«Valorization of solid metal waste for the production of platform chemicals (VFAs) through the fixation of CO_2 using anaerobic granular sludge and homoacetogen bacteria strains»

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CYPRUS UNIVERSITY OF TECHNOLOGY

Environmental Engineering Laboratory

Aim of the study

- Carbon dioxide mitigation.
- Achieve the new EU climate targets.
- Production of important platform chemicals.
- Study the production of hydrogen using solid waste metals.
- Study the industrial interest.

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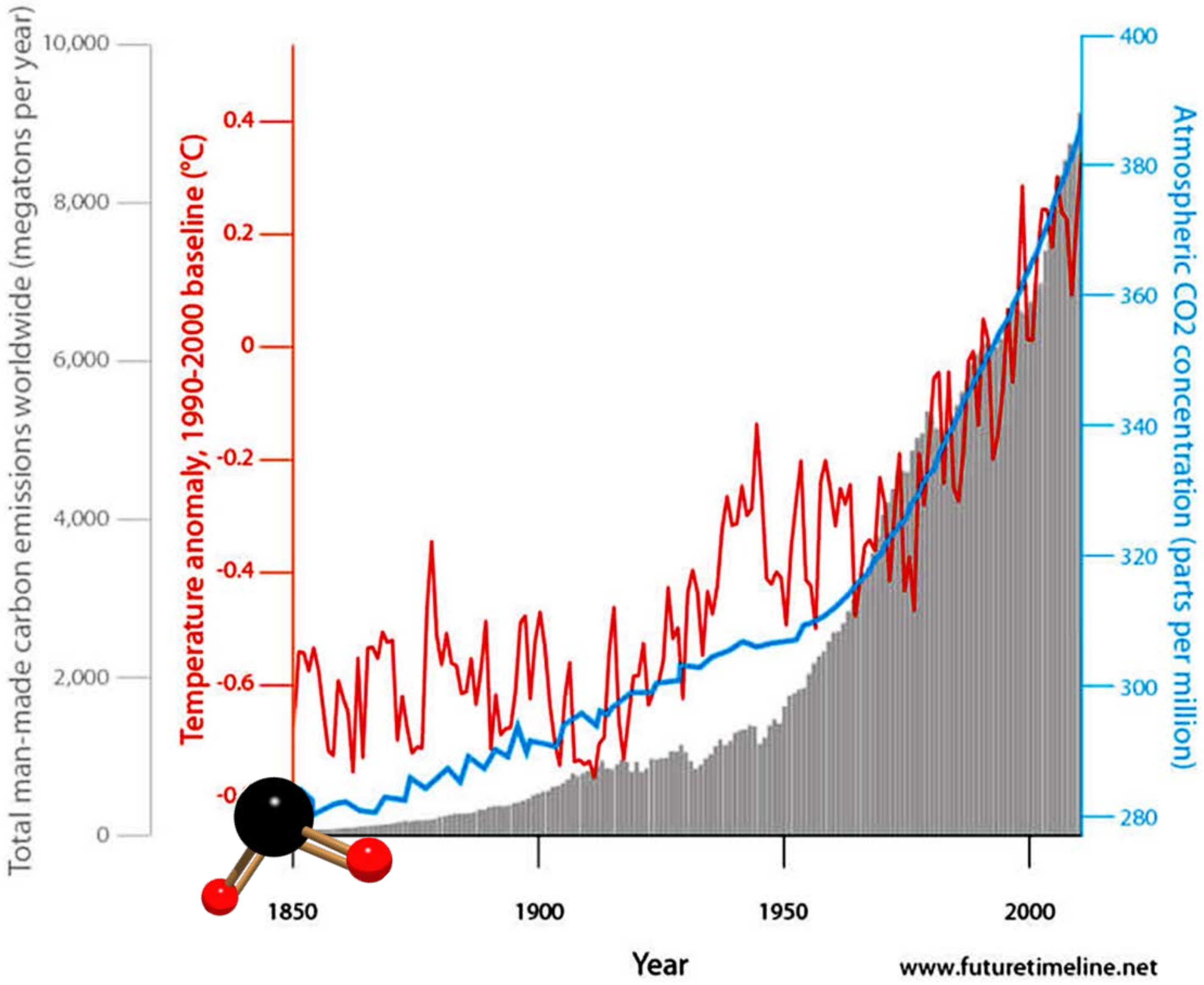
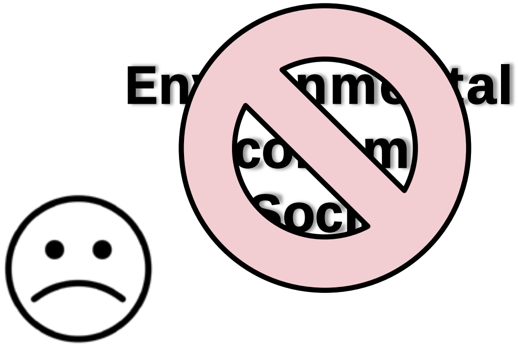




Carbon dioxide accuses of:

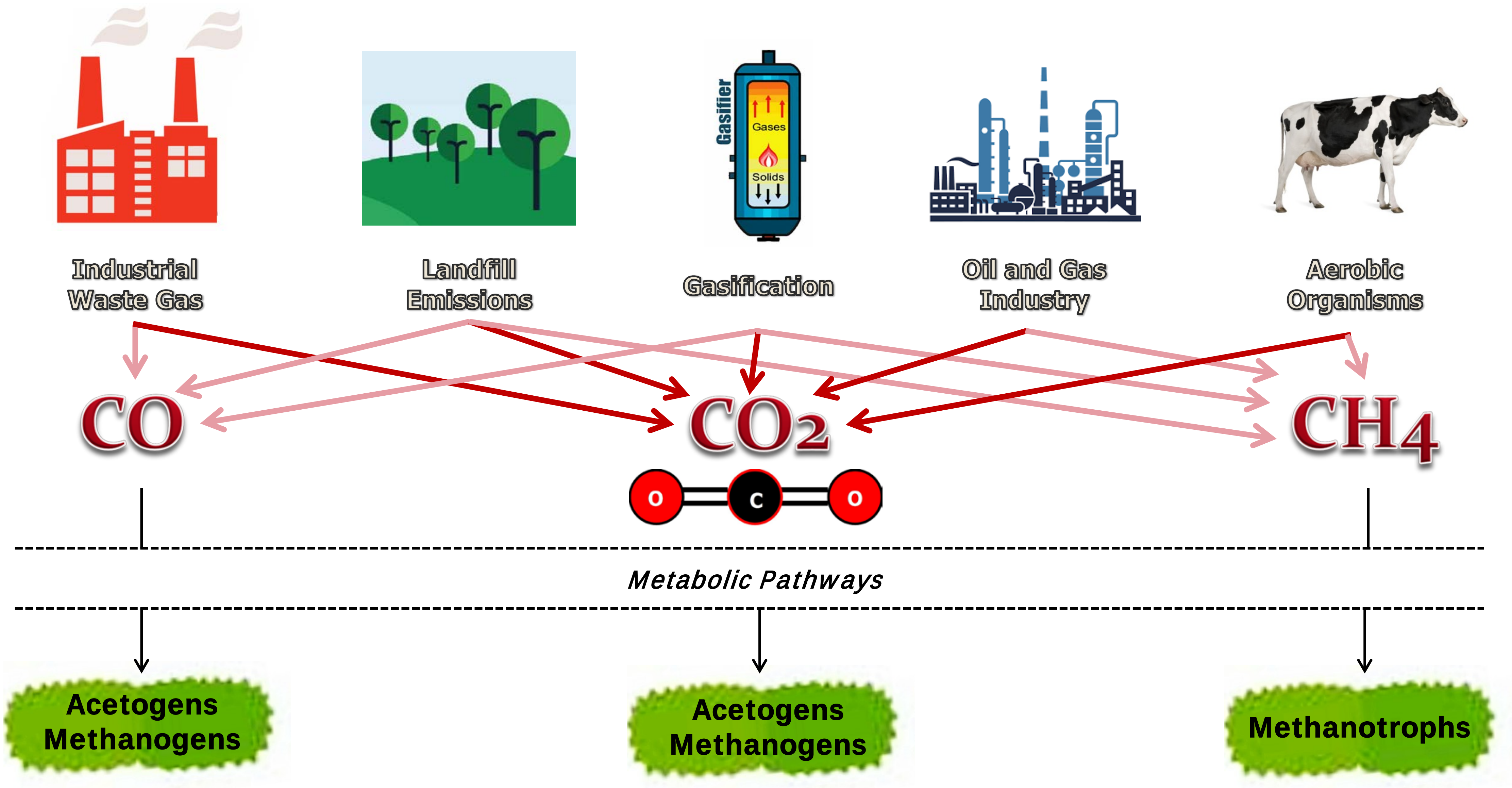
- Global warming
- Ocean acidification
- Rise of sea level
- Cyclones, storms, floods, fires, geography changes
- Extinction of animal species, elimination of plants
- Threat to social and economic development
- Mental and Physical consequences – Climate anxiety
- 23% of deaths related to air quality
- GDP – 0,79 % global annual losses
- CO_2 taxes for EU members

