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Valorisation of Agricultural residues to produce H_2 through Two Stage Anaerobic Digestion process

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UNIVERSITÀ di VERONA

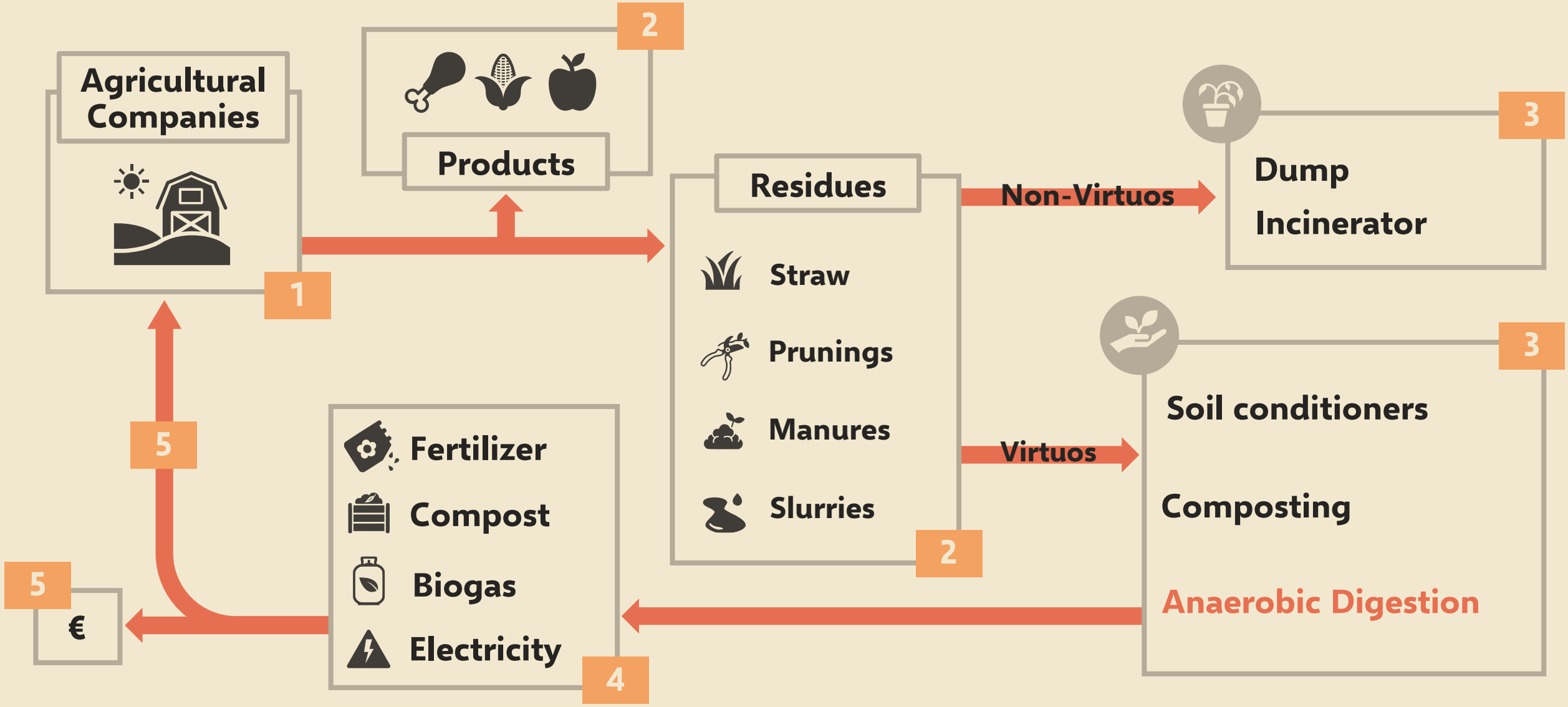
Introduction
Agricultural Sector

	Europe	Italy
Agricultural companies	9’100 k	83 K
Vegetal products (cereal + oilseed)	170.0 Mt	18.3 Mt
Animal products (meat + milk/dairy)	176.2 Mt	21.9 Mt
Agricultural residues	Gt	Gt

*http://dati.istat.it/Index.aspx?DataSetCode=DCSP_COLTIVAZIONI

Introduction

Agricultural residues as a Resource

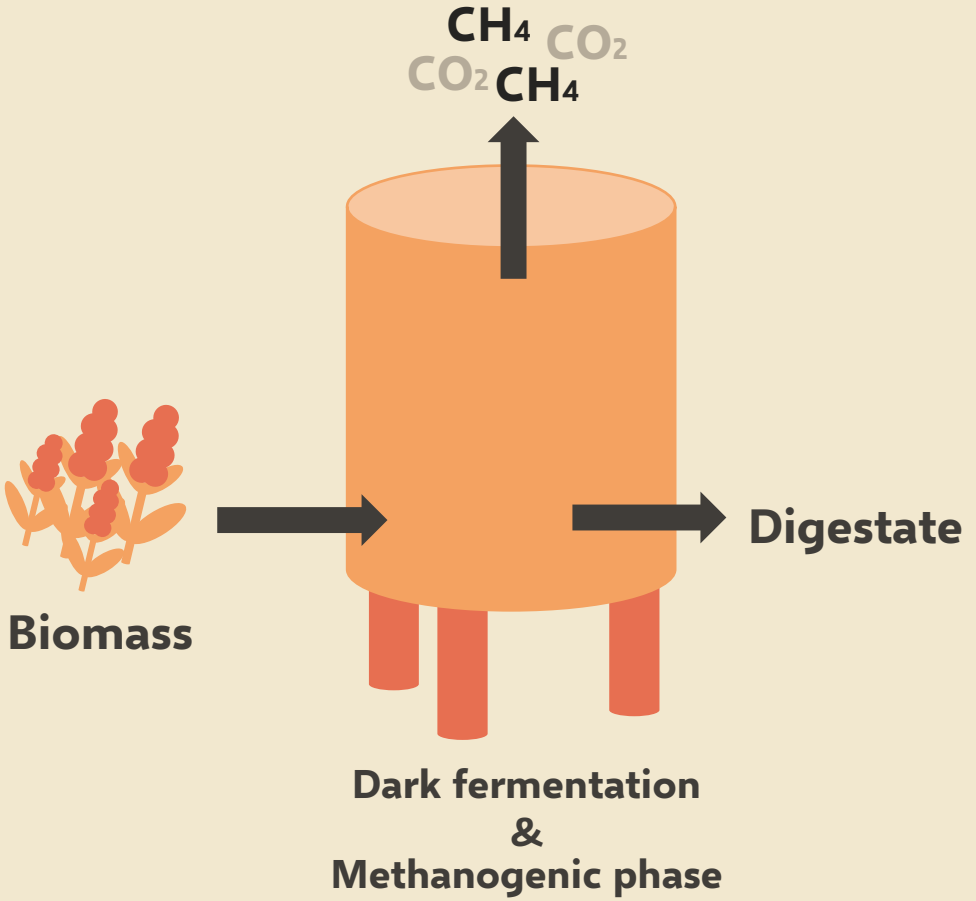


Introduction

Anaerobic Digestion

Existing plants:

