VALORGAS

DARK FERMENTATION OPTIMIZATION BY ANAEROBIC DIGESTED SLUDGE RECIRCULATION: EFFECTS ON HYDROGEN PRODUCTION

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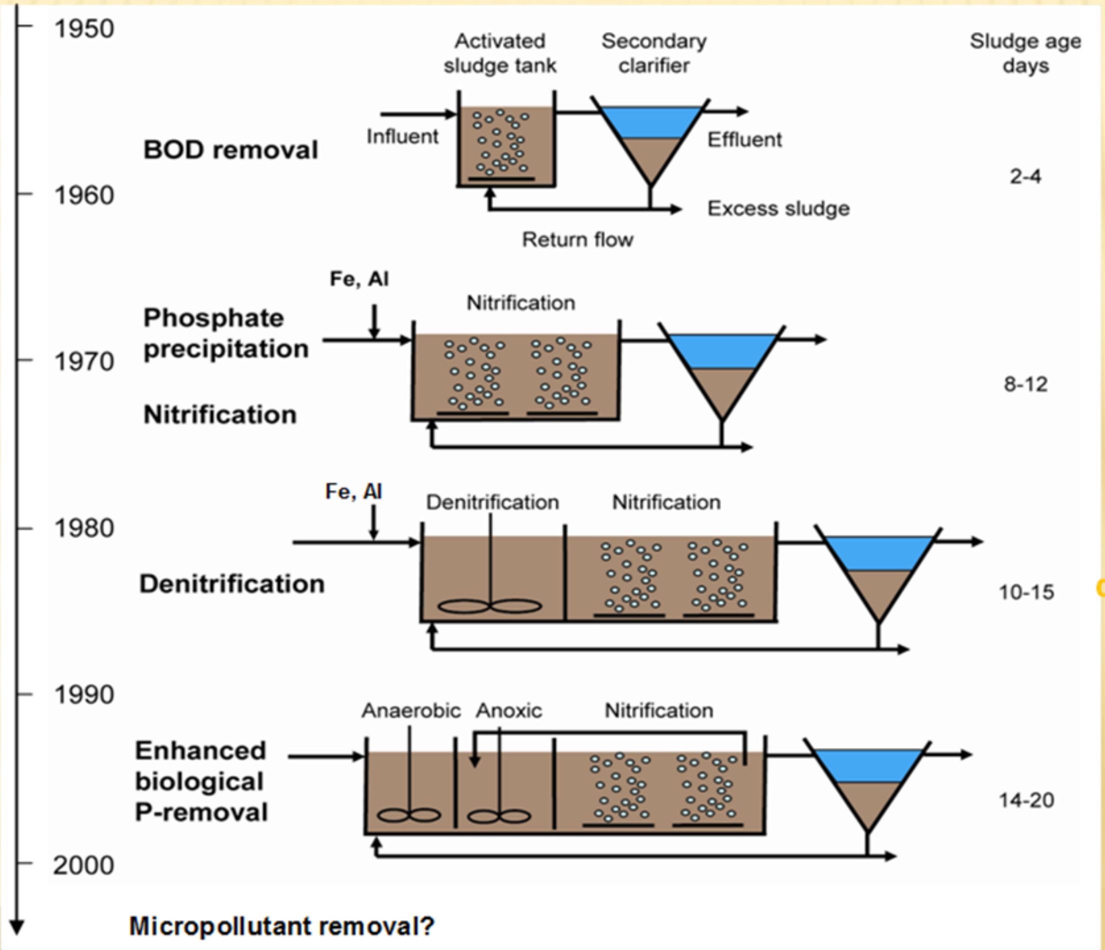
Integration of water cycle and wet waste



