Ministero dello sviluppo economico

Piano triennale 2019-2021 della Ricerca di Sistema Elettrico Nazionale

Progetto

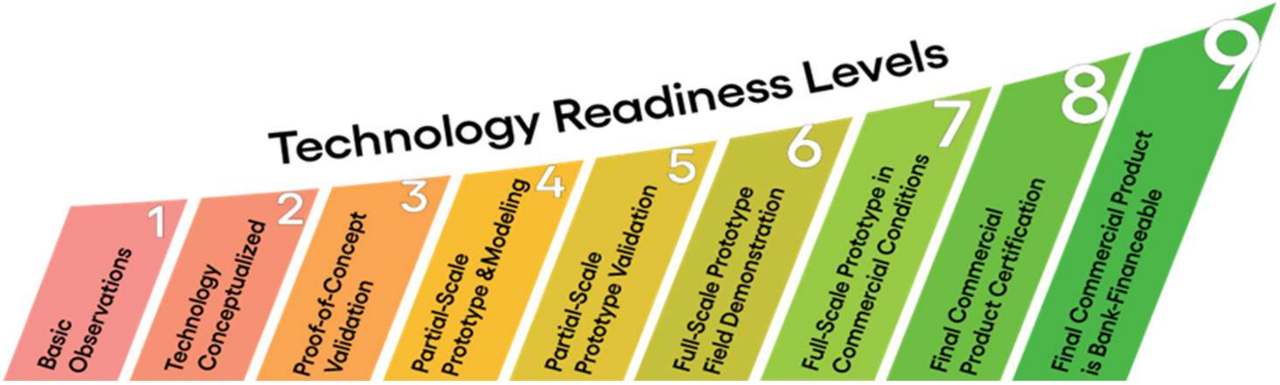
MODSEN

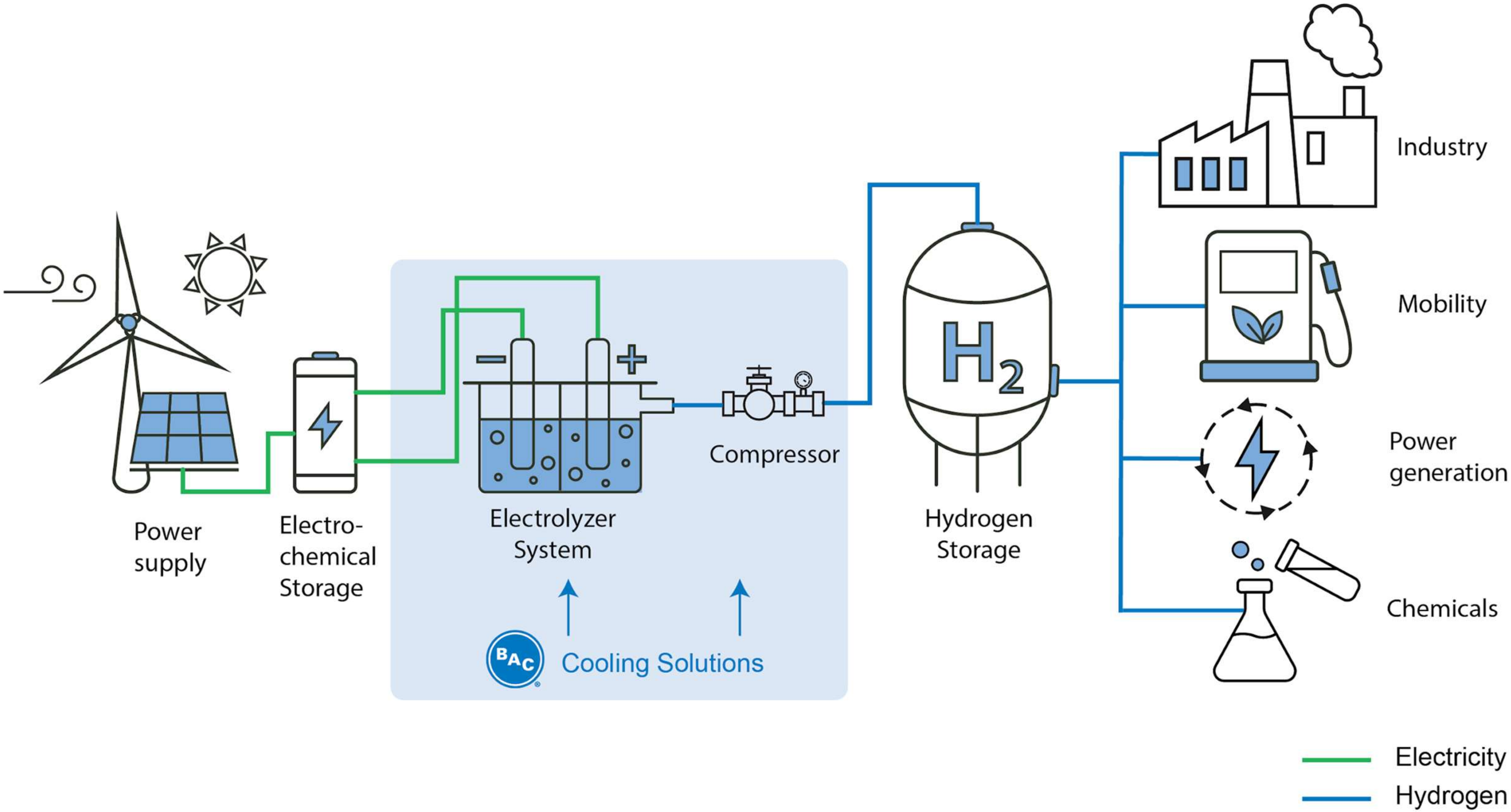
MODel of Saving electric ENergy from organic waste fermentation

Lead Partner:
Gruppo Veritas - Green Propulsion Laboratory
Partners:
Università Ca' Foscari Venezia
Università degli Studi di Padova
Fondazione Ca Foscari/ 9-Tech/ RCV Impianti

OBJECTIVES OF THE PROJECT

- Develop and validate the microbiological production of hydrogen from wastewater and organic waste
- Optimize the process at laboratory scale in order to transfer it to pilot scale (TRL 7)
- Integrate and improve the hydrogen separation, storage, and energy conversion chain
- Assess the energy and environmental sustainability, as well as the industrial replicability, through energy analysis and LCA




Power
supply
Electro-
chemical
Storage
Electrolyzer
System
Compressor
Cooling Solutions
BAC
H2
Hydrogen
Storage
Industry
Mobility
Power
generation
Chemicals
Electricity
Hydrogen

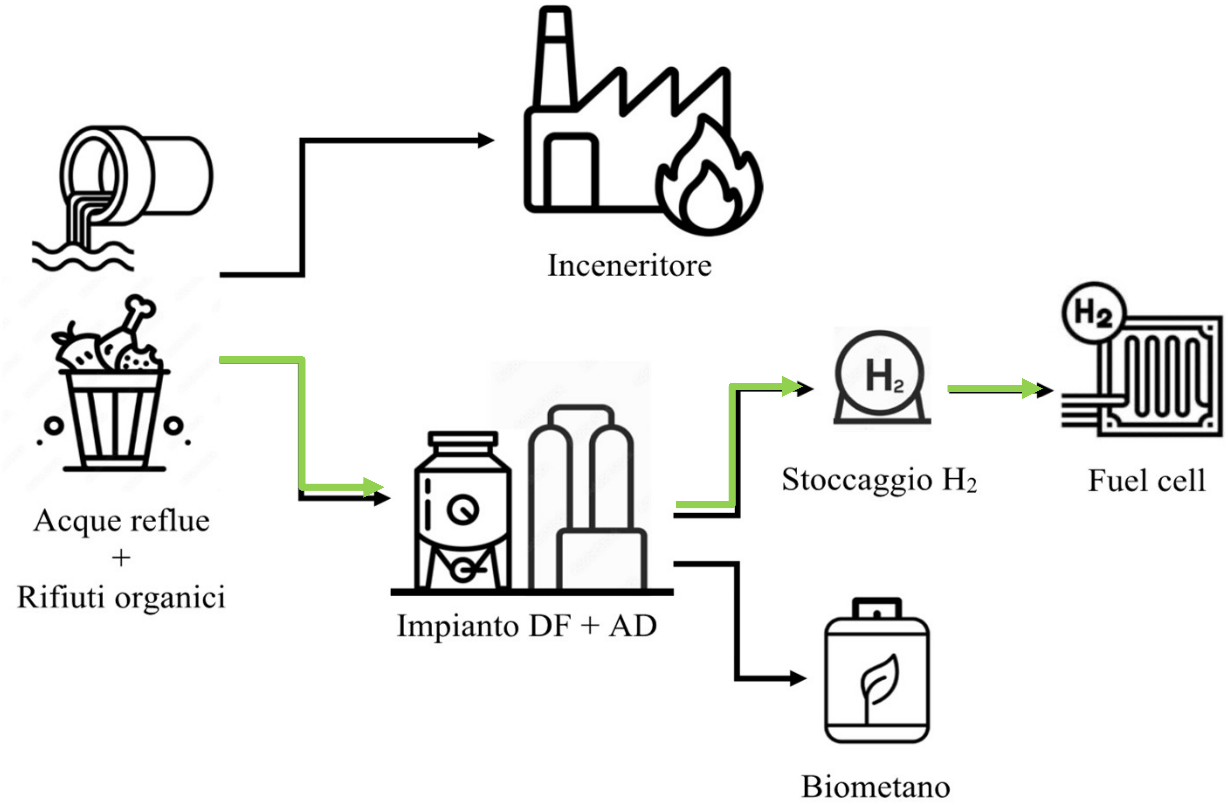
Dark fermentation

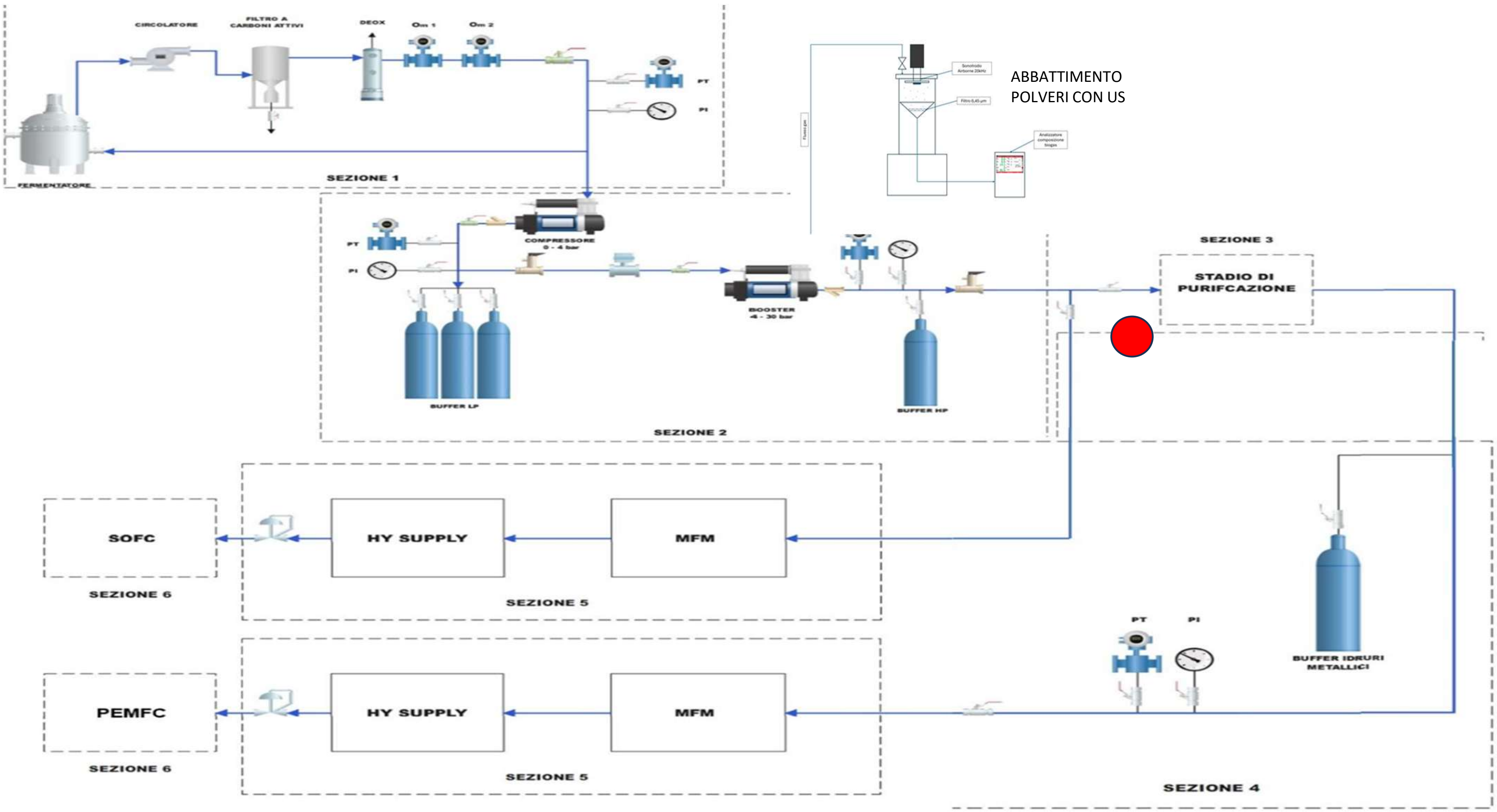
$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

Organic wastes→ Substrate, fonte di glucosio

sewage sludge→ Inoculum, source of bacteria

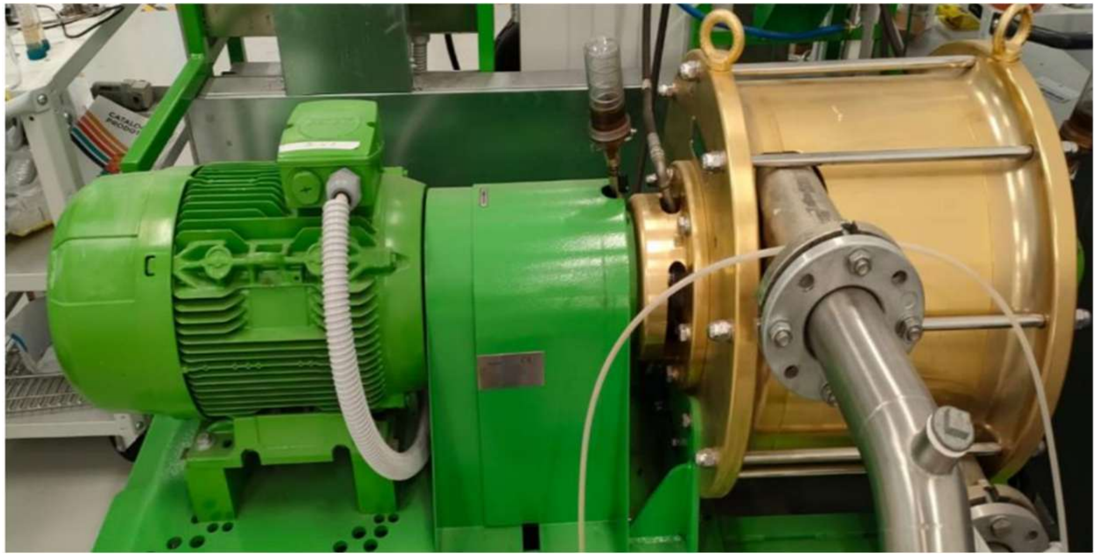
Other products of the process: CH_4, H_2S, H_2O




CIRCOLATORE
FILTRO A CARBONI ATTIVI
DEOX
Om 1
Om 2
PT
PI
FERMENTATORE
SEZIONE 1
Flusso gas
Sonotrodo Airborne 20kHz
Filtro 0,45 µm
Analizzatore composizione biogas
ABBATTIMENTO
POLVERI CON US
PT
PI
COMPRESSORE
0 - 4 bar
BOOSTER
4 - 30 bar
BUFFER LP
BUFFER HP
SEZIONE 2
SEZIONE 3
STADIO DI PURIFCAZIONE
SOFC
HY SUPPLY
MFM
SEZIONE 6
SEZIONE 5
PT
PI
BUFFER IDRURI METALLICI
PEMFC
HY SUPPLY
MFM
SEZIONE 6
SEZIONE 5
SEZIONE 4

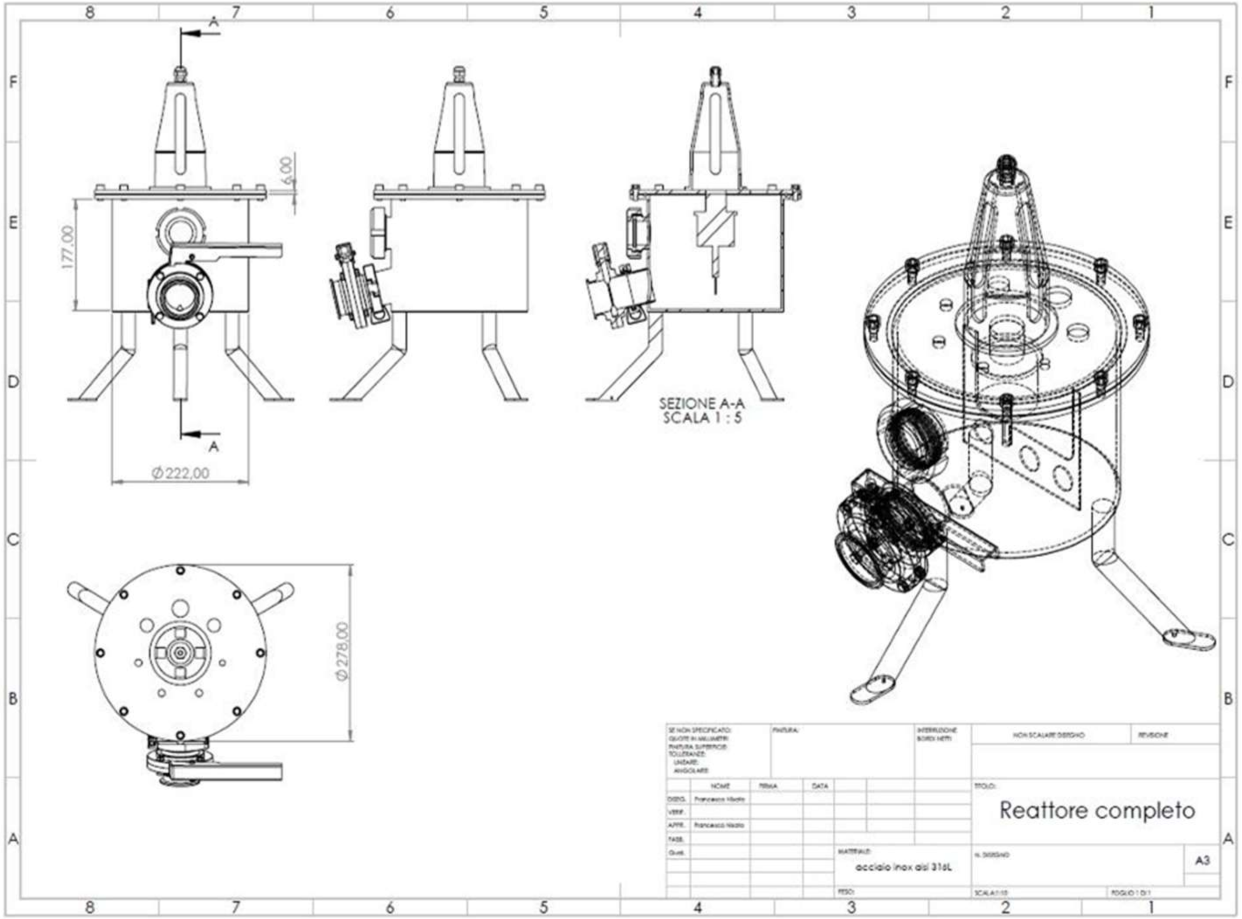
Preparation of Organic substate

Hydrodynamic Cavitation for Sludge/Biomass Treatment

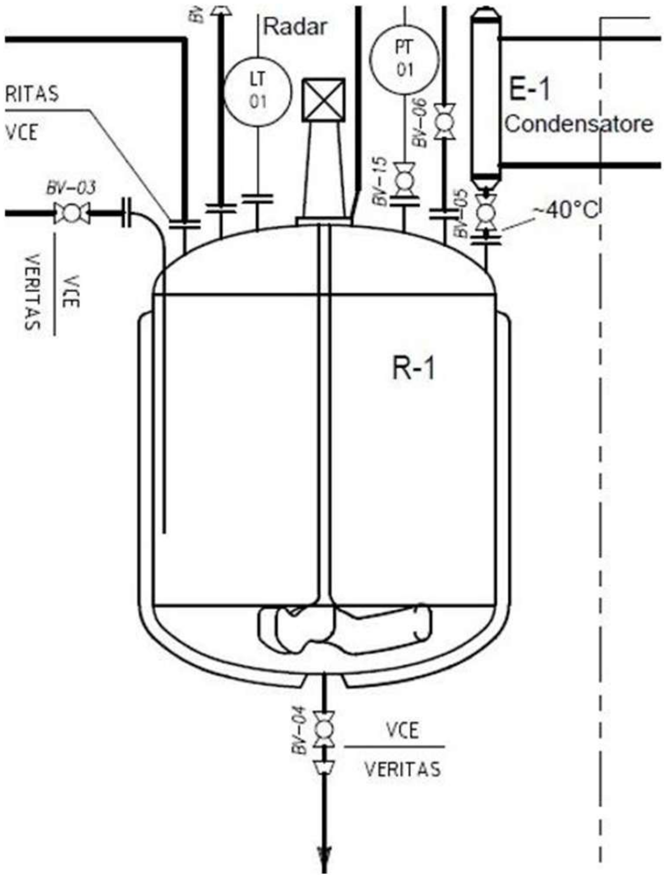


Implementation of a hydrodynamic cavitation system in the substrate pretreatment line.
Due to the poor homogenization of the two substrates and to increase nutrient bioavailability, hydrodynamic cavitation was tested in order to improve homogenization of the treatment mixture.

Design and Start-Up of Fermenters: 4 liters



Design and Start-Up of Fermenters: 400 liters



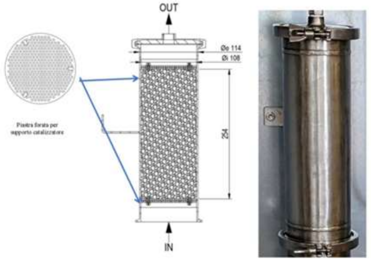
Gas Purification System

The gas generated from the fermentation of market waste and civil sludge undergoes a first purification stage.

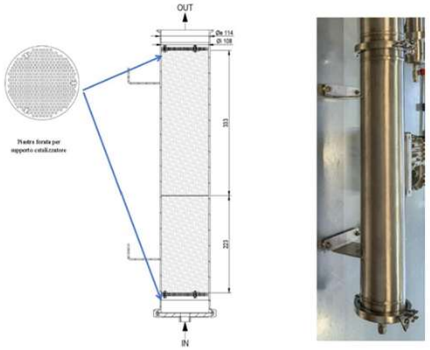
This stage includes:

1. Activated carbon filtration:
   - reduction of water content;
   - removal of contaminants such as H2S, VOCs and siloxanes.
2. Deoxygenation system (Deoxo):
   - removal of molecular oxygen from the gas mixture;
   - reduction of safety risks during compression.

After purification, the gas is dehumidified and deoxygenated, making it suitable for the pre-compression stage.



deossigenatore



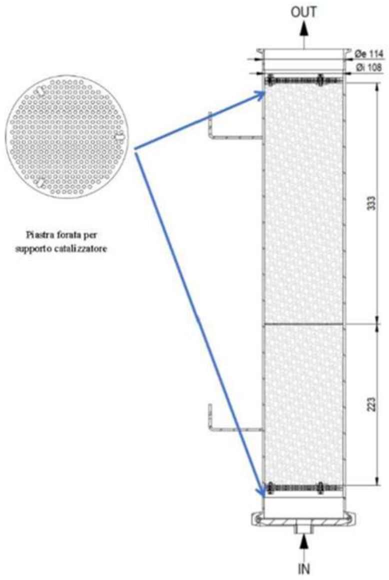
desolforatore

Desulfurization Process

The desulfurization process removes contaminants such as:

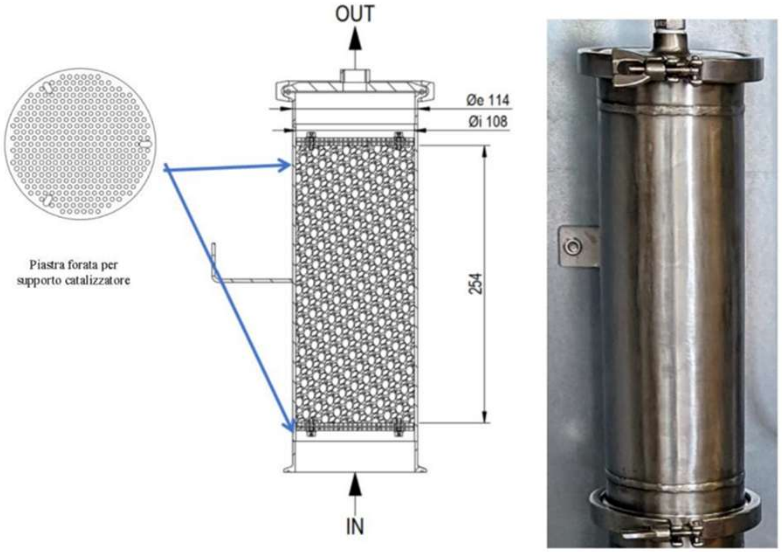
- H2S
- VOCs
- Siloxanes

The process prevents catalyst poisoning and protects the deoxygenation catalyst. Removal occurs through adsorption on activated carbon arranged in two layers.



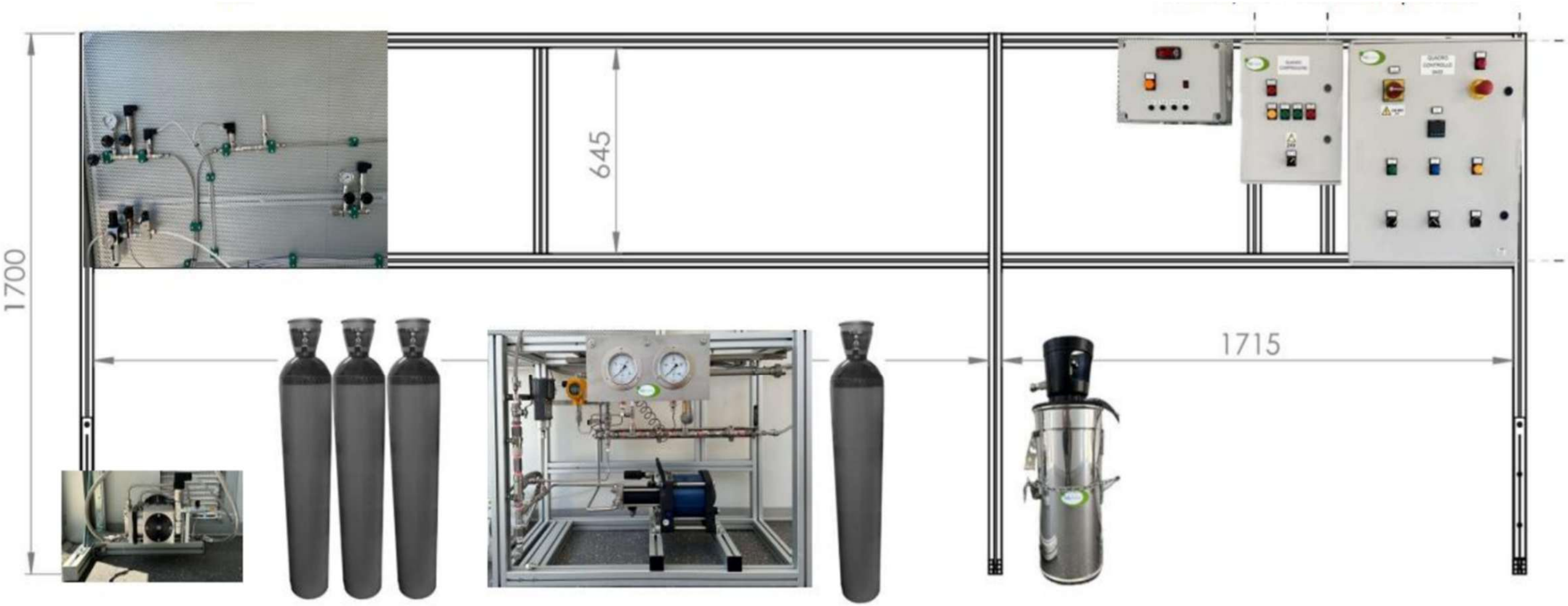
Deoxygenation Process

The deoxygenation process removes oxygen from the gas stream to prevent combustion risks.
Oxygen reacts with hydrogen to form water using a palladium catalyst.
The catalytic bed is designed to guarantee adequate residence time.



deossigenatore

Hydrogen storage set up



1° stadio compressione
da 0 a 4 bar

2° stadio compressione
da 4 a 30 bar

Bombola di stoccaggio
idruri (dopo
purificazione)a 30 bar
H2 puro al 99,9999%

Hydrogen Separation

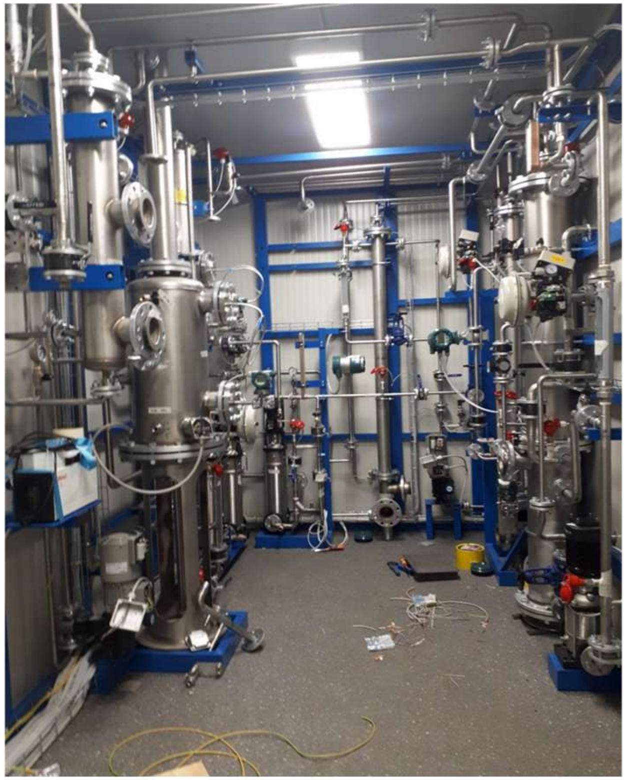
Physical separation of CO2

PDMSXA-10 polymeric membranes were selected for initial tests.
Advantages:

- good gas permeability;
- effective H2/CO_2 separation;
- lower cost than metallic or ceramic membranes;
- operational simplicity.