- Italy 1’555
- EU 10’000

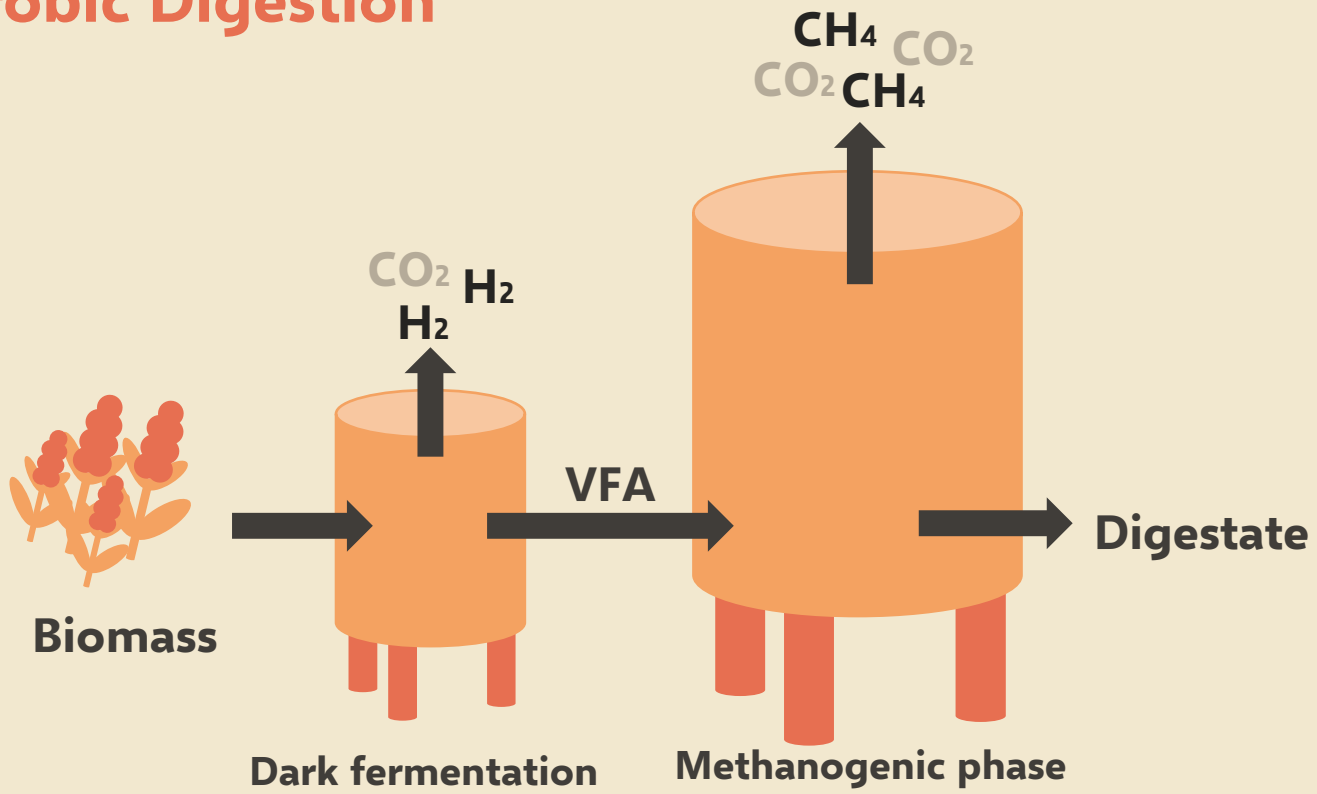


MonoStage

Hydrolysis → Acidogenesis → Acetogenesis → Methanogenesis

Introduction

Two Stage Anaerobic Digestion



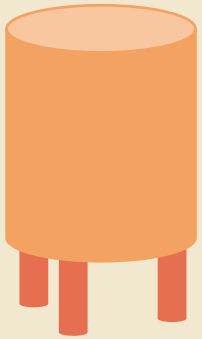
TwoStage

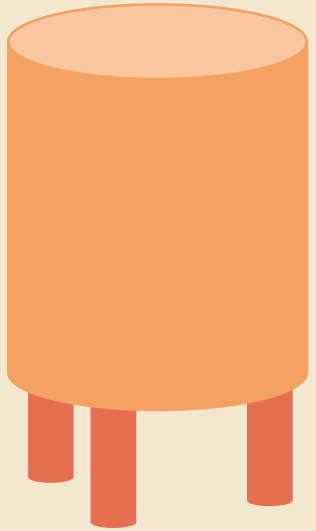
Hydrolysis → Acidogenesis → Acetogenesis → Methanogenesis

Introduction

Ideal Optimal Parameters

Dark fermentation		Methanogenic phase
CSTR, UASB	REACTOR	CSTR, UASB, AFBR
12 h-3 d	HRT	>15 d
>37 kgCOD/m³d)	OLR	OLR <20 kgCOD/m³d
Mesophilic	TEMPERATURE	Thermophilic, Mesophilic
5.5–6.5	pH	7–8
15–35	C/N	50
Agricultural/Municipal Digestate	INOCULUM	Agricultural/Municipal Digestate





Which are the best parameters for agricultural residues?

*D. Bertasini, F. Battista, F. Rizzioli, N. Frison, D. Bolzonella, 2023. Decarbonization of the European natural gas grid using hydrogen and methane biologically produced from organic waste: A critical overview

Material and Methods

Analyzed Substrate

Wheat straw for mushroom cultivation (MS)

What is MS?

Carbon Source

Nitrogen Source

Wheat Straw

Hen manure

Fungal Spores

Water

Straw Bale

Product (Mushroom)

Residues SM

Material and Methods

Experimental Plan

1

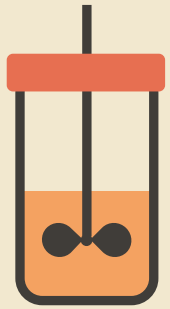
Substrate Characterization

Standard Methods

2

Dark Fermentation

Continuous Stirred Tank Reactor



3

Methanogenic Phase

BioMethanation Potential

Material and Methods

Substrates' characterization 1

METHODs

SOLIDS

Gravimetric method

CARBON CONTENT

Total Chemical Oxigen Demand Titration

NITROGEN CONTENT

Spectroscopic method

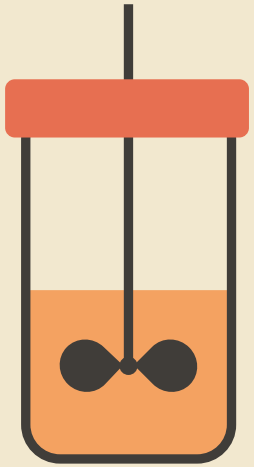
Agricultural digestate - Inoculum				
TS	TVS	TVS/TS	tCOD	TKN
%	%	%	g/L	g/L
4.1	2.7	65.7	44.3	11.2

MS Residues				
TS	TVS	TVS/TS	tCOD	TKN
%	%	%	g/KgTS	g/KgTS
29.2	26.1	89.2	866.6	60.2

Material and Methods

Dark Fermentation 2

Dark fermentation



CSTR	REACTOR
???	HRT
???	OLR
(Controlled) 38 °C	TEMPERATURE
(Controlled) 5.5 – 6.5	pH
±21	C/N
Agricultural Digestate	INOCULUM

HRT

The HRT parameter was the subject of studies, to see which was best for this type of substrate.

