

Inorganic Gasses into Organic Acids for Polyhydroxyalkanoates Production: An Integrated Lab-Scale System for the Syngas Fermentation Coupled PHA Production

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#Biomass-to-Material

#GasFermentation

#Biomaterials

#Biotechnology

#PHB

#Biochar

#Bioplastics

#Anaerobes

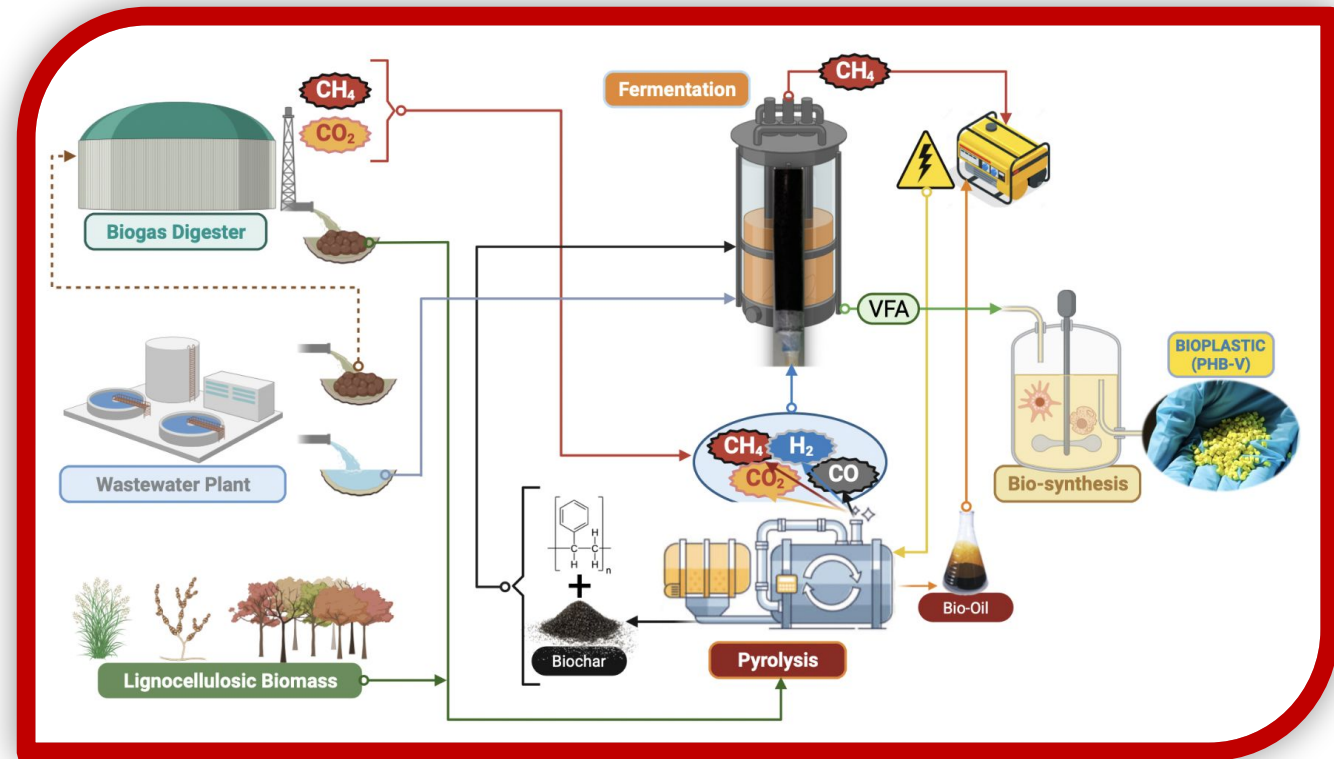
#GreenEconomy

#Gas-to-VFA

Proposed Approach

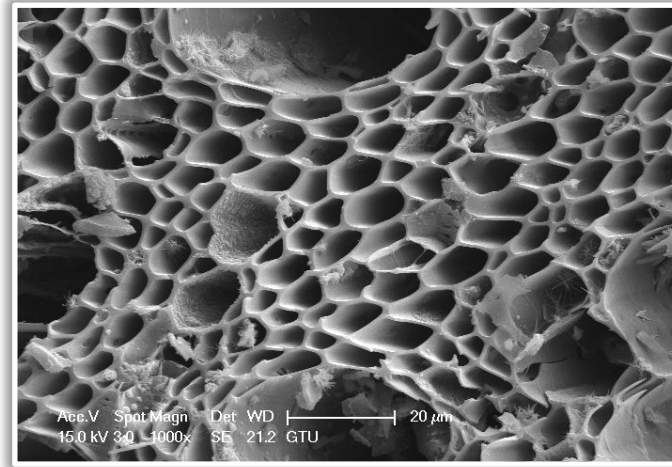
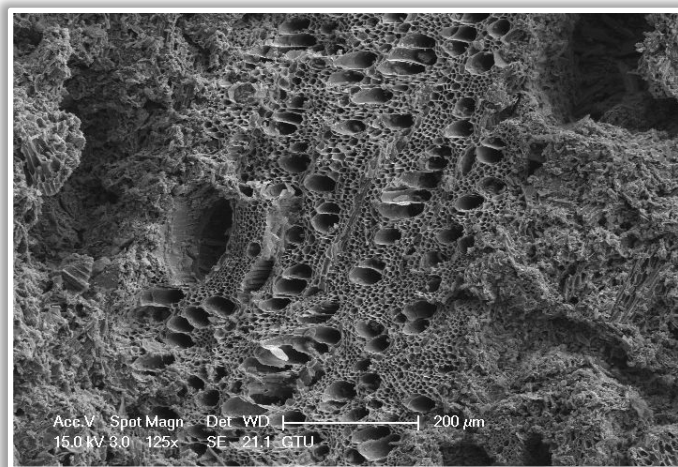
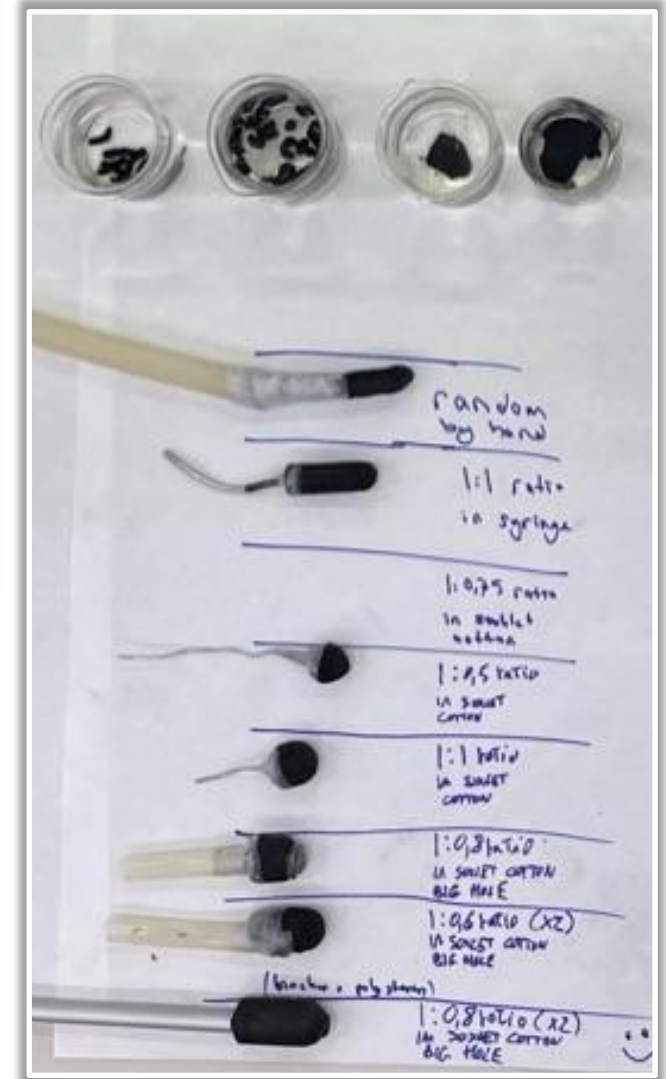
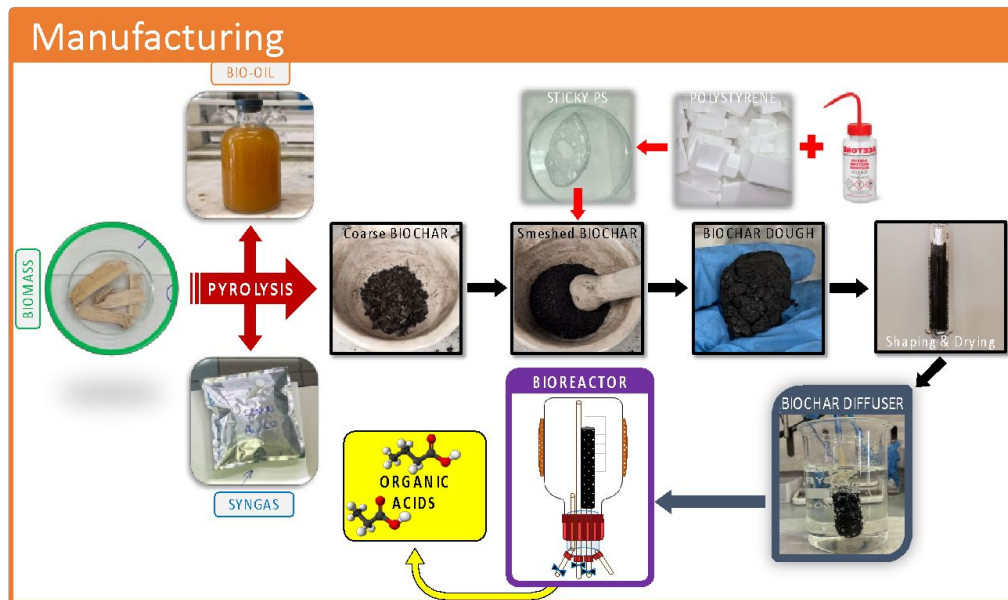
- Biomass materials (wooden and/or organic waste) can be thermally converted into **C1 rich syngas**, **energy-rich bio-oil**, and porous carbonous **biochar**.
- **Syngas** and **biochar** can be utilized by **syngas fermentation** technology which can convert **C1 gasses** and H_2 into the **organic acids (VFA)**.
- Porous and conductive **biochar** material is proposed to enhance **anaerobic conversion**.
- **Bio-oil** as a liquid fuel and **CH_4 (Methane)** as a gas fuel can be theoretically used to recover energy that is required for pyrolysis.
- N and P rich **wastewaters** can be used as nutrient source for both sequential biological systems (thanks to **MMC** technology).
- **PHAs** are the target final products as value-added biodegradable plastics.