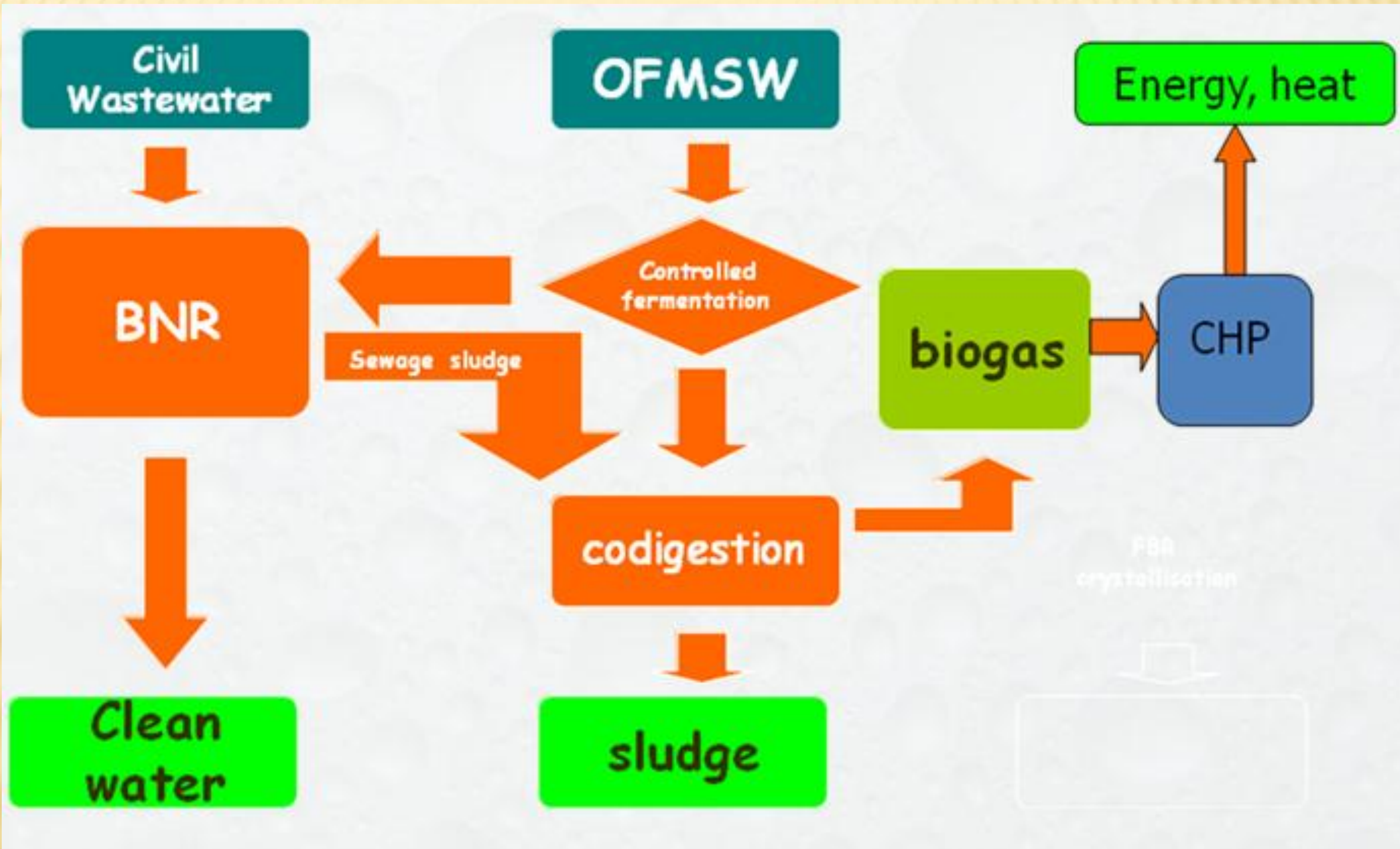
In Italia

Molto diffuso

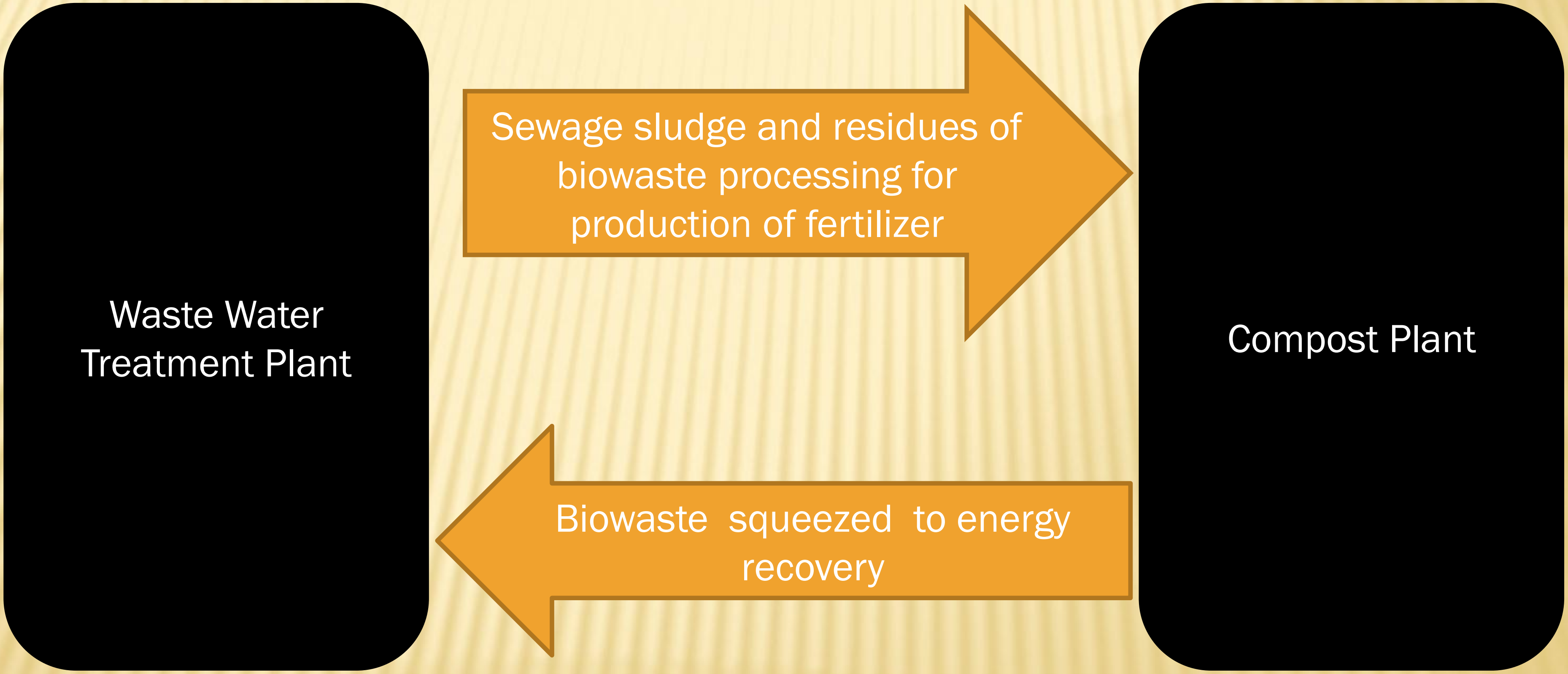
Mediamente diffuso (in aree sensibili)

