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Unidad Académica Juriquilla

Implementing an optimization strategy in real time to improve biological hydrogen production

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Ideas for a sustainable world
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LIPATA Laboratorio de Investigación en Procesos Avanzados de Tratamiento de Aguas

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Hydrogen

As energetic vector

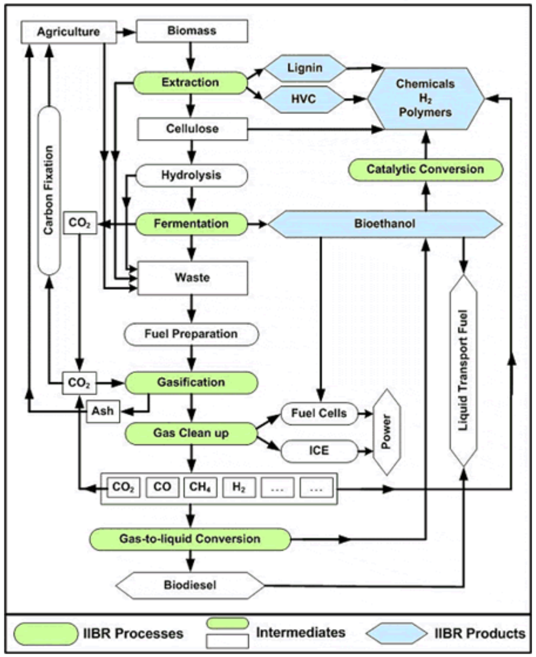
- ✓ Heat of combustion: 120 kJ/g

  Gasoline: 45 kJ/g
- ✓ 1kg de H_2 = 2.4 kg de CH_4
- ✓ High utilization efficiency
- ✓ Water as combustion product

Used in Biorefineries

- ✓ Methanol production
- ✓ Products from syngas

INTENSIFIED INTEGRATED BIOREFINERY (IIBR)



Methods for hydrogen production

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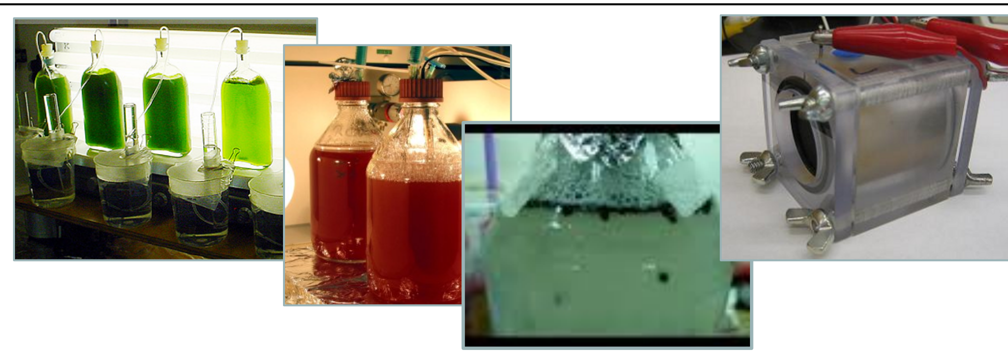
- Conventional (96%)
  - Reforming processes
  - Pyrolysis
  - Gasification

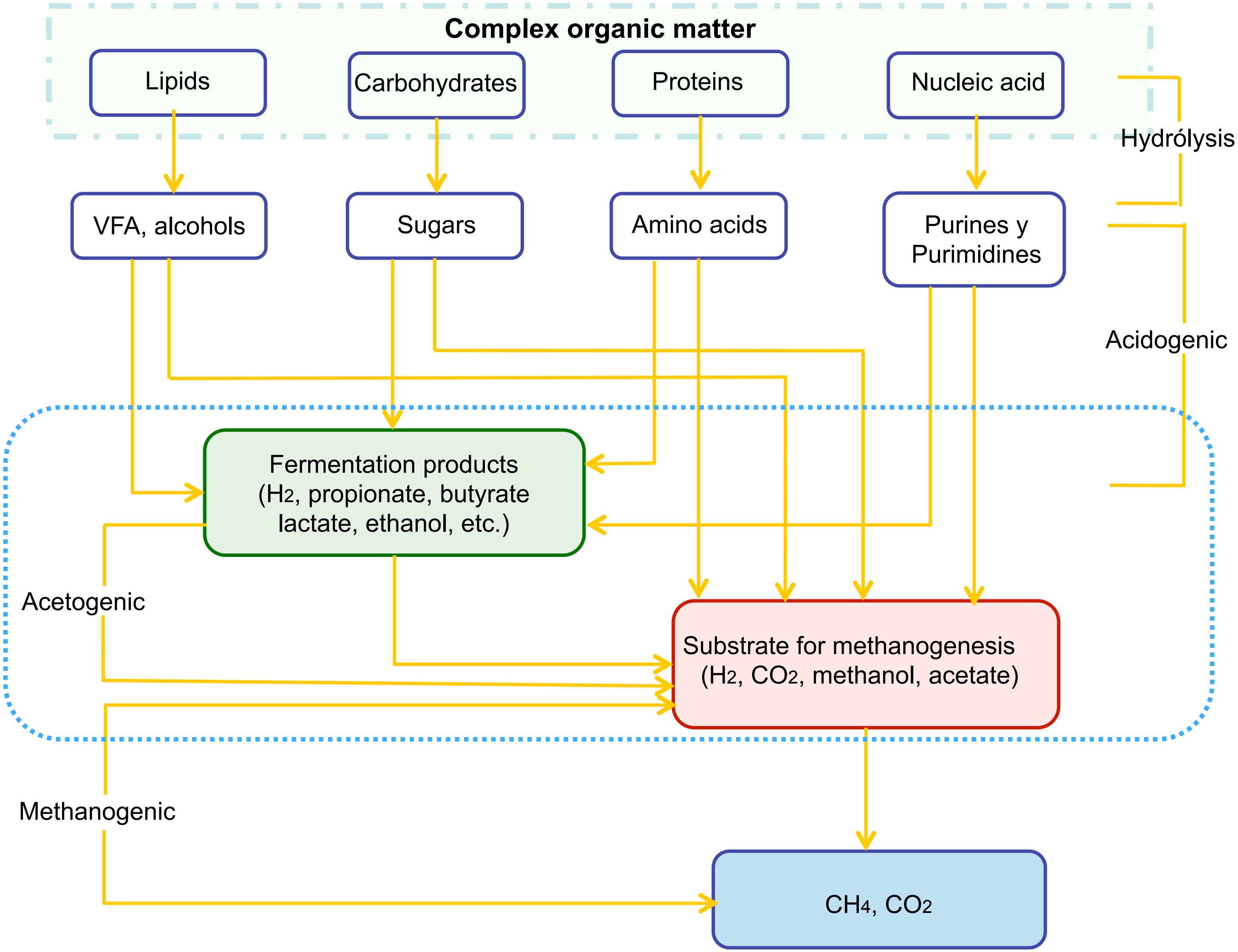
  (Biomass, Carbon)
- Electrolysis (4% H_2O)

- Biological
  - Biophotolysis
  - Photo-fermentation
  - Bioelectrochemical systems
  - **Dark-fermentation**



Waste

Dark fermentation



Reactions

Stoichiometry

Theoretical equation:

$$C_6H_{12}O_6 + 12H_2O \rightarrow 6CO_2 + 12H_2$$

(12 mol H_2/mol glucose)

Reactions

Stoichiometry (*Clostridium* bacteria)

Thermophilic:

$\mathbf{C_6H_{12}O_6 + 2H_2O \rightarrow C_2H_4O_2 + 2CO_2 + 4H_2}$ **:** Acetic
(4mol H_2/mol glucose)

Reactions

Stoichiometry (*Clostridium* bacteria)

Mesophilic

$C_6H_{12}O_6 + 2H_2O \rightarrow C_2H_4O_2 + 2CO_2 + 4H_2$: Acetic
(4mol H_2/mol glucose)
$C_6H_{12}O_6 + 2H_2O \rightarrow 2C_4H_7O_2 + 2CO_2 + 2H_2$: Butiric
(2mol H_2/mol glucose)

Side reactions

Methane
CO2 + 4 H2 → CH4 + 2H2O
Solvents: acetone, ethanol, butanol

Inoculum

Pure culture

Clostridium acetobutylicum, C. butyricum, C. termocellum, etc

Enterobacter aerogenes, E. cloacae…

Escherichia coli

Consortium

- Viable for industrial application

- Robust against environmental changes

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Factors influencing

Some factors affecting fermentative hydrogen production

- Inoculum (Lo et al., 2008; Jo et al., 2008)
- Substrate (Zheng et al., 2008; Lee et al., 2008)
- pH (Chen et al., 2005; Das and Veziroglu, 2008)
- Temperature (Lin et al., 2008; Montes-Moncivais et al., 2007)