Hybrid Thermochemical-Biological Biorefinery



Methodology

Biochar Based Diffuser Manufacturing



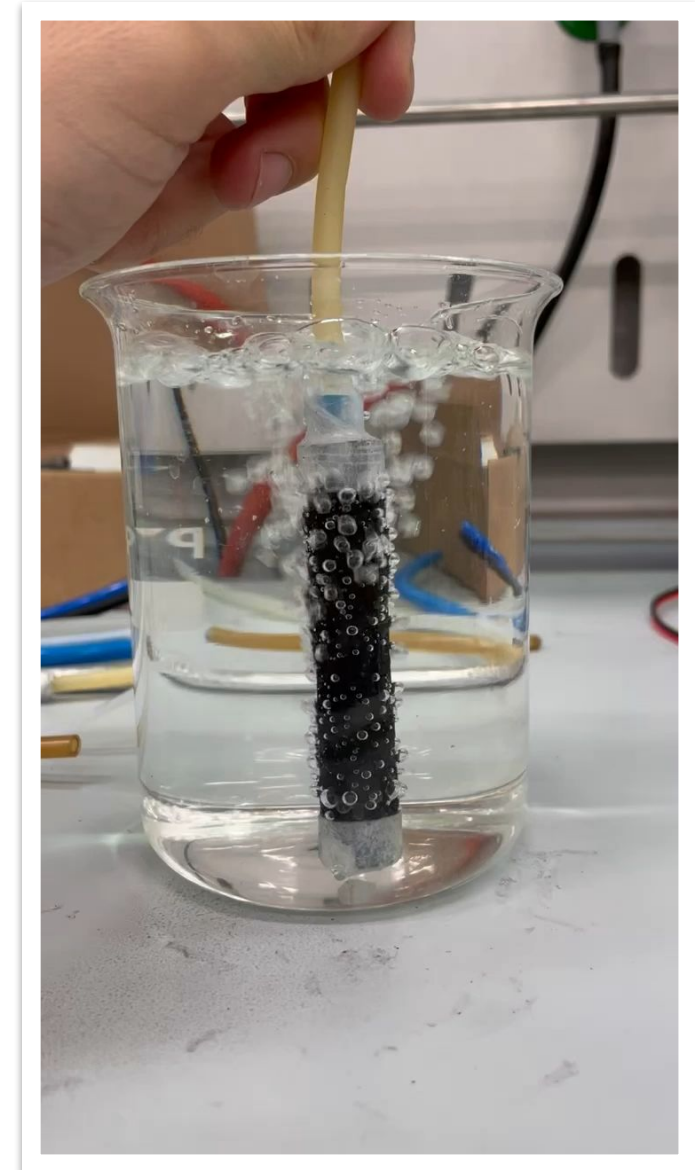
Methodology

First Complete Biochar Based Diffusers

- One of the initial **complete biochar-based** diffusers are presented to the right-side.
- At this moment we are able to manufacture even more **standardized shapes** at bigger scales with different geometry.
- A novel biomass originated **carbon-based affordable product** was achieved.

