Recent advances in biological biogas upgrading and valorization

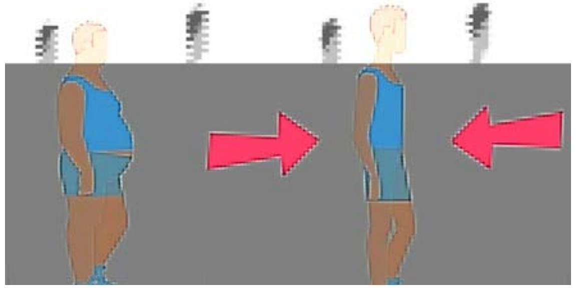
Raúl Muñoz

Institute of Sustainable Processes, University of Valladolid (Spain)

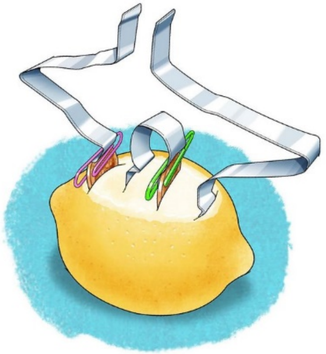
16TH IWA World Conference on Anaerobic Digestion
Accelerating natural cycles with anaerobic digestion

Change in AD perception

Waste Reduction Technology



Electricity production



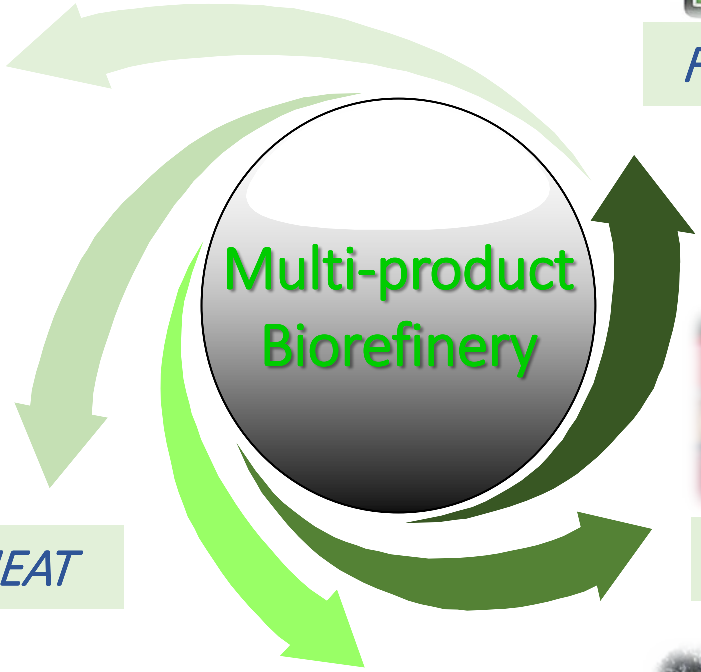
Multi-product Biorefinery

AD as a multi-product Biorefinery

- **Anaerobic Digestion as an effective Carbon and Nutrient recycling platform**

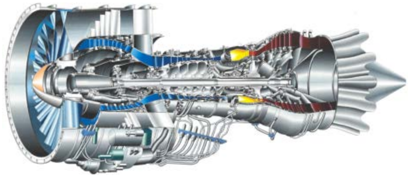
FINE & BULK CHEMICALS

BIOFERTILIZERS



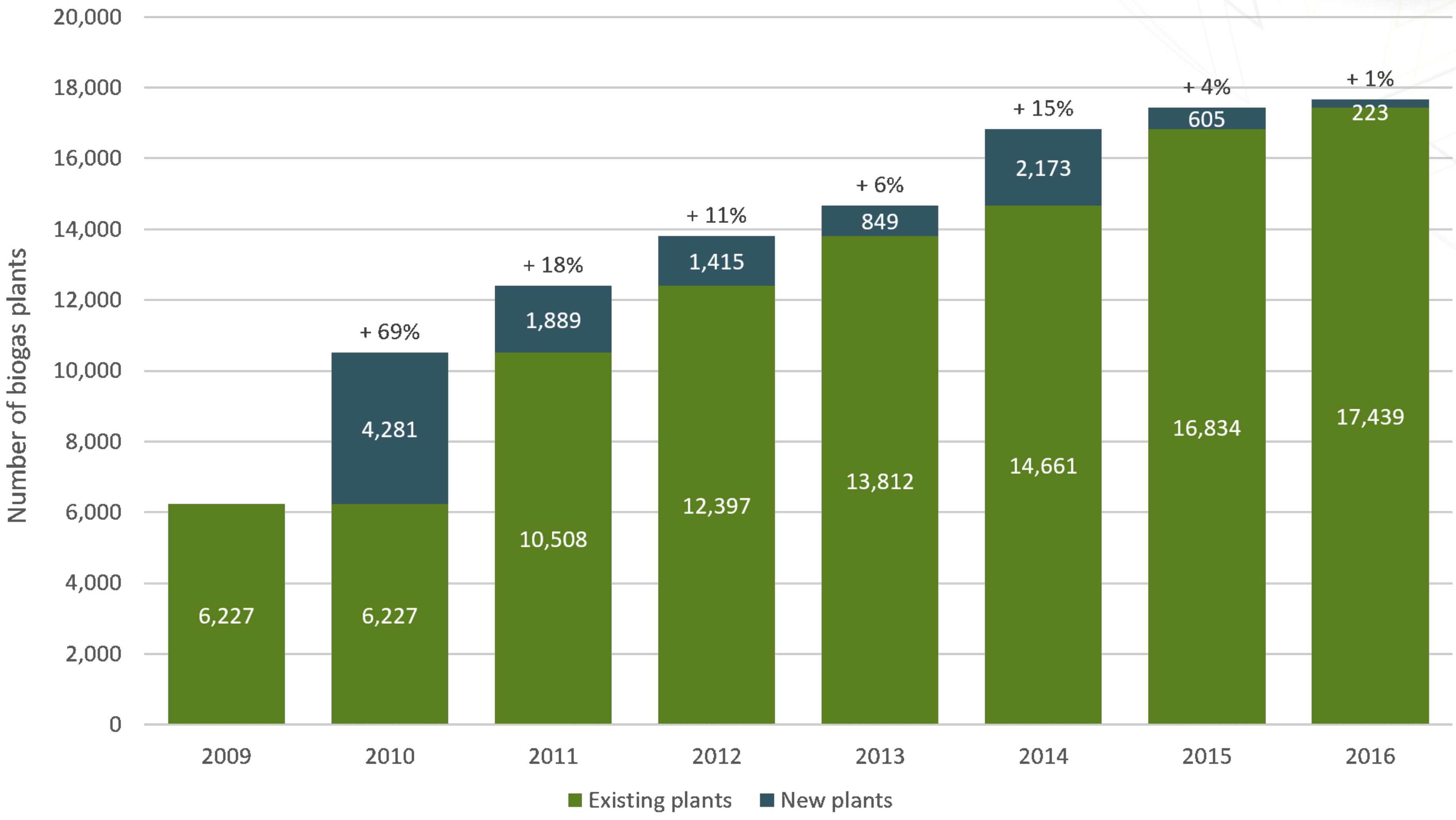
BIOMETHANE FOR VEHICLES

ELECTRICITY & INDUSTRIAL HEAT



BIOMETHANE FOR NATURAL GAS GRIDS

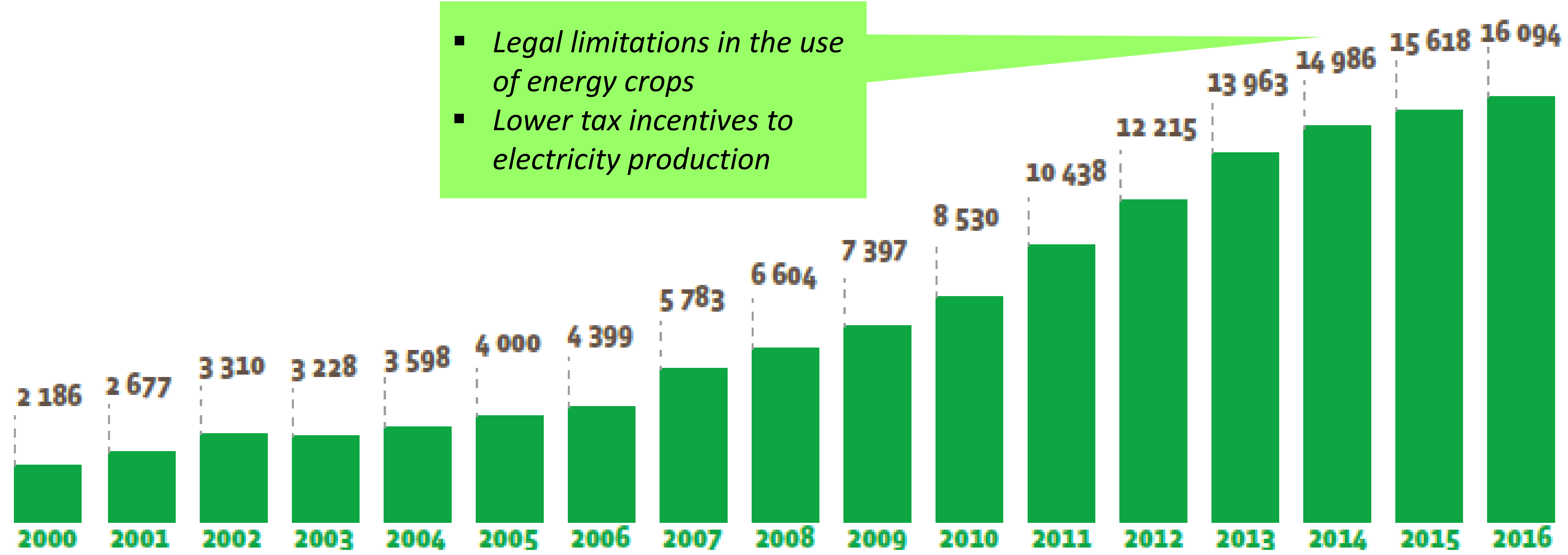
Biogas production plants in Europe



*(EBA, **2018**)*

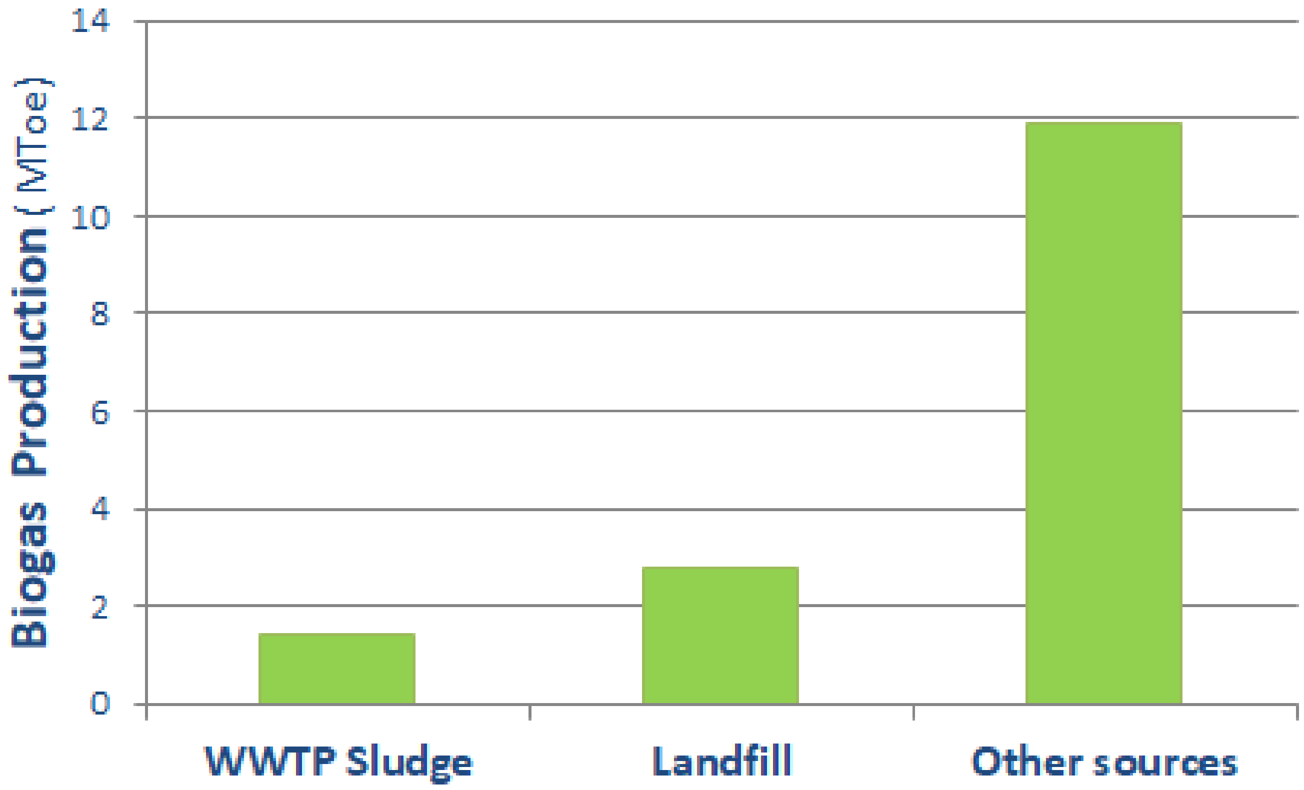
Primary energy production from Biogas in Europe

Evolution of primary biogas energy production in European union (EU 28) since 2000 (in ktoe)



Source: EurObserv'ER 2017

Primary energy production from Biogas in Europe

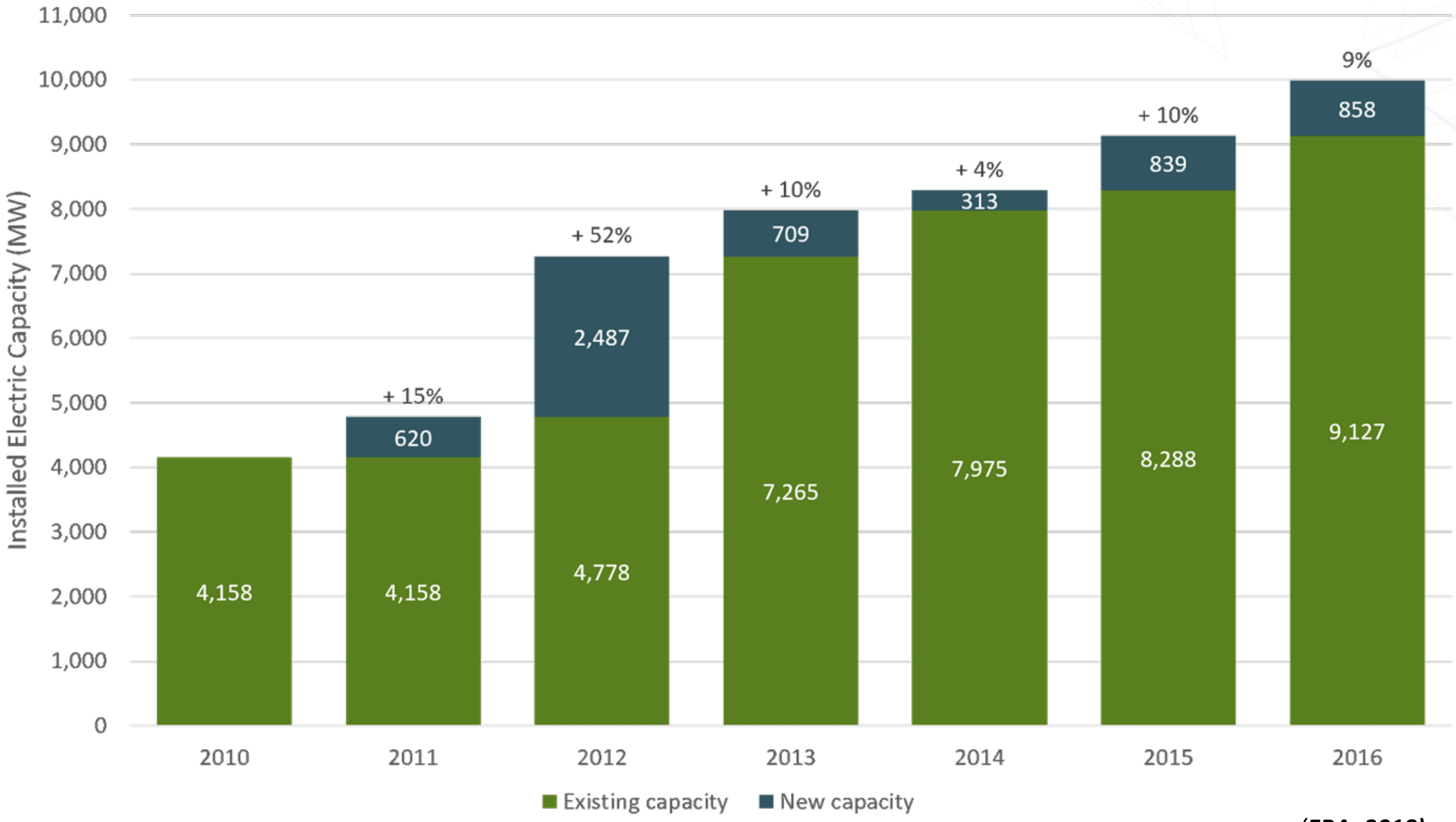


(EBA, 2018)

Other sources
Livestock waste, urban solid waste, energy crops, etc

- **Annual production of biogas in the EU will reach 41 Mtoe in 2030 (EBA)**
- **Estimated annual production potential of biogas in the world can reach 658 Mt CH_4**

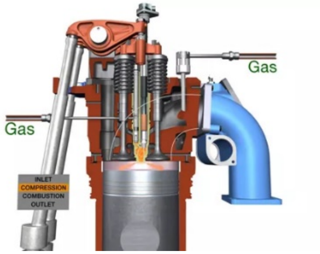
Electric capacity from Biogas in Europe



(EBA, 2018)

