ICAPP 2019

1st International Conference on Advanced Production and Processing

Biological conversion of Greenhouse Gases into added value bio-products: Moving towards GHG Biorefineries

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Institute of Sustainable Processes
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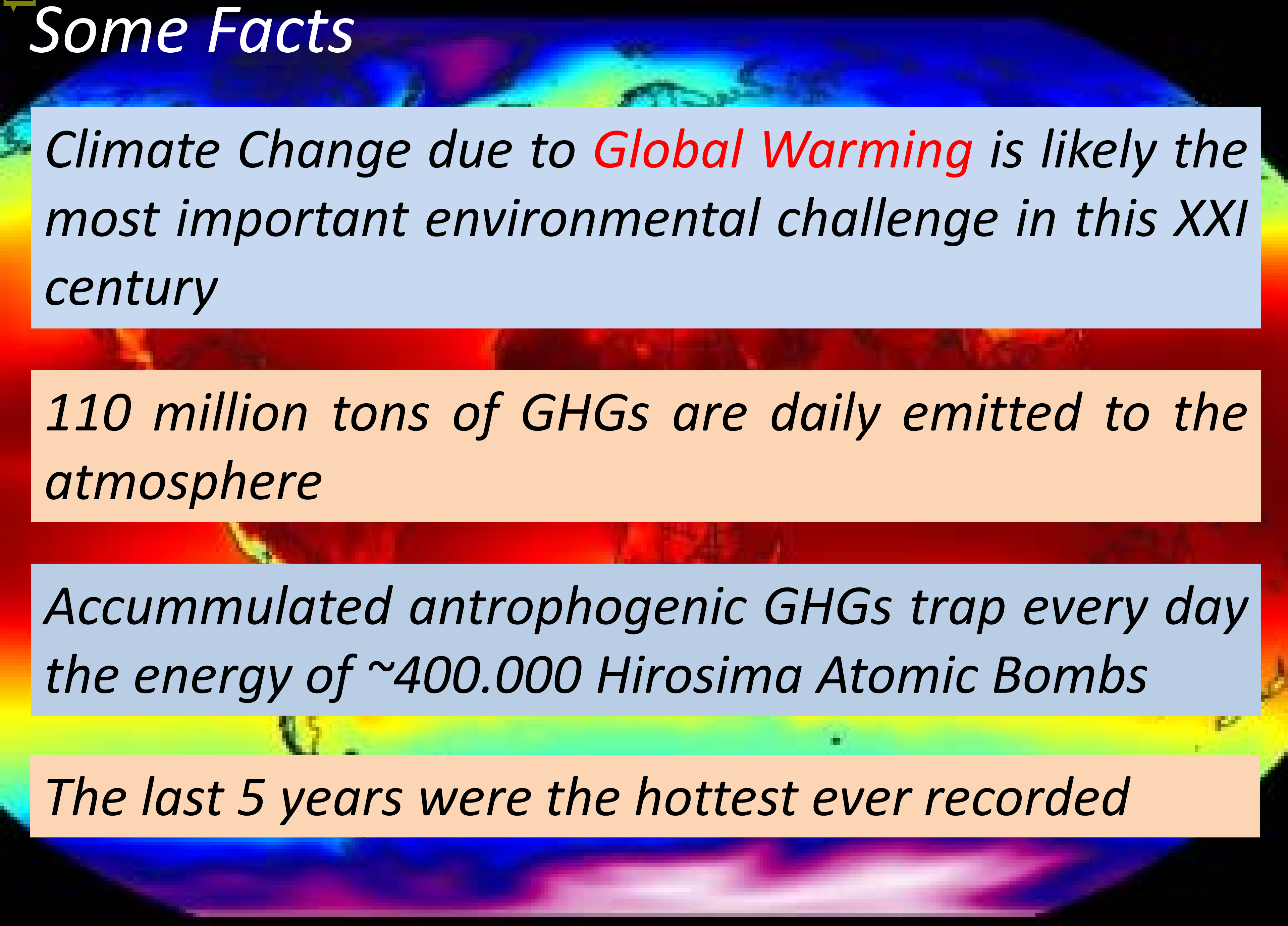


Some Facts

Climate Change due to Global Warming is likely the most important environmental challenge in this XXI century

110 million tons of GHGs are daily emitted to the atmosphere

Accummulated antrophogenic GHGs trap every day the energy of ~400.000 Hirosima Atomic Bombs

The last 5 years were the hottest ever recorded

EUROPEAN COMMISSION

PRESS RELEASE

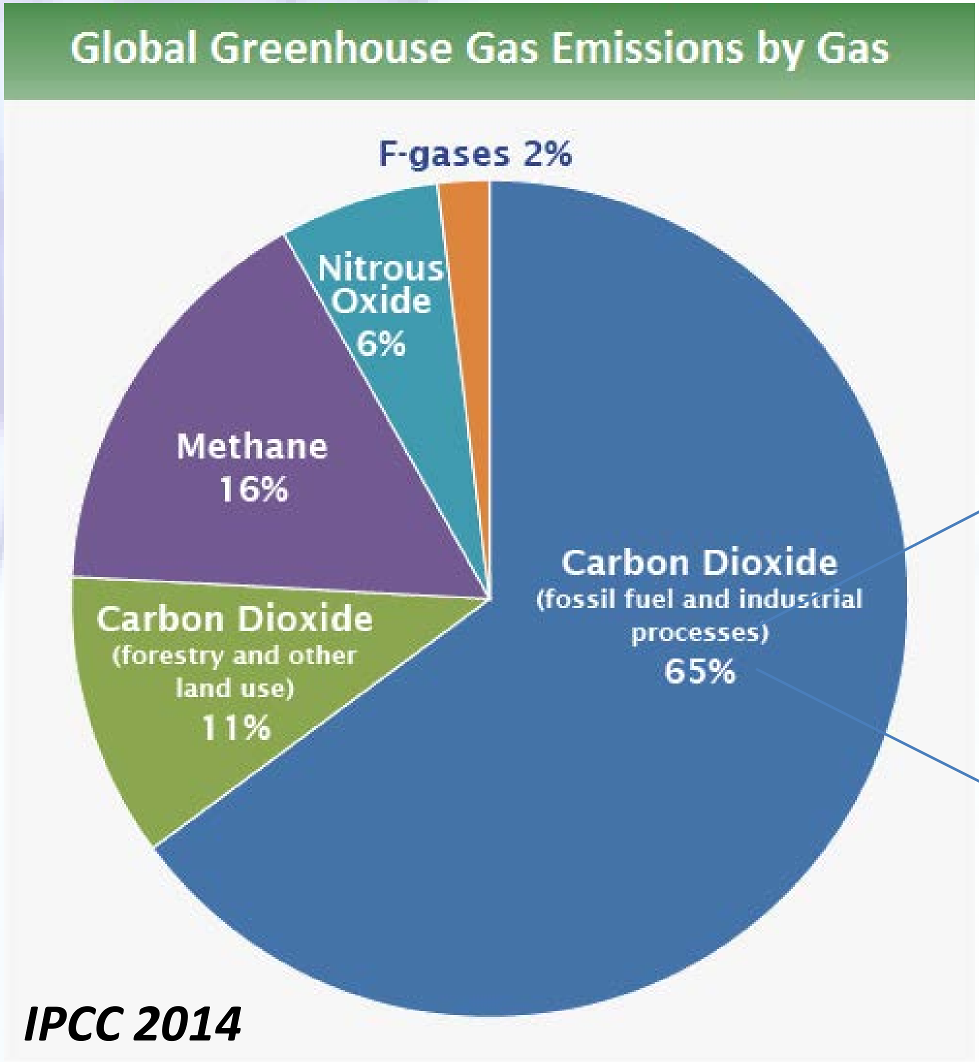
October 2014

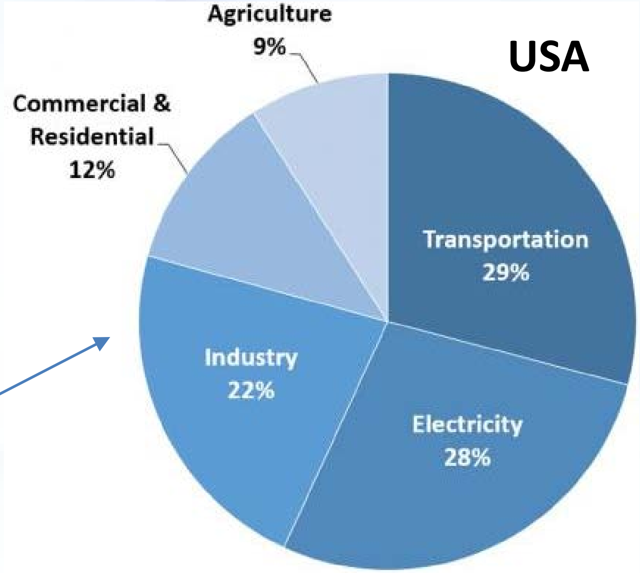
[2030 Climate and Energy Goals](#)

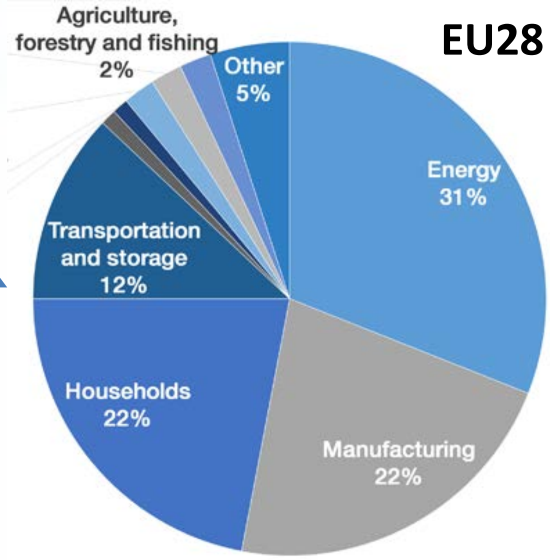
[for a Competitive, Secure and Low-Carbon EU Economy](#)

Ambitious objective for EU-GHG emissions: 40% by 2030

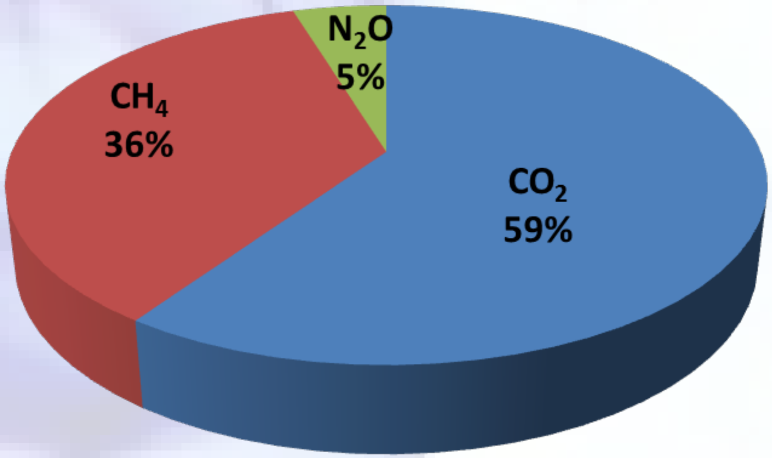
What is the most important GHG Worldwide?





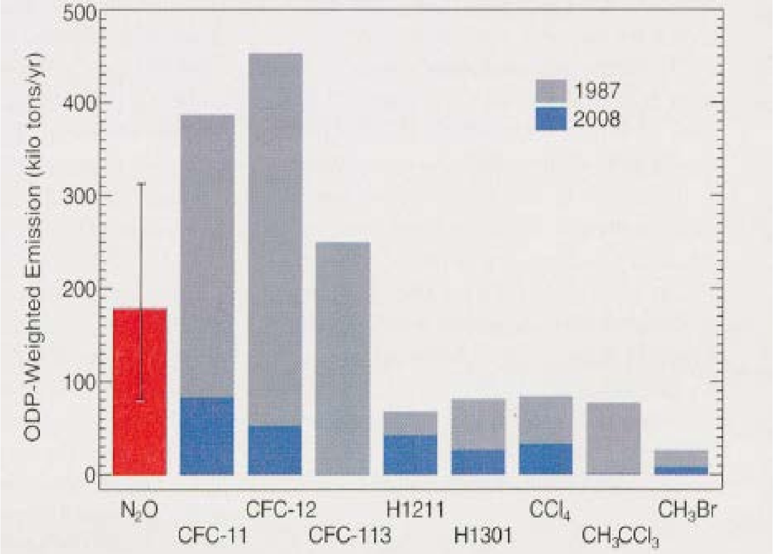


Global Warming



European Commission JCR 2012; O'connor et al. 2010

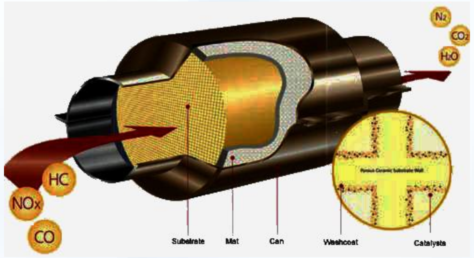
O_3 Depletion



Science, 326: 123-125

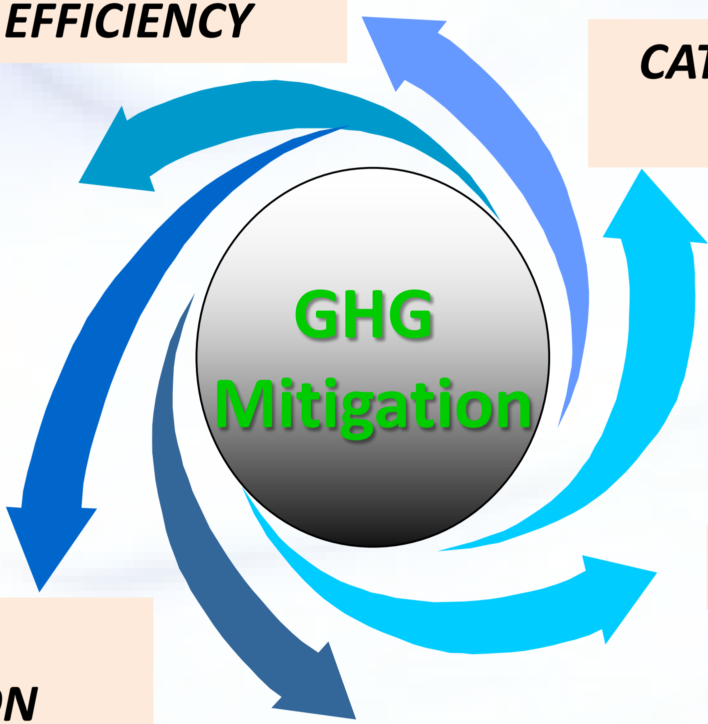
Active Abatement of CH_4 & N_2O is also needed