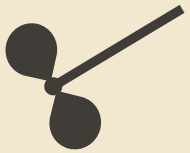
In particular, for the production of VFAs and H_2.

These were the values tested in terms of days:

18 – 12 – 10 – 7 – 6 – 4 – 1.5

To avoid mixing problems

TS were set at 5%



OLR

18 – 12 – 10 – 7 – 6 – 4 – 1.5

2.2 – 3.3 – 4.0 – 5.7 – 6.7 – 10.0 – 26.7

gCOD/L*d

The highest possible OLR was tried to be used. But the value is then resulting from the HRT and a TS content set to 5%.

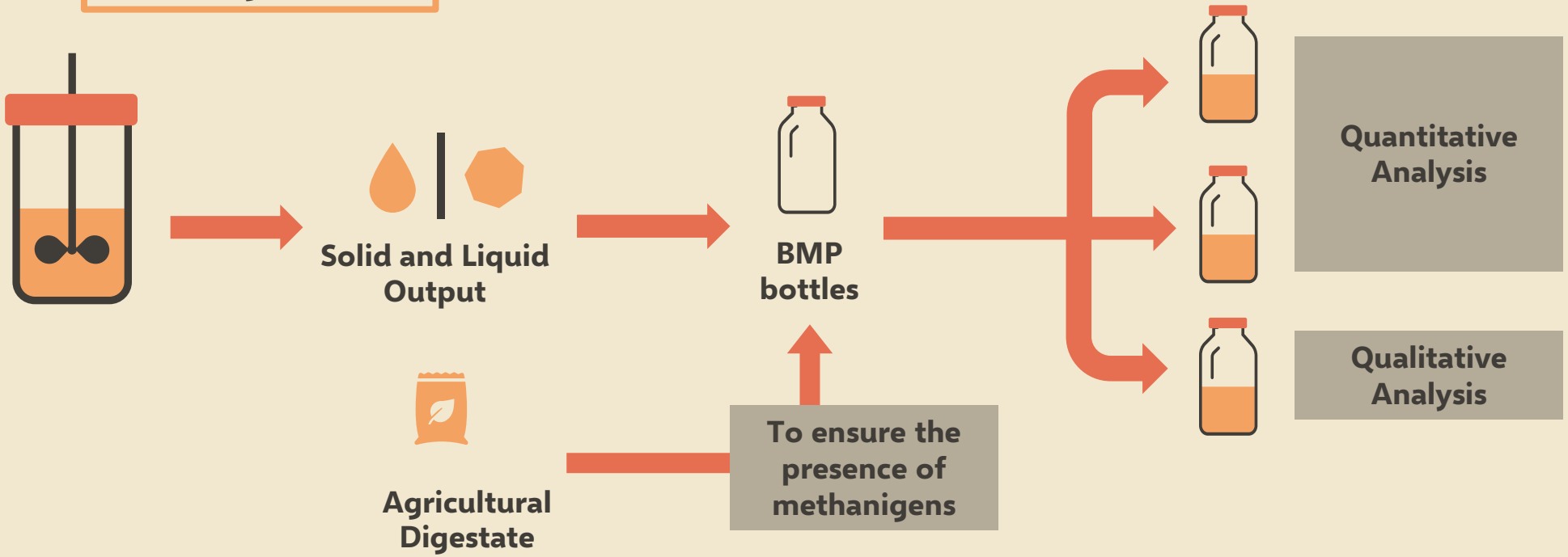
Analysis Time

3 x HRT

Material and Methods

Methanogenic phase 3

Methanogenic Phase



To the test how Dark Fermentation affected the biodegradability of the substrate

Parameters

Temperature	pH Value	Substrate : Inoculum Ratio (VS)	Trial duration
38 °C	7-8	1 : 1	50 Days

Material and Methods

Output

METHODs

GAS - Quantitative

Water Displacement

GAS - Qualitative

Analyzer Biogas 5000

Volatile Fatty Acids

Ion Chromatography

Hydrogen Content

Estimated

RESULTs

Gas production Rate
(m3 gas/KgVS*d)

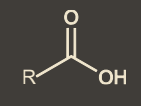
Gas Composition

Methane production Rate
(m3 CH_4/KgVS*d)

CH_4

VFAs Composition

VFAs Productivity



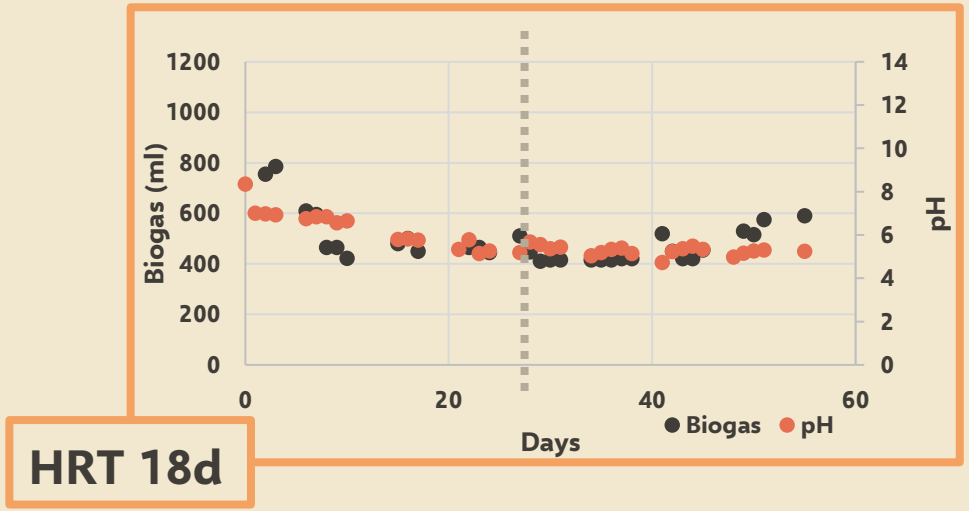
Hydrogen production Rate
(m3 H_2/KgVS*d)

