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<u>Fermentative hydrogen production from food – industry wastes in a CSTR-type reactor: The influence of Hydraulic Retention Time</u>

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Renewable Energy Resources

- Growing energy demands
- Decreasing reserves of fossil fuel resources
- Environmental problems



Renewable Energy Resources

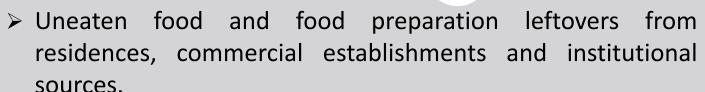
BIOMASS: Biological (organic) material that can be converted into <u>biofuels</u> (CH_4 , H_2 , bio-ethanol, bio-diesel).

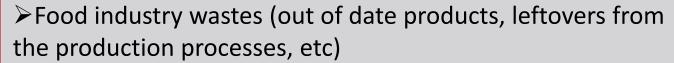


agricultural residues forest residues livestock residues energy crops

municipal and industry wastes and wastewaters

Food Waste







Food industry wastes used in this study

> The mixture of seven out of date solid baby foods at different flavors





Rich in carbohydrates, which are an ideal substrate for fermentative hydrogen production.

Food waste has been proven to be highly desirable substrate for anaerobic fermentation due to its high digestibility and well balanced carbon and nutrient contents.(*Zhang et al., 2007*)

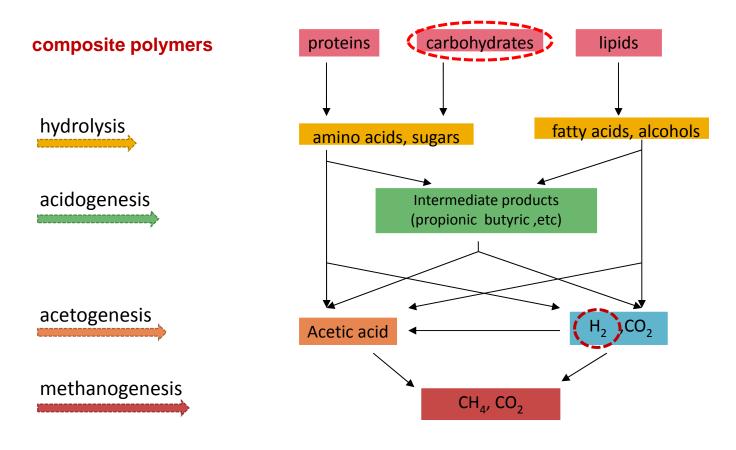
Aim of this study



The investigation of the influence of the Hydraulic Retention
 Time (HRT) on fermentative hydrogen production using as substrate the solid waste streams of a food industry in a CSTR – type reactor.

Fermentative hydrogen production

- ► It is carried out in the dark, under anaerobic conditions
- ➤ It is directly related to the acidogenic stage of anaerobic digestion process.



➤It is well founded, that **carbohydrates** are the main source of hydrogen during fermentative processes.

Fermentative Hydrogen Production

Metabolic pathways - reactions

Production of acetic acid:

• $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$

Production of butyric acid:

• $C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + 2CO_2 + 2H_2$

Production of propionic acid:

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

Production of lactic acid:

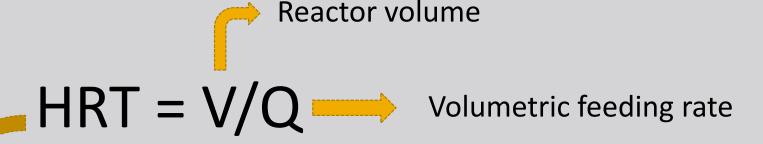
- $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$
- $C_6H_{12}O_6 \rightarrow CH_3CHOHCOOH + CH_3CH_2OH + CO_2$
- $2C_6H_{12}O_6 \rightarrow 3CH_3COOH + 2CH_3CHOHCOOH$

Production of ethanol:

• $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

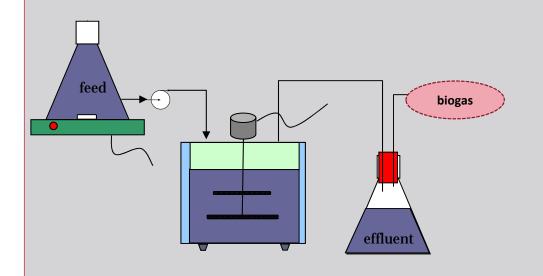
Fermentative Hydrogen Production

Hydraulic Retention Time (HRT)



important parameter that influences the hydrogen production rate and operational stability of a hydrogen-producing reactor.