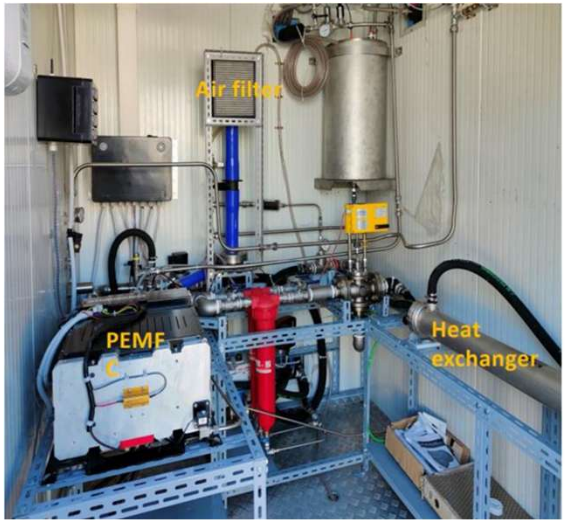
Chemical separation of CO2

Chemical adsorption using potassium carbonate: $\mathrm{K}2CO3 + CO2 + HO \rightarrow 2KHCO3$



PEM fuel cell, HyPMTM HD 30

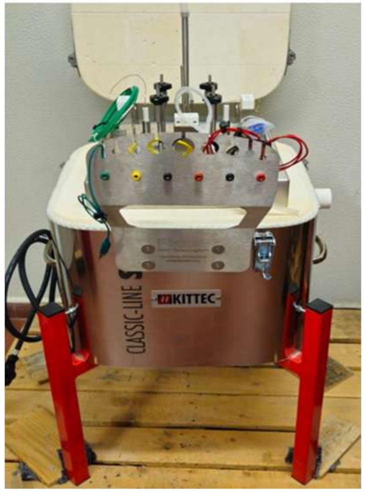
- dry hydrogen fuel (≥99.98%);
- nominal power: 33 kW;
- peak efficiency: 55%;
- operating temperature range: -10°C to 55°C.



SOFC technology was investigated in order to reduce the need for deep gas purification.

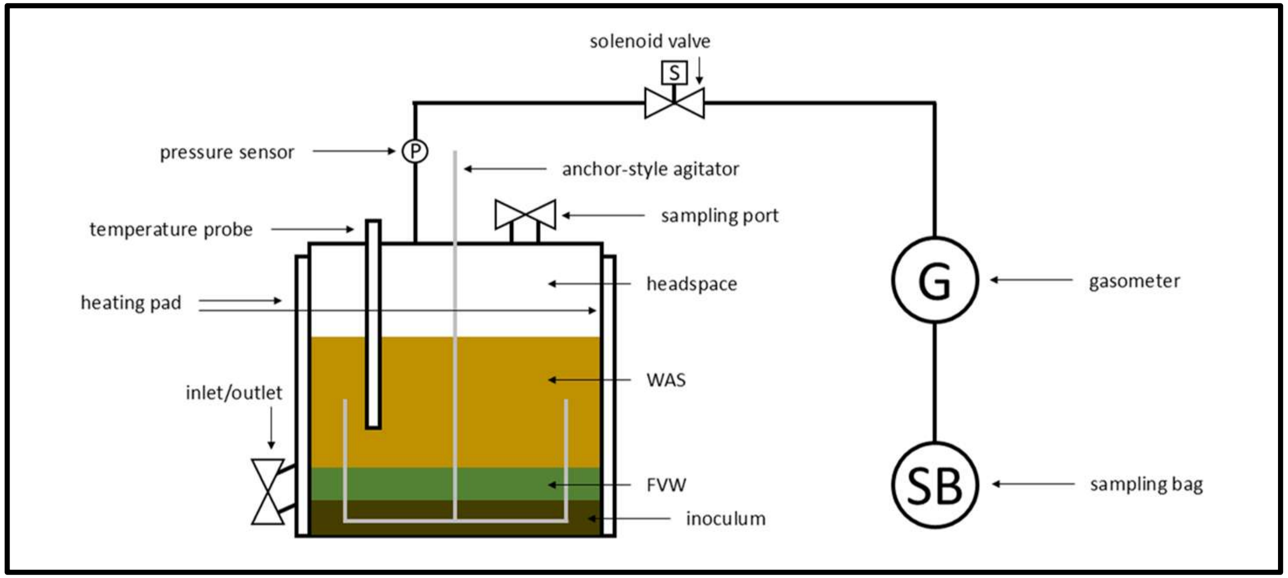
A Ni-YSZ anode was prepared through wet impregnation of NiO on commercial 8YSZ powder.
Performance was tested under:
- 10% H_2 – 90% Ar;
- 10% H_2 + 20% CO_2 – 70% Ar.

Results:
- CO_2 reduced power output by about 8% at 900°C;
- at lower temperatures (600–650°C), the effect became beneficial.

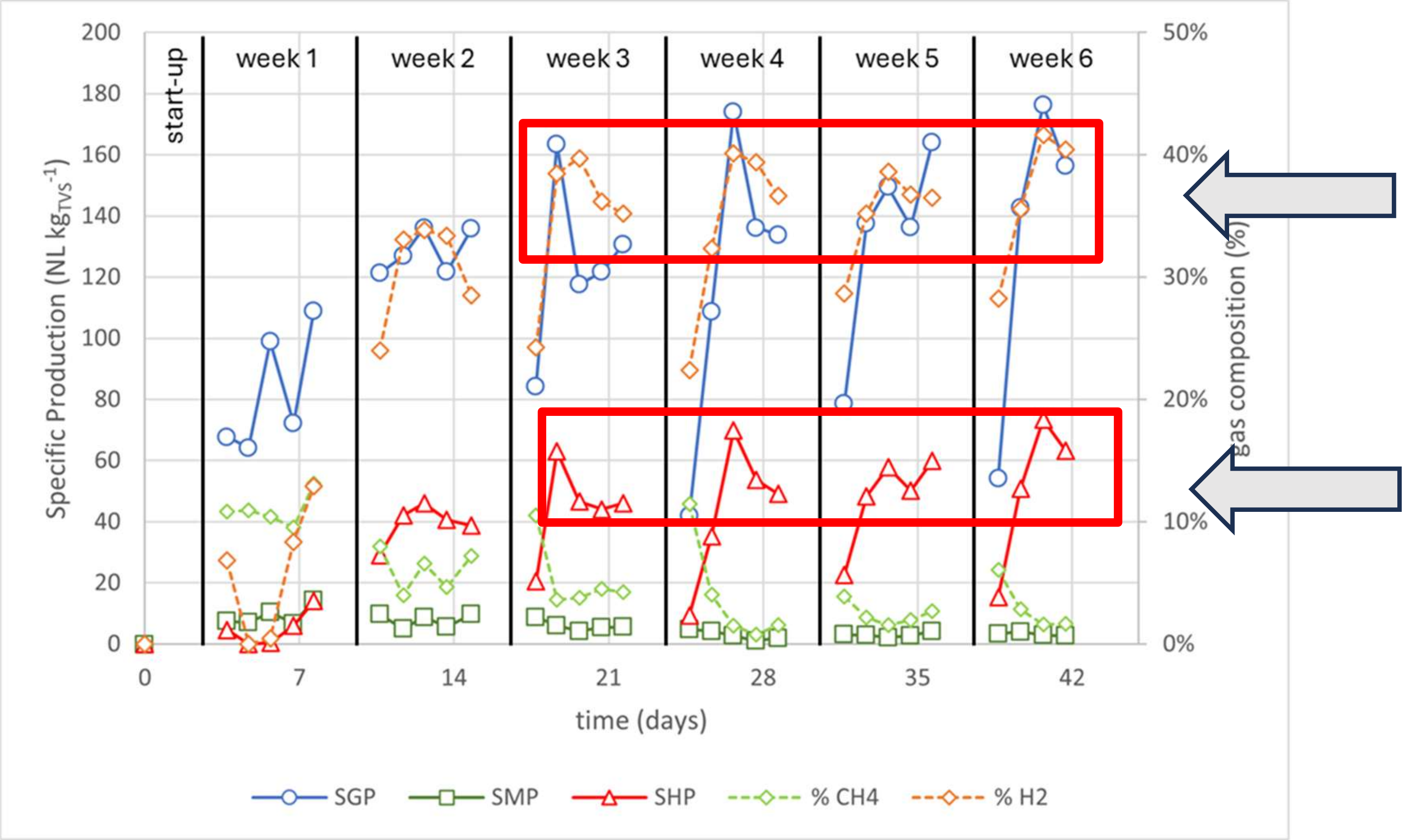


MARKET WASTES

SLUDGE

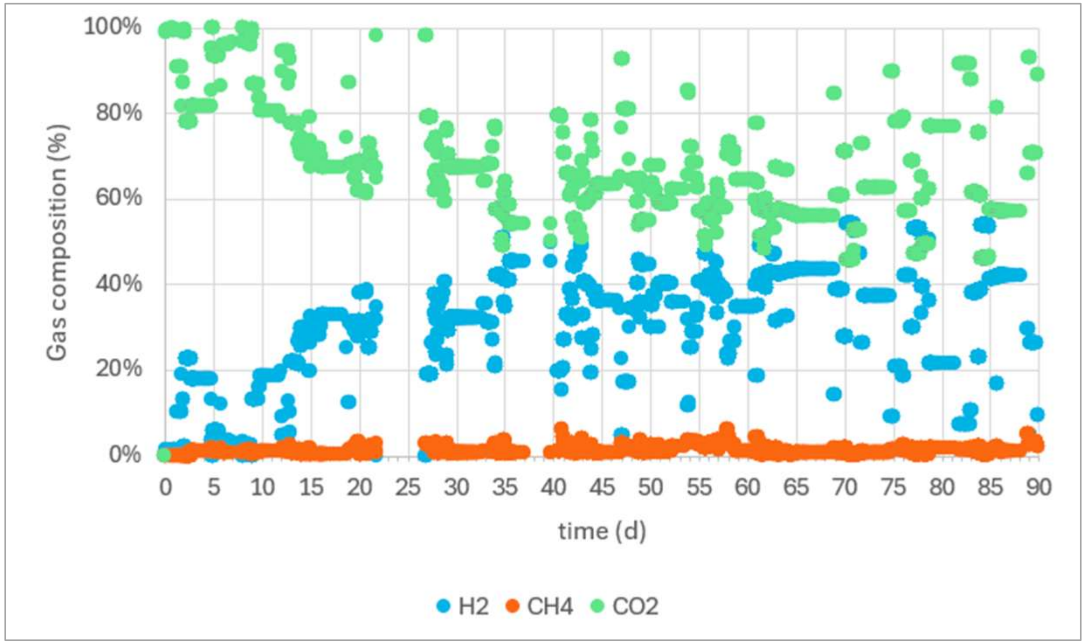


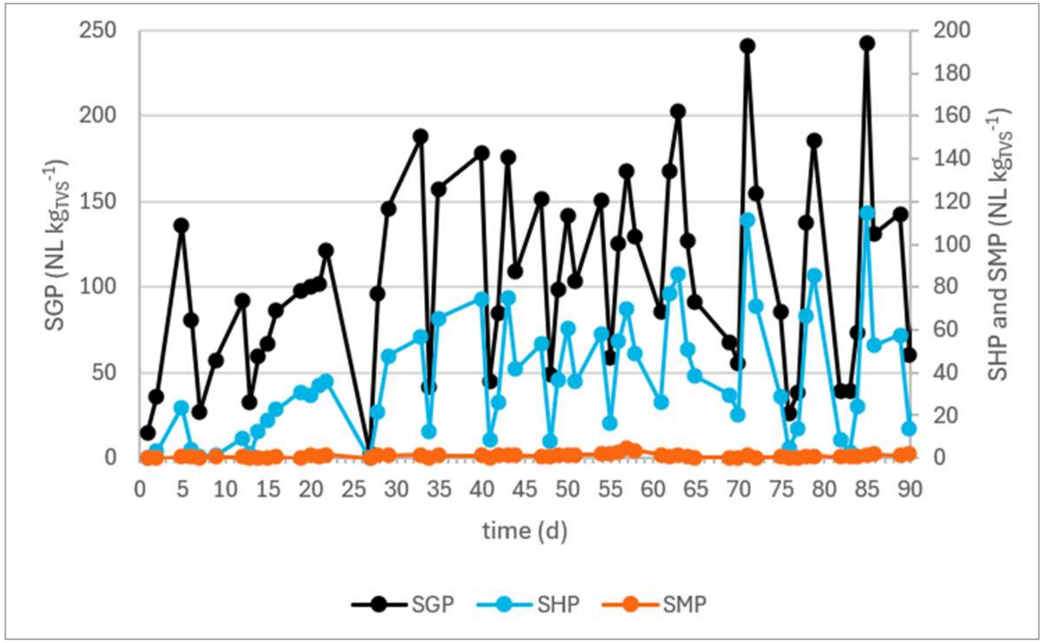
- Test duration: 43 d
- Volume: **4 L**
- **HRT**: 3.0 d
- **OLR**: 12 ± 1 $kg_{TVS}\ m^{-3}\ d^{-1}$
- **pH**: 5.5- controlled
- **T**: 37 °C
- Feeding: **1** $L_{WAS}\ d^{-1}$ + **270** $g_{FVW}\ d^{-1}$ (5 days/week)



- $\%H_2$: **37** ± 2 %

- SHP: **54** ± 10 NL_{H2} kg_{TVS}^{-1}

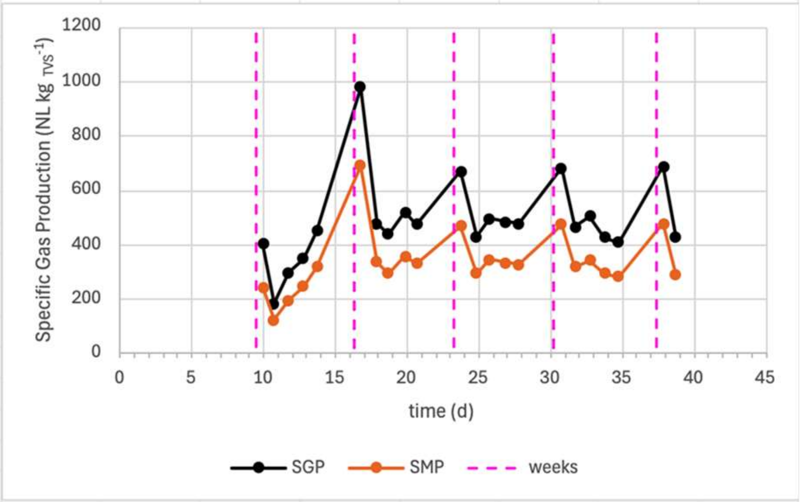




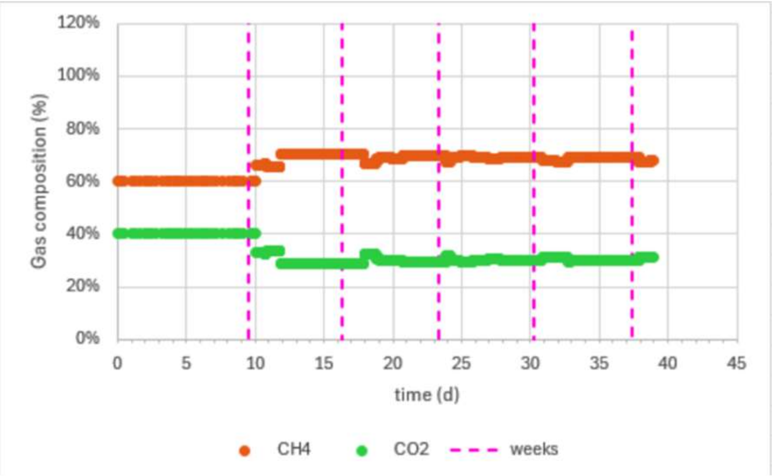
%H_2: **40** ± 2 %

15 NL kgTVS^{-1} d^{-1}

- Test duration: **45 Giorni**
- Volume : **350 L**
- **HRT**: 17.5 d
- **OLR**: 1.0 ± 0.1 $kg_{TVS}\ m^{-3}\ d^{-1}$
- **pH**: not controlled
- **T**: 37 °C
- Feeding: **15** $L_{DFE}\ d^{-1}$ (5 days/week)



- pH: ~ **7.7**
- SGP: ~ **500** NL kg_{TVS}^{-1}
- SMP: ~ **350** $NL_{CH4}\ kg_{TVS}^{-1}$
- %CH_4: ~ **65.4** %
- GPR: ~ **0.394** NL $L_{reactor}^{-1}$



65.000 ton/y

258.335 ton/y

Dark Fermentation

10 m^3 of H_2 for ton of waste

+

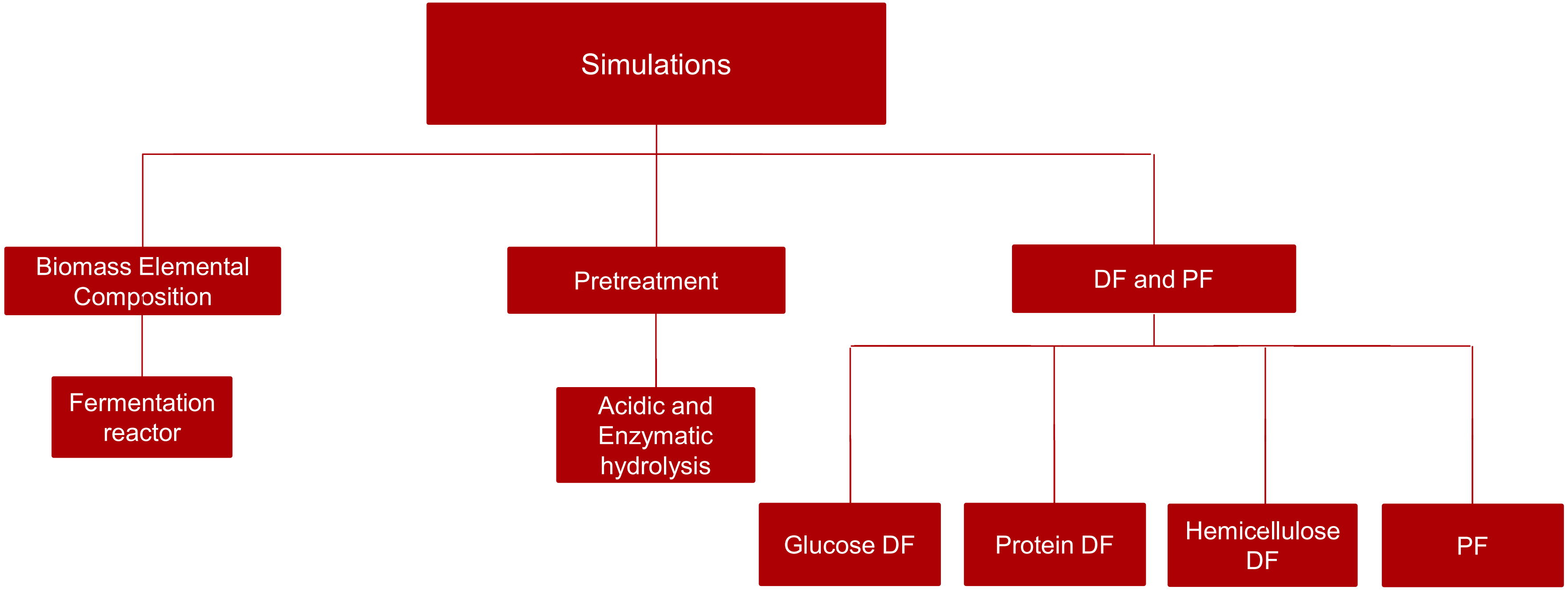
Anaerobic Digestion

70 m^3 of CH_4 for ton of waste

Anaerobic Digestion

60 m^3 of CH_4 for ton of waste

What we did …


Simulations

Biomass Elemental Composition

Fermentation reactor

Pretreatment

Acidic and Enzymatic hydrolysis

DF and PF

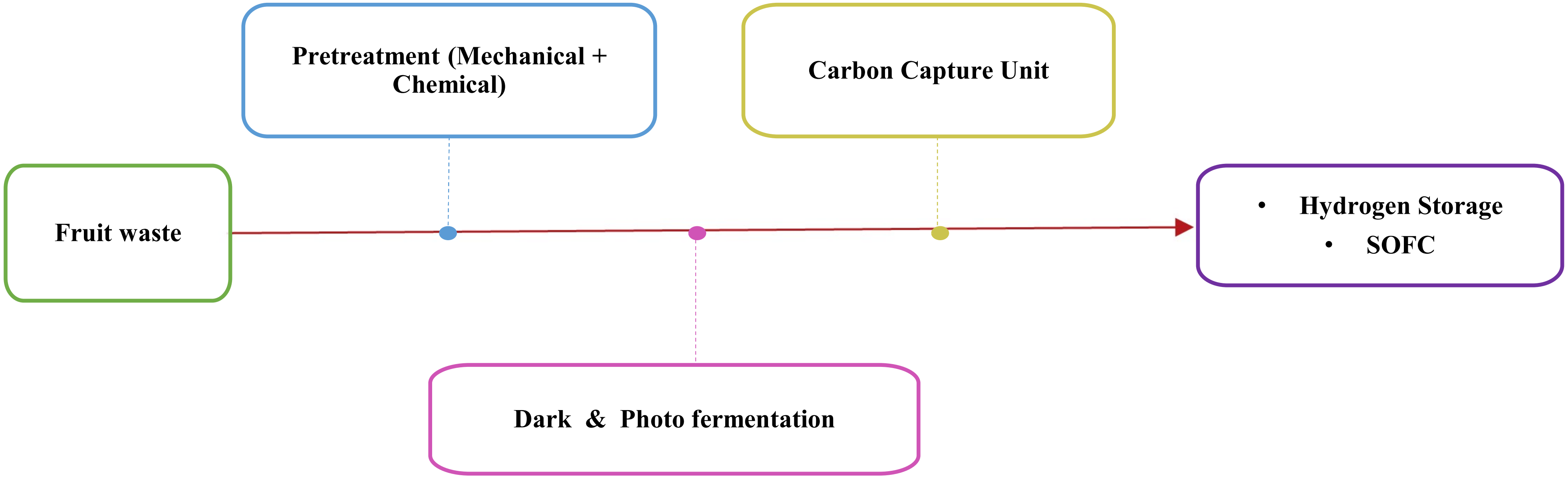
Glucose DF

Protein DF

Hemicellulose DF

PF

System Overview:

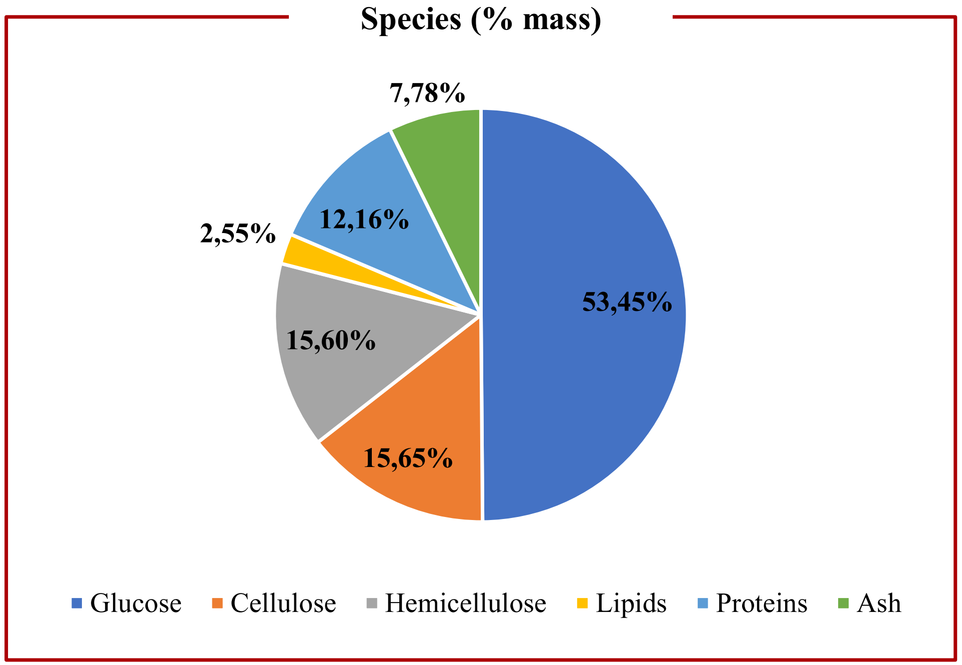


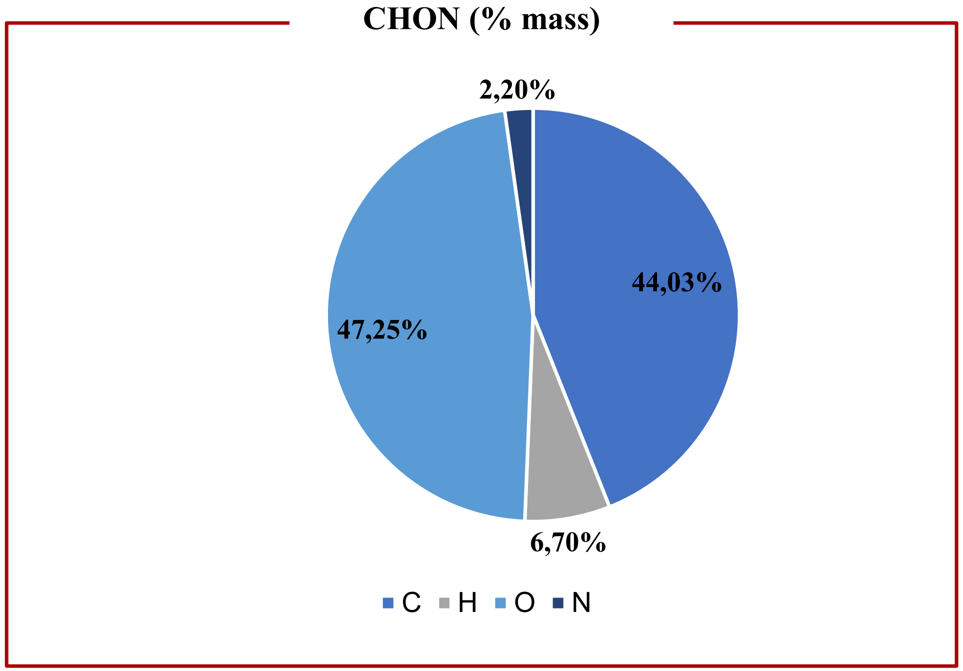
Biomass Characterization: Methodology & Key Results

300000 random mixture generated.