Parameters		Biochar-Diffuser
Material(s)	-	Biochar, Polysterene
Biochar : PS ¹ Ratio	<i>M:M</i>	2.0
Active Length ²	<i>mm</i>	65.0
Outer Diameter	<i>mm</i>	14.0 ± 1.5
Inner Diameter	<i>mm</i>	8.5 ± 0.5
Bulk Volume	<i>mL</i>	≈ 6.0

¹ Polystrene, ² Length of the non-covered active part of the diffuser



Methodology

Analytical Methods and COD Approach

COD as a Single Unit to Track Chemical Energy Flow

- **Chemical oxygen demand (COD)** as a widely used unit mainly for water treatment purposes so far.
- Mainly monitored just for indirect measurement of the organic content of liquid samples' (e.g. wastewaters).
- Number of equivalent amount of oxygen required to oxidize all available organic compounds in a given volume of sample.
- In fact, **COD** is directly correlated to the energy content of any solid, liquid, and gas samples.

$$1\text{kg COD} = 0.125 \text{ kmol } e^- \approx 15 \text{ Mjoule}$$

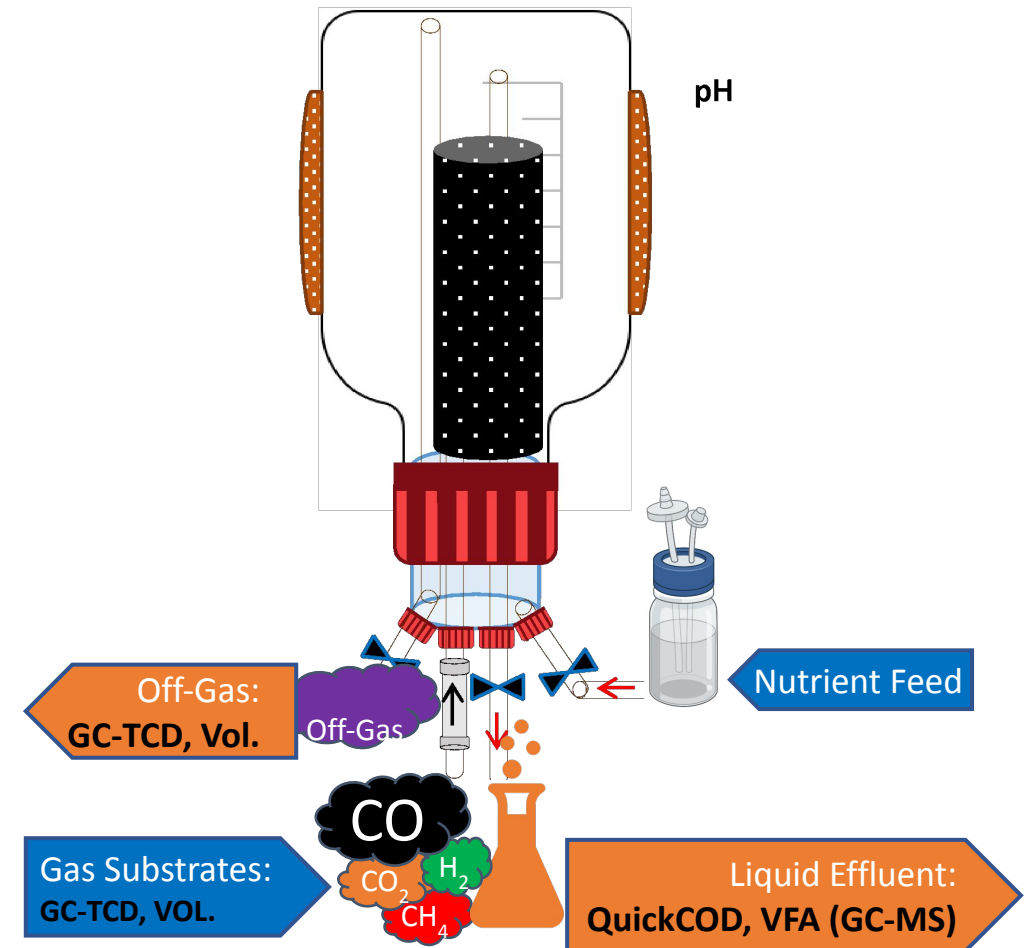
$$[\text{e.g.: } 1\text{L-H}_2 \times 0.084 \text{ g-H}_2/\text{L} \times 7.94 \text{ g-COD/g-H}_2 = 0.67\text{g-COD/L-H}_2]$$

- Allow to track chemical energy flow in biorefinery systems.

COD reactants = COD products

- Instead of mass balance, COD balance can be made for any biorefinery which usually deal with variety of input and output.