H_2

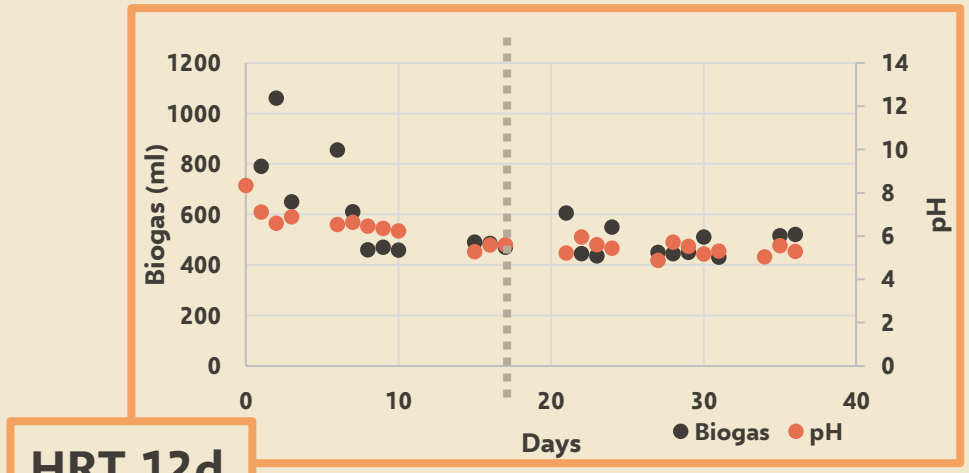
Results

Steady state

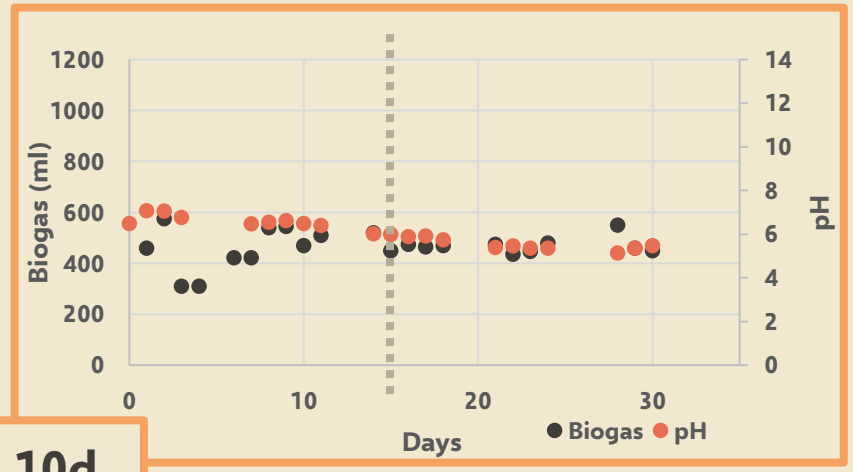
At around one and a half HRT, steady state was reached for all tests



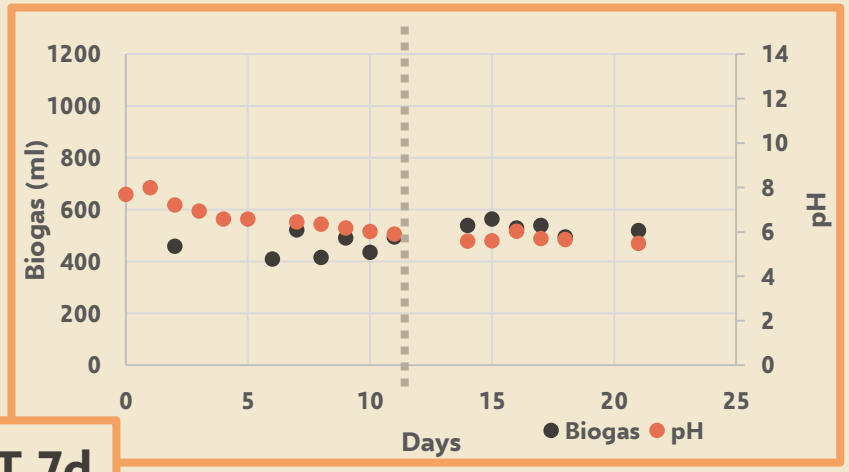
HRT 18d



HRT 12d



HRT 10d

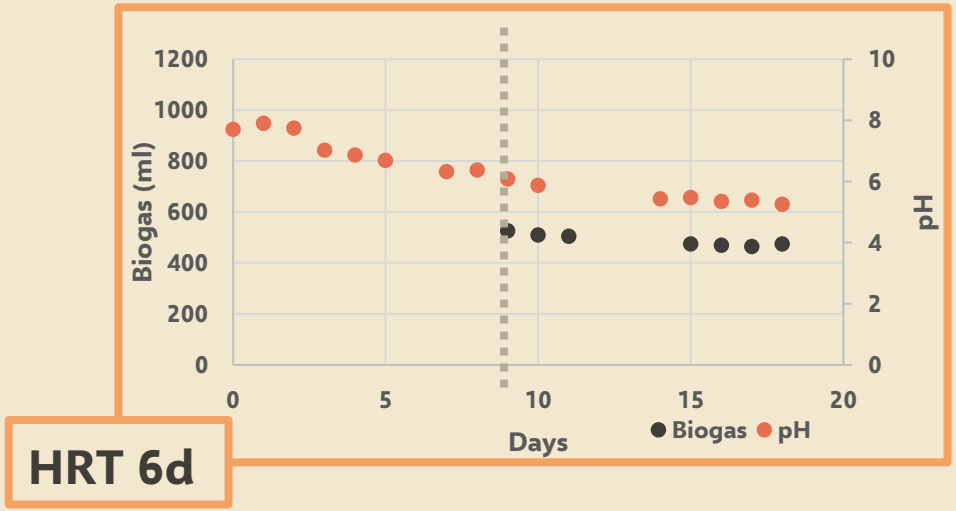


HRT 7d

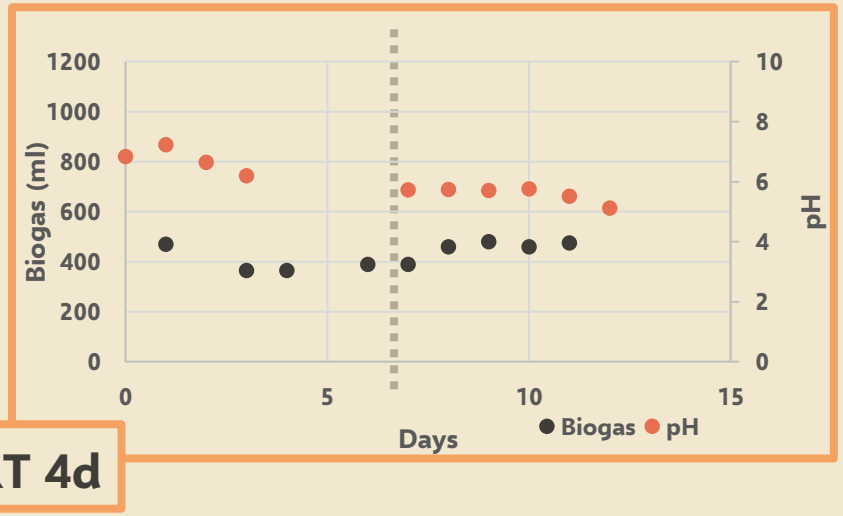
Results

Steady state

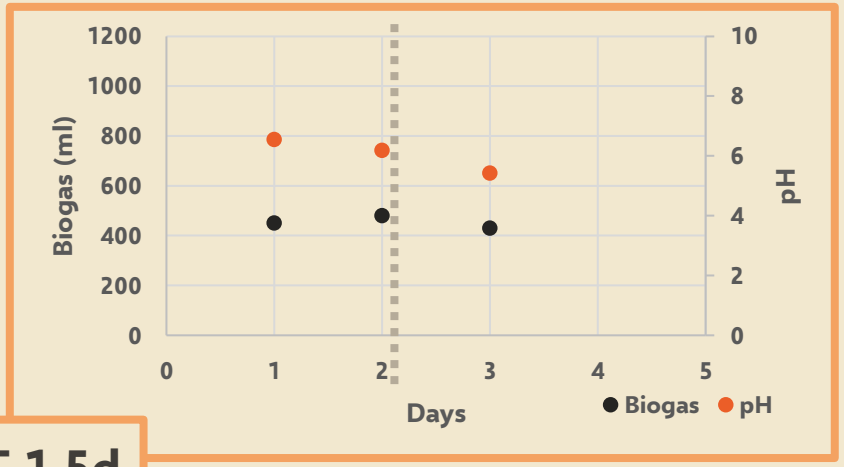
At around one and a half HRT, steady state was reached for all tests