INCREASED ENERGY EFFICIENCY



CATALYTIC /NON-CATALYTIC N_2O REDUCTION

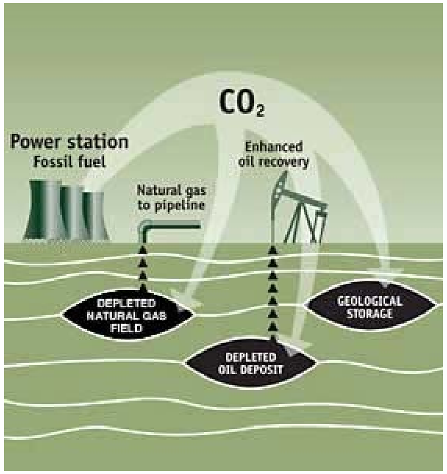
RENEWABLE ENERGY PRODUCTION



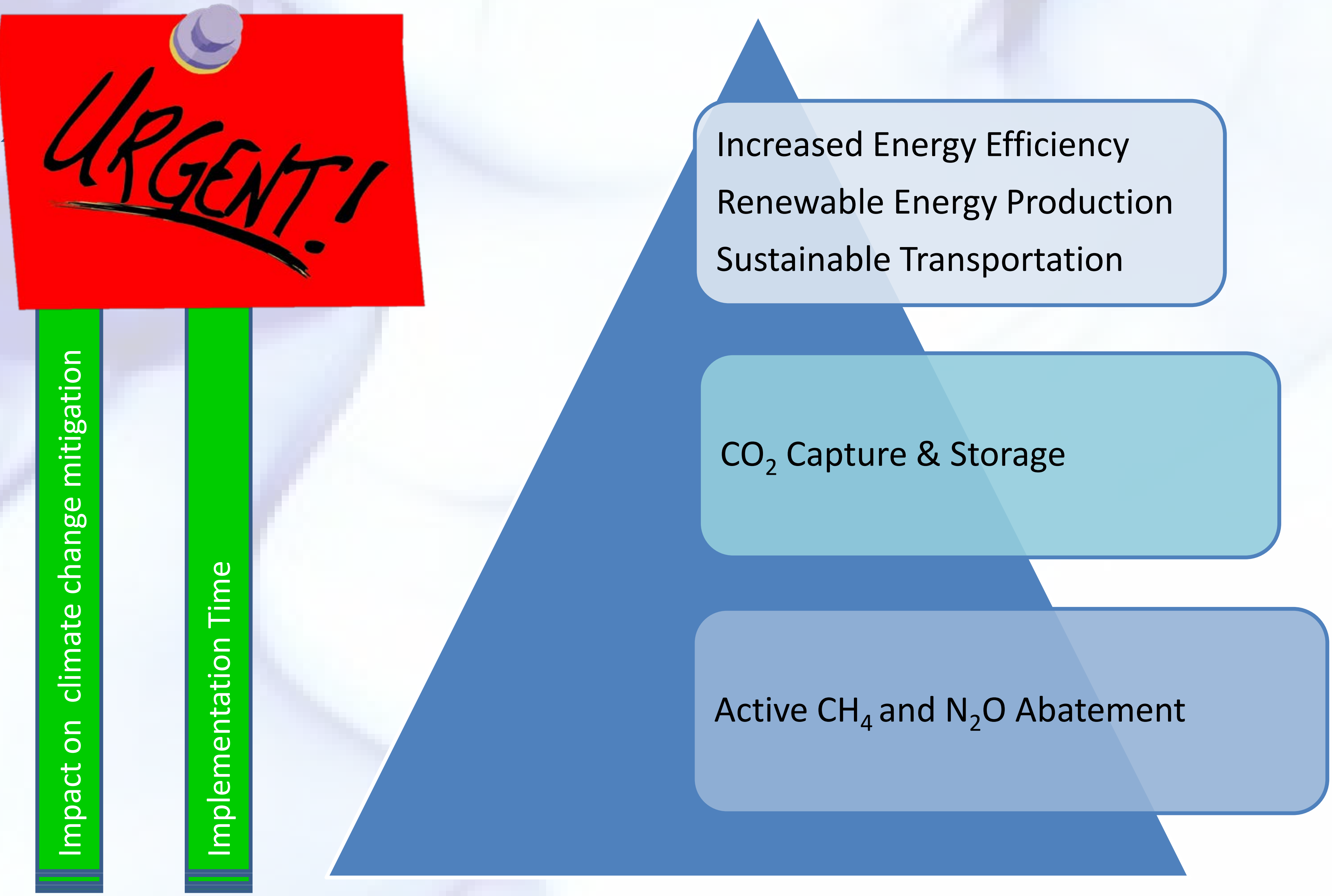
CH_4 FLARING

SUSTAINABLE TRANSPORTATION

CO_2 CAPTURE & STORAGE



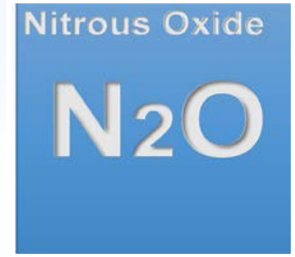
Climate Change Mitigation Strategies



End-of-the-pipe GHG abatement is dominated by..

- Absorption
- Adsorption
- Membrane separation

- Flaring
- Adsorption

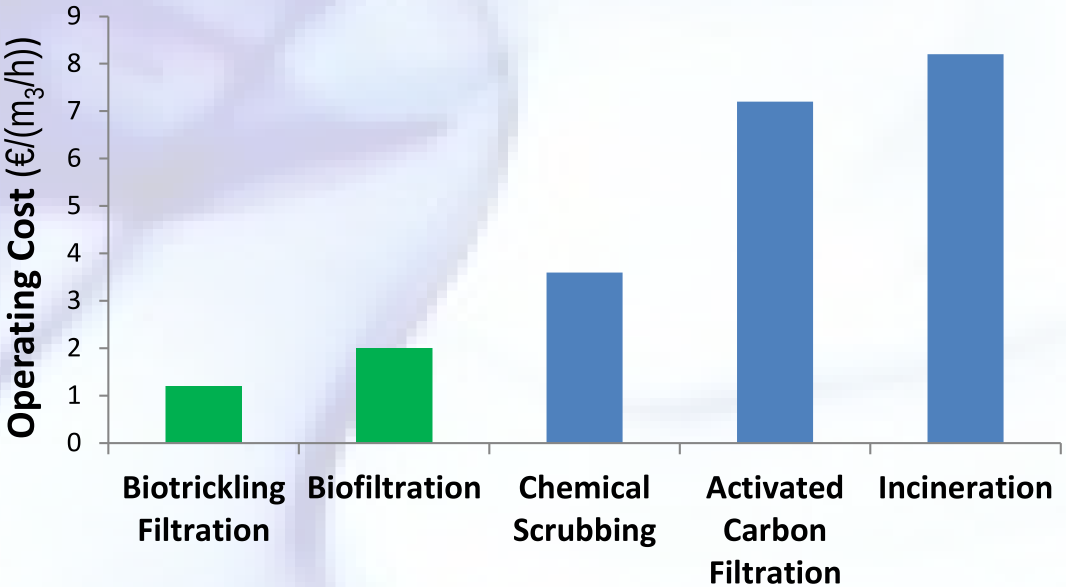


- Selective catalytic reduction
- Selective non-catalytic reduction
- Adsorption
- Scrubbing

- ❑ High Operating Cost
- ❑ High Environmental Impact
- ❑ No Resource Recovery out of GHG mitigation

Biotechnologies for the abatement of gas pollutants:

- low operating costs
- low environmental impacts
- allow for pollutant valorization



Biot Adv, 2012, 30:1354-1363

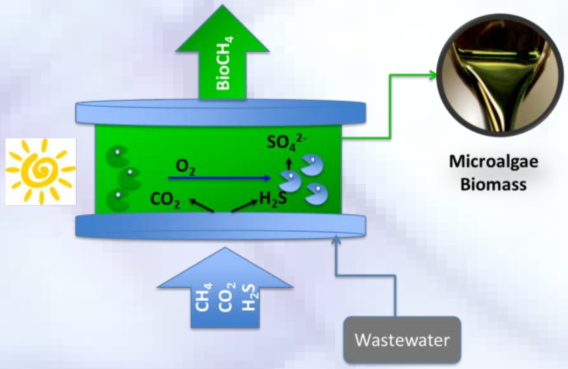
but limitations to overcome…

Limitations to be overcome in GHG abatement ***Biotechnologies:***

Nutrient Availability →	Limited photosynthetic CO_2 fixation
Limited Understanding of N_2O Microbiology →	No biotechnologies available for N_2O abatement
No Resource Recovery →	Poor process economics
Limited GHG mass transfer rates →	High investment costs

Overcoming Limitations

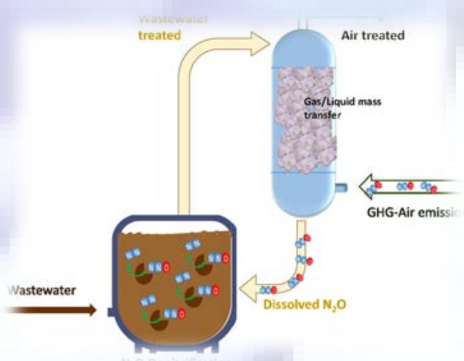
@ University of Valladolid



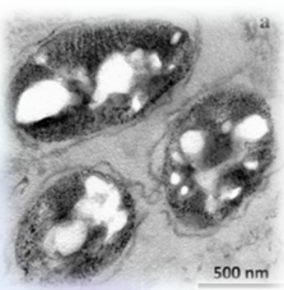
Photosynthetic CO_2 fixation from biogas

Overcoming GHG abatement Limitations

High-Mass Transfer Bioreactors



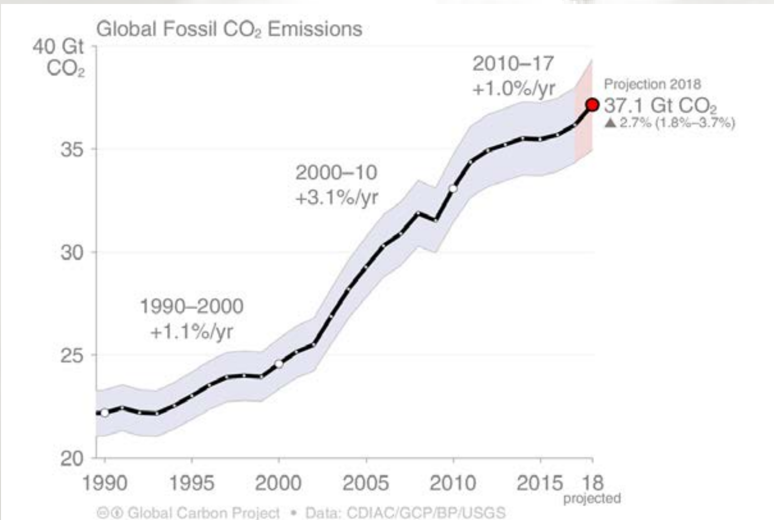
Innovative Biological Processes for N_2O abatement



Biopolymer Production from CH_4

Cosmetics Production from CH_4

Can Microalgae fix all CO_2 from flue gases?



(Global Carbon Budget 2018)

Table 1. Total world nutrient capacity of ammonia, phosphoric acid and potash, 2015-2020 (thousand tonnes)

Year	2015	2016	2017	2018	2019	2020
Ammonia (NH_3) as N	174 781	181 228	185 222	186 804	186 920	188 310
Phosphoric acid (H_3PO_4) as P_2O_5	57 422	58 385	60 955	61 995	63 036	64 677
Potash as K_2O	52 942	55 974	58 111	61 576	62 136	64 486
Total (N+ P_2O_5+K_2O)	285 145	295 587	304 287	310 374	312 092	317 474

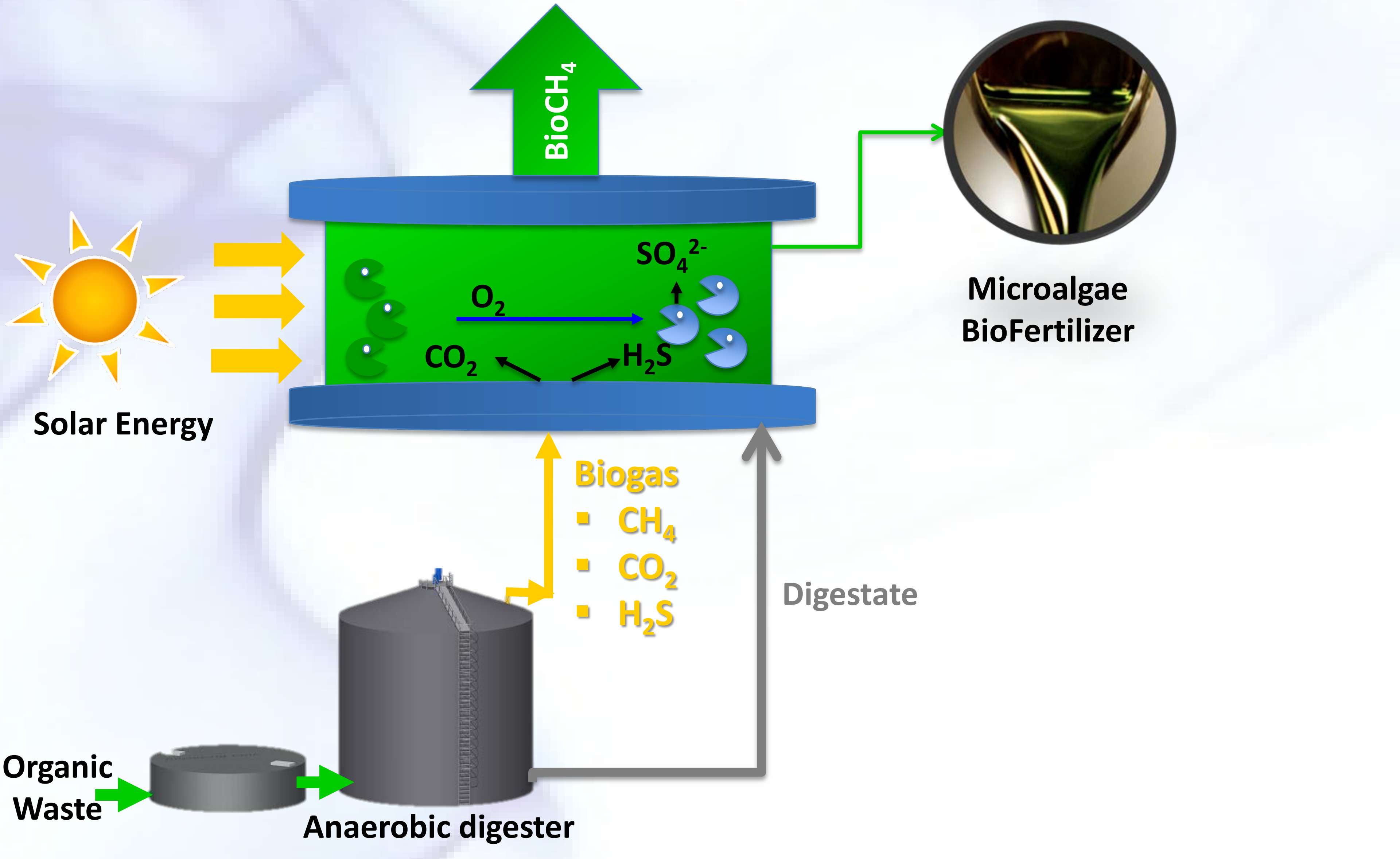
(FAO 2018)