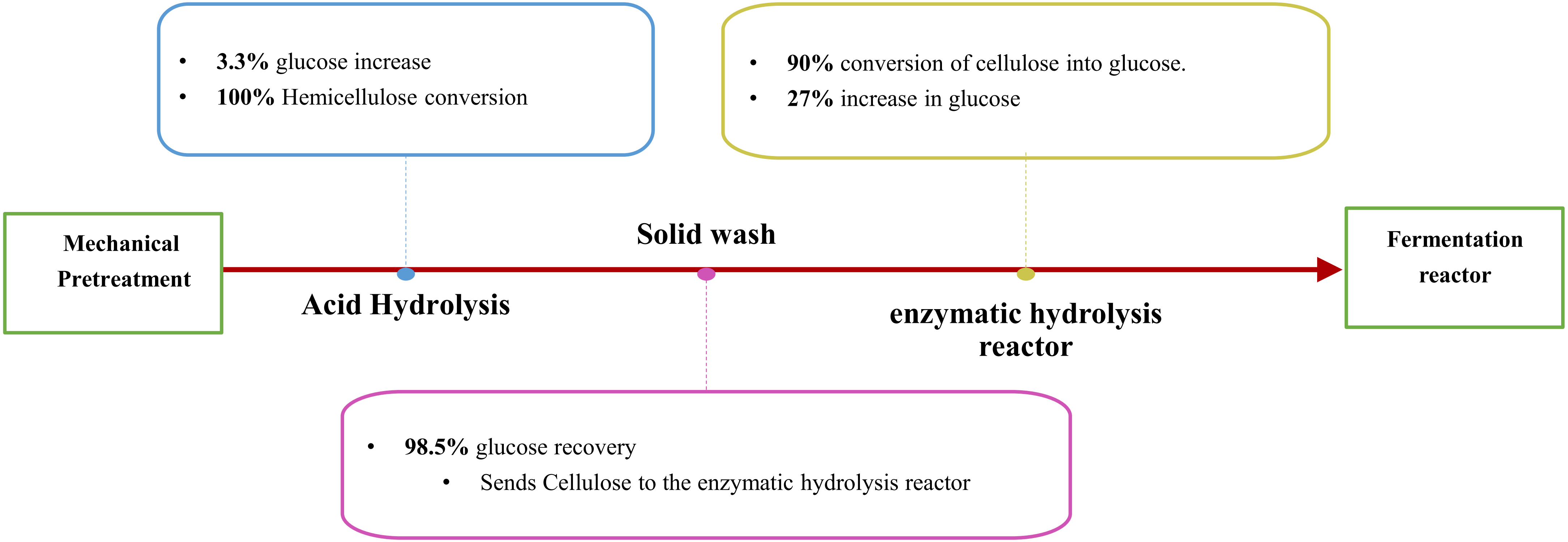
Conversion to Representative Species

CHON Composition





Chemical Pretreatment: Acid Hydrolysis, Solid Washing & Enzymatic Hydrolysis



- **3.3%** glucose increase
- **100%** Hemicellulose conversion

- **90%** conversion of cellulose into glucose.
- **27%** increase in glucose

Mechanical Pretreatment

Acid Hydrolysis

Solid wash

enzymatic hydrolysis reactor

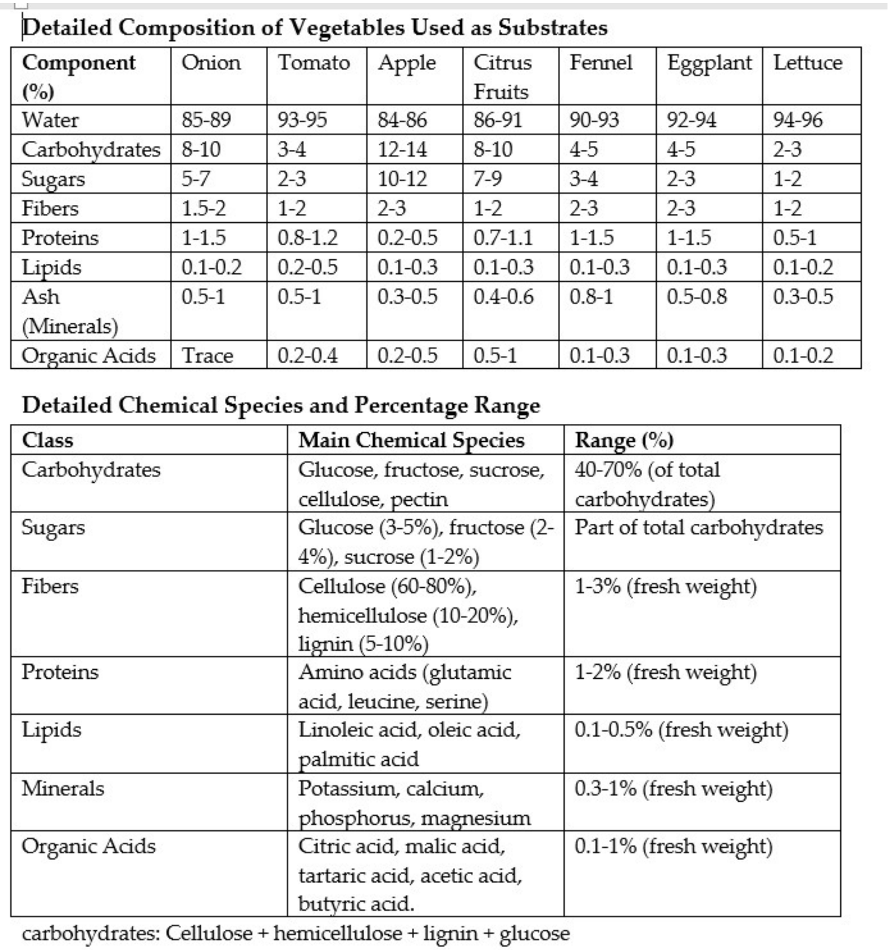
Fermentation reactor

- **98.5%** glucose recovery
    - Sends Cellulose to the enzymatic hydrolysis reactor

Overall: 29.7 % glucose increase and full Hemicellulose conversion into fermentable sugars

1. Biomass Elemental Composition

Data



Detailed Composition of Vegetables Used as Substrates

Component (%)	Onion	Tomato	Apple	Citrus Fruits	Fennel	Eggplant	Lettuce
Water	85-89	93-95	84-86	86-91	90-93	92-94	94-96
Carbohydrates	8-10	3-4	12-14	8-10	4-5	4-5	2-3
Sugars	5-7	2-3	10-12	7-9	3-4	2-3	1-2
Fibers	1.5-2	1-2	2-3	1-2	2-3	2-3	1-2
Proteins	1-1.5	0.8-1.2	0.2-0.5	0.7-1.1	1-1.5	1-1.5	0.5-1
Lipids	0.1-0.2	0.2-0.5	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.2
Ash (Minerals)	0.5-1	0.5-1	0.3-0.5	0.4-0.6	0.8-1	0.5-0.8	0.3-0.5
Organic Acids	Trace	0.2-0.4	0.2-0.5	0.5-1	0.1-0.3	0.1-0.3	0.1-0.2

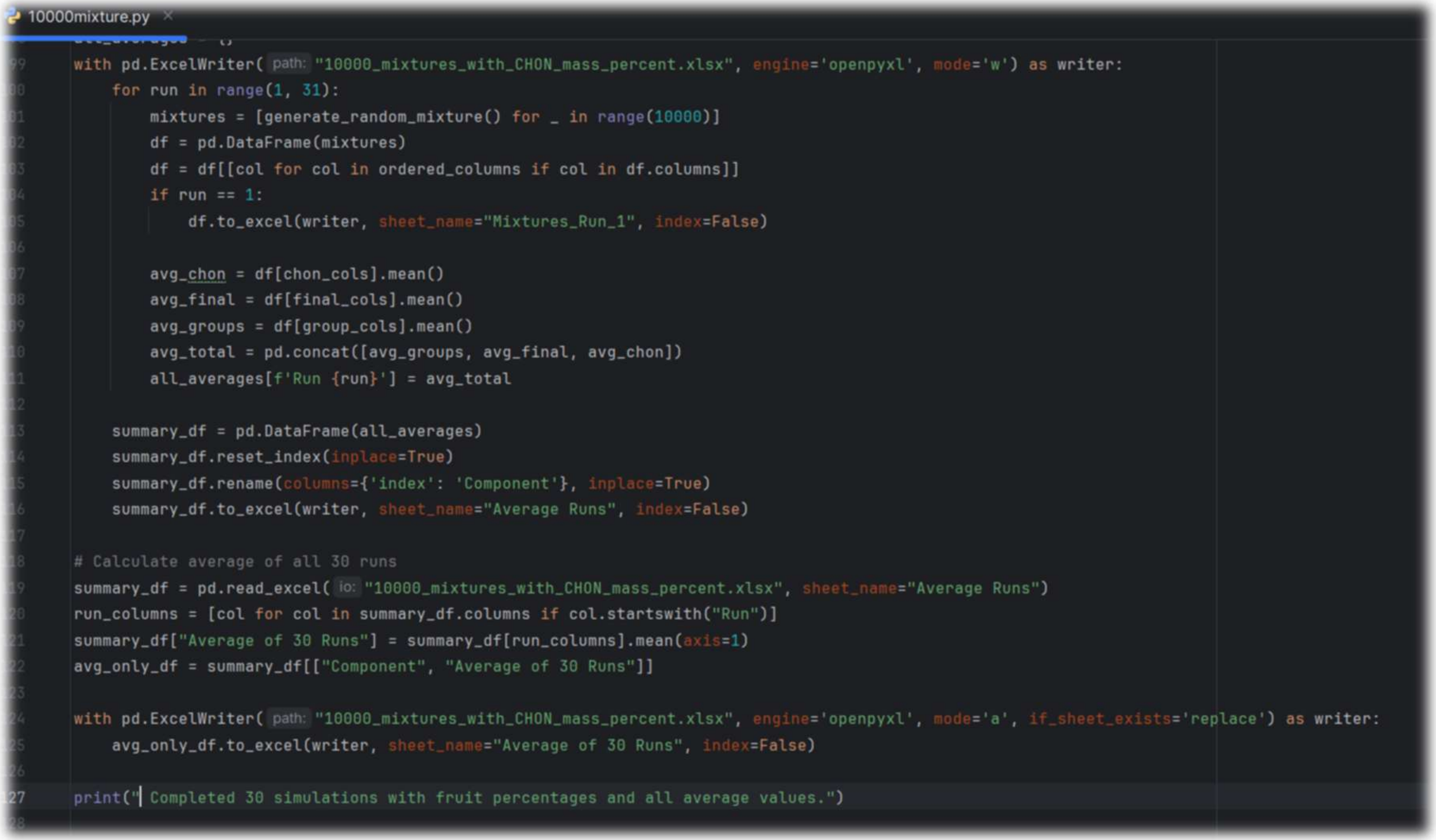
Detailed Chemical Species and Percentage Range

Class	**Main Chemical Species**	**Range (%)**
Carbohydrates	Glucose, fructose, sucrose, cellulose, pectin	40-70% (of total carbohydrates)
Sugars	Glucose (3-5%), fructose (2-4%), sucrose (1-2%)	Part of total carbohydrates
Fibers	Cellulose (60-80%), hemicellulose (10-20%), lignin (5-10%)	1-3% (fresh weight)
Proteins	Amino acids (glutamic acid, leucine, serine)	1-2% (fresh weight)
Lipids	Linoleic acid, oleic acid, palmitic acid	0.1-0.5% (fresh weight)
Minerals	Potassium, calcium, phosphorus, magnesium	0.3-1% (fresh weight)
Organic Acids	Citric acid, malic acid, tartaric acid, acetic acid, butyric acid.	0.1-1% (fresh weight)

carbohydrates: Cellulose + hemicellulose + lignin + glucose

1. Biomass Elemental Composition

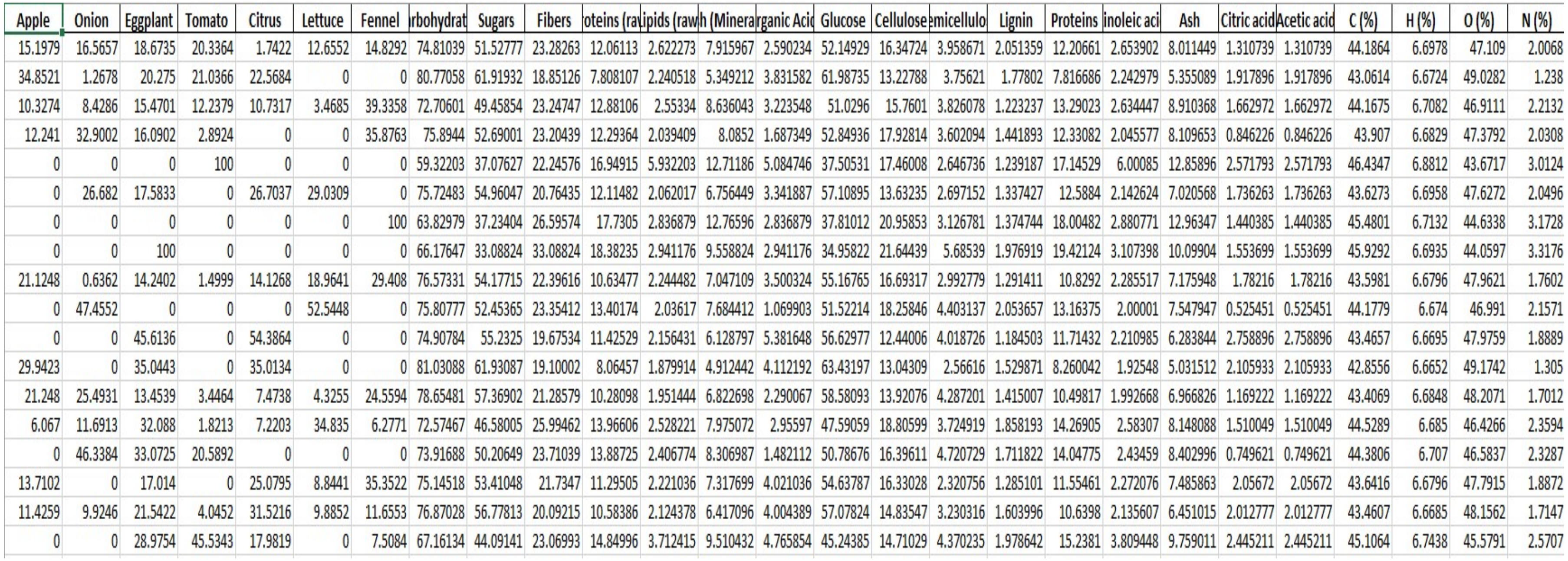
Python



```python
with pd.ExcelWriter("10000_mixtures_with_CHON_mass_percent.xlsx", engine='openpyxl', mode='w') as writer:
    for run in range(1, 31):
        mixtures = [generate_random_mixture() for _ in range(10000)]
        df = pd.DataFrame(mixtures)
        df = df[[col for col in ordered_columns if col in df.columns]]
        if run == 1:
            df.to_excel(writer, sheet_name="Mixtures_Run_1", index=False)

        avg_chon = df[chon_cols].mean()
        avg_final = df[final_cols].mean()
        avg_groups = df[group_cols].mean()
        avg_total = pd.concat([avg_groups, avg_final, avg_chon])
        all_averages[f'Run {run}'] = avg_total

    summary_df = pd.DataFrame(all_averages)
    summary_df.reset_index(inplace=True)
    summary_df.rename(columns={'index': 'Component'}, inplace=True)
    summary_df.to_excel(writer, sheet_name="Average Runs", index=False)

# Calculate average of all 30 runs
summary_df = pd.read_excel("10000_mixtures_with_CHON_mass_percent.xlsx", sheet_name="Average Runs")
run_columns = [col for col in summary_df.columns if col.startswith("Run")]
summary_df["Average of 30 Runs"] = summary_df[run_columns].mean(axis=1)
avg_only_df = summary_df[["Component", "Average of 30 Runs"]]

with pd.ExcelWriter("10000_mixtures_with_CHON_mass_percent.xlsx", engine='openpyxl', mode='a', if_sheet_exists='replace') as writer:
    avg_only_df.to_excel(writer, sheet_name="Average of 30 Runs", index=False)

print(" Completed 30 simulations with fruit percentages and all average values.")
```

1. Biomass Elemental Composition

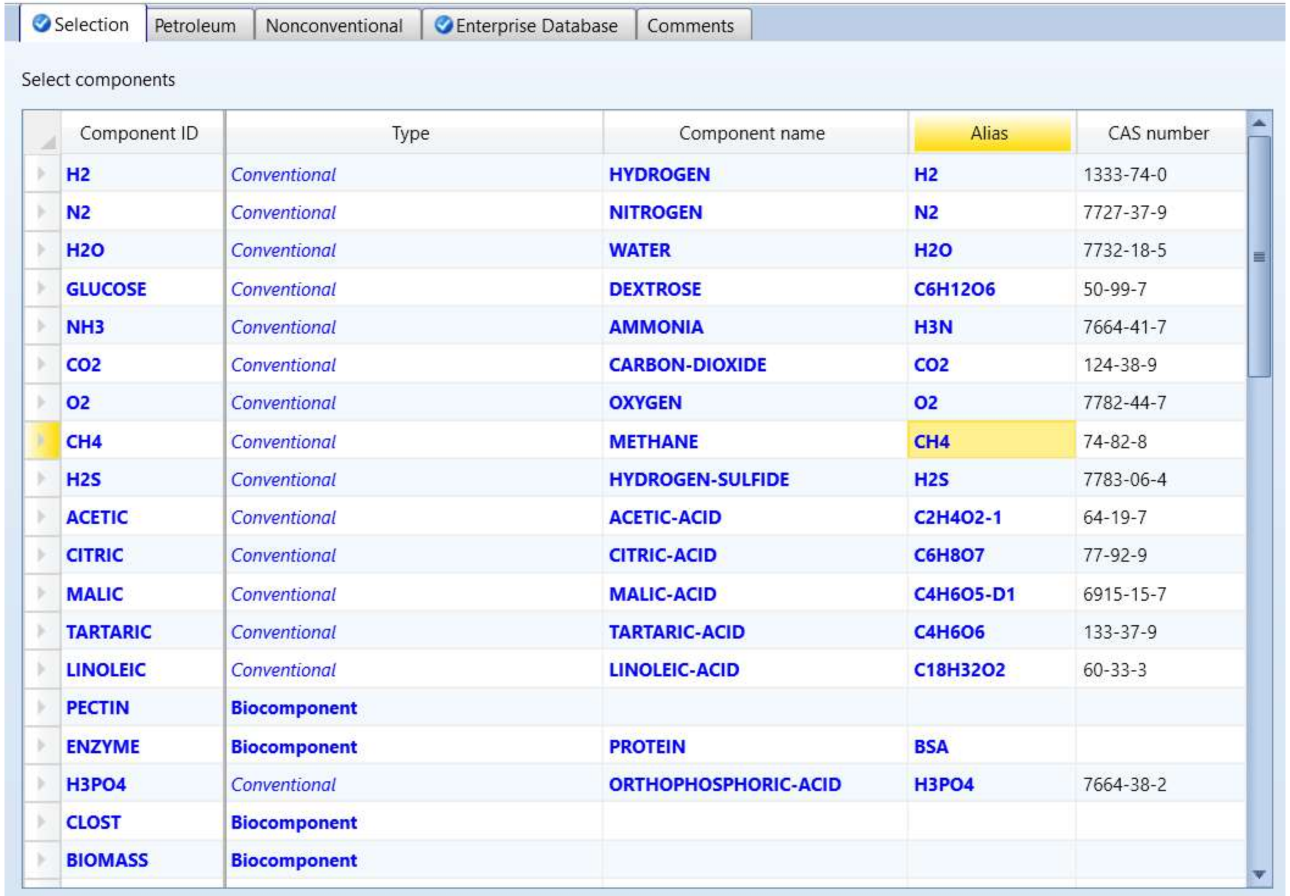
Python Results, 1st sheet



Apple	Onion	Eggplant	Tomato	Citrus	Lettuce	Fennel	rbohydrat	Sugars	Fibers	oteins (ra	ipids (raw	h (Minera	rganic Acid	Glucose	Cellulose	emicellulo	Lignin	Proteins	inoleic aci	Ash	Citric acid	Acetic acid	C (%)	H (%)	O (%)	N (%)
15.1979	16.5657	18.6735	20.3364	1.7422	12.6552	14.8292	74.81039	51.52777	23.28263	12.06113	2.622273	7.915967	2.590234	52.14929	16.34724	3.958671	2.051359	12.20661	2.653902	8.011449	1.310739	1.310739	44.1864	6.6978	47.109	2.0068
34.8521	1.2678	20.275	21.0366	22.5684	0	0	80.77058	61.91932	18.85126	7.808107	2.240518	5.349212	3.831582	61.98735	13.22788	3.75621	1.77802	7.816686	2.242979	5.355089	1.917896	1.917896	43.0614	6.6724	49.0282	1.238
10.3274	8.4286	15.4701	12.2379	10.7317	3.4685	39.3358	72.70601	49.45854	23.24747	12.88106	2.55334	8.636043	3.223548	51.0296	15.7601	3.826078	1.223237	13.29023	2.634447	8.910368	1.662972	1.662972	44.1675	6.7082	46.9111	2.2132
12.241	32.9002	16.0902	2.8924	0	0	35.8763	75.8944	52.69001	23.20439	12.29364	2.039409	8.0852	1.687349	52.84936	17.92814	3.602094	1.441893	12.33082	2.045577	8.109653	0.846226	0.846226	43.907	6.6829	47.3792	2.0308
0	0	0	100	0	0	0	59.32203	37.07627	22.24576	16.94915	5.932203	12.71186	5.084746	37.50531	17.46008	2.646736	1.239187	17.14529	6.00085	12.85896	2.571793	2.571793	46.4347	6.8812	43.6717	3.0124
0	26.682	17.5833	0	26.7037	29.0309	0	75.72483	54.96047	20.76435	12.11482	2.062017	6.756449	3.341887	57.10895	13.63235	2.697152	1.337427	12.5884	2.142624	7.020568	1.736263	1.736263	43.6273	6.6958	47.6272	2.0496
0	0	0	0	0	0	100	63.82979	37.23404	26.59574	17.7305	2.836879	12.76596	2.836879	37.81012	20.95853	3.126781	1.374744	18.00482	2.880771	12.96347	1.440385	1.440385	45.4801	6.7132	44.6338	3.1728
0	0	100	0	0	0	0	66.17647	33.08824	33.08824	18.38235	2.941176	9.558824	2.941176	34.95822	21.64439	5.68539	1.976919	19.42124	3.107398	10.09904	1.553699	1.553699	45.9292	6.6935	44.0597	3.3176
21.1248	0.6362	14.2402	1.4999	14.1268	18.9641	29.408	76.57331	54.17715	22.39616	10.63477	2.244482	7.047109	3.500324	55.16765	16.69317	2.992779	1.291411	10.8292	2.285517	7.175948	1.78216	1.78216	43.5981	6.6796	47.9621	1.7602
0	47.4552	0	0	0	52.5448	0	75.80777	52.45365	23.35412	13.40174	2.03617	7.684412	1.069903	51.52214	18.25846	4.403137	2.053657	13.16375	2.00001	7.547947	0.525451	0.525451	44.1779	6.674	46.991	2.1571
0	0	45.6136	0	54.3864	0	0	74.90784	55.2325	19.67534	11.42529	2.156431	6.128797	5.381648	56.62977	12.44006	4.018726	1.184503	11.71432	2.210985	6.283844	2.758896	2.758896	43.4657	6.6695	47.9759	1.8889
29.9423	0	35.0443	0	35.0134	0	0	81.03088	61.93087	19.10002	8.06457	1.879914	4.912442	4.112192	63.43197	13.04309	2.56616	1.529871	8.260042	1.92548	5.031512	2.105933	2.105933	42.8556	6.6652	49.1742	1.305
21.248	25.4931	13.4539	3.4464	7.4738	4.3255	24.5594	78.65481	57.36902	21.28579	10.28098	1.951444	6.822698	2.290067	58.58093	13.92076	4.287201	1.415007	10.49817	1.992668	6.966826	1.169222	1.169222	43.4069	6.6848	48.2071	1.7012
6.067	11.6913	32.088	1.8213	7.2203	34.835	6.2771	72.57467	46.58005	25.99462	13.96606	2.528221	7.975072	2.95597	47.59059	18.80599	3.724919	1.858193	14.26905	2.58307	8.148088	1.510049	1.510049	44.5289	6.685	46.4266	2.3594
0	46.3384	33.0725	20.5892	0	0	0	73.91688	50.20649	23.71039	13.88725	2.406774	8.306987	1.482112	50.78676	16.39611	4.720729	1.711822	14.04775	2.43459	8.402996	0.749621	0.749621	44.3806	6.707	46.5837	2.3287
13.7102	0	17.014	0	25.0795	8.8441	35.3522	75.14518	53.41048	21.7347	11.29505	2.221036	7.317699	4.021036	54.63787	16.33028	2.320756	1.285101	11.55461	2.272076	7.485863	2.05672	2.05672	43.6416	6.6796	47.7915	1.8872
11.4259	9.9246	21.5422	4.0452	31.5216	9.8852	11.6553	76.87028	56.77813	20.09215	10.58386	2.124378	6.417096	4.004389	57.07824	14.83547	3.230316	1.603996	10.6398	2.135607	6.451015	2.012777	2.012777	43.4607	6.6685	48.1562	1.7147
0	0	28.9754	45.5343	17.9819	0	7.5084	67.16134	44.09141	23.06993	14.84996	3.712415	9.510432	4.765854	45.24385	14.71029	4.370235	1.978642	15.2381	3.809448	9.759011	2.445211	2.445211	45.1064	6.7438	45.5791	2.5707

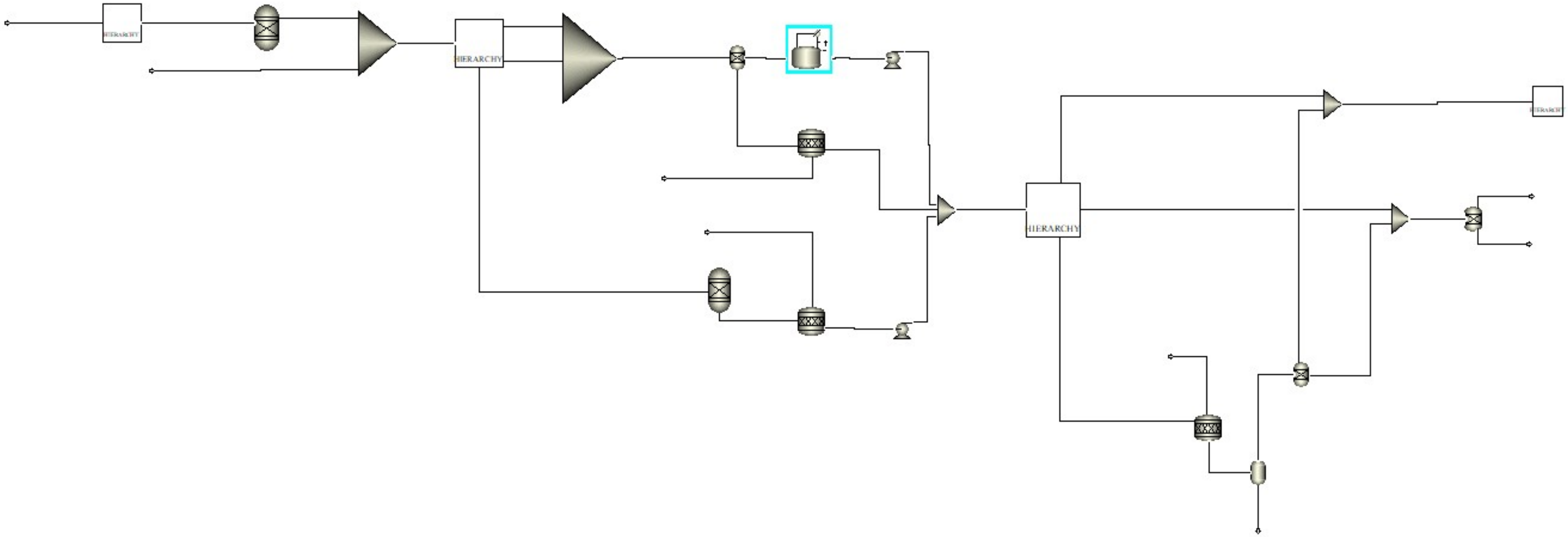
Hydrogen Production Via Fermentation
Properties Section - Components

65 Components



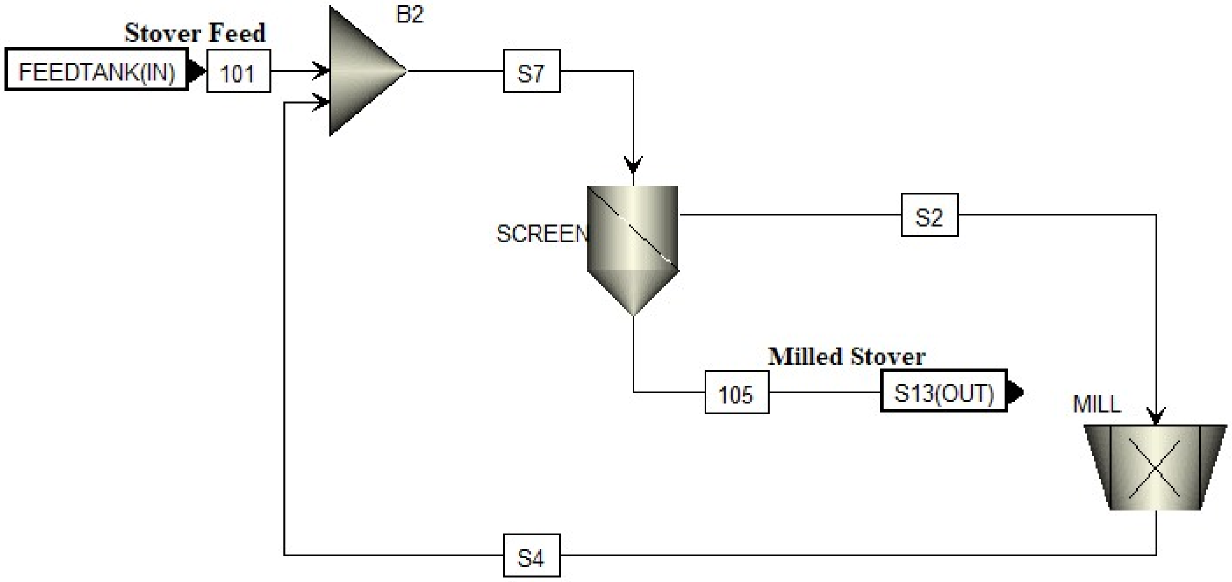
Component ID	Type	Component name	Alias	CAS number
H2	*Conventional*	HYDROGEN	H2	1333-74-0
N2	*Conventional*	NITROGEN	N2	7727-37-9
H2O	*Conventional*	WATER	H2O	7732-18-5
GLUCOSE	*Conventional*	DEXTROSE	C6H12O6	50-99-7
NH3	*Conventional*	AMMONIA	H3N	7664-41-7
CO2	*Conventional*	CARBON-DIOXIDE	CO2	124-38-9
O2	*Conventional*	OXYGEN	O2	7782-44-7
CH4	*Conventional*	METHANE	CH4	74-82-8
H2S	*Conventional*	HYDROGEN-SULFIDE	H2S	7783-06-4
ACETIC	*Conventional*	ACETIC-ACID	C2H4O2-1	64-19-7
CITRIC	*Conventional*	CITRIC-ACID	C6H8O7	77-92-9
MALIC	*Conventional*	MALIC-ACID	C4H6O5-D1	6915-15-7
TARTARIC	*Conventional*	TARTARIC-ACID	C4H6O6	133-37-9
LINOLEIC	*Conventional*	LINOLEIC-ACID	C18H32O2	60-33-3
PECTIN	Biocomponent			
ENZYME	Biocomponent	PROTEIN	BSA	
H3PO4	*Conventional*	ORTHOPHOSPHORIC-ACID	H3PO4	7664-38-2
CLOST	Biocomponent			
BIOMASS	Biocomponent			