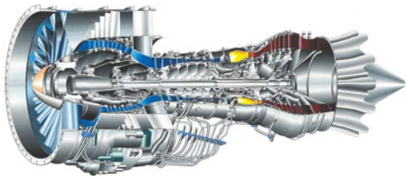
Biogas quality requirements

INTERNAL COMBUSTION ENGINEES



Siloxanes < 9-44 ppm_v
H_2S <200-1000 ppm_v

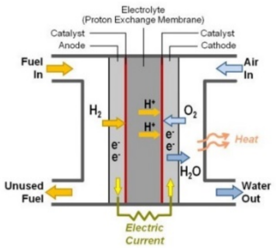
TURBINES & MICROTURBINES



Siloxanes < 0.006 ppm_v
H_2S <10000 ppm_v

Upgrading Requirements

FUEL CELLS



Siloxanes < 1 ppm_v
H_2S <10 ppm_v

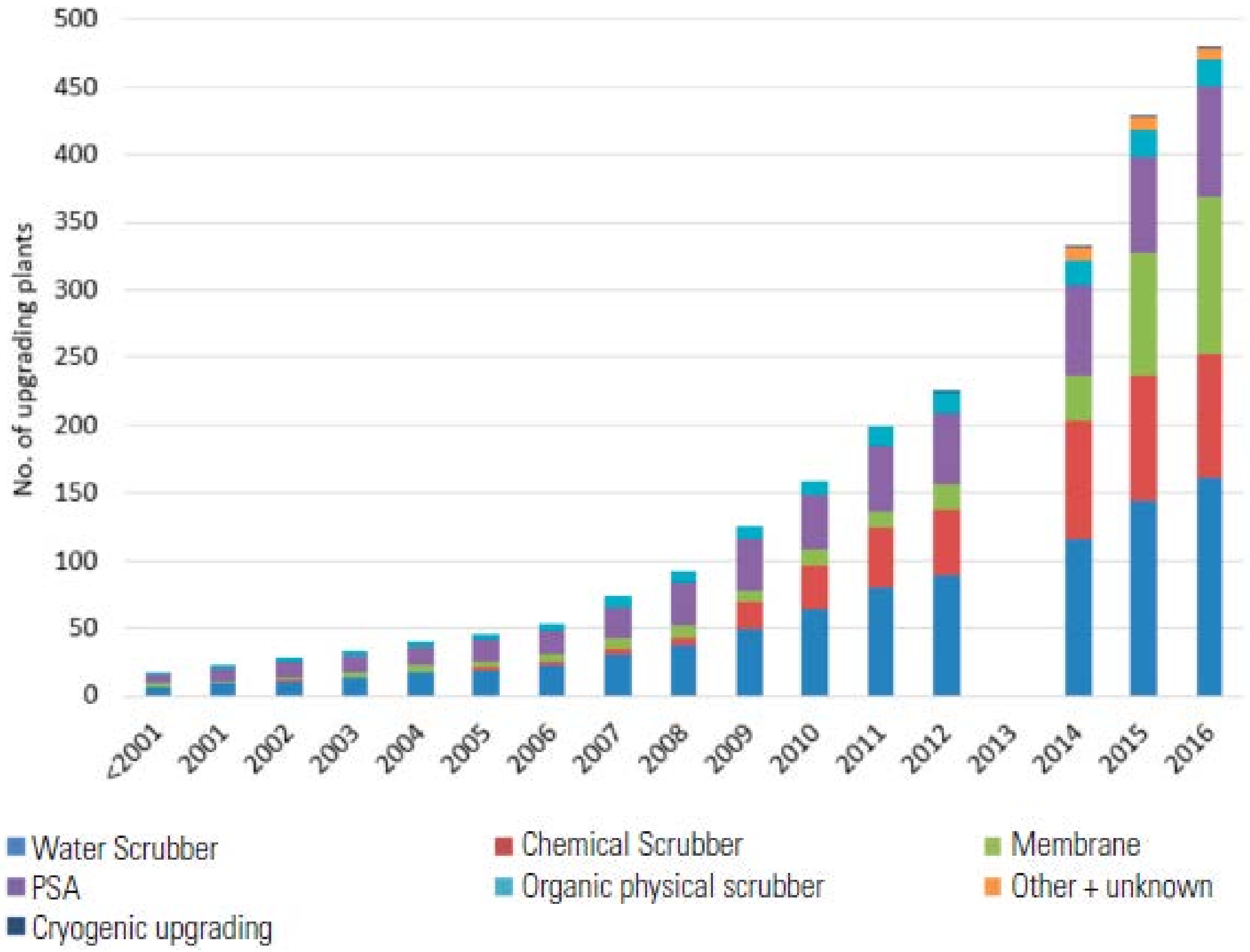
INJECTION INTO NATURAL GAS GRIDS

Standard EN 16723-1

VEHICLE FUEL

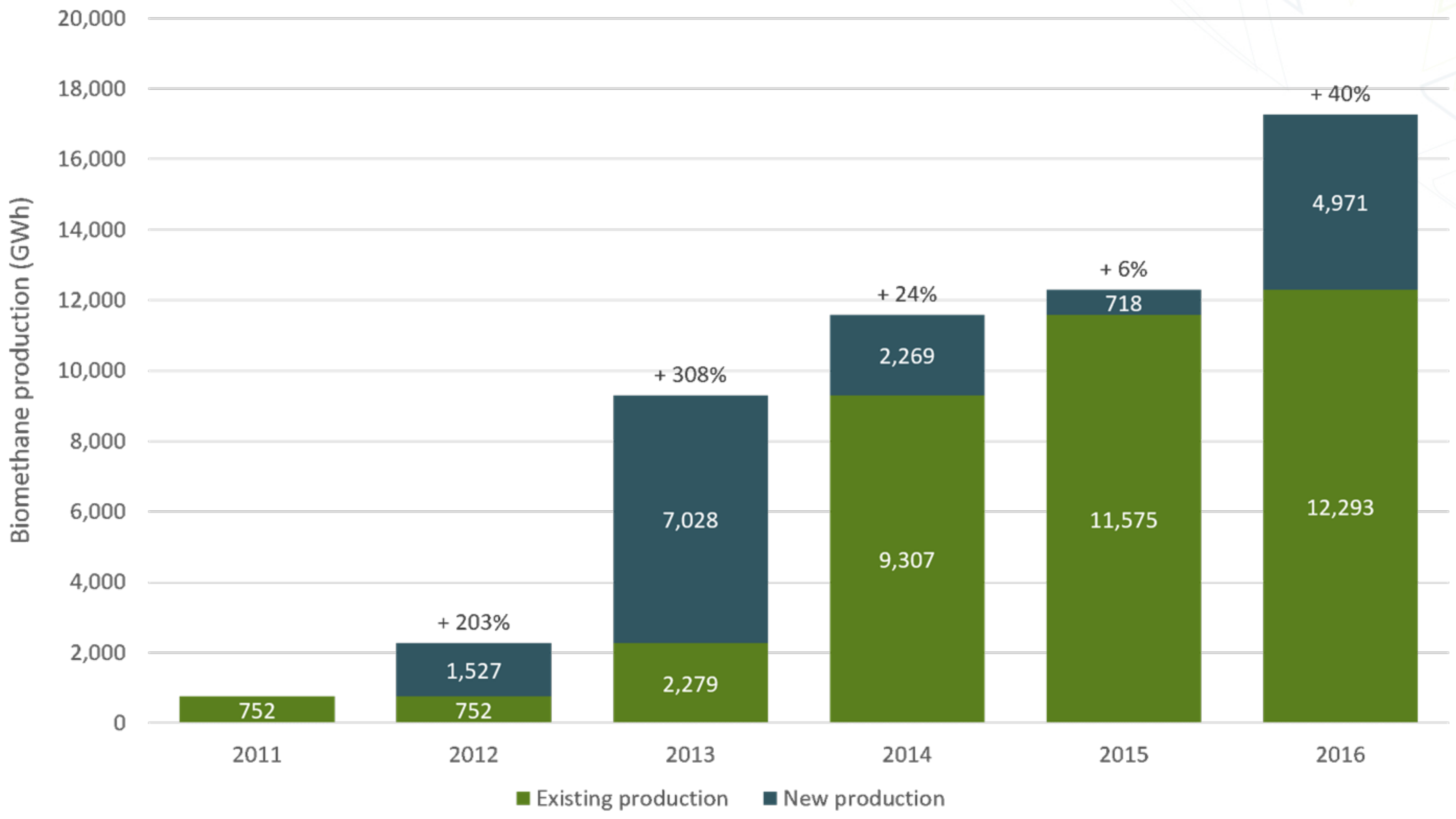
Standard EN 16723-2

Biogas upgrading plants in the IEA Bioenergy Task 37 group countries



(IEA Bioenergy 2018)

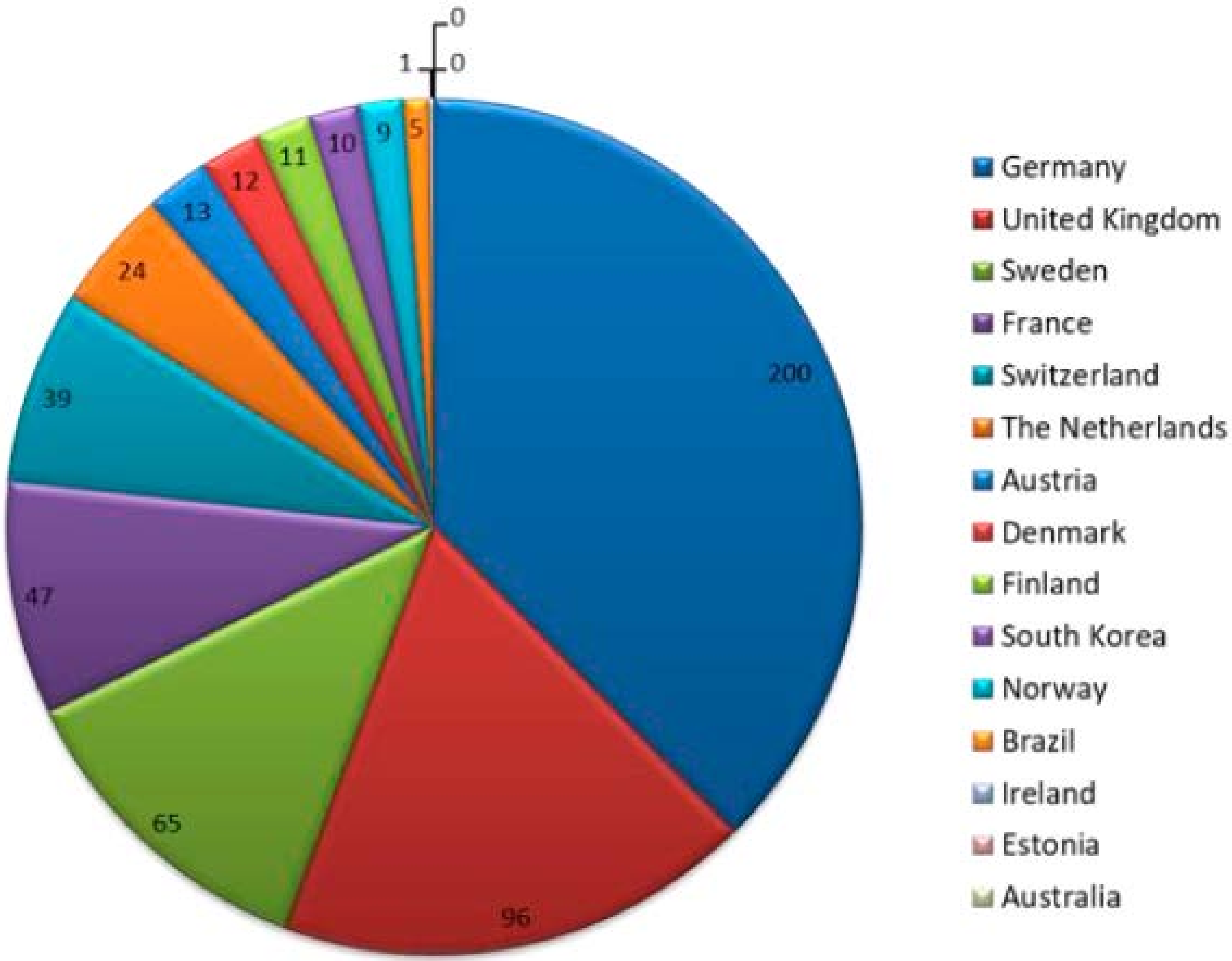
Biomethane production in Europe



(EBA, 2018)

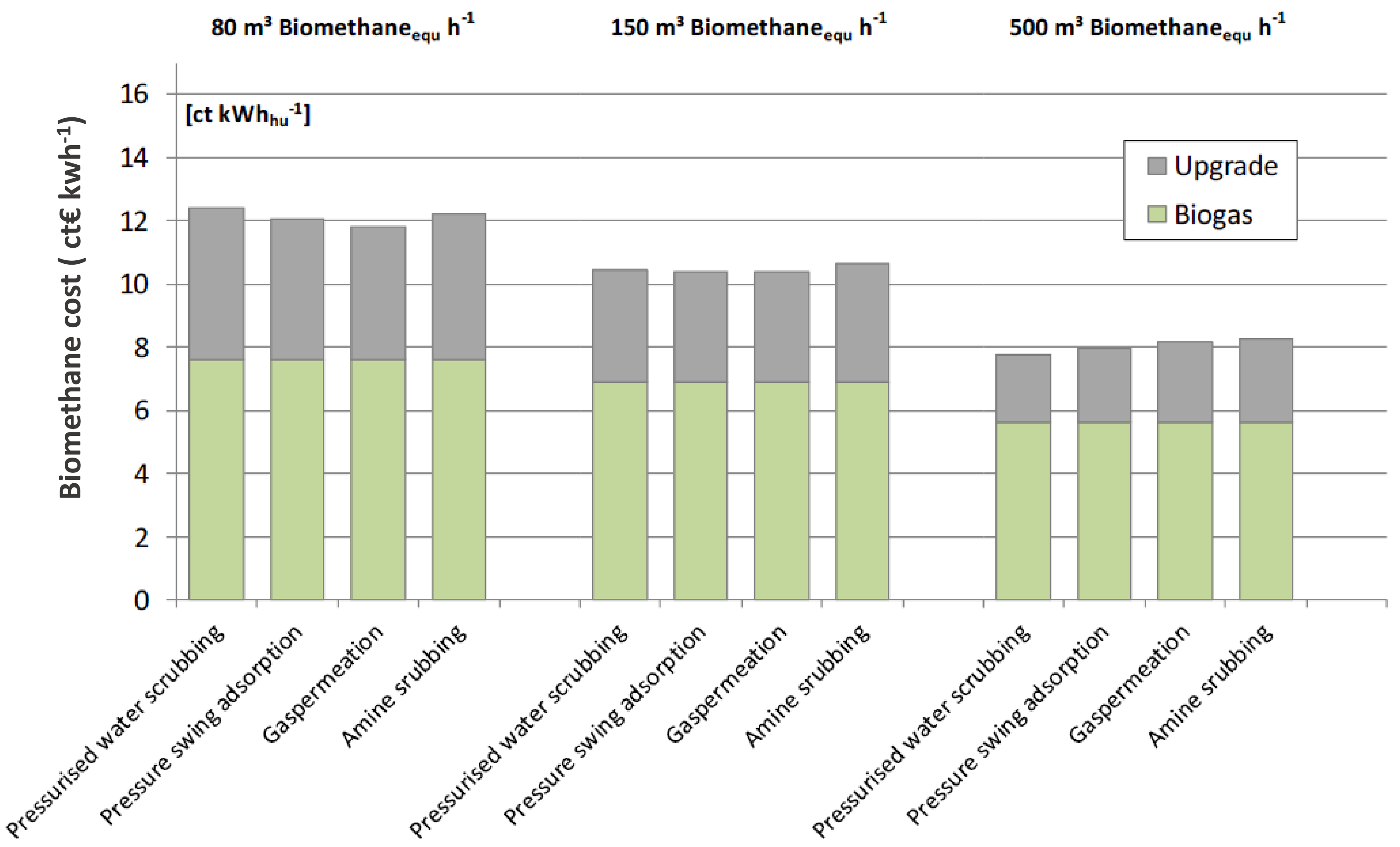
Distribution of Biogas upgrading plants in the IEA Task 37 group countries

2017



(EBA, 2018)

The price of Biomethane

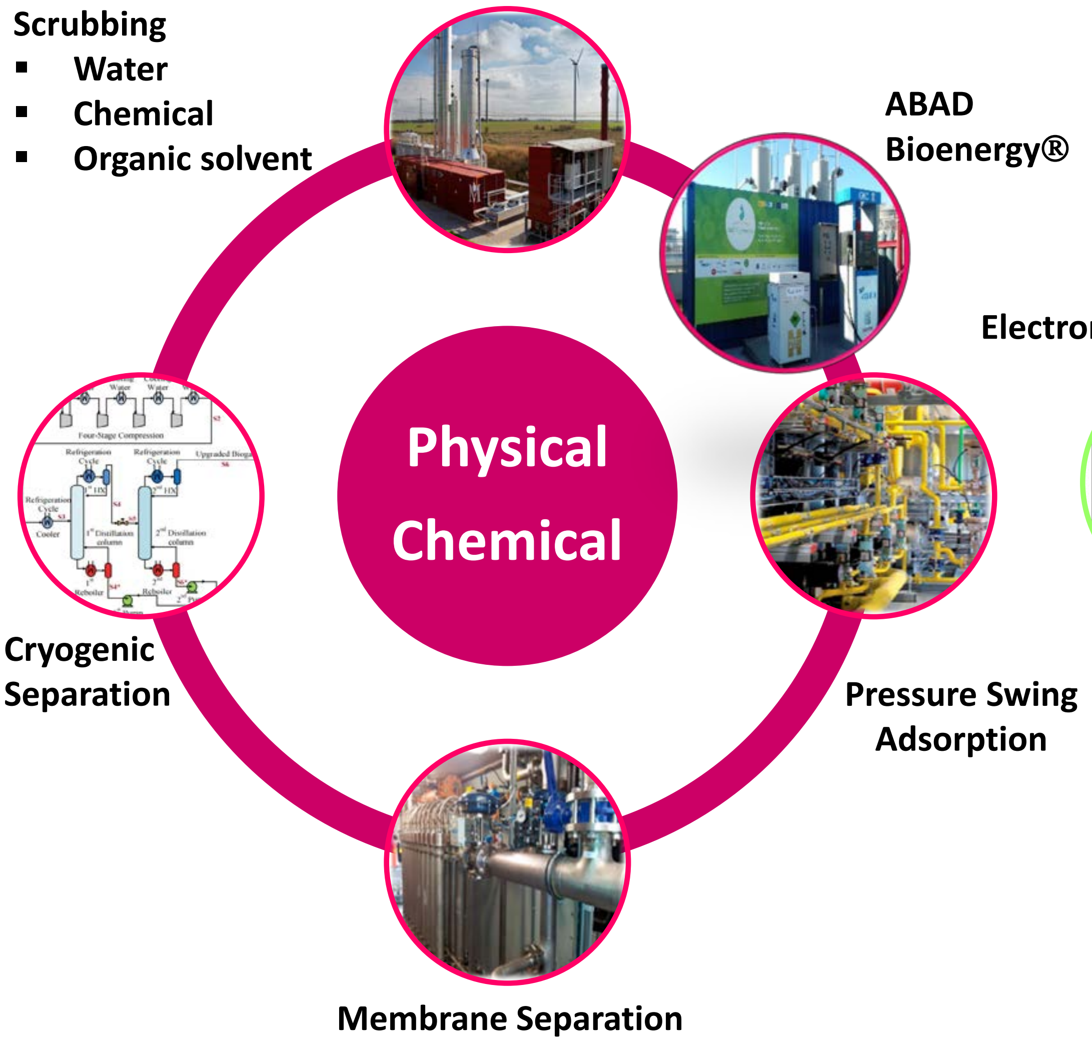


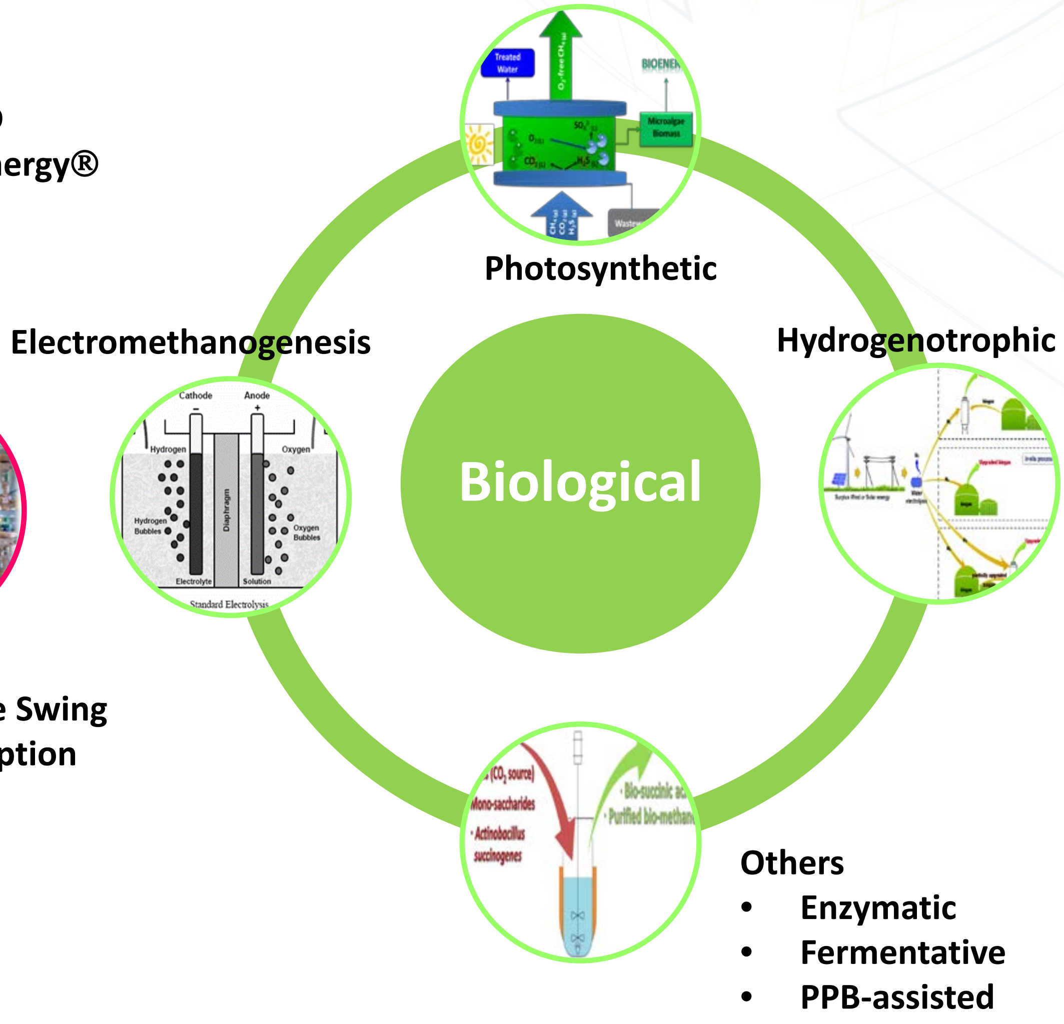
(Biosurf, 2016)