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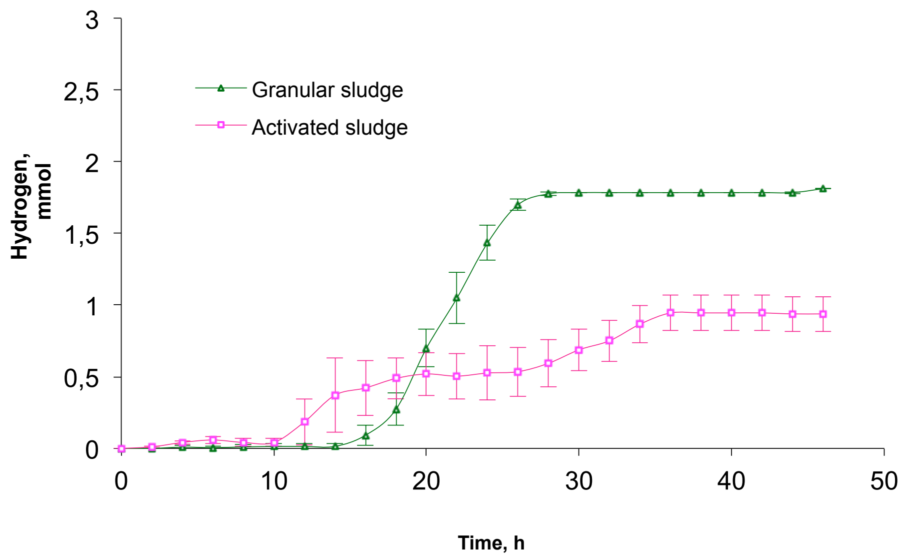
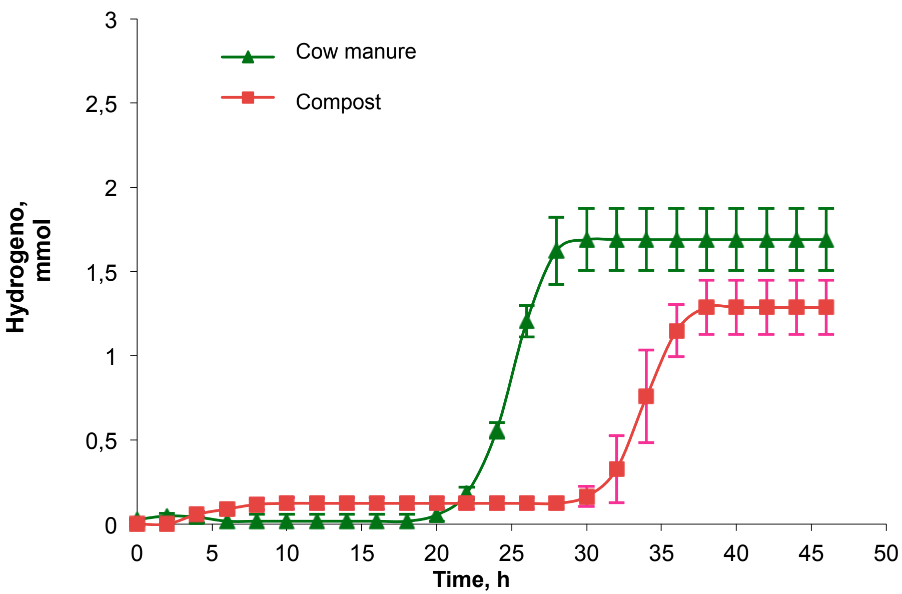
Inoculum



GS → 1.79 mmol

AS → 0.94 mmol



CM → 1.69 mmol

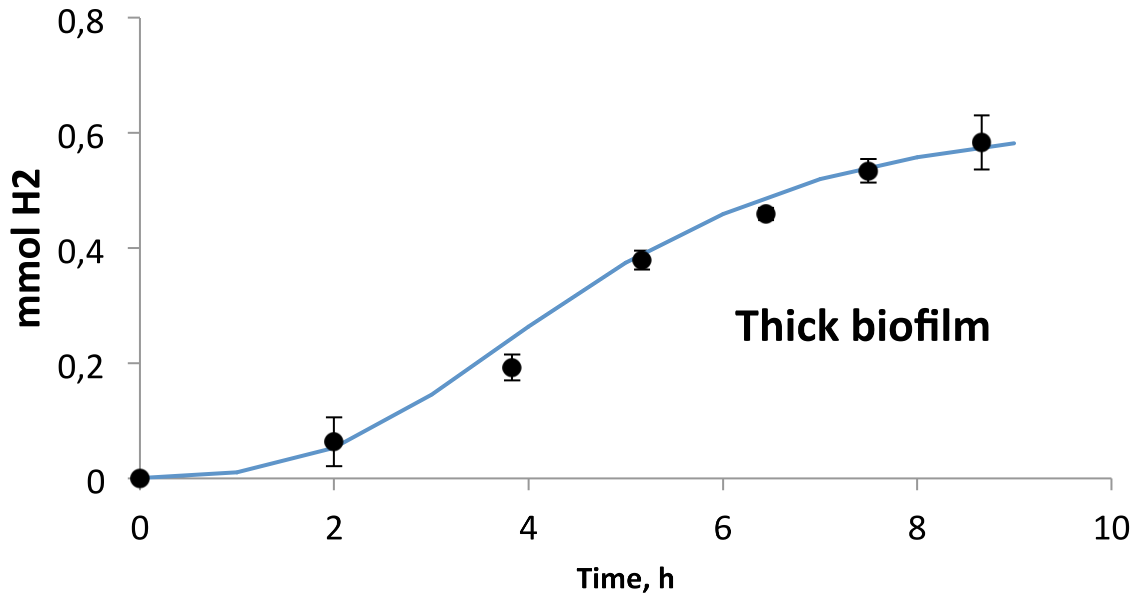
CO → 1.29 mmol

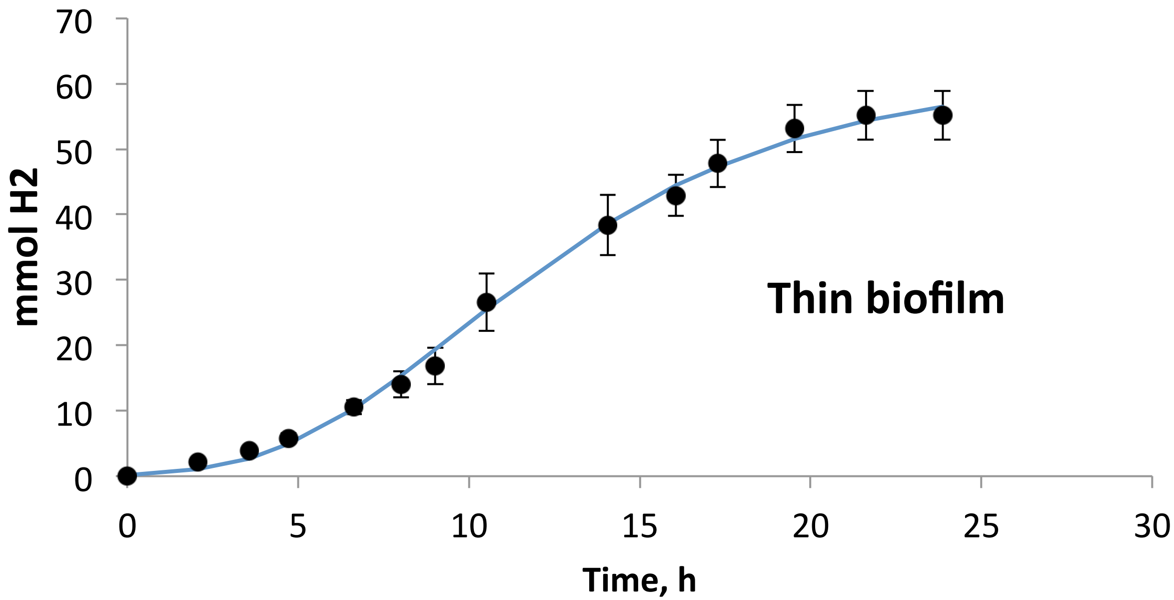
Montes Moncivias et al., (2006)

Biomass retention

- Disperse growth: SS in the effluent

Thickness of biofilms





Hernández et al., (2011)

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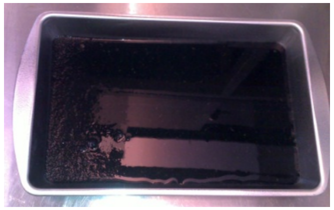
Thickness of biofilms

- Thin biofilms are more suitable for hydrogen production
- Thick biofilm developed a bacterial community oriented to the production of propionate

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$$

Inoculum pretreatment

Heat pretreatment



Anaerobic granular sludge from a UASB

24 h @ 104 °C

Grounded and sieved (0.01 cm diameter)

Generation of hydrogen producing bacteria with a more viable method

HRT and pH were used as the pressure selection inducers:

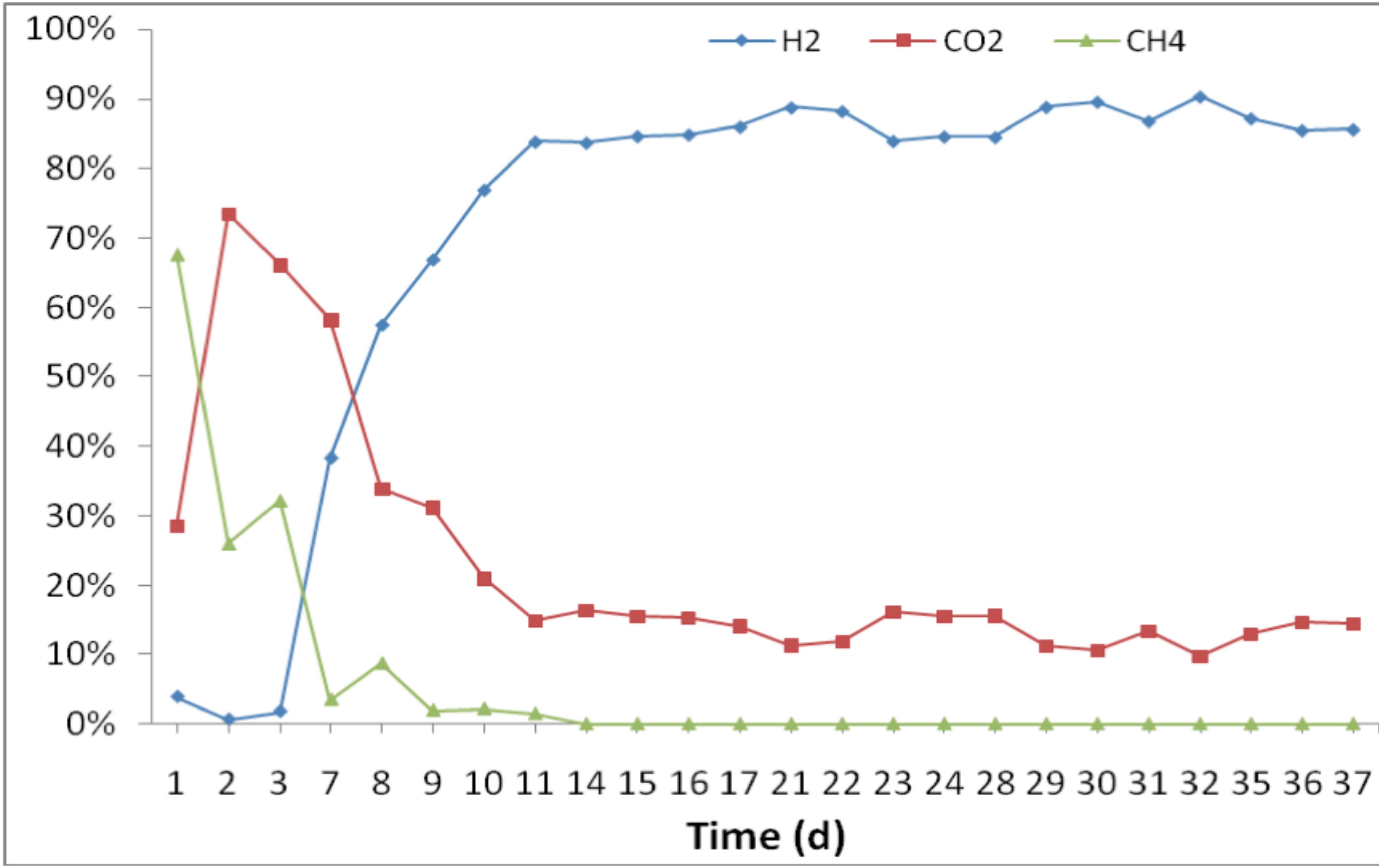
An UASB reactor was used.

The pH was controlled at 5.0 ± 0.1 and HRT was fixed at 6 h

Mesophilic conditions (35°C) and

7.3 ± 0.4 gVSS/L

Factors influencing



Hernández et al., (2012)

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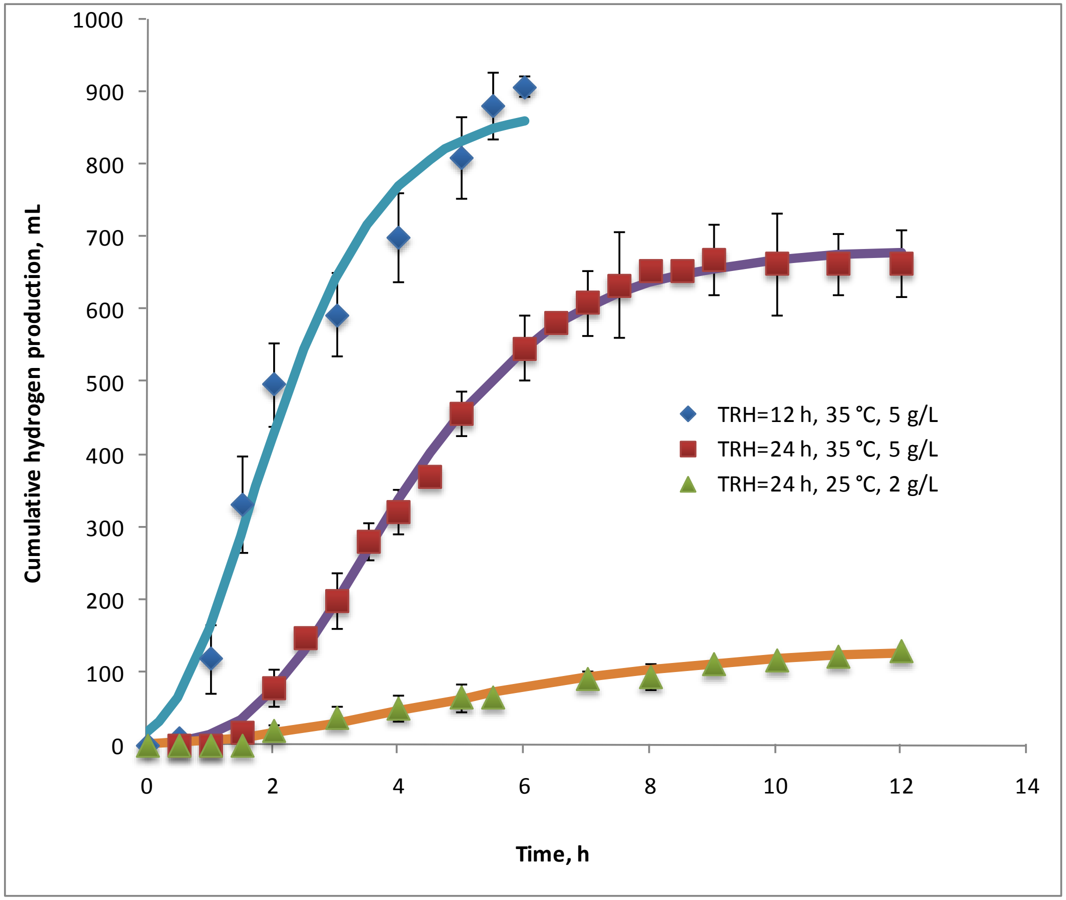
Tequila vinasses



pH:	3.88±0.1
Sugars:	7.0 g/L
Sulphate:	1.4 g/L
Phenols:	57 mg/L

Buitron & Carvajal (2010)

Optimization of H_2 production

- Once a biohydrogen production process has been developed, the operational conditions have to be optimized in order to achieve a desirable performance

- Limited data on optimization strategies:

1. Model predictive control strategy: asymptotic online observer Aceves-Lara et al., (2010)
2. Fuzzy control Huang et al., (2012)

Optimization of H_2 production

- ✓ One of the most important operating parameters is the organic loading rate (OLR)

- ✓ Changes in OLR influence:
  1. Metabolic paths.
  2. Population dynamics.

- ✓ Because the process changes over time it is important to:

Evaluate the effect of OLR on the process.

Implement a real-time optimization strategy.

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Objectives

- ✓ To design and implement a real-time optimization strategy for computing the optimal feed flow which maximize and stabilize the hydrogen production

