

***METHANE PRODUCTION AFTER FERMENTATION OF THE ORGANIC FRACTION OF MUNICIPAL SOLID WASTE FOR THE SELECTIVE PRODUCTION OF METABOLITES UNDER DIFFERENT pH AND REACTION TIMES***

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Pipyn and Verstraete (1981) - Thermodynamically, methane production is best from lactic acid and ethanol

OFMSW fermentation without pH control produces large amounts of ethanol and lactic acid (Jojoa-Unigarro and González-Martínez, 2021)

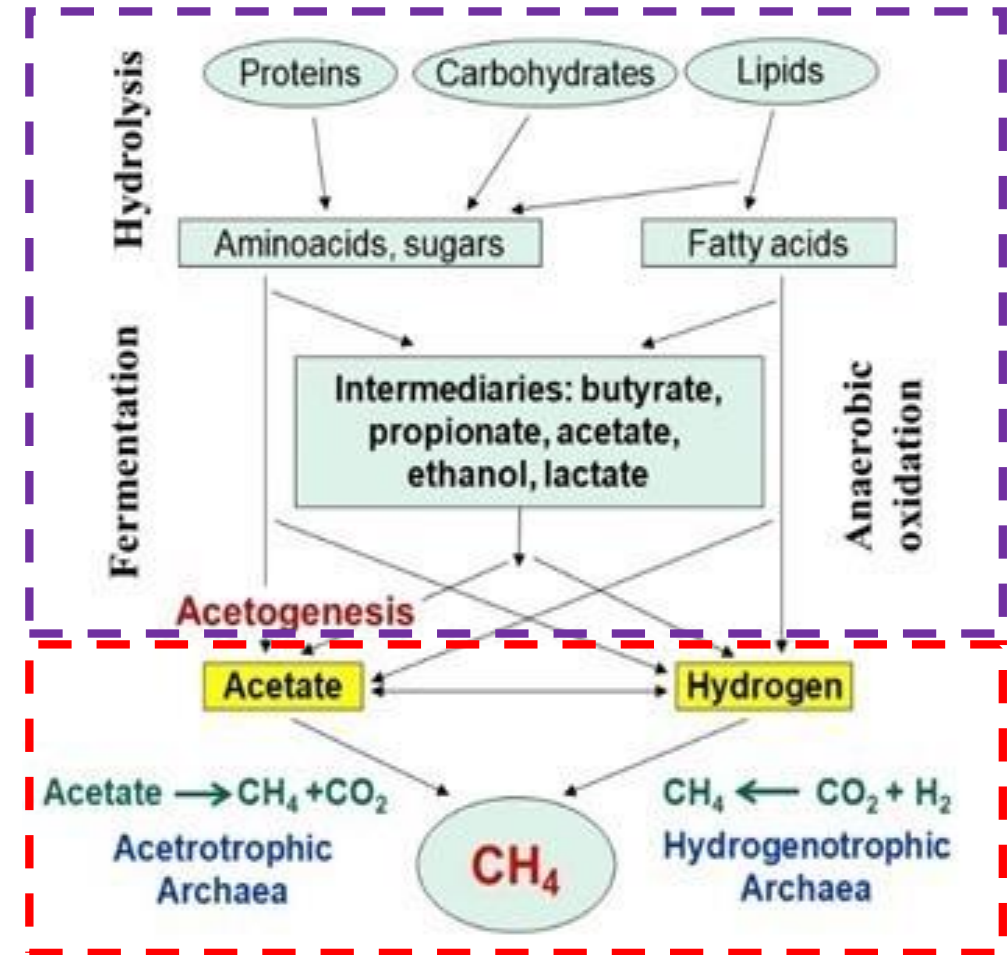
pH and reaction time are the most important variables during OFMSW fermentation

The objectives of this work:

- Evaluate the effects of pH and reaction time on the selectivity of products during OFMSW fermentation.
- Determine the effects of fermentation on the specific methane production methanization kinetics.