CO_2 Removal Technologies

CO_2 Removal Technologies

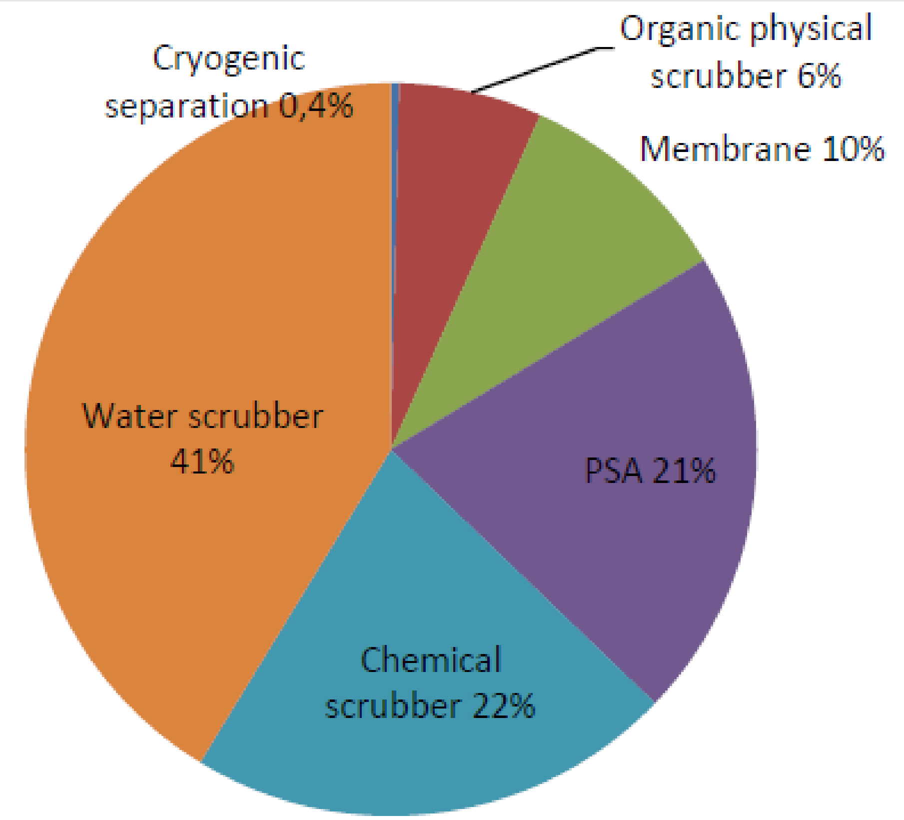
A large portfolio of technologies





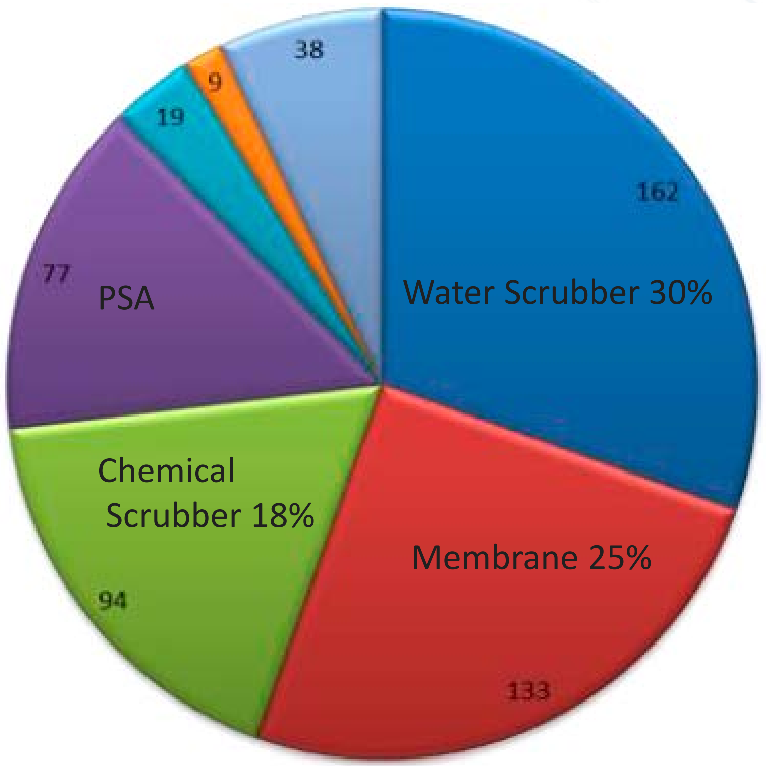
Distribution of CO_2 removal technologies in IEA Task 37 group countries

2012



(IEA, **2014**)

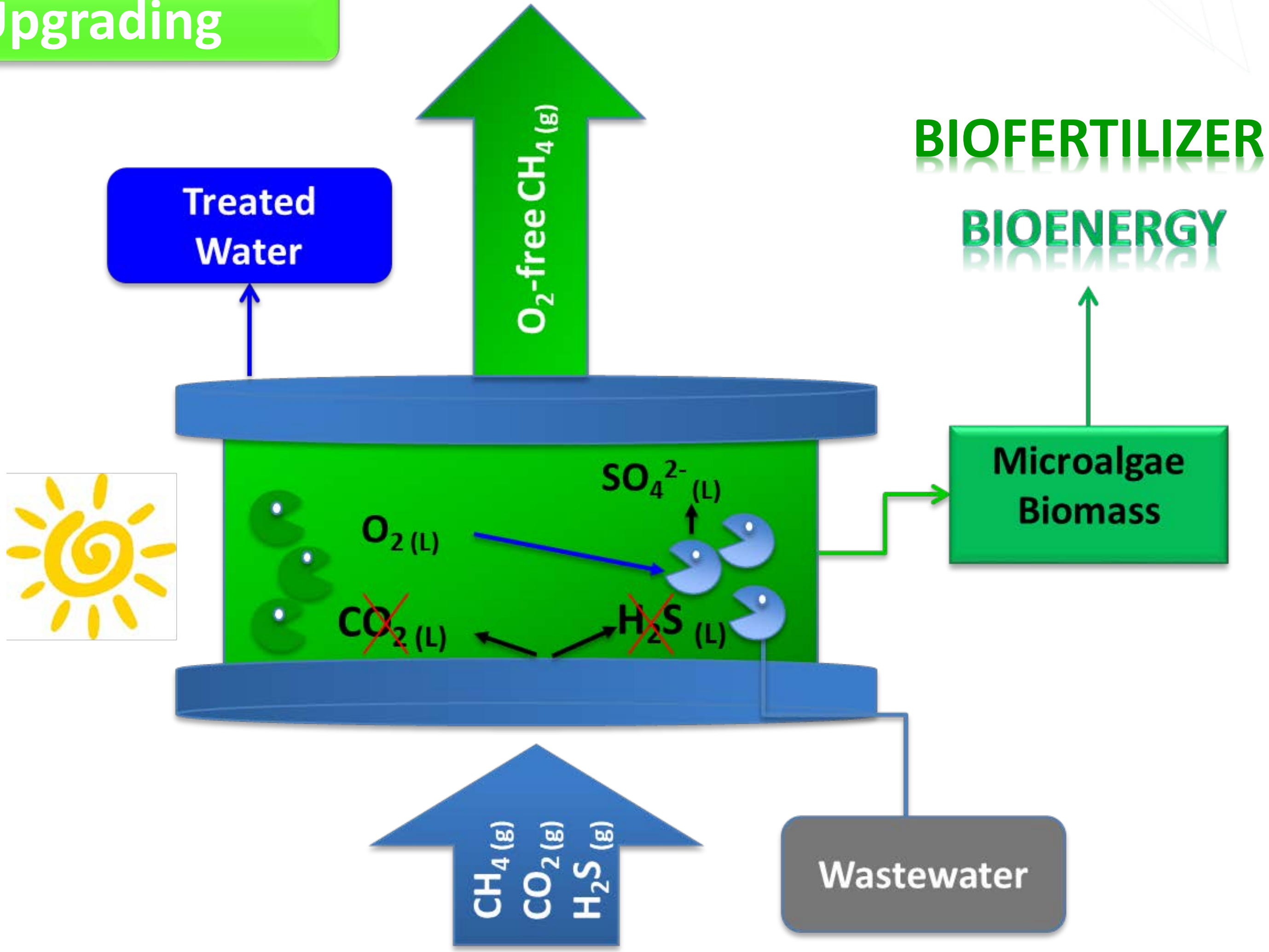
2017



(IEA, **2018**)

Biological CO_2 Removal Technologies

Photosynthetic Upgrading



Biological CO_2 Removal Technologies

INCOVER

Photosynthetic Upgrading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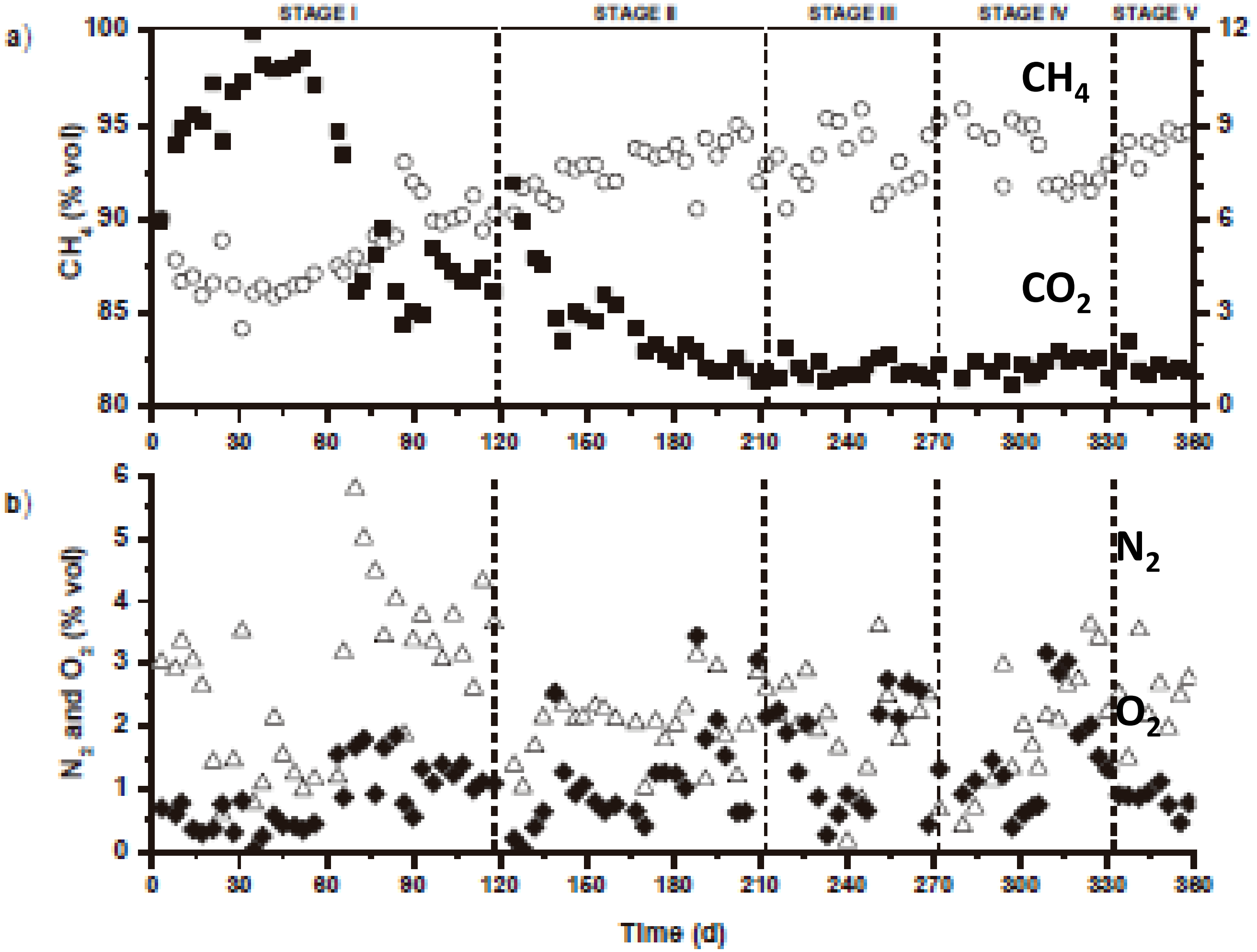
journal homepage: www.elsevier.com/locate/biortech

ELSEVIER

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,*]



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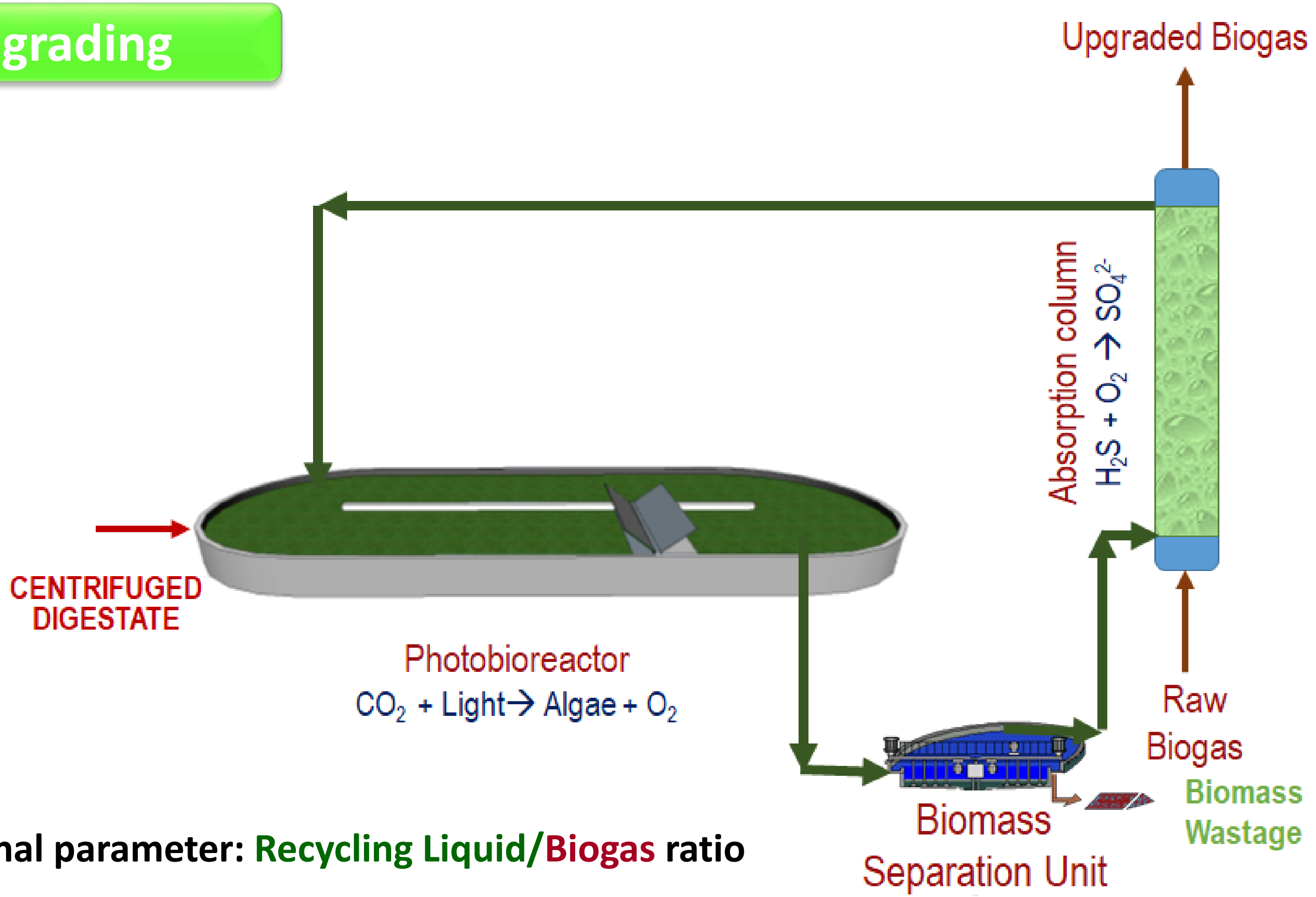
Biological CO_2 Removal Technologies

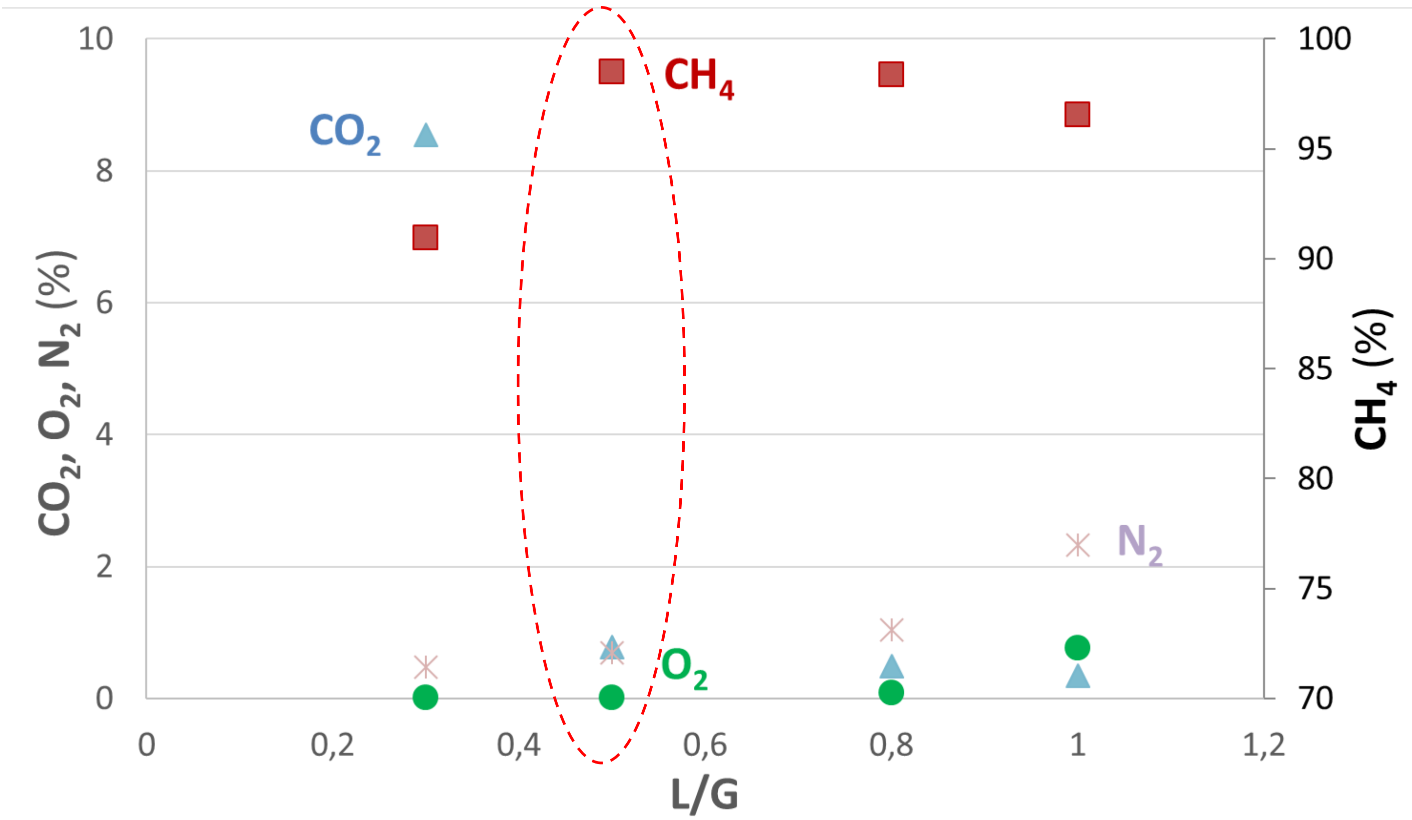
Photosynthetic Upgrading



Key operational parameter: Recycling Liquid/Biogas ratio

Biological CO_2 Removal Technologies

Photosynthetic Upgrading



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Biological CO_2 Removal Technologies