HRT 6d



HRT 4d



HRT 1.5d

Results

Volatile Fatty Acids

Samples recovered

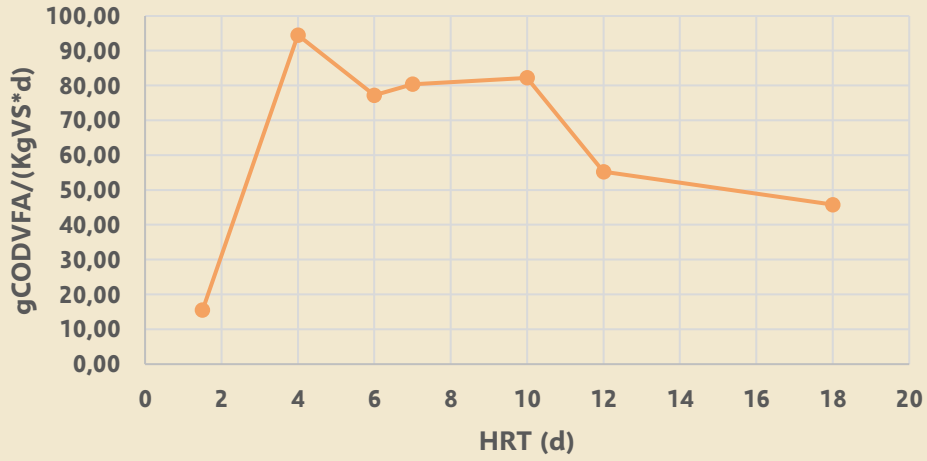
during D.F.

Yield = gCOD/KgVS

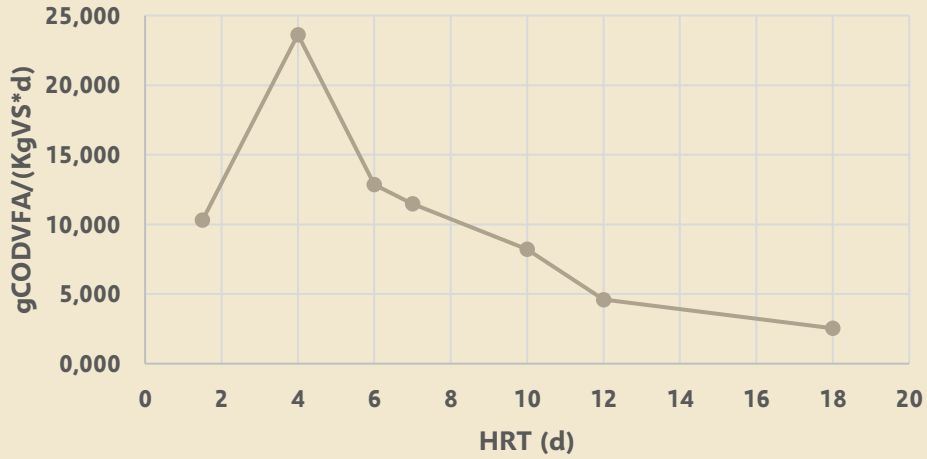
Productivity = gCOD/(KgVS*d)

HRT	VFAs Yields	VFAs Productivity
-	(gCOD VFA/kgVS)	(gCOD VFA/(kgVS*d))
18	45.8	2.5
12	55.2	4.6
10	82.2	8.2
7	80.4	11.5
6	77.2	12.9
4	**94.5**	**23.6**
1.5	15.5	10.3