Analytical Equipments and Analysis Methods



(1) Thermochemical Conversion

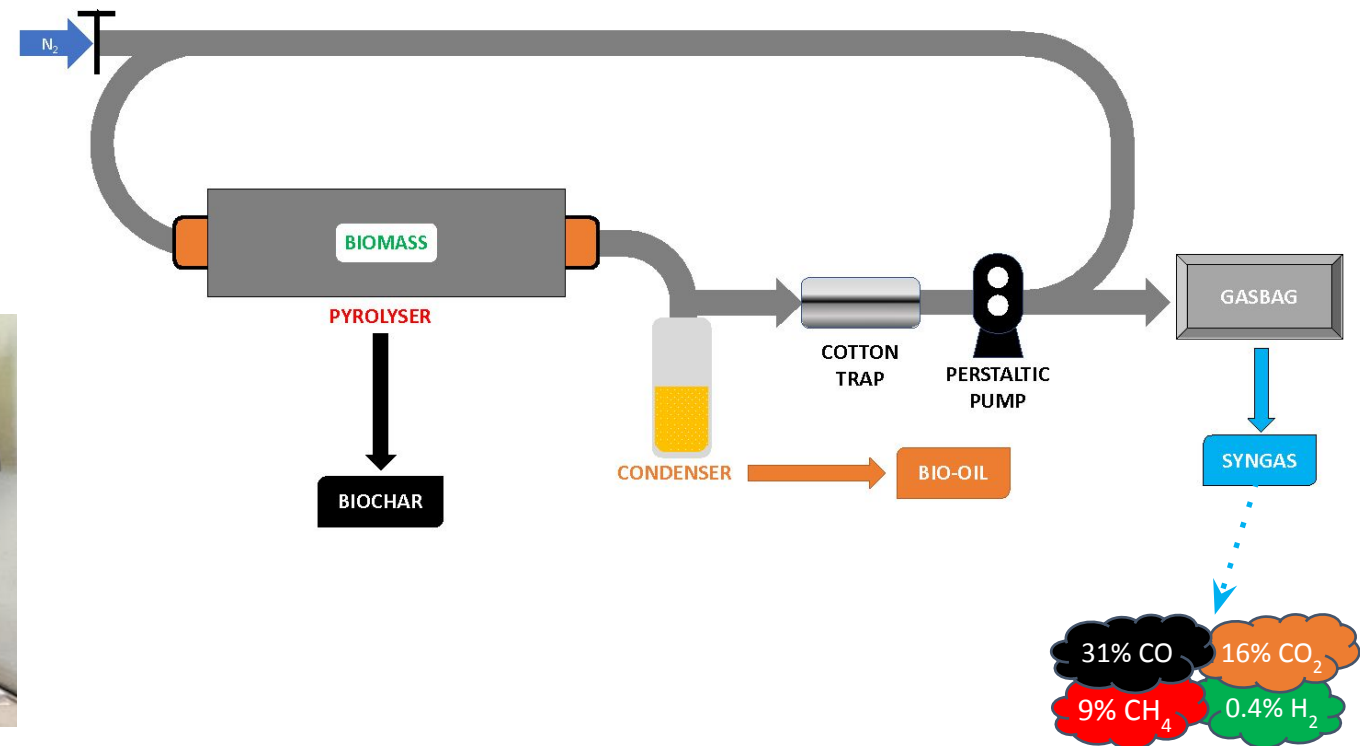
- Biomass is an abundant renewable source in the earth.
- Pyrolysis is an ancient and efficient thermochemical technique for biomass' chemical conversion.

Intermediate Pyrolysis Conditions

- **Fir Sawdust** used as representative lignocellulosic biomass.
- Batch pyrolysis conducted at moderate heating rate (**550°C for 30 minutes**) under gas recirculation.