*EUROPEAN GREEN DEAL

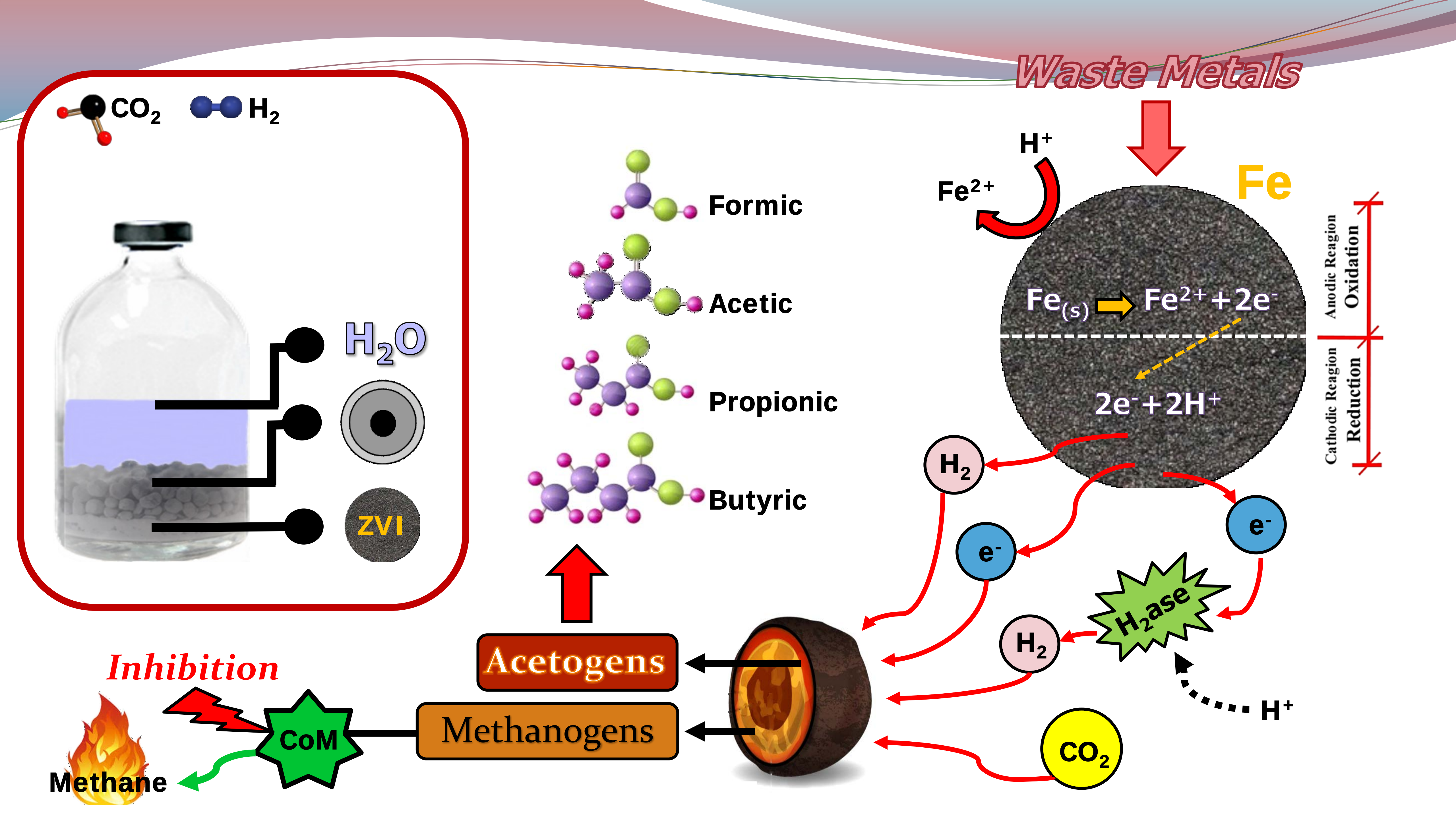
*EU – CLIMATE NEUTRAL

* PARIS AGREEMENT

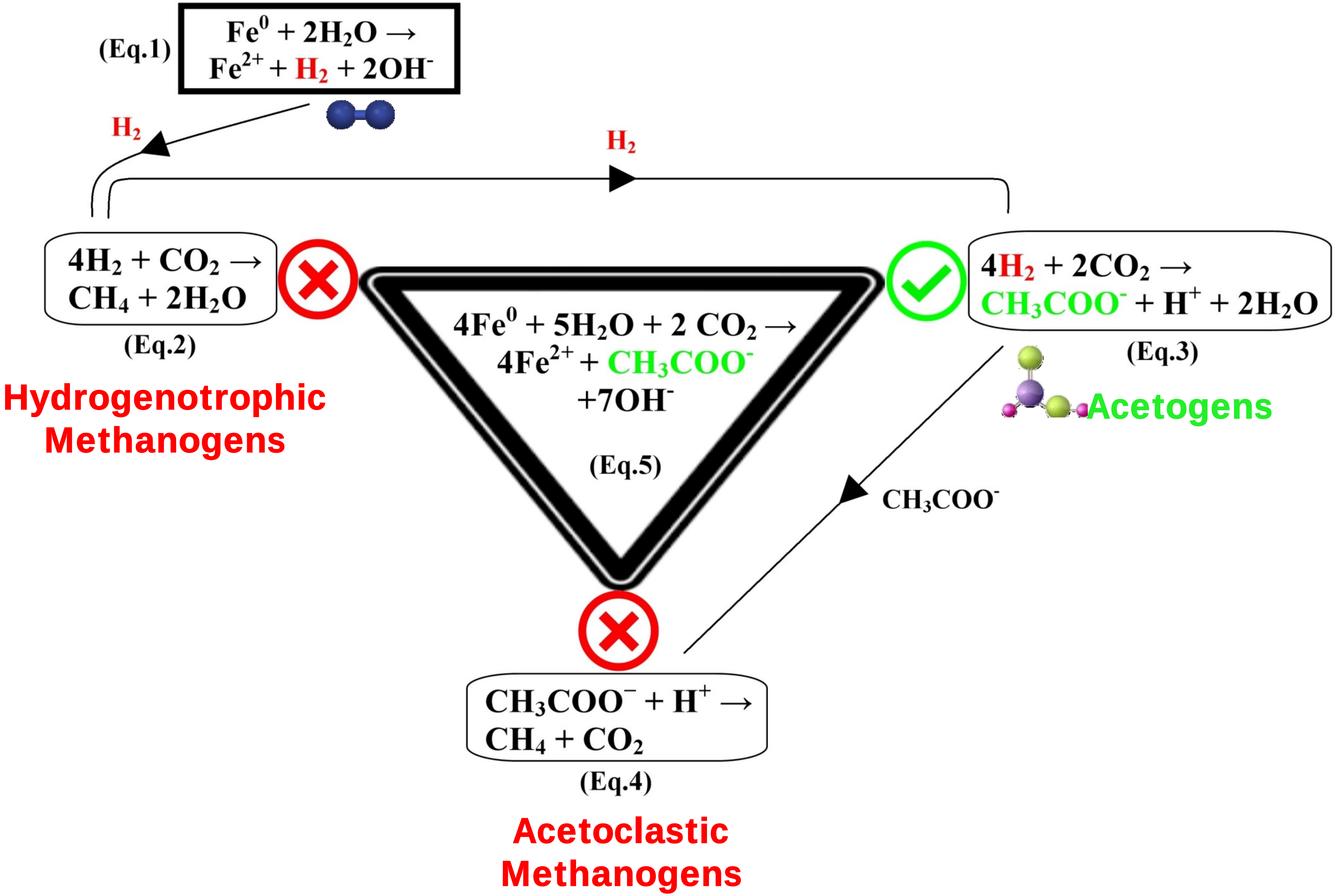
On the 12th of December 2015 has been signed the "Paris Agreement" which is the first-ever universal, legally binding global climate change agreement, adopted at the Paris climate conference. The Governments agreed to limit global warming to well below 2°C {COM(2016) 110 final)}. On the other hand, the EU promotes the "Green Deal" which is a new growth strategy that aims to transform the EU into climate neutral by 2050 {COM(2019) 640 final}



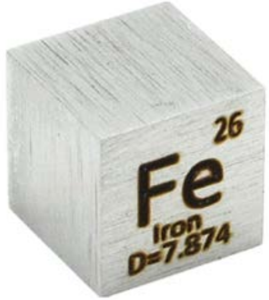
Gasifier
Gases
Solids
Industrial Waste Gas
Landfill Emissions
Gasification
Oil and Gas Industry
Aerobic Organisms
CO
CO2
CH4
O
C
O
Metabolic Pathways
Acetogens Methanogens
Acetogens Methanogens
Methanotrophs

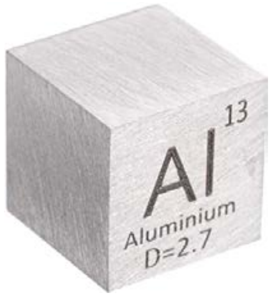


Waste Metals
CO2
H2
H2O
ZVI
Formic
Acetic
Propionic
Butyric
H+
Fe2+
Fe
Fe(s) → Fe2+ + 2e-
2e- + 2H+
Anodic Reagion
Oxidation
Cathodic Reagion
Reduction
H2
e-
e-
H2ase
H2
H+
CO2
Acetogens
Methanogens
Inhibition
CoM
Methane


(Eq.1)
$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$
H_2
H_2
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$
(Eq.2)
Hydrogenotrophic Methanogens
$4Fe^0 + 5H_2O + 2\ CO_2 \rightarrow 4Fe^{2+} + CH_3COO^- + 7OH^-$
(Eq.5)
$4H_2 + 2CO_2 \rightarrow CH_3COO^- + H^+ + 2H_2O$
(Eq.3)
Acetogens
CH_3COO^-
$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$
(Eq.4)
Acetoclastic Methanogens

Abiotic Hydrogen Production Protocols





Under anaerobic conditions

ZVI 50 µm

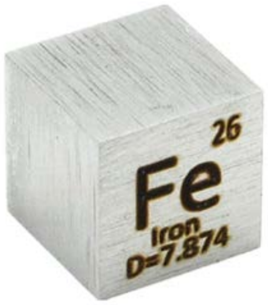
Waste Fe metal 800 µm
Waste Fe metal (white) 1 x 1 mm
Waste Fe metal (black) 8 x 5 mm
Steel wool waste

Waste Al foil
Waste Al beverage cans
Waste Al metal 2 x 2 mm

Magnesium ribbon

Under investigation

Hydrogen



ZVI

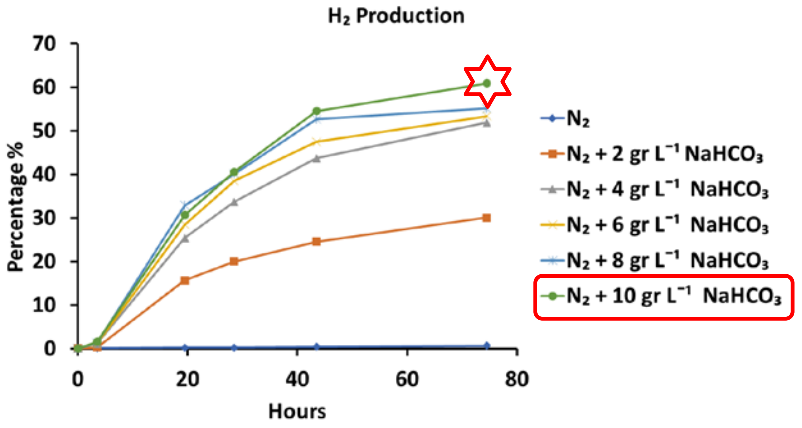
50 µm

Serum Bottles of 160 ml
Working Volume: 65 ml
Incubation: ~ 33 tC° - Agitation: ~ 100 rpm – pH 6-7

