ₂ O	175.6
Na ₂ S·9 H ₂ O	240.2
Pyridoxine·HCl	205.6
Thiamine·HCl	300.8
Riboflavin	376.6
Nicotinic acid	123.1
Calcium D-(+)-pantothenate	476.5
Thioctic acid	206.3
p-Aminobenzoic acid	314.8
Biotin	244.3
Folic acid	441.4
Vitamin B12	1355.4
Nitriloacetic acid	275.1
MnSO ₄ ·H ₂ O	169.0
Fe(SO ₄) ₂ (NH ₄) ₂ ·6H ₂ O	392.1
CoCl ₂ ·6H ₂ O	237.9
ZnSO ₄ ·7H ₂ O	287.6
CuCl ₂ ·2H ₂ O	170.5
NiCl ₂ ·6H ₂ O	237.7
Na ₂ MoO ₄ ·2H ₂ O	241.9
Na ₂ SeO ₄	142.0

Component <i>j</i>	Molar mass [kg/kmol]
Na ₂ WO ₄	293.8
HCl	36.5
FeCl ₂ ·4H ₂ O	198.8
ZnCl ₂	136.3
MnCl ₂ ·4H ₂ O	197.9
H ₃ BO ₃	61.8
CoCl ₂ ·6H ₂ O	237.9
CuCl ₂ ·2H ₂ O	170.5
NiCl ₂ ·6H ₂ O	237.7
Na ₂ MoO ₄ ·2H ₂ O	241.9

*Repetition unit molecular weight of 684.6 kg/kmol

**Dummy molecular weight due to lack of composition data

A.3 CONSTANTS

<i>microorganism energy_{ik}</i>	Microorganism growth energy base contribution of utility <i>k</i> in system <i>i</i> [MJ/kmol]
<i>capacity</i>	Fraction of the total operating time in which natural sunlight is available (0.18 [7])
<i>coefficient_{ij}</i>	Main reaction coefficients of component <i>j</i> in system <i>i</i> (Table 3.1)
<i>compression_i</i>	Base electricity consumption for compression in system <i>i</i> [MJ/kmol of main component of system <i>i</i>] (Table 3.2)
<i>concentration_{ij}</i>	Concentration in the feed stream of component <i>j</i> in system <i>i</i> [g/m ³] (Table 2.1 – Table 2.4)
<i>cooling_i</i>	Base cooling utility consumption in system <i>i</i> [MJ/kmol of main component of system <i>i</i>] (Table 3.2)
<i>heating_i</i>	Base heating utility consumption in system <i>i</i> [MJ/kmol of main component of system <i>i</i>] (Table 3.2)
<i>irradiance</i>	Radiant flux or irradiance of light received by the photoreactor [kW/m ²]
<i>light_i</i>	Electricity consumption associated with artificial light requirement in system <i>i</i> [MJ/kmol of main component of system <i>i</i>]
<i>molar mass_j</i>	Molecular weight of component <i>j</i> [kg/kmol]
<i>photosensitizer energy_{ik}</i>	Photosensitiser synthesis energy base contribution of utility <i>k</i> in system <i>i</i> [MJ/kmol]
<i>reaction enthalpy_i</i>	Reaction enthalpy of the main reaction in system <i>i</i>

A.4 PARAMETERS

$conversion_{ij}$	Fraction of CO ₂ that undergoes a chemical reaction in system i
$efficiency_{ik}$	Deviation from ideality of utility k consumption in system i
$ideality_i$	Deviation from ideality of the photoreactor area in system i
$purge_i$	Fraction of recycle stream that leaves the process as waste/off-gas in system i
$recovery_{ij}$	Fraction of component j in system i that is recovered as product

A.5 VARIABLES

$microorganism_{ik}$	Microorganism growth energy contribution of utility k in system i [MW]
$cooling\ utilities_i$	Total cooling utilities consumption in system i [MW]
$electricity_i$	Total electricity consumption in system i [MW]
$final\ product_{ij}$	Product molar flow of component j in system i [kmol/s]
$feed\ energy_{ik}$	Process feed utility k consumption in system i [MW]
$fresh\ feed_{ij}$	Process feed molar flow of component j in system i [kmol/s]
$heating\ utilities_i$	Total heating utilities consumption in system i [MW]
$photosensitizer_{ik}$	Photosensitiser synthesis energy contribution of utility k in system i [MW]
$power_i$	Energy per unit of time required to carry out the chemical reaction [MW]
$purge\ flow_{ij}$	Purge molar flow of component j in system i [kmol/s]
$reaction\ product_{ij}$	Product molar flow of component j in system i [kmol/s]
$reactor\ feed_{ij}$	Reactor inlet molar flow of component j in system i [kmol/s]
$recycle_{ij}$	Recycle stream molar flow of component j in system i [kmol/s]
$separation\ feed_{ij}$	Separation inlet molar flow of component j in system i [kmol/s]
$volumetric\ flow_i$	Fresh feed initial volumetric flow in system i [m ³ /s]