«Valorization of solid metal waste for the production of platform chemicals (VFAs) through the fixation of CO₂ using anaerobic granular sludge and homoacetogen bacteria strains»

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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
- CO2 taxes for EU members
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}.
Hydrogenotrophic Methanogens

\[
\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-
\]  
(Eq.1)

\[
4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\]  
(Eq.2)

Acetoclastic Methanogens

\[
4\text{Fe}^0 + 5\text{H}_2\text{O} + 2\text{CO}_2 \rightarrow 4\text{Fe}^{2+} + \text{CH}_3\text{COO}^- + 7\text{OH}^-
\]  
(Eq.5)

\[
\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_4 + \text{CO}_2
\]  
(Eq.4)

Acetogens

\[
4\text{H}_2 + 2\text{CO}_2 \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ + 2\text{H}_2\text{O}
\]  
(Eq.3)
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
Abiotic Hydrogen Production Protocol #1
25 gr/L Fe(0) (50 μm) - Headspace 100% N₂
NaHCO₃ - 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% CO₂
NaHCO₃ - 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) - NaHCO₃ 10 gr/L - Headspace 100% CO₂
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) - NaHCO₃ 10 gr/L - Headspace 100% CO₂
pH - a: 4 b: 5 c: 6 d: 7 e: 8

ZVI
50 μm

Serum Bottles of 160 ml
Working Volume: 65 ml
Incubation: ~33°C - Agitation: ~100 rpm - pH 6-7
Abiotic Hydrogen Production Protocol #1
Waste Fe 800 μm - NaHCO₃ 10 gr/ L - Headspace 100 % CO₂
Waste Fe - a: 25 gr/ L  b: 100 gr/ L  c: 200 gr/ L

Abiotic Hydrogen Production Protocol #2
Waste Fe 3x1 mm - NaHCO₃ 10 gr/ L - Headspace 100 % CO₂
Waste Fe - a: 25 gr/ L  b: 100 gr/ L

Abiotic Hydrogen Production Protocol #3
Waste Fe 7x5 mm - NaHCO₃ 10 gr/ L - Headspace 100 % CO₂
Waste Fe - a: 25 gr/ L  b: 100 gr/ L

Abiotic Hydrogen Production Protocol #4
Waste Fe wool - NaHCO₃ 10 gr/ L - Headspace 100 % CO₂
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

DAYS 0-15

B Cycle

DAYS 15-27

Experimental bottles with contents.
Gas Composition (%)

VFAs (mg/L)

CYCLE A

CYCLE B
A Cycle

DAYS 0-15

CH4: Fully inhibited
CO2: 3 refeeds

Acetic Acid
pH 6: ~1736 mg/l

B Cycle

DAYS 15-27

CH4: Fully inhibited
CO2: 2 refeeds

Acetic Acid
pH 6: ~2027 mg/l

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°C - Agitation: ~ 100 rpm

A Cycle

Sub-Cycle

DAYS
0-7

B Cycle

Sub-Cycle

DAYS
7-15

DAYS
15-27
Gas Composition (%)

VFAs (mg/L)

**CYCLE A**

- **Sub-cycle A**
- **Sub-cycle B**

**VFAs (mg/L)**

**CYCLE B**

- **STDEV < 1.10**
- **STDEV < 0.98**

- Flash CO₂
- H₂
- CH₄
- CO₂

- Flash CO₂
- Formic acid
- Acetic acid
- Propionic acid
- Butyric acid

Time (Days)
Thermal treatment
### A Cycle

<table>
<thead>
<tr>
<th>DAYS</th>
<th>Sub-Cycle</th>
<th>pH Inhibition</th>
<th>Thermal Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-7</td>
<td>CH4: ~50%</td>
<td>Ph 6 $\rightarrow$ pH ~4</td>
<td>CH4: Fully Inhibited</td>
</tr>
<tr>
<td></td>
<td>CO2: 1 refeeds</td>
<td>CH4: ~40%</td>
<td>CH4: Day 27</td>
</tr>
<tr>
<td></td>
<td>Acetic Acid</td>
<td>CO2: 2 refeeds</td>
<td>CO2: 2 refeeds</td>
</tr>
<tr>
<td></td>
<td>pH 6: ~ 60 mg/l</td>
<td>New Medium</td>
<td>Acetic Acid</td>
</tr>
</tbody>
</table>

### B Cycle

<table>
<thead>
<tr>
<th>DAYS</th>
<th>Sub-Cycle</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-15</td>
<td>pH 6: ~ 390 mg/l</td>
<td>pH 6: ~ 1400 mg/l</td>
</tr>
<tr>
<td>15-27</td>
<td>pH 6: ~ 1400 mg/l</td>
<td></td>
</tr>
</tbody>
</table>
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°C - Agitation: ~ 100 rpm

A Cycle

B Cycle

DAYS 0-15

DAYS 15-22

A Cycle

B Cycle
**A Cycle**

**DAYS 0-15**
- CH4: Fully inhibited
- BES: 3-10 mM BES
- CO2: 2 refeeds

**DAYS 15-22**
- CH4: Fully inhibited
- BES: 4-10 mM BES
- CO2: 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
A Cycle

DAYS 0-24

CH4: Fully inhibited
NaCl: 60gr/l, 90gr/l
CO2: 3 refeeds

TOTAL VFAs MAX
NaCl 90gr/l : 600mg/l
BIOREACTOR - EX-SITU H₂ PRODUCTION
Homoacetogen Enrichment
A continuous feed with 100 % CO₂ - 80 ml/sec - TC° 33
Waste iron 666 gr/L - BES 4 mM - pH 6-7

Airlock
CO₂ Cylinder
Waste Fe
Acetogens
Lake sample

Bio-reactor B
Reactor A
Gas Composition (%)

VFA (mg/L)

Reactor A

Bio-reactor B
Acetobacterium

Next-Generation sequencing

**Reactor A**

<table>
<thead>
<tr>
<th>DAYS 0-60</th>
<th>DAYS 0-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4: No</td>
<td>CH4: Fully inhibited</td>
</tr>
<tr>
<td>CO2: 100% continuous</td>
<td>CO2: continuous</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>H2: continuous</td>
</tr>
<tr>
<td>0 mg/l</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Acetic Acid</strong></td>
</tr>
<tr>
<td></td>
<td>7000 mg/l</td>
</tr>
</tbody>
</table>
Conclusions - Future work

- A new approach for CO₂ 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 H₂?
"...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-

Thank you!