Abiotic Hydrogen Production Protocol #1

25 gr/L Fe(0) (50 µm) – Headspace 100 % N_2

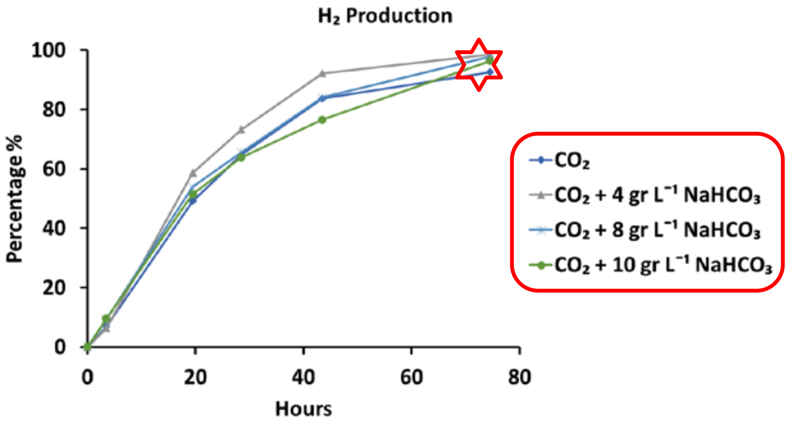
$NaHCO_3$ – a: 0 gr/L b: 2 gr/L c: 4 gr/L d: 6 gr/L e: 8 gr/L f: 10 gr/L



Abiotic Hydrogen Production Protocol #2

25 gr/L Fe(0) (50 µm) – Headspace 100 % CO_2

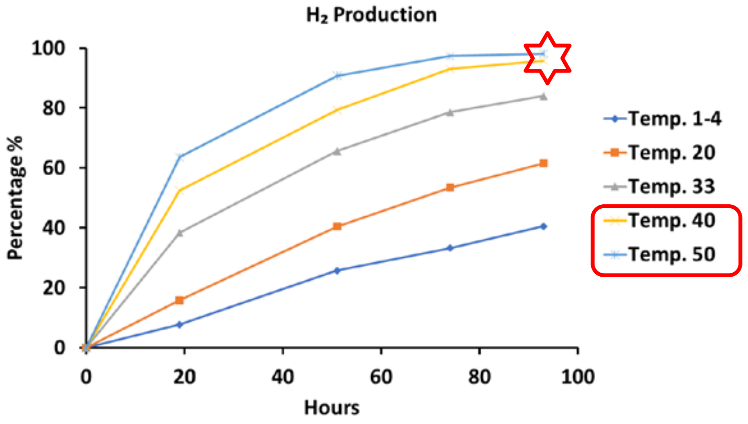
$NaHCO_3$ – a: 0 gr/L b: 4 gr/L c: 8 gr/L d: 10 gr/L



Abiotic Hydrogen Production Protocol #3

25 gr/L Fe(0) (50 µm) - $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

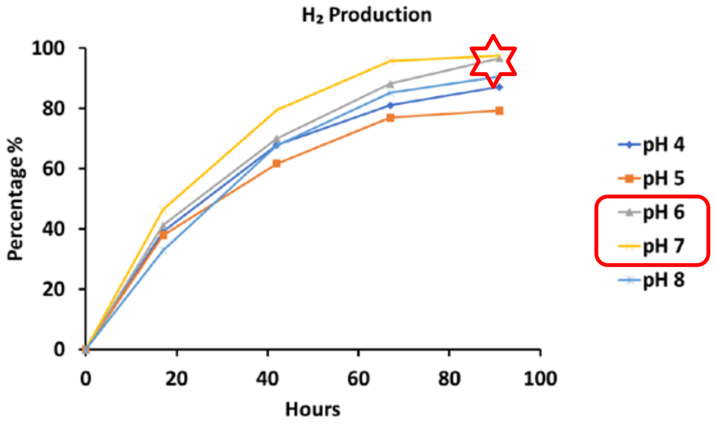
Temperature – a: 1-4 C° b: 20 C° c: 30 C° d: 40 C° e: 50 C°

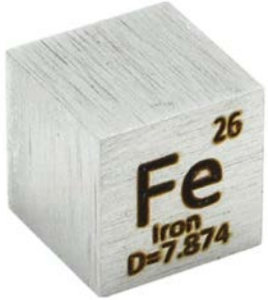


Abiotic Hydrogen Production Protocol #4

25 gr/L Fe(0) (50 µm) - $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

pH – a: 4 b: 5 c: 6 d: 7 e: 8





1

Waste Fe 800 µm

2

Waste Fe (white) 3x1 mm

3

Waste Fe (black) 7x5 mm

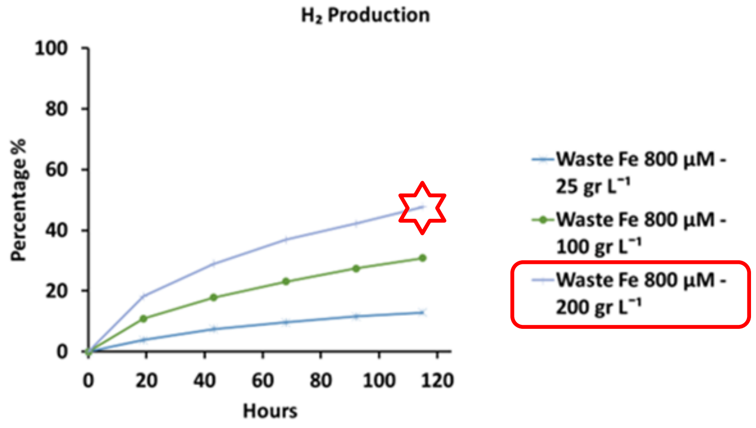
4

Waste Fe wool

Abiotic Hydrogen Production Protocol #1

Waste Fe 800 µm - $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

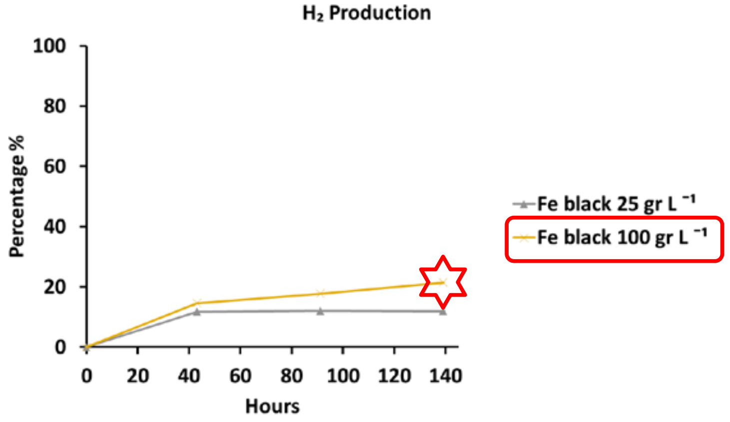
Waste Fe – a: 25 gr/L b: 100 gr/L c: 200 gr/L