World fossil-fuel carbon emissions in 2018 ~ **10000 million tons C**

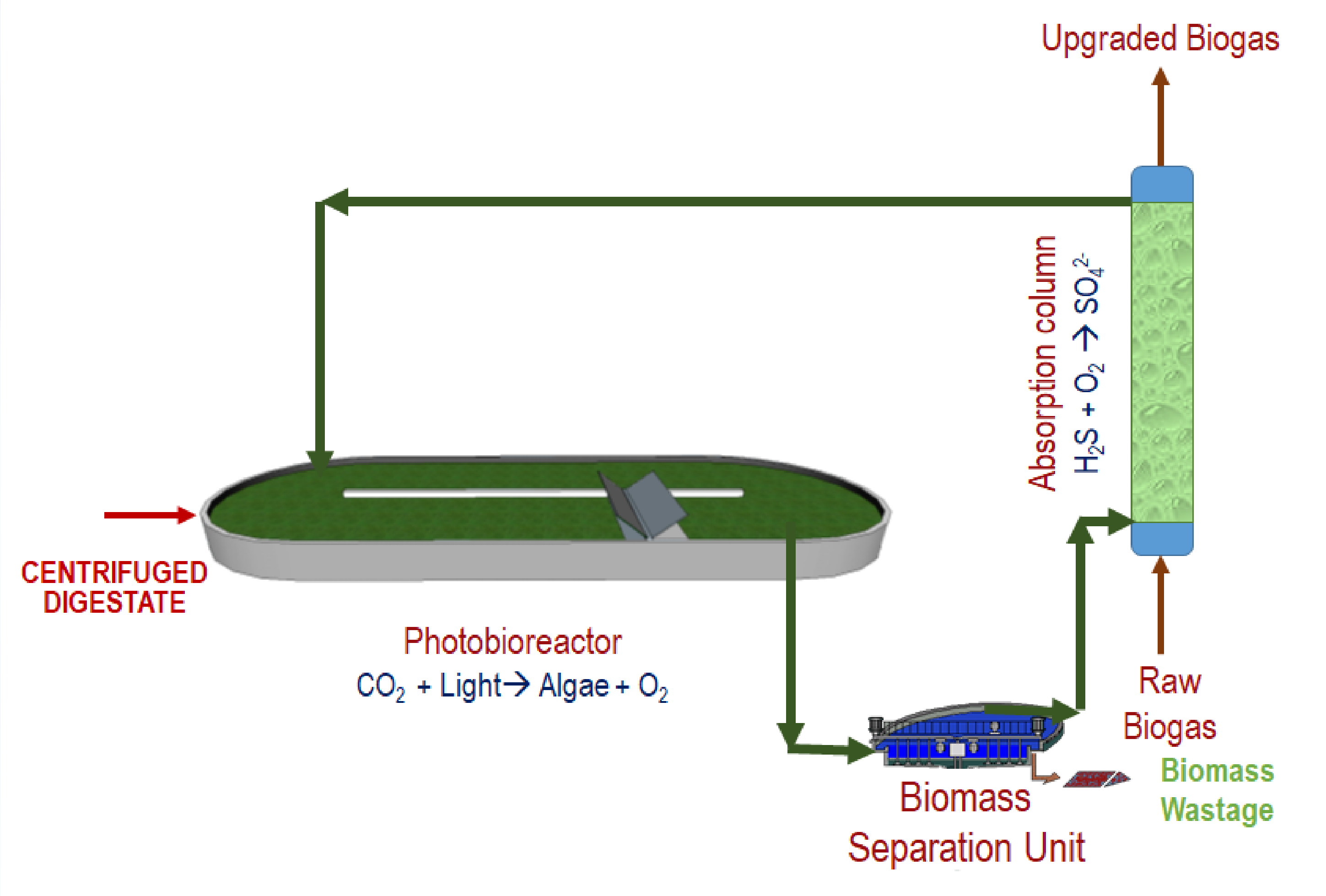
Theoretical Nitrogen Demand for Photosynthetic CO_2 Fixation
1380 million tons

World fertilizer (N+P_2O_5 +K_2O) production capacity in 2018 =**187 million tons**

Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

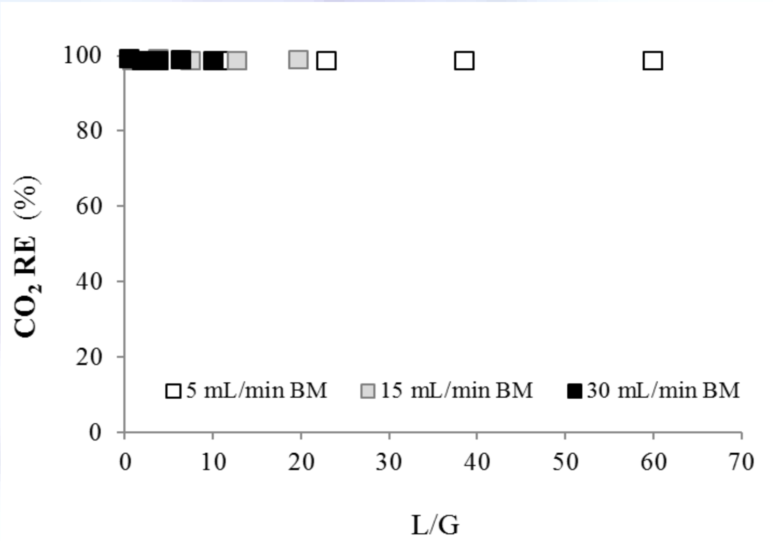


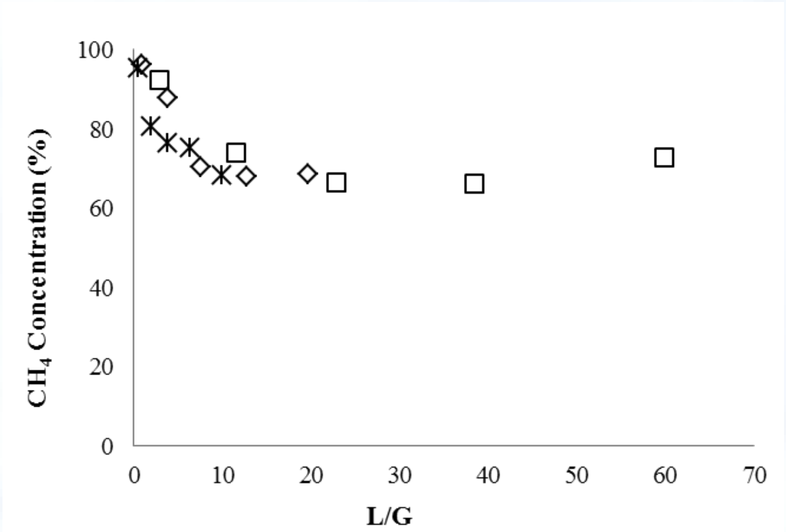
Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

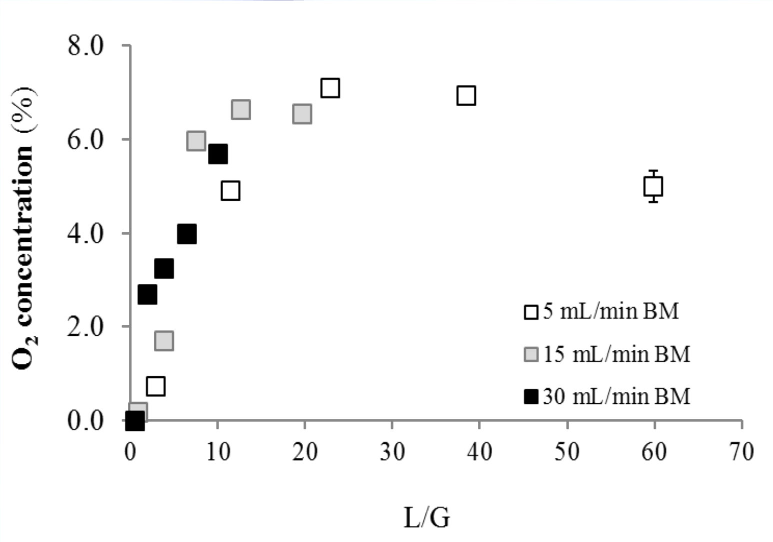


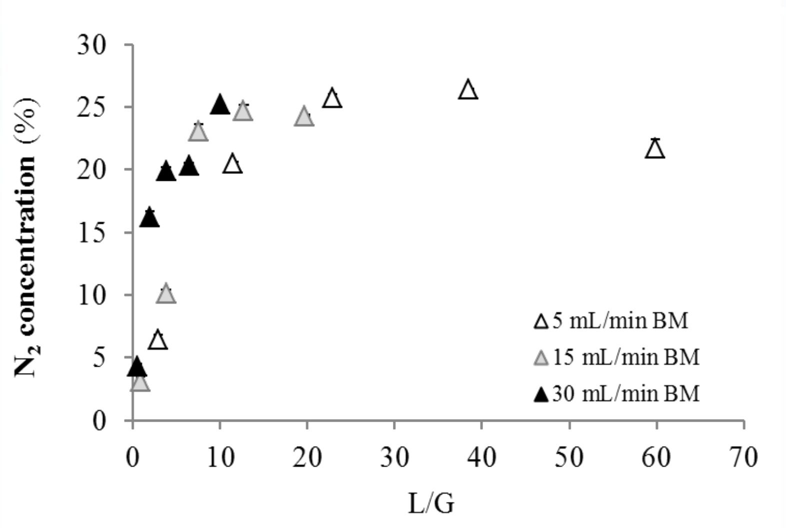
Key operational parameter: Recycling Liquid/Biogas ratio

Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

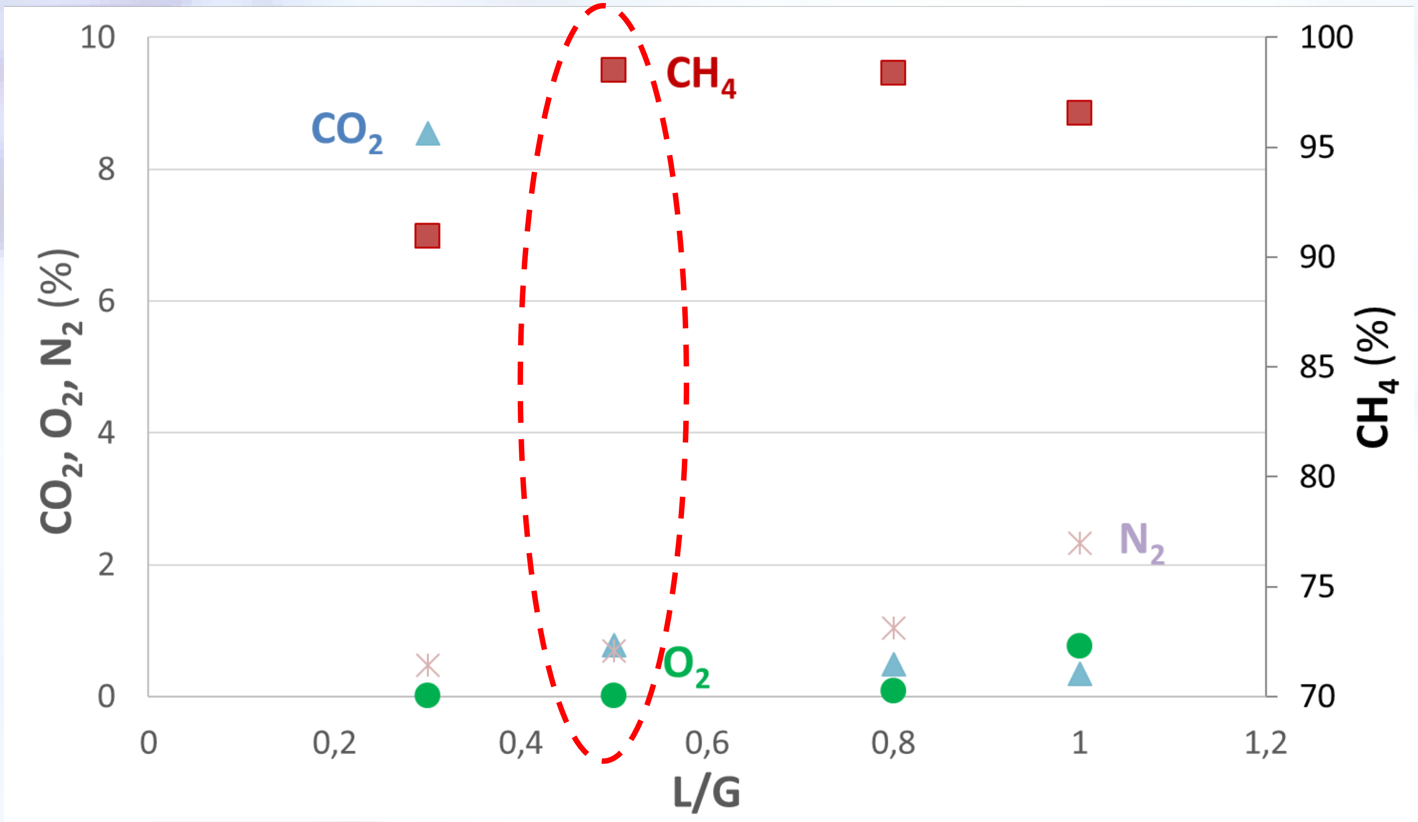








Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

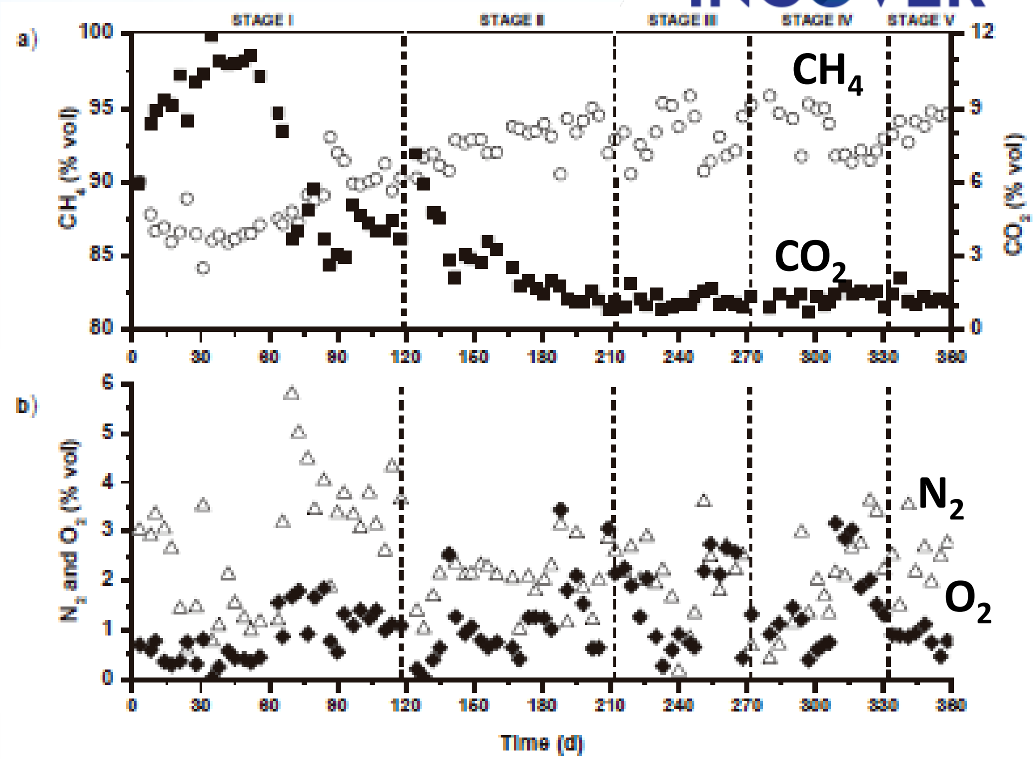


Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

Contents lists available at ScienceDirect
Bioresource Technology
journal homepage: www.elsevier.com/locate/biortech