Hydrogen Production Via Fermentation
Simulation Section – Main Flowsheet

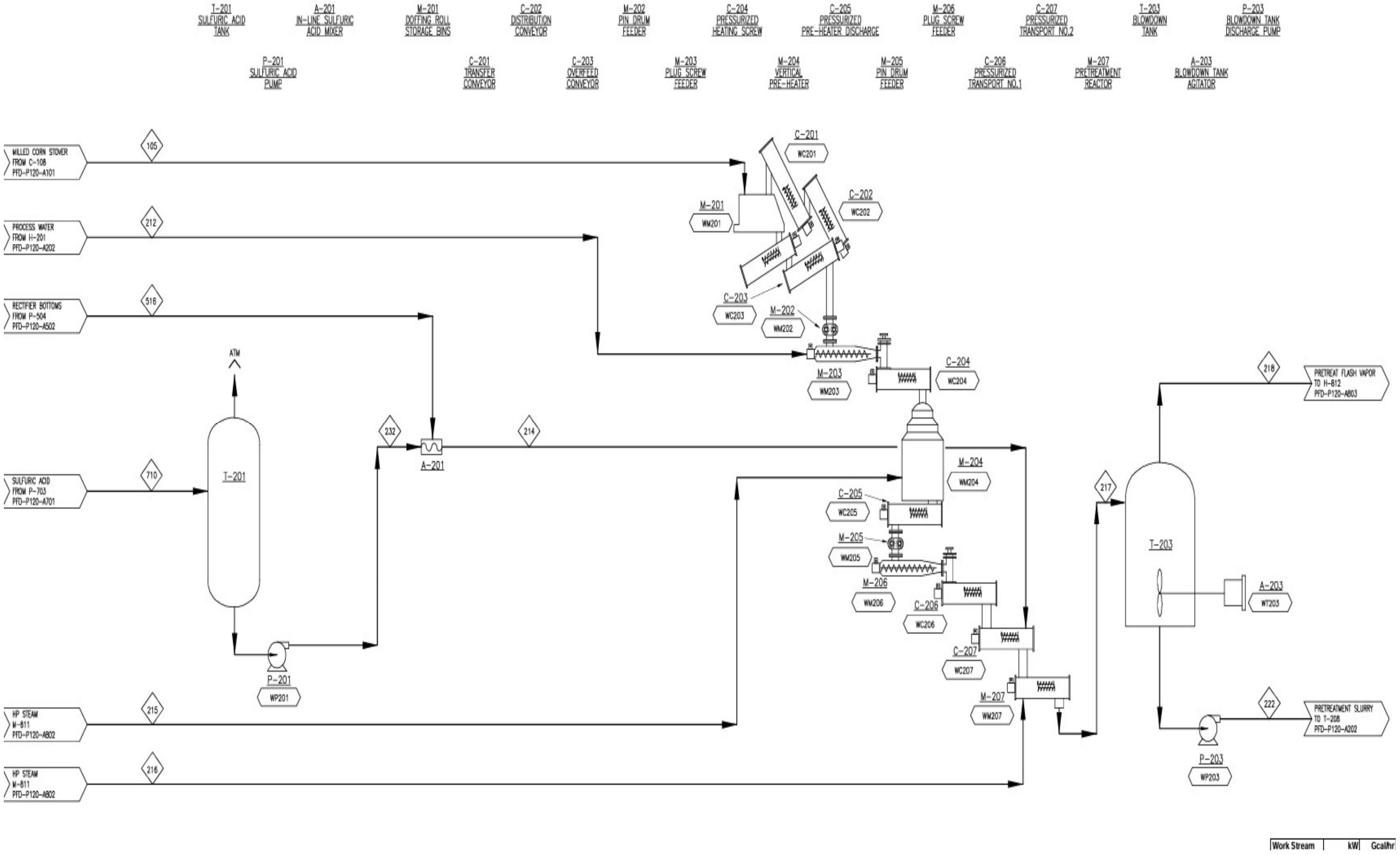


500 Kg of food waste : 10% Dry Biomass (50 Kg) ; 90% (450 Kg)

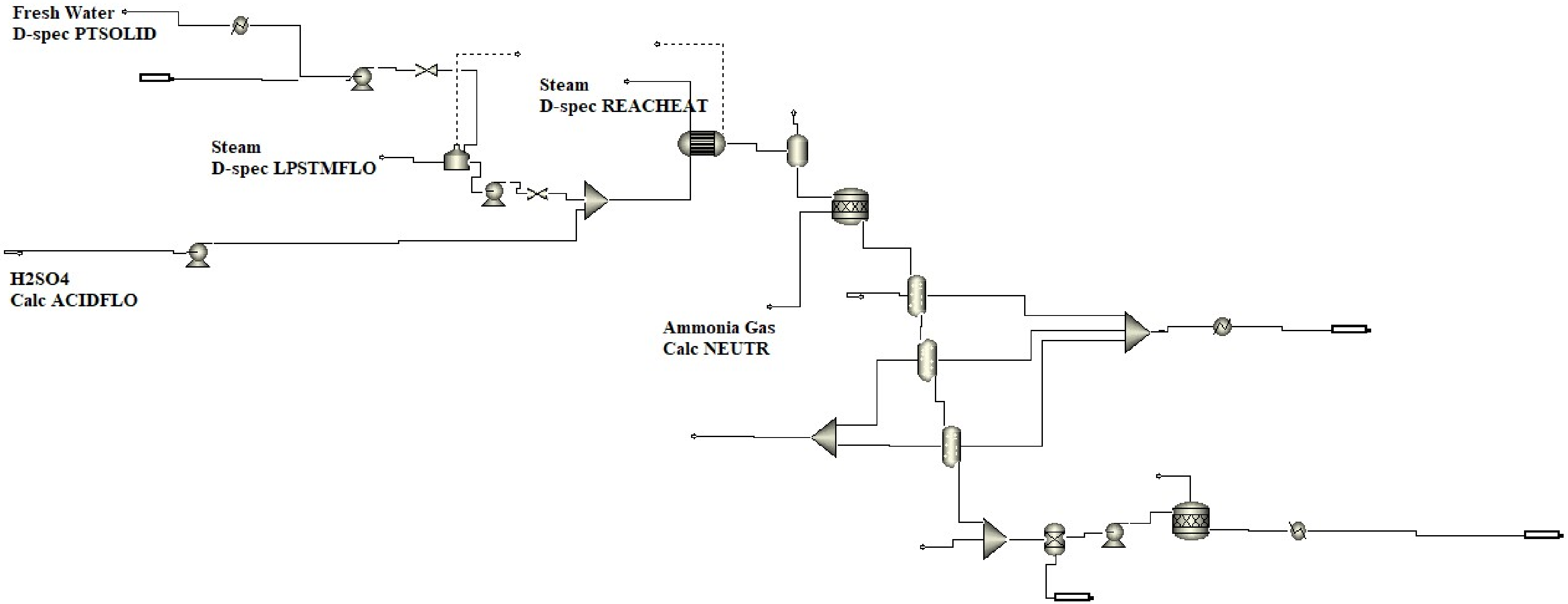
Hydrogen Production Via Fermentation
Solid Handling



Hydrogen Production Via Fermentation pretreatment

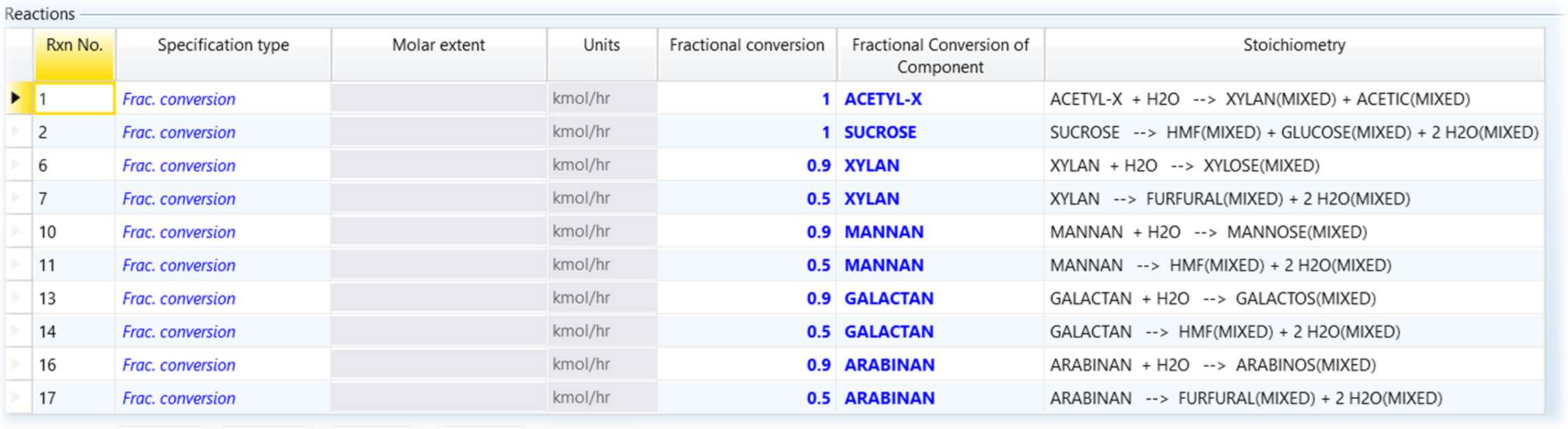


Hydrogen Production Via Fermentation
pretreatment



Hydrogen Production Via Fermentation

Reactions of acidic pretreatment (Breaking Hemicellulose)



Reactions

	Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
▶	1	*Frac. conversion*		kmol/hr	**1**	**ACETYL-X**	ACETYL-X + H2O --> XYLAN(MIXED) + ACETIC(MIXED)
	2	*Frac. conversion*		kmol/hr	**1**	**SUCROSE**	SUCROSE --> HMF(MIXED) + GLUCOSE(MIXED) + 2 H2O(MIXED)
	6	*Frac. conversion*		kmol/hr	**0.9**	**XYLAN**	XYLAN + H2O --> XYLOSE(MIXED)
	7	*Frac. conversion*		kmol/hr	**0.5**	**XYLAN**	XYLAN --> FURFURAL(MIXED) + 2 H2O(MIXED)
	10	*Frac. conversion*		kmol/hr	**0.9**	**MANNAN**	MANNAN + H2O --> MANNOSE(MIXED)
	11	*Frac. conversion*		kmol/hr	**0.5**	**MANNAN**	MANNAN --> HMF(MIXED) + 2 H2O(MIXED)
	13	*Frac. conversion*		kmol/hr	**0.9**	**GALACTAN**	GALACTAN + H2O --> GALACTOS(MIXED)
	14	*Frac. conversion*		kmol/hr	**0.5**	**GALACTAN**	GALACTAN --> HMF(MIXED) + 2 H2O(MIXED)
	16	*Frac. conversion*		kmol/hr	**0.9**	**ARABINAN**	ARABINAN + H2O --> ARABINOS(MIXED)
	17	*Frac. conversion*		kmol/hr	**0.5**	**ARABINAN**	ARABINAN --> FURFURAL(MIXED) + 2 H2O(MIXED)

Hydrogen Production Via Fermentation

Reactions of acidic pretreatment (Breaking Hemicellulose)

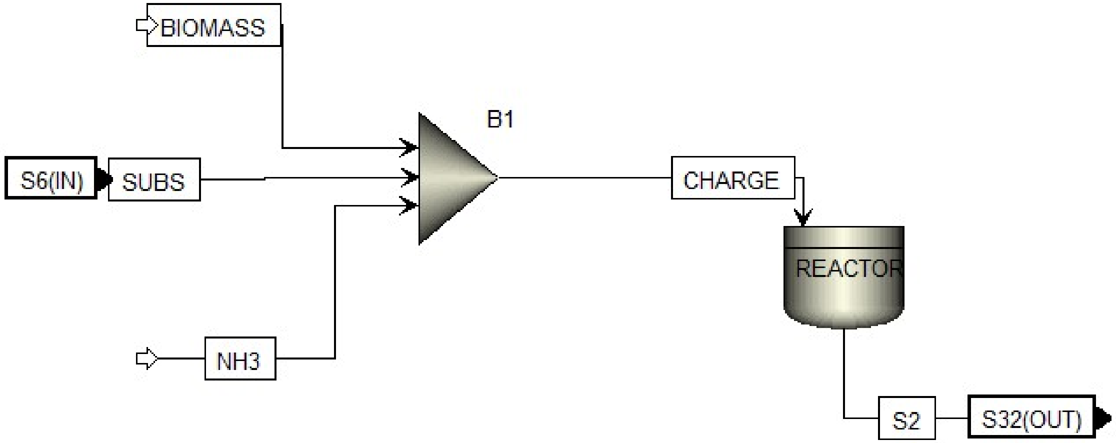
Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	*Frac. conversion*		kmol/hr	**0.9**	**CELLULOS**	CELLULOS + H2O --> GLUCOSE(MIXED)
2	*Frac. conversion*		kmol/hr	**1**	**CELLOB**	CELLOB + H2O --> 2 GLUCOSE(MIXED)

Reactions of Enzymatic hydrolysis pretreatment (Breaking Cellulose)

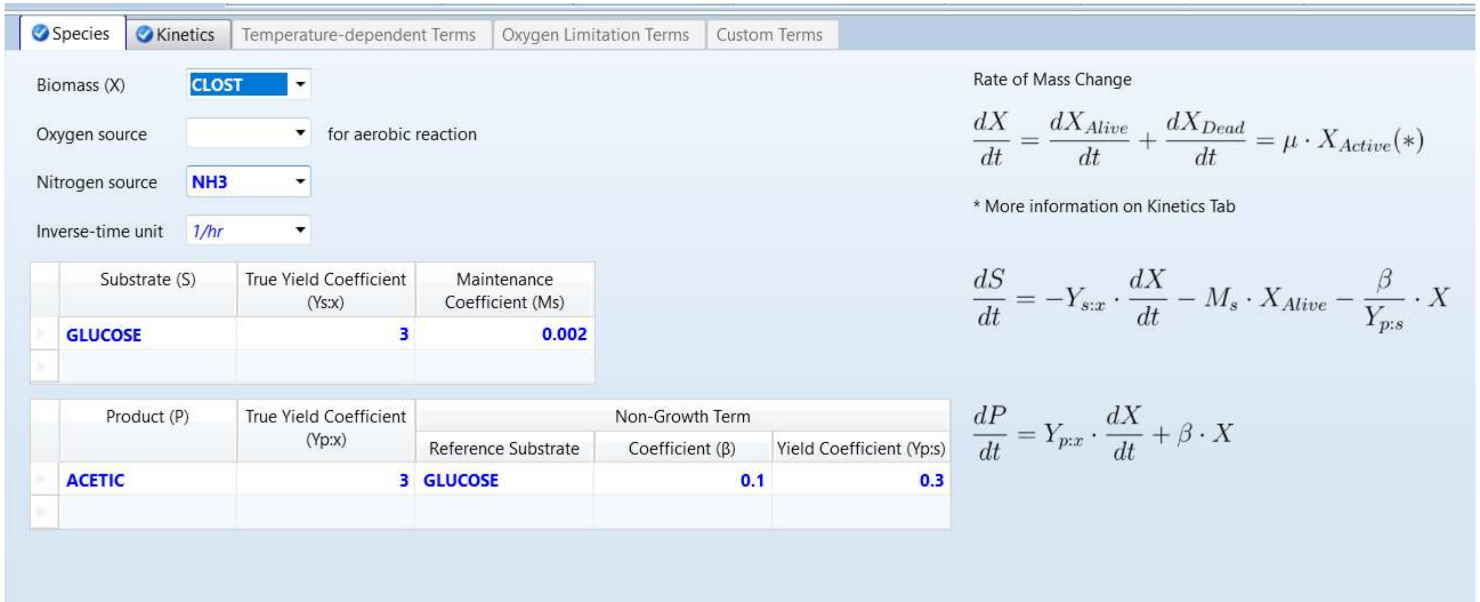
Hydrogen Production Via Fermentation

Dark Fermentation of Glucose



Hydrogen Production Via Fermentation

Dark Fermentation of Glucose (Reaction)



Biomass (X) CLOST

Oxygen source for aerobic reaction

Nitrogen source NH3

Inverse-time unit *1/hr*

Substrate (S)	True Yield Coefficient (Ys:x)	Maintenance Coefficient (Ms)
GLUCOSE	**3**	**0.002**

Product (P)	True Yield Coefficient (Yp:x)	Non-Growth Term		
		Reference Substrate	Coefficient (β)	Yield Coefficient (Yp:s)
ACETIC	**3**	**GLUCOSE**	**0.1**	**0.3**

Rate of Mass Change

$$\frac{dX}{dt} = \frac{dX_{Alive}}{dt} + \frac{dX_{Dead}}{dt} = \mu \cdot X_{Active}(*)$$

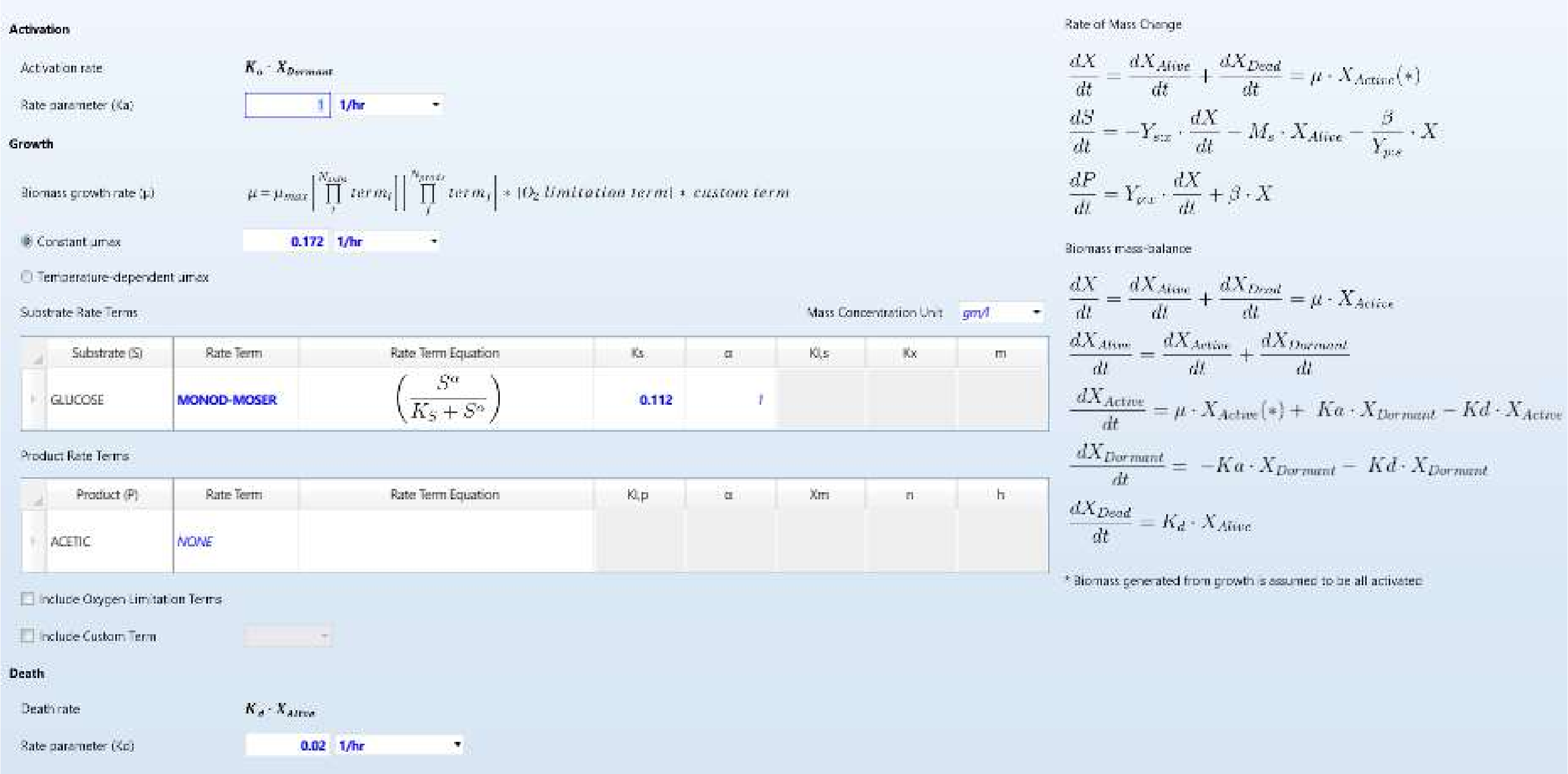
* More information on Kinetics Tab

$$\frac{dS}{dt} = -Y_{s:x} \cdot \frac{dX}{dt} - M_s \cdot X_{Alive} - \frac{\beta}{Y_{p:s}} \cdot X$$

$$\frac{dP}{dt} = Y_{p:x} \cdot \frac{dX}{dt} + \beta \cdot X$$

Hydrogen Production Via Fermentation

Dark Fermentation of Glucose (Reaction)



Activation

Activation rate $K_a \cdot X_{Dormant}$

Rate parameter (Ka) 1 1/hr

Growth

Biomass growth rate (μ) $\mu = \mu_{max}\left[\prod_{i}^{N_{subs}} term_i\right]\left[\prod_{j}^{N_{prods}} term_j\right] * [O_2\ limitation\ term] * custom\ term$

● Constant μmax 0.172 1/hr

○ Temperature-dependent μmax

Substrate Rate Terms

Mass Concentration Unit gm/l

Substrate (S)	Rate Term	Rate Term Equation	Ks	α	KI,s	Kx	m
GLUCOSE	MONOD-MOSER	$\left(\frac{S^{\alpha}}{K_S + S^{\alpha}}\right)$	0.112	1			

Product Rate Terms

Product (P)	Rate Term	Rate Term Equation	KI,p	α	Xm	n	h
ACETIC	NONE						

☐ Include Oxygen Limitation Terms

☐ Include Custom Term

Death

Death rate $K_d \cdot X_{Alive}$

Rate parameter (Kd) 0.02 1/hr

Rate of Mass Change

$$\frac{dX}{dt} = \frac{dX_{Alive}}{dt} + \frac{dX_{Dead}}{dt} = \mu \cdot X_{Active}(*)$$

$$\frac{dS}{dt} = -Y_{s:x} \cdot \frac{dX}{dt} - M_s \cdot X_{Alive} - \frac{\beta}{Y_{p:s}} \cdot X$$

$$\frac{dP}{dt} = Y_{p:x} \cdot \frac{dX}{dt} + \beta \cdot X$$

Biomass mass-balance

$$\frac{dX}{dt} = \frac{dX_{Alive}}{dt} + \frac{dX_{Dead}}{dt} = \mu \cdot X_{Active}$$

$$\frac{dX_{Alive}}{dt} = \frac{dX_{Active}}{dt} + \frac{dX_{Dormant}}{dt}$$

$$\frac{dX_{Active}}{dt} = \mu \cdot X_{Active}(*) + Ka \cdot X_{Dormant} - Kd \cdot X_{Active}$$

$$\frac{dX_{Dormant}}{dt} = -Ka \cdot X_{Dormant} - Kd \cdot X_{Dormant}$$

$$\frac{dX_{Dead}}{dt} = K_d \cdot X_{Alive}$$

* Biomass generated from growth is assumed to be all activated

Hydrogen Production Via Fermentation

Dark Fermentation of Glucose (Result)

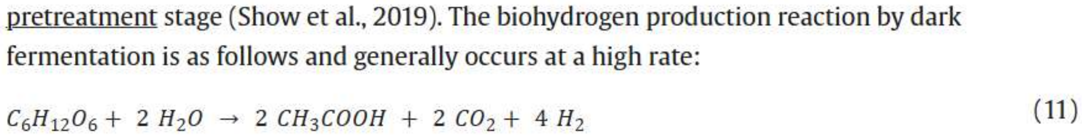
ELSEVIER

Bioresource Technology
Volume 364, November 2022, 128134

Review

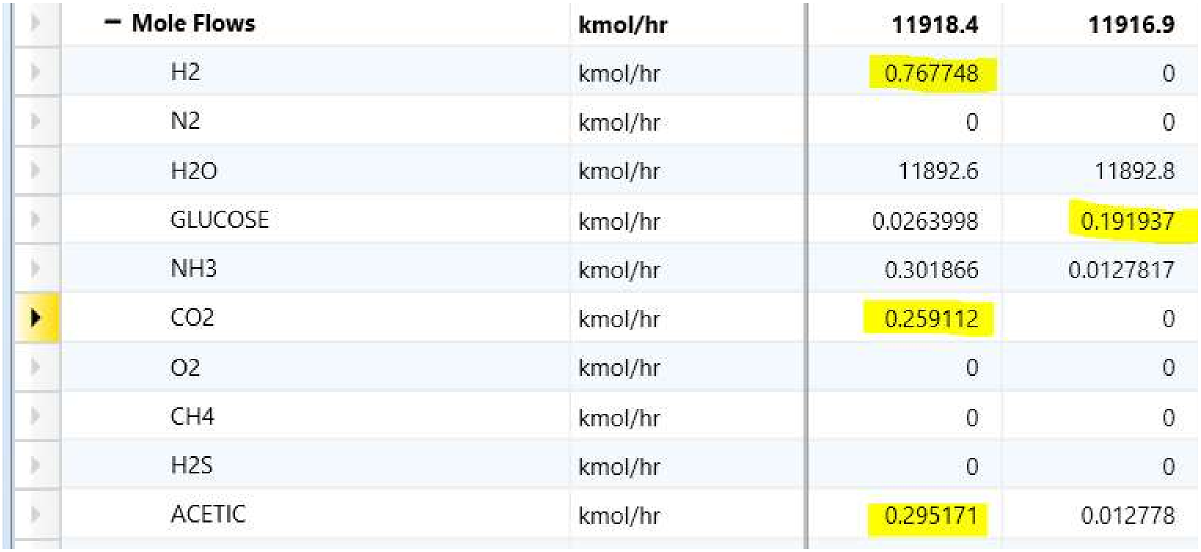
Microalgae-derived hydrogen production towards low carbon emissions via large-scale outdoor systems

Young Joon Sung [a][b][1], Byung Sun Yu [a][1], Ha Eun Yang [a], Dong Hoon Kim [a], Ju Yeon Lee [a], Sang Jun Sim [a]



pretreatment stage (Show et al., 2019). The biohydrogen production reaction by dark fermentation is as follows and generally occurs at a high rate:

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 2\ CO_2 + 4\ H_2 \tag{11}$$



− Mole Flows	kmol/hr	11918.4	11916.9
H2	kmol/hr	0.767748	0
N2	kmol/hr	0	0
H2O	kmol/hr	11892.6	11892.8
GLUCOSE	kmol/hr	0.0263998	0.191937
NH3	kmol/hr	0.301866	0.0127817
CO2	kmol/hr	0.259112	0
O2	kmol/hr	0	0
CH4	kmol/hr	0	0
H2S	kmol/hr	0	0
ACETIC	kmol/hr	0.295171	0.012778

Hydrogen Production Via Fermentation

Dark Fermentation of Protein (Reaction)

$$C_3H_7O_2N + H_2O \rightarrow \frac{1}{3}CH_3COOH + \frac{2}{3}CH_3CH_2COOH + NH_3 + \frac{1}{3}CO_2 + \frac{1}{3}H_2 \qquad (3)$$

Not in mass balance

Reaction 3 (Corrected): Alanine to Propionic Acid
3 ALANINE + 4 H2O → 2 PROPIONIC_ACID + 3 NH3 + 3 CO2 + 4 H2

$$C_3H_7O_2N + H_2O \rightarrow \frac{1}{2}CH_3CH_2CH_2COOH + NH_3 + CO_2 + H_2 \qquad (4)$$

$$C_3H_7O_3N + H_2O \rightarrow CH_3COOH + NH_3 + CO_2 + H_2 \qquad (5)$$

$$C_3H_7O_3N \rightarrow \frac{1}{2}C_4H_8O_2 + NH_3 + CO_2 \qquad (6)$$

$$C_4H_7O_4N + 2H_2O \rightarrow CH_3COOH + NH_3 + 2CO_2 + 2H_2 \qquad (7)$$

$$C_4H_7O_4N \rightarrow C_3H_7O_2N + CO_2 \qquad (8)$$

$$C_6H_{13}O_2N + 2H_2O \rightarrow C_5H_{10}O_2 \text{ (isovalerate)} + NH_3 + CO_2 + 2H_2 \qquad (9)$$

Hydrogen Production Via Fermentation

Dark Fermentation Results

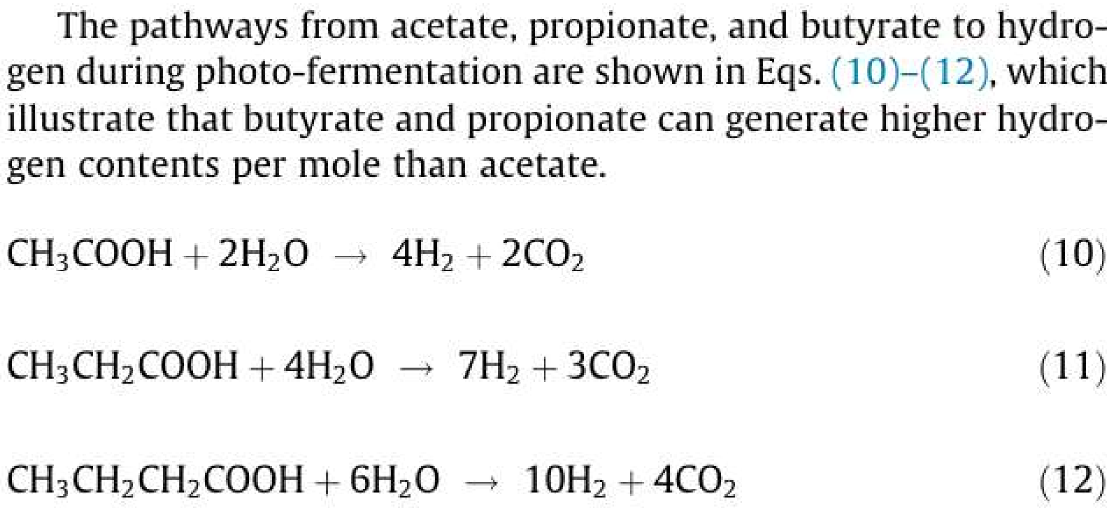
From 500 Kg Fruit waste

Mole Flows	kmol/hr	
H2	kmol/hr	0.808906
CO2	kmol/hr	0.304062
ACETIC	kmol/hr	0.320554

Mass Flows	kg/hr	
H2	kg/hr	1.630657
CO2	kg/hr	13.38173
ACETIC	kg/hr	19.25008

Hydrogen Production Via Fermentation

Photo Fermentation (Reactions)



The pathways from acetate, propionate, and butyrate to hydrogen during photo-fermentation are shown in Eqs. (10)–(12), which illustrate that butyrate and propionate can generate higher hydrogen contents per mole than acetate.