Abiotic Hydrogen Production Protocol #3

Waste Fe 7x5 mm - $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

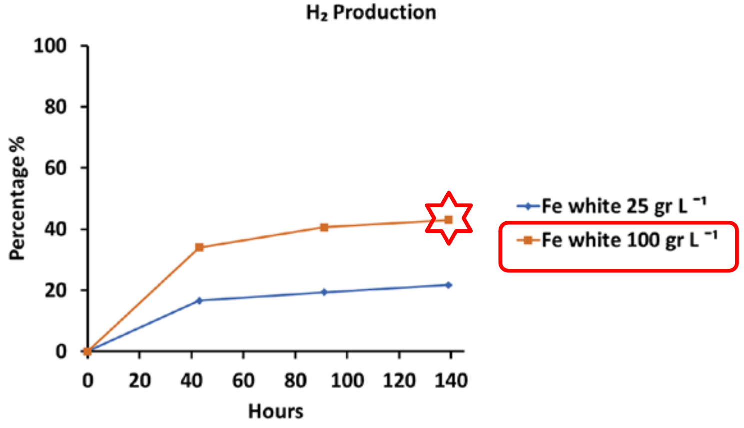
Waste Fe – a: 25 gr/L b: 100 gr/L



Abiotic Hydrogen Production Protocol #2

Waste Fe 3x1 mm - $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

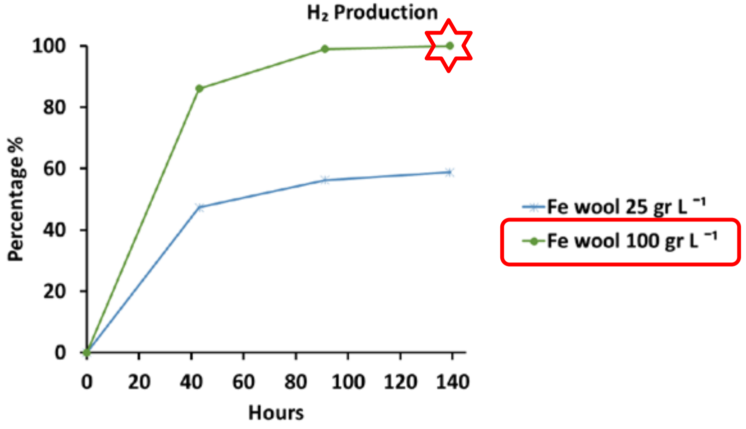
Waste Fe – a: 25 gr/L b: 100 gr/L



Abiotic Hydrogen Production Protocol #4

Waste Fe wool- $NaHCO_3$ 10 gr/L – Headspace 100 % CO_2

Waste Fe – a: 25 gr/L b: 100 gr/L



Experimental Protocol #1

Chemical inhibition of Methanogenesis

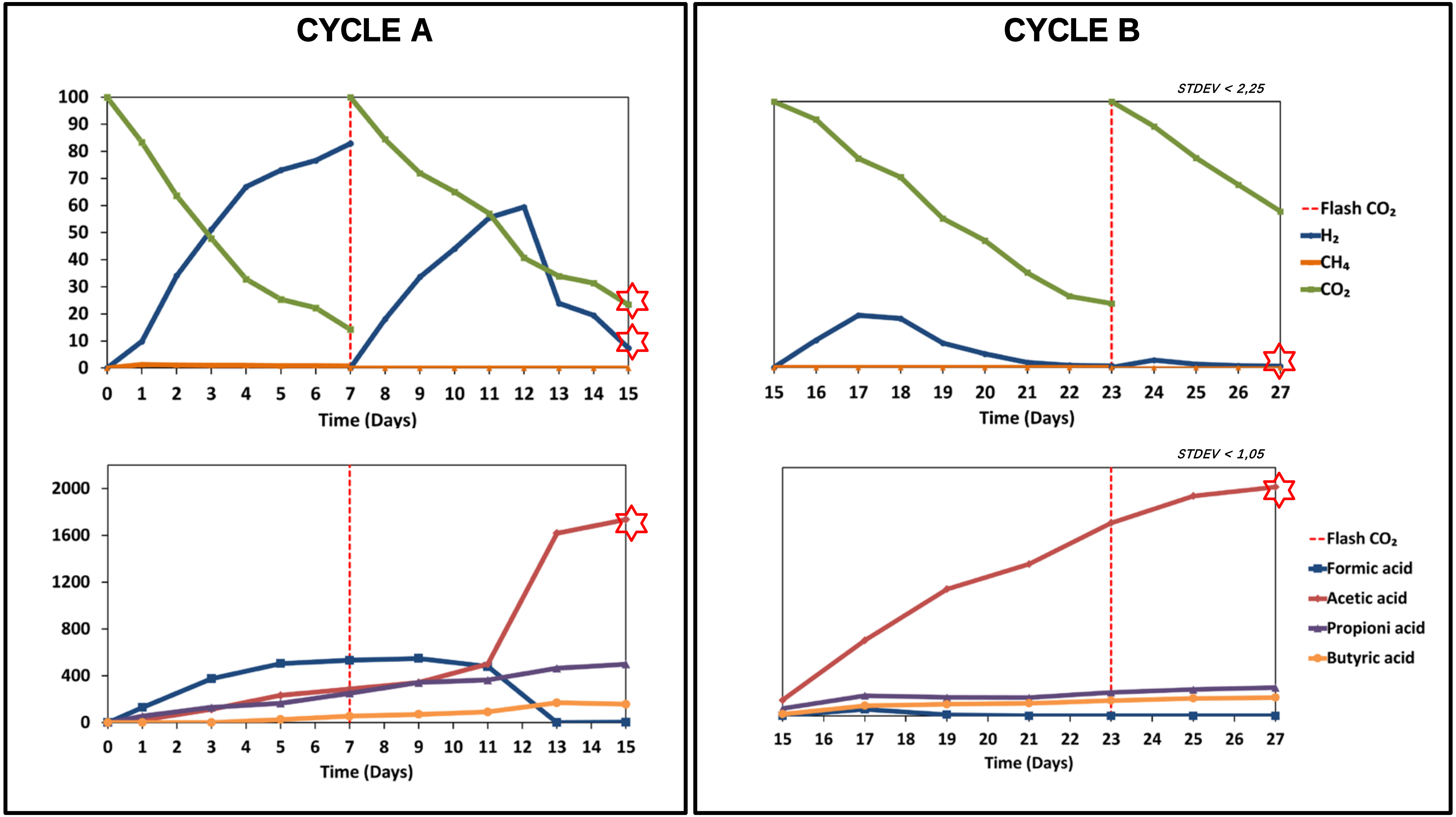
100 gr/l GrSL - 100 gr/l Fe(0) – pH 6 - 50 mM BES

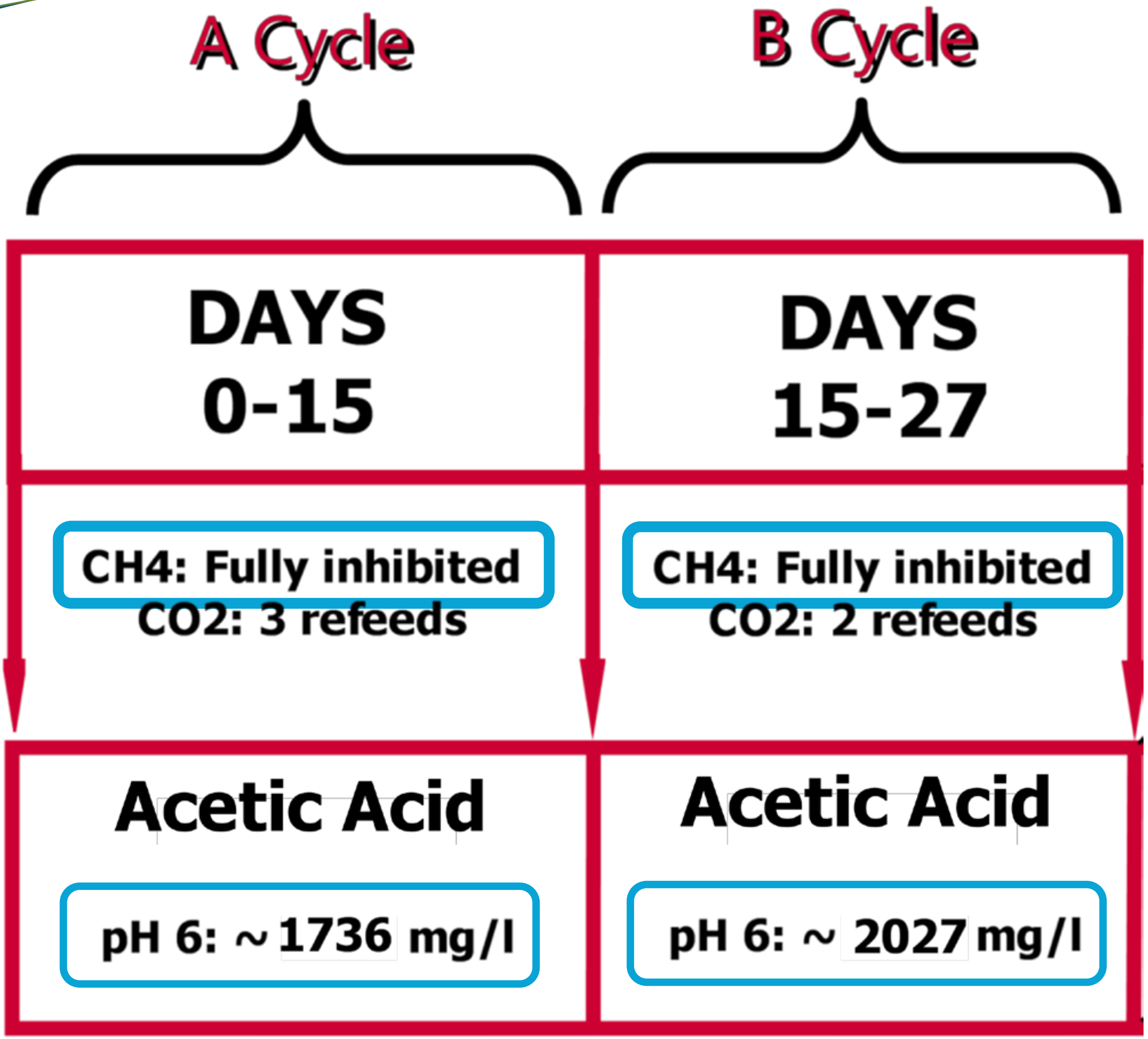
Serum Bottles of 250ml
Working Volume: 100 ml
Incubation: ~ 33 tC° - Agitation: ~ 100 rpm

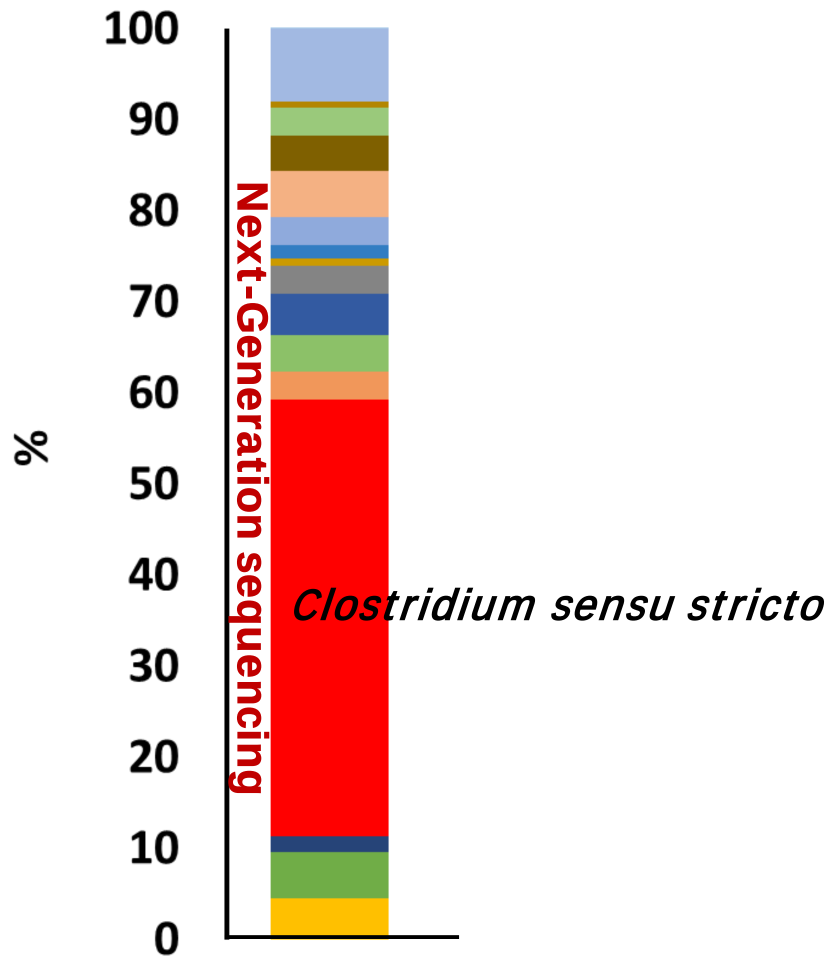
A Cycle	B Cycle
DAYS 0-15	DAYS 15-27

Gas Composition (%)

VFAs (mg / L)