Free energy changes of CH<sub>4</sub> production from different substrates

Substrate	Free energy $\Delta G^0$ per mol CH <sub>4</sub> produced (kJ)
Acetic acid	-31.0
Propionic acid	-32.3
Butyric acid	-32.7
Lactic acid	-68.8
Ethanol	-59.5



Main transformations during anaerobic digestion

## Method.

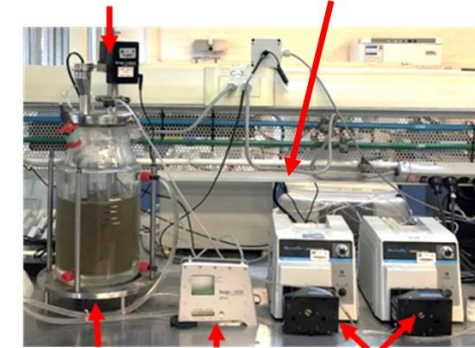
### Operation condition and assembly fermentation test:

- Temperature 35° C
- Reactor volume 3 L
- pH = 4, 5 and 6
- Fermentation time= 1, 3 and 6 days
- Solids concentration 4% VS
- The digestate was centrifuged to obtain a liquid and a solid.

### Operation condition and assembly methanisation test:

- Temperature 35° C
- 400 ml work volume
- 8 g<sub>VS</sub> inoculum (UASB sludge)
- Phosphate buffer at pH 7
- Inorganic nutrients added
- **Substrate – Fermented OFMSW**
- Liquid fraction: 25, 50, 100 and 150 mL
- Solid fraction: 4, 8, 16 and 24 g

Stirring system      pH automatic control

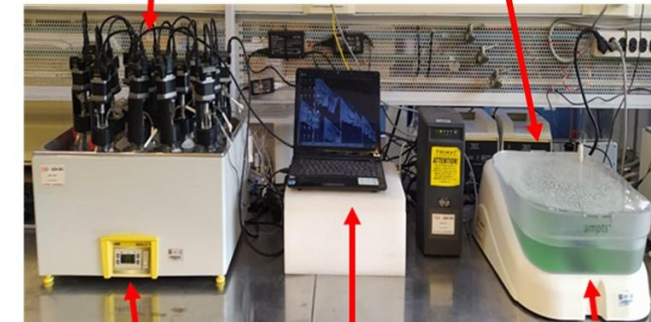


Fermentation reactor      BPC® μFlow      Acid and base pumps

Fermentation reactor system

Methanization reactors with stirring system

Automatic biogas measurement device

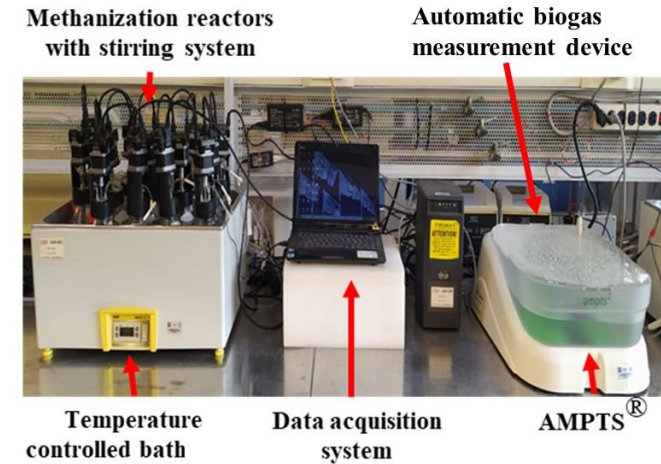
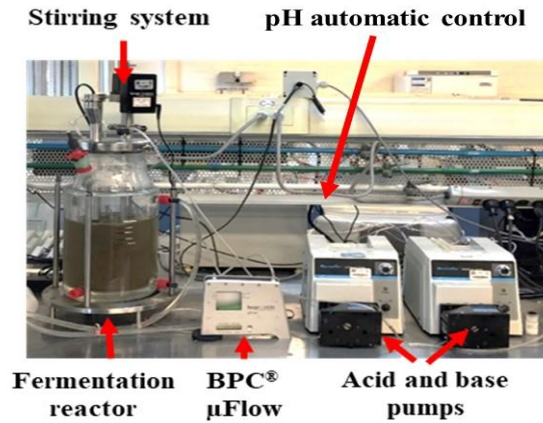
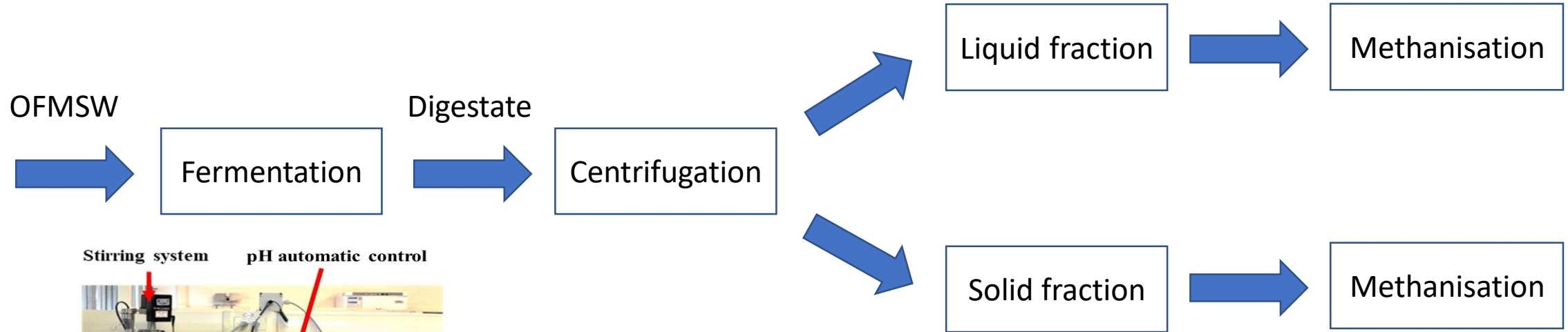