Casi sporadici

The logic of integrated cycles

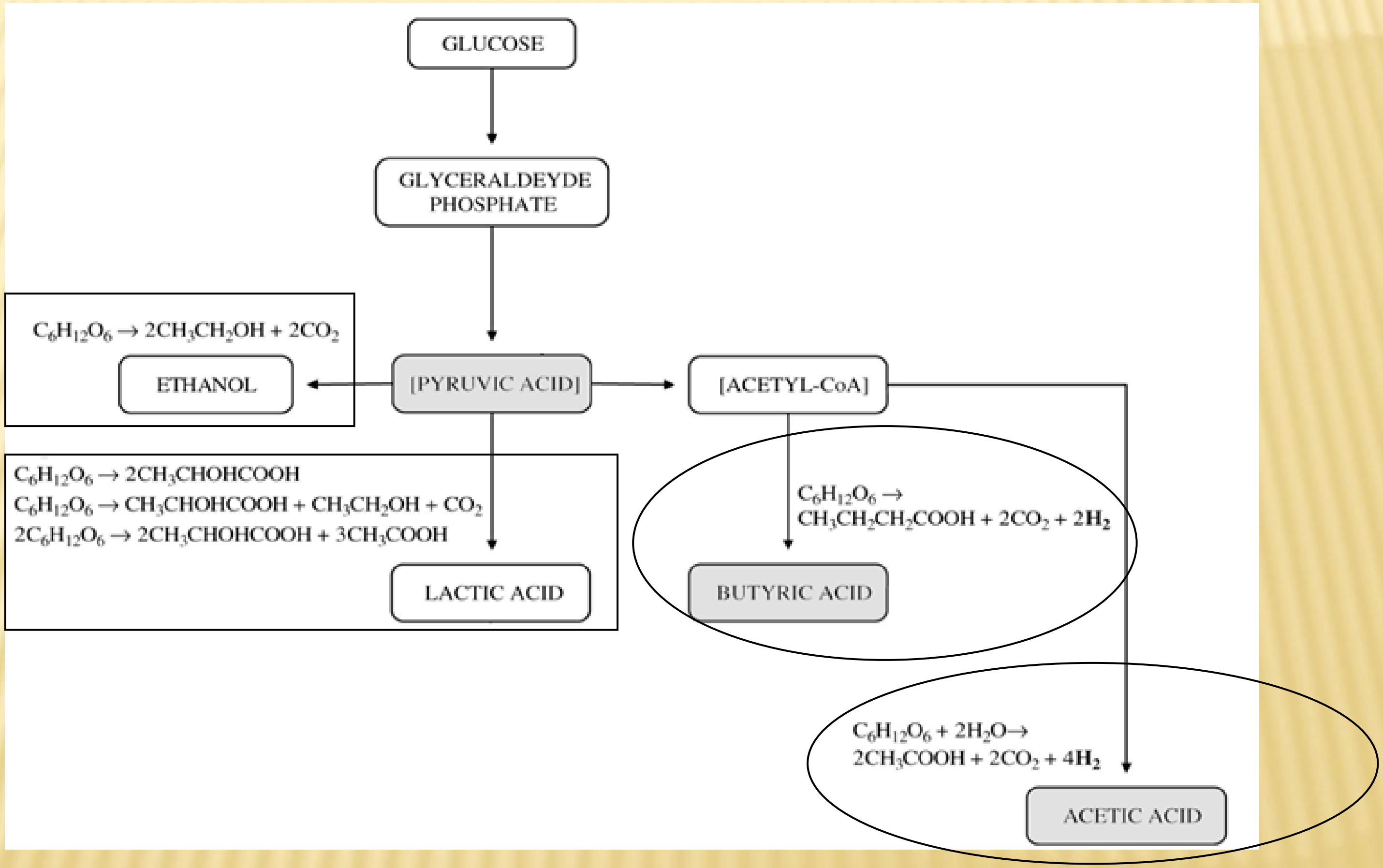


New synergies



Dark Fermentation: main metabolic pathways

Hydrogen can be produced by anaerobic bacteria, grown in the dark on carbohydrate-rich substrates.