Photosynthetic Upgrading

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INCOVER

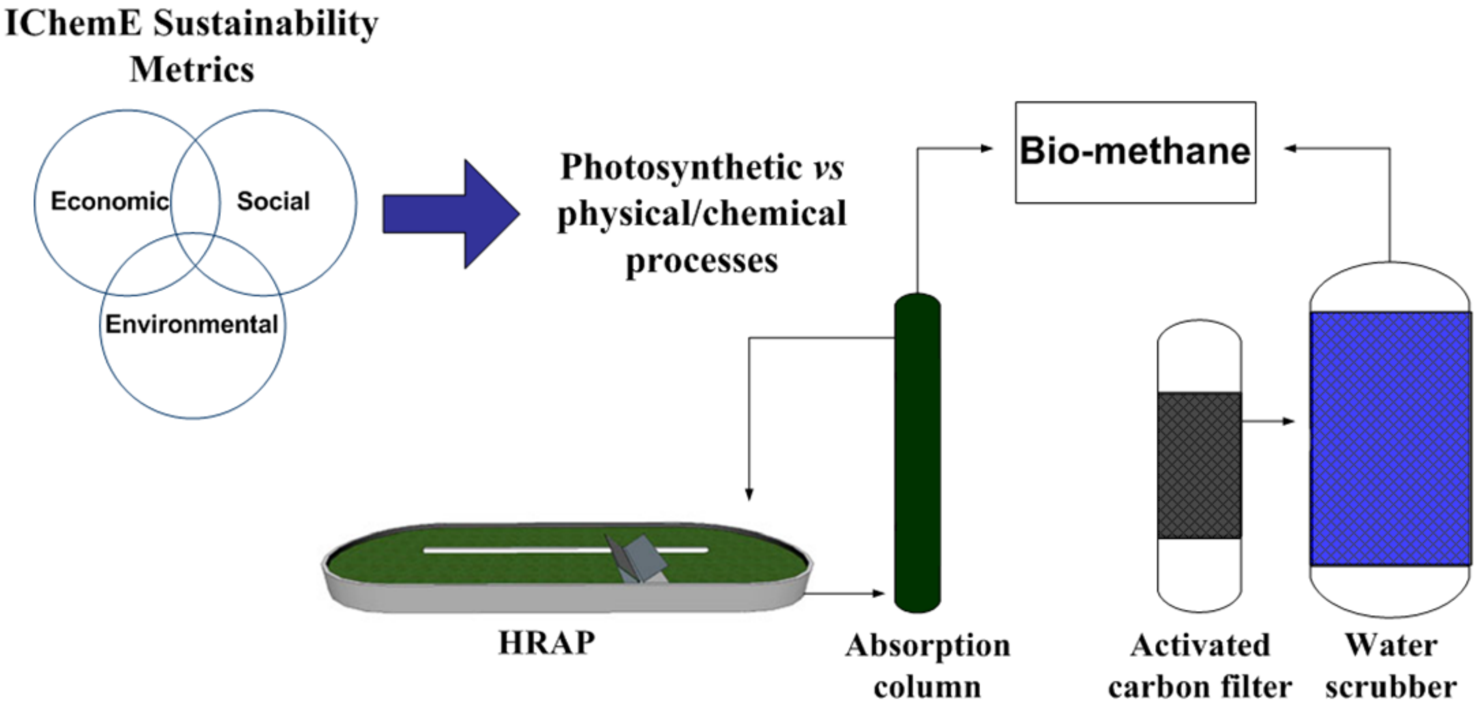
European Commission

HORIZON 2020

Biological CO_2 Removal Technologies

Photosynthetic Upgrading

IChemE
Sustainability



Upgrading Capacity: 300 Nm^3/h of biogas

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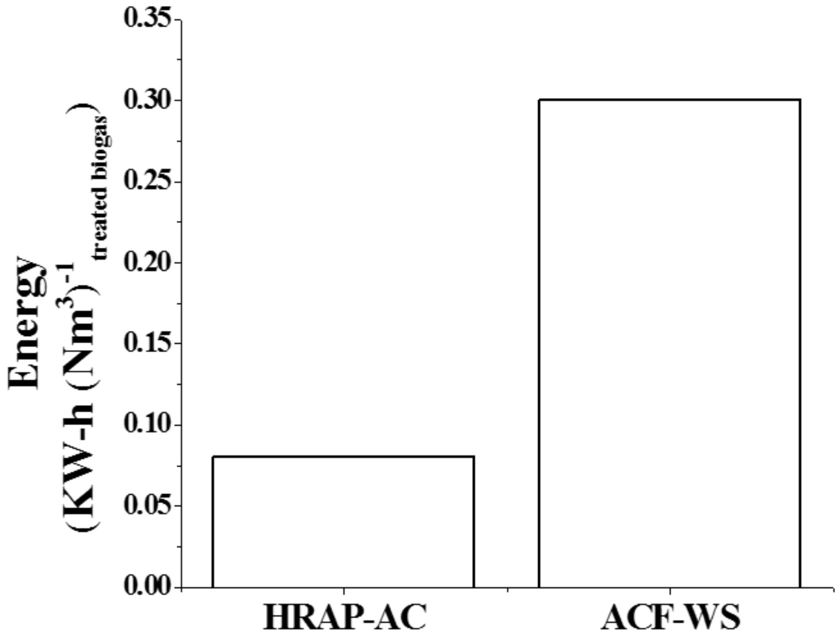
Biological CO_2 Removal Technologies

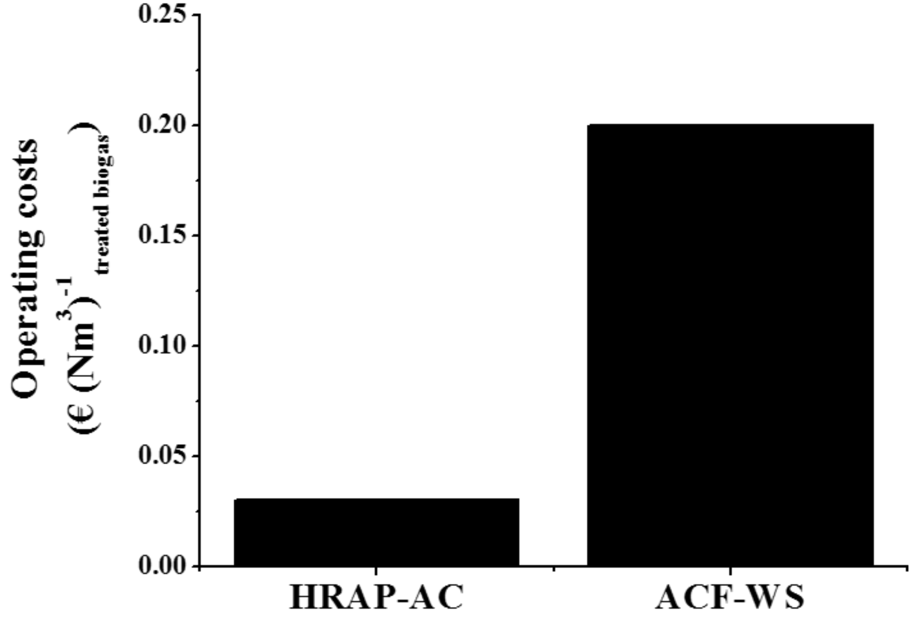
Photosynthetic Upgrading

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,*]





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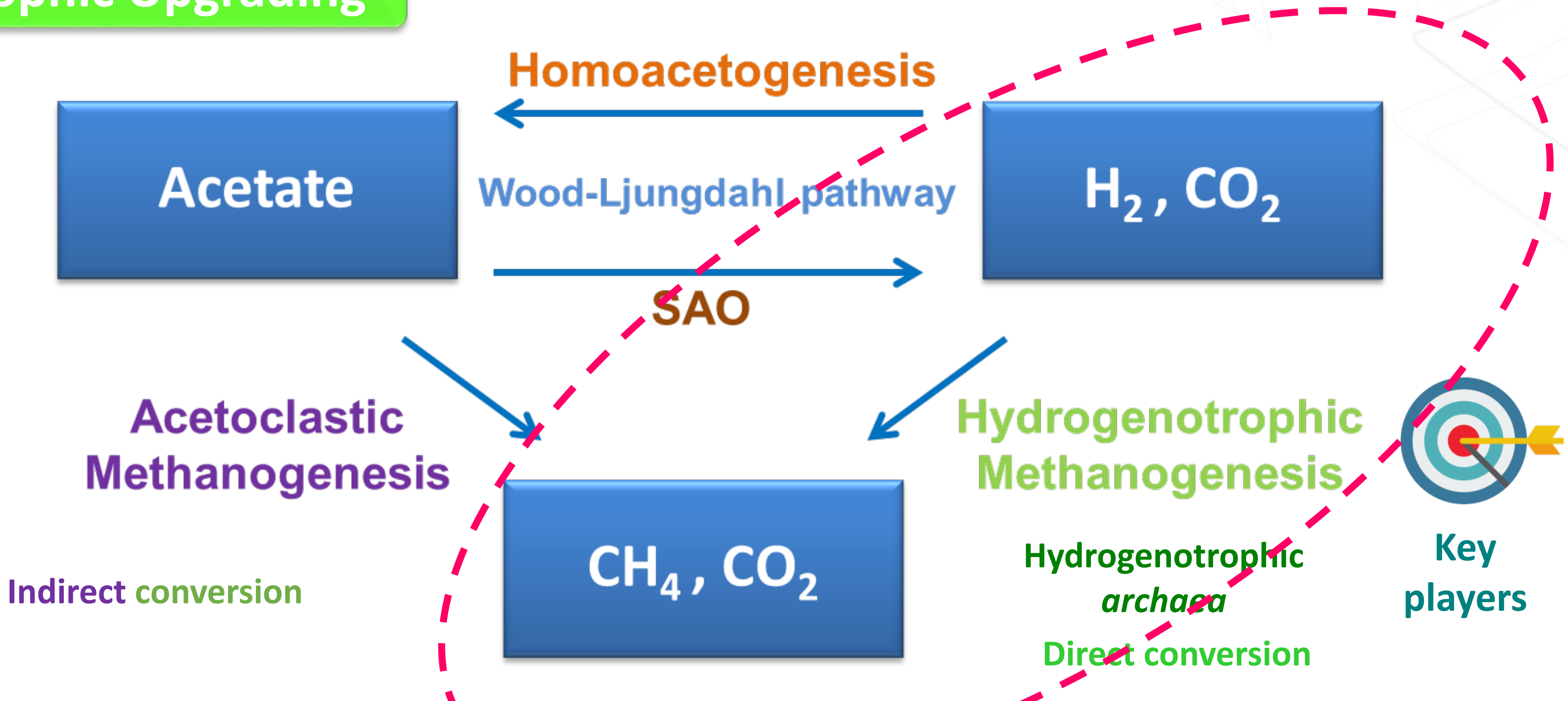
Biological CO_2 Removal Technologies

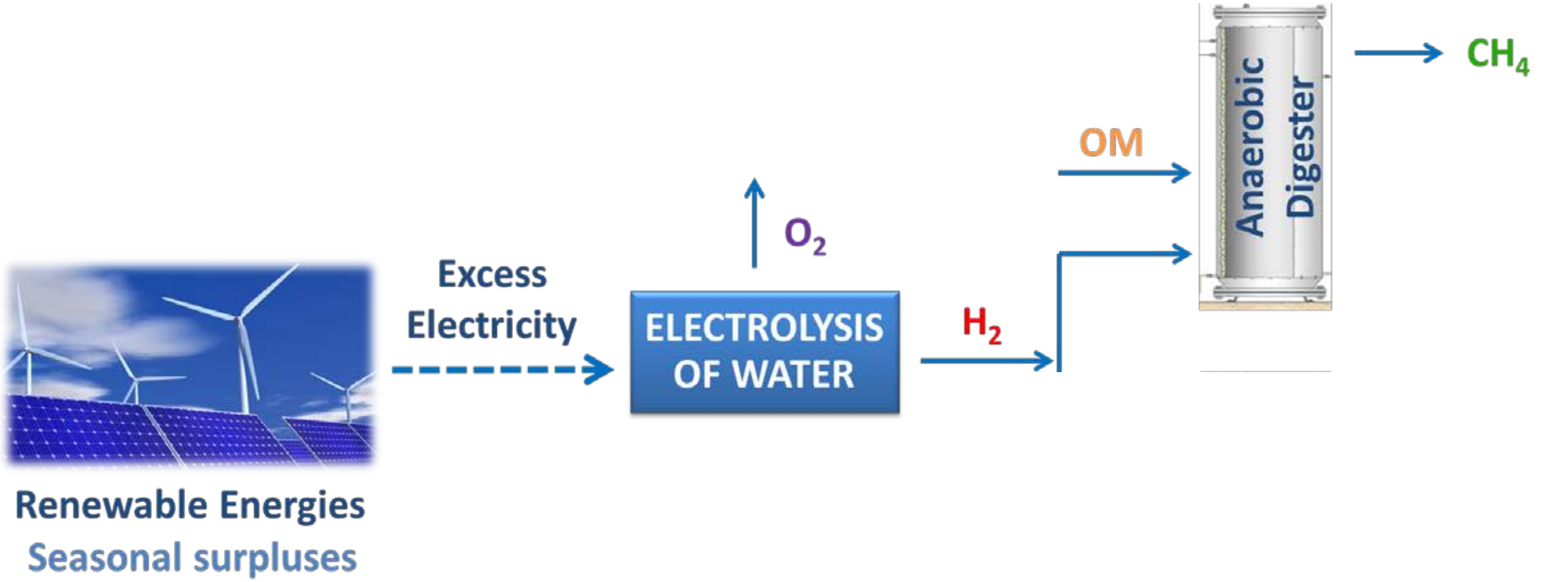
Hydrogenotrophic Upgrading

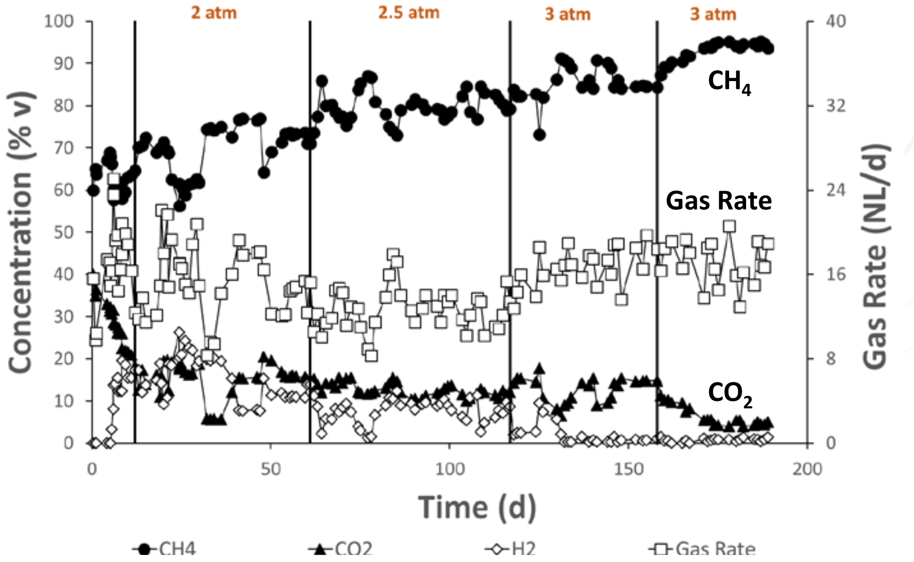


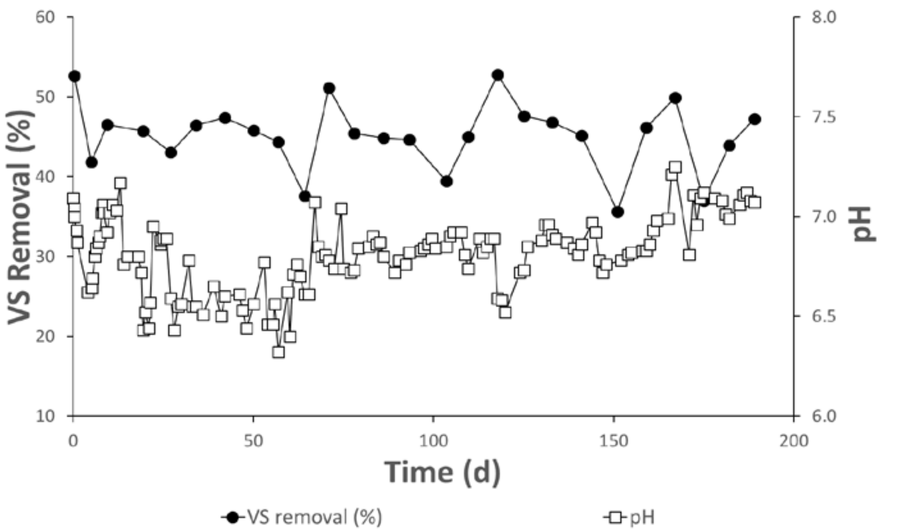
$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$
$$\Delta G^0 = -130.4 \text{ kJ mol}^{-1}$$