Temperature controlled bath

Data acquisition system

AMPTS®

Methanisation system



pH : 4, 5 and 6

Fermentation time : 1, 3 and 6 days

- 9 digestates were obtained

- Liquid fraction: 25, 50, 100 and 150 mL
- Solid fraction: 4, 8, 16 and 24 g

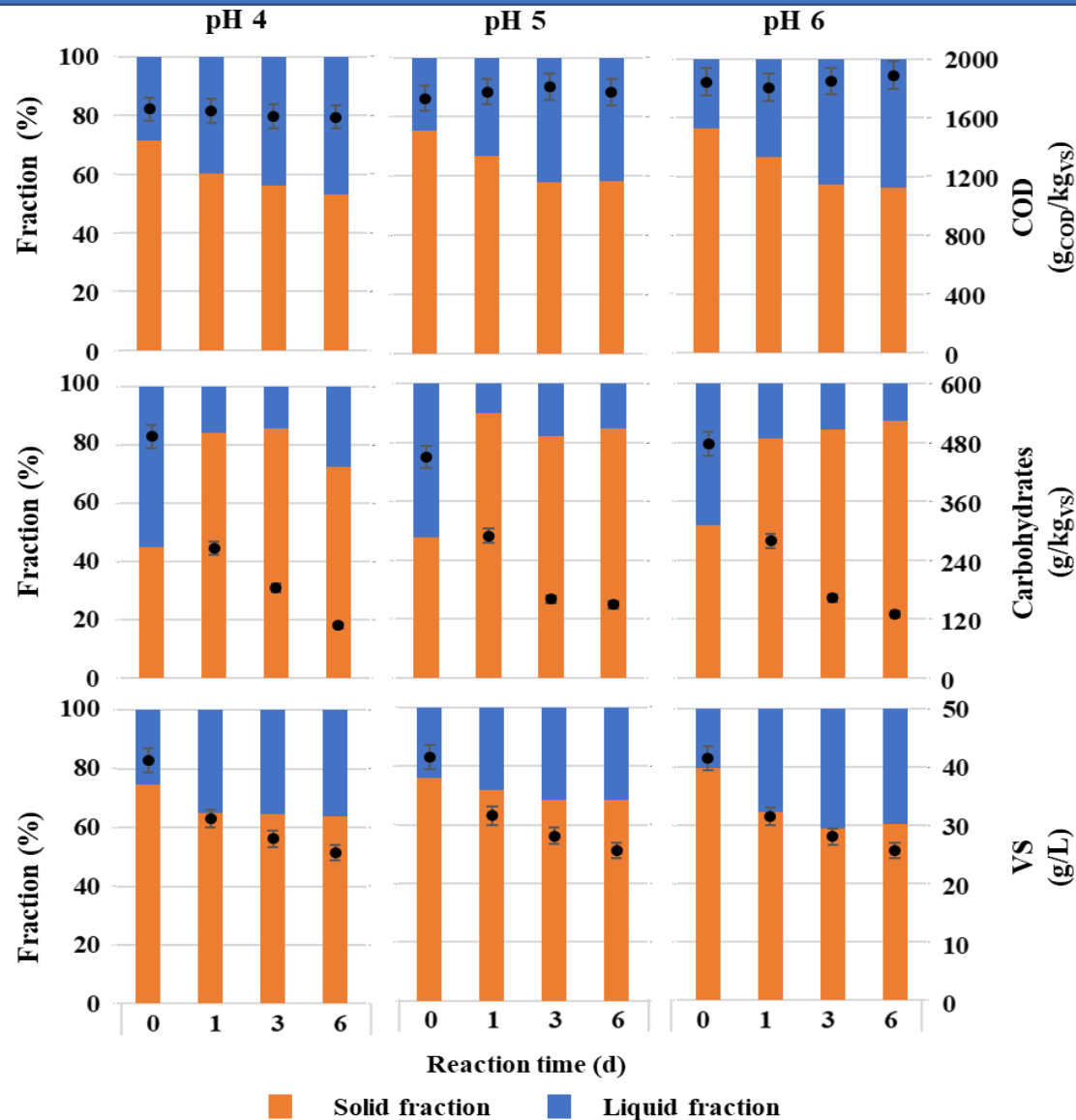


Figure. Distribution of COD, carbohydrates, and volatile solids among liquid and solid fractions over reaction time.

### COD

- The COD/SV ratio remains constant as the fermentation time increases

### Carbohydrates

- Increasing the fermentation time decreases the concentration of carbohydrates in the fermentation reactor.

### Volatile solids

- Increasing the fermentation time decreases the concentration of VS in the fermentation reactor.