A Cycle
B Cycle
DAYS
0-15
DAYS
15-27
CH4: Fully inhibited
CO2: 3 refeeds
CH4: Fully inhibited
CO2: 2 refeeds
Acetic Acid
pH 6: ~1736 mg/l
Acetic Acid
pH 6: ~ 2027 mg/l


100
90
80
70
60
50
40
30
20
10
0
%
Next-Generation sequencing
Clostridium sensu stricto

Experimental Protocol #2

pH and Thermal Inhibition of Methanogenesis

Serum Bottles of 250ml
Working Volume: 100 ml
Incubation: ~ 33 tC° - Agitation: ~ 100 rpm

A Cycle

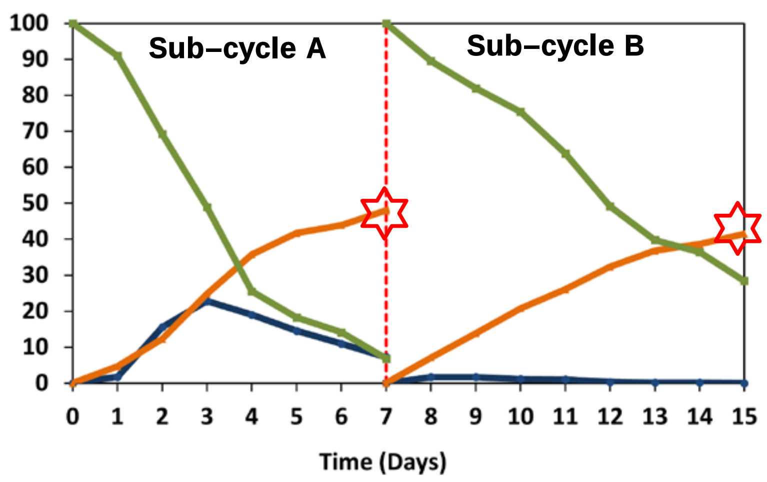
B Cycle

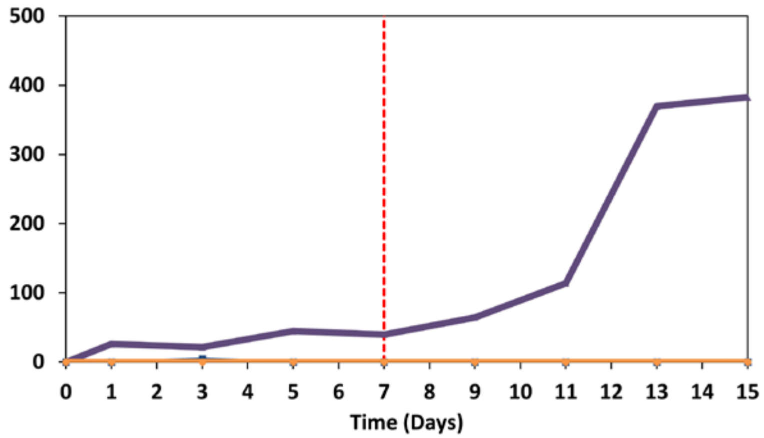
Sub-Cycle	Sub-Cycle	
DAYS 0-7	DAYS 7-15	DAYS 15-27

Gas Composition (%)

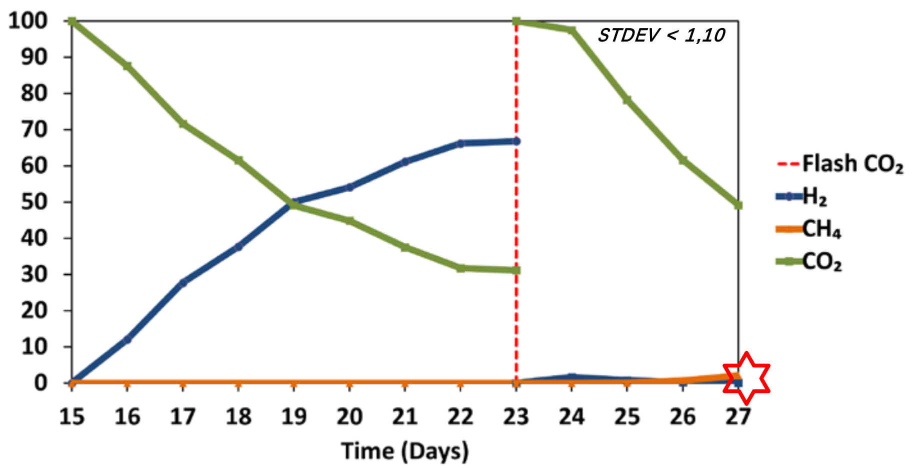
VFAs (mg / L)