Biological CO_2 Removal Technologies

Hydrogenotrophic *In-situ* Upgrading







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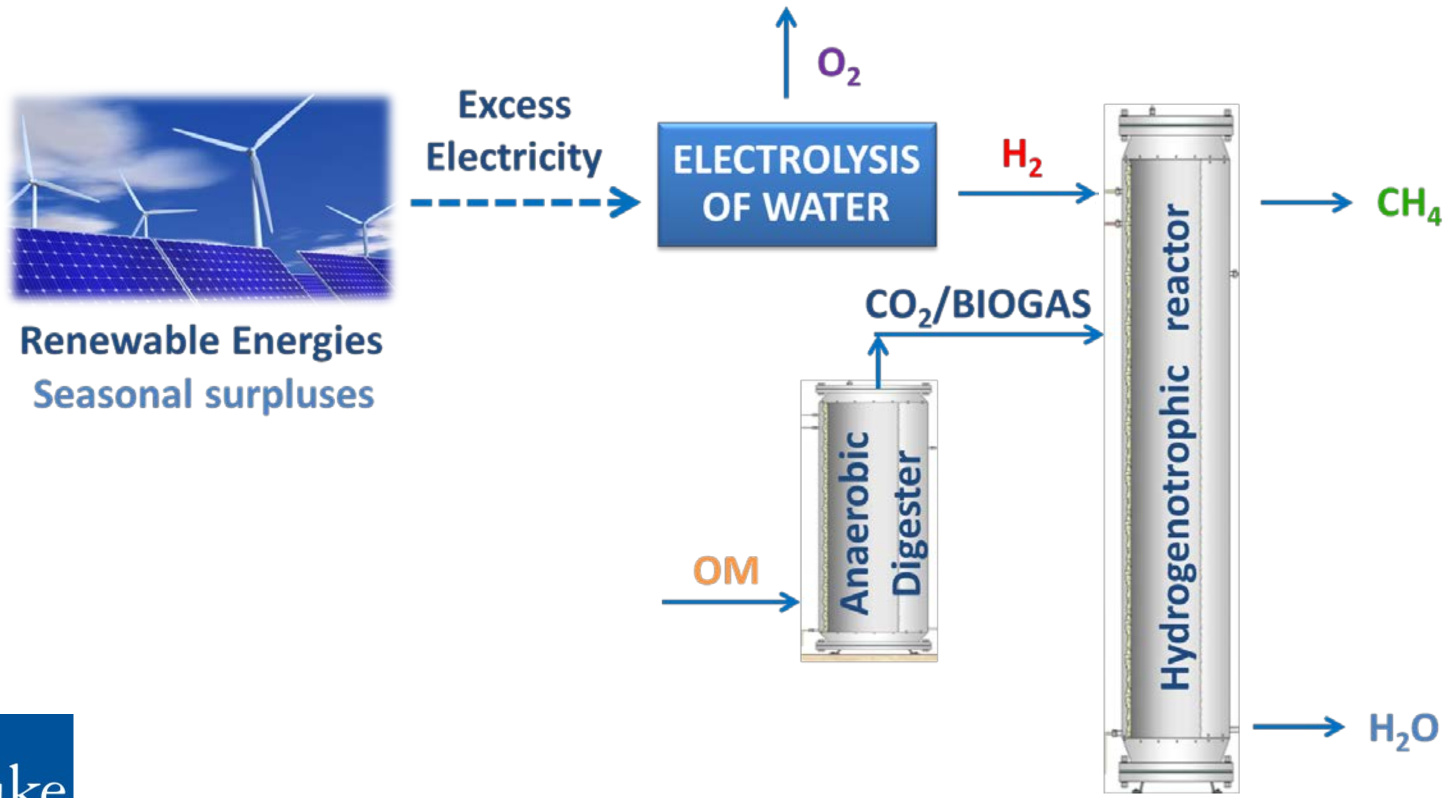
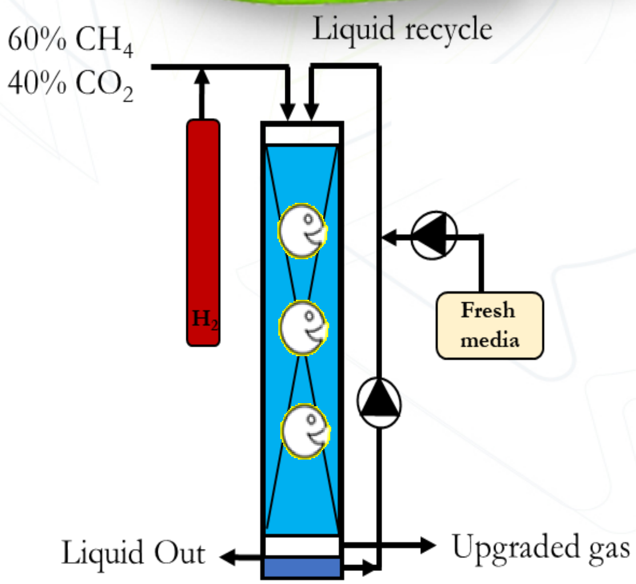
Biological CO_2 Removal Technologies

Hydrogenotrophic *Ex-situ* Upgrading

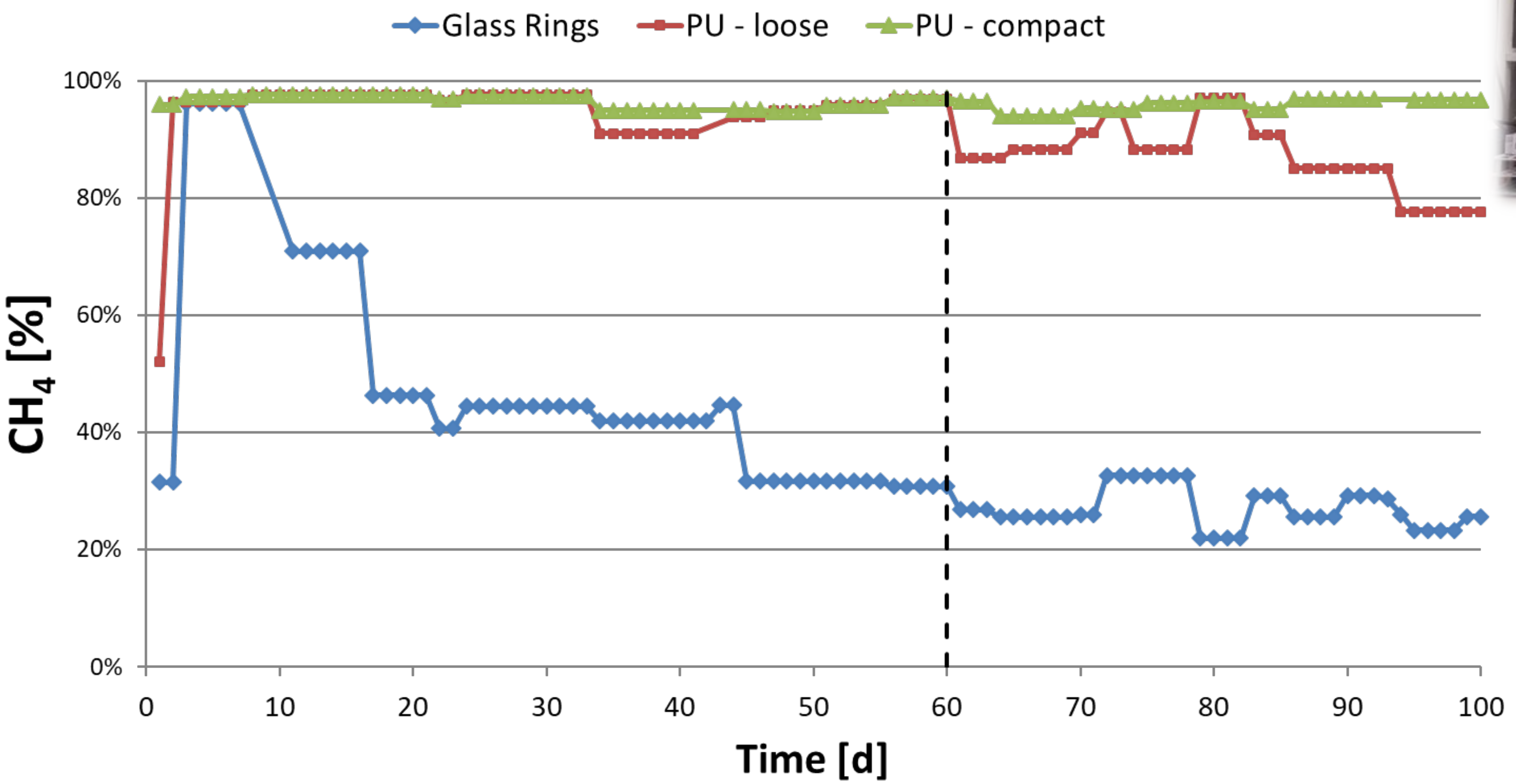




Influent Biogas Composition (CH_4:CO_2)	30:70	45:55	60:40
Final [CH_4] (% vol/vol)	98	98	98
Final [CO_2] (% vol/vol)	1.2	1.5	1.5
Upgrading Capacity (m^3 m^{-3} d^{-1})	13	11	9.5

Biological CO_2 Removal Technologies

Hydrogenotrophic *Ex-situ* Upgrading



Biological CO_2 Removal Technologies

Hydrogenotrophic *Ex-situ* Upgrading

Pilot Scale

Full Scale: in 2-3 years

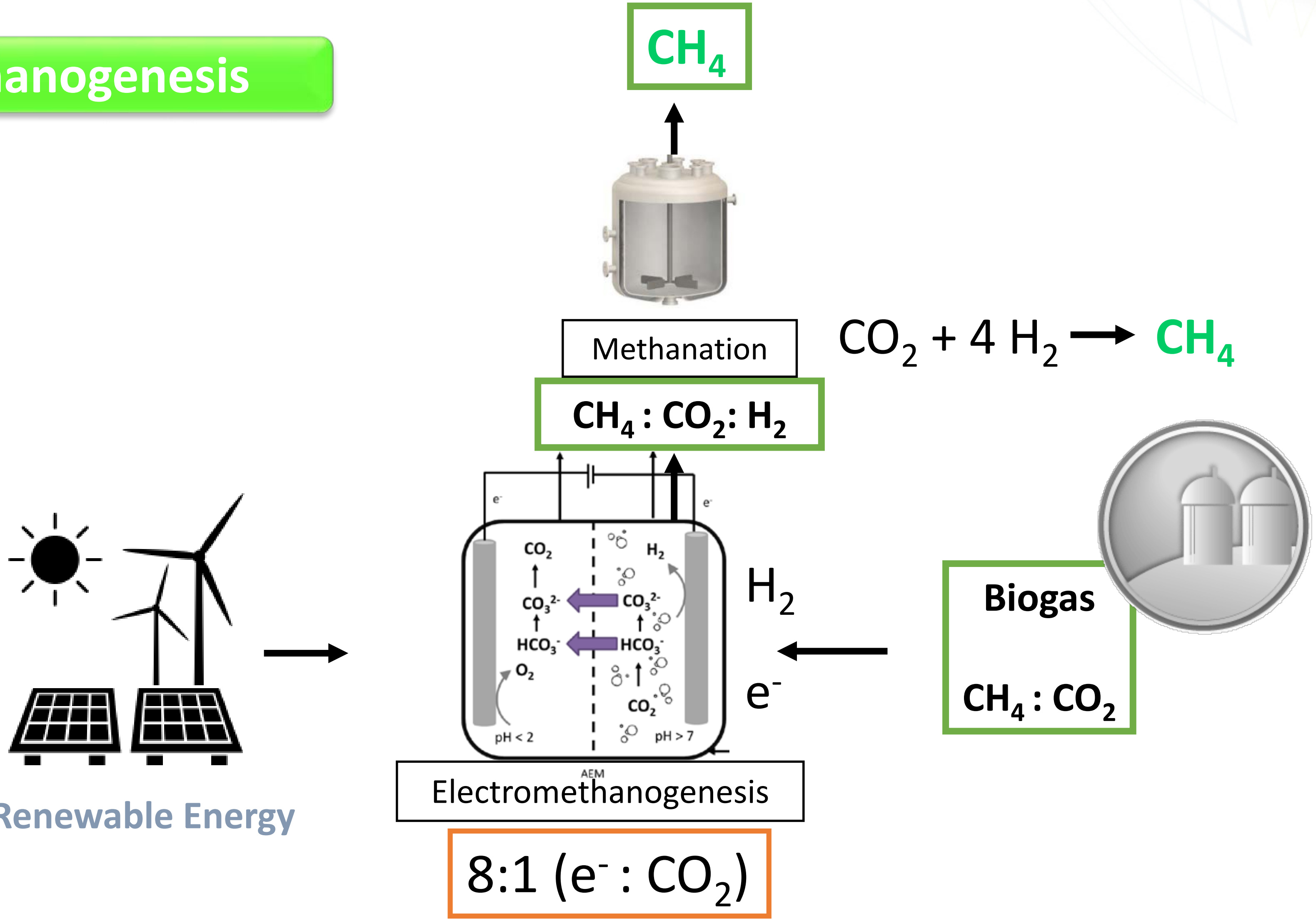
<u>BioUpgrade Project - Lemvig Biogas plant</u>

<u>eFUEL Project - Midtfyn Biogas Plant</u>

DTU

Biological CO_2 Removal Technologies

Electromethanogenesis



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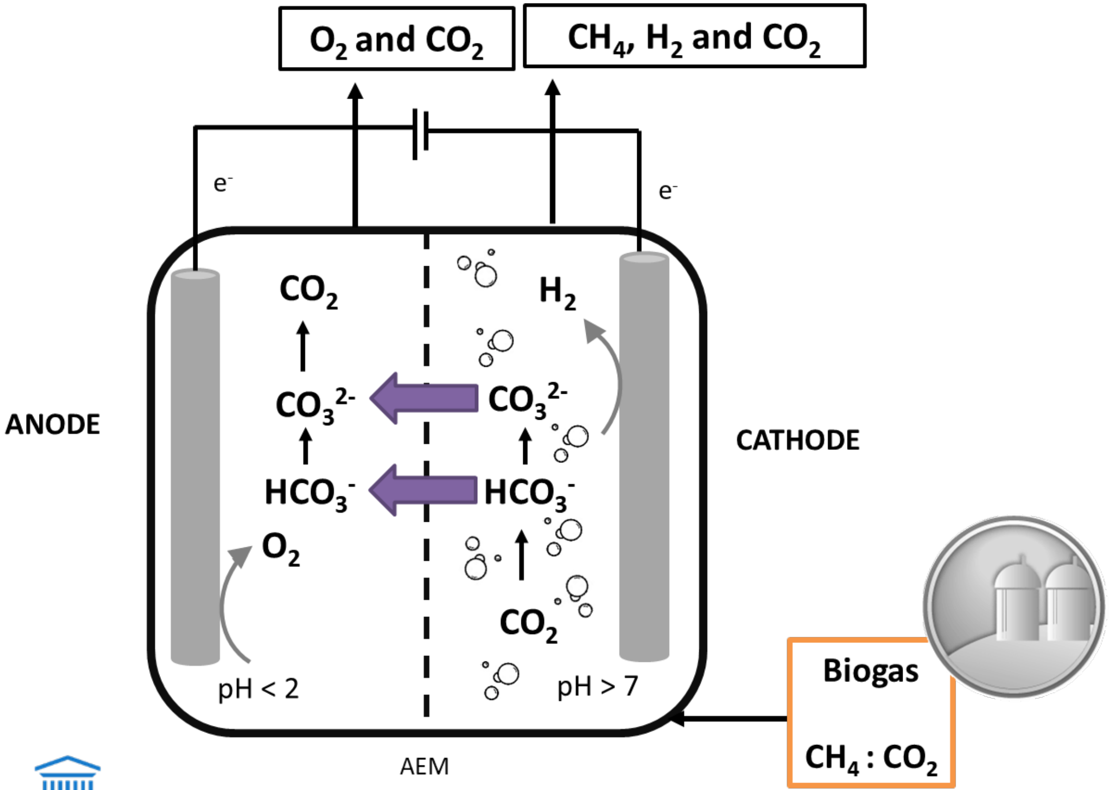
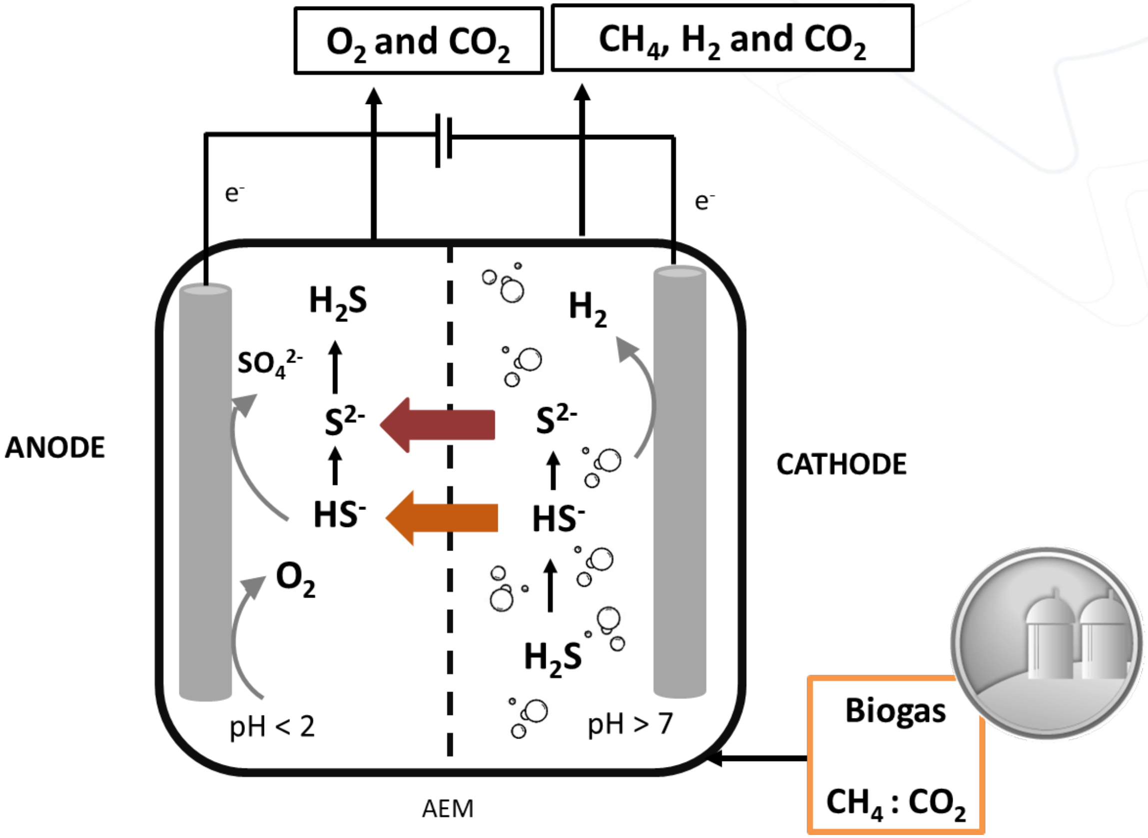
Biological CO_2 Removal Technologies