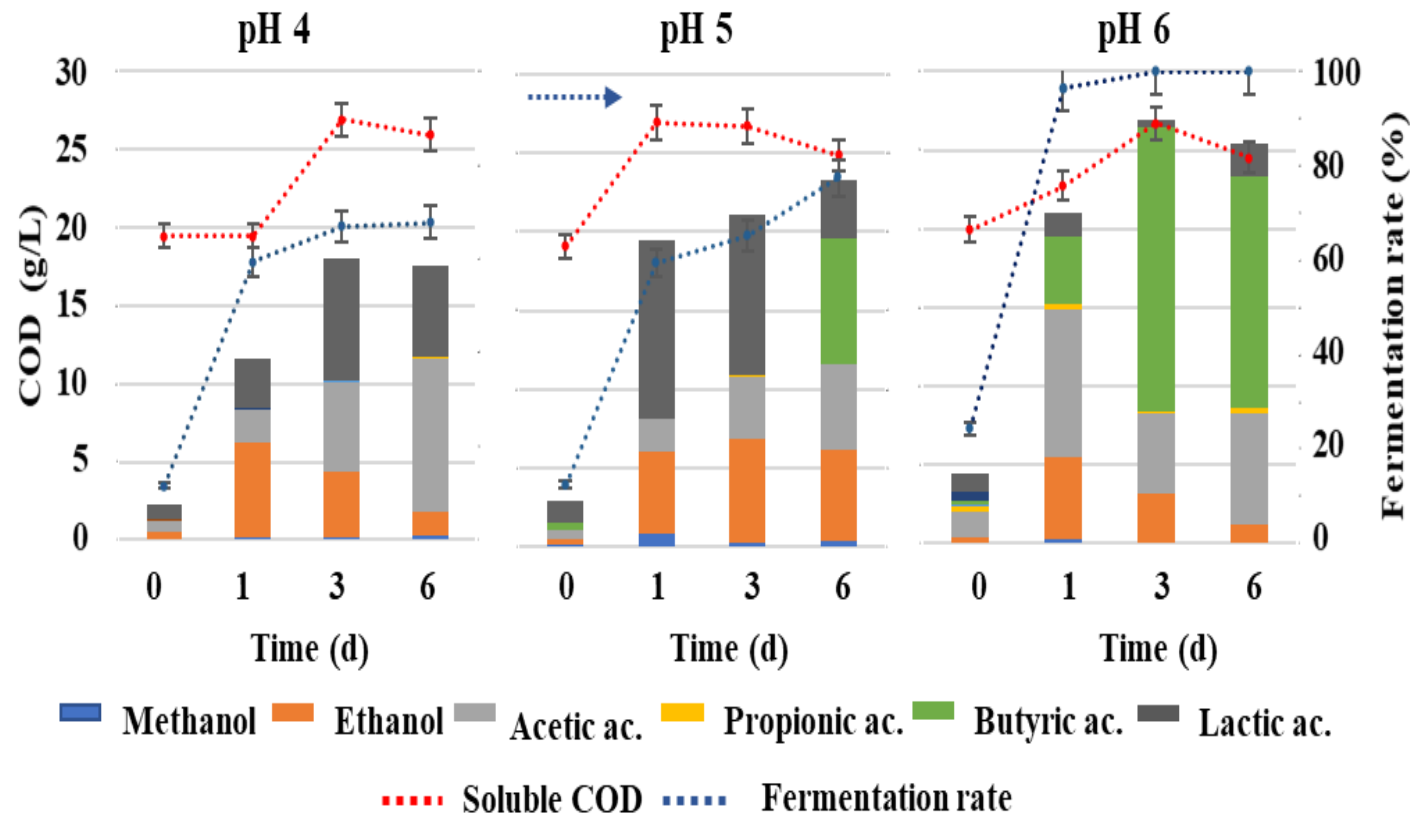


Figure . Metabolites produced during fermentation under different pH values. Comparison of soluble COD with the fermentation rate

pH 4:

- High ethanol production, which decreases over time

pH 5

- High production of lactic acid, which decreases with time and the concentration of ethanol remains constant with time.

pH 6

- High production of acetic acid at one day of fermentation and high production of butyric acid at 3 days of fermentation