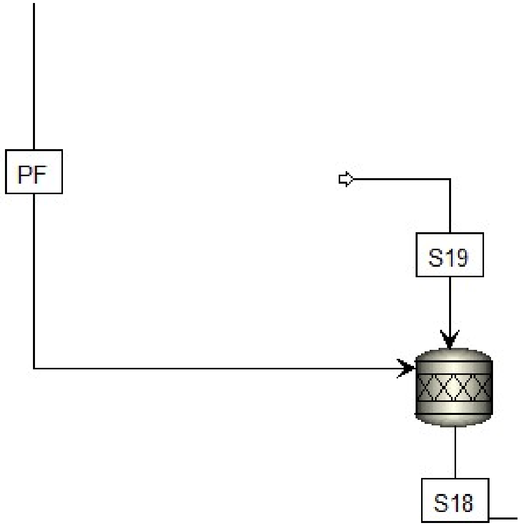
$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2 \tag{10}$$

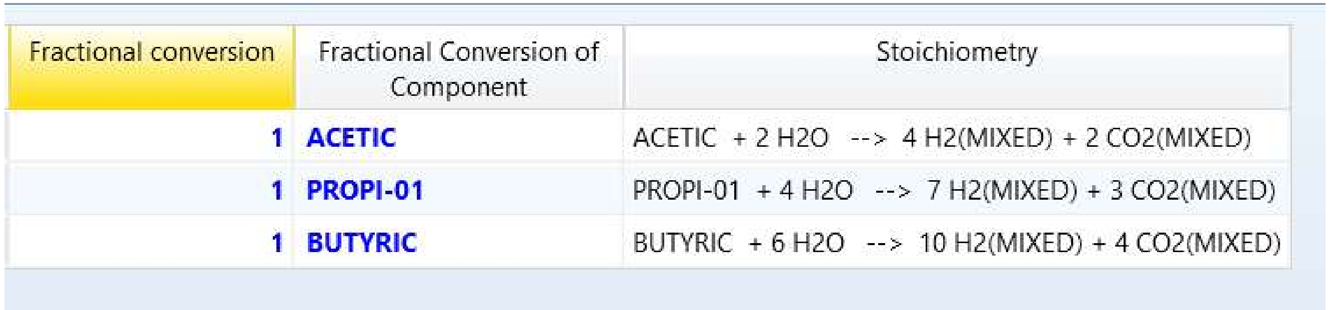
$$CH_3CH_2COOH + 4H_2O \rightarrow 7H_2 + 3CO_2 \tag{11}$$

$$CH_3CH_2CH_2COOH + 6H_2O \rightarrow 10H_2 + 4CO_2 \tag{12}$$

Hydrogen Production Via Fermentation

Photo Fermentation (Reactions)





Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	**ACETIC**	ACETIC + 2 H2O --> 4 H2(MIXED) + 2 CO2(MIXED)
1	**PROPI-01**	PROPI-01 + 4 H2O --> 7 H2(MIXED) + 3 CO2(MIXED)
1	**BUTYRIC**	BUTYRIC + 6 H2O --> 10 H2(MIXED) + 4 CO2(MIXED)

Hydrogen Production Via Fermentation

Photo Fermentation (Results)

From 500 Kg Fruit waste

Mole Flows	kmol/hr	
H2	kmol/hr	1.186623
CO2	kmol/hr	0.576618

Mass Flows	kg/hr	
H2	kg/hr	2.39209
CO2	kg/hr	25.37684

Hydrogen Production Via Fermentation

Purification

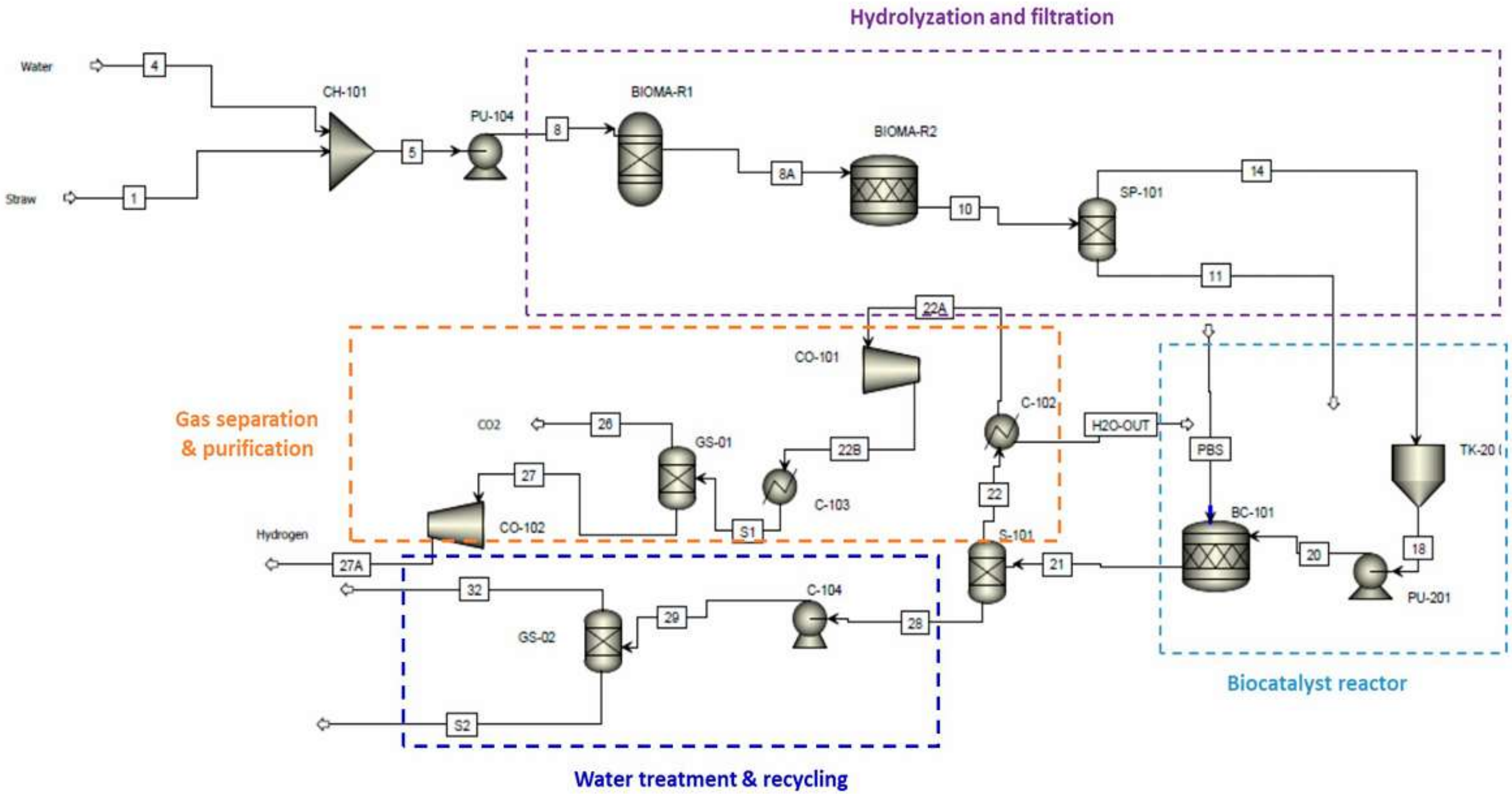
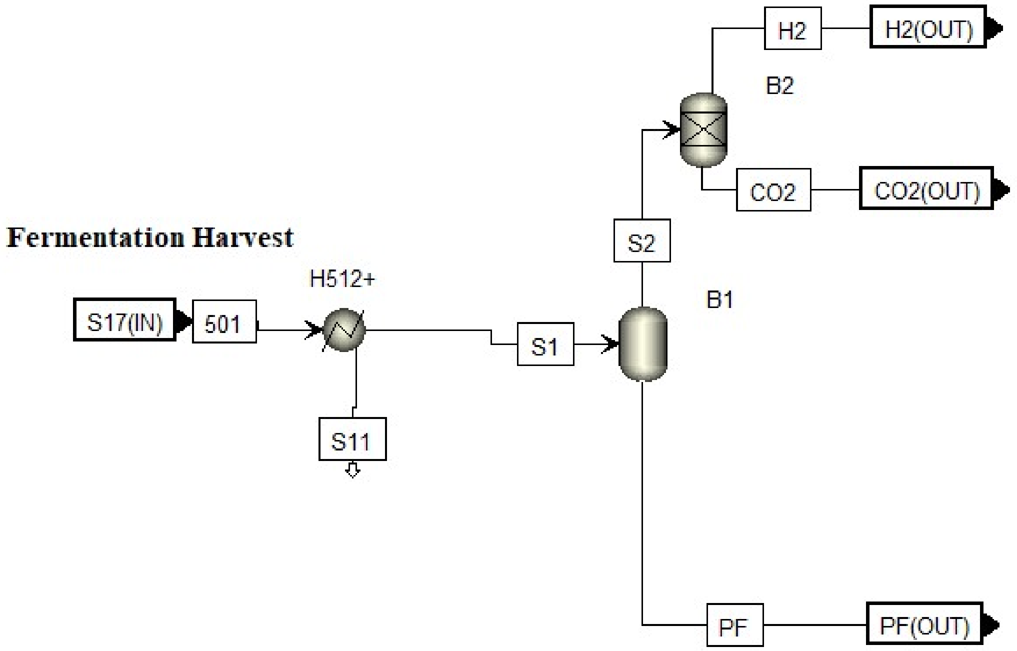


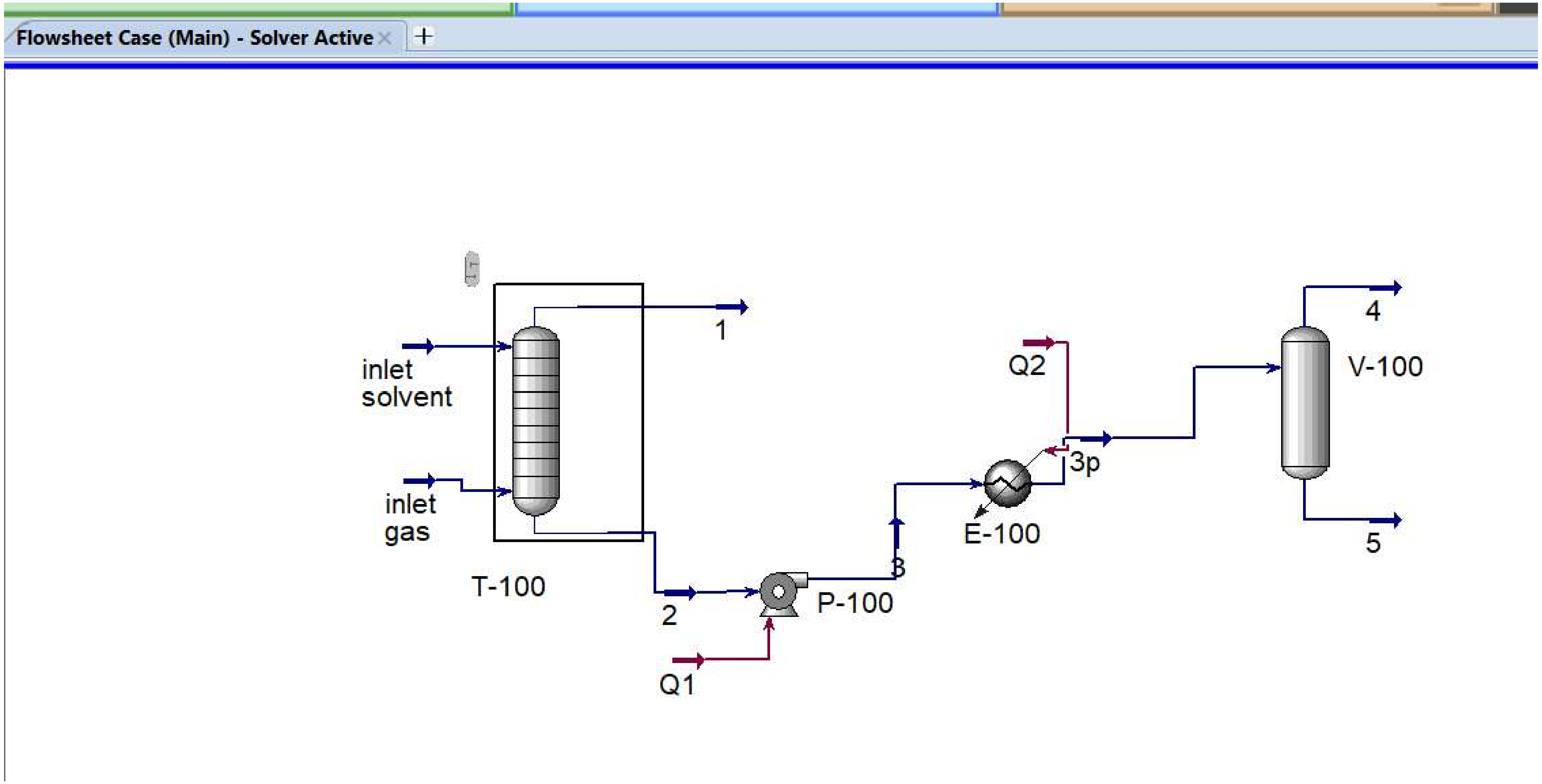
Figure 3. Process overview for hydrogen production with ASPEN Plus.

Hydrogen Production Via Fermentation

Purification

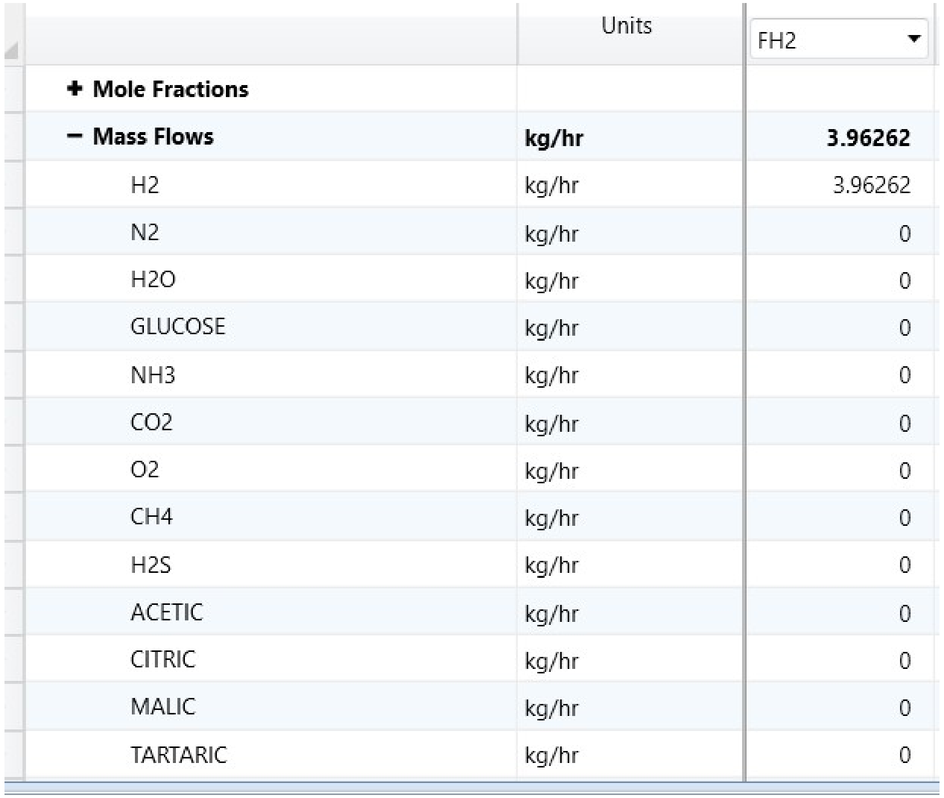


Current stage: Amine based Carbon Capture (By MEA)

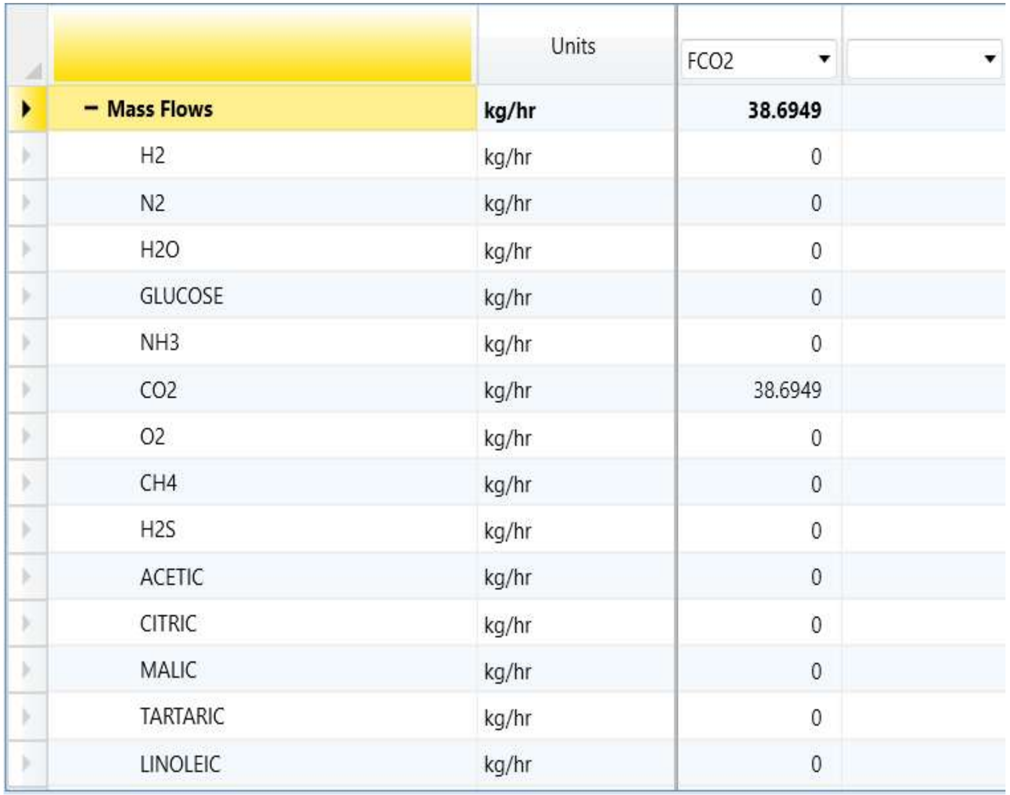


Looking for best Method for CCU

Final Result



	Units	FH2
+ Mole Fractions		
− Mass Flows	**kg/hr**	**3.96262**
H2	kg/hr	3.96262
N2	kg/hr	0
H2O	kg/hr	0
GLUCOSE	kg/hr	0
NH3	kg/hr	0
CO2	kg/hr	0
O2	kg/hr	0
CH4	kg/hr	0
H2S	kg/hr	0
ACETIC	kg/hr	0
CITRIC	kg/hr	0
MALIC	kg/hr	0
TARTARIC	kg/hr	0

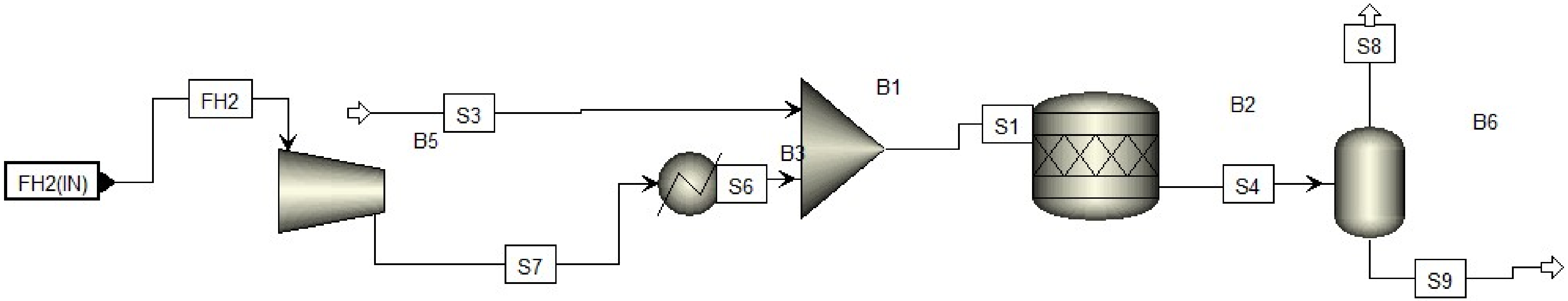


	Units	FCO2	
− Mass Flows	**kg/hr**	**38.6949**	
H2	kg/hr	0	
N2	kg/hr	0	
H2O	kg/hr	0	
GLUCOSE	kg/hr	0	
NH3	kg/hr	0	
CO2	kg/hr	38.6949	
O2	kg/hr	0	
CH4	kg/hr	0	
H2S	kg/hr	0	
ACETIC	kg/hr	0	
CITRIC	kg/hr	0	
MALIC	kg/hr	0	
TARTARIC	kg/hr	0	
LINOLEIC	kg/hr	0	

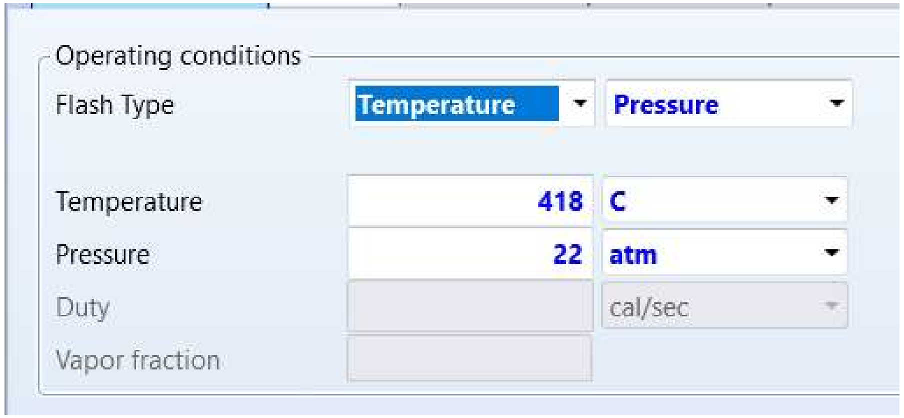
Final Result

The results obtained from the Aspen Plus simulation of hydrogen production via dark fermentation and photo-fermentation of fruit-based food waste show a hydrogen production rate of 3.963 kg/h and a carbon dioxide production rate of 38.723 kg/h, corresponding to approximately 0.079 kg H_2/kg and 0.774 kg CO_2/kg of dry waste. These values align closely with those reported by Cheng et al. (2011), who investigated a two-stage process involving dark and photo-fermentation of cassava starch. In their study, the total hydrogen yield reached 0.075 kg H_2/kg—very similar to the value obtained in this simulation. Although Cheng et al. did not report CO_2 mass flow explicitly, the theoretical stoichiometry of combined dark and photo-fermentation (which can reach up to 12 mol H_2/mol glucose with 6 mol CO_2/mol) suggests a CO_2/H_2 molar ratio near 0.5:1. In this simulation, the CO_2/H_2 molar ratio is approximately 0.44:1.

Hydrogen Storage
Metal Hydrides

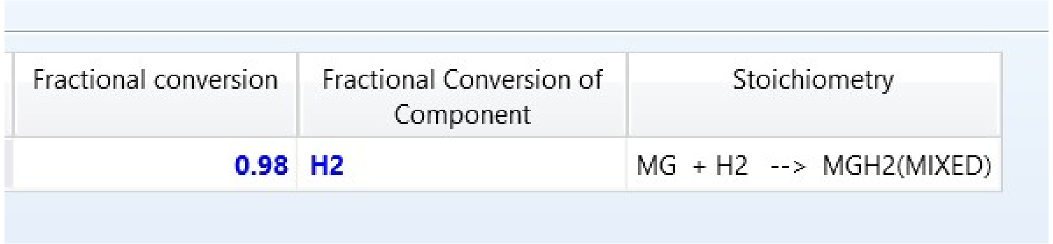


Hydrogen Storage
Metal Hydrides (Charging Phase)



Operating conditions

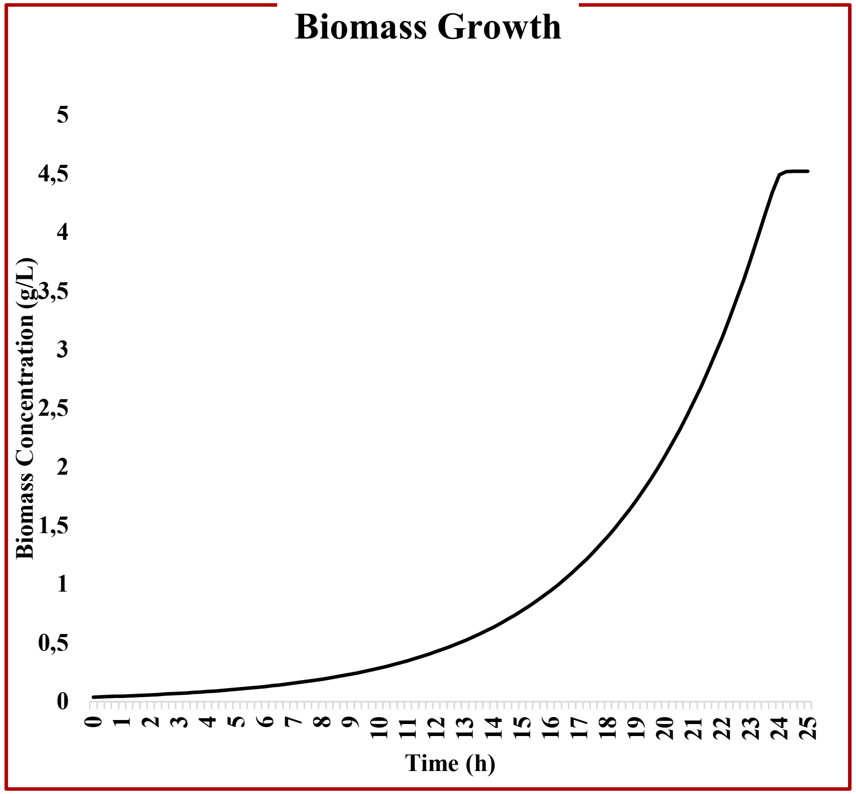
Flash Type	Temperature	Pressure
Temperature	418	C
Pressure	22	atm
Duty		cal/sec
Vapor fraction		

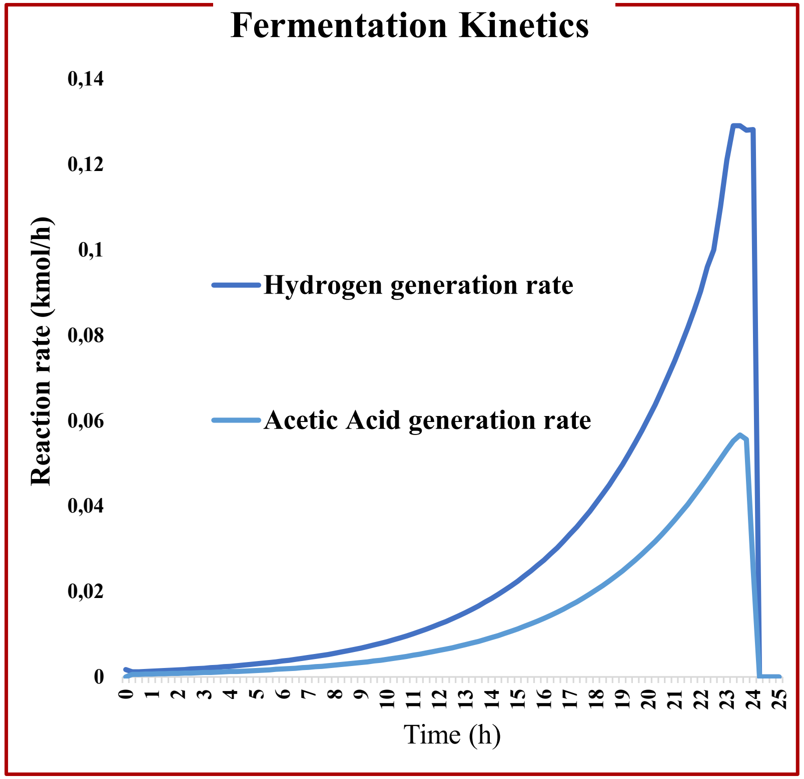


Fractional conversion	Fractional Conversion of Component	Stoichiometry
0.98	H2	MG + H2 --> MGH2(MIXED)

Dark Fermentation: Glucose (Theoretical)

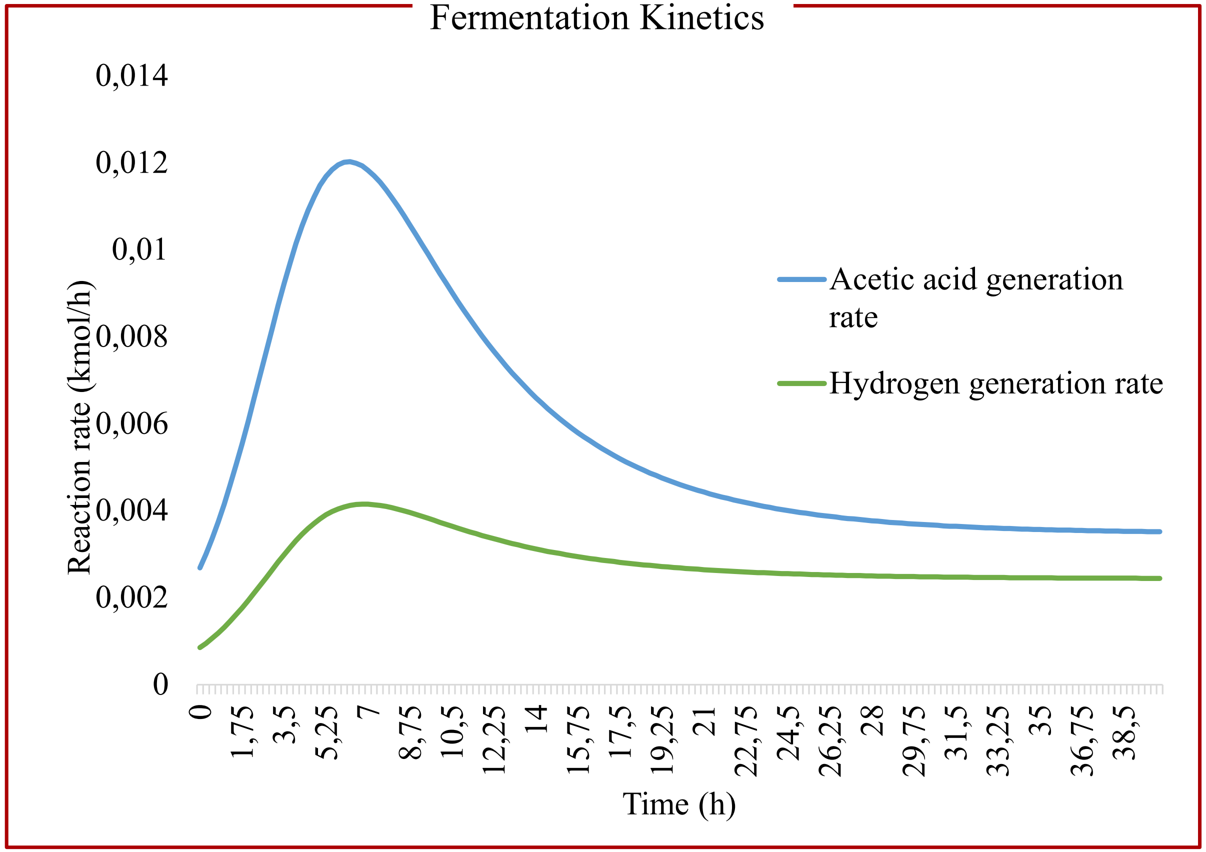
$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2$$