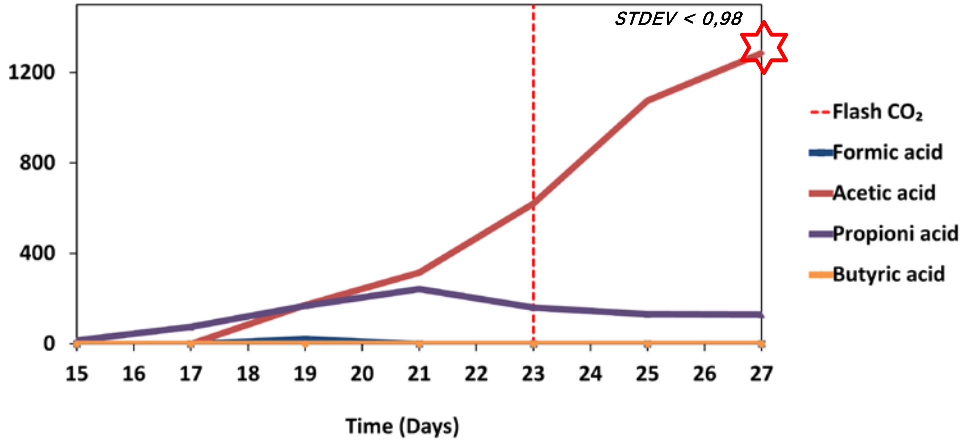
CYCLE A



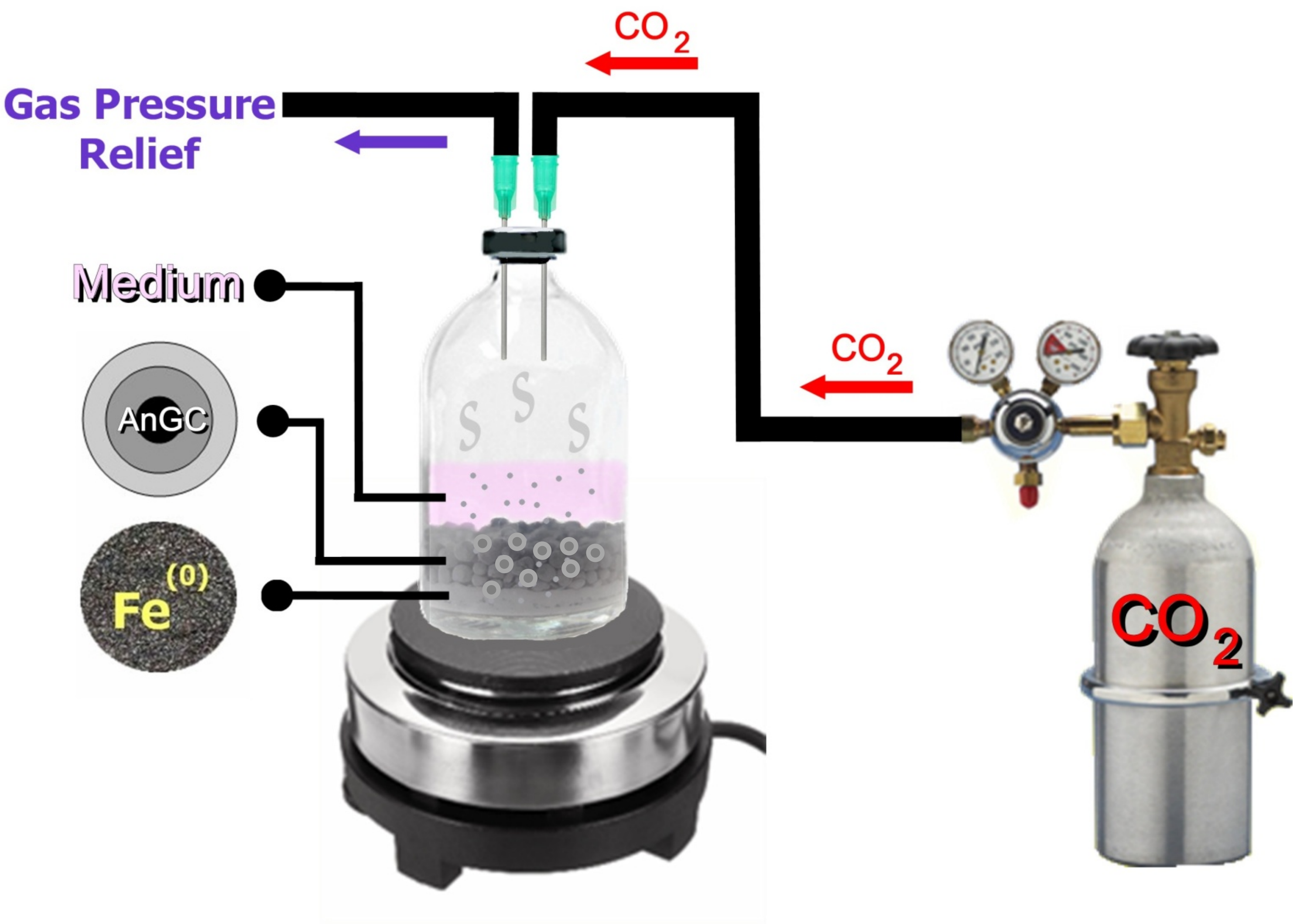


CYCLE B





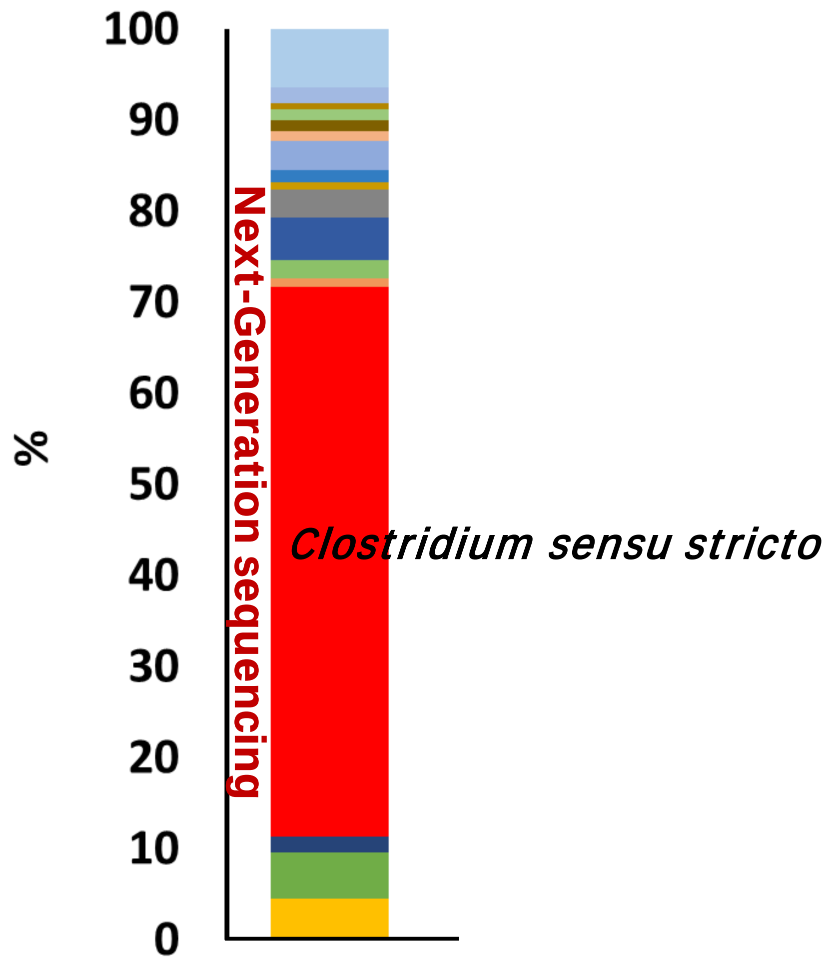
Thermal treatment



A Cycle

B Cycle

Sub-Cycle	Sub-Cycle	
DAYS 0-7	**DAYS 7-15**	**DAYS 15-27**
CH_4: ~50% CO_2: 1 refeeds	pH Inhibition Ph 6 -> pH ~4 CH_4: ~40% CO_2: 2 refeeds New Medium	Thermal Inhibition CH_4: Fully Inhibited CH_4: Day 27 CO_2: 2 refeeds
Acetic Acid pH 6: ~ 60 mg/l	Acetic Acid pH 6: ~ 390 mg/l	Acetic Acid pH 6: ~ 1400 mg/l



Experimental Protocol #3

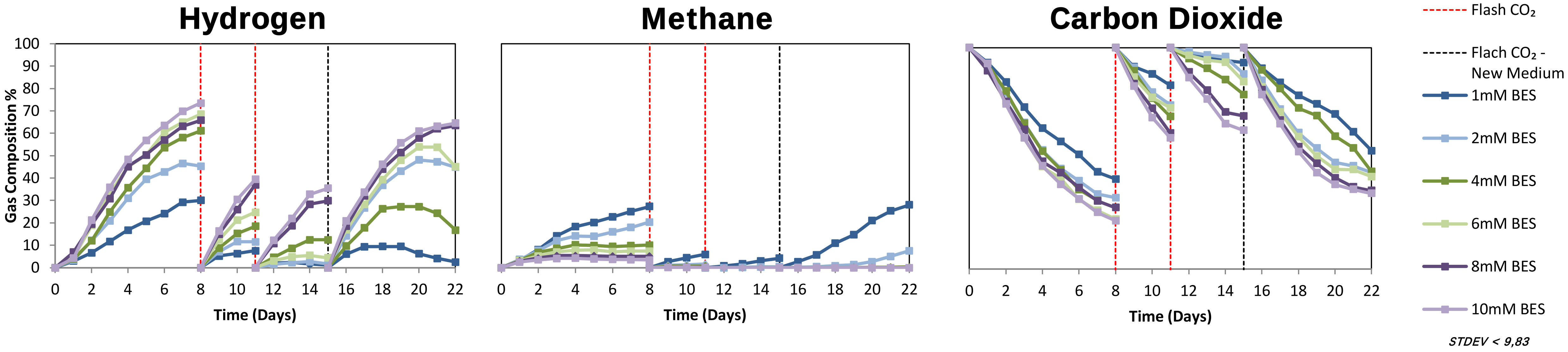
Chemical Inhibition of Methanogenesis

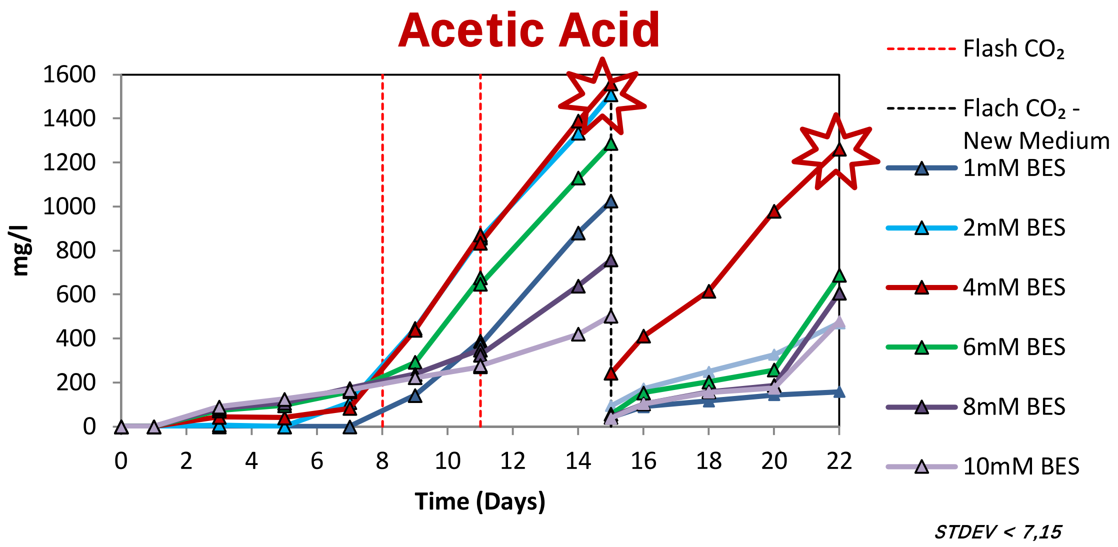
100 gr/l GrSL - 100 gr/l Fe(0) – BES

BES – a: 1mM b: 2mM, c: 4mM, d: 6mM, e: 8mM, f: 10mM

Serum Bottles of 250ml
Working Volume: 100 ml
Incubation: ~ 33 tC° - Agitation: ~ 100 rpm

A Cycle	B Cycle
DAYS 0-15	DAYS 15-22





Formic acid
Propionic acid
Butyric Acid

380 mg/l

A Cycle	B Cycle
DAYS 0-15	**DAYS 15-22**
CH_4: Fully inhibited BES: 3-10 mM BES CO_2: 2 refeeds	CH_4: Fully inhibited BES: 4-10 mM BES CO_2: 1 refeeds New Medium
Acetic Acid MAX 2mM BES: 1509 mg/l 4mM BES: 1558 mg/l	Acetic Acid MAX 4mM BES: 1262 mg/l

Experimental Protocol #4

Methanogenesis inhibition using NaCl

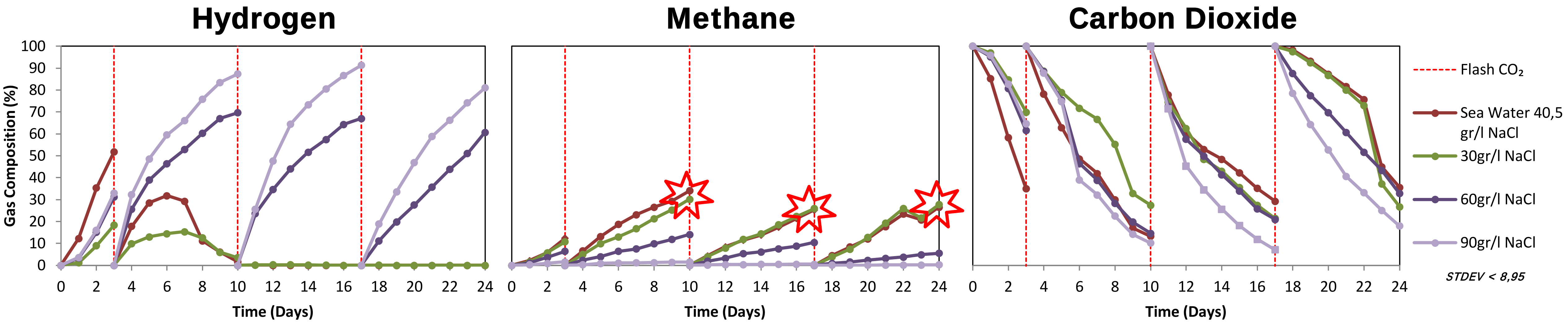
100 gr/l GrSL - 100 gr/l Fe(0) – NaCl

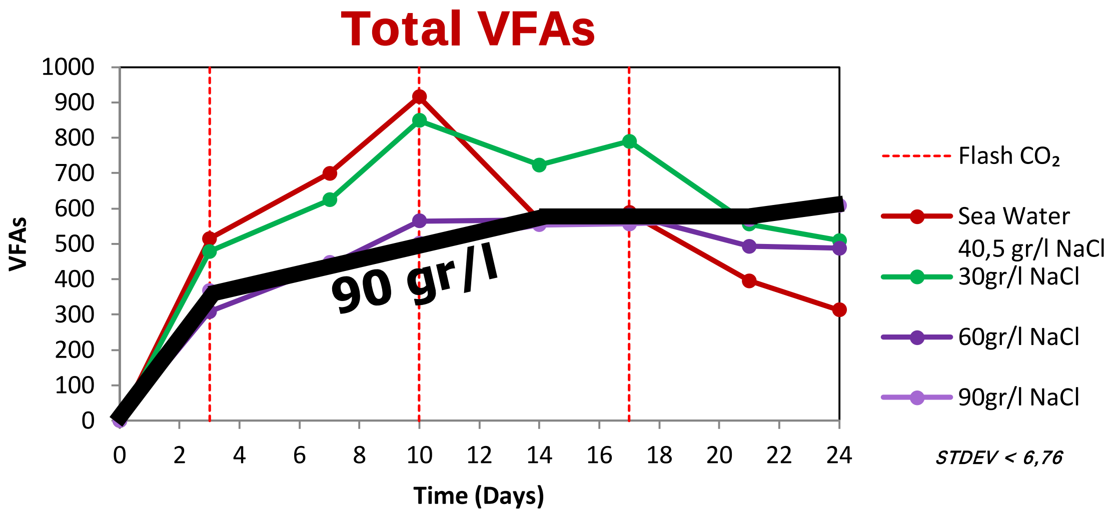
NaCL - a: 30gr/l, b: 40,5gr/l, c: 60gr/l, d: 90gr/l