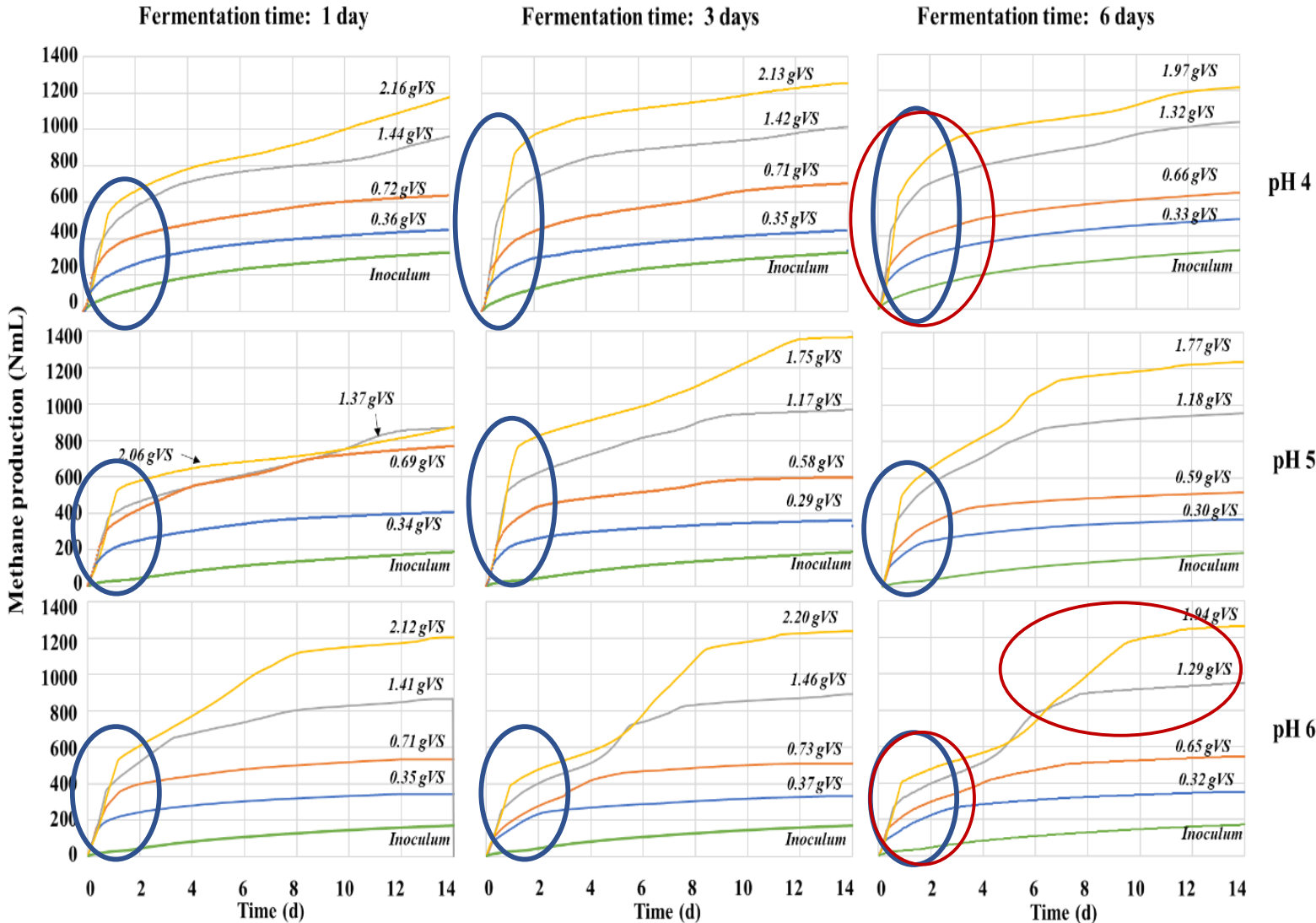


Figure. Methane production from the liquid fractions of fermented digestates at different pH values and fermentation times

- In all the curves, as the initial mass of VS increases, the generated volume of methane increases proportionally.
- When the pH of the fermentation decreases, it is observed that the curves present a single methanization stage.
- In the first stage of methanization between 55-75% of the total methane is produced