Yield



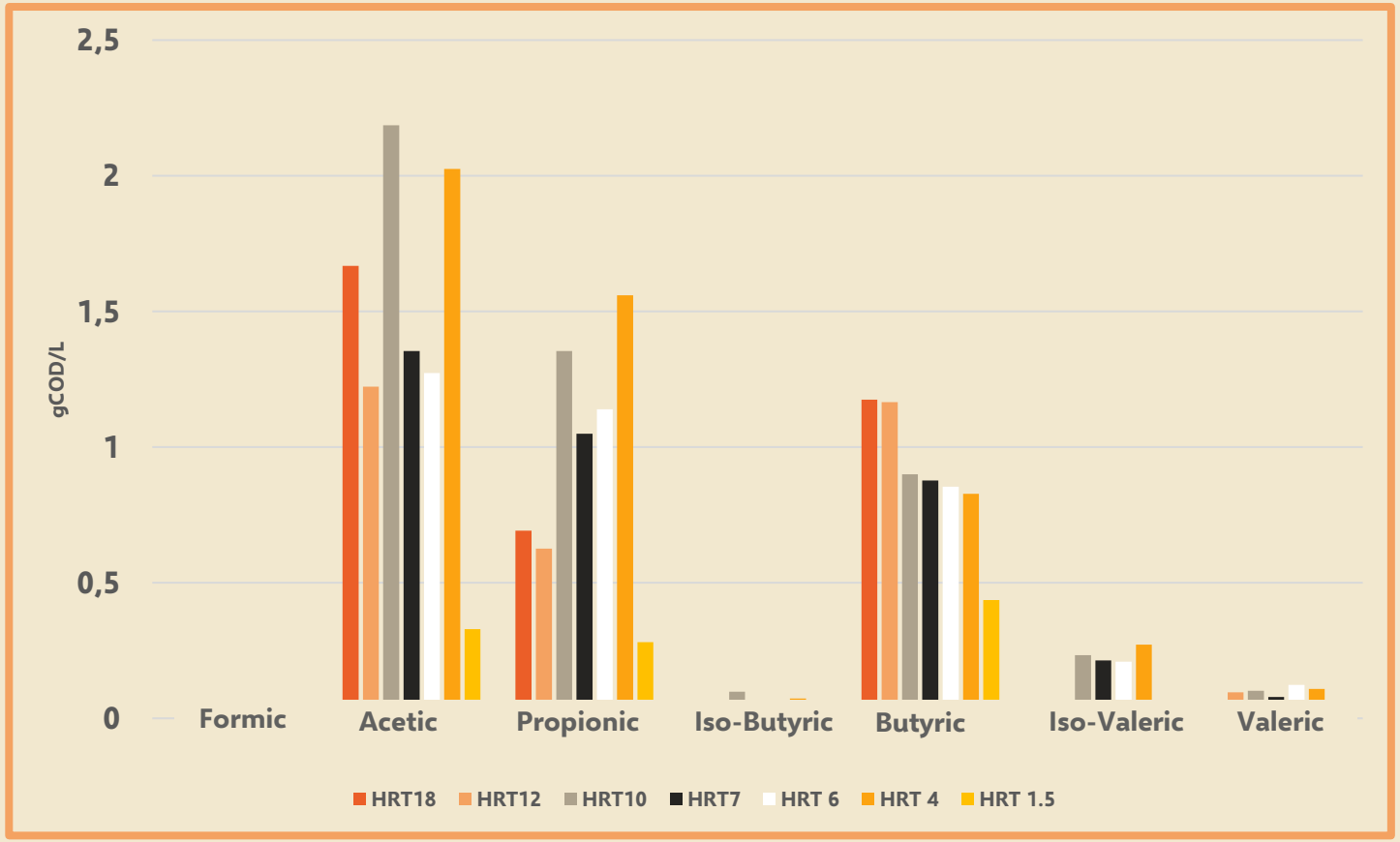
Productivity



Results

Volatile Fatty Acids

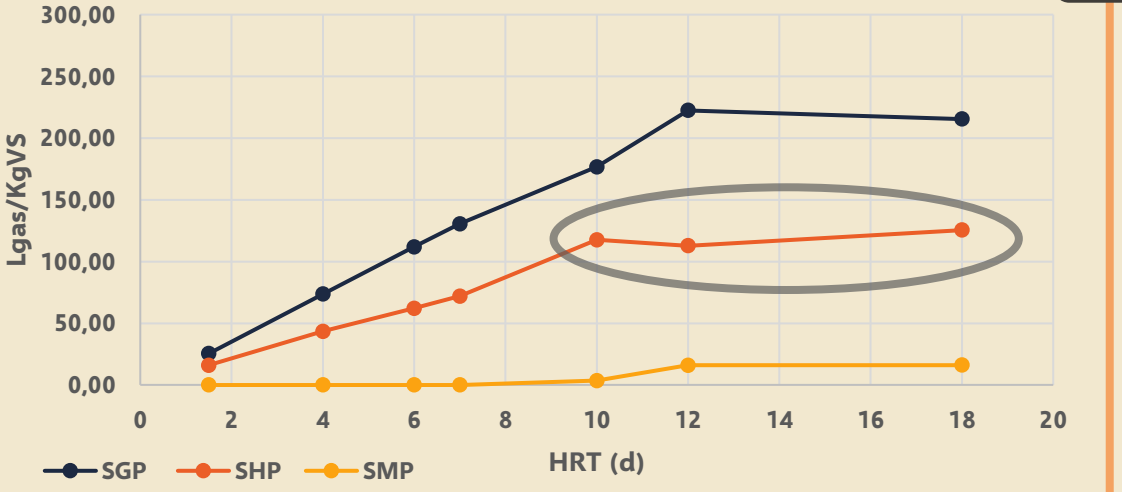
- The main VFAs produced during SM fermentation are **short-chain**: Acetic acid, Propionic acid and Butyric acid
- Iso-Valeric acid and Valeric acid aren't produced at HRT 18 days



Results

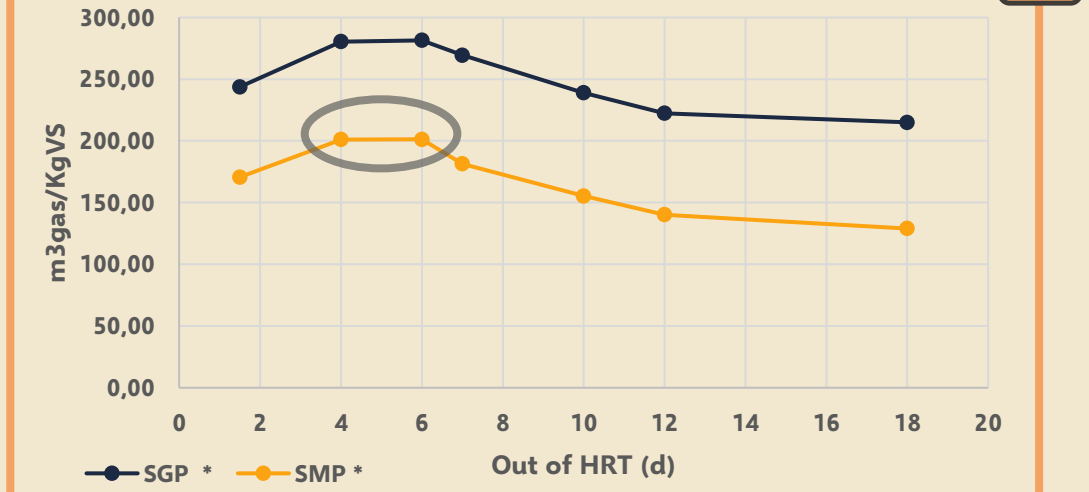
Gas production - Yield

Dark Fermentation



From the test with the 10-day HRT value, the reactor yield peaks at about 100 LH2/KgVS, maintaining similar values for the two tests at higher HRT.

Methanogenic Phase



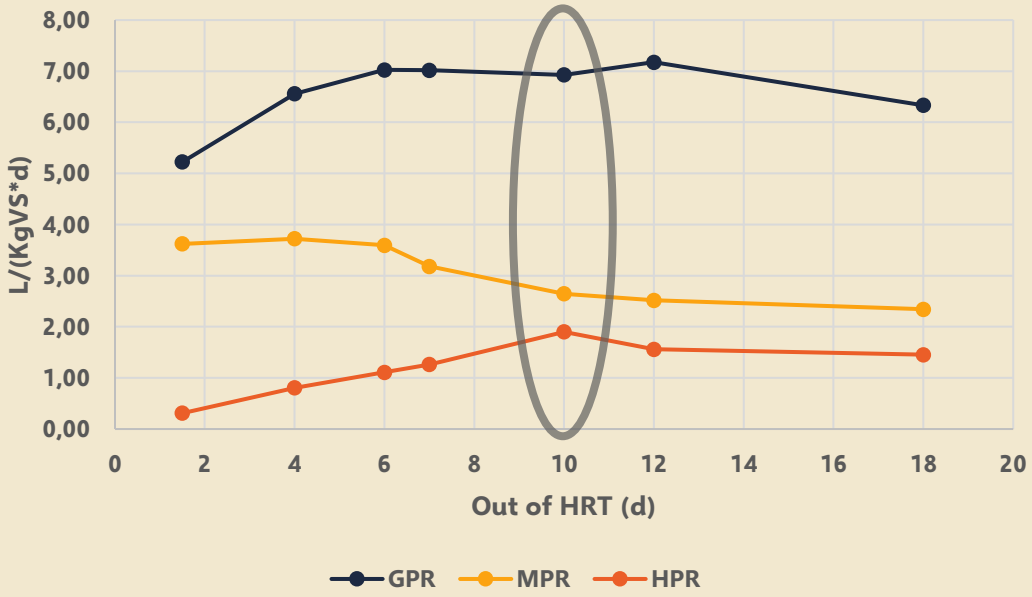
50d

The tests HRT 4 and HRT 6 days reported the best yield in biogas and methane production (about 200 LCH4/KgVS), during the methanogenic phase.