Serum Bottles of 250ml
Working Volume: 100 ml
Incubation: ~ 33 tC° - Agitation: ~ 100 rpm

A Cycle

DAYS 0-24


Hydrogen
Methane
Carbon Dioxide
Gas Composition (%)
Time (Days)
Flash CO_2
Sea Water 40,5 gr/l NaCl
30gr/l NaCl
60gr/l NaCl
90gr/l NaCl
STDEV < 8,95


Total VFAs
VFAs
Time (Days)
90 gr/l
Flash CO_2
Sea Water 40,5 gr/l NaCl
30gr/l NaCl
60gr/l NaCl
90gr/l NaCl
STDEV < 6,76

A Cycle

DAYS
0-24

CH_4: Fully inhibited
NaCl: 60gr/l, 90gr/L
CO_2: 3 refeeds

TOTAL VFAs MAX

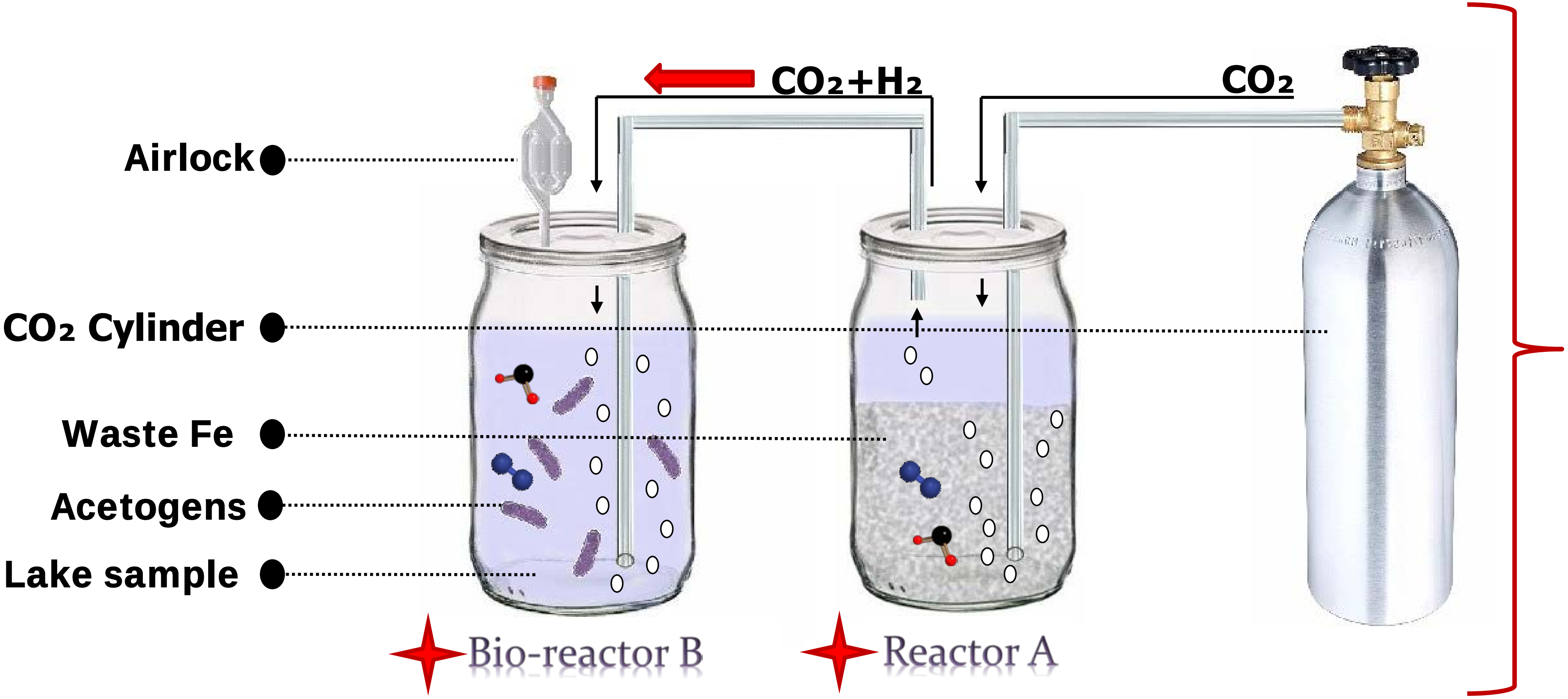
NaCl 90gr/l : 600mg/l

BIOREACTOR - EX-SITU H_2 PRODUCTION

Homoacetogen Enrichment

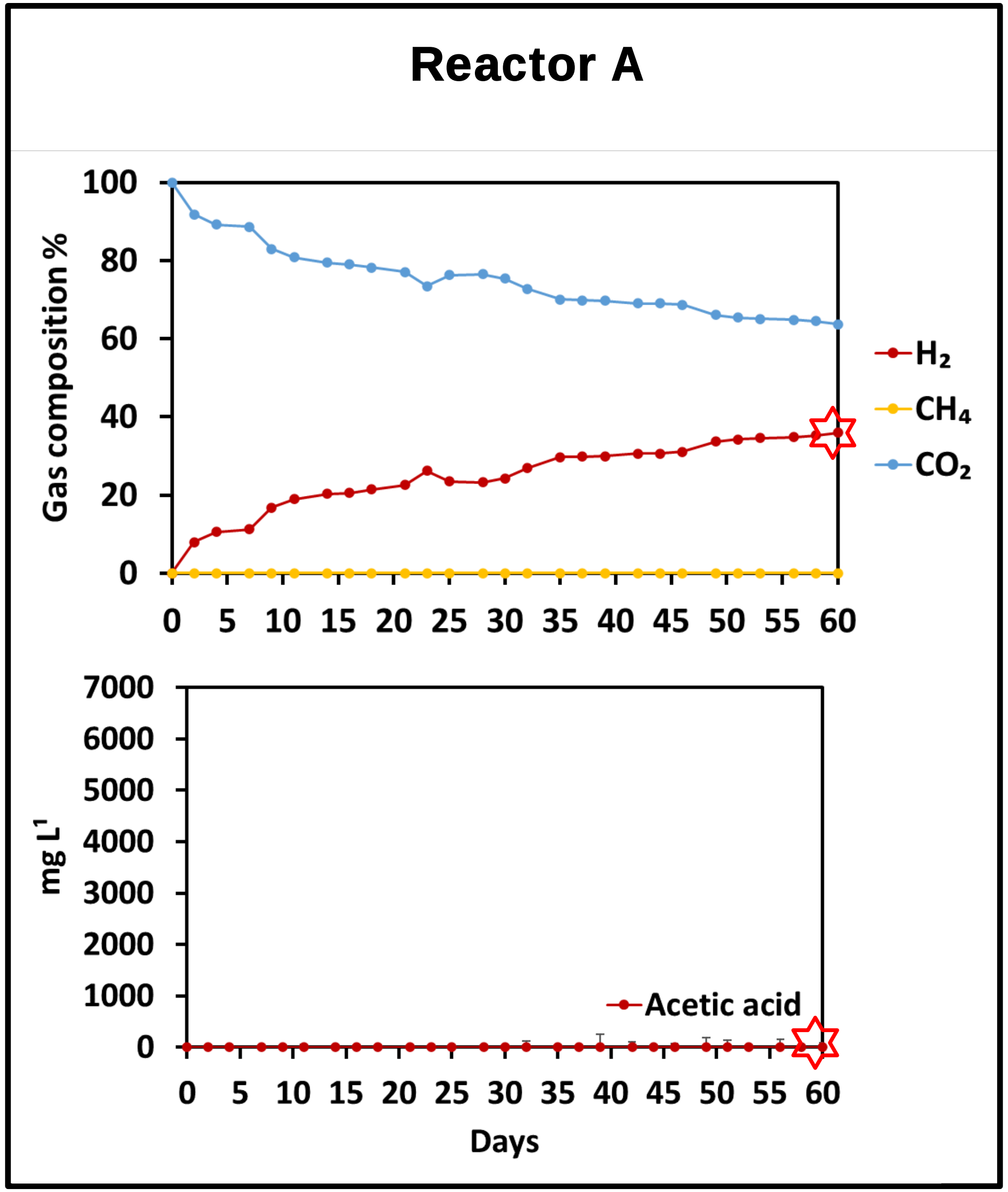
A continuous feed with 100 % CO_2 - 80 ml/sec - TC° 33