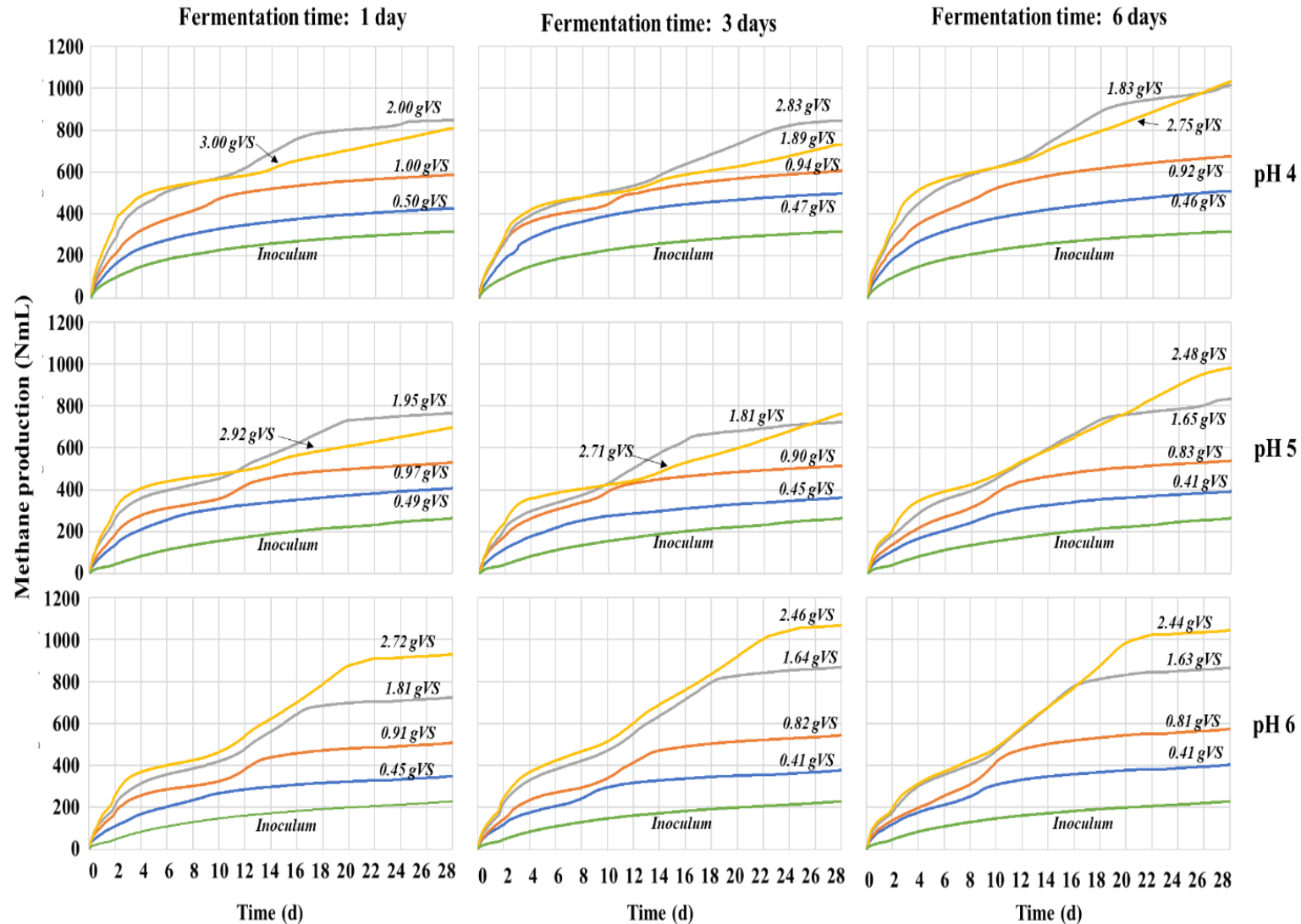


Figure. Methane production from the solid fractions of fermented digestates at different pH values and fermentation times

- In general, increasing the initial mass of VS increases the volume of methane.
- At a pH of 4 and 5 with the highest VS mass, 28 days of methanation were not enough.
- At the first stage of methanation, between 45-60% of total methane is generated, this increases when the pH decreases



pH	FT	Fraction (as VS)	Methane production in first stage			
			% of first stage over final	CH <sub>4</sub> production (NL/kg <sub>VS</sub> )	CH <sub>4</sub> production (combined) (NL/kg <sub>VS</sub> )	
1	Liq	0,35	59±4	83	207	
	Sol	0,65	69±3	124		
4	3	Liq	0,35	75±6	132	237
	Sol	0,65	66±7	106		
6	Liq	0,36	65±4	108	257	
	Sol	0,64	64±7	149		
5	1	Liq	0,28	59±6	68	181
	Sol	0,72	64±7	113		
5	3	Liq	0,31	69±8	151	272
	Sol	0,69	60±9	121		
6	Liq	0,32	53±17	101	206	
	Sol	0,68	53±9	105		
6	1	Liq	0,35	64±11	109	201
	Sol	0,65	56±9	91		
6	3	Liq	0,41	52±14	107	212
	Sol	0,59	53±9	105		
6	Liq	0,40	49±12	112	209	
	Sol	0,60	51±9	97		

$$M_{TVS} \cdot SMP_T = m_{LVS} \cdot SMP_L + m_{SVS} \cdot SMP_S$$

$M_{TVS}$ : Total volatile solids

$SMP_T$ : Total specific methane production

$m_{LVS}$  and  $m_{SVS}$ : Mass of volatile solids in the liquid and solid fractions

$SMP_L$  and  $SMP_S$ : Specific methane production in the liquid and solid fractions