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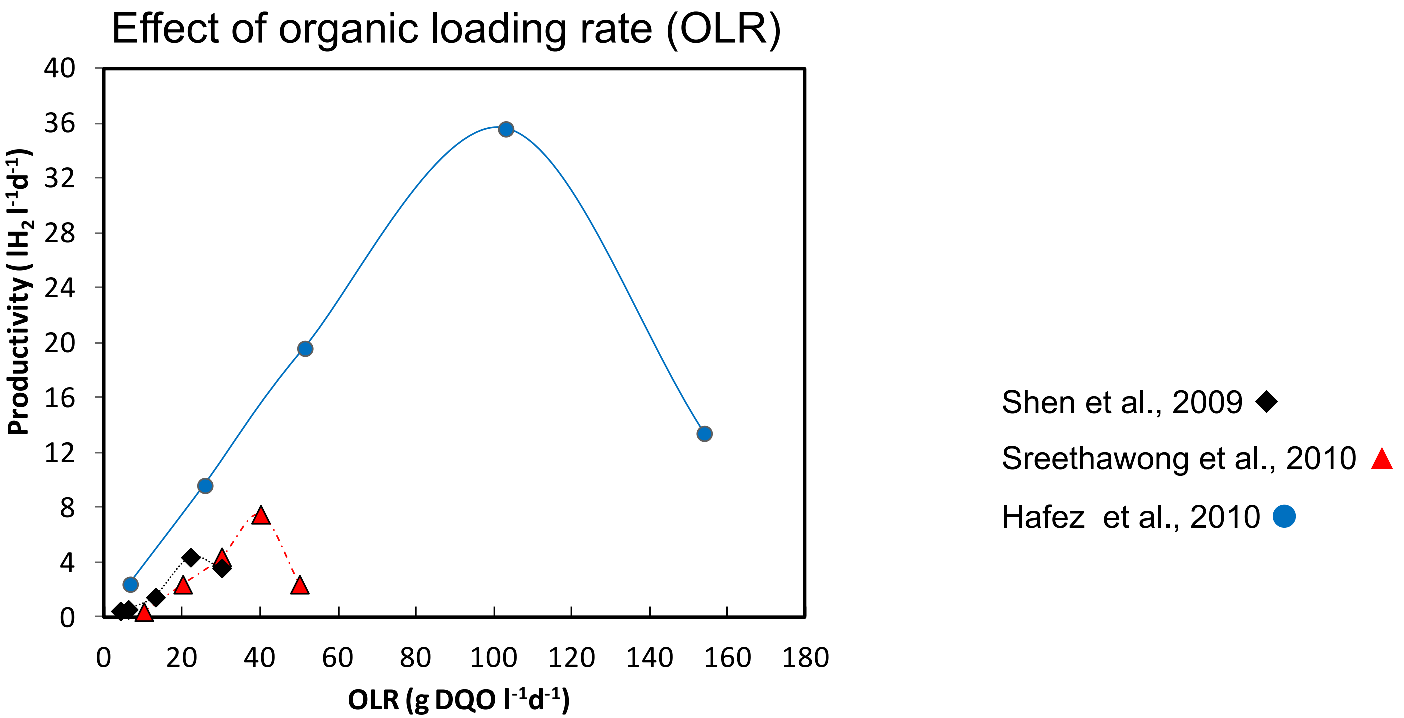
Materials and Methods

Experimental procedure

Step 1: Study effect of OLR over the productivity.

Function Productivity *vs.* OLR



Experimental procedure

Step 2: Implementation of the optimization strategy.

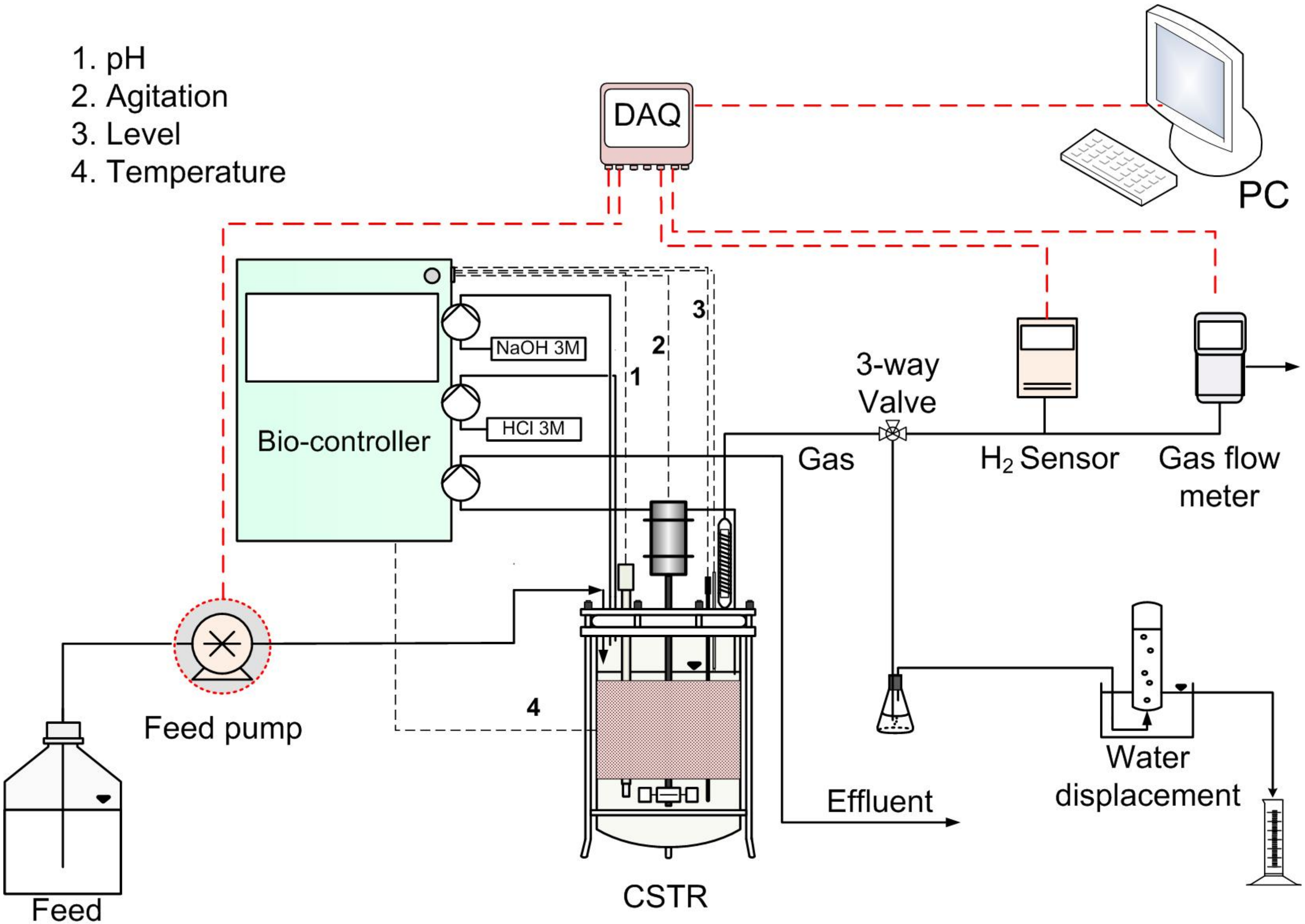
Maximize and stabilize the productivity

- ✓ The real-time optimization strategy involves the continuous evaluation of the H_2 productivity to calculate **the optimal feed flow**.
- ✓ Optimal solution subject to a **HRT working range (4 -12 h)** and a **corrected productivity standard deviation of 1%**.
- ✓ **For that the objective function is updated** considering the last experimental data.

Experimental conditions

- CSTR Applikon 1.25L (0.9L useful).
- 37 °C.
- TRH from 6 and 24 h
- Implementation software: Matlab.
- pH 5.5.
- Glucose (5, 10,15 y 20 g/L) + mineral salts
- Inoculum (sludge pretreated at 100 °C for 24h).