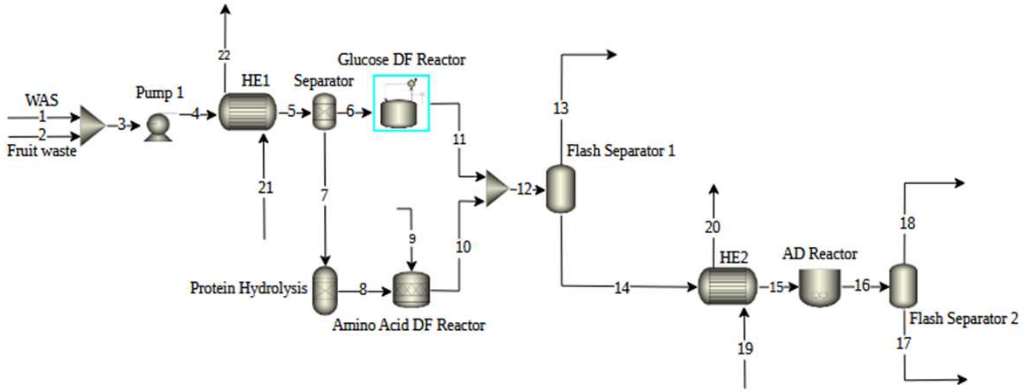


$$3.57 \, \frac{mol\ H_2}{mol\ glucose} \quad \& \quad 1.83 \, \frac{mol\ acetic\ acid}{mol\ glucose}$$

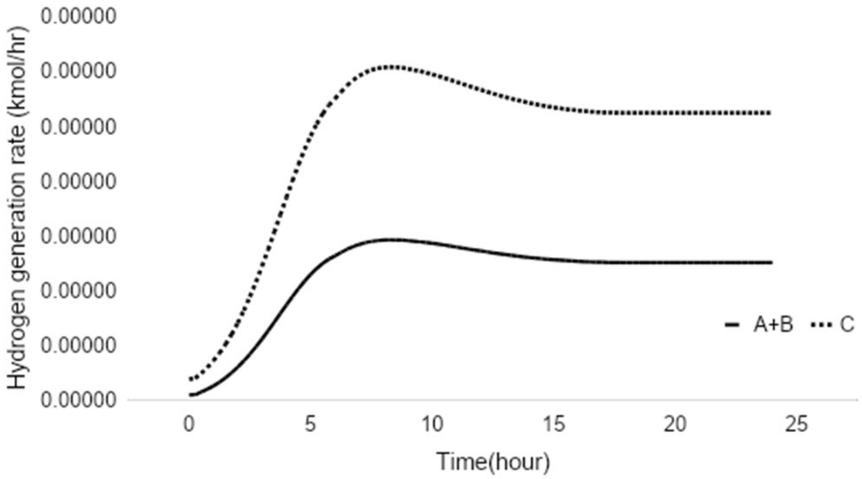
Dark Fermentation: Glucose (Hydrogen Partial-Pressure Inhibition)



Component	**Simulation**	**Experimental valid range**
Hydrogen	$\mathbf{1.76}\ \frac{mol_{H_2}}{mol_{glucose}}$	$\mathbf{1.4-2.4}\frac{mol_{H_2}}{mol_{glucose}}$
Acetic Acid	$\mathbf{0.96}\ \frac{mol_{acetic}}{mol_{H_2}}$	$\mathbf{0.75-1.5}\ \frac{mol_{acetic}}{mol_{H_2}}$



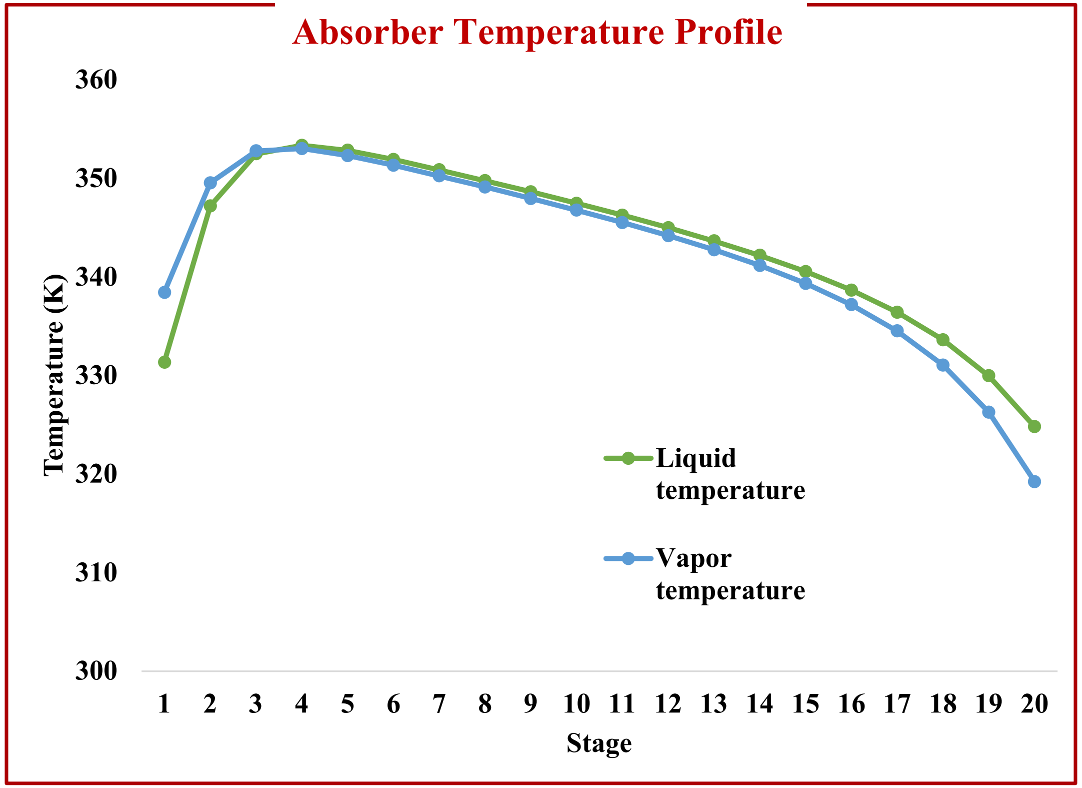
Schematizzazione del processo integrato di dark fermentation e digestione anaerobica in Aspen Plus

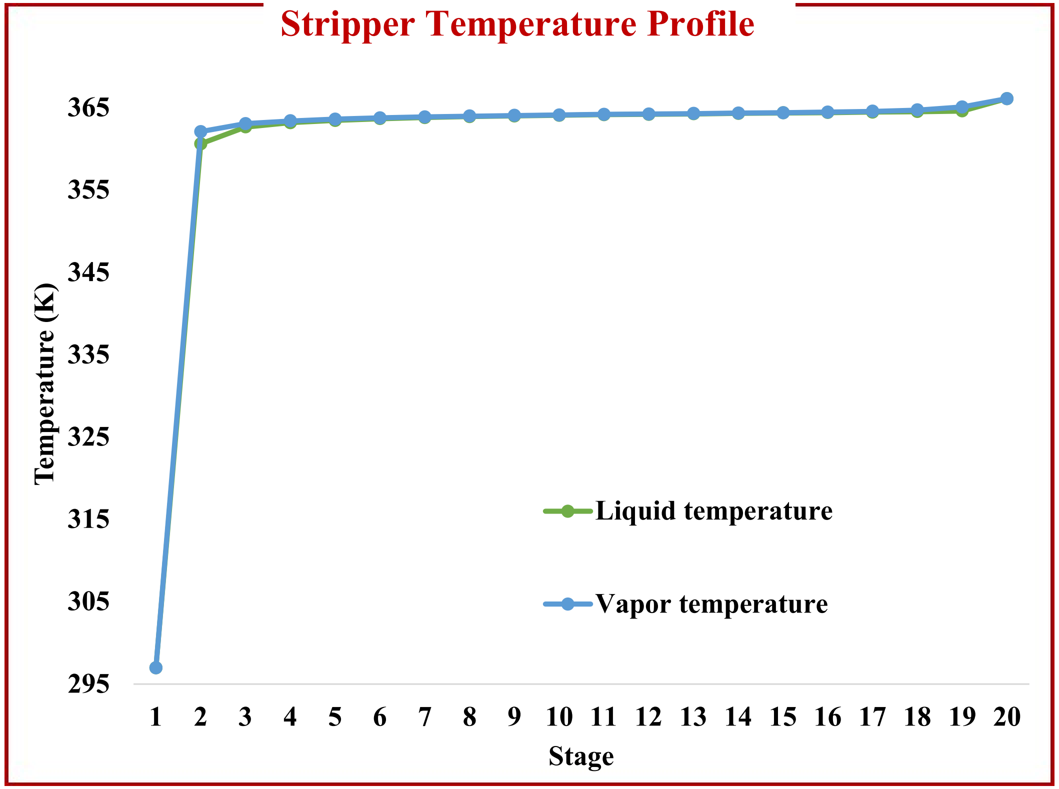


Parameter	**Value from Simulation**		**Experimental range**
	Mix A+B	Mix C	
Acetic acid	10.21	10.3	4.8-29.0
Butyric acid	8.46	8	0-13.4
HPR	0.79	0.8	0.7-0.83
Hydrogen per Glucose	1.54	1.54	1.45-2.5
	0.51	0.52	0.4-0.6
	0.49	0.48	0.4-0.5

Parameter	**Value from Simulation**		**Notes**
	Mix A+B	Mix C	
Residual glucose conversion	99.9	99.88	Near-complete degradation
Acetic acid conversion	99.52	99.48	Primary methanogenic substrate
Methane production rate	54.18	58.24	Primary energy output
Specific methane yield	123.47	124.44	High-efficiency conversion

CCU-Absorber & Stripper

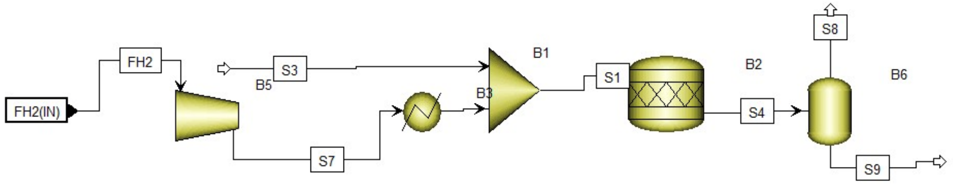

Absorber Temperature Profile


Stripper Temperature Profile

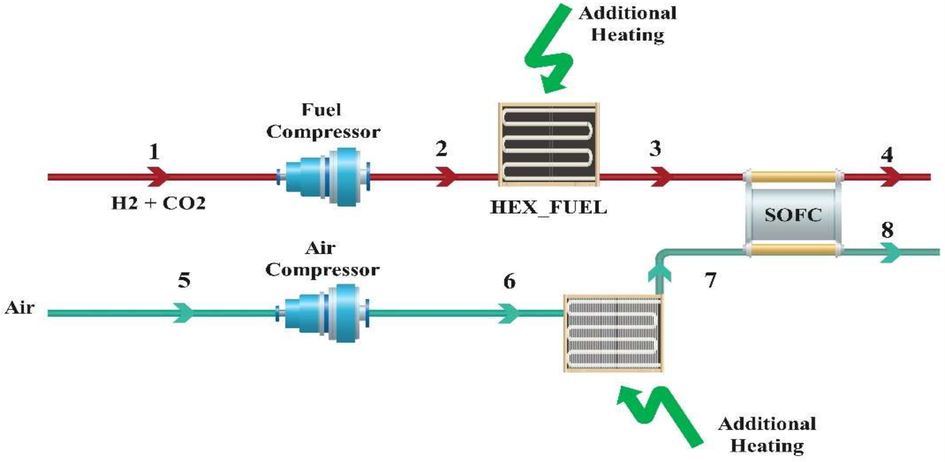
CO_2 capture efficiency: ≈ 69% & H_2 loss: $< 0.01\%$

Metal Hydride Hydrogen Storage & SOFC

$$\mathrm{Mg\,(s) + H_2\,(g)} \rightarrow MgH_2\mathrm{(s)}$$

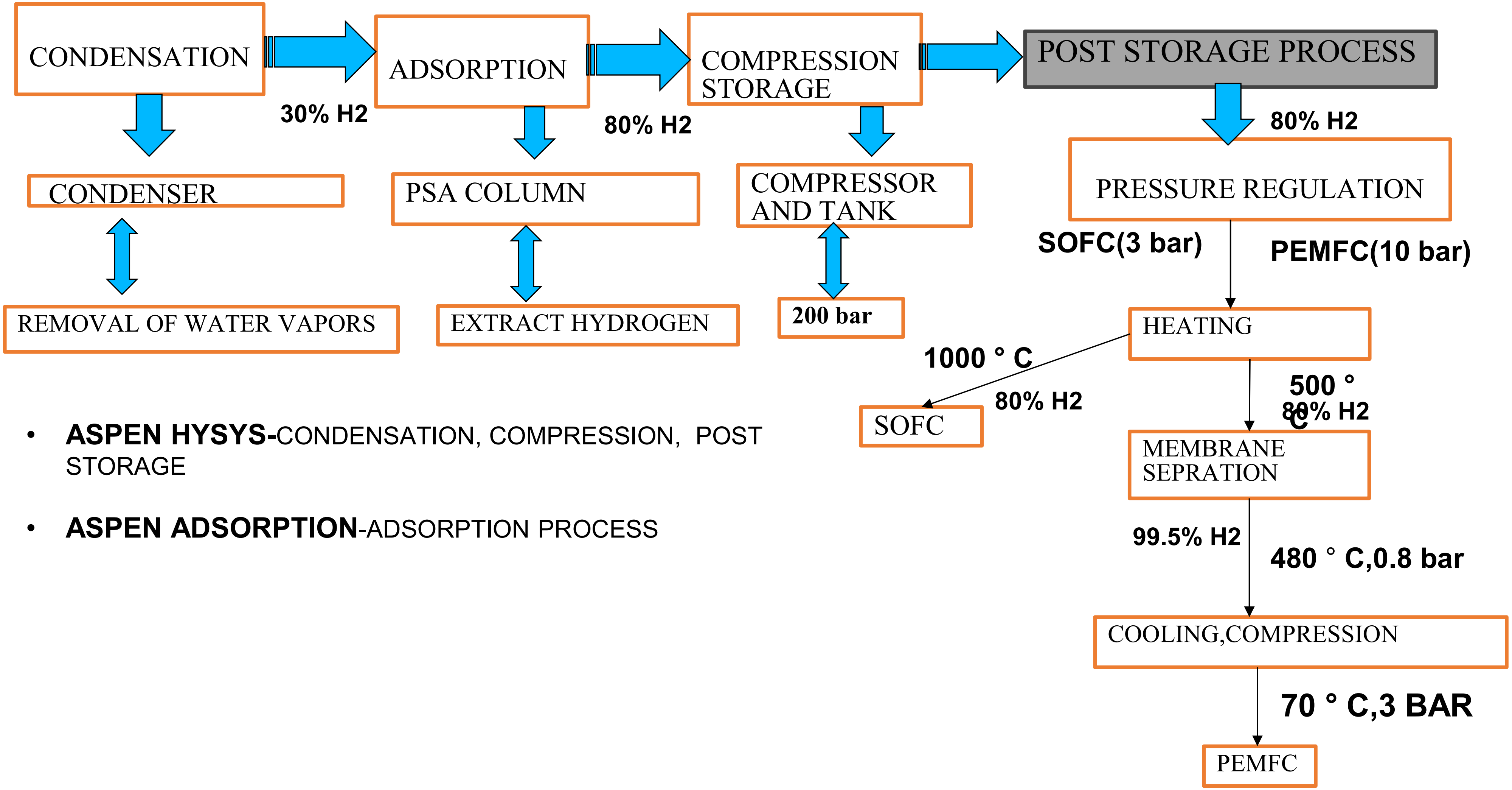


- **98% absorption of Hydrogen**



- **Voltage: 0.861 V**
- **operating Power: 68.82 kW AC**
- **Efficiency: 49.4%**
- **Fuel utilization: 85%**

PURIFICATION PROCESS PATH



CONDENSATION

30% H2

ADSORPTION

80% H2

COMPRESSION STORAGE

POST STORAGE PROCESS

80% H2

CONDENSER

REMOVAL OF WATER VAPORS

PSA COLUMN

EXTRACT HYDROGEN

COMPRESSOR AND TANK

200 bar

PRESSURE REGULATION

SOFC(3 bar)

PEMFC(10 bar)

HEATING

1000 ° C

80% H2

SOFC

500 ° C

80% H2

MEMBRANE SEPRATION

99.5% H2

480 ° C,0.8 bar

COOLING,COMPRESSION

70 ° C,3 BAR

PEMFC

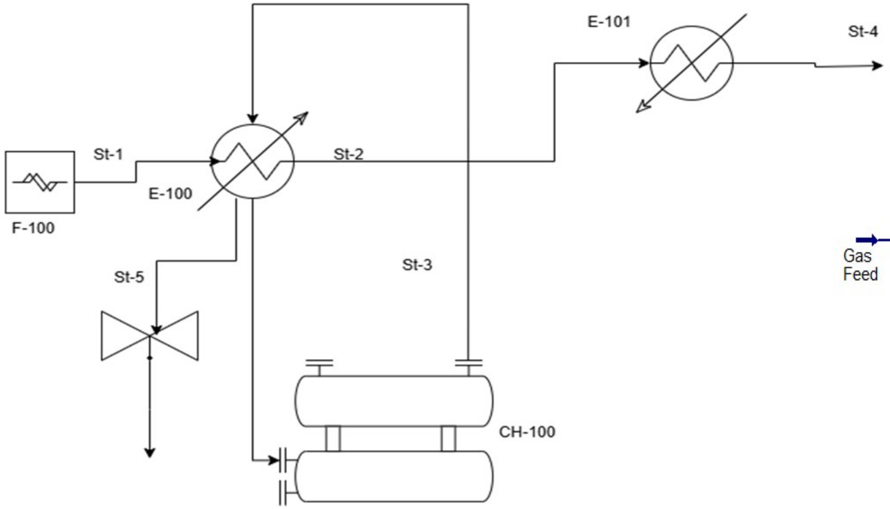
- **ASPEN HYSYS-**CONDENSATION, COMPRESSION, POST STORAGE
- **ASPEN ADSORPTION**-ADSORPTION PROCESS

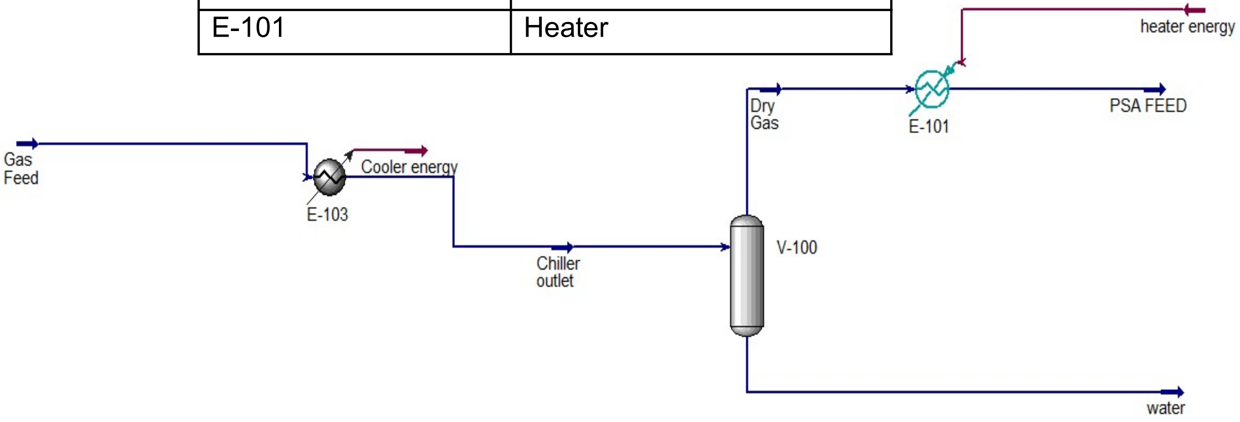
CONDENSATION

- Improve Hydrogen Purity
- Protect Equipment
- Ensure Fuel Cell Compatibility

Stream Number	Stream Name	Temperature(°C)
St-1	Dark Fermentation Gas Flow	40
St-2	Dry Gas	10
St-3	Chilled Water	5
St-4	PSA Feed	40-70
St-5	Condensed Water	-

EQUIPMENT CODE	EQUIPMENT NAME
F-100	Gas Flow Meter
CH-100	Chiller
E-100	Condenser
E-101	Heater



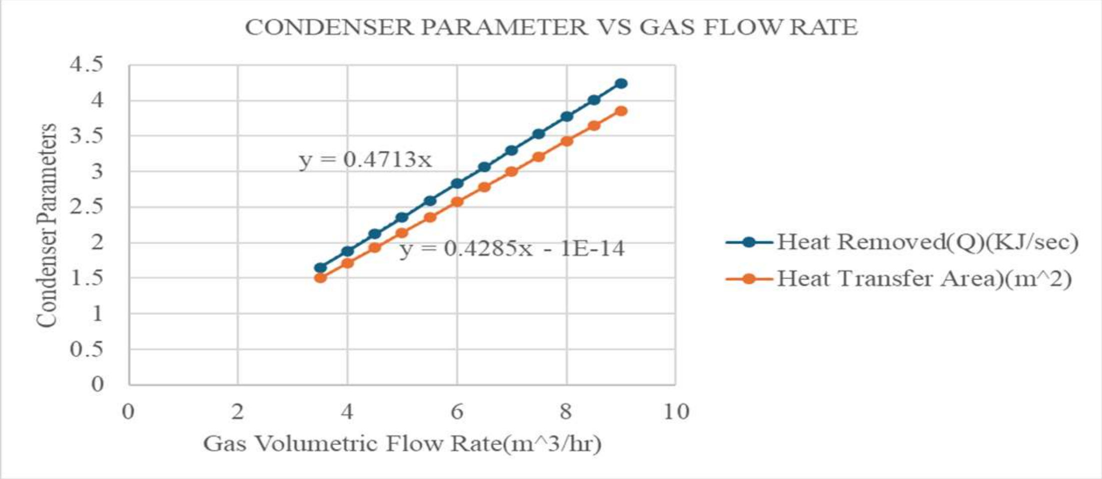


CONDENSATION RESULTS

- **98% water removed**
- **Calculate condenser duty and heat transfer area**

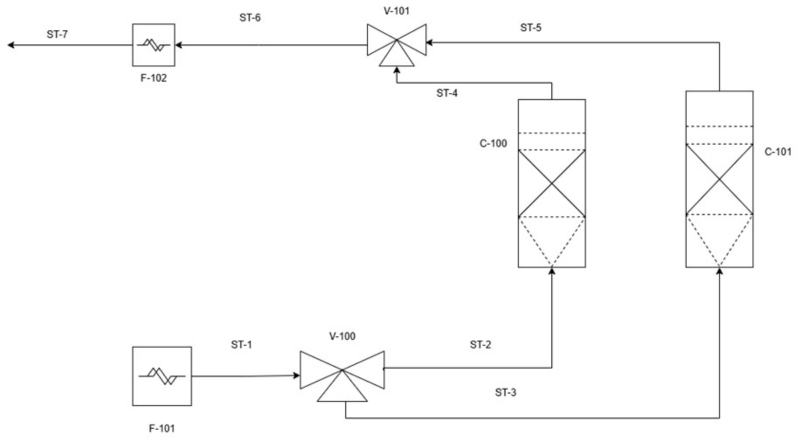
GAS	INITIAL MOLAR COMPOSITION-(y1)(estimated)	FINAL MOLAR COMPOSITION-(y2)(through simulation)
H_2O	0.0782	0.0014
CO_2	0.3664	0.3968
H_2	0.2782	0.2956
O_2	0.0056	0.0061
CH_4	0.0042	0.0046
N_2	0.2728	0.2956

PARAMETER	UNIT	VALUE
$\boldsymbol{Volumetric\ flow\ rate}$	m^3/hr	3.5
	mole/sec	0.404
$\boldsymbol{moles\ of\ water\ before\ condensation}$	mole/sec	0.0315
moles of water after condensation	mole/sec	0.029
$\dot{\boldsymbol{Q}}(\boldsymbol{Condenser\ Duty})$	kJ/sec	1.65
$\boldsymbol{A}(\boldsymbol{Heat\ Transfer\ Area})$	m^2	1.5

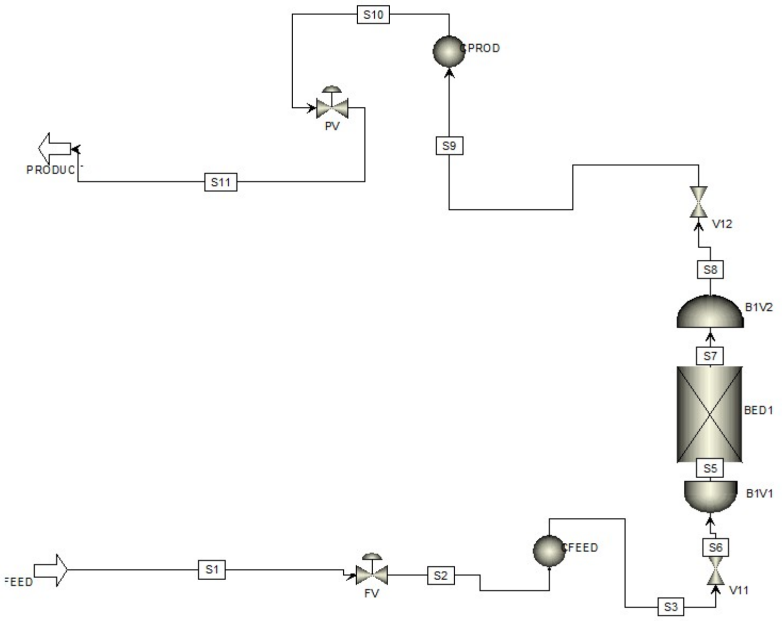


ADSORPTION

- Pressure Swing Adsorption(PSA)
- Separate hydrogen
- Gas mixture flows through an **adsorption column** packed with porous materials (e.g., **Zeolite 13X**, **Activated Carbon**).
- **Adsorption, depressurization, purge, and repressurization**
- Designed to achieve **≥80% hydrogen purity**

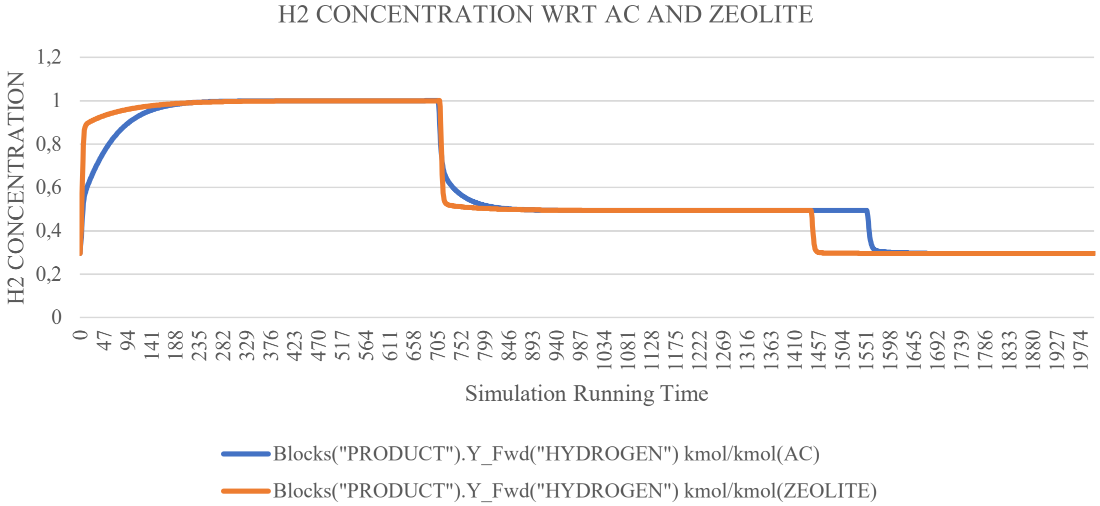


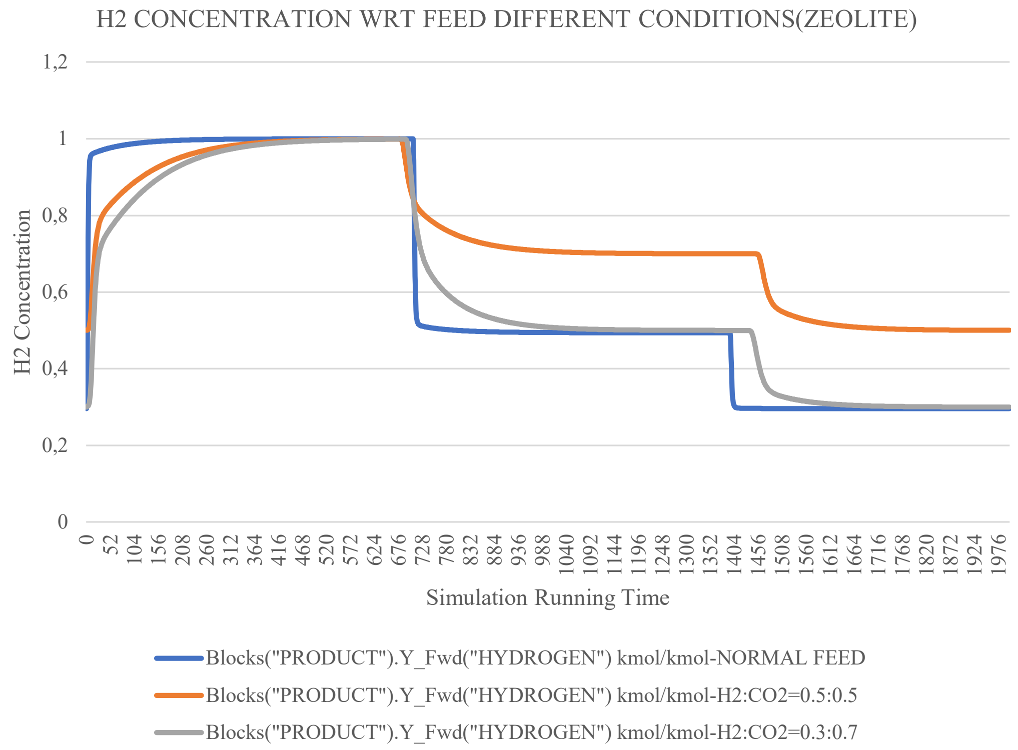
EQUIPMENT CODE	**EQUIPMENT NAME**
F-101	**Gas Feed Flow Meter**
V-100	**Feed Valve**
C-100,C-101	**Adsorption Column**
V-101	**Product Valve**
F-102	**Product Flow Meter**