Experimental procedure - Reactor



- ➤ CSTR type reactor
- > V = 0.4 L
- >T = 35°C
- \rightarrow HRTs = 12, 8, 6 and 4 h.

- > Start up: 2 d as a batch reactor.
- ➤ **Inoculum:** indigenous microbial species, contained in the substrate
- > Inoculum characteristics:
 - \circ TSS = 10.57 g/L
 - \circ VSS = 10.56 g/L
 - \circ pH = 6.87
 - \circ TCOD = 22.6 g/L

Experimental procedure - Feed





Feed characterization

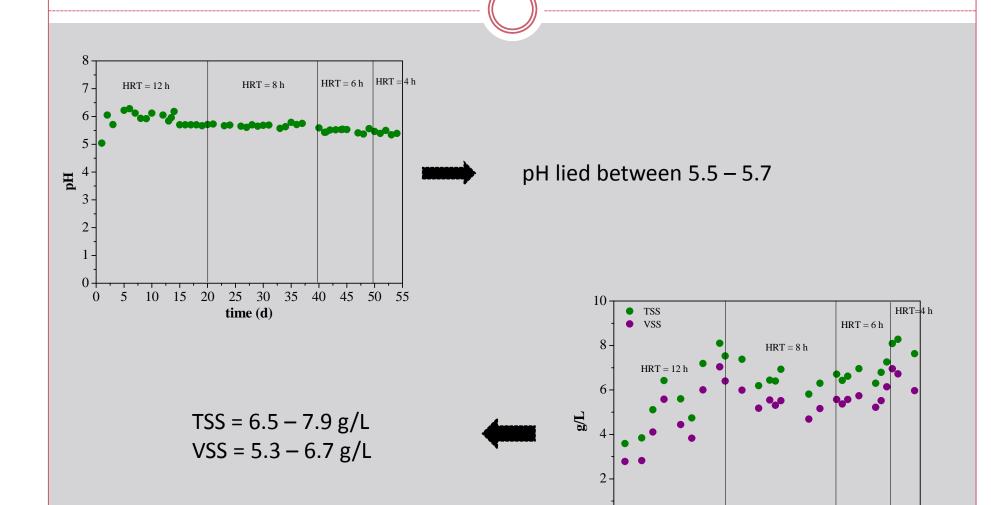
Aqueous solution of the mixture of the seven solid baby foods.

	рН	11.61 ± 0.44
	TSS (g/L)	13.4 ± 1.05
	VSS (g/L)	10.8 ± 0.42
7	Total Carbohydrates (g/L)	12.43 ± 0.73
So	oluble Carbohydrates (g/L)	7.94 ± 0.35
	Total COD (g/L)	21.30 ± 4.07
	Soluble COD (g/L)	12.85 ± 1.90

+ 5 g/L NaOH + 6.8 g/L KH $_2$ PO $_4$ + 2g/L urea + 0.5 g/L yeast extract

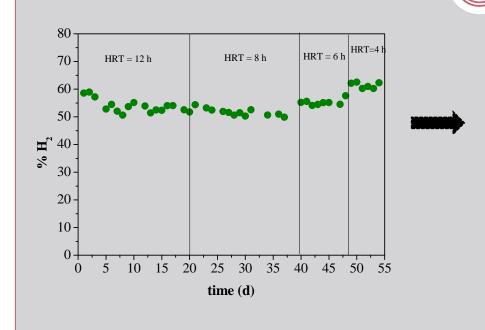
+ $(NH_4)_2HPO_4$ (7.21 g/L) + $FeSO_4 * 7H_2O$ (0.7 g/L) + trace metals

10 mL/ L feed

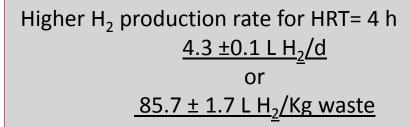


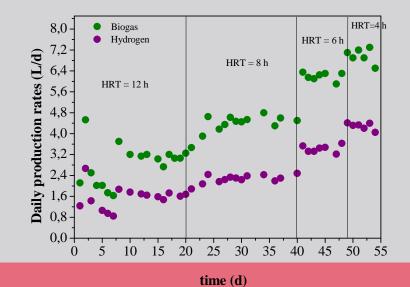
5 10 15 20 25 30 35 40 45 50 55

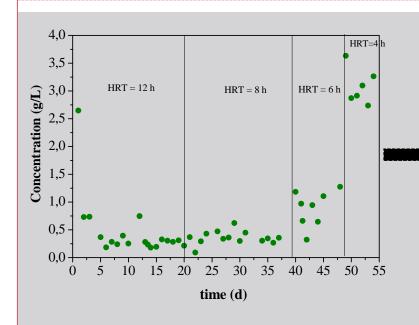
time (d)