Experimental implementation



Experimental implementation

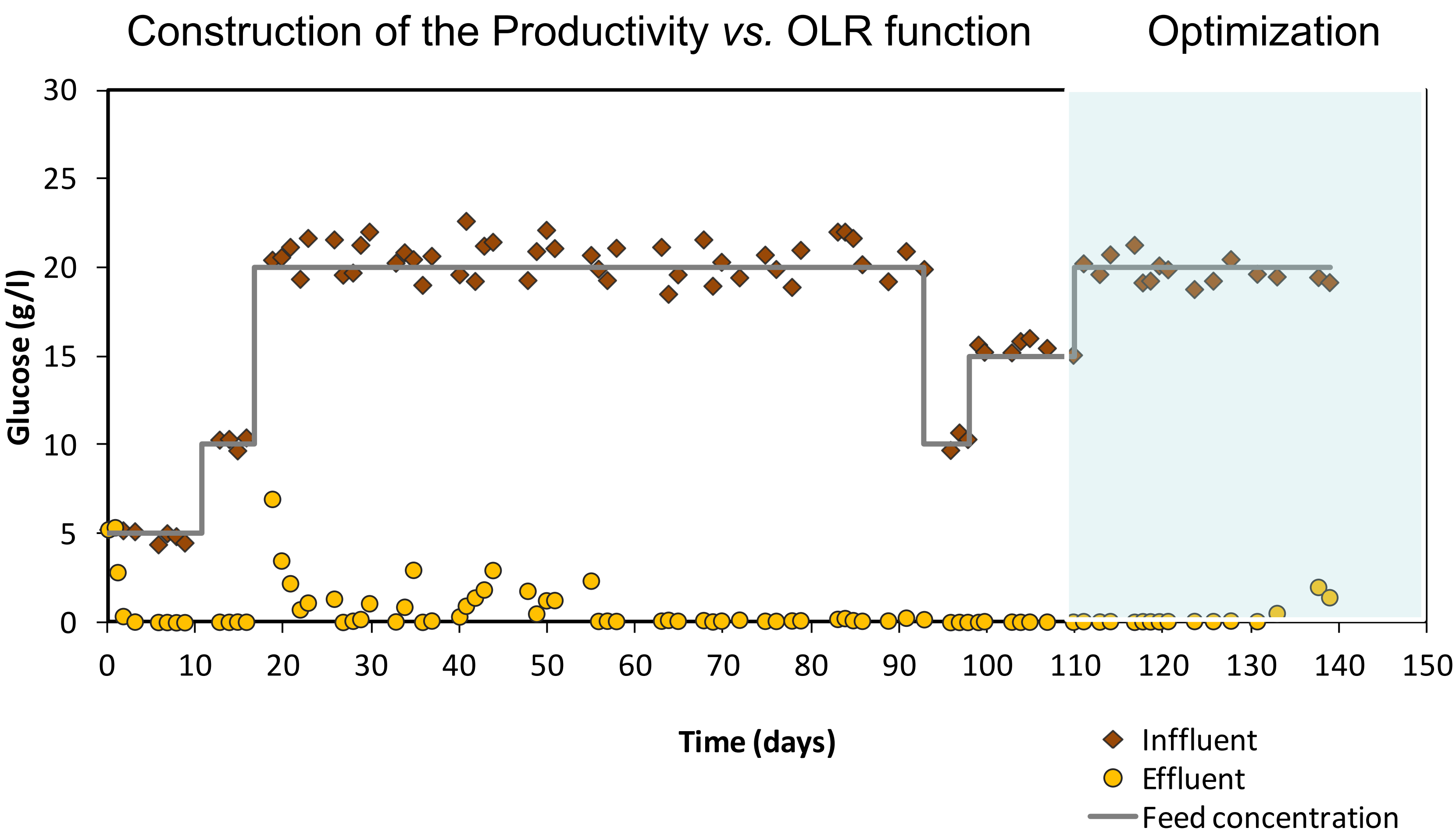
Analytical methodology

Analysis	Methodology
Liquid phase	
Glucose	Dubois
Volatile fatty acids and alcohols	Gas chromatography
COD	Hach
Biomass (VSS)	Gravimetry

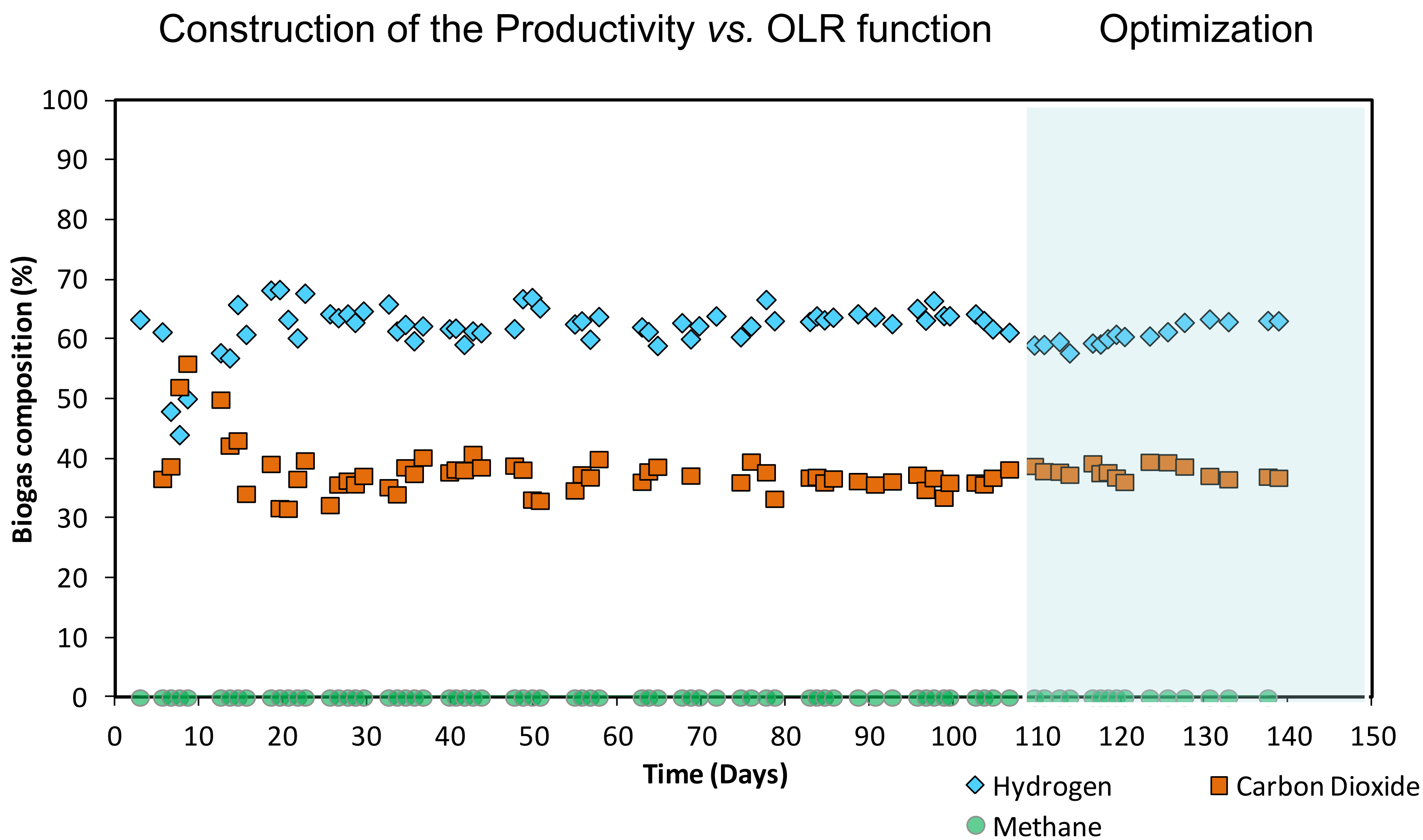
Gas phase	
Composition of biogas	GC TCD and H_2 sensor
Biogas flow (H_2)	Water displacement and flowmeter online

Results

Evolution of substrate concentration



Biogas composition (H_2,CO_2,CH_4)