In more detail, dark fermentation process produce a mixed biogas containing primarily hydrogen and carbon dioxide

Dark Fermentation: Optimization

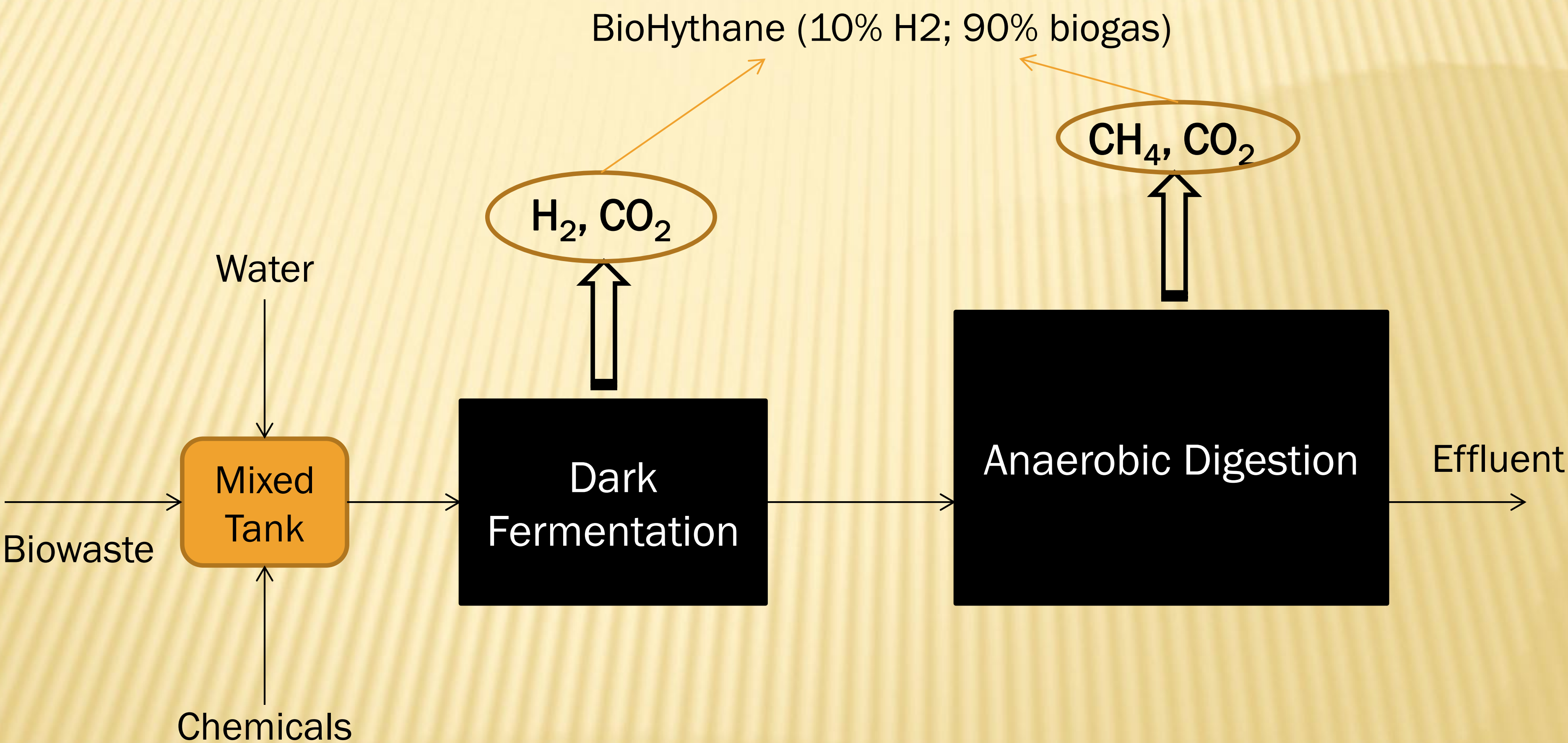
Dark Fermentation optimization means to promote the metabolic pathways that have hydrogen as gaseous product

Optimal operating conditions for hydrogenase enzyme:

- Temperature condition: 55°C
- pH: 5.5 (range of the functionality : 5 – 6)

To maintain pH to desired value, it is usually necessary to dose chemicals to buffer acidifying action, produced by the fermentation products.