Seasonal variation of biogas upgrading coupled with digestate treatment in an outdoors pilot scale algal-bacterial photobioreactor

David Marín[a,c], Esther Posadas[a], Patricia Cano[a], Victor Pérez[a], Saúl Blanco[b], Raquel Lebrero[a], Raúl Muñoz[a,*]



Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

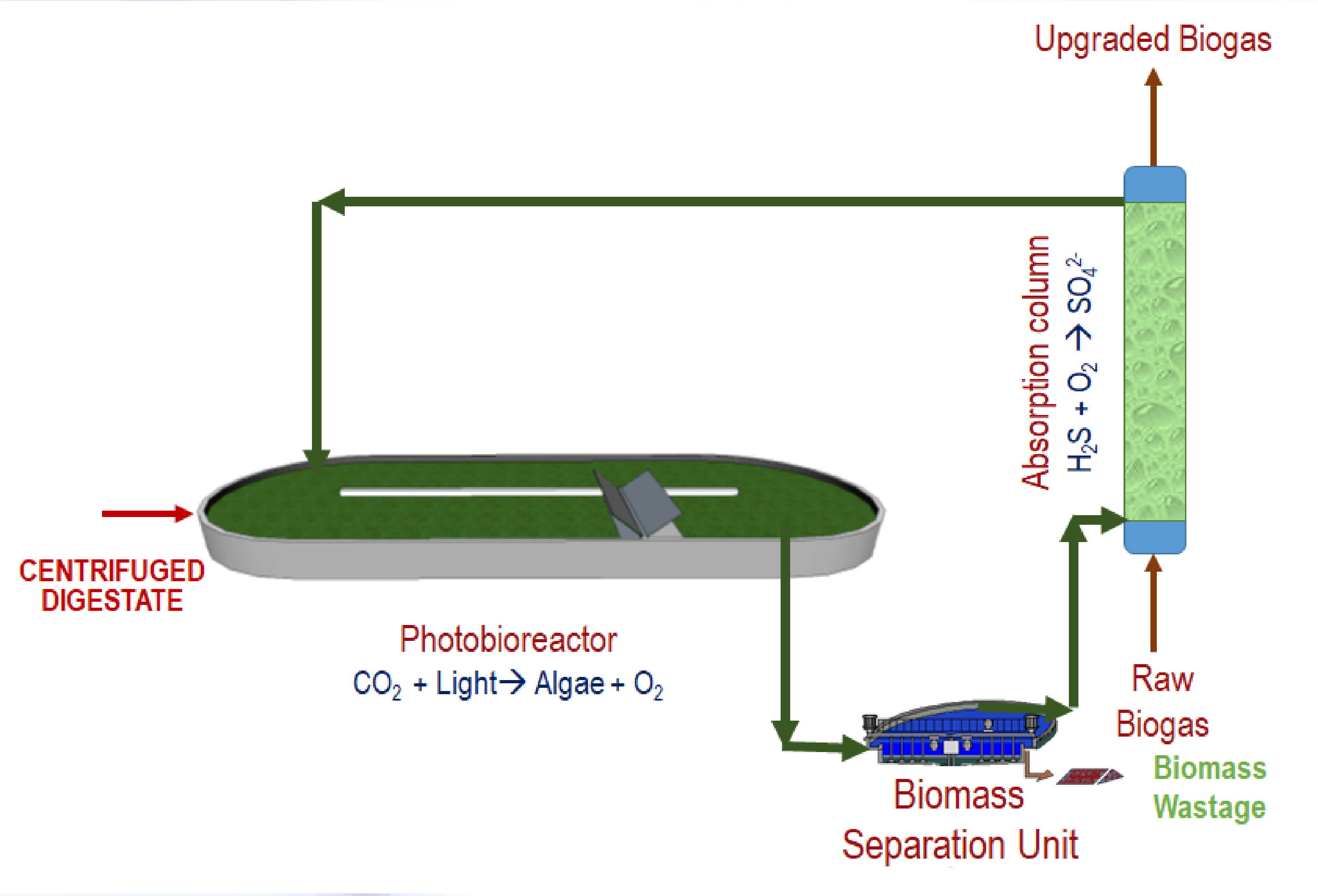
INCOVER

aqualia

European Commission

HORIZON 2020

Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery

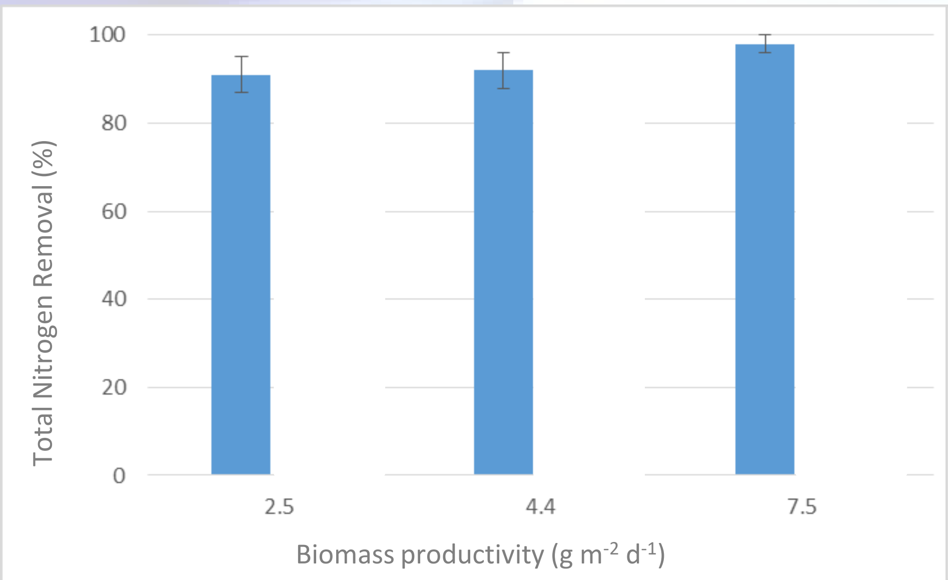


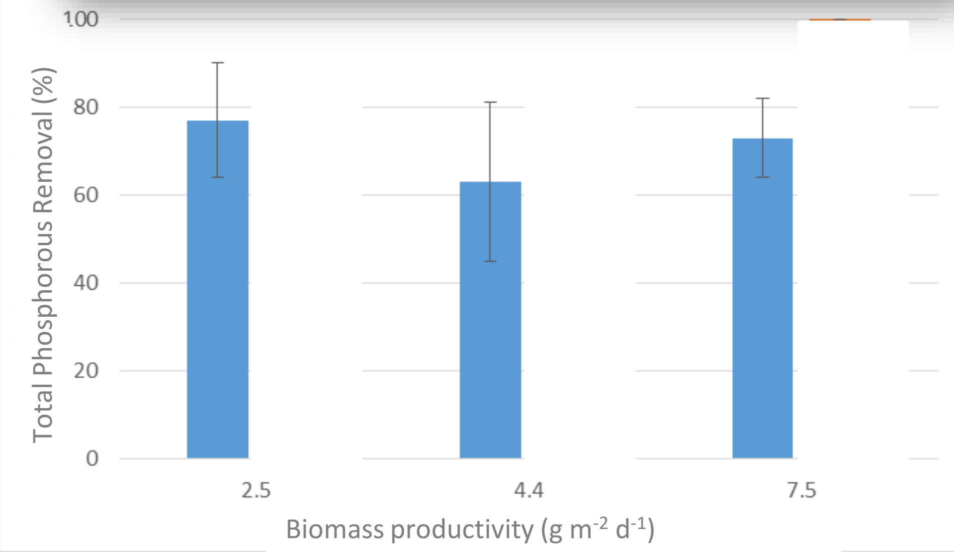
Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery


Contents lists available at ScienceDirect
Algal Research
journal homepage: www.elsevier.com/locate/algal

Photosynthetic biogas upgrading to bio-methane: Boosting nutrient recovery via biomass productivity control

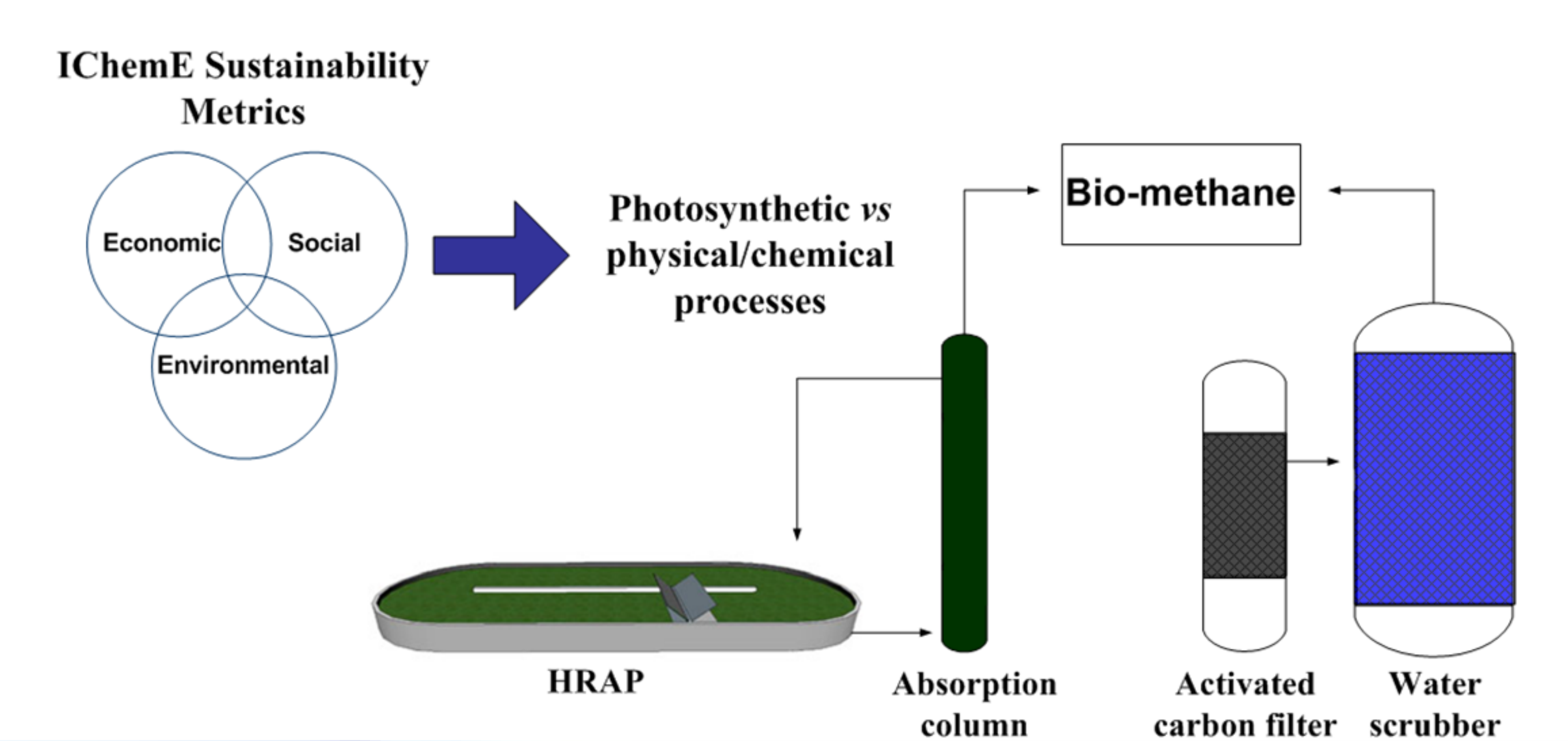
Alma Toledo-Cervantes [a], Mayara L. Serejo [b], Saúl Blanco [c,1], Rebeca Pérez [a], Raquel Lebrero [a], Raúl Muñoz [a,*]





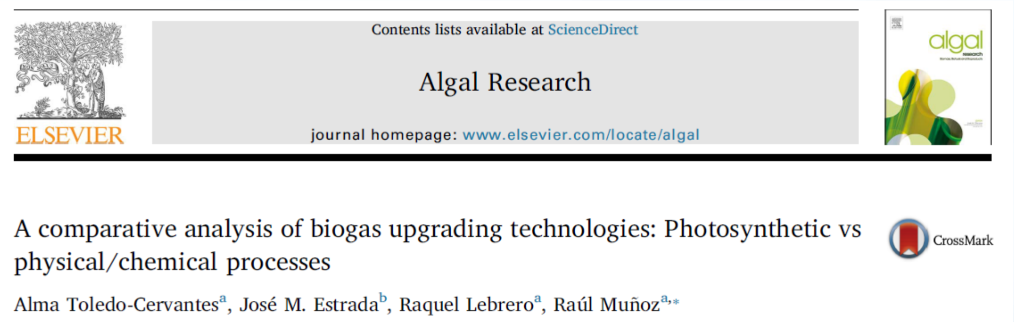
Removal

Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery



Upgrading Capacity: 300 Nm^3/h of biogas

Photosynthetic CO_2 fixation as a tool for Biogas upgrading & Nutrient Recovery



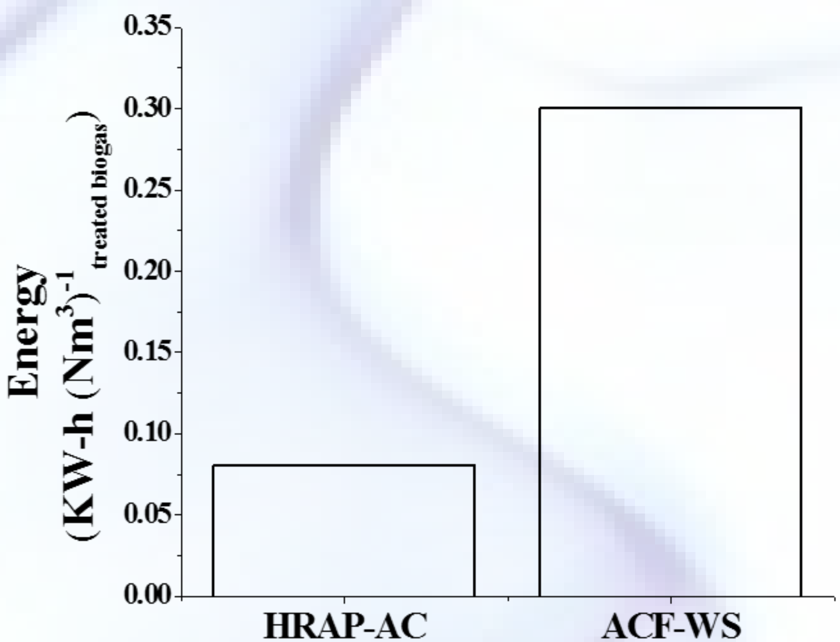
Contents lists available at ScienceDirect