Intermediate Pyrolysis Derived Real Syngas

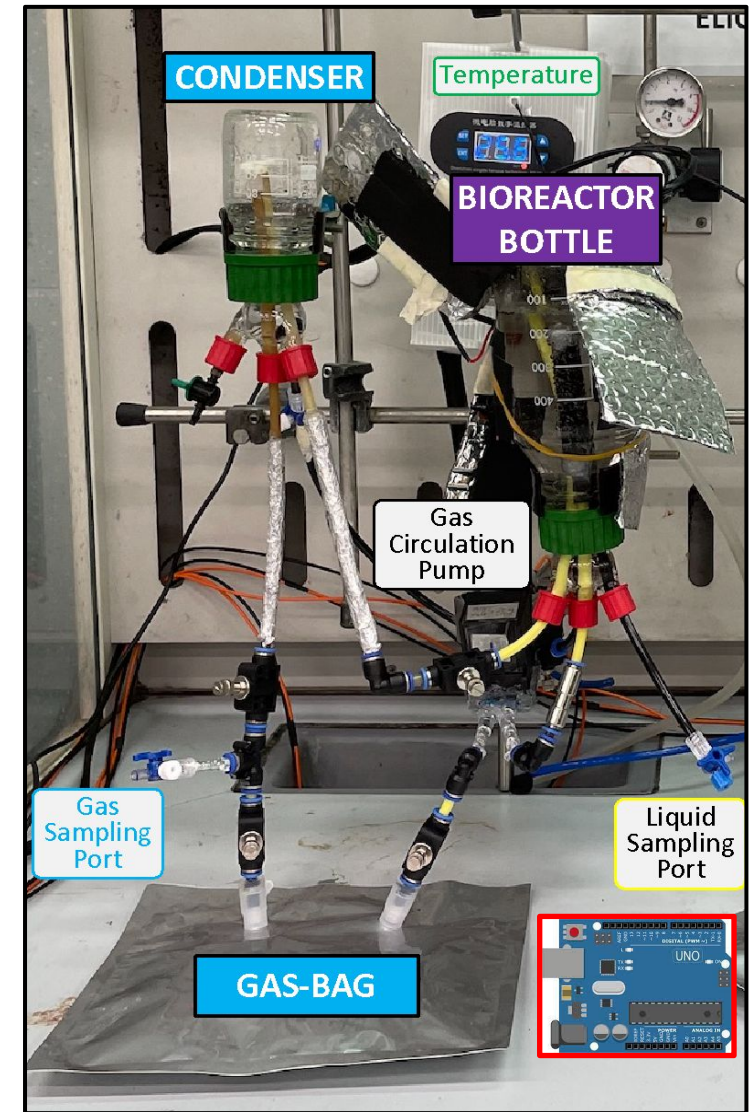
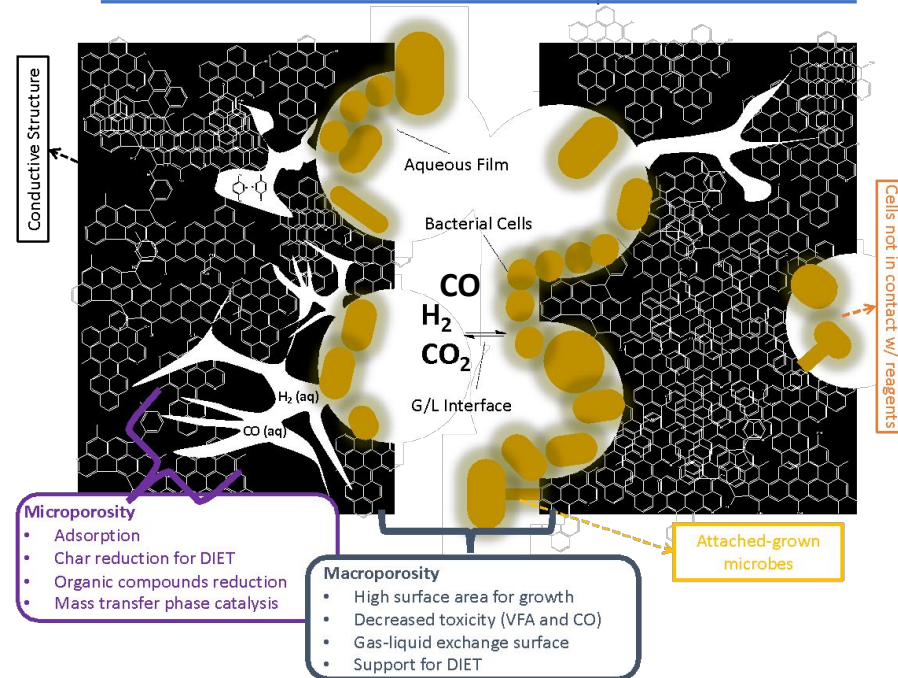


(2) Syngas Fermentation

Integration of MMC and Biochar Composite Material

- Bioreactor set-up was designed and constructed by the research team.
- Arduino is the key tool for configurable (flexible) bioreactor set-up with cost-efficiency.
- Four-ported (tetrapod) bottle caps provides sufficient inlet and outlet for such complex bioreactors.
- Pneumatic adapters and pipes together with gas-tight valves and pumps are required for such system.
- A small condenser bottle was combined to minimize water vapor losses.

Parameters		R-1 Syngas Reactor
Substrate Material	-	Syngas
Operational Method	-	Daily Fed Continuous
Temperature Set	°C	36.0
Total Wet Volume	mL	500.0
Hydraulic Retention Time	days	25
Average Gas Loading Rate	g-COD/L-day	0.53 ± 0.14
Sodium Bicarbonate Level	g/L	40.0
Start-Mix Concentration	g-COD/L	10.0
Inoculum : Glucose : Medium	COD basis	40% : 50% : 10%
Initial BES Concentration	mM	10.0