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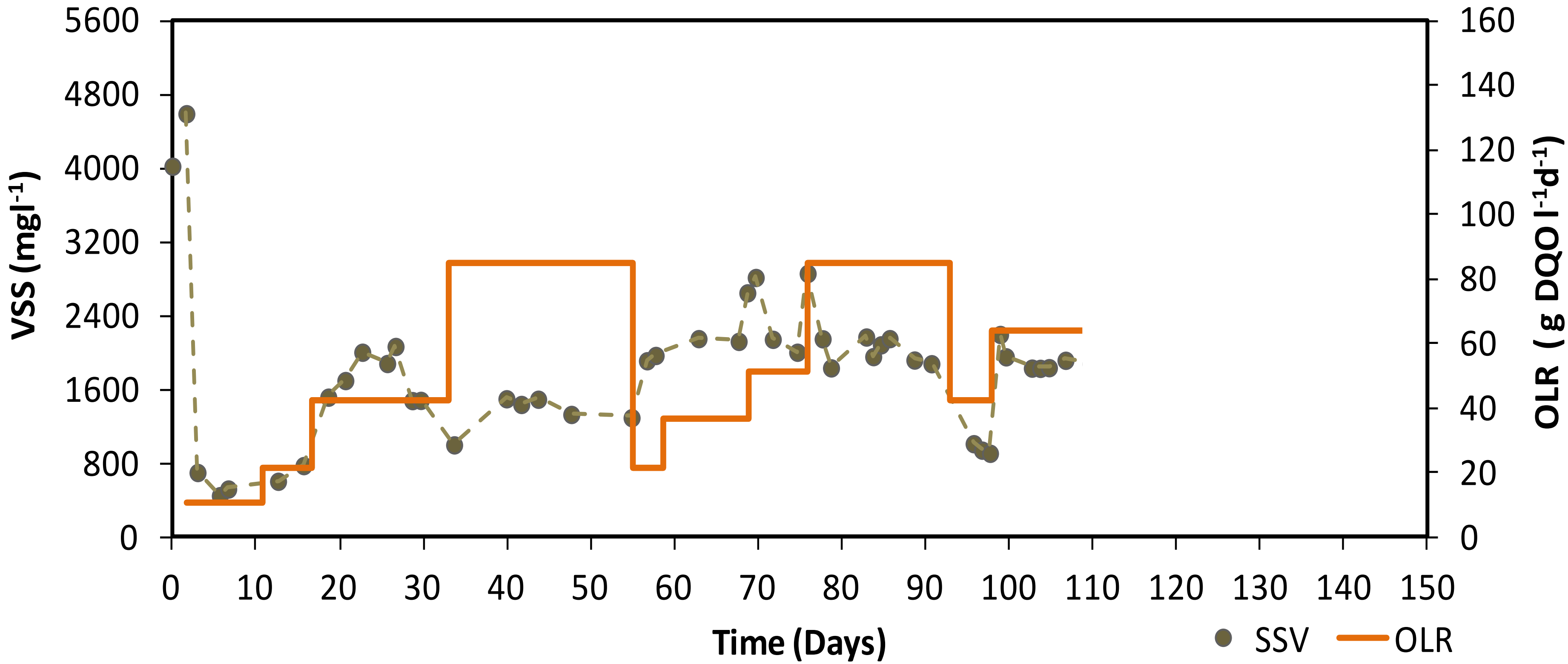
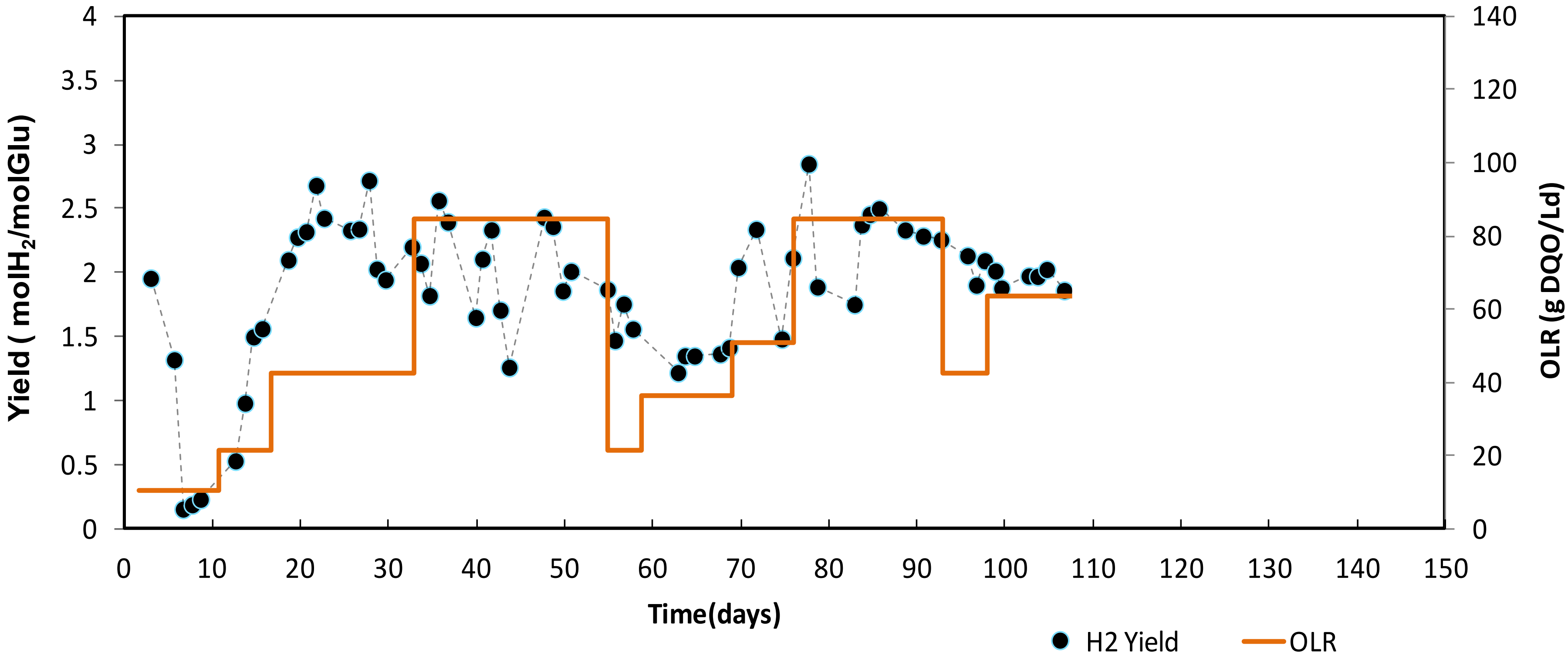
Volatile suspended solids (VSS, biomass)