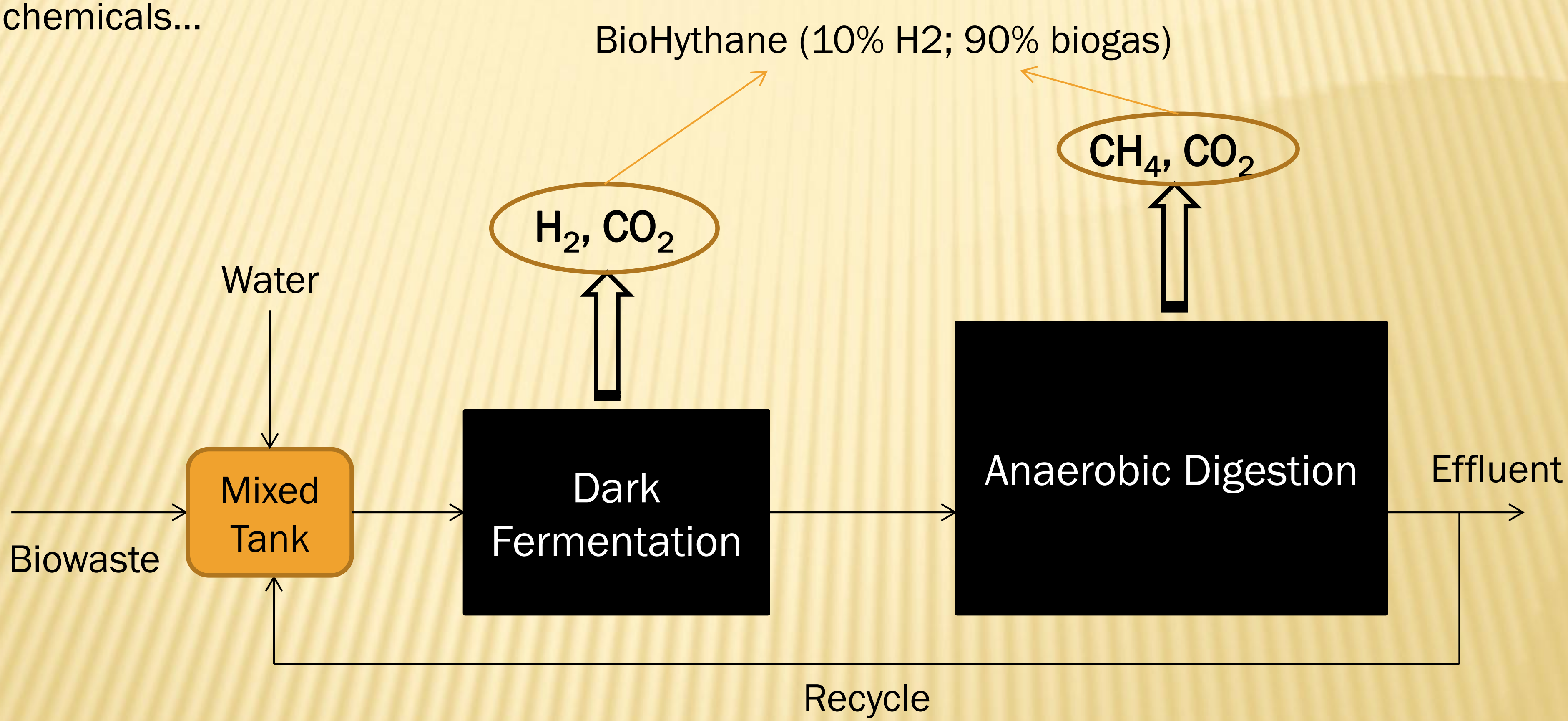
Dark Fermentation + Anaerobic Digestion: BioHythane



The use of external chemicals entails a high production costs of Biohythane

Dark Fermentation + Anaerobic Digestion: BioHythane

In the first phase reactor, to maintain pH to desired value, instead to use external chemicals...



With this system, the production of hydrogen by DF of biowaste is obtained without external pH control because the recirculated second phase sludge supports the DF with buffering agents (mainly ammonia)

Biohythane, what is that?

Biofuel that can be of great interest in the transportation sector

The addiction of 10% of hydrogen in biogas:

- Enhances combustion, with a consequent improvement in thermal efficiency and power output.
- Allows a drastic reduction of hydrocarbons (HC) emissions.

Biohythane: State of the art

A lot of important car and truck industries worldwide are now investing towards this kind of fuel. Ashok Leyland is developing a four-cylinder, four-litre 63-KW engine for hythane-CNG blend through a joint research and development programme with the ministry of new and renewable energy and Indian Oil Corp, Volvo has equipped a crew of V70 model for the use of biohythane, and they are now circulating in Sweden for few years.

The European Union has set the target of increasing the share of biofuels and so-called alternative fuels, including natural gas, in traffic to 10 and 20 %, respectively, by 2020.

In order to overcome these barriers, a European project called GasHighWay has been established, aiming at promoting the uptake of gaseous vehicle fuels, namely biomethane and CNG, and especially the realisation of a comprehensive network of filling stations for these fuels spanning Europe from the north, Finland and Sweden, to the south, Italy - in other words: the GasHighWay.

AIM OF THIS WORK

Previous studies have evidenced that the hydrogen production rate decrease in correspondence with ammonia concentration increase in the system, due to the action of sludge recirculation.

Starting from this evidence, the aim of this work was to individuate the sludge recirculation ratio that allows to keep a stable biological process while maximizing the hydrogen yield.

Substrates

Composition of treated biowaste
(WW = Wet Weight; DW = Dry Weight)

Waste Class	% WW	% DW
Fruit and vegetable	38 – 46	30 – 38
Other food waste	13 – 16	12 – 19
Paper and cardboard	13 - 18	15 - 19
Plastic	5 – 10	7 – 14
Inerts	3 – 9	14 – 19
Unclassified materials	10 – 20	13 – 25