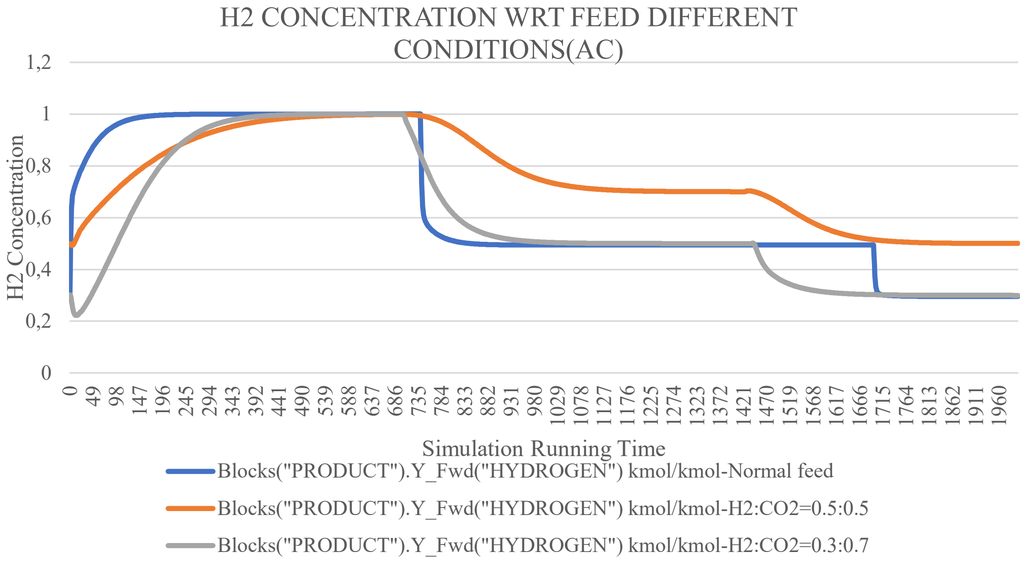


Gas Type	**Adsrobent Type**	**Adsorbent Capacity(mole/kg)**
CO_2	**Zeolite**	**4**
N_2	**Zeolite**	**1**
O_2	**Activated Carbon**	**0.2**

ADSORPTION


H2 CONCENTRATION WRT AC AND ZEOLITE
H2 CONCENTRATION
1,2
1
0,8
0,6
0,4
0,2
0
0 47 94 141 188 235 282 329 376 423 470 517 564 611 658 705 752 799 846 893 940 987 1034 1081 1128 1175 1222 1269 1316 1363 1410 1457 1504 1551 1598 1645 1692 1739 1786 1833 1880 1927 1974
Simulation Running Time
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol(AC)
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol(ZEOLITE)

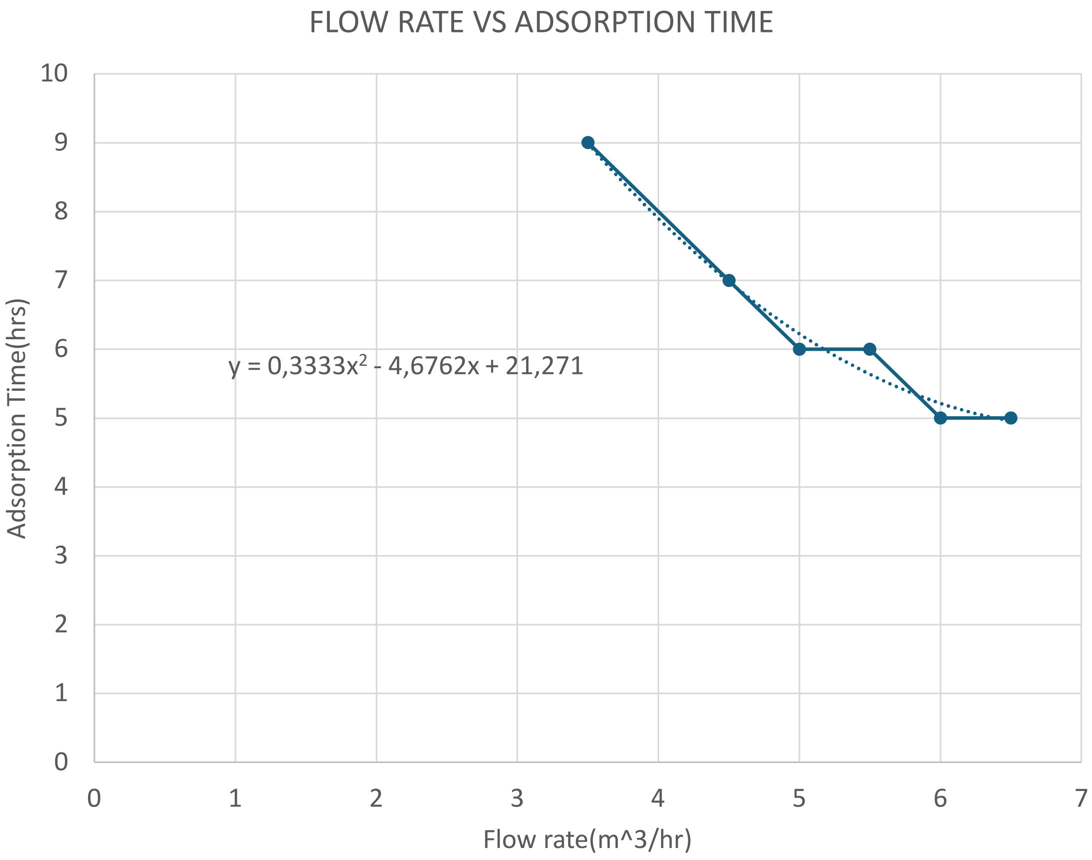

H2 CONCENTRATION WRT FEED DIFFERENT CONDITIONS(ZEOLITE)
H2 Concentration
1,2
1
0,8
0,6
0,4
0,2
0
0 52 104 156 208 260 312 364 416 468 520 572 624 676 728 780 832 884 936 988 1040 1092 1144 1196 1248 1300 1352 1404 1456 1508 1560 1612 1664 1716 1768 1820 1872 1924 1976
Simulation Running Time
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-NORMAL FEED
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-H2:CO2=0.5:0.5
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-H2:CO2=0.3:0.7


H2 CONCENTRATION WRT FEED DIFFERENT CONDITIONS(AC)
H2 Concentration
1,2
1
0,8
0,6
0,4
0,2
0
0 49 98 147 196 245 294 343 392 441 490 539 588 637 686 735 784 833 882 931 980 1029 1078 1127 1176 1225 1274 1323 1372 1421 1470 1519 1568 1617 1666 1715 1764 1813 1862 1911 1960
Simulation Running Time
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-Normal feed
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-H2:CO2=0.5:0.5
Blocks("PRODUCT").Y_Fwd("HYDROGEN") kmol/kmol-H2:CO2=0.3:0.7

ADSORPTION

Gas Components	Initial molar concentration(y_1)	Final(required) molar concentration(y_2)
H_2	0.314	0.80
CO_2	0.366	0.15
O_2	0.0065	0
N_2	0.314	0.05

PARAMETERS	UNIT	VALUE
$V_{bed}(volume\ of\ bed)$	**m^3**	**5.4**
$d(diameter\ of\ bed)$	**m**	**1.90**
$l(length\ of\ bed)$	**m**	**5.7**
$t_{ads}(recalculated\ time\ of\ adsorptio$	**hrs**	**9**
$t_{cyclic}\ (recalculated\ cyclic\ time)$	**hrs**	**13**
$No\ of\ beds$	**-**	**3**

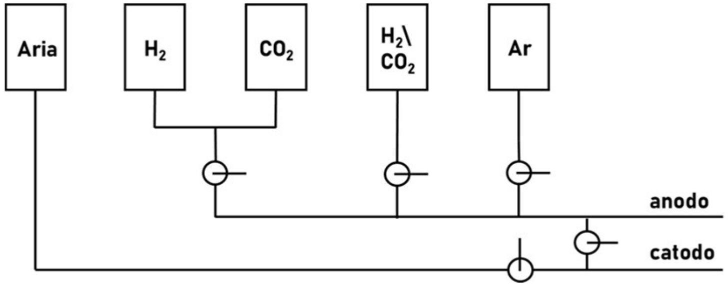


Fonte	**Temperature °C**	**Peak specific power mW/cm²**	
(A. Le Gal La Salle)	800	537	20% H_2 - 20% CO - 10% CO_2 – 50 % N_2

Design del set-up di cella

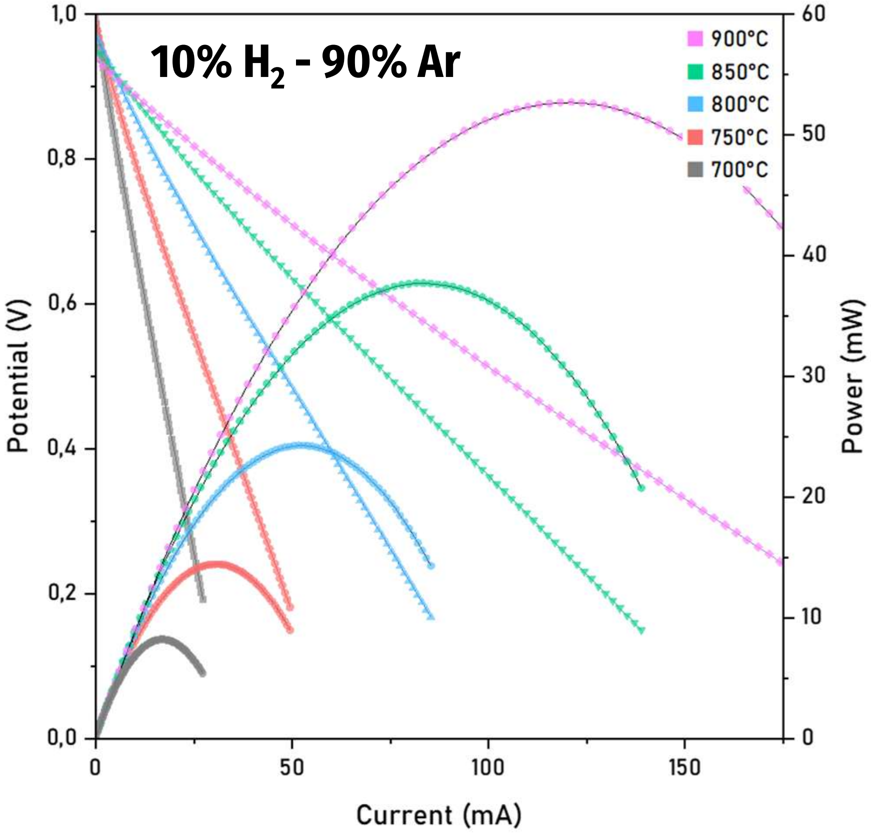
Fiaxell

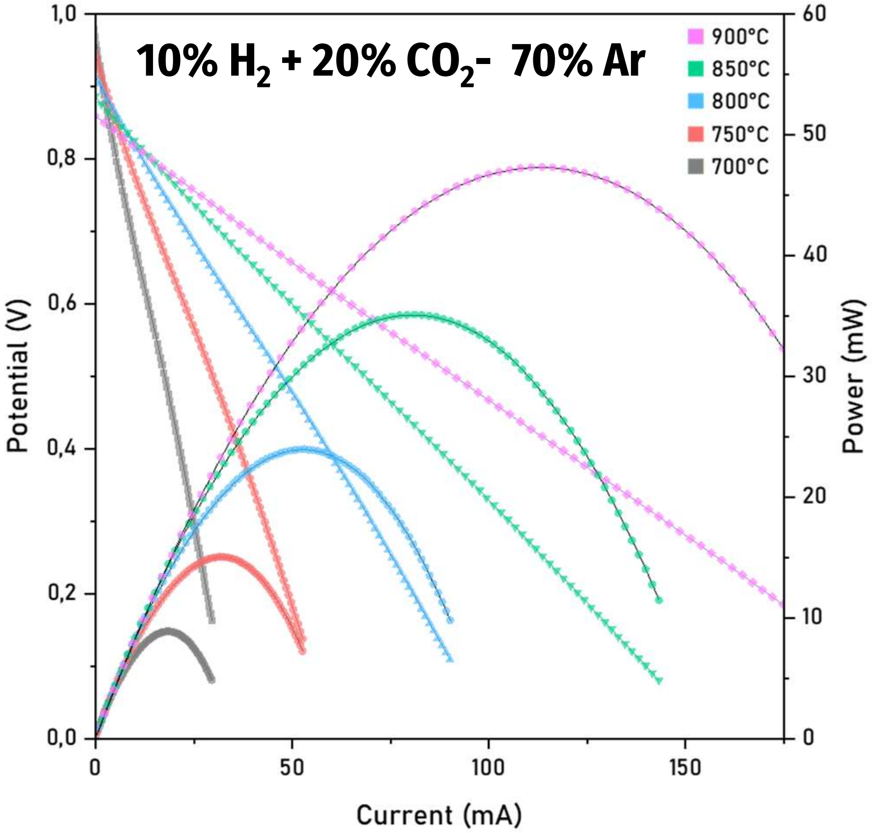
SOFC Technologies™



- fornace Kittec Squadro SQ11 con flangia di alloggiamento in INCONEL® 601
- raccorderia Swagelok in AISI 316
- sistema di MFC per misura e controllo dei gas

First test: commercial cell Ni-YSZ/YSZ/LSCF


10% H_2 - 90% Ar


10% H_2 + 20% CO_2- 70% Ar

First test: commercial cell Ni-YSZ/YSZ/LSCF

	Power density (Ω·cm^{-2})	
Temperature (°C)	**10% H_2 - 90% Ar**	**10% H_2 + 20% CO_2- 70% Ar**
700	8.2	8.8
750	14.4	15.0
800	24.3	23.9
850	37.7	35.1
900	52.7	47.3

- Dirty” hydrogen shows better performance at low temperatures: favorable coking effects
- Performance decreases above 800°C due to Ni nanoparticle coverage and RWGS occurring as a parallel reaction
- 10% power loss at 900°C

SOFC MODELING IN AVL CRUISE™ M

- Use of a **Pre-defined SOFC model** → **complex setup procedure** involving*:
  - ***Simulation procedure***
  - ***Reactions/electrochemical parameters*** (numerical stability)
  - ***Carrier (Argon) substitution*** *(N/A):* **Ar↔N_2** (ammonia decomp. suppression)

Enabled reactions

✓ **Reversed Water-Gas shift (RWGS)**
$CO_2 + H_2 \leftrightarrow CO + H_2O$
✓ **Methane steam reforming (MSR)**
$CH_4 + H_2O \leftrightarrow CO + 3H_2$
✗ **Ammonia decomp. rate (ADR)**
$NH_3 \leftrightarrow N_2 + 3H_2$

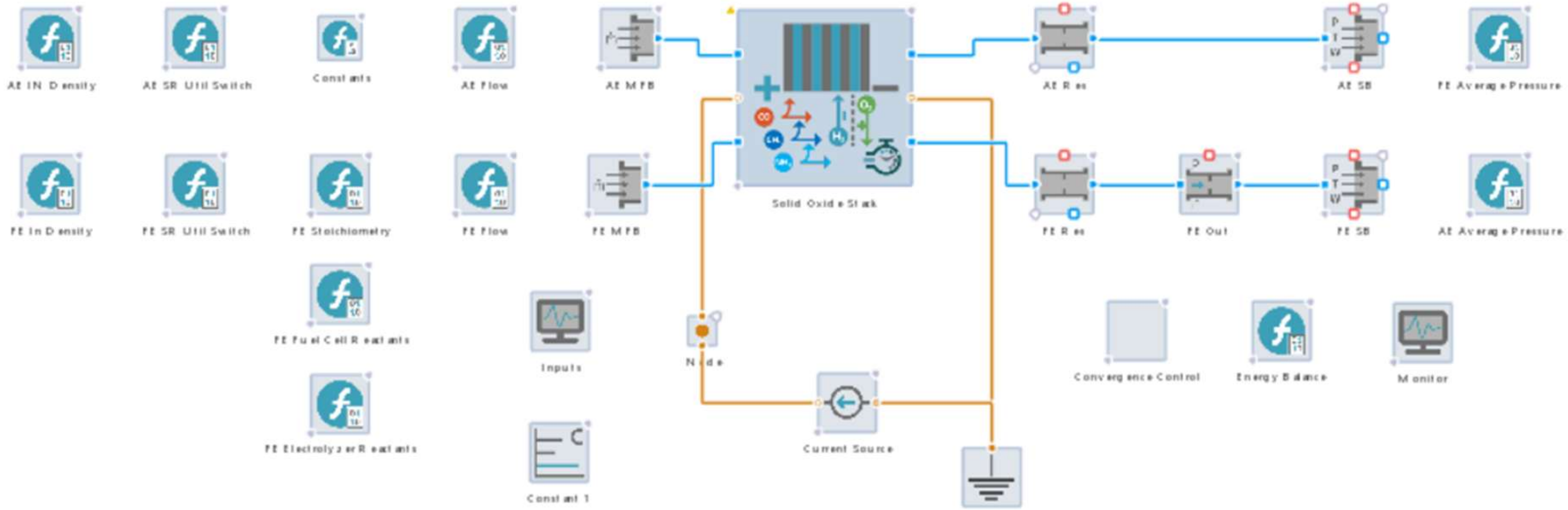
- **Area scaling** in CRUISE M for **numerical stability** (1.13→113 cm^2, 3→300 cm^2)
- **State-of-the-art materials** (Ni-YSZ/YSZ, same as experimental setups), **default current density** (2-2.5 A/cm^2)

Final Model

Input
Fuel Mixtures

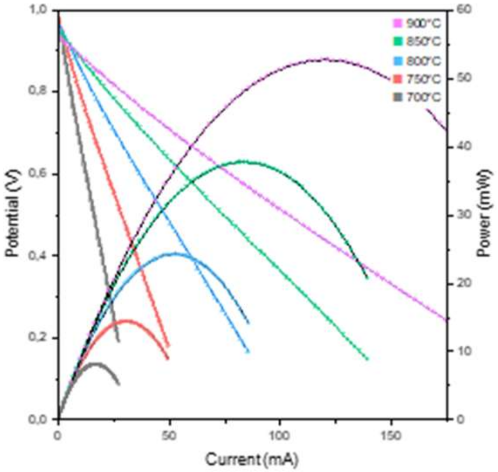
Output
I-V curves for each case

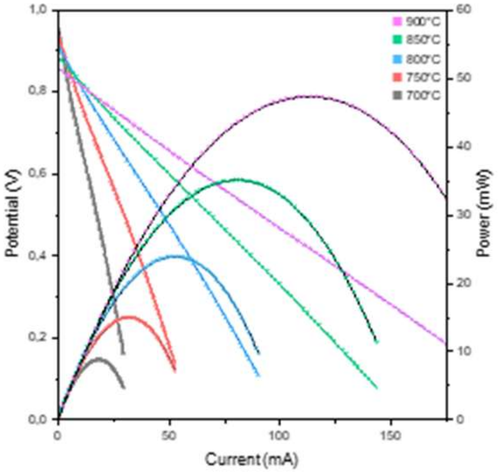
Postprocessing
Cruise M→Matlab I-V-P curves

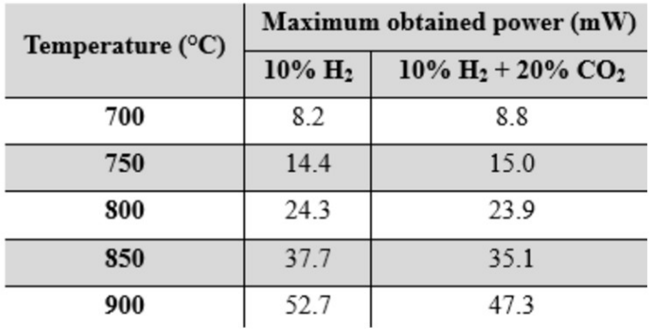


* For brevity, only key steps are outlined and not explained

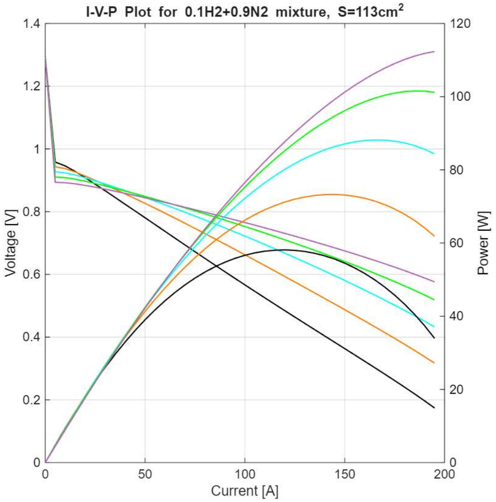
FIRST SIMULATION SET – EXPERIMENTAL VALIDATION



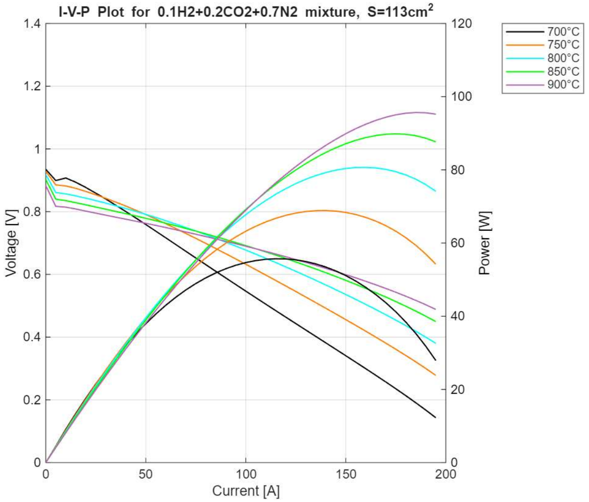




Temperature (°C)	Maximum obtained power (mW)	
	10% H_2	10% H_2 + 20% CO_2
700	8.2	8.8
750	14.4	15.0
800	24.3	23.9
850	37.7	35.1
900	52.7	47.3



Left: $0.1H_2+0.9N_2$;



Right: $0.1H_2+0.2CO_2+0.7N_2$

Validation Results

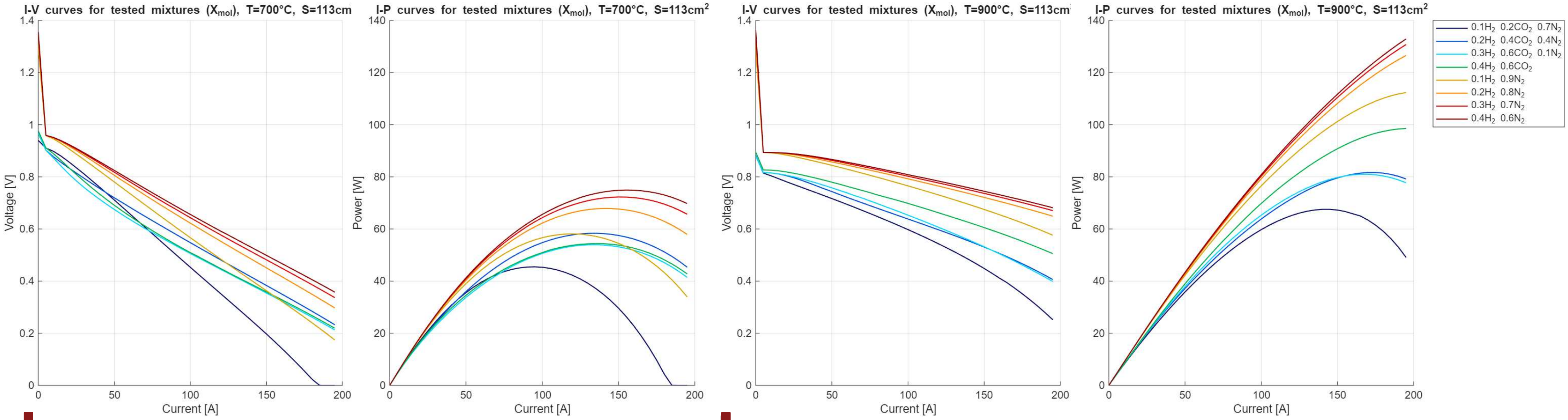
☑ **CO_2 reduces maximum power at high T**

☑ **Performance penalty between the two mixtures ↓ as T↓**

→ Consistent modeling of activation, ohmic and transport losses

➢ Model presents localized numerical artifact at I = 0-5 A, and is more optimized

First simulation set – Sensitivity analysis (700°C and 900°C)



700°C

CO_2-free mixtures

- **Best performances** as $X_{H_2}\uparrow$ ($X_{N_2}\downarrow$)
- **Base $0.1H_2$+$0.9N_2$ overtaken by sensitivity CO_2-mix**

CO_2-containing mixtures

- **$0.2H_2$+$0.4CO_2$+$0.4N_2$** is the **best case**
- **Frequent overlapping** at low I

900°C

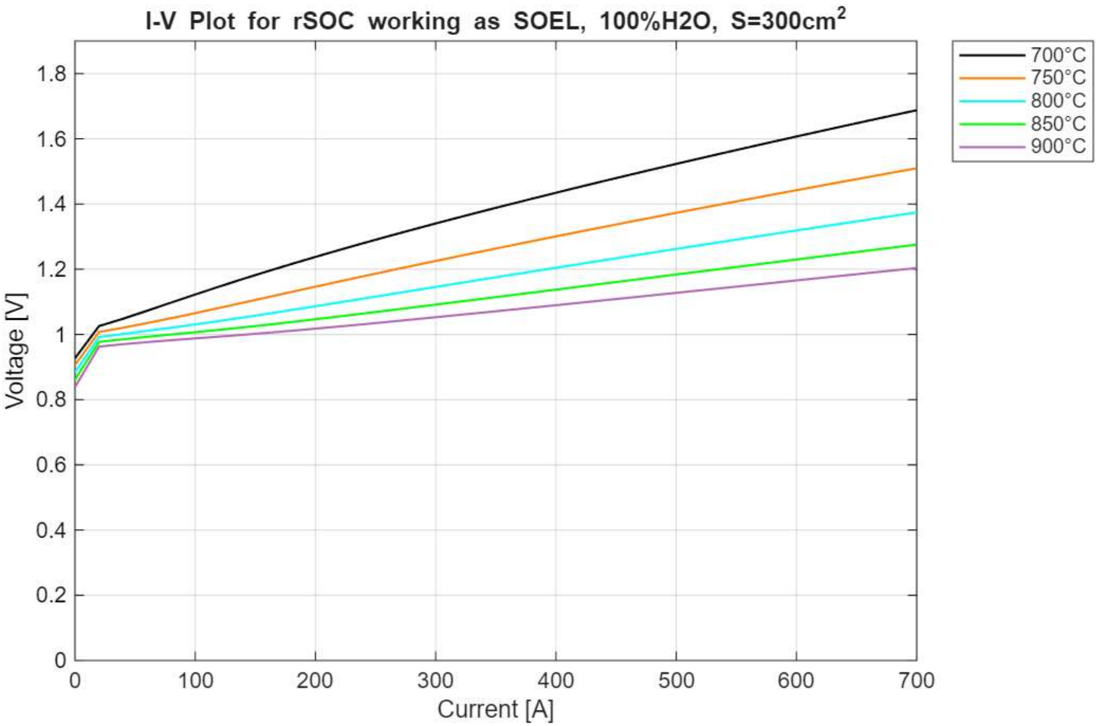
CO_2-free mixtures

- **Always best performing across all I**, clear distinction from CO_2 mix

CO_2-containing mixtures

- **Worst performances**, growing as X_{H2}, $X_{CO2}\uparrow X_{N2}\downarrow$
- **Overlapping of intermediate mixtures**

SECOND SIMULATION SET – REVERSIBLE SOFC TO SOEL



- **Reverse modeling in CRUISE M** with data postprocessing

- **Cell V increases with I** → activation, ohmic, and concentration **overpotentials effects** (reversed SOFC case)

- **Higher T :**

→ **lower electrolysis V** at any I, due to reduced overpotentials

→ **same H_2 production rate at lower electrical energy input** → advantage of high-T electrolysis

CONCLUSIONS

Overall **consistent baseline experimental validation and further modeling of mixtures**

KEY FINDINGS

☑ **Temperature and H_2 availability** (pure or from SMR) as synergistic key improvement factor