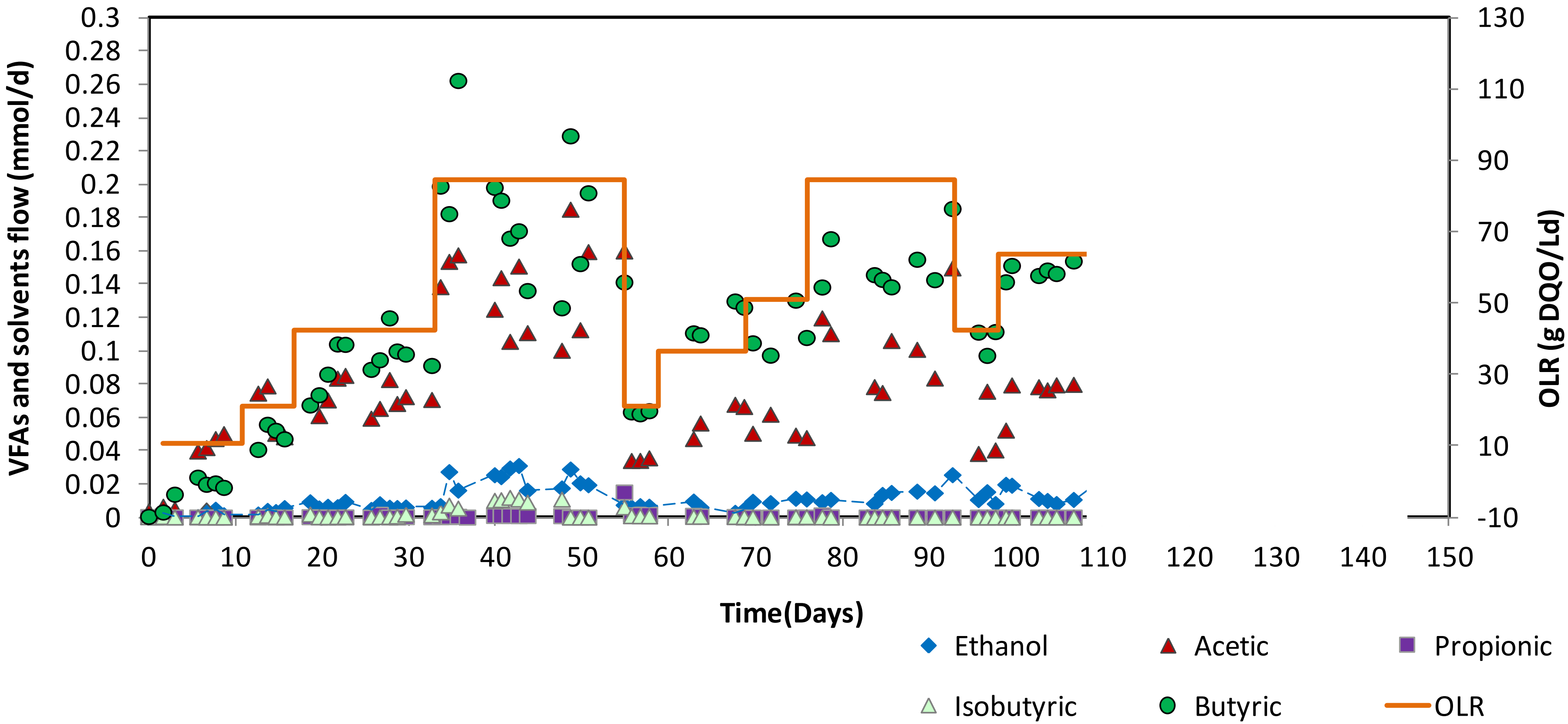


H2 yield

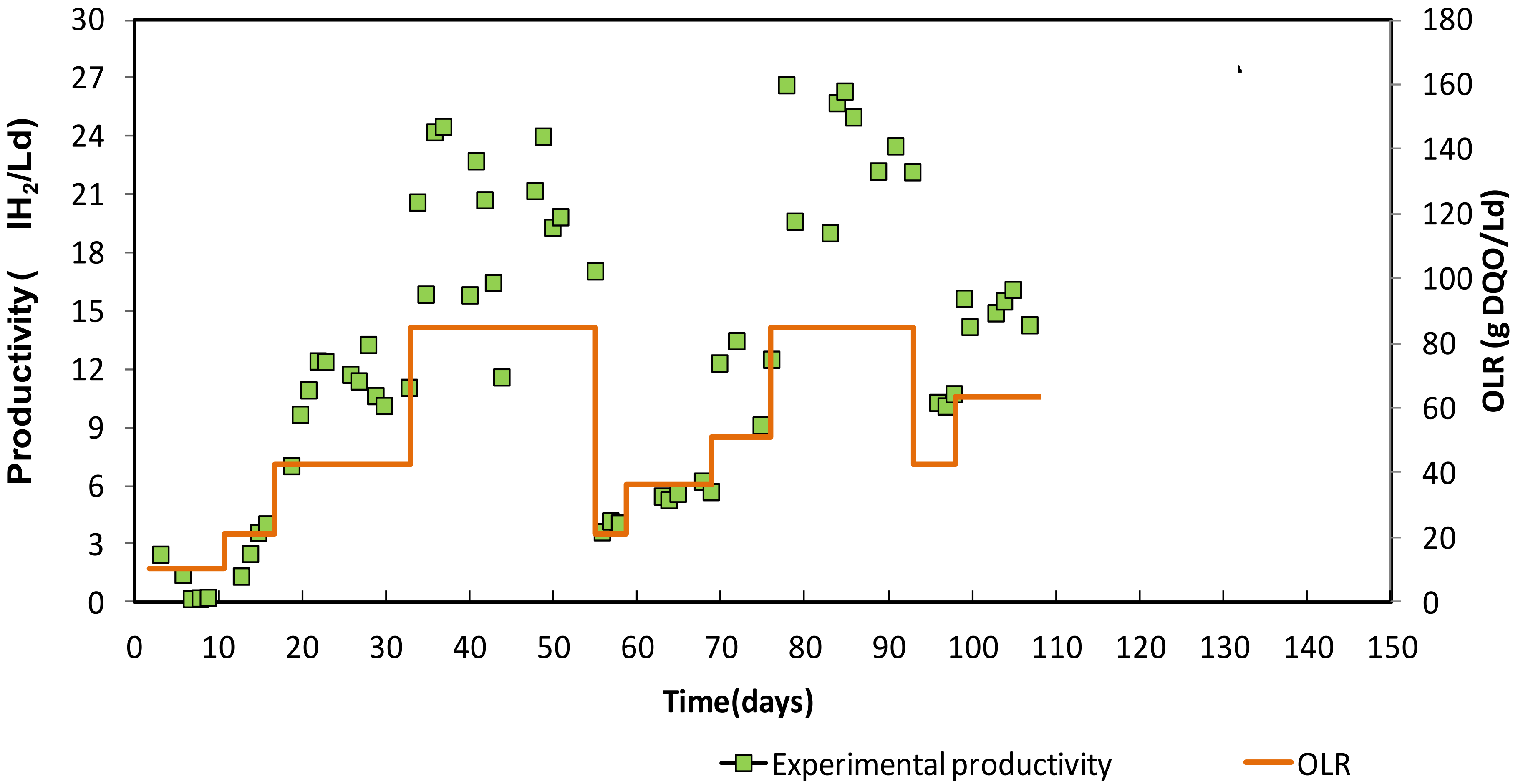


Yield (molH2/molGlu)
OLR (g DQO/Ld)
Time(days)
H2 Yield
OLR
0
0.5
1
1.5
2
2.5
3
3.5
4
0
20
40
60
80
100
120
140
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

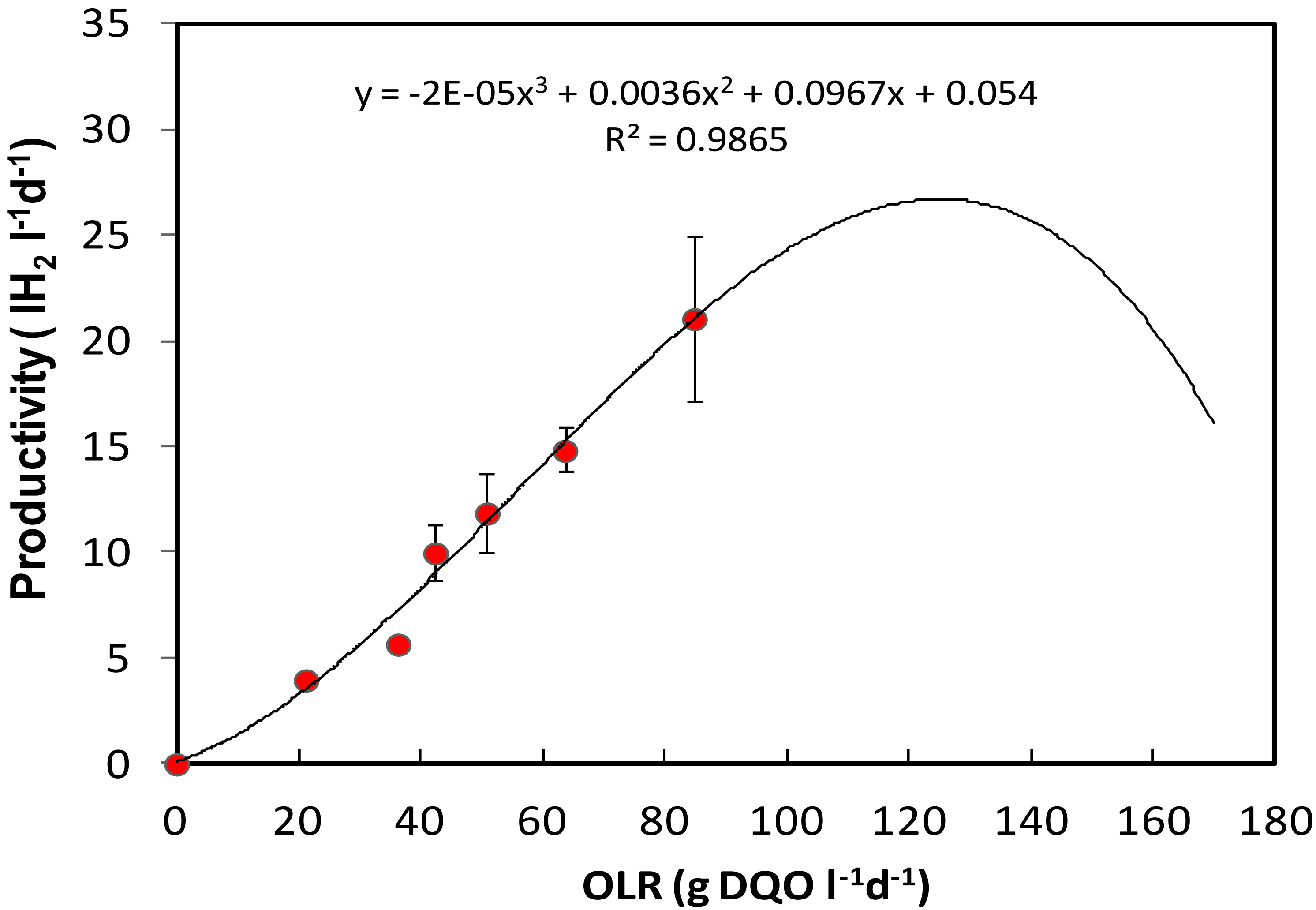
By-products


0.3
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
VFAs and solvents flow (mmol/d)
130
110
90
70
50
30
10
-10
OLR (g DQO/Ld)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
Time(Days)
Ethanol
Acetic
Propionic
Isobutyric
Butyric
OLR