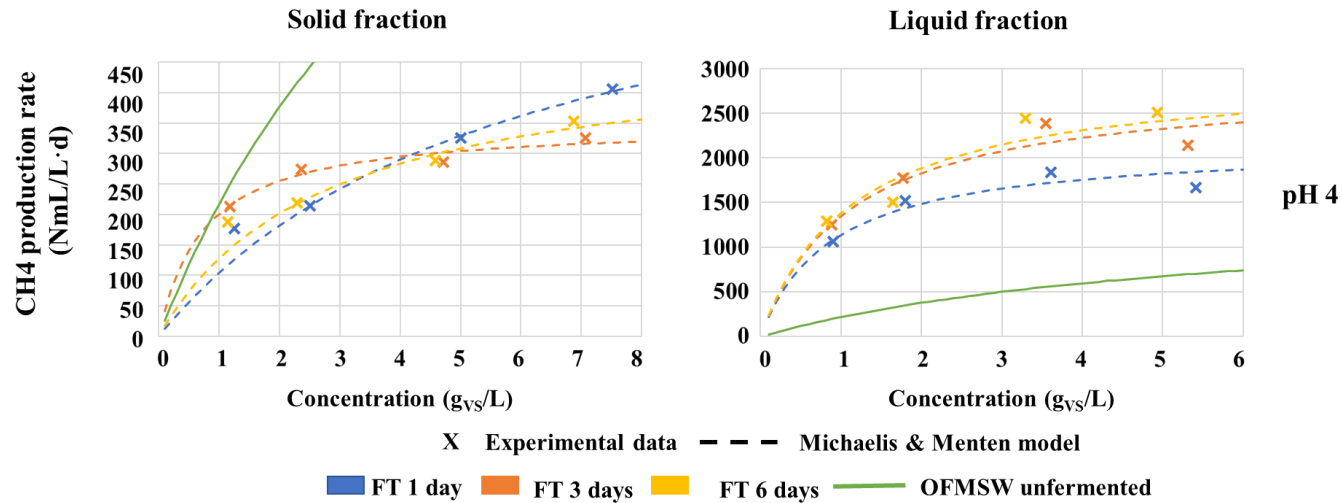
$$SMP_T = f_L \cdot SMP_L + f_S \cdot SMP_S$$

$f_L$  and  $f_S$ : fraction as VS for liquid and solid fraction

Table. Specific methane production from the liquid and solid fermented digestates from OFMSW at first methanization stage

- The highest methane production was achieved at pH 5 and a fermentation time of 3 days
- Solid fraction contributes between 40 to 49% of the specific production

## Michaelis and Menten modeling of liquid and solid fractions fermented at pH 4



The figure shows the methanation modeling for digestates fermented at pH 4 and in the table 3 the kinetic parameters of the liquid and solid fractions for each digestate.

- Decreasing the fermentation pH increases  $V_{max}$  of the liquid fraction of the digestate.
- A shorter fermentation time increases  $V_{max}$  of the solid fraction of the digestate.
- High  $K_m$  values, lower affinity of the substrate to methanization

### Kinetic parameters of the liquid and solid fractions

		$V_{max}$ (NmL/L·d)			$K_m$ (gvs/L)			Regression coefficients		
		1	3	6	1	3	6	1	3	6
Liquid fraction	pH 4	2146	2846	2974	0.9	1.1	1.2	0.933	0.957	0.887
	pH 5	1366	2306	2248	0.3	0.8	1.0	0.913	0.972	0.914
	pH 6	1512	1232	1454	0.8	0.5	0.5	0.879	0.985	0.902
Solid fraction	pH 4	717	349	479	5.9	0.7	2.8	0.999	0.958	0.901
	pH 5	414	326	222	2.6	2.2	1.5	0.985	0.989	0.916
	pH 6	479	317	222	5.0	2.5	1.4	0.964	0.982	0.816



- Lower pH values and shorter fermentation allow better ethanol and lactic acid production.
- Higher pH values and longer fermentation times promote acetic and butyric acid formation
- During fermentation, hydrolysis mainly occurs during the first day causing total carbohydrates and COD to decrease with time.
- Hydrolysis rates decrease with fermentation time at all different pH values.
- The first methanization stage of the liquid fractions requires 1 to 2 days, and the solid fractions from 4 to 8 days.
- Liquid and solid fractions together represent 49 to 69% of total methane production
- Independently of pH and duration, OFMSW fermentation allows better and faster methanization

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**Thank you for your attention!!!**