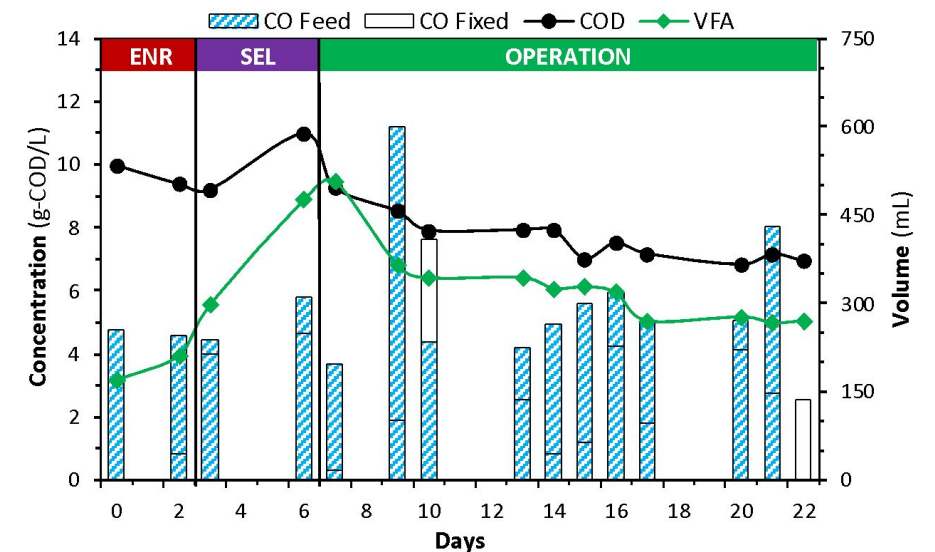
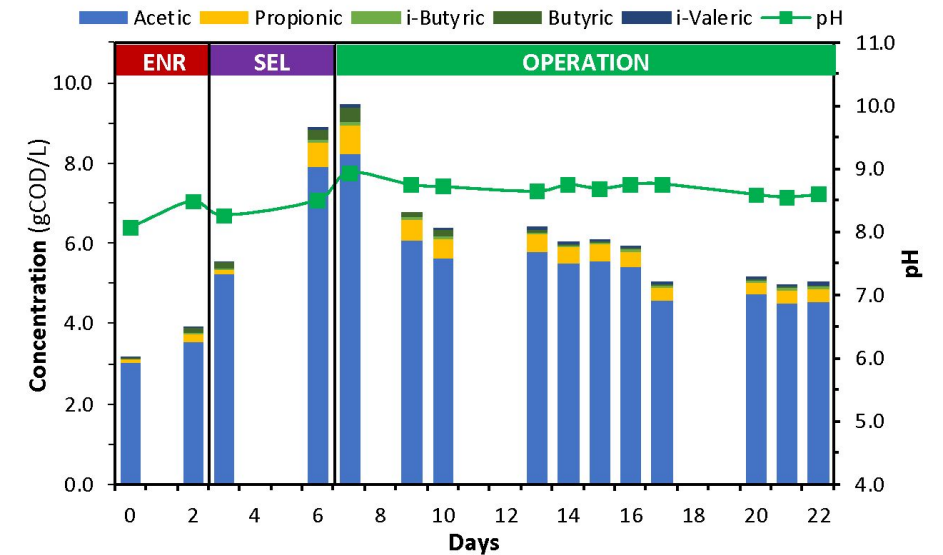