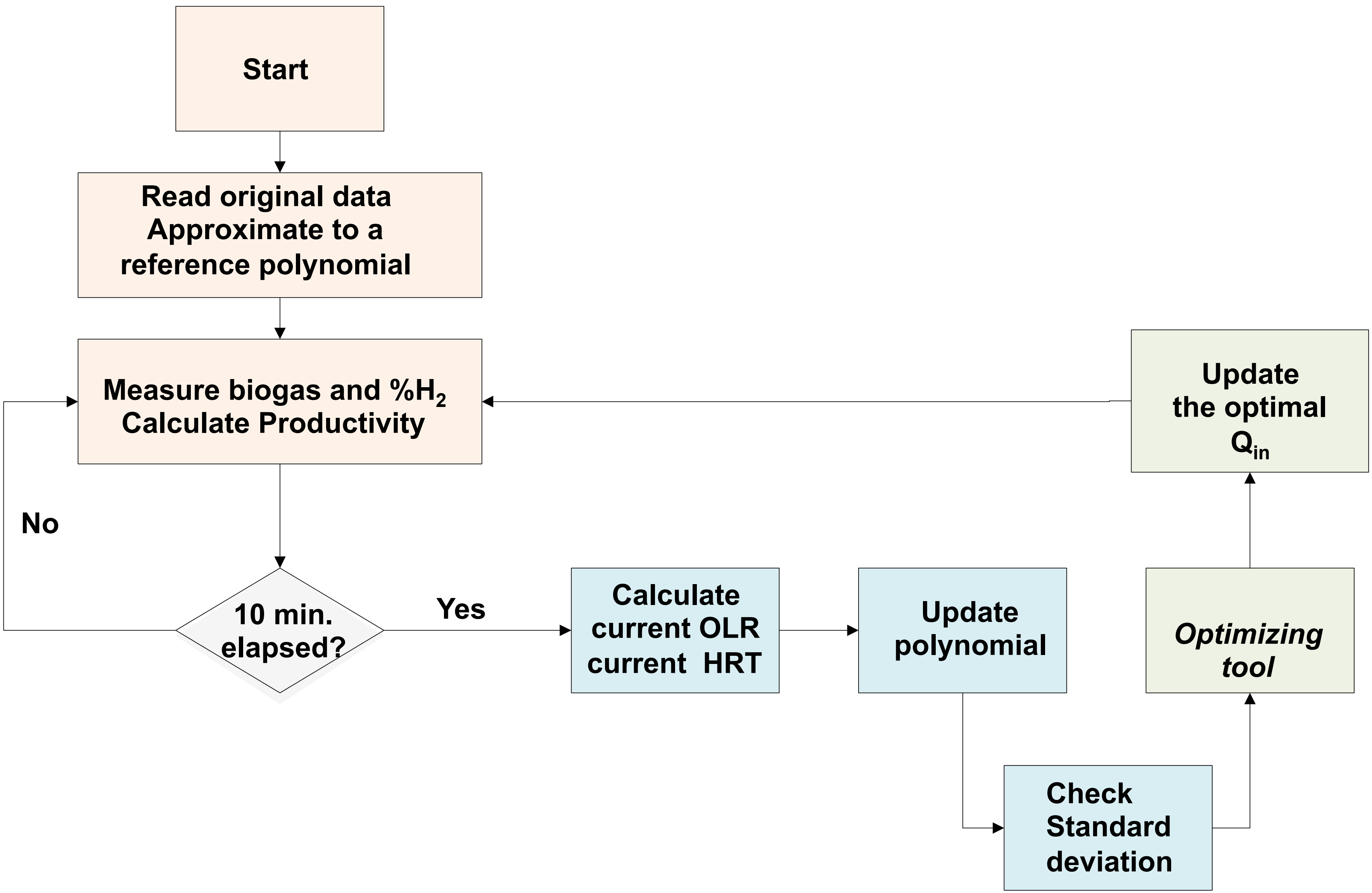
Volumetric productivity of H_2



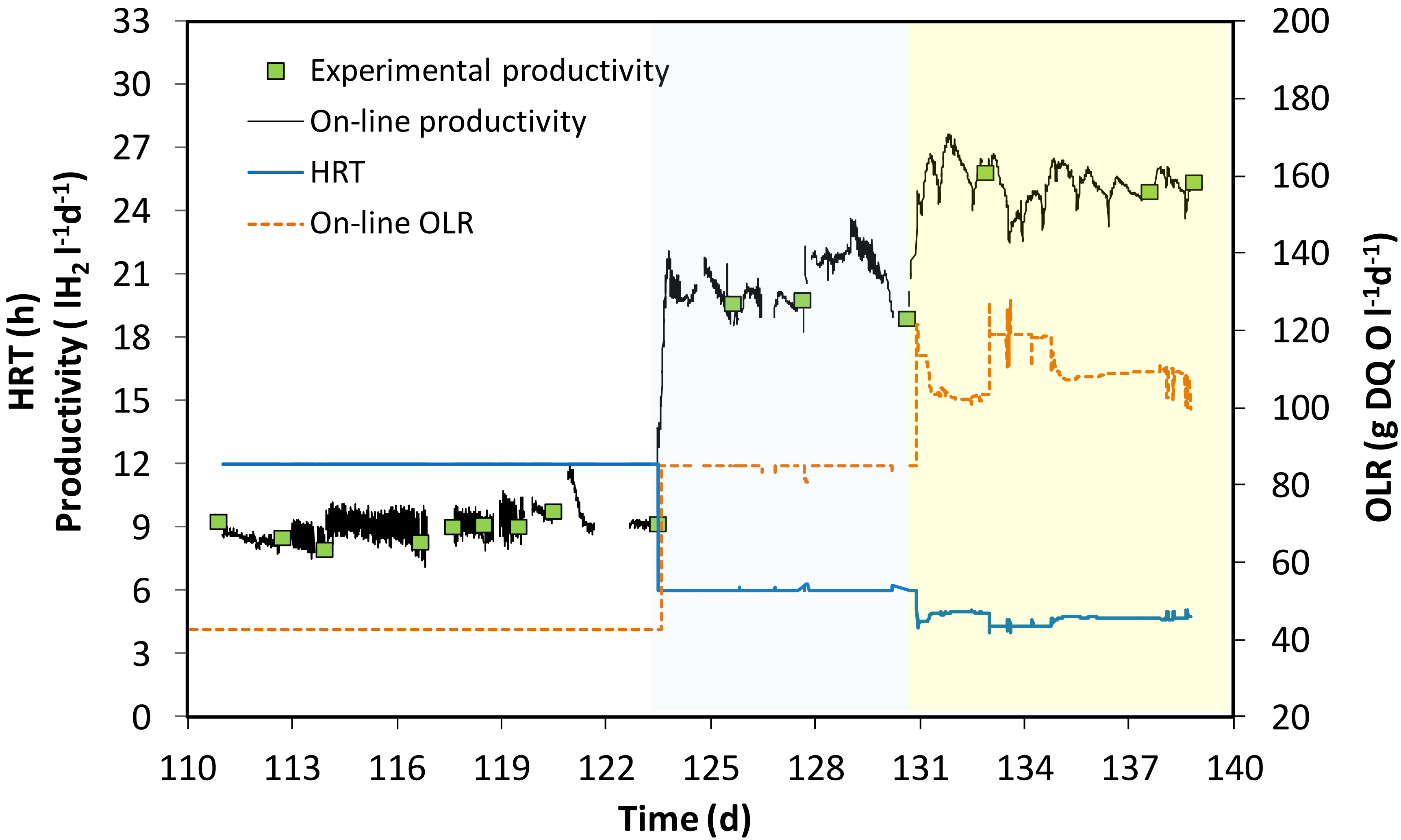
Volumetric productivity *vs.* OLR



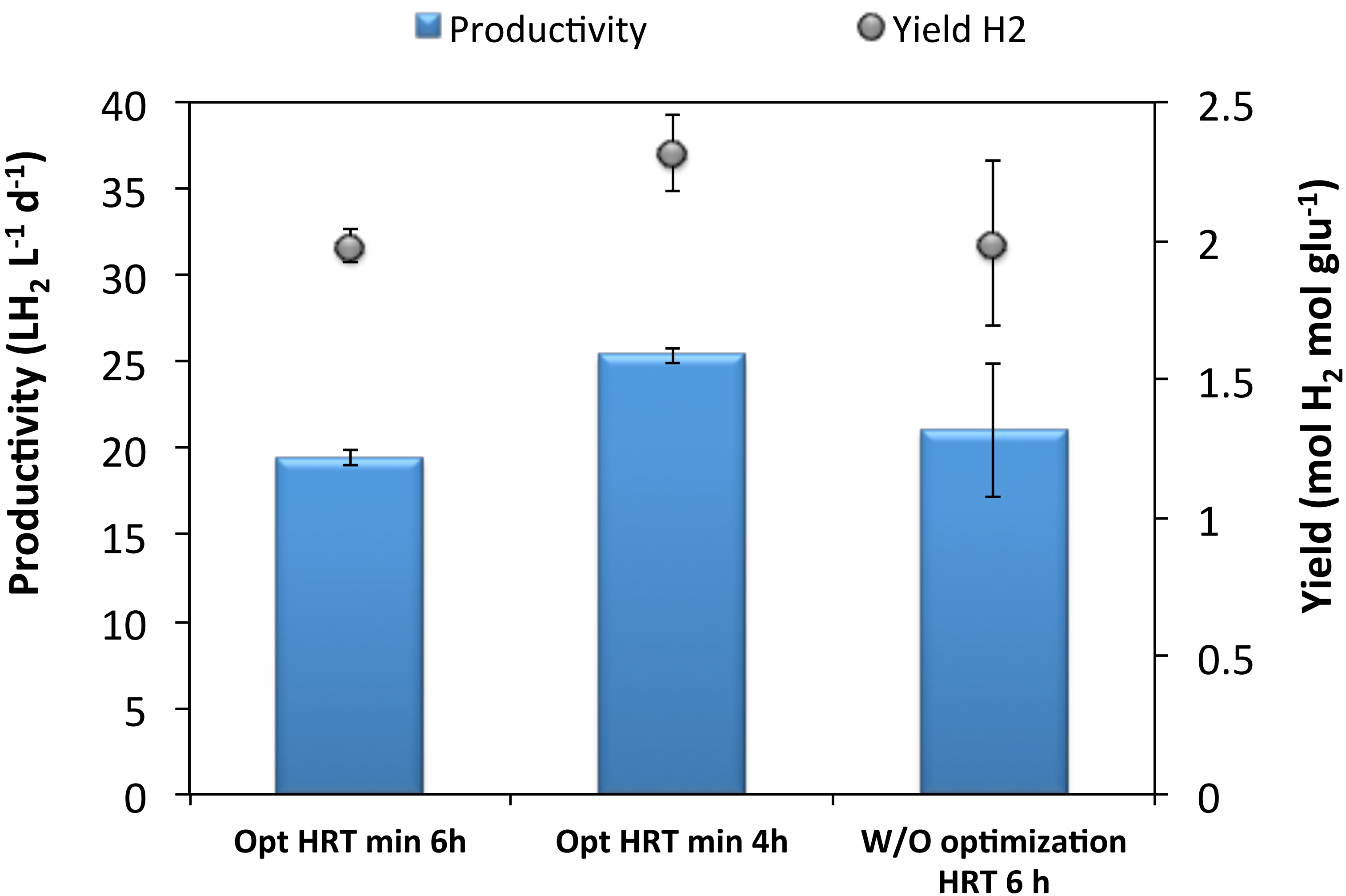
Solution algorithm



Real-time optimization



Active biomass producing H_2



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Conclusions

Conclusions

- ✓ A simple real-time optimization strategy was implemented to maximize the H_2 volumetric productivity by computing the optimal feed flow.

- ✓ Maximum H_2 volumetric productivity was increased by 25% and stability was substantially improved.

- ✓ H_2 productivity was increased during the operation around the optimal OLR (120 $g[COD]l^{-1}d^{-1}$) because the process was carried out mainly by active biomass producing H_2.

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