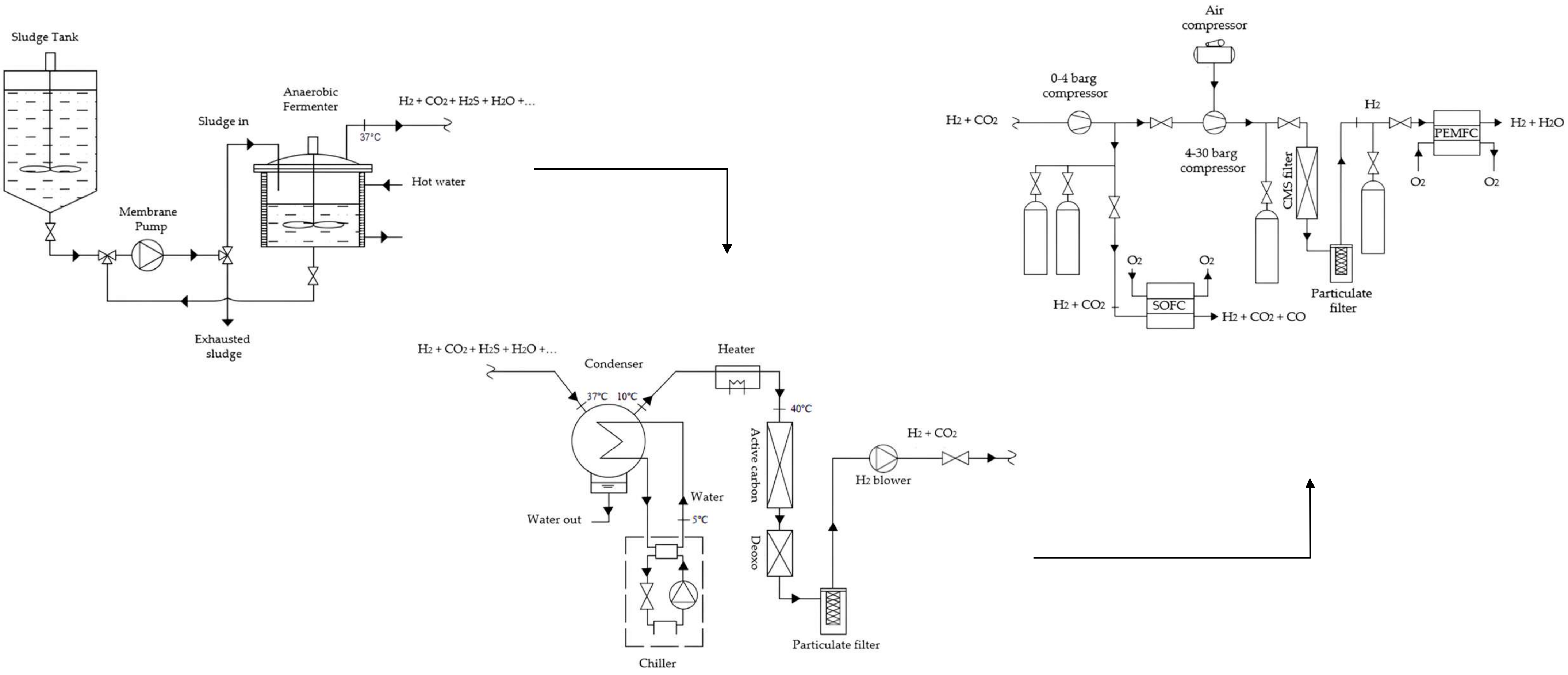
☑ **Carrier gas** acts as **diluent**, **worsening performance**

☑ **CO_2** acts as diluent and active reactant → **dual-sided effect**, **even competitive** in mixtures at low T

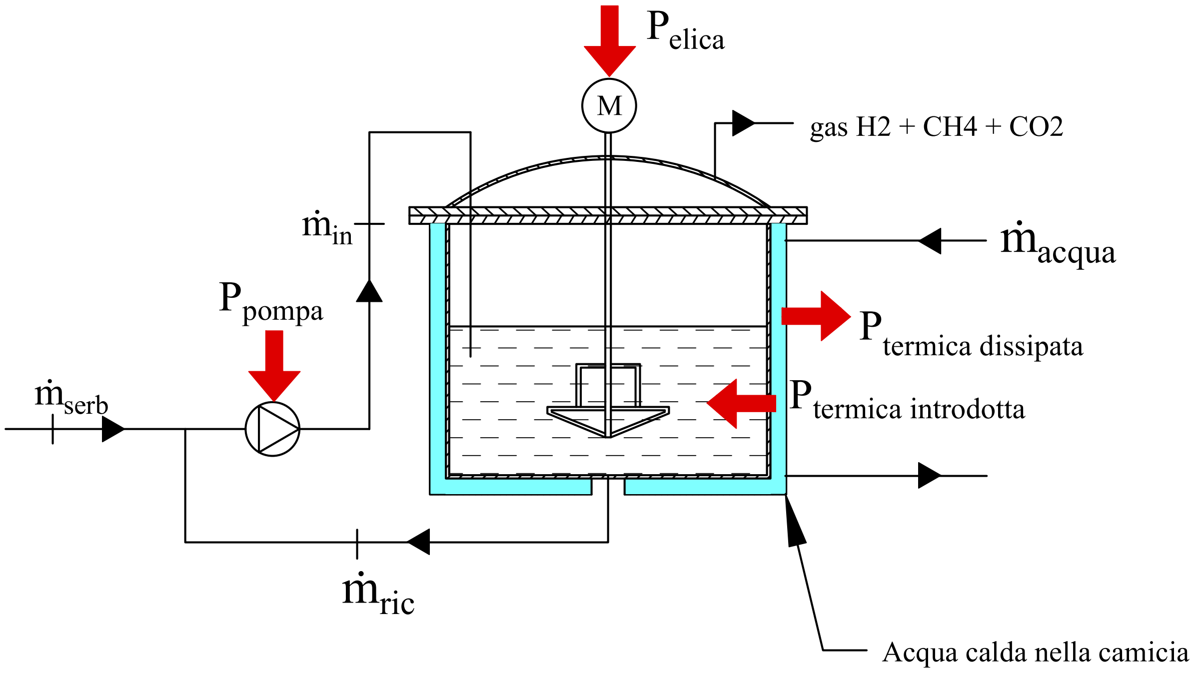
☑ **RWGS and SMR regulate performance** when CH_4 or CO_2 are present with H_2

→ **Best improvements and performances obtained with H_2-CH_4 blends at high T**

☑ **As T↑, curves become flatter** (losses influence) and **performance gap generally narrows**


Sludge Tank
Membrane Pump
Sludge in
Anaerobic Fermenter
37°C
$H_2 + CO_2 + H_2S + H_2O + \ldots$
Hot water
Exhausted sludge
$H_2 + CO_2 + H_2S + H_2O + \ldots$
Condenser
37°C
10°C
Heater
40°C
Active carbon
Deoxo
Water out
Water
5°C
Chiller
Particulate filter
H_2 blower
$H_2 + CO_2$
Air compressor
0-4 barg compressor
$H_2 + CO_2$
4-30 barg compressor
CMS filter
H_2
PEMFC
$H_2 + H_2O$
O_2
O_2
O_2
O_2
SOFC
$H_2 + CO_2$
$H_2 + CO_2 + CO$
Particulate filter

Energy model of the fermentation module



- **Mud/substrate mix feed pump**
- **Mixing propeller**
- **Electric resistance for heating the water inside the jacket**

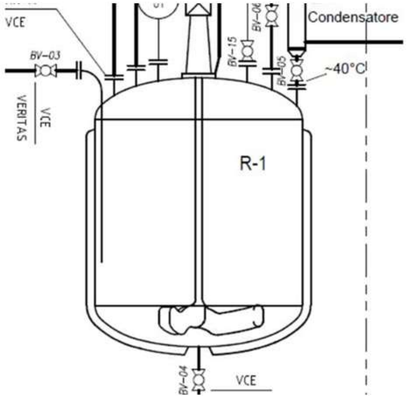
$$E_{netta} = E_{prodotta} - (E_{pompa} + E_{elica} + E_{term})$$

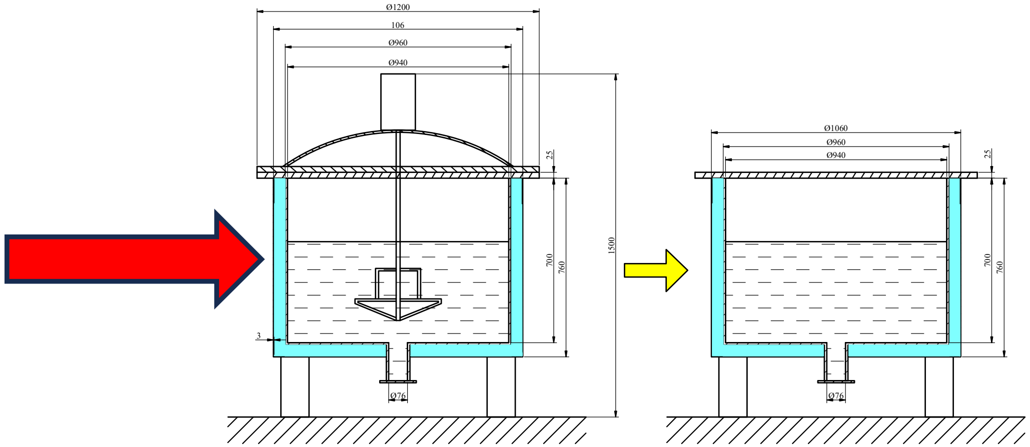
$$E_{term} = E_{warm\_up} + E_{loss}$$

For sludge heating

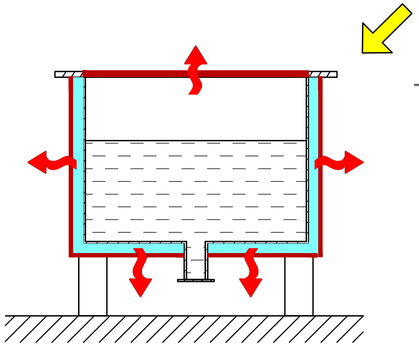
To counteract heat dissipation

Estimation of thermal dissipation





- Internal tank volume of approximately 480 L, filled to approximately 3/5.
- Overall dimensions: maximum height of 1500 mm and maximum diameter of 1200 mm. Outer jacket filled with approximately 150 L of water-glycol solution, maintained at a temperature of 35 to 40°C.
- Outer jacket thickness of 3 mm and no external insulation.
- **Steel inox 316**



	Area m^2
Lateral area	2.53
Bottom area	0.88
Upper area	0.69

How to reduce thermal dissipation

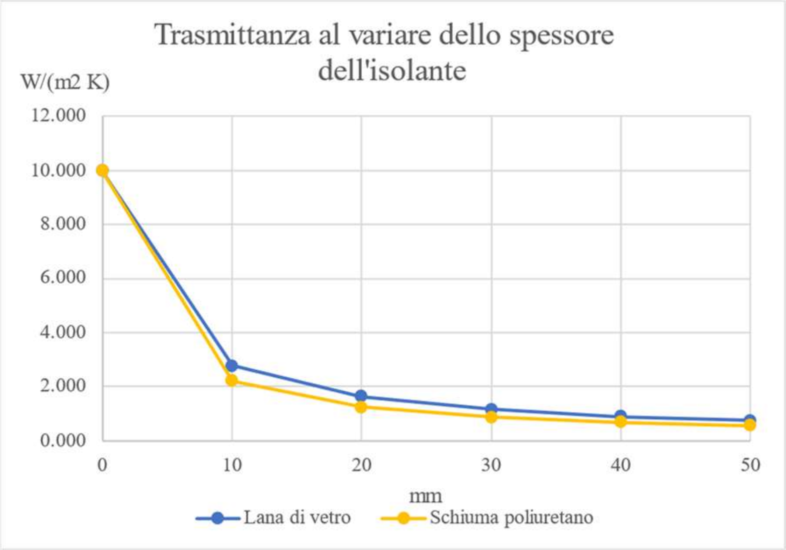
$$U = \frac{1}{\boxed{\frac{s_i}{k_i}} + \frac{s}{k} + \frac{1}{h_a}}$$

$$U = \frac{1}{\boxed{\frac{r1}{k_i}\ln\left(\frac{r3}{r2}\right)} + \frac{r1}{k}\ln\left(\frac{r2}{r1}\right) + \frac{1}{h_a}}$$

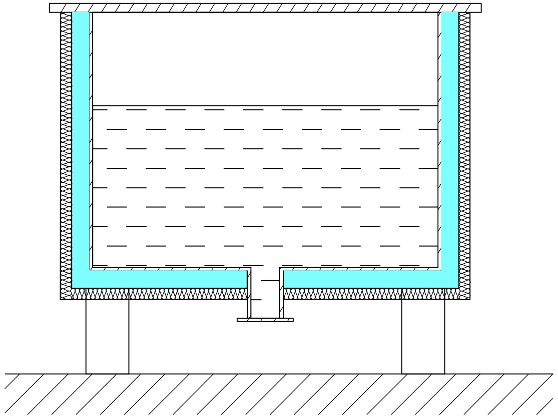
Since there are no reference standards yet, the following materials are proposed for the model in question (in compliance with fire classifications):

Glass wool: k_i equal to approximately 0.038 W/(m K), non-combustible, no toxic gases in the event of combustion

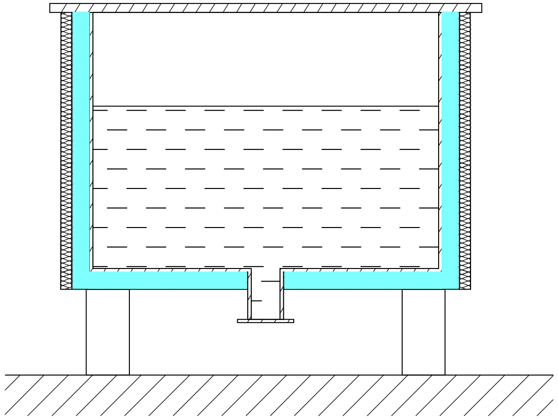
Rigid polyurethane foam: k_i values between 0.022 and 0.028 W/(m K), presence of organic material ⇒ must be coupled with a lining of non-combustible or fire-resistant material



Solution with complete insulation of the jacket



Solution with lateral insulation of the jacket

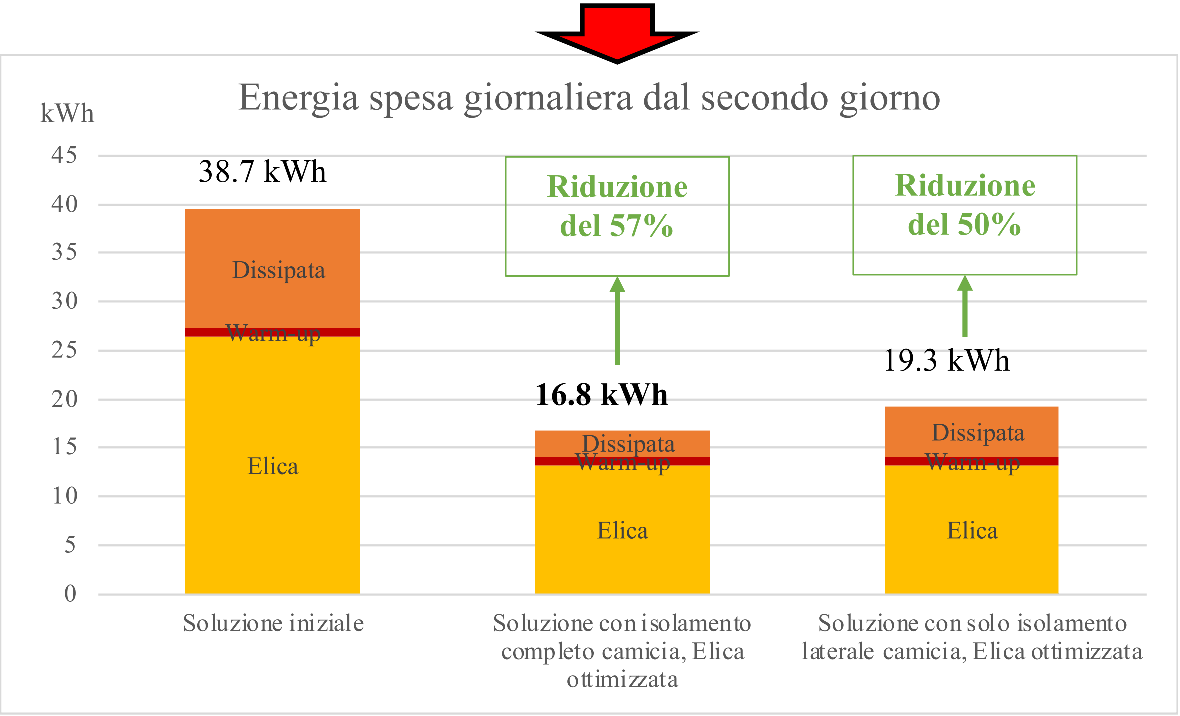


Global consumption estimation

$$\boxed{\mathrm{E_{H2}} = \mathrm{E_{pompa}} + \mathrm{E_{elica}} + \mathrm{E_{term}} = \mathrm{E_{pump}} + \mathrm{E}_{propeller} + \mathrm{E_{diss}} + \mathrm{E_{warm\_up}}}$$

Laboratory tests suggest operating the impeller with on/off intervals of 5/55 s.

The analysis suggests thermally insulating the fermenter with 40 mm polyurethane insulation.



Energy balance

- **Experimental tests on a pre-pilot plant (45 L)**
- **SHP performance exceeded the initial project estimates (58.08 NLH_2/kgTVS)**

System energy balance

Pathway 1 – SOFC with minimum gas purification

- Energy produced: 9.2 kWh/day
- Energy consumed: 9.3 kWh/day

Pathway 2 – PEM with deep purification

- Energy produced: 8.4 kWh/day
- Energy consumed: 16.1 kWh/day

Operational conclusions

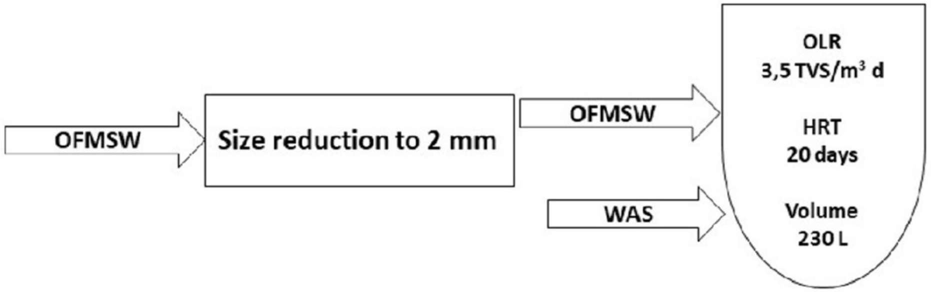
- The SOFC configuration proved to be the preferred solution.
- The increase in methane production in the two-stage process directly improves the overall energy balance.

Main critical energy consumptions

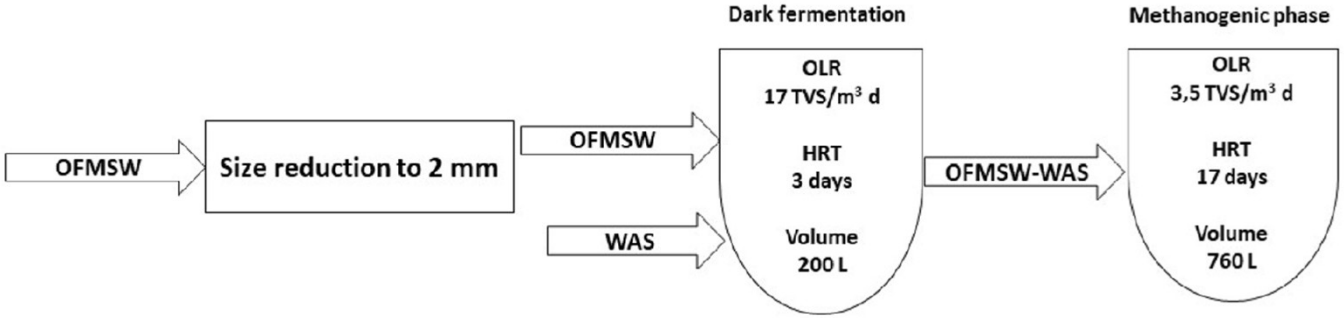
- mixing/agitation;
- reactor heating.

Parametro	**Valore**
SHP average	58 ± 15 NL_{H2}/kg_{TVS}
SMP average	1,4 ± 0,9 NL_{CH4}/kg_{TVS}
SGP average	145 ± 28 NL/kg_{TVS}
CH_4	1%
H_2	39,9%
HPR	0,83 ± 0,21 NL H_2 L^{-1} reactor d^{-1}
GPR	2,09 ± 0,41 NL H_2 L^{-1} reactor d^{-1}

Mono Stage Anaerobic Digestion



Double Stage Anaerobic Digestion



D. Bolzonella et al., “Producing Biohythane from Urban Organic Wastes,” Waste Biomass Valor, vol. 11, no. 6, pp. 2367–2374, Jun. 2020, doi: 10.1007/s12649-018-00569-7

Experimental data vs literature

(D. Bolzonella *et al.*, “Producing Biohythane from Urban Organic Wastes,” *Waste Biomass Valor*, vol. 11, no. 6, pp. 2367–2374, Jun. 2020, doi: 10.1007/s12649-018-00569-7)

Process	**Test condtions**	**SMP (Nm³ CH_4/kg TVS)**
Single phase	Batch (BMP, potential value)	0,45
Double phase	Batch (BMP, potential value)	0,60
Single phase	Semicontinuous (70-75% of theoretical)	0,34
Single phase	Semicontinuous (75% of potential batch)	0,45
Double phase	Semicontinuous (+15-18% with respect to single phase)	0,39-0,40
Caso realistico adottato	Semicontinuous double phase	0,40

H2 storage using metahydride technology

Advantages :

- High storage capacity(7.6 wt%);
- Economically substainable
- Safe
- C=270g (3 Nm^3) of H_2

Disadvantages :

- $T_{des} > 300°C$
- Slow Kinetics

Reaction:

- $$M + \frac{x}{2}H_2 \rightleftharpoons MH_2 + \Delta H$$


From left to right: MyH2_3000; metal hydride powders; charging process; discharging process

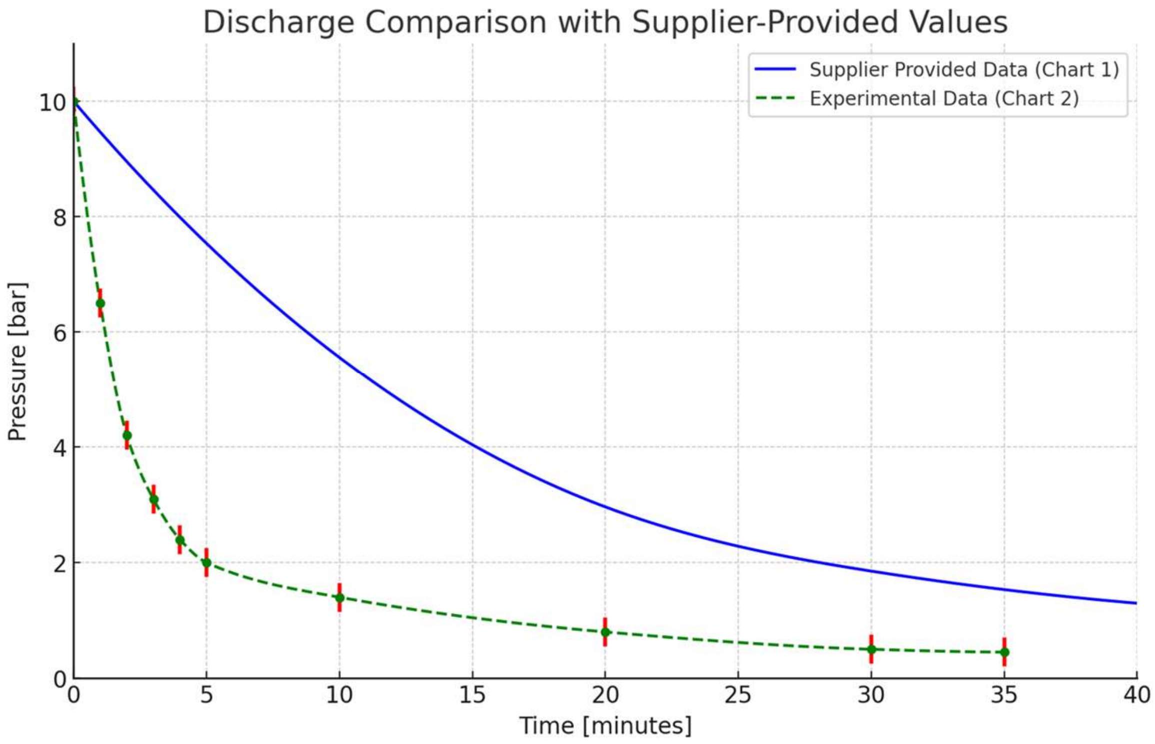
Possible solutions:

- Ball milling (nanocrystalline powder with high specific surface area).
- The addition of elements such as Ni, Ce, Nb, Ti, $LaNi_5$, FeTi, Fe, Co, and Cr improves the process kinetics.
- The addition of graphite reduces activation cycles and improves adsorption kinetics.
- At high concentrations, negative effects on the desorption process may occur.

Technical difficulties:

There are still critical issues related to the thermal conductivity and mechanical stability of the materials, which still need to be resolved.

- The system was immersed in room-temperature water to dissipate heat during the hydrogen charging phase.
- Hydrogen was supplied via an electrolyzer, with a progressive increase in pressure from 5 to 10 bar.
- The charging phase was completed in 2 hours; the final internal pressure (valve closed) reached approximately 10 bar.
- The temperature remained stable throughout the charging phase, likely due to the effective heat dissipation provided by the water bath.
- During the discharging phase (valve open), the pressure decreased rapidly from 10 to 2 bar in 5 minutes.
- Hydrogen continued to be released at lower flow rates for an additional 30 minutes, until complete depletion.
- To accelerate the discharging phase in future tests, immersion in warm water (≤ 55°C) is recommended.



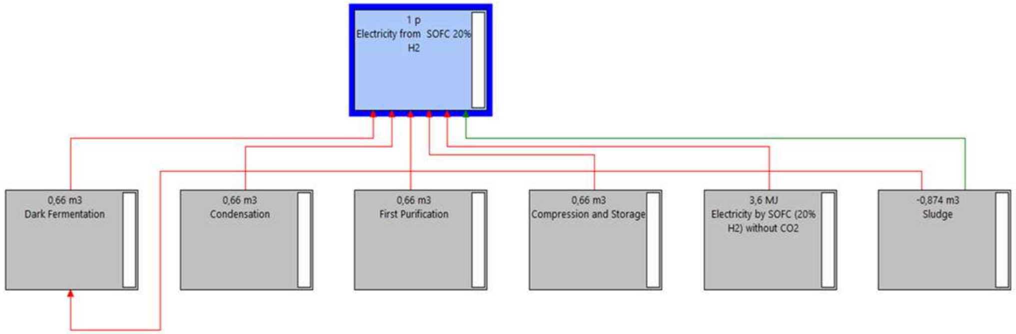
- Estimated total energy consumption: ≈ 19.5 kWh/day
- Reactor heating → 3.96 kWh/day (~20%) → maintaining 37°C
- Compressors (upgrading + storage) → 4.25 kWh/day (~22%)
- Mechanical agitator → 2.24 kWh/day (~11%) with suitable optimization strategies
- Chiller (gas purification) → 6.6 kWh/day
- Other consumptions (pumps, hydrides, AC/DC conversion, gas heater) → ~2.4 kWh/day (~13%)

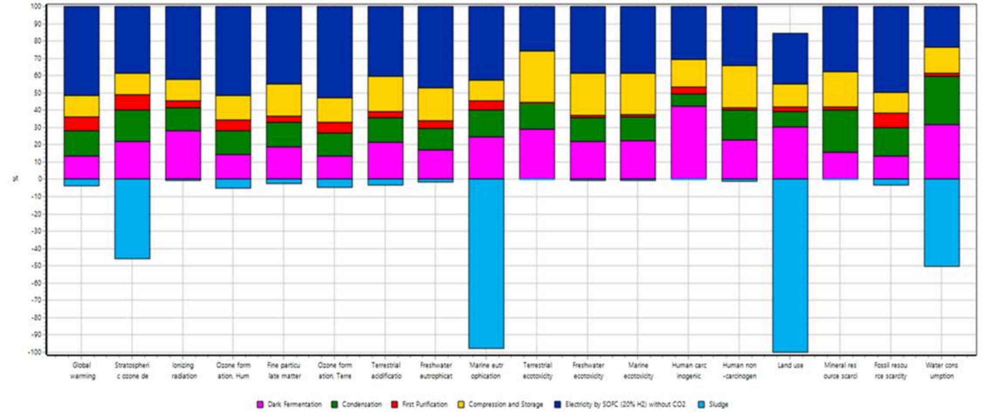
Energy optimization strategies

- Intermittent mixing (5 s/min) → significant reduction in agitator energy consumption (~11% of total)
- Thermal insulation of the fermenter → reduction of heat losses up to 57% → strong impact on heating demand
- Optimization of purification and compression stages

Life Cycle Assessment

- The study was conducted according to ISO 14040:2006 and ISO 14044:2006 standards, using the ReCiPe 2016 (H) method in SimaPro software, with a functional unit of 1 Wh of electricity produced.
- Although impactful, dark fermentation valorizes waste by avoiding the impacts associated with conventional disposal.
- H_2 purification is the most energy-intensive stage and contributes the most to Global Warming Potential (GWP).
- Higher H_2 concentration → improved fuel cell efficiency and reduced GWP.
- Water consumption is generally low, but it increases with more intensive purification stages.
- SOFCs are more efficient and less environmentally impactful than PEMFCs due to lower purification requirements.





Method: ReCiPe 2016 Midpoint (H) V1.08 / World (2010) H / Characterization
Analyzing 1 p 'Electricity from SOFC 20% H2';

Life Cycle Assessment

- The LCA considers the entire MODSEN supply chain, with a functional unit of 1 kWh of electricity produced.
- Compression and storage significantly contribute to the environmental impact due to high energy and material consumption.
- SOFCs show lower environmental impact than PEMFCs thanks to reduced purification requirements and greater CO_2 tolerance.
- Higher H_2 concentration → reduction in GWP and resource consumption.
- The overall impact is mainly dominated by gas upgrading and energy conversion technology.

Summary of LCA results: hydrogen via dark fermentation.

Parameter	Value	Notes
GWP SOFC (20% H_2)	4.15 kg CO_2eq/kWh	-
GWP SOFC (50% H_2)	2.82 kg CO_2eq/kWh	Higher efficiency leads to lower emissions.
GWP SOFC (efficienza 44.8%)	4.66 kg CO_2eq/kWh	Increase in emissions due to lower efficiency (RWSH effect)
GWP PEMFC (20% H_2)	6.96 kg CO_2eq/kWh	Higher impact compared to SOFC
GWP PEMFC (50% H_2)	4.60 kg CO_2eq/kWh	Improved performance with higher-purity hydrogen
Consumo acqua SOFC (20% H_2)	0.0657 m^3/kWh	It increases up to 0.0815 m^3/kWh under reduced efficiency conditions
Consumo acqua PEMFC (20% H_2)	0.0832 m^3/kWh	-

COHERENT

Community Hydrogen, Emissions Trading, and Renewable Energy for Inclusive Net-Zero Transition

COHERENT aims to accelerate the transition to zero-inertia, 100% renewable energy systems by integrating hydrogen production, advanced AI, and inclusive policy frameworks at community level. The project's objectives are fourfold:

- develop modular multienergy models that capture local resource strengths and socio-economic factors
- design and implement hydrogen-based community trading mechanisms and a tailored Community Emissions Trading Scheme (C-ETS)
- validate next-generation low carbon technologies (e.g., electrolysers, fuel cells, heat pumps) through lab-based testbeds and real-time digital simulators
- formulate inclusive policies ensuring that disadvantaged groups can participate equitably in net-zero transitions.