(2) Syngas Fermentation

Integration of MMC and Biochar Composite Material

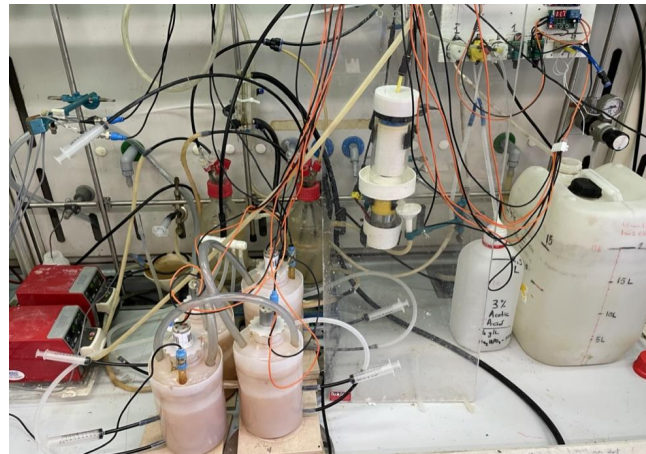
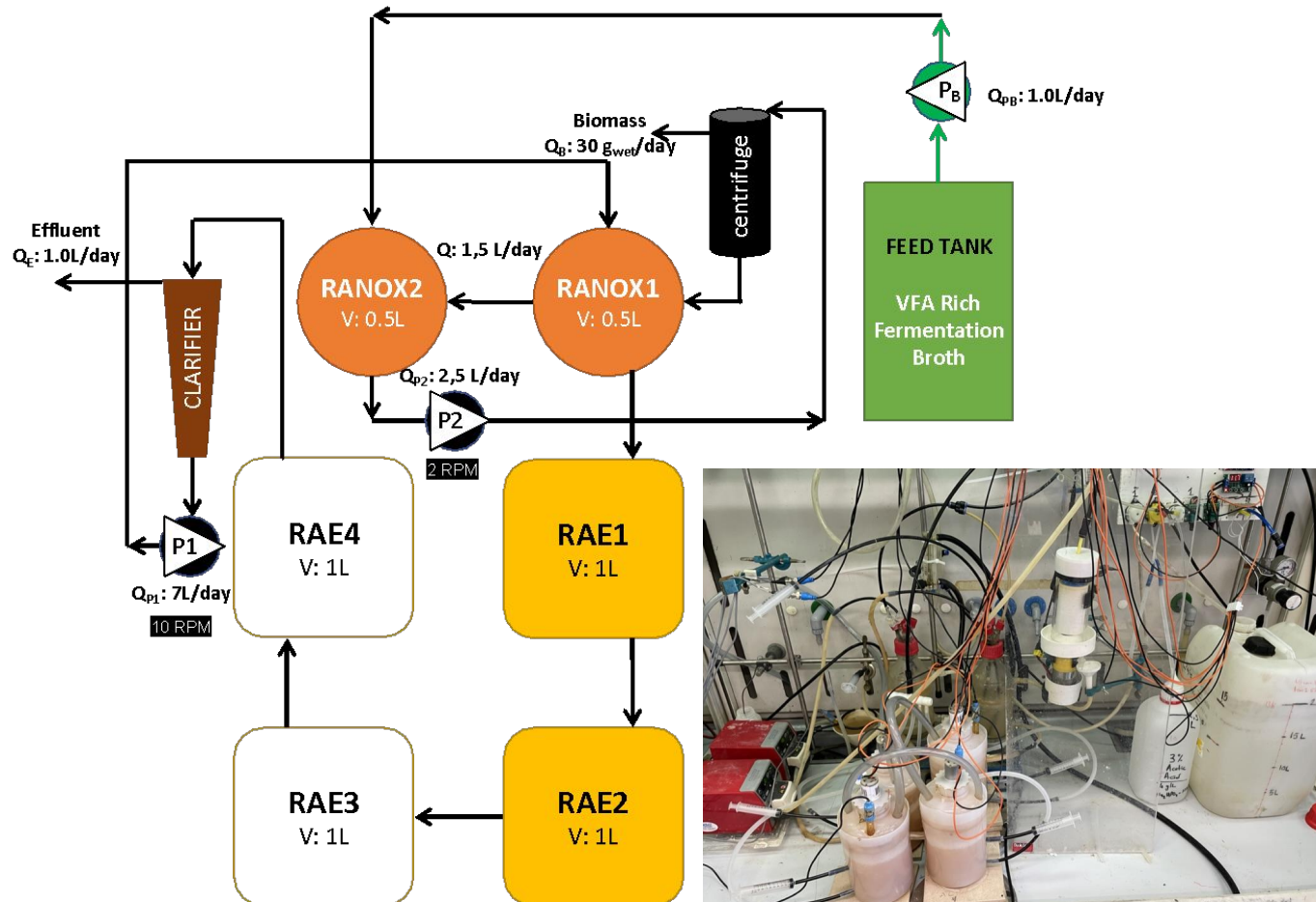
- Over 75% of effluent COD was contributed by VFA production.
- Low effluent suspended COD content (< 250ppm) with pH 8.5 is favorable for the subsequent PHA bio-accumulation process.
- Initial glucose originated COD is extracted from the performance estimations.
- These promising preliminary results suggesting that, this biochar based real syngas fermentation approach can be exploited for the production of VFA-rich liquids.
- To achieve better productivities, larger biochar diffuser is required, which should occupy most of the wet volume.

Parameters	Unit	Syngas Reactor (R-1)
Total Input	<i>g-COD</i>	11
Total Output	<i>g-COD</i>	10
Overall COD Recovery	%	> 90%
Effluent VFA to COD Ratio	%	77% ± 6
Diffuser _{BASED} VFA _{NET} Productivity	<i>g-COD/L-day</i>	5.0
Volumetric _{WET} VFA _{NET} Productivity	<i>g-COD/L-day</i>	0.06



(3) PHB Bio-Accumulation

Fully Continuous Lab-Scale System:



- Instead of much more common fully aerobic feast/famine operation, where especially C/P ratio has to be regulated, a sequential microaerophilic - aerobic PHA accumulation system is proposed ^{REF}.
- To avoid any chemical adjustment (presence of nutrients; N / P) for the fermentation effluent prior to the PHA accumulation system.
- Feast and famine regimes are sustained via sequential several reactors.
- A continuous small-scale centrifuge was developed to ensure continuous biomass withdrawal.
- 34% of PHB content has achieved by the MMC so far.

Conclusion



Integrated but simplified biorefinery approach for PHA from biomass.



Direct bio-utilisation of pyrolysis derived real syngas with biochar presence is possible.



Acetic acid and nutrient rich fermentation broth with $\text{pH} \approx 8$ is ideal for PHA-producers.



No chemical adjustment or pre-treatment is required, thanks to sequential MMC systems.



Chemical methanogen inhibitor (BES) increasing the cost.



Gasifier derived syngas bio-utilisation still required to be confirmed.



Syngas fermentation productivity should be increased (larger and better bio-diffusers).



Thank you for your attention!



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