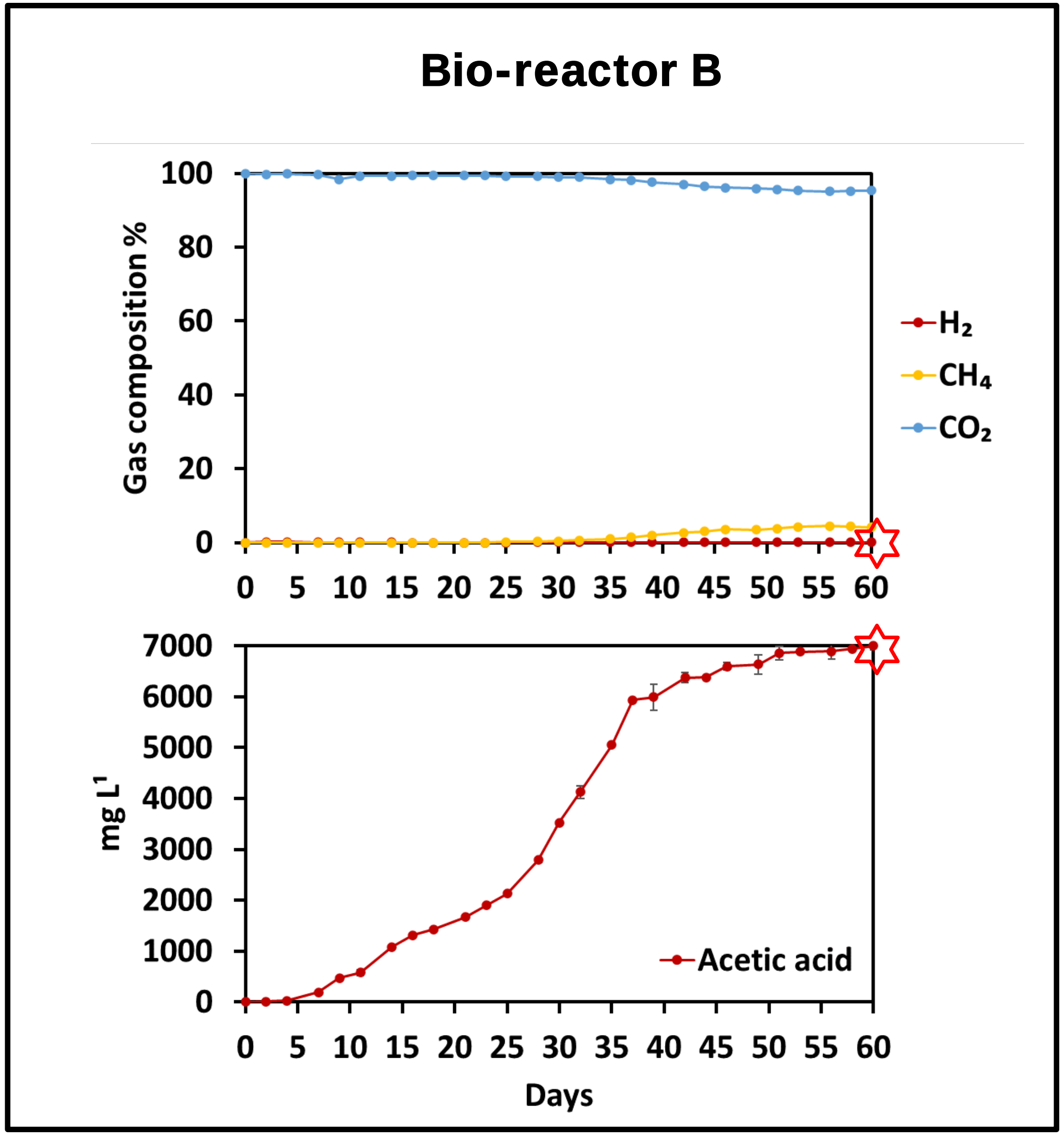
Waste iron 666 gr/L – BES 4 mM – pH 6-7



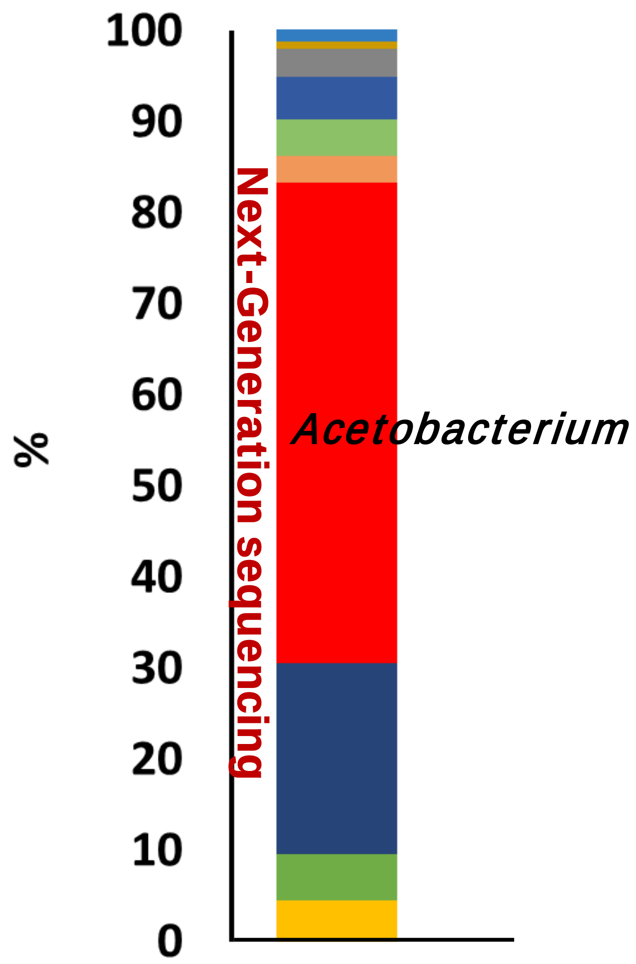
Gas Composition (%)

VFAs (mg / L)



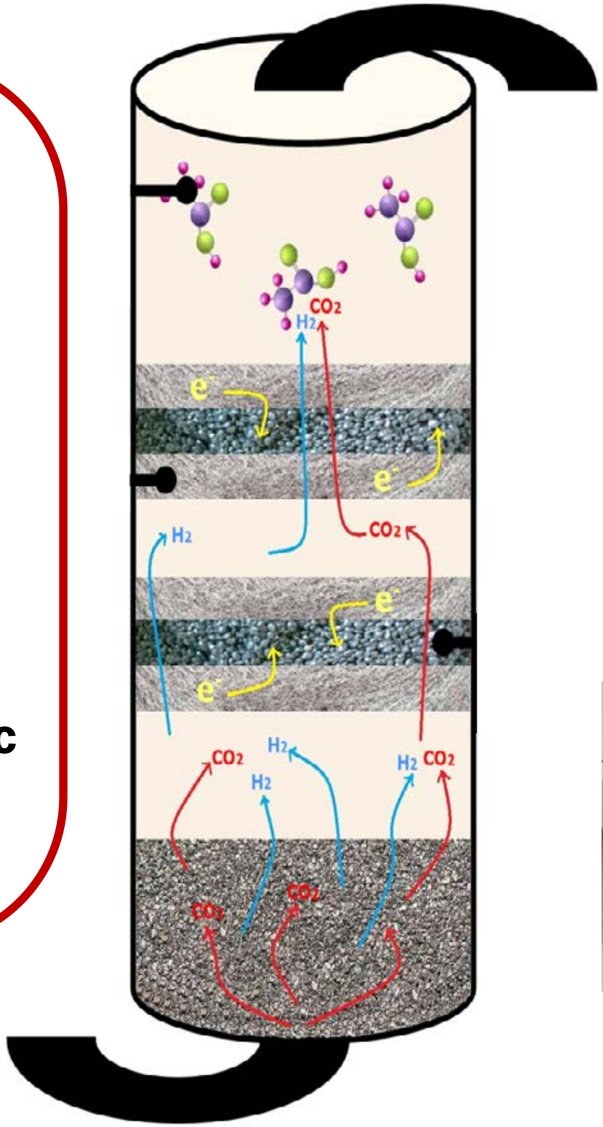


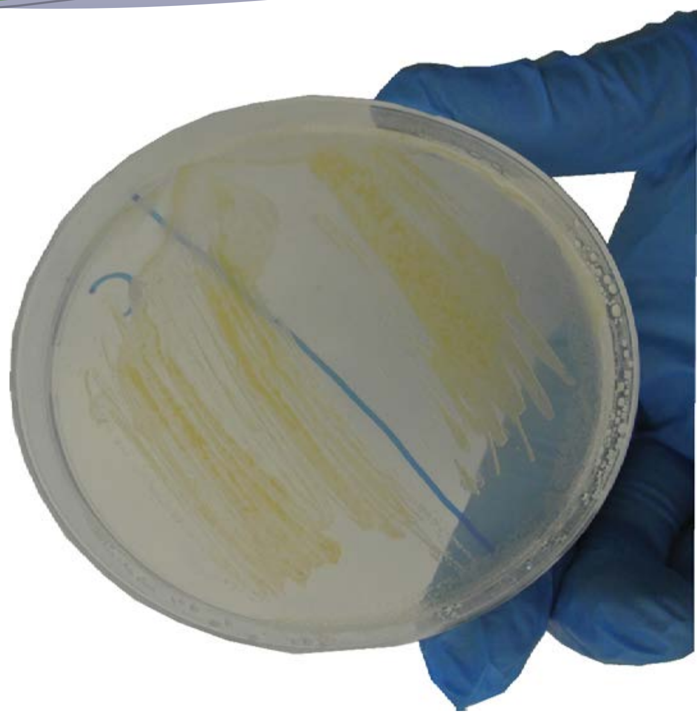
Reactor A	Bio-reactor B
DAYS 0-60	DAYS 0-60
CH_4: No CO_2: 100% continious	CH_4: Fully inhibited CO_2: continious H_2: continious
Acetic Acid 0 mg/l	Acetic Acid 7000 mg/l

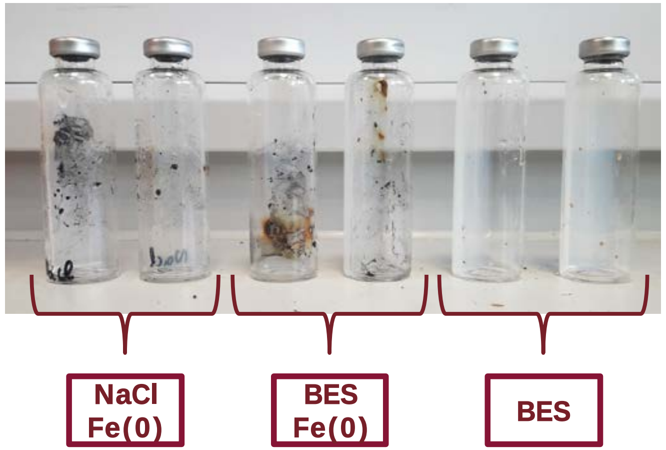


Conclusions – Future work

- A new approach for CO_2 utilization (as a sole carbon source)
- Contribute to climate change mitigation.
- Sustainability
- The production of acetic acid and other VFAs under ambient conditions is tangible.
- Different kinds of waste metals in a circular economy concept.
- Anaerobic granular sludge – the danger of contamination.
- Mechanism regarding the production of acetic acid by acetogens and metallic iron. Direct electron transfer or indirect though H_2?





Thank you!

"...on opening the incubator, I experienced one of those rare moments of intense emotion which reward the research worker for all his pains..."

-Félix d'Herelle-