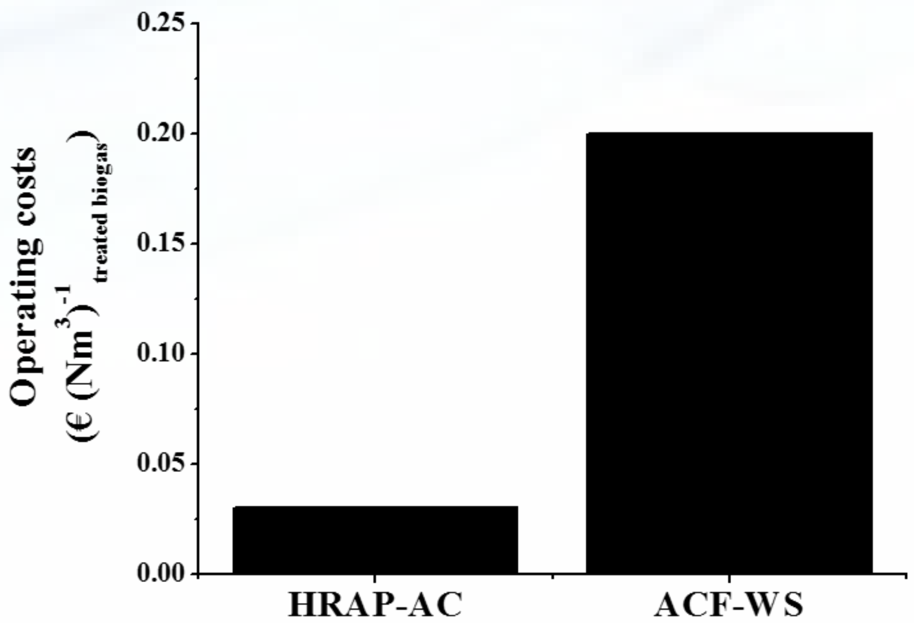
Algal Research

journal homepage: www.elsevier.com/locate/algal

A comparative analysis of biogas upgrading technologies: Photosynthetic vs physical/chemical processes

Alma Toledo-Cervantes[a], José M. Estrada[b], Raquel Lebrero[a], Raúl Muñoz[a,*]





The need for Biological N_2O Abatement technologies

Heterotrophic denitrification with organic matter as e-donor

$$3N_2O + CH_3OH \rightarrow 3N_2 + 2H_2O + CO_2$$ **(ΔG°´ = - 1013.3 kJ)**

N_2O nitrification to nitrate and nitrite

$$N_2O + 2O_2 + H_2O \rightarrow 2NO_3^- + 2H^+$$ **(ΔG°´ = - 87.4 kJ)**

$$N_2O + O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$$ **(ΔG°´ = - 15 kJ)**

N_2O assimilation into biomass

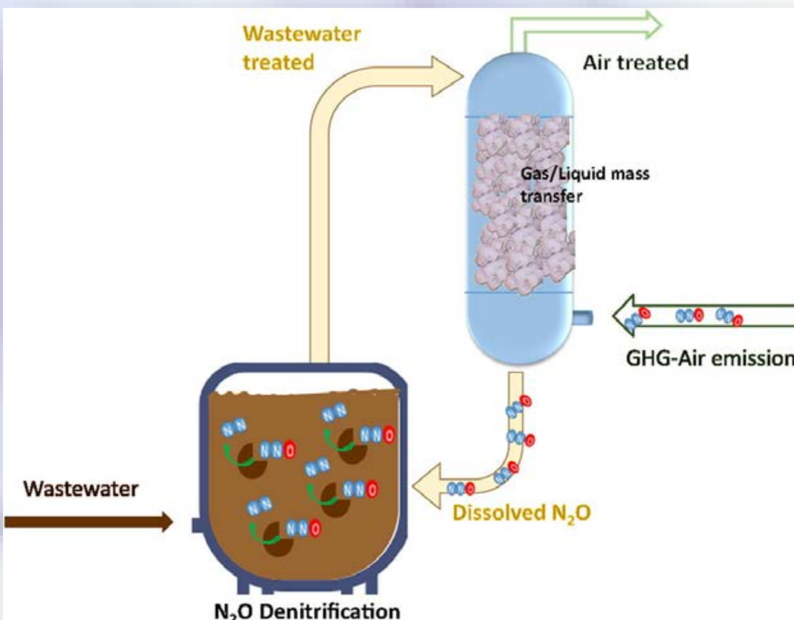
$$N_2O \rightarrow C_5H_7NO_2$$

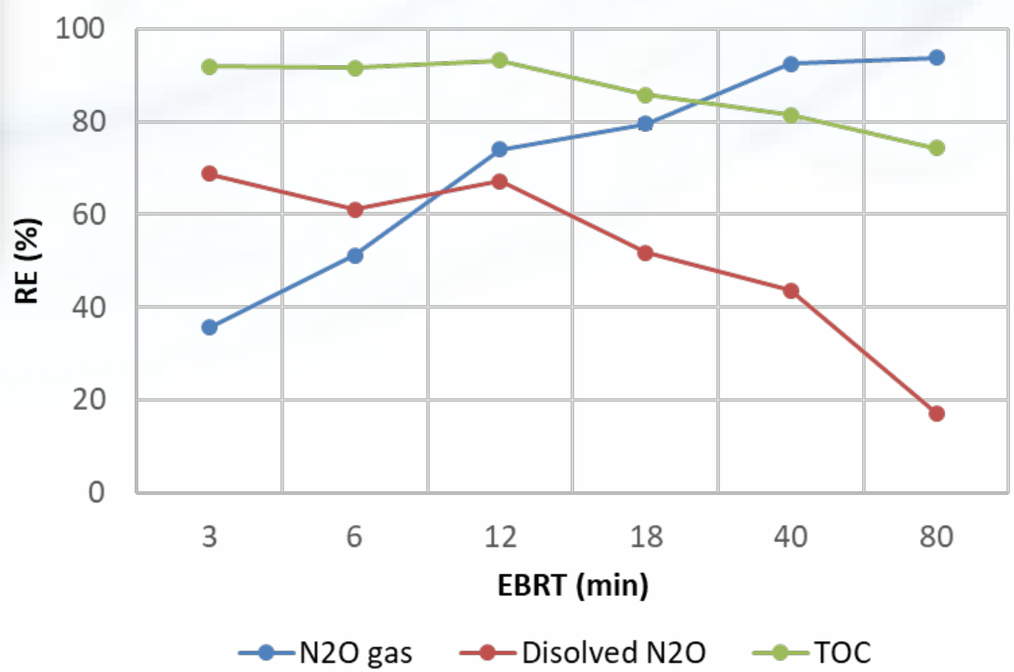
The need for **Biological** N_2O Abatement technologies

Chemical Engineering Journal 288 (2016) 28–37
Contents lists available at ScienceDirect
Chemical Engineering Journal
ELSEVIER
journal homepage: www.elsevier.com/locate/cej

Simultaneous biological nitrous oxide abatement and wastewater treatment in a denitrifying off-gas bioscrubber

Osvaldo D. Frutos [a,b,1], Guillermo Quijano [a,1], Rebeca Pérez [a,1], Raúl Muñoz [a,*]



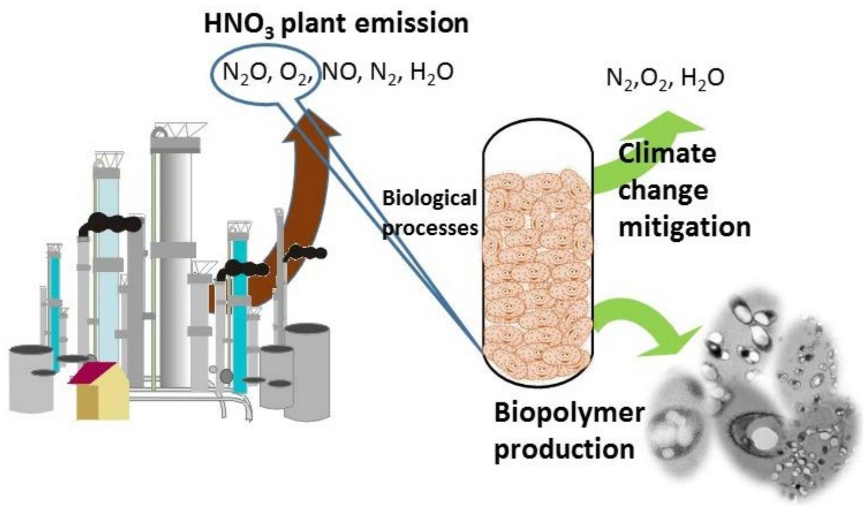


WWTP N_2O emission:

- N_2O = 100 ppm_v
- O_2 = 210000 ppm_v

Wastewater: Synthetic Domestic WW
WW Residence Time: 5 hours
Microorganisms: Activated sludge

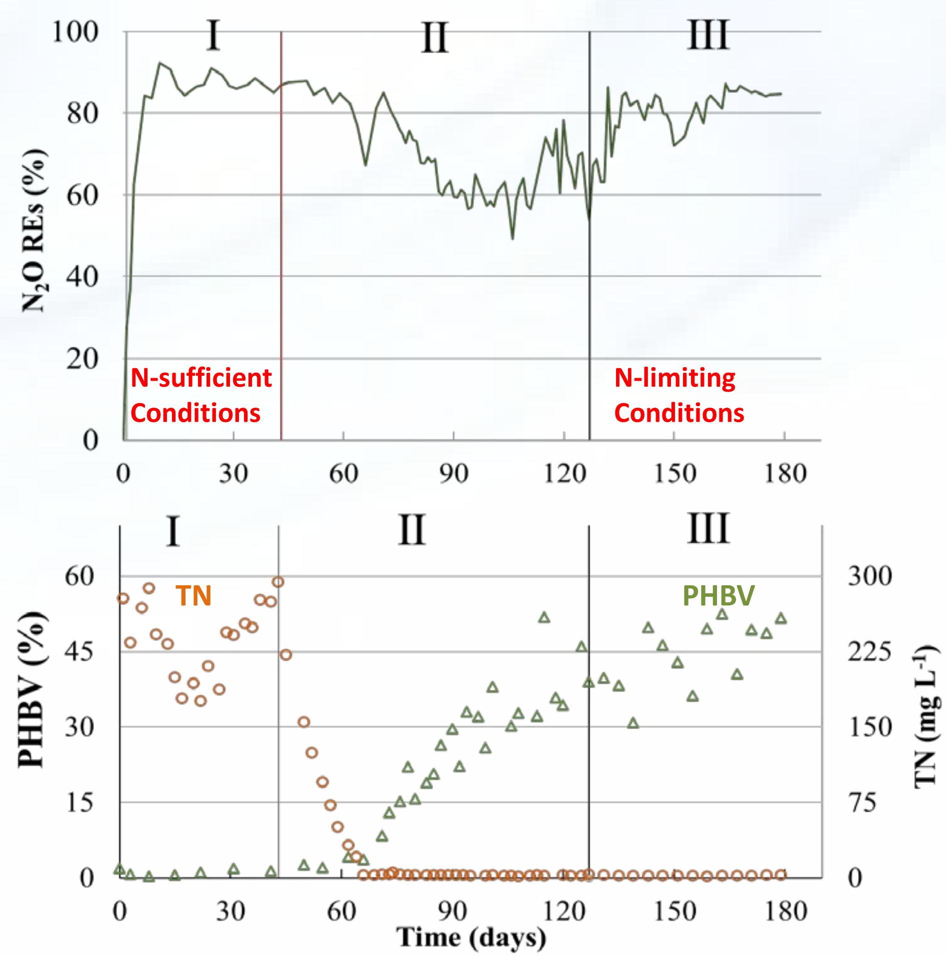
The need for Biological N_2O Abatement technologies



Environmental Science & Technology
Article
pubs.acs.org/est

Nitrous Oxide Abatement Coupled with Biopolymer Production As a Model GHG Biorefinery for Cost-Effective Climate Change Mitigation

Osvaldo D. Frutos,[†,‡] Irene Cortes,[†] Sara Cantera,[†] Esther Arnaiz,[†] Raquel Lebrero,[†] and Raúl Muñoz*[,†,§]

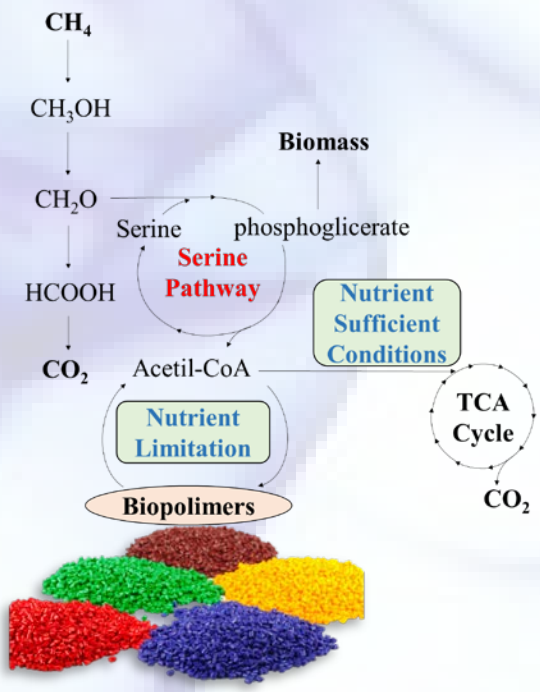


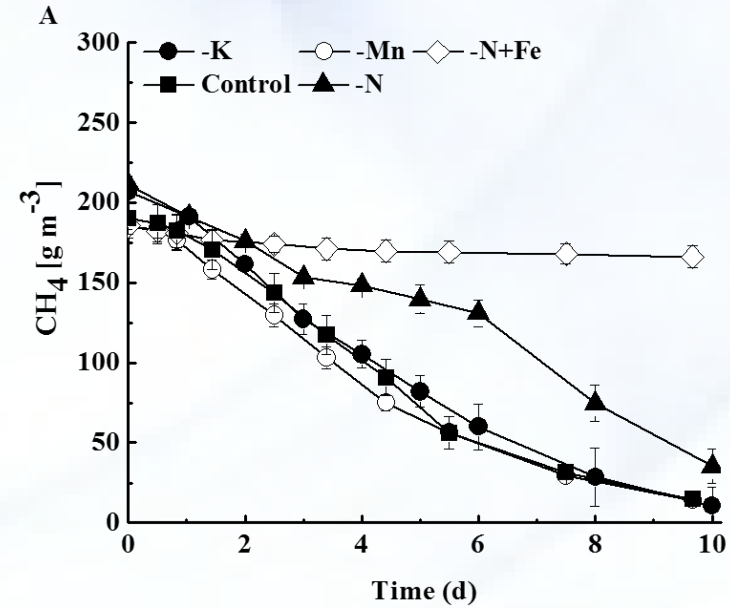
Industrial N_2O emission:

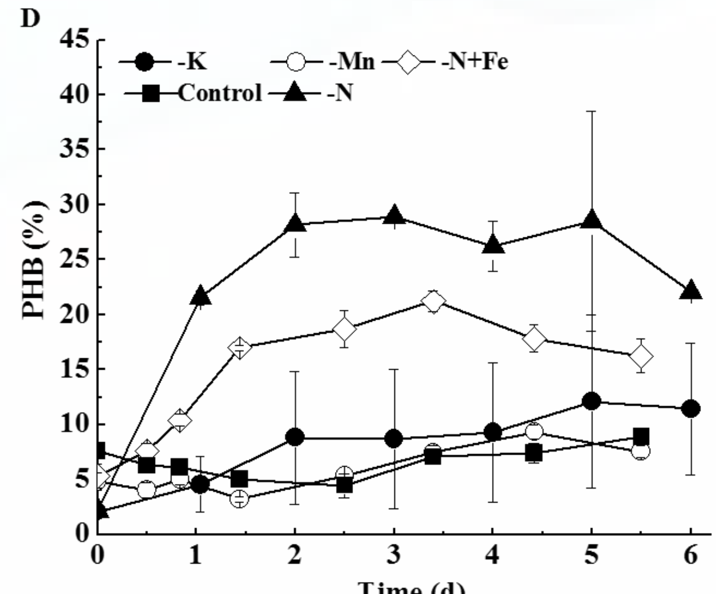
- N_2O = 4000 ppm$_v$
- O_2 = 11000 ppm$_v$

Reactor: Bubble Column
Gas Residence Time: 17 min
Bacterial strain: *Paracoccus denitrificans*
e-donor: *metanol*

Biological CH_4 Abatement coupled to Biopolymer Production





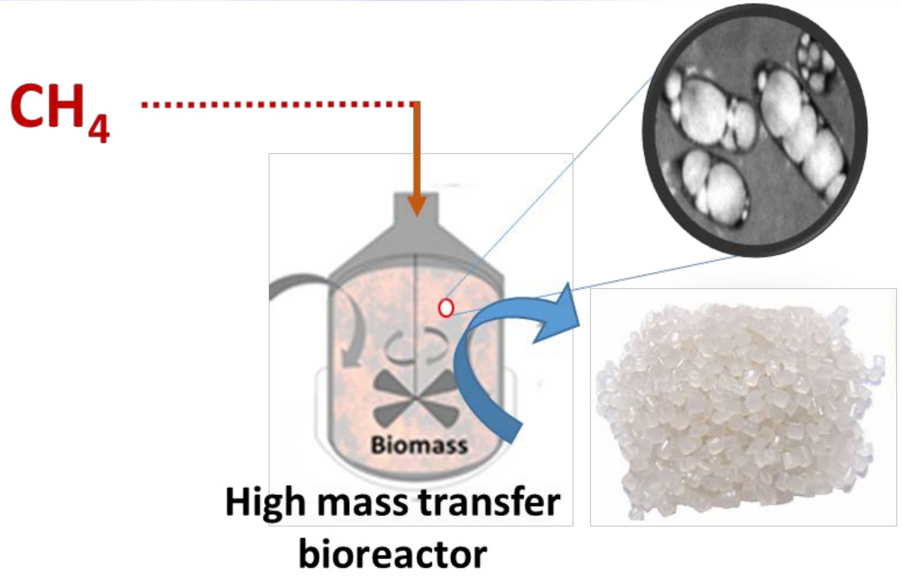


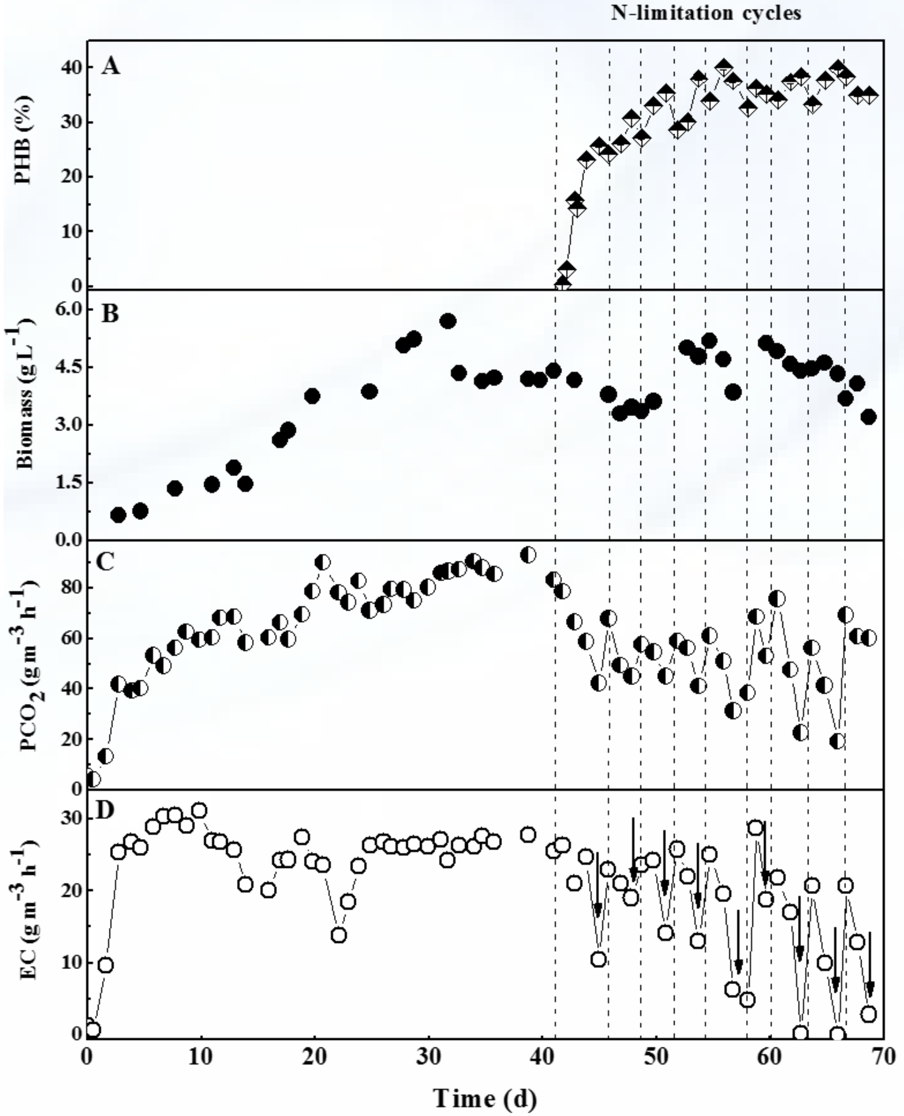
Landfill CH_4 emission:

- CH_4 = 33%
- O_2 = 66%

Reactor: Gas-Tight 2-L Bottles
Bacterial strain: *Methylocystis Hirsuta*
Nutrient Limited*:* N, K, Mn and N +Fe

Biological CH_4 Abatement coupled to Biopolymer Production





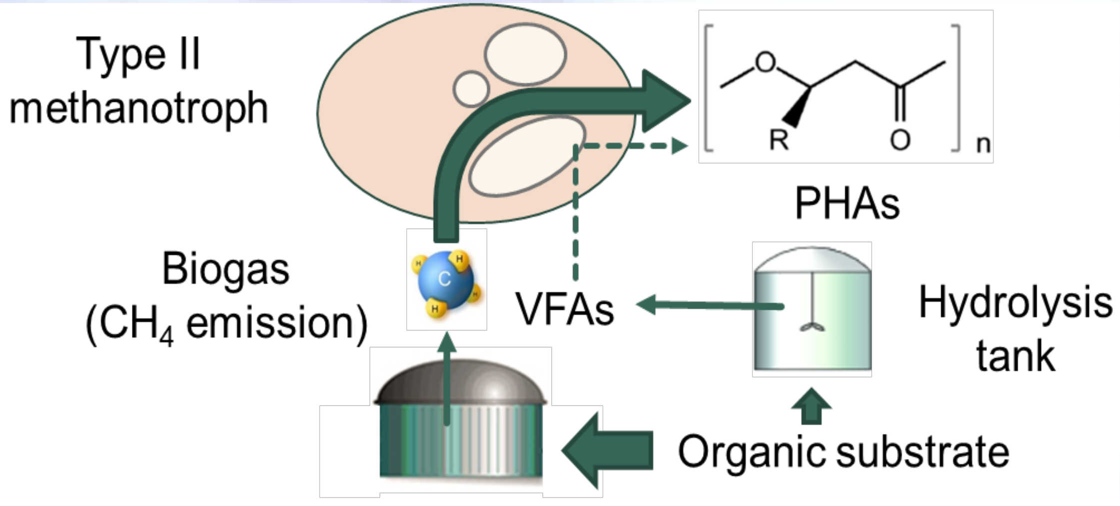
Landfill CH_4 emission:

- CH_4 = 4%
- O_2 = 20%

Reactor: Bubble Column

Bacterial strain: *Methylocystis Hirsuta*

Biological CH_4 Abatement coupled to Biopolymer Production



Contents lists available at ScienceDirect
Chemical Engineering Journal
journal homepage: www.elsevier.com/locate/cej
ELSEVIER

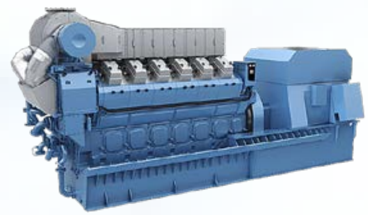
Biogas-based polyhydroxyalkanoates production by *Methylocystis hirsuta*: A step further in anaerobic digestion biorefineries

Juan C. López, Esther Arnáiz, Laura Merchán, Raquel Lebrero, Raúl Muñoz*
Department of Chemical Engineering and Environmental Technology, School of Industrial Engineerings, University of Valladolid, C/Dr. Mergelina s/n, 47011 Valladolid, Spain

URBIOFIN
urban biorefinery

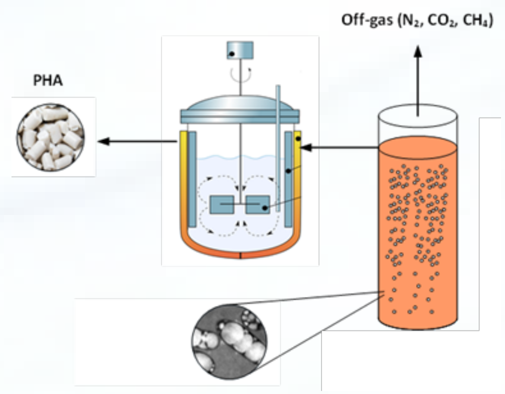
Culture condition	PHA		
	PHA content (wt %)	HB fraction (mol %)	HV fraction (mol %)
Biogas	43.1 ± 1.8	100	0
Biogas + Acetic acid	52.3 ± 0.7	100	0
Biogas + Propionic acid	47.9 ± 0.7	98	2
Biogas + Butyric acid	52.2 ± 2.1	100	0
Biogas + Valeric acid	53.8 ± 0.8	75	25