Electromethanogenesis





- HCO_3^- as main charge balancing ion
- Simultaneous desulphurization

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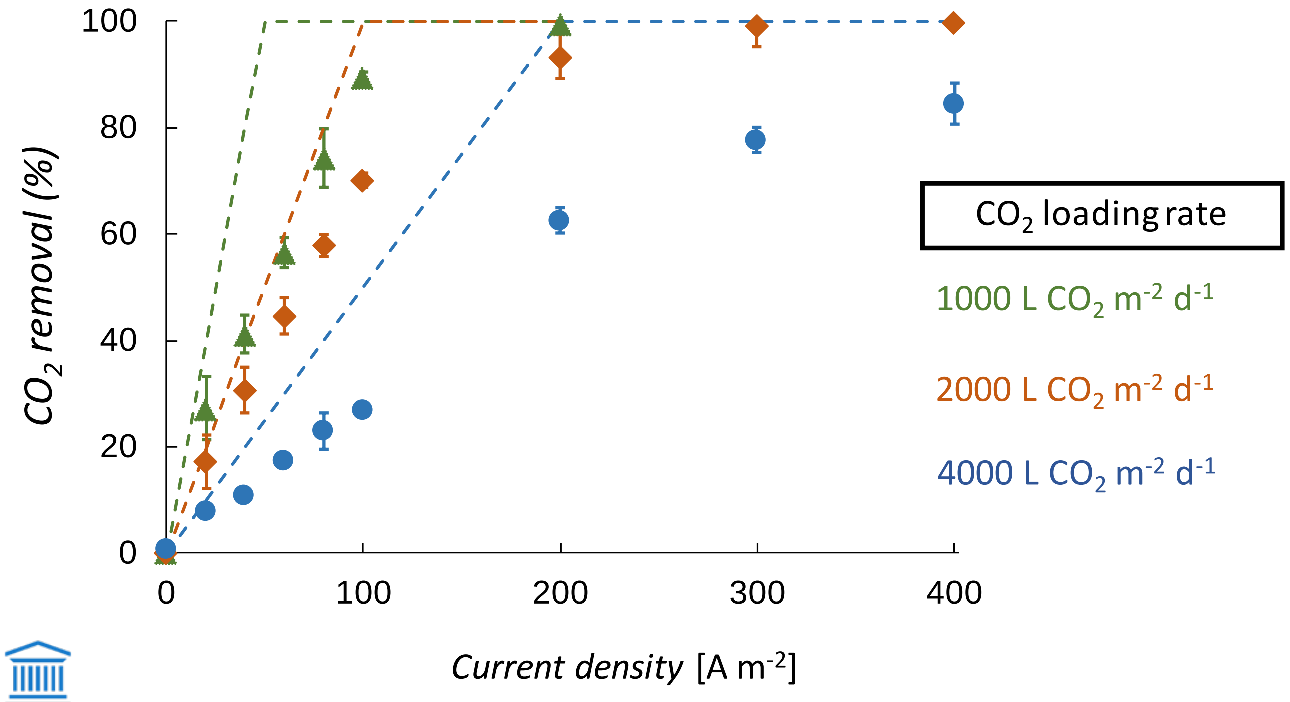
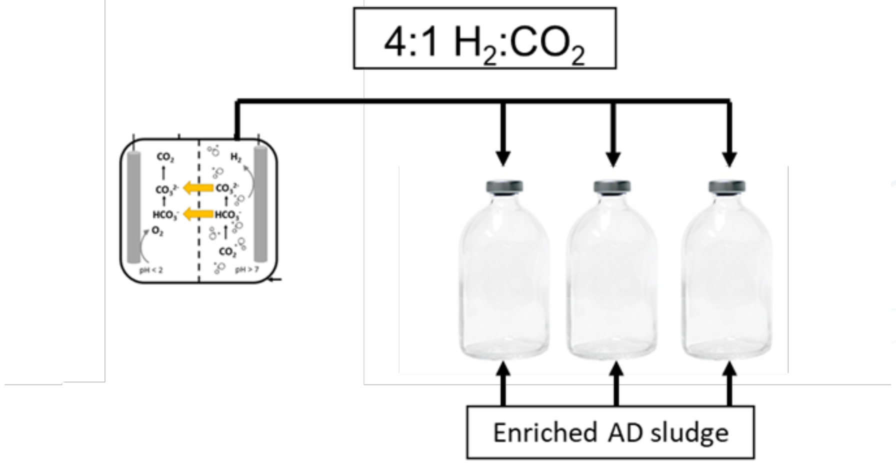
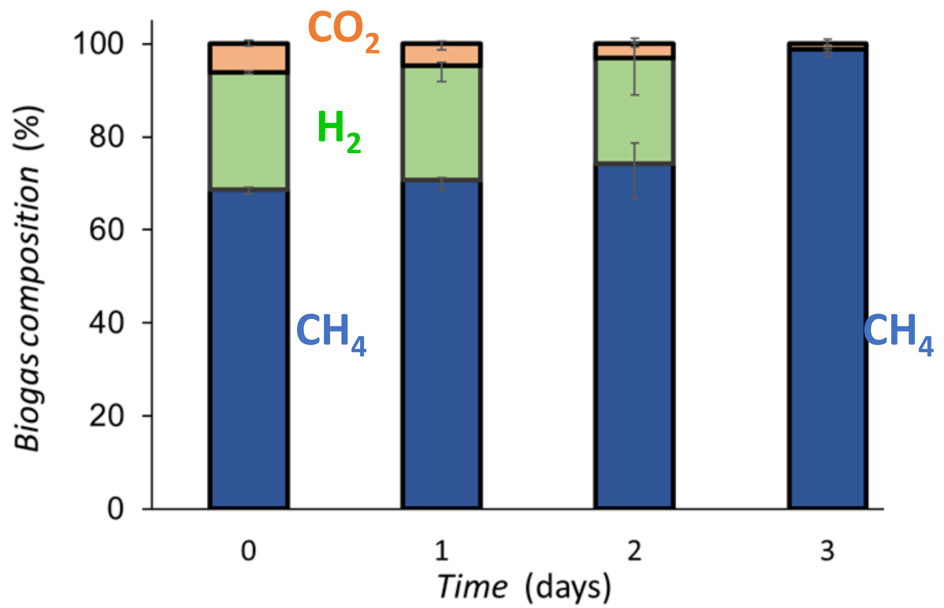
Electromethanogenesis







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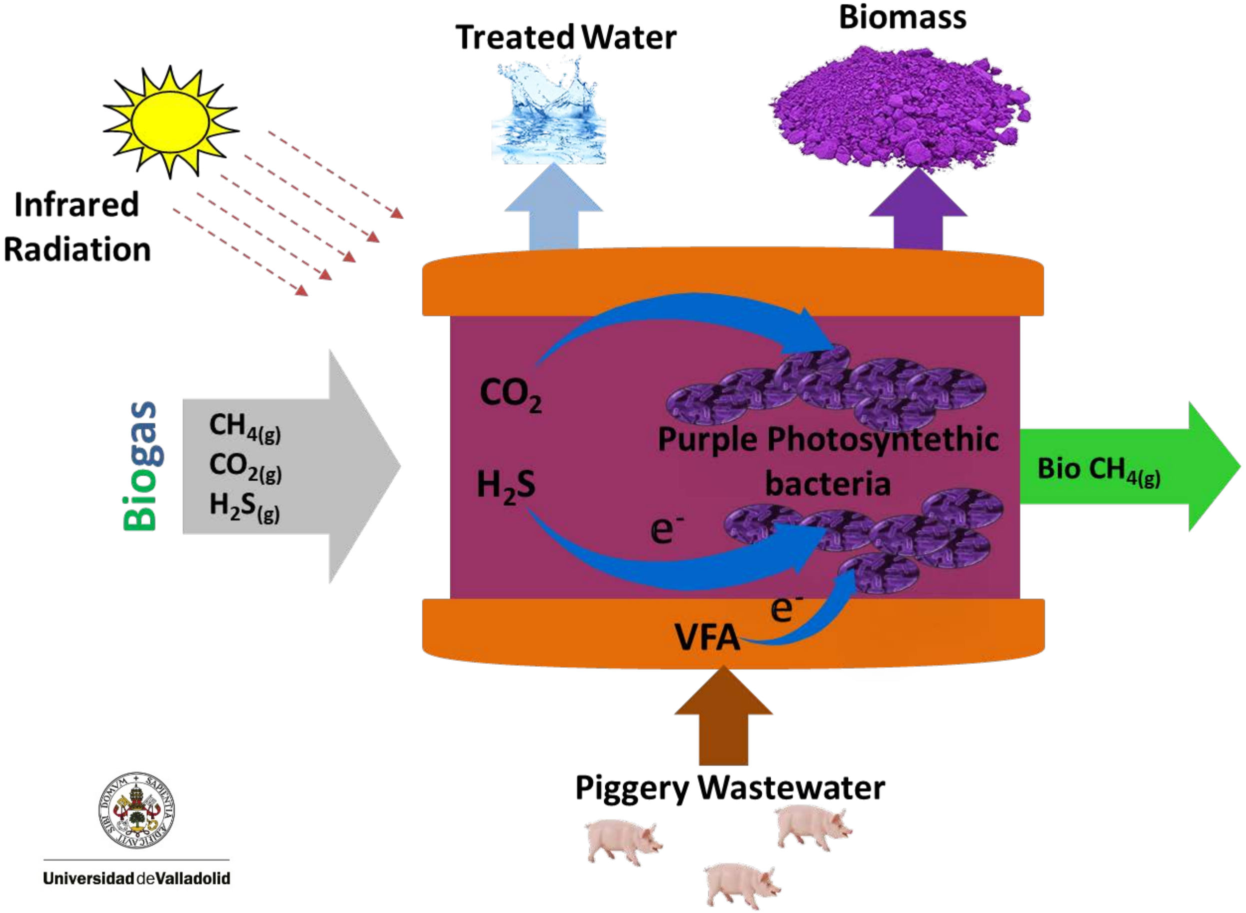
Biological CO_2 Removal Technologies

PPB-assisted Upgrading



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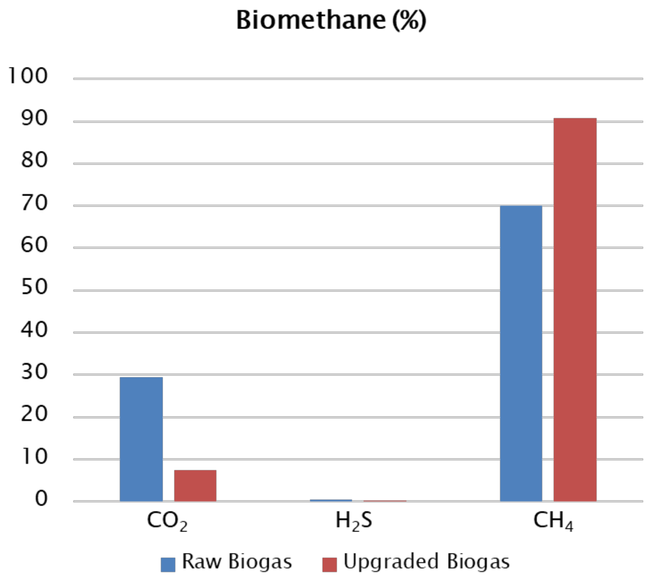
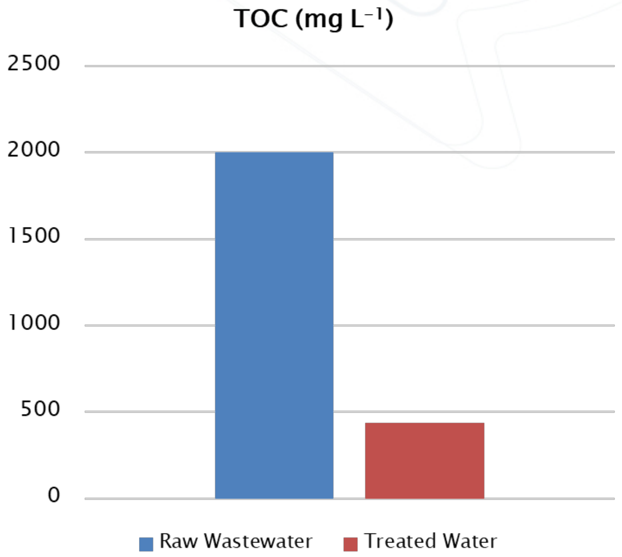
Assessing the potential of purple phototrophic bacteria for the simultaneous treatment of piggery wastewater and upgrading of biogas

David Marín[a,b,c], Esther Posadas[a], Dimas García[a,b,c], Daniel Puyol[d], Raquel Lebrero[a,b], Raúl Muñoz[a,b,*]





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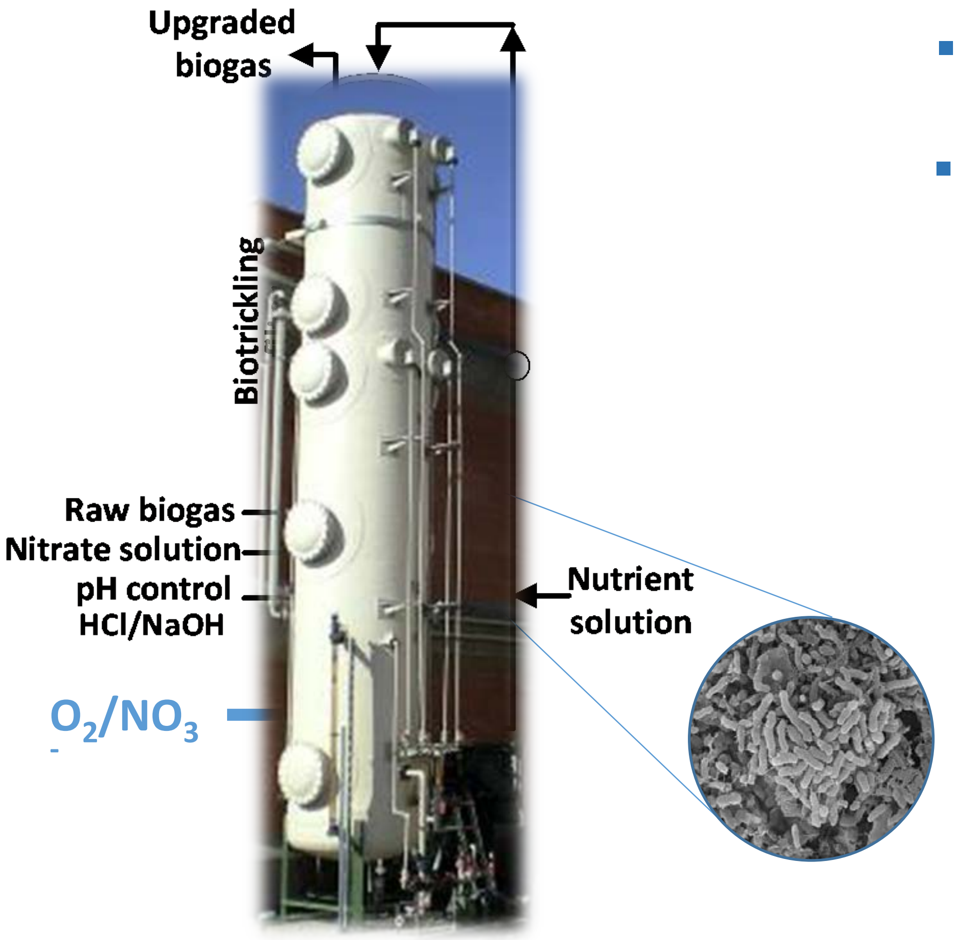
H_2S Removal Technologies

Biological H_2S Removal Technologies

Biotrickling Filtration



- Based on the action of lithoautotrophs: H_2S as energy source
- e- acceptor: O_2 or NO_3^-
- EBRT = 2-16 min → H_2S-RE = 99%

Aerobic

$$H_2S + 0.5O_2 \rightarrow S + H_2O$$

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

Anoxic

$$3H_2S + NO_3^- \rightarrow 3S + 0.5\,N_2 + 3H_2O$$

$$3H_2S + 4NO_3^- \rightarrow 3SO_4^{2-} + 2N_2 + 6H^+$$

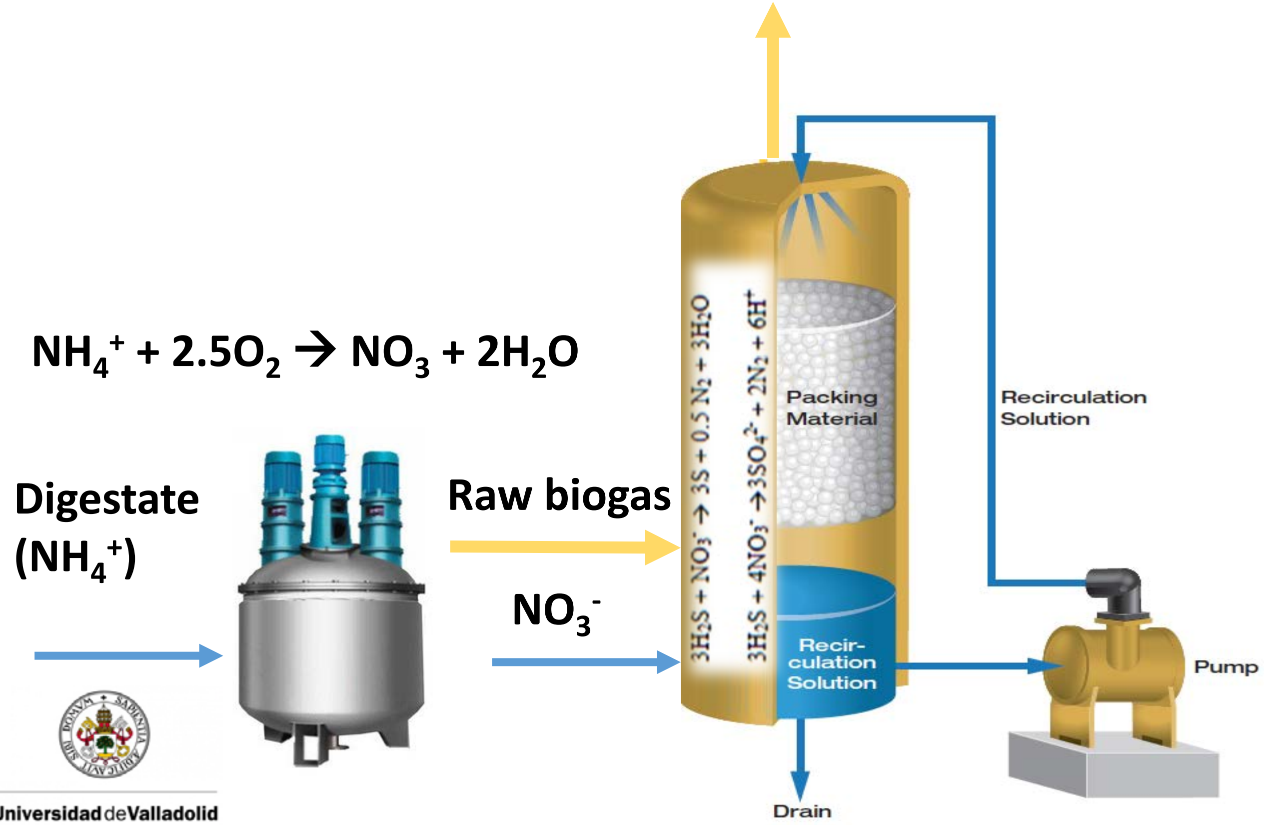
UAB Universitat Autònoma de Barcelona

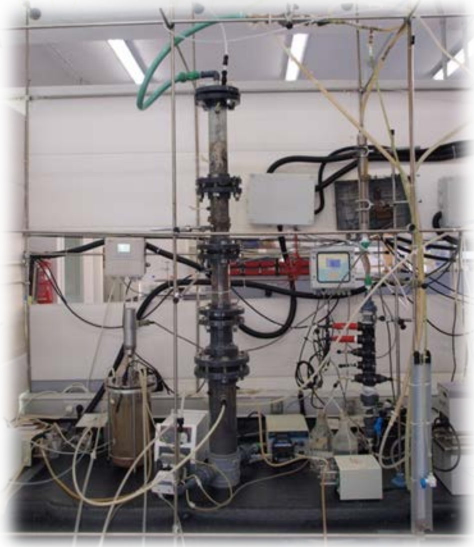
Biological H_2S Removal Technologies

Biotrickling Filtration

NITRIFICATION TANK BIOTRICKLING FILTER

$$NH_4^+ + 2.5O_2 \rightarrow NO_3 + 2H_2O$$





- H_2S-EC = 280 gS m^{-3} h^{-1} (RE = 96%)
- EBRT= 3 min

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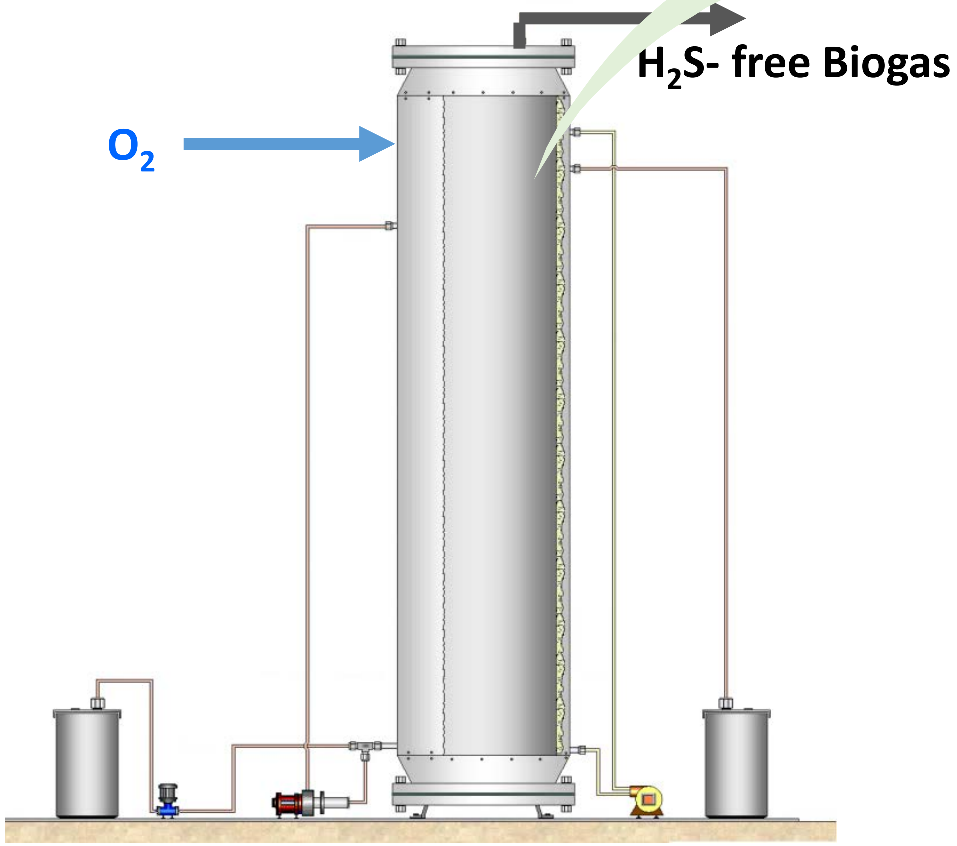
URBIOFIN
urban biorefinery

Biological H_2S Removal Technologies

Microaerobic AD



- No need for external desulfurization
- No impact on AD
- Periodical cleaning of AD headspace

Biological H_2S Removal Technologies

Microaerobic AD

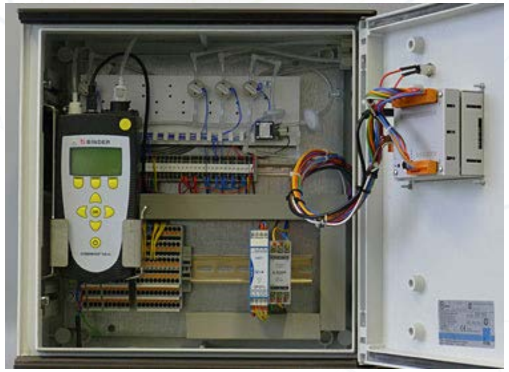
O_2 generator

93 ± 3 % O_2

2400m³ sludge digester

O_2 inyection into the headspace

WWTP for 100,000 p.e.