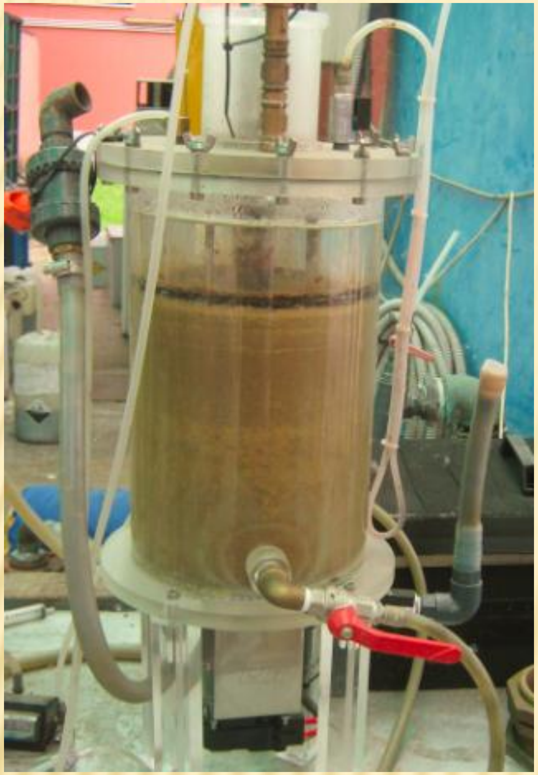
Pre – Treatment step of substrates

- Grinding
- Deferrization
- Sifting

Characterization of the food waste after pre-treatment step

Parameters	Units	Average	SD	Max	Min
TS	g/Kg_{WW}	238	29.3	323.8	232.6
TVS	g/Kg_{WW}	233.6	21.9	261.3	191.3
COD	g/Kg_{DW}	945.8	150.4	1,126.5	658.6
TKN	g/Kg_{DW}	19.4	9.2	29.8	8.5
P_{TOT}	g/Kg_{DW}	7.4	3	11.1	3.4

Experimental set - up



- Type of reactor: CSTR
- Used Volume: 4.5L
- Operating temperature: 55°C

		Run I	Run II	Run III	Run IV
HRT	d	3	3	3	3
OLR	Kg/m^3d	16	16	16	16
α (sludge recirculation ratio)		0.33	0.42	0.66	1

The recirculated sludge used was collected from a pilot digester and then, before of its use, treated with separation process by evaporation unit in order to maintain the ammonia concentration to about 500 mg/L.

Characterization of anaerobic sludge before treatment with evaporator unit

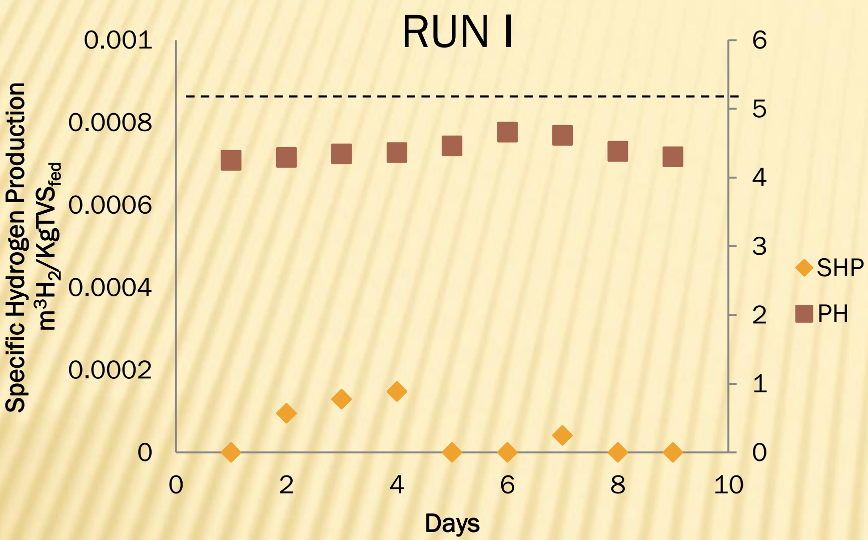
Par.	Units	Average	SD
TS	g/Kg	15.1	2.9
TVS	g/Kg	9.5	2.4
pH		8.2	0.1
VFA	mgCOD/L	640	350
Alk 6	$mgCaCO_3/L$	3,527	551
Alk 4	$mgCaCO_3/L$	5,184	408
NH_4^+	$mgN\text{-}NH_4^+/L$	1,190	152

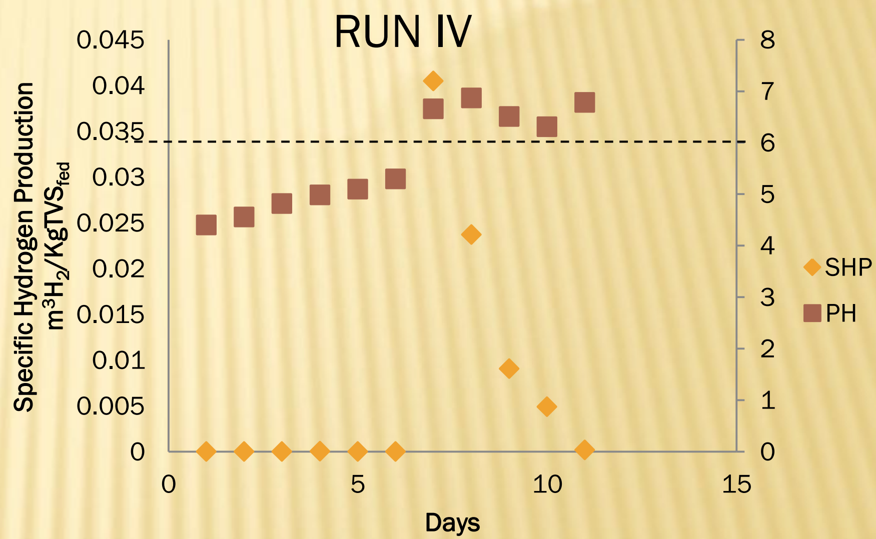
Characterization of anaerobic sludge after treatment with evaporator unit