Biological CH_4 Abatement coupled to Biopolymer Production

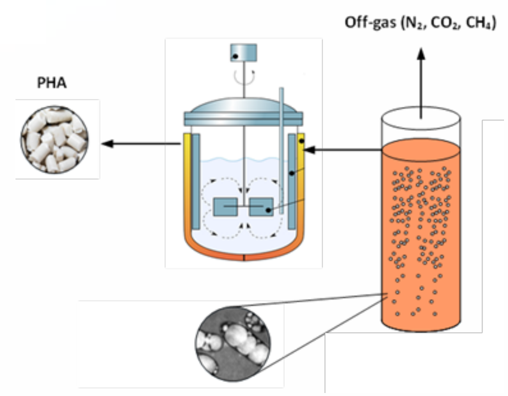


100 % biogas to CHP

1000 Nm^3 biogas h^{-1}

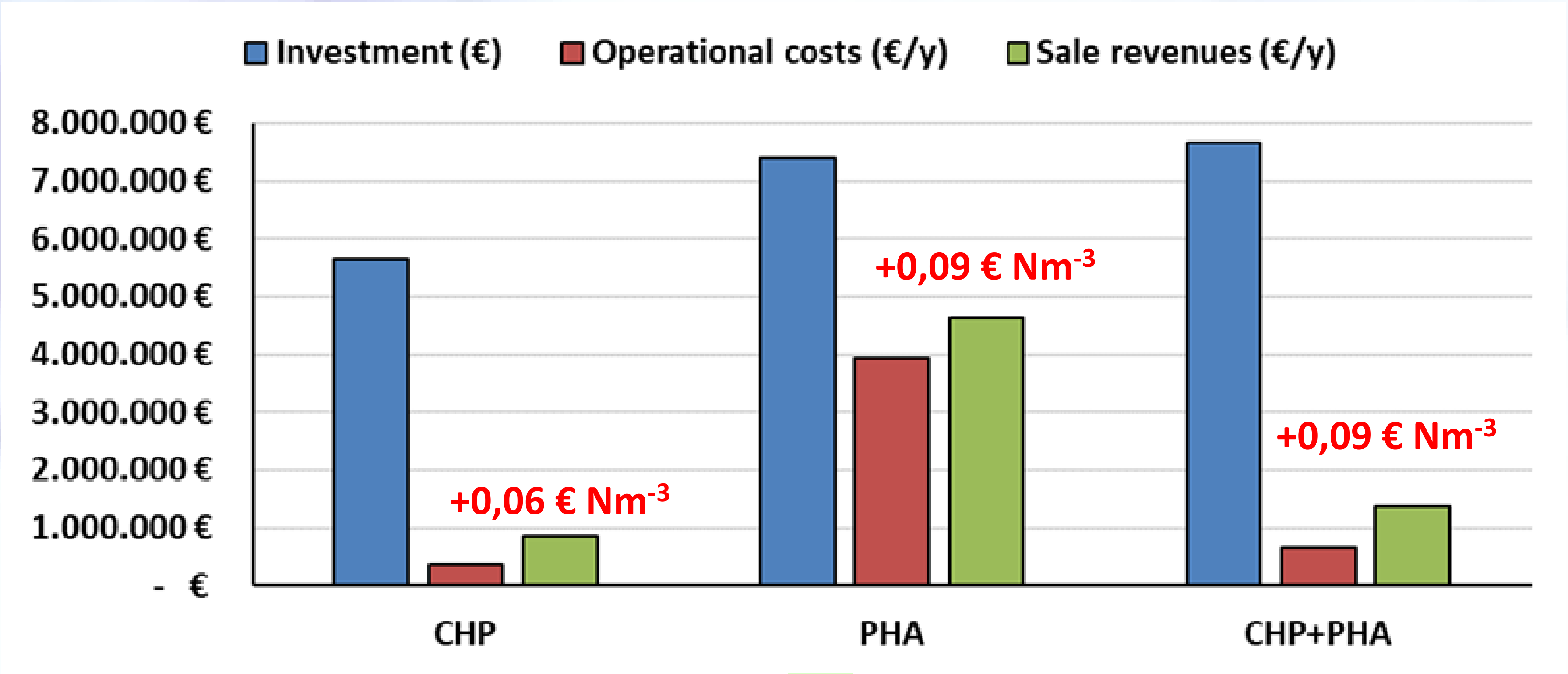


100 % biogas to PHA



55 % biogas to CHP+ 45 % biogas to PHA

Biological CH_4 Abatement coupled to Biopolymer Production



PHA production ~ 1,900 kg PHA d^{-1}
PHA selling price ~ 7,1 € kg^{-1}

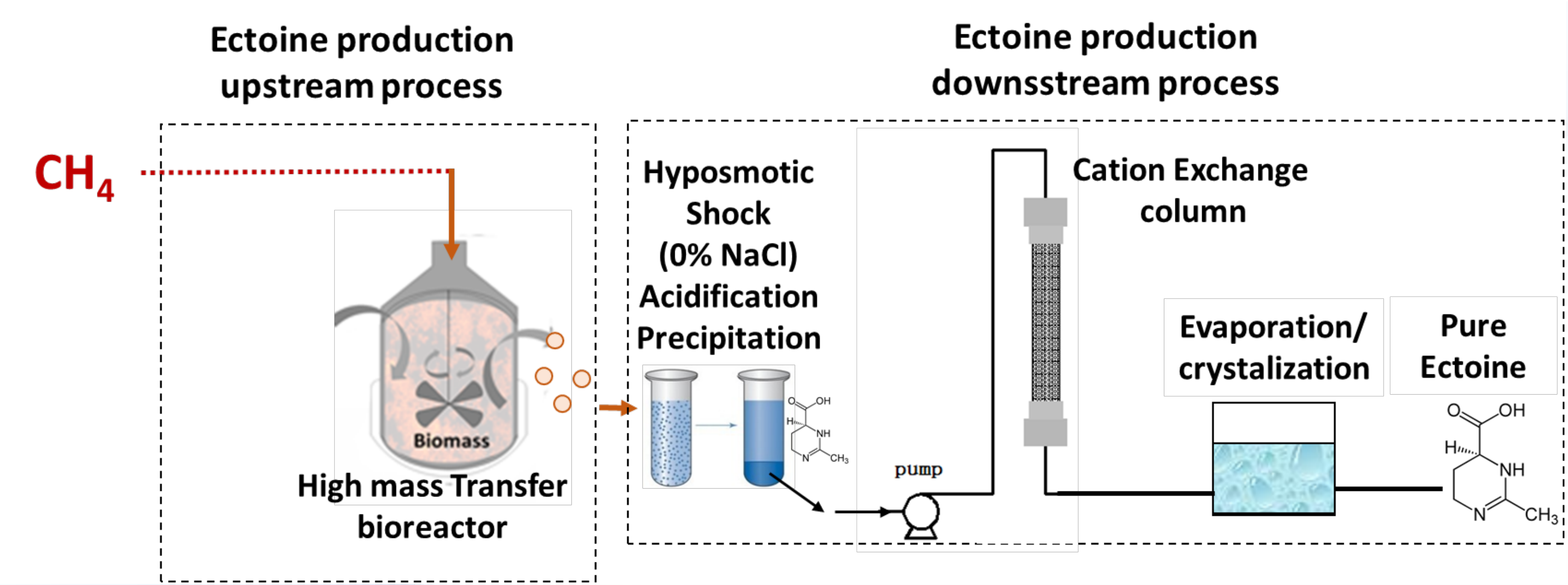
PHA production ~ 800 kg PHA d^{-1}
PHA selling price ~ 4,4 € kg^{-1}

Biological CH_4 Abatement coupled to Ectoine Production

Contents lists available at ScienceDirect
Chemical Engineering Journal
journal homepage: www.elsevier.com/locate/cej
ELSEVIER
Short communication

Ectoine *bio-milking* in methanotrophs: A step further towards methane-based bio-refineries into high added-value products

Sara Cantera, Raquel Lebrero, Suní Rodríguez, Pedro A. García-Encina, Raúl Muñoz *



Microbial protective compound → High salinity
Raw material in Cosmetic Industry
Market Value: 1300 € kg^{-1}

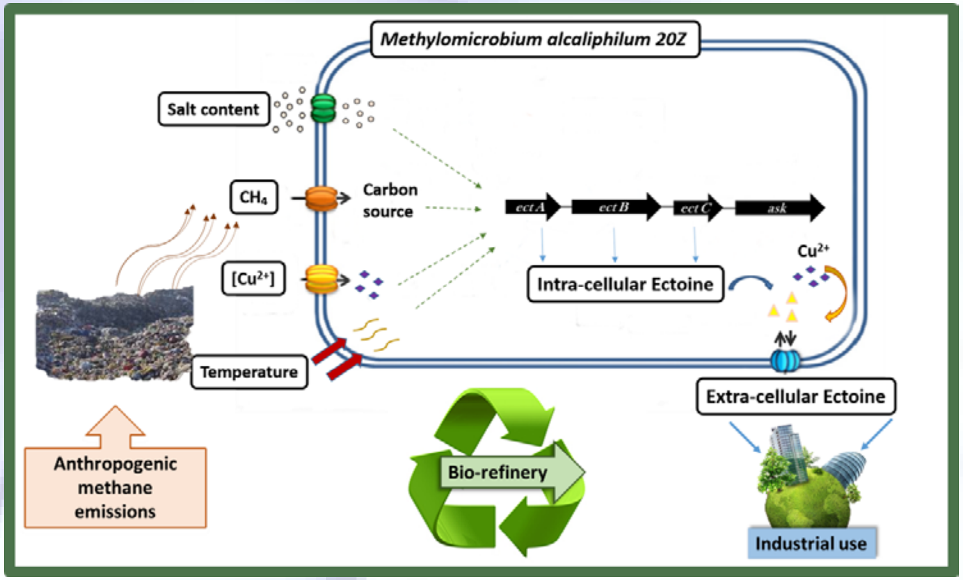
Biological CH_4 Abatement coupled to Ectoine Production

Contents lists available at ScienceDirect
Journal of Environmental Management
journal homepage: www.elsevier.com/locate/jenvman

Research article

Valorization of CH_4 emissions into high-added-value products: Assessing the production of ectoine coupled with CH_4 abatement

Sara Cantera, Raquel Lebrero, Lidia Sadornil, Pedro A. García-Encina, Raúl Muñoz*



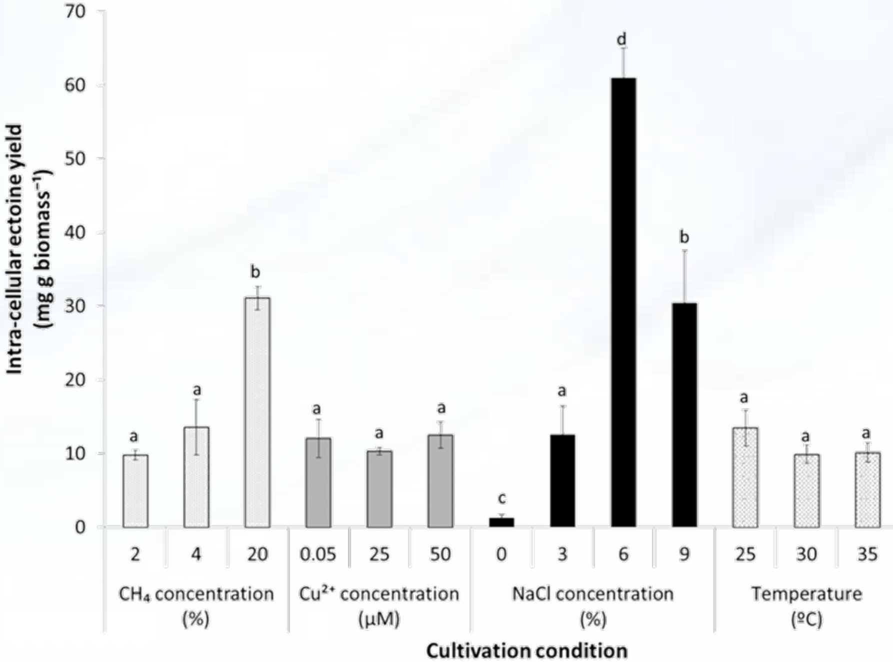
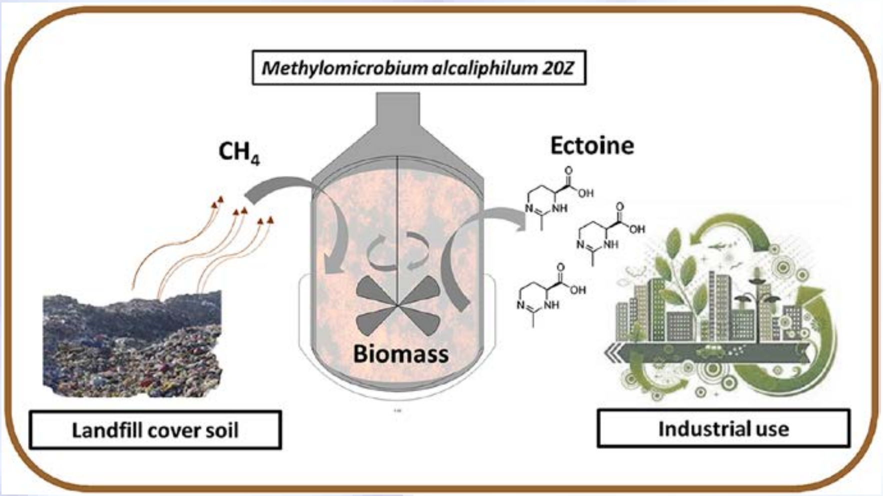


Table 1
Cultivation conditions evaluated during *Methylomicrobium alcaliphilum 20Z* batch cultivation tests.

Test series (TS)	Operating conditions			
	CH_4 (%)	Cu^{2+} (µM)	NaCl (%)	T (°C)
TS1	2, 4, 20	0.05	3	25
TS2	20	0.05, 25, 50	3	25
TS3	20	0.05	0, 3, 6, 9	25
TS4	20	0.05	3	25, 30, 35
TS5	20	50	6	30

Biological CH_4 Abatement coupled to Ectoine Production



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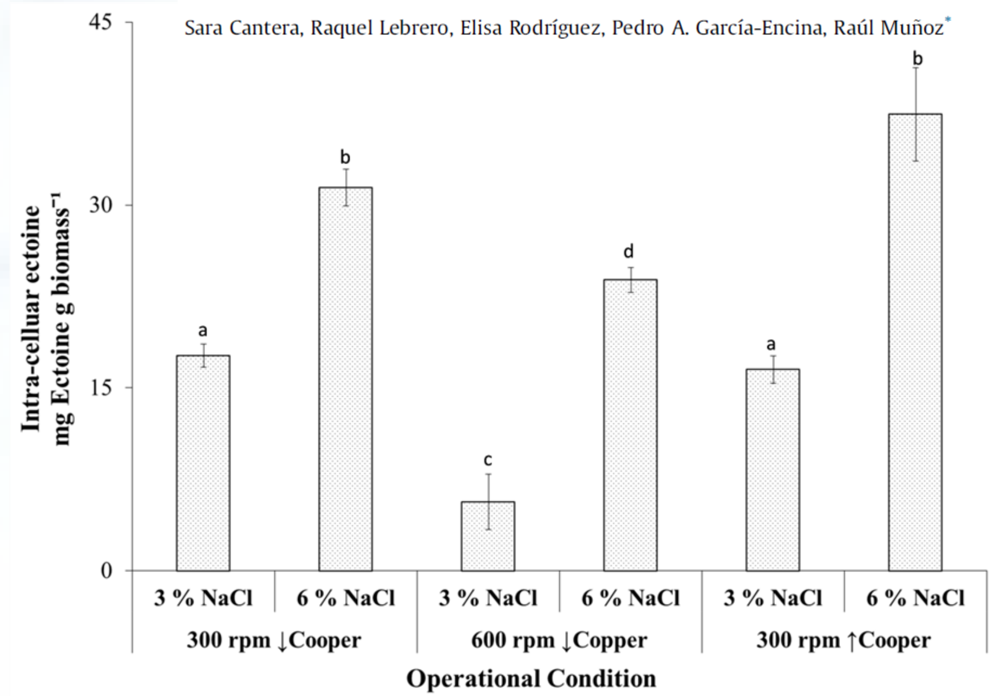
Continuous abatement of methane coupled with ectoine production by *Methylomicrobium alcaliphilum 20Z* in stirred tank reactors: A step further towards greenhouse gas biorefineries

Sara Cantera, Raquel Lebrero, Elisa Rodríguez, Pedro A. García-Encina, Raúl Muñoz*



Landfill CH_4 emission:

- CH_4 = 4%
- O_2 = 20%

Reactor: Stirred Tank Reactor

Bacterial strain: *Methylomicrobium Alcaliphilum*

TLR 5 → DEEP PURPLE → **TLR 7**

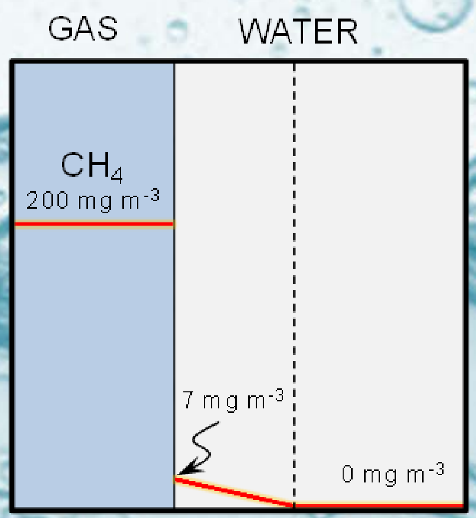
High Mass Transfer Bioreactors

Two Phase Partitioning Bioreactors

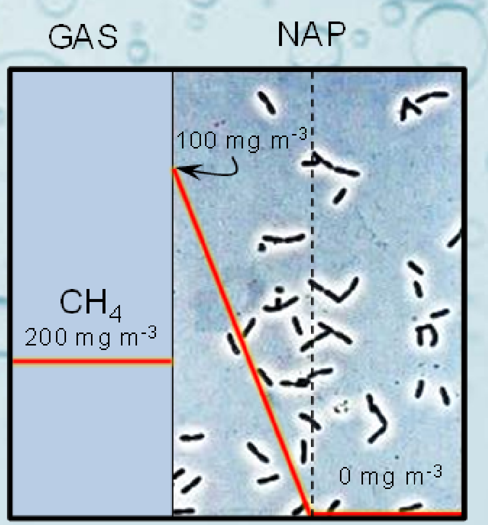
TPPBs are based on the addition of an immiscible, non-volatile, biocompatible and non-biodegradable organic solvent with a high affinity for the target gas pollutant…..

$$F_{G/A} = K_1 a_{G/A} \left(\frac{[GHG]_G}{H_{GHG}} - [GHG]_A \right)$$

	MERITs
✓	NEW AND EFFICIENT PATHWAY FOR VOC MASS TRANSFER
✓	INCREASED PROCESS STABILITY AS A RESULT OF BUFFER CAPACITY OF THE ORGANIC PHASE
✓	THE PRESENCE OF THE ORGANIC PHASE INCREASES THE GAS-WATER INTERFACIAL AREA.