Biogas composition

Infra-red & electrochem.

(CH_4, CO_2, O_2, N_2 ,H_2S)

Biogas flow rate

Ultrasonic flowmeter

aqualia

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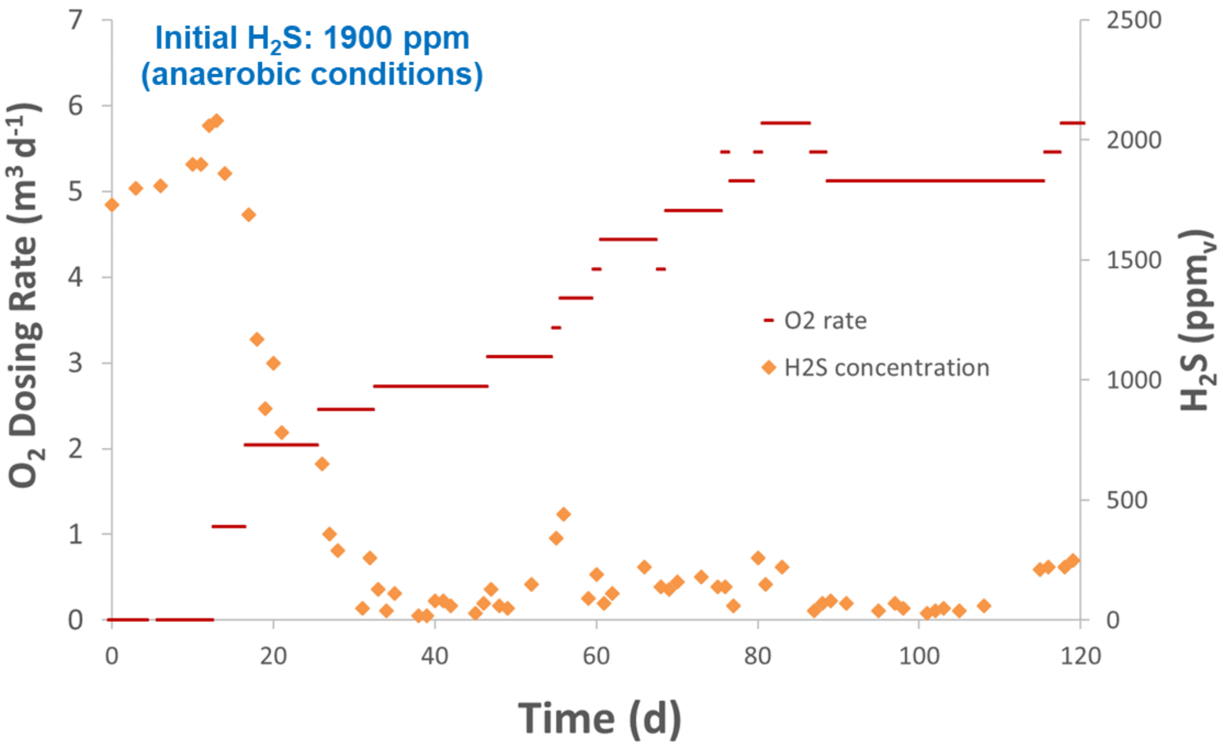
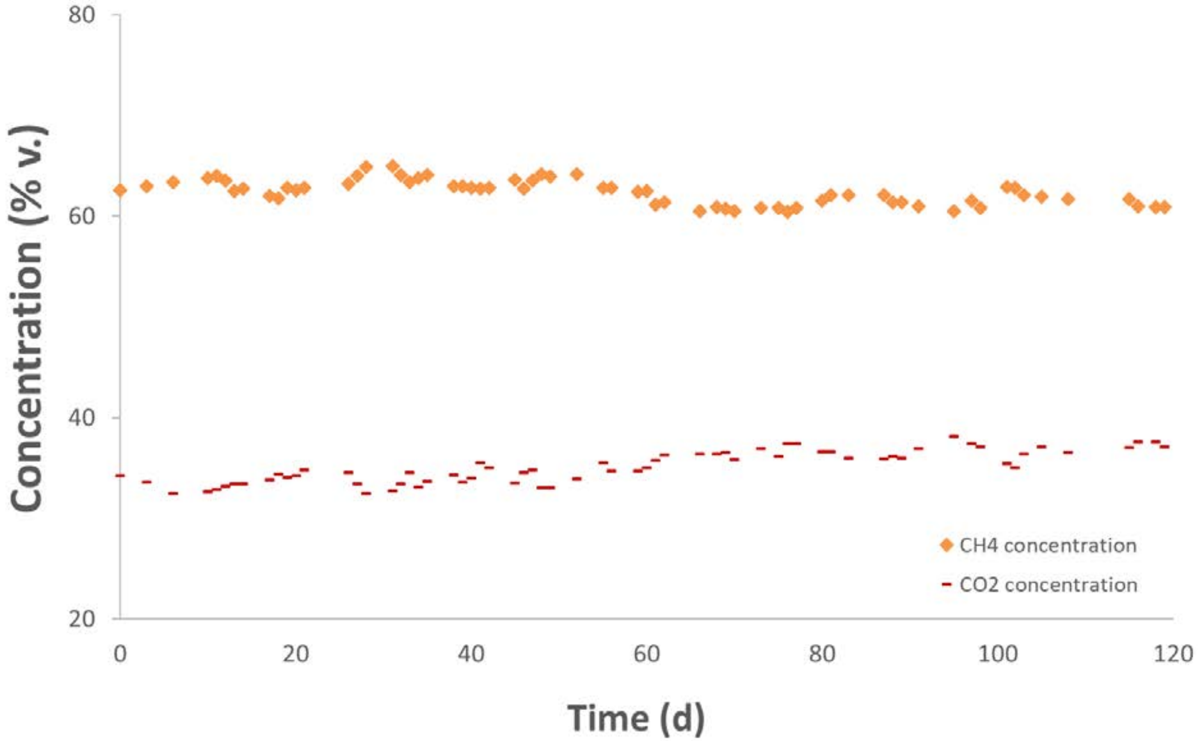
Biological H_2S Removal Technologies

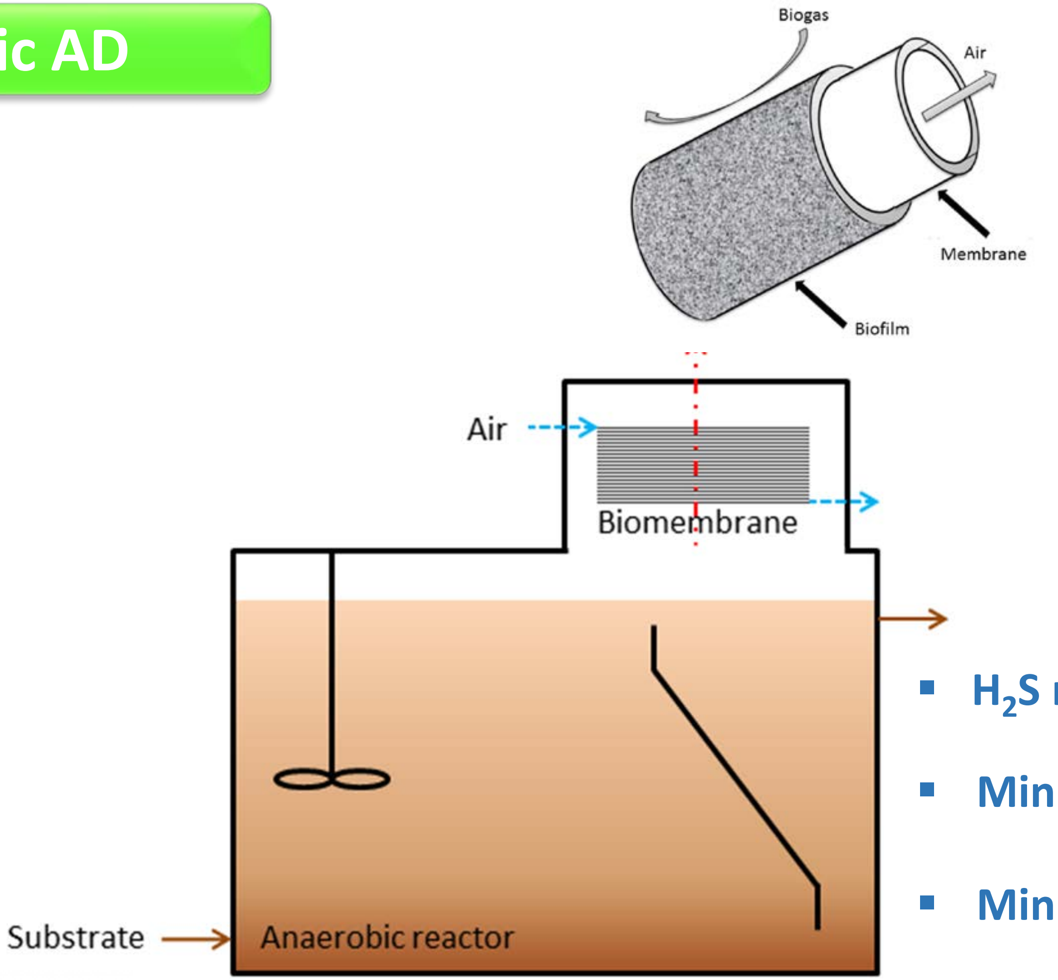
Microaerobic AD





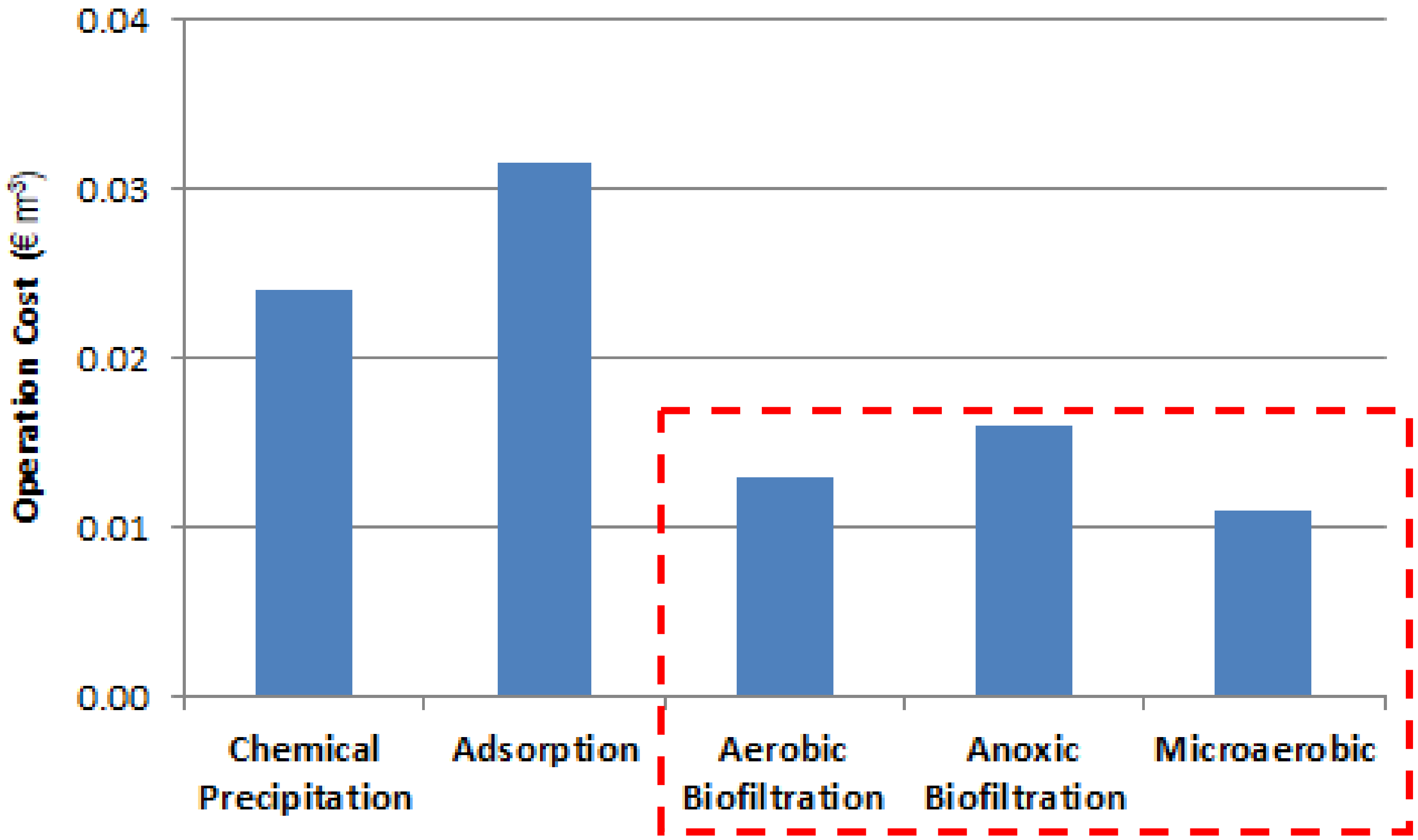
Biological H_2S Removal Technologies

Microaerobic AD



- **H_2S removal over 99%**
- **Minimum N_2 or O_2 contamination** of biogas
- **Minimum sulfur deposits** outside the membrane surface

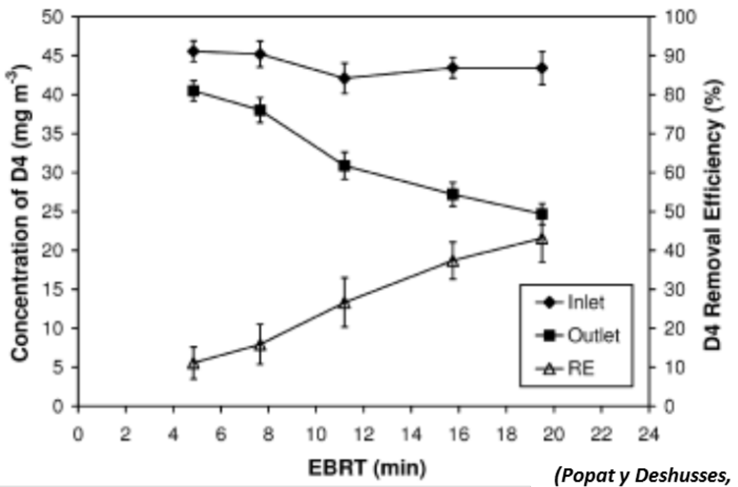
Operating Cost of H_2S Removal Technologies



Siloxanes Removal Technologies

Biological Siloxane Removal Technologies

- Siloxanes are biodegradable
- Siloxanes removal is limited by gas-liquid mass transfer

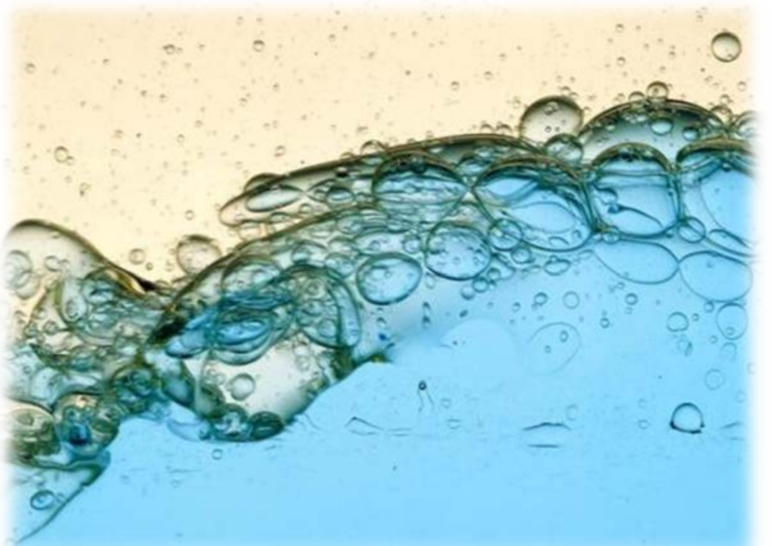


(Popat y Deshusses, 2008)