Results

Gas production – Production Rate

TSAD – Both Processes



HRT	GPR (Lgas/KgVS*d)	MPR (Lgas/KgVS*d)	HPR (Lgas/KgVS*d)
18	6.33	2.34	1.45
12	7.18	2.52	1.56
10	6.93	**2.65**	**1.90**
7	7.02	3.18	1.26
6	7.02	3.59	1.11
4	6.56	3.72	0.81
1.5	5.23	3.62	0.31

HRT d + 50d

Assuming to removing CO_2 from the biogas, the HRT 10 days reported the best biohythane production rate (4.55 Lgas/(KgVS*d)), composed by:

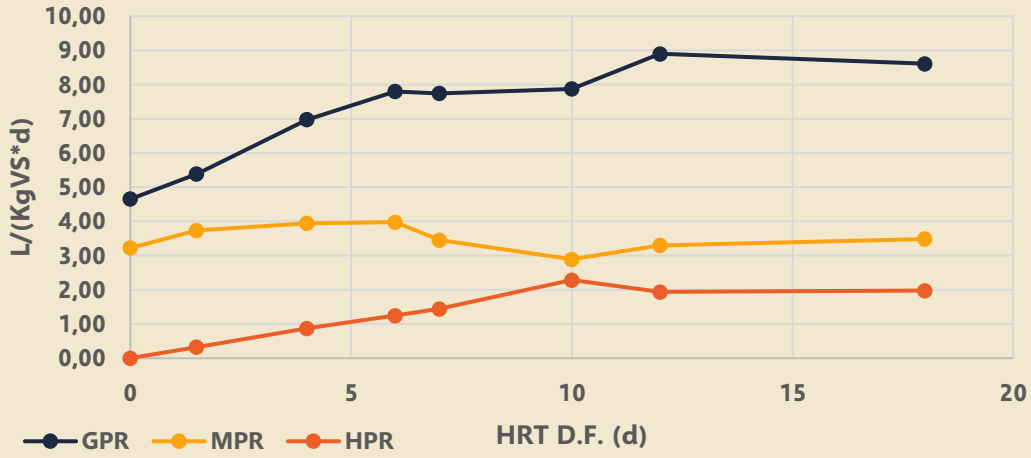
Methane	Hydrogen
58.2%	41.8%

Results

Gas Production - Compared to Fresh Substrate

Comparison of mono stage and two stage AD production rate, imposing a total HRT of 50 days for each process.

HRT D.F.	GPR	MPR	HPR	MPR+HPR	
-	(Lgas/KgVS*d)	(LCH4/KgVS*d)	(LH2/KgVS*d)	(Lgas/KgVS)	
18	8,61	3,48	1,98	5,46	TSAD
12	8,90	3,30	1,93	5,23	
10	7,88	2,89	2,28	5,17	
7	7,74	3,45	1,44	4,89	
6	7,80	3,98	1,24	5,22	
4	6,97	3,94	0,87	4,81	
1.5	5,38	3,73	0,32	4,05	
0	4,65	3,22	0,00	3,22	MSAD



HRT d + MP d = 50

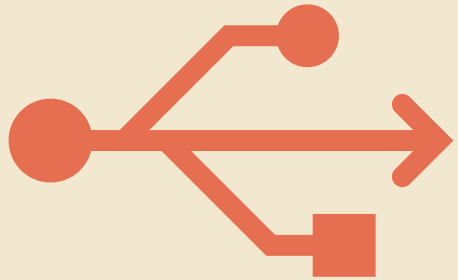
Methane + Hydrogen Production Rate

5.46 max — **Two Stage AD with HRT 50 days** > **Mono Stage AD with HRT 50 days** — **3.22**

Results

Conclusion

- The TSAD process is also **feasible** for MS as substrate
- During the Dark Fermentation tests, the 10-day HRT value reporting the **best hydrogen yield** at about **100 LH_2/KgVS.** HRT 12 and 18 days also reached similar values.
- Dark Fermentation test outputs with **HRT 4 and 6** reported the best theoretical **methane yield (200 LCH_4/KgVS)**, during the BMP tests.
- According to this series of experiments, applying **two stage** anaerobic digestion to MS residues would lead to **better yields** (H_2 and CH_4) than a classic mono stage.



Future Prospects

Other residues

- **Once the feasibility of the TSAD process on MS has been verified, one can move on to study the process on other more easily hydrolyzable agricultural residues.**
- Implementing codigestion among multiple substrates could affect yields.
- The influence of changing other operational parameters could be tested.
- The feasibility of the process could be tested on higher TRLs, as is already happening at the agricultural level.

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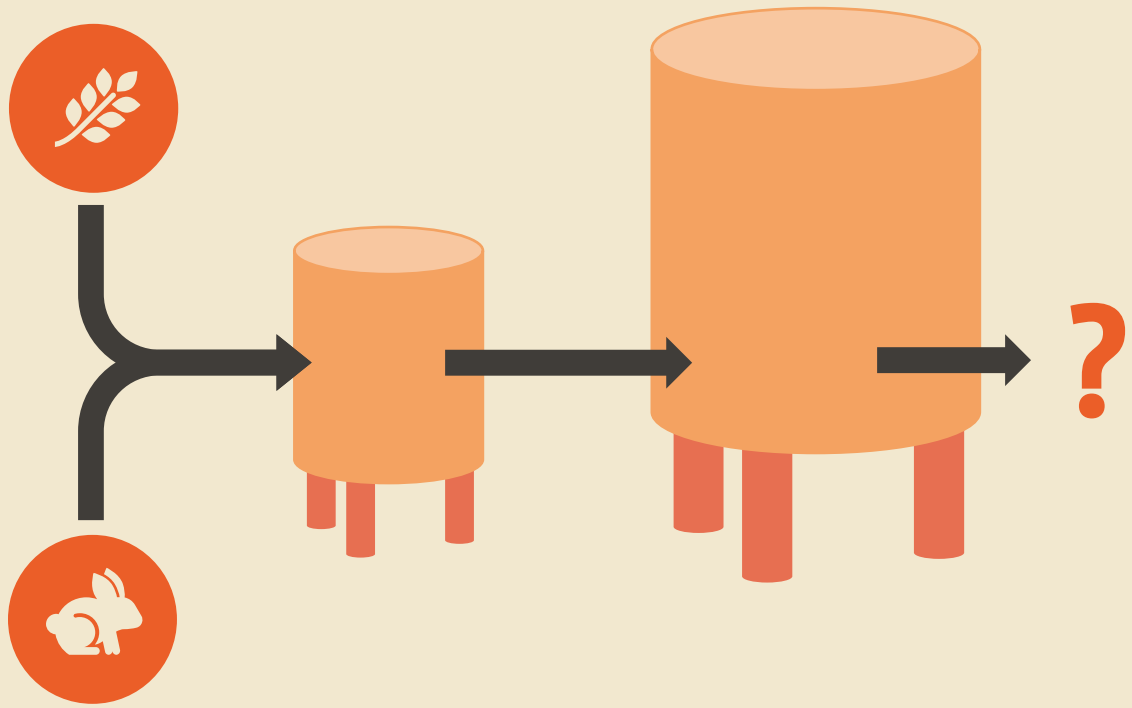