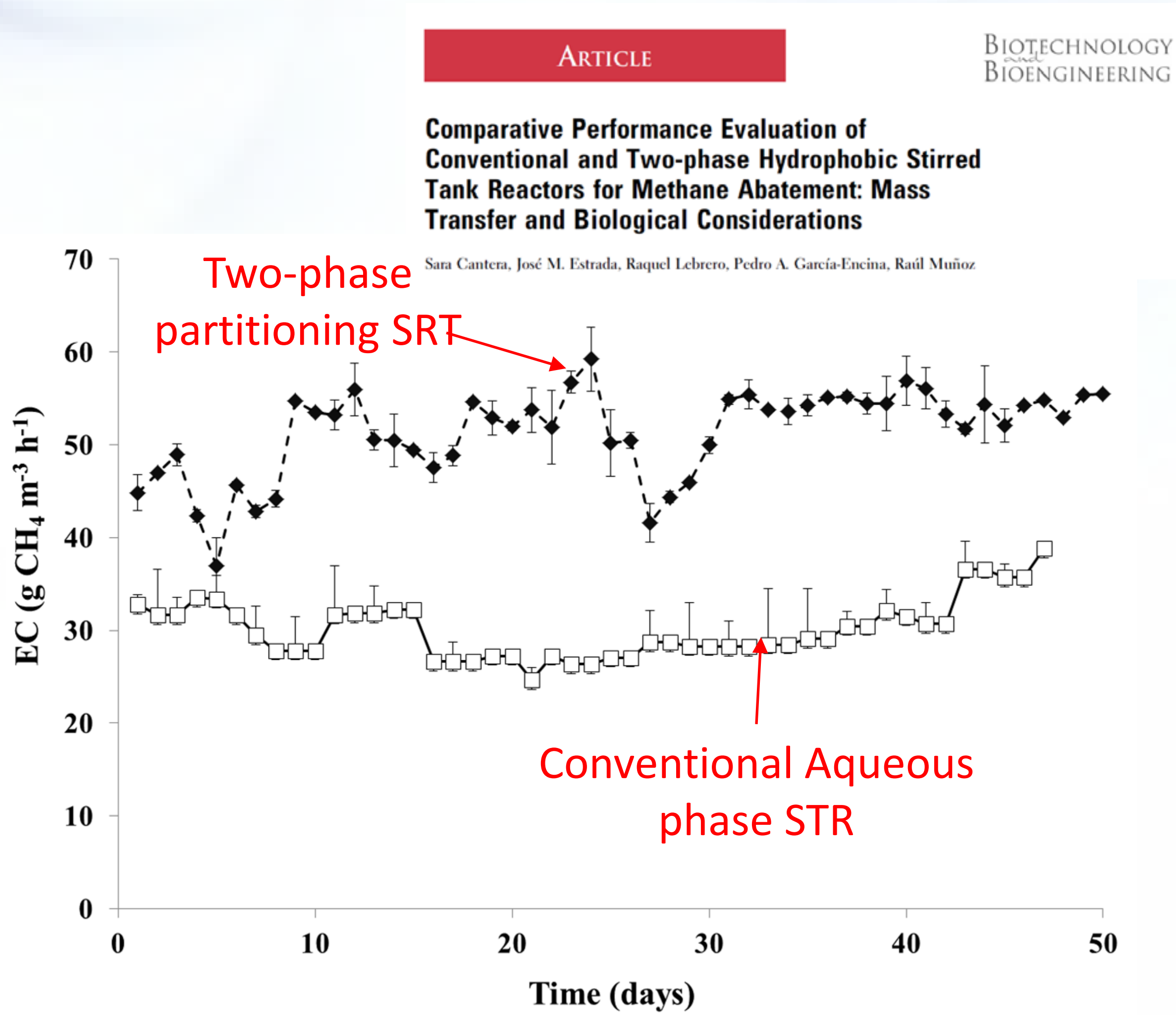
Driving force = 7 mg m^{-3}



Driving force = 100 mg m^{-3}

High Mass Transfer Bioreactors

Two Phase Partitioning Bioreactors


ARTICLE

BIOTECHNOLOGY and BIOENGINEERING

Comparative Performance Evaluation of Conventional and Two-phase Hydrophobic Stirred Tank Reactors for Methane Abatement: Mass Transfer and Biological Considerations

Sara Cantera, José M. Estrada, Raquel Lebrero, Pedro A. García-Encina, Raúl Muñoz

Landfill CH_4 emission:

- CH_4 = 4%
- O_2 = 20 %

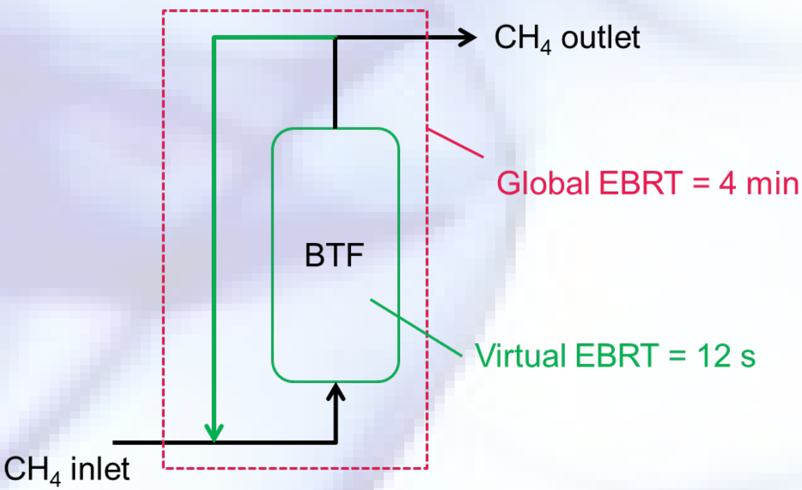
Reactor: Stirred Tank Reactor

Bacterial strain: *Mixed consortium*

NAP: 10 % of silicone oil

High Mass Transfer Bioreactors

Internal Gas Recycling Bioreactors



High K_la increases at a negligible pressure drop→

EC increase by a factor of 2.5

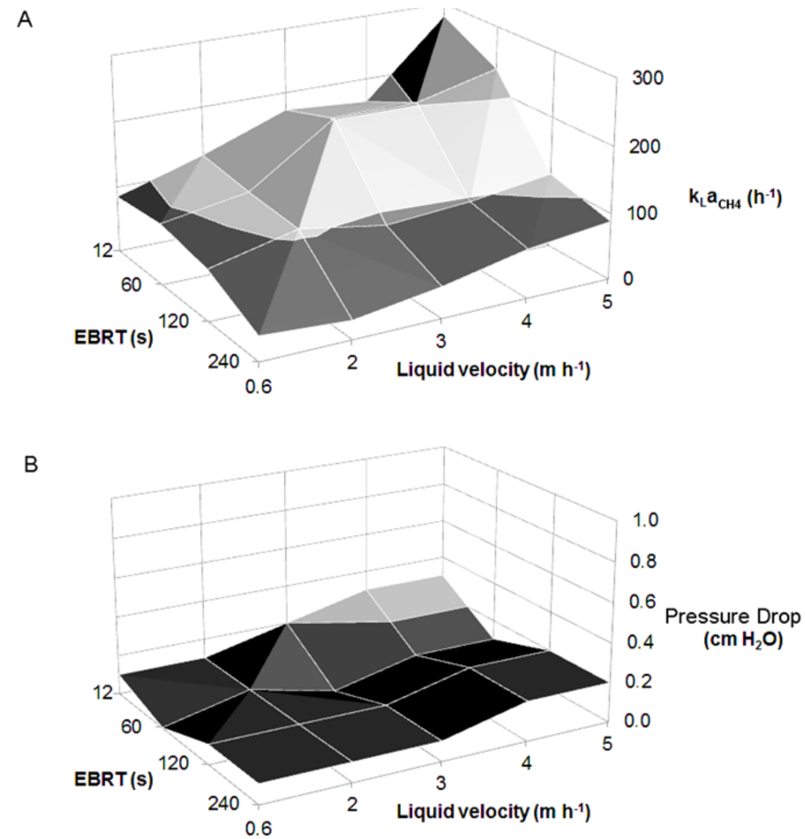
Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

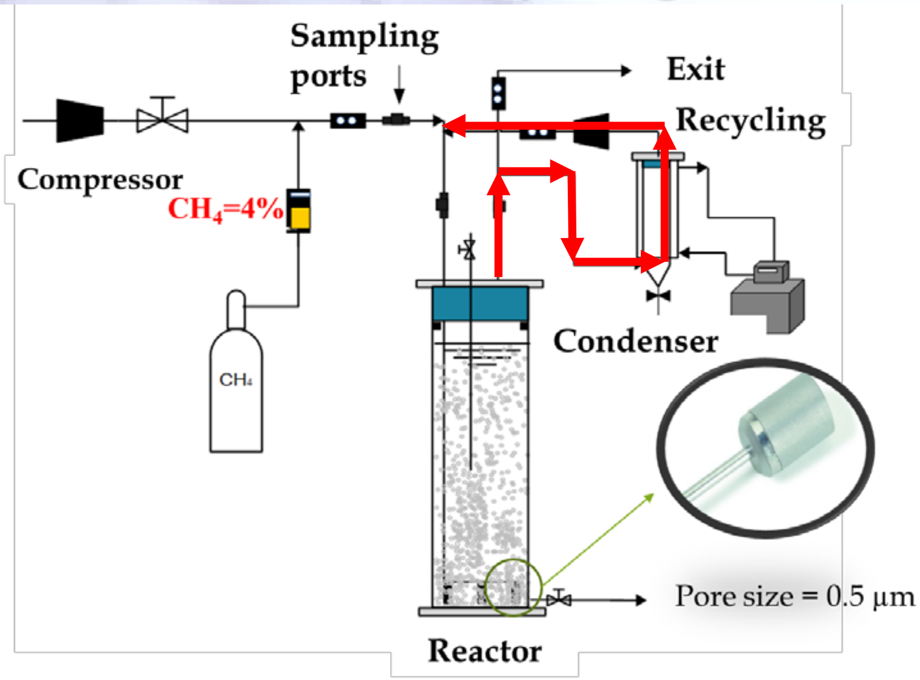
Methane abatement in a gas-recycling biotrickling filter: Evaluating innovative operational strategies to overcome mass transfer limitations

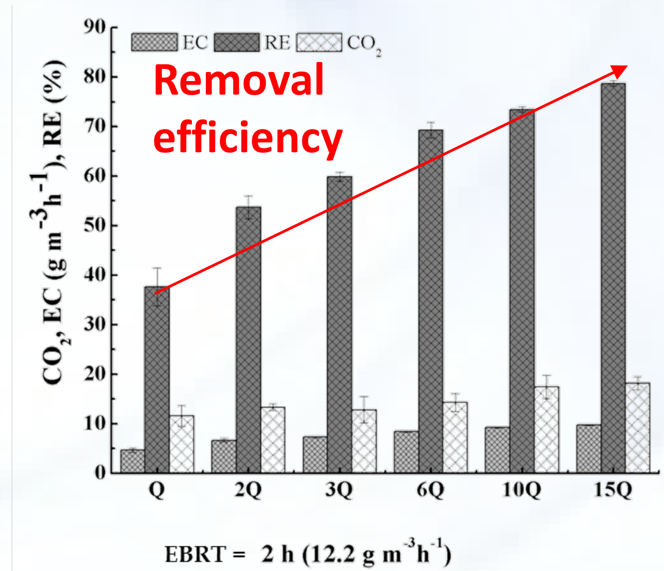
José M. Estrada, Raquel Lebrero, Guillermo Quijano, Rebeca Pérez, Ivonne Figueroa-González, Pedro A. García-Encina, Raúl Muñoz *

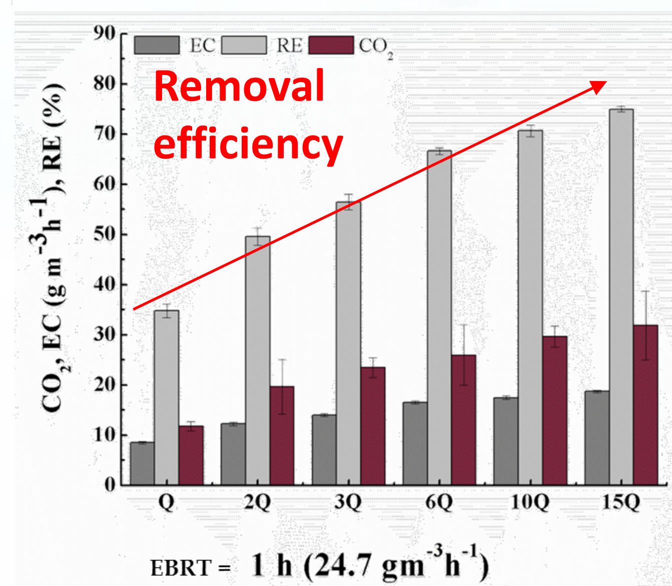


High Mass Transfer Bioreactors

Internal Gas Recycling Bubble Column







Landfill CH_4 emission:

- CH_4 = 4%
- O_2 = 20%

Reactor: Bubble Column

Bacterial strain: *Methylocystis Hirsuta*

Take HOME Message

- **Microalgae biotechnology** represents a promising platform for the bioconversion of biogas to biomethane coupled to nutrient recovery from digestates
- **Two-stage bioscrubbers** based on heterotrophic N_2O reduction were successfully engineered for the abatement of N_2O from WWTP emissions using WW as e-donor
- **N_2O abatement** from industrial emissions can be **coupled to biopolymer production**
- **Diluted CH_4 emissions and biogas** can be successfully valorized into **biopolymers** and **ectoine** in high-mass transfer bioreactors
- **Nitrogen limitation** supported the **highest biopolymer accumulation**, while **Valeric Acid** supplementation allowed **tailoring the composition of the PHBV copolymer**.
- **Two-phase partitioning** and **Internal Gas-Recycling bioreactors** can significantly enhance the gas-liquid mass-transfer of CH_4

Acknowledgments

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HORIZON 2020

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Thank you for your Attention

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