Par.	Units	Average	SD
TS	g/Kg	12.6	3.8
TVS	g/Kg	7.3	2.8
pH		8.5	0.3
VFA	mgCOD/L	331.6	230.1
Alk 6	$mgCaCO_3/L$	2,162.3	312.6
Alk 4	$mgCaCO_3/L$	3,236.9	485.7
NH_4^+	$mgN\text{-}NH_4^+/L$	562.8	60.6

Results & Discussion (Run I & IV)

The Run I and Run IV have given the worst results with a not significant hydrogen production

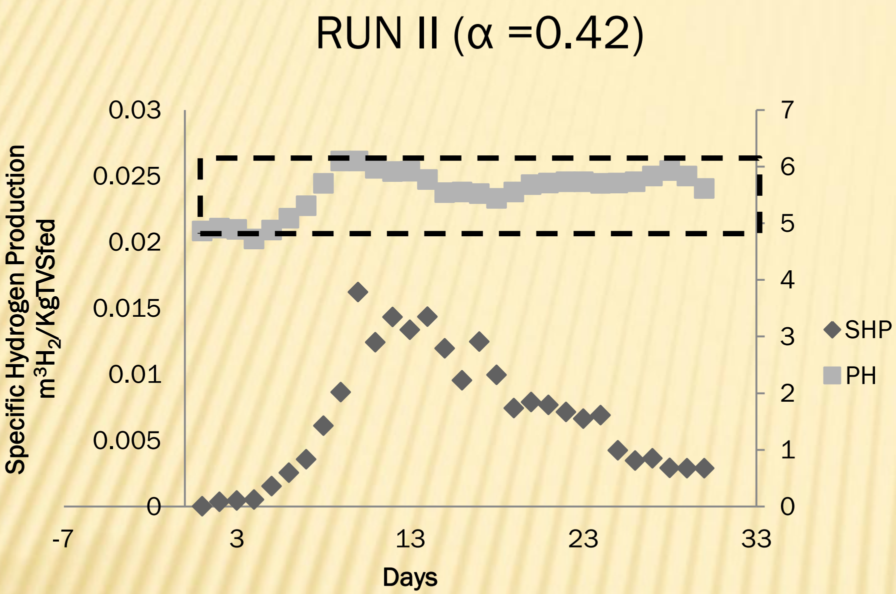


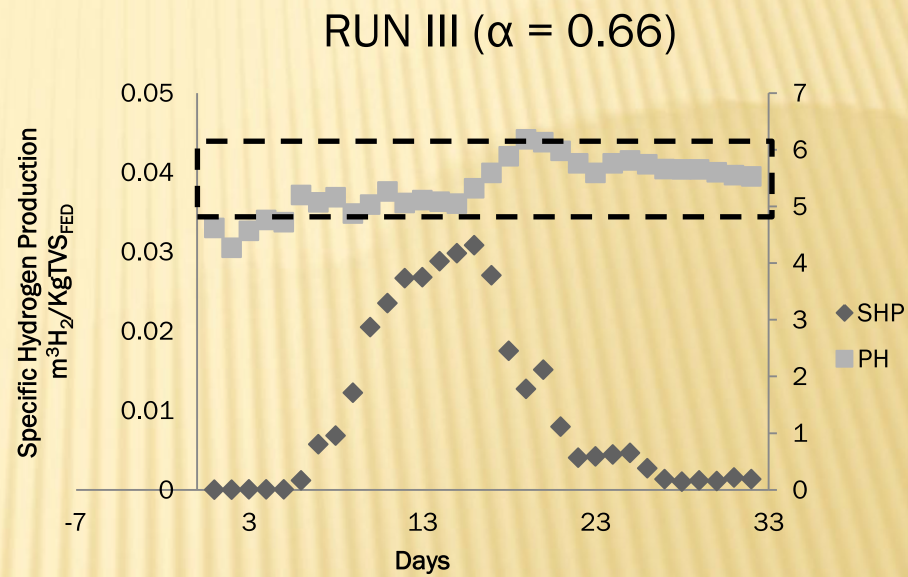


With α = 0.33, pH maintained in range between 4.2 and 4.6. This low pH value could be explained by the low alkalinity in the system (stabilized at 800 mgCaCO3/L). This value of alkalinity was not sufficient to buffer the acids produced from fermentative process.

With α = 1, pH system remained in range between 6.7 and 7 after seven days. In correspondence of these conditions, was not observed hydrogen production, instead was observed a small production of methane.

Results & Discussion (Run II & Run III)