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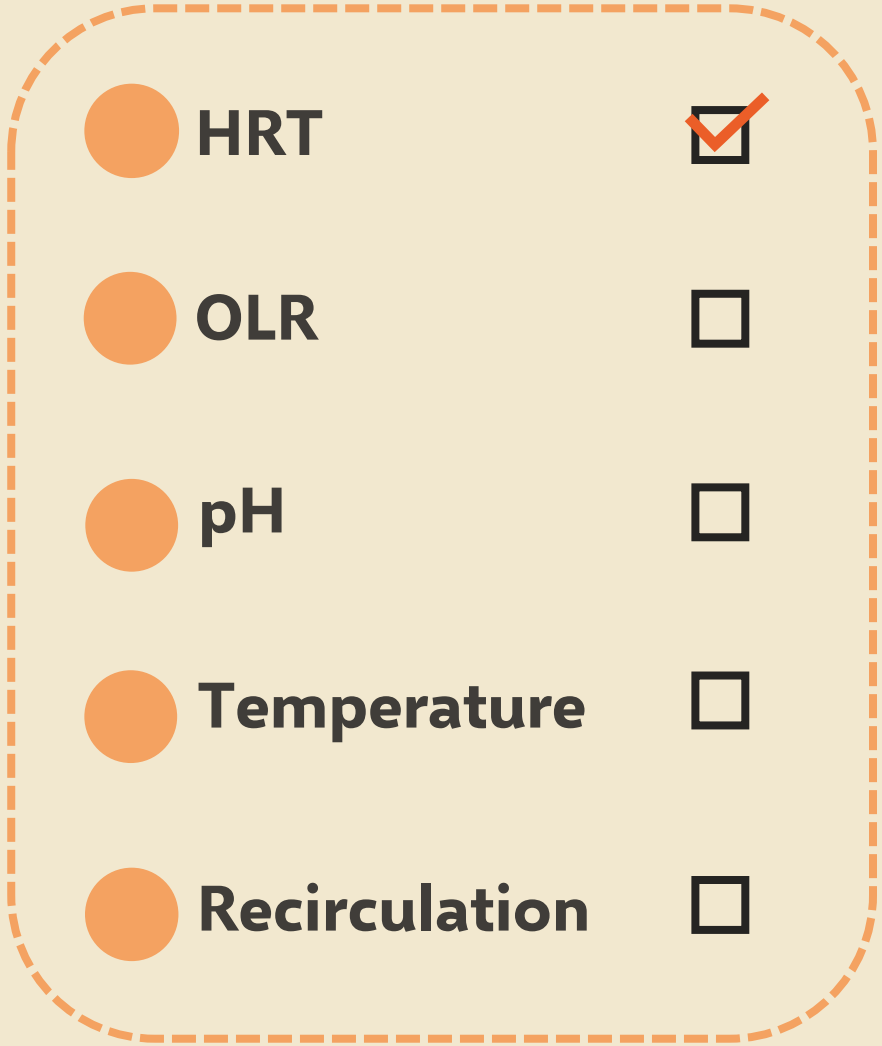

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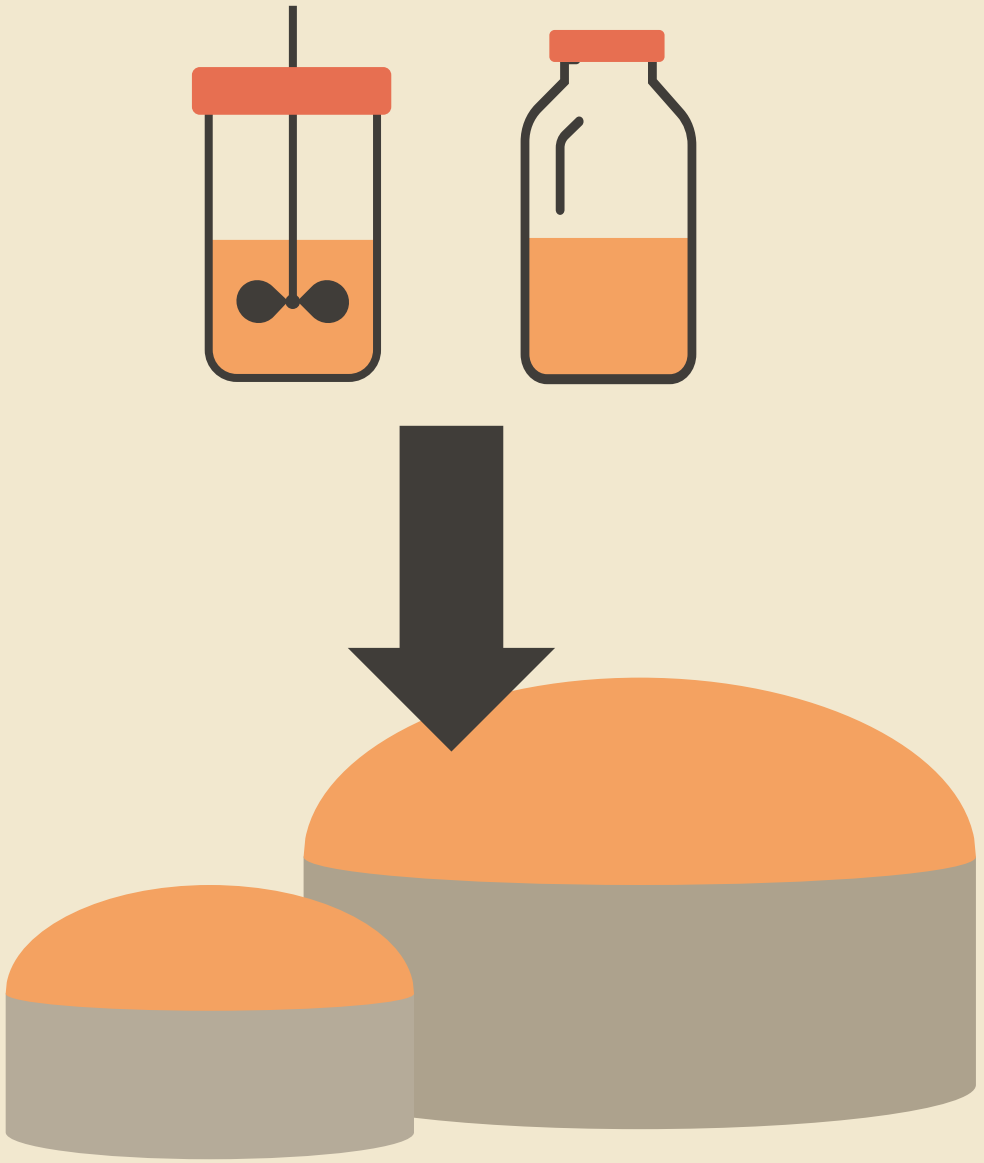

Thank you for the attention