Two-Phase Partitioning Bioreactors

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

e. g.
Silicone oil
Heptamethylnonane



Biological Siloxane Removal Technologies

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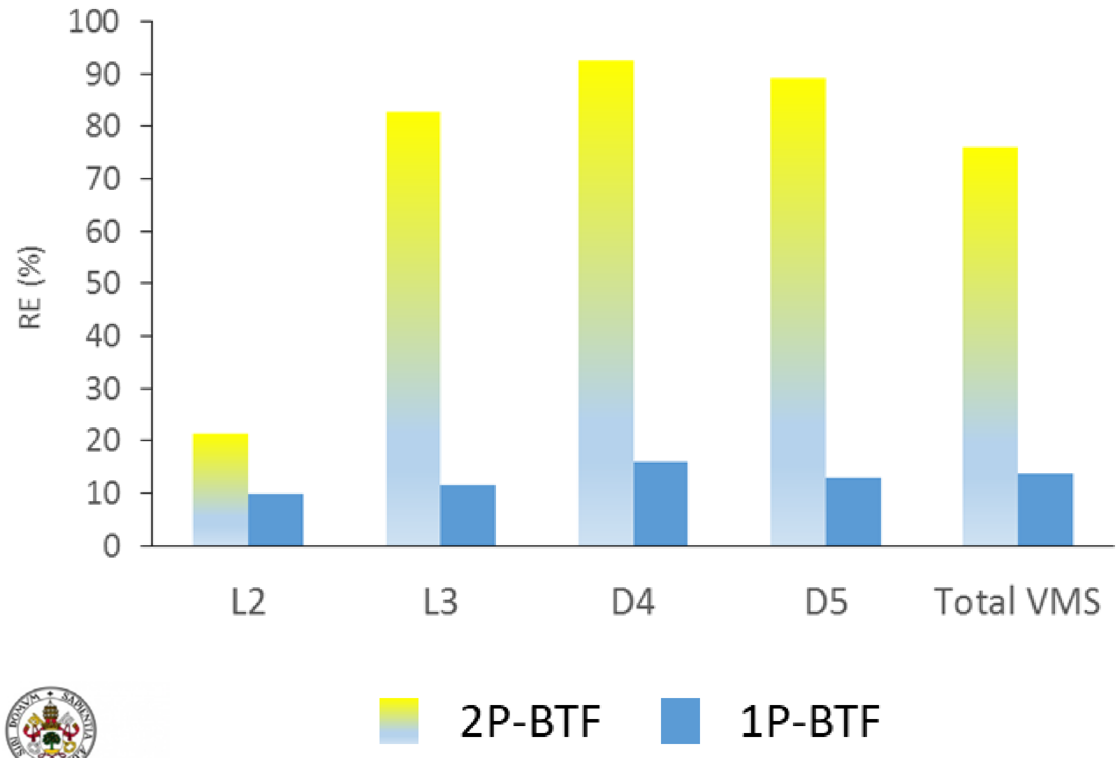
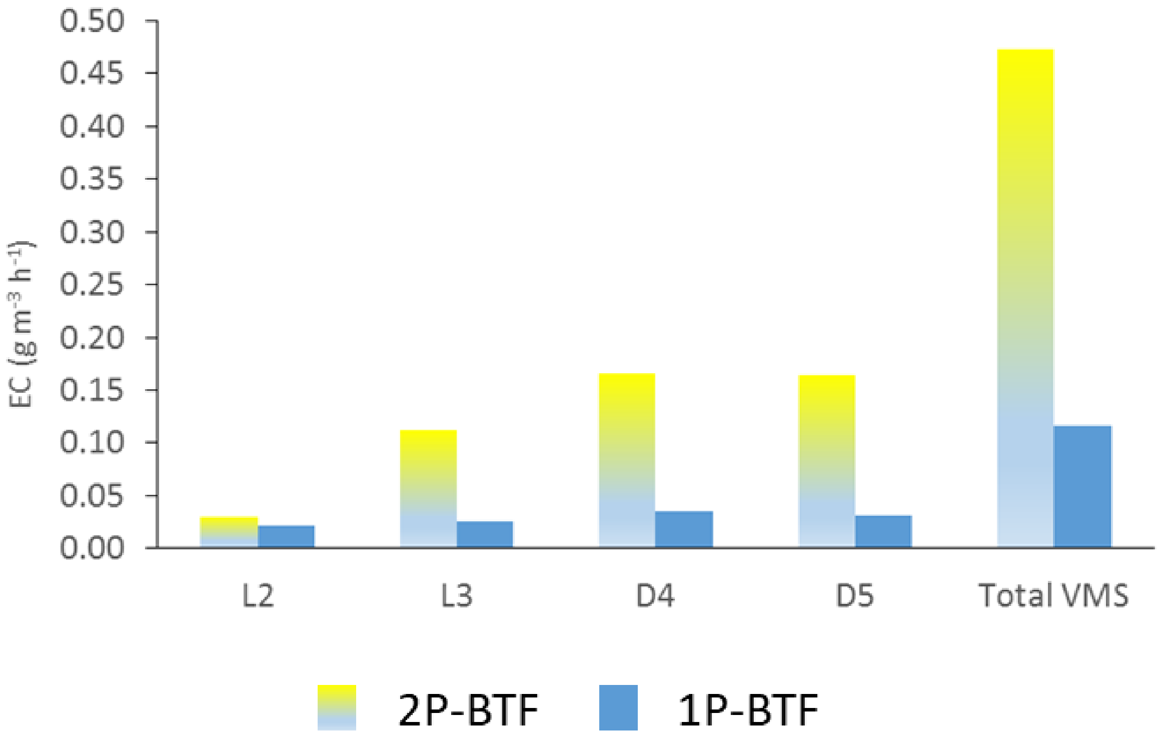
Two-phase partitioning Bioreactors





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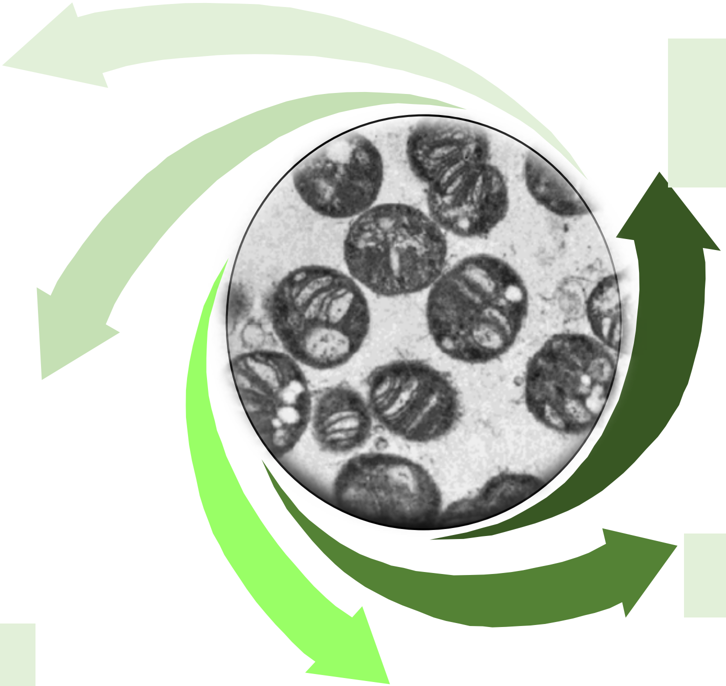
Biogas bioconversion into commercial bioproducts

Biogas bioconversion into commercial bioproducts

BIOPOLYMERS



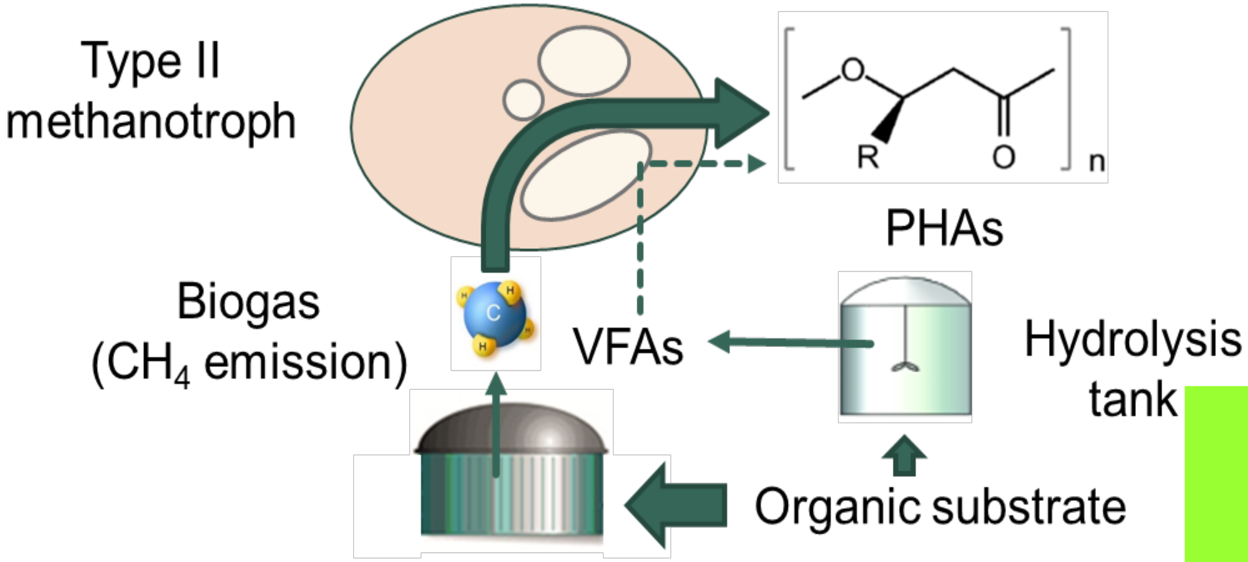
CHEMICAL BUILDING BLOCKS

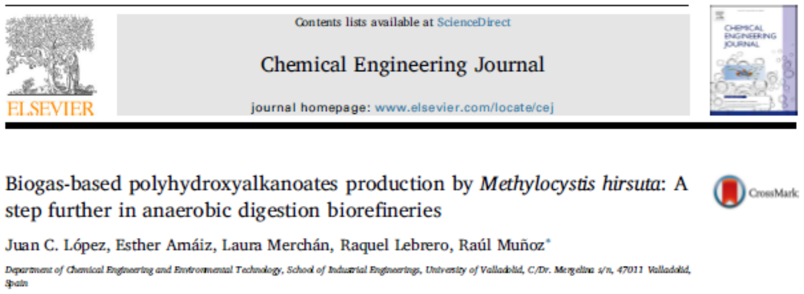
ECTOINE

EXOPOLYSACCHARIDES

SINGLE CELL PROTEIN

Biogas bioconversion into commercial bioproducts

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ELSEVIER

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

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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

URBIOFIN
urban biorefinery

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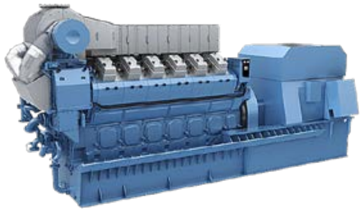
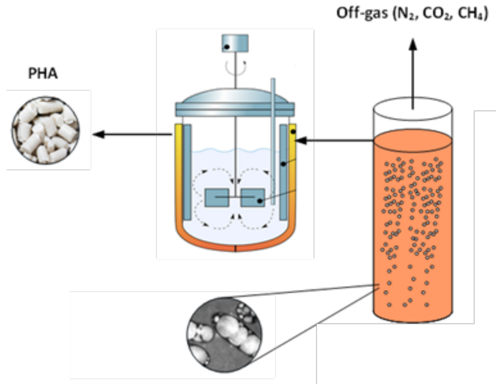
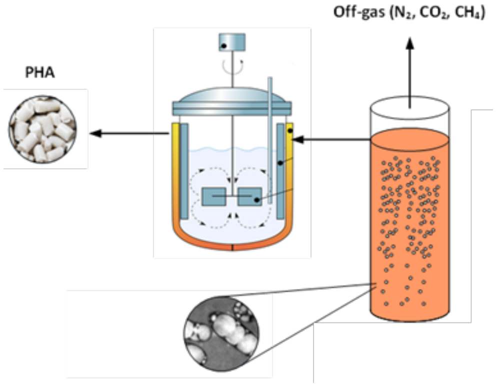


100 % biogas to CHP

1000 Nm^3 biogas h^{-1}



100 % biogas to PHA



55 % biogas to CHP+ 45 % biogas to PHA

IChemE
Sustainability

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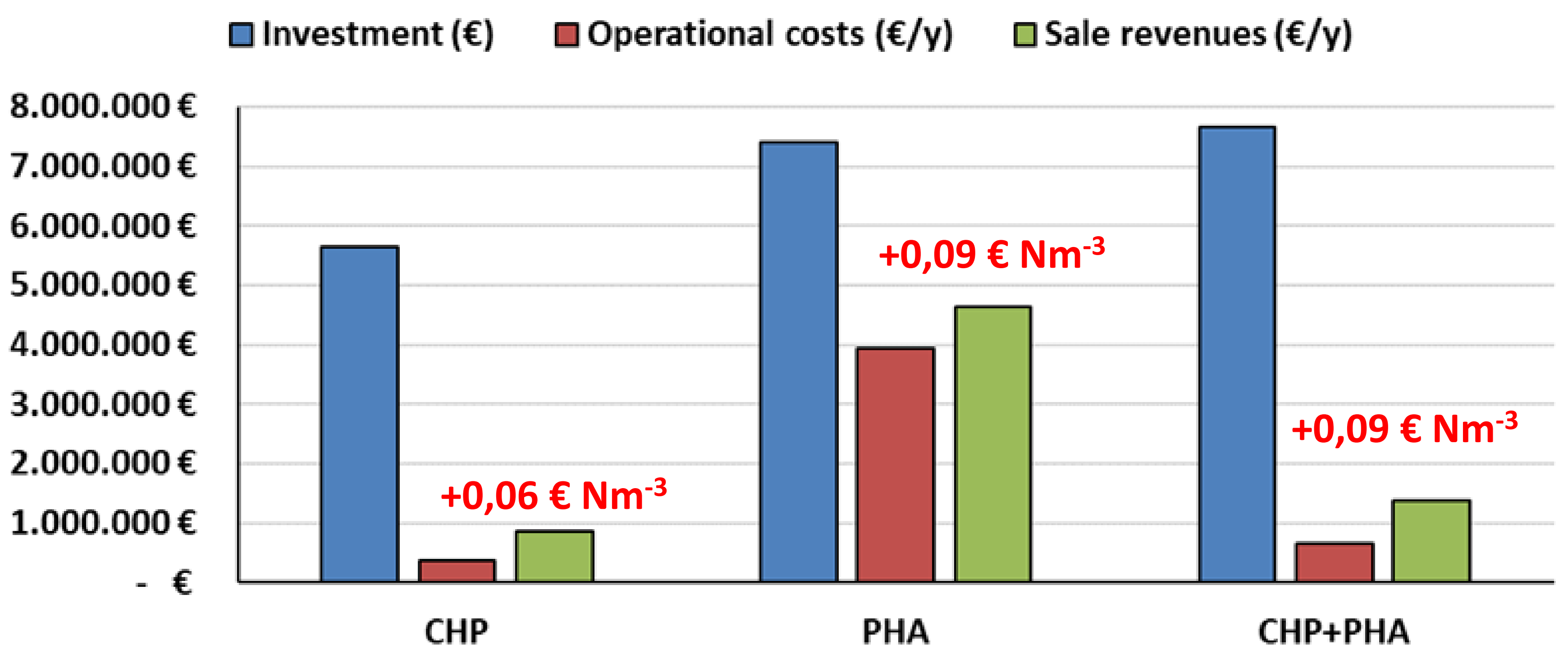

PHA production ~ 1,900 kg PHA d^{-1}
PHA selling price ~ 7,1 € kg^{-1}

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

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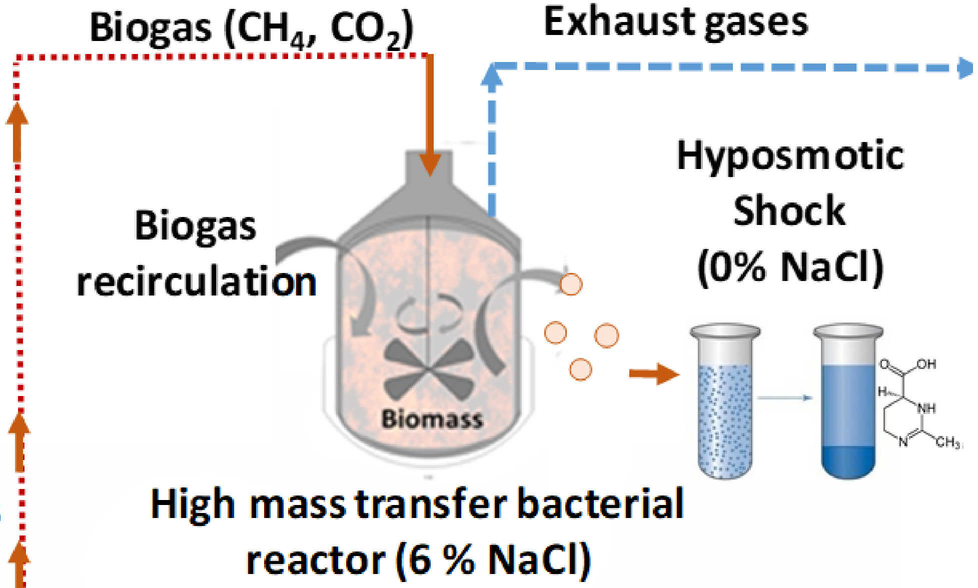
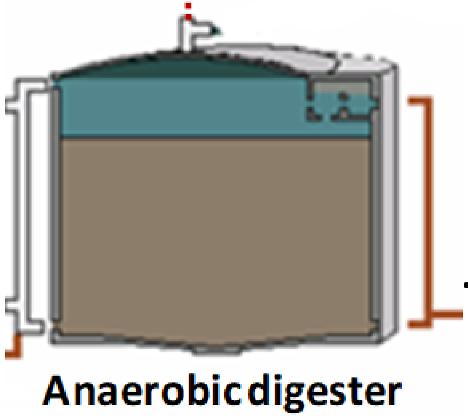
Biogas bioconversion into commercial bioproducts





Ectoine is an osmotic cell protector with a high market value (> 1000 € kg^{-1})

TLR 5 → DEEP PURPLE → TLR 7

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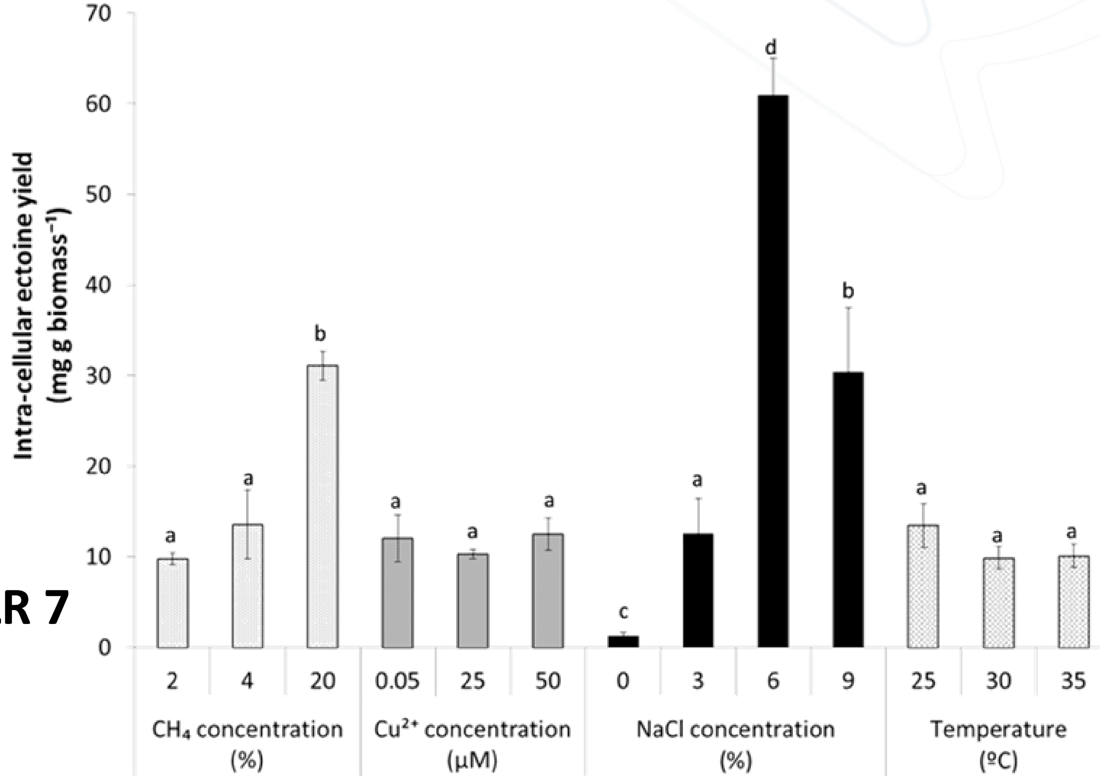
Research article

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*



TAKE HOME MESSAGES

- Anaerobic digestion can be engineered as a multi-product biorefinery
- Biotechnologies for biogas upgrading are being successfully scale-up and validated
- Power-to-gas has attracted most research efforts in the field of biological biogas upgrading
- Biological desulfurization methods provide high H_2S-REs at low operating costs
- TPPB can support an effective siloxane removal
- Biogas represents a valuable feedstock for the production of commodities and high-added value products

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Co-authors

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Thank you for your Attention

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