Hydrogen content in the gas phase lied between 50-60 %





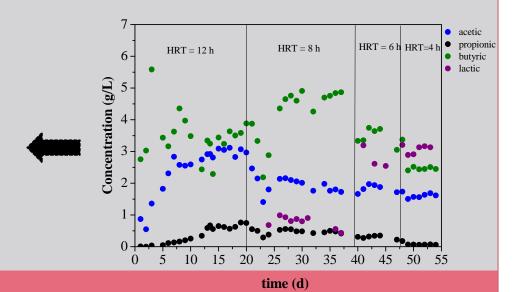


HRT =12 and 8 h complete carbohydrates' consumption

HRT = 6 h is a slight increase in their concentration

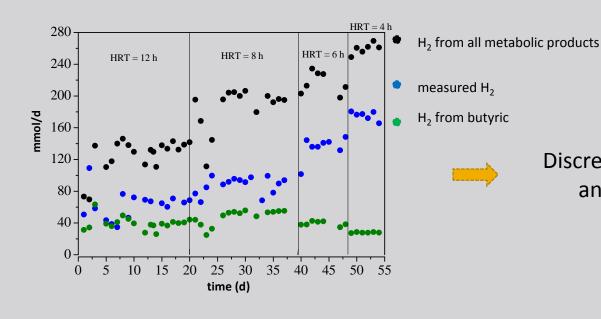
HRT = 4 h carbohydrate accumulation

Main metabolic products:
Acetic acid
Propionic acid
butyric acid
lactic acid





H₂ balance taking into account the concentrations of acetic, butyric and propionic acids.



Discrepancy between predicted and measured hydrogen production rates



 $C_6H_{12}O_6 \rightarrow 3CH_3COOH$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

 $C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + 2CO_2 + 2H_2$
 $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$

Characteristic	Value				
	HRT = 12 h	HRT = 8 h	HRT = 6 h	HRT = 4 h	
Content in hydrogen (%)	52.43 ± 1.03	50.95 ± 0.75	55.70 ± 1.34	61.47 ± 1.06	
Acetic acid (g/L)	2.94 ± 0.12	2.00 ± 0.17	1.83 ± 0.10	1.57 ± 0.05	
Butyric acid (g/L)	3.19 ± 0.52	4.71 ± 0.19	3.46 ± 0.16	2.45 ± 0.05	
Propionic acid (g/L)	0.63 ± 0.08	0.50 ± 0.05	0.26 ± 0.08	0.07 ± 0.00	
Lactic acid (g/L)	-	0.77 ± 0.20	2.89 ± 0.36	3.03 ± 0.14	
Soluble COD measured (g/L)	15.59 ± 0.69	17.10 ± 0.30	15.60 ± 0.48	16.98 ± 0.36	
Soluble COD theoretical (g/L)	10.58	12.95	13.09	12.79	

Characteristic	Value				
	HRT= 12 h	HRT= 8 h	HRT= 6 h	HRT= 4 h	
L H ₂ /L reactor/d	4.13 ± 0.14	5.63 ± 0.15	8.72 ± 0.32	10.79 ± 0.21	
L H ₂ / kg waste	96.27 ± 3.36	87.60 ± 2.40	101.75 ± 3.71	83.94 ± 1.63	
L H ₂ / kg VS waste	98.24 ± 3.43	89.40 ± 2.45	103.84 ± 3.79	85.67 ± 1.66	
mol H ₂ /mol consumed carbohydrates	0.71 ± 0.03	0.73 ± 0.03	0.56 ± 0.03	0.49 ± 0.02	

When the concentration of butyric acid maximized

Conclusions

- ➤ The influence of the hydraulic retention time was investigated during fermentative hydrogen production of food industry wastes in a CSTR—type reactor.
- The reactor operated at HRTs of 12, 8, 6 and 4 h, using indigenous microbial species.
- The maximum hydrogen production yield was obtained for the HRT of 8 h and was 0.73 ± 0.03 mol H_2 /mol consumed carbohydrates which corresponded to 87.60 ± 2.40 L H_2 /kg waste.
- ➤ It was demonstrated that solid wastes of food industry can be exploited for hydrogen production in continuous bioreactors, in a viable and effective process.

Thank you for your attention !!!