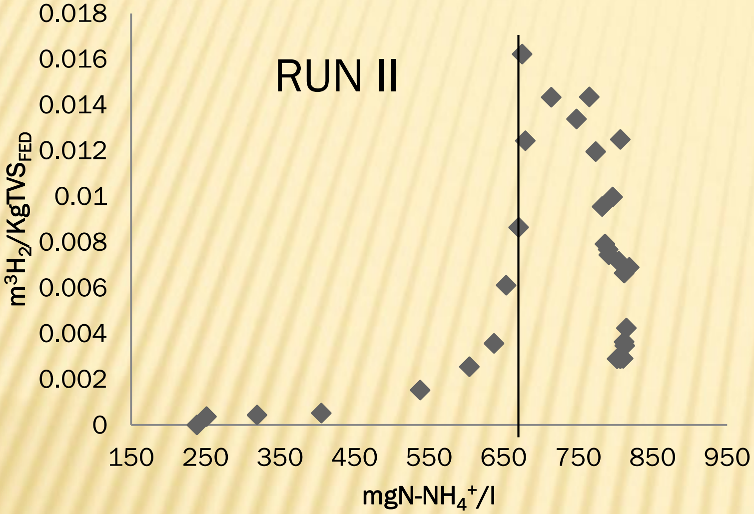


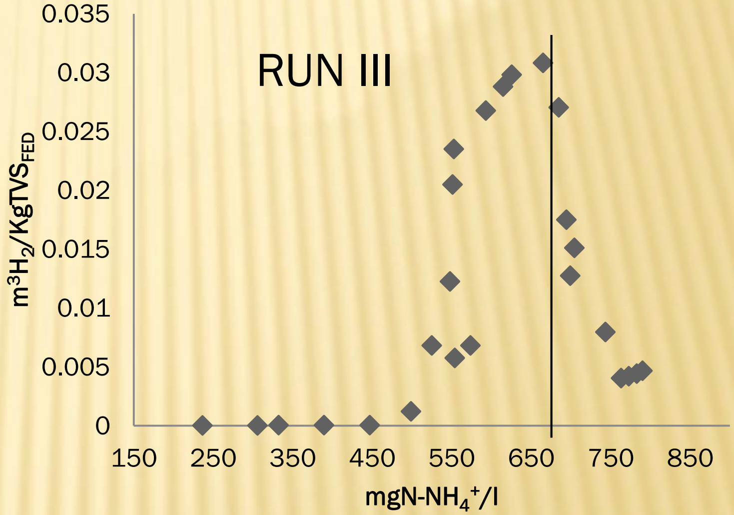
The trend of the hydrogen production, expressed as specific hydrogen production (SHP), in both of these runs, showed an initial low hydrogen production, due to the lag time, then a fast increase until a maximum value; after few days the production decreased though pH remains in the range of the functionality.

Why?

Results & Discussion (Run II & Run III)

Specific Hydrogen Production versus Ammonia concentration in Run II and Run III





The hydrogen yields increased in both Runs with the increasing of ammonia concentration until the same threshold value (about 670 $mgN\text{-}NH_4^+/L$), beyond which it decrease sharply. The increase of ammonia concentration, until a value close to 670 $mgN\text{-}NH_4^+/L$, allows an increase in the hydrogen production as it support the dark fermentation with alkalinity, but exceeded this value the ammonia could act an inhibitor of the biological process of hydrogen production.

Characterization of effluent and gas yields of Run II and Run III in the condition of maximum H_2 production

Parameters	Units	Run II	Run III
Characterization of effluent			
TS	g/Kg	71 ± 0.4	44 ± 4
TVS	g/Kg	48 ± 0.2	33 ± 4
COD	g/Kg_{WW}	67 ± 0.3	46 ± 2
TKN	g/Kg_{WW}	2 ± 0.1	1.1 ± 0.1
P_{TOT}	g/Kg_{WW}	1 ± 0.1	0.22 ± 0.02
pH		5.8 ± 0.2	5.5 ± 0.2
VFA	mgCOD/L	11,156 ± 1,372	15,352 ± 1,395
Acetic Acid	mgCOD/L	1,066 ± 100	3,344 ± 696
Butyric Acid	mgCOD/L	3,442 ± 496	5,747 ± 996
Alkalinity (pH = 4)	$mgCaCO_3/L$	4,768 ± 135	3,483 ± 463
NH_4^+	$mgN\text{-}NH_4^+/L$	677 ± 3	675 ± 14
Gas yields			
Gas Production (GP)	L/d	2.4 ± 1.5	3 ± 0.2
Specific Gas Production (SGP)	$m^3_{biogas}/KgTVS_{fed}$	0.033 ± 0.01	0.094 ± 0.05
Gas Production Rate (GPR)	$m^3_{biogas}/m^3_{reactor}d$	0.48 ± 0.03	0.84 ± 0.06
H_2	%	35 ± 8	40 ± 10
Specific Hydrogen Production (SHP)	$m^3_{Hydrogen}/KgTVS_{fed}$	0.014 ± 0.002	0.03 ± 0.002

Conclusion

A dark fermentation process optimized for the hydrogen production was tested in four different recirculation conditions.

- Run I and IV, the sludge recirculation ratio was respectively 0.33 and 1, was not shown hydrogen production.

- In the remaining two runs, the sludge recirculation ratios were 0.42 and 0.66, the hydrogen yields increased with the increasing of ammonia concentration until the same threshold value (about 670 mgN-NH4+/L), beyond which it decrease sharply.

  - From this study, the ammonia concentration greater than a threshold value of approximately 670 mgN-NH4+/L showed inhibition towards the biological process of hydrogen production

- The optimal hydrogen production was found using a recirculated sludge ratio of 0.66. However, this condition is not maintained stable for continuous accumulation of ammonia in the system due to the sludge recirculation.

Master di Ingegneria Chimica della depurazione delle acque e delle energie rinnovabili

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Dipartimento di Scienze ambientali, Informatica e Statistica

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Valorisation of Food Waste to Biogas

Grazie