Biomethanation of Olive Oil Mill Waste. Influence of the production process on the energy yield

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Abstract. This work shows the results of up to 9 batch methanation trials of olive pomace from olive oil mills with a two-phase separation process, compared to the pâté obtained in a multi-phase separation process.

The main inhibitors of anaerobic digestion in this type of substrates are the olive stone, due to its high lignin content, and the high content of polyphenols, slightly higher in the case of the pâté from the multiphase decanters. In both cases, samples were tested without stone content and different substrate-water dilutions were used, mainly in the ratio 70/30 to mitigate the inhibitory effect of phenolic compounds.

In the light of the results obtained, it is possible to affirm that the behavior of pâté is different from pomace; biogas production starts with a delay and needs more time to reach total degradation. If we consider the results obtained when treating the substrate with 70% pomace and 70% pâté, pâté, in absolute terms, has a higher energy potential than pomace, 43.5 L methane/kg pâté compared to 31.1 L methane/kg pomace

Keywords: Anaerobic digestion, Olive-oil mill waste, Biogas production.

1 Introduction

The European Union has updated its renewable energy targets, increasing the goal from 22% to 42.5% by 2030 with the new DIRECTIVE (EU) 2023/2413 [1]. This directive supports the EU's REPowerEU Plan, aiming for 35 billion cubic meters of sustainable biomethane production annually by 2030 [2]. In Spain, the "Biogas Roadmap" sets a target of 10.41 TWh/year of biogas production by 2030 [3]. The Spanish Gas Association (Sedigas) estimates a biomethane production potential of 163 TWh/year, with 3.9% from agro-industrial waste [4].

Spain leads global olive oil production, averaging 1325 thousand tonnes annually over the last decade, representing 44% of global production [5,6]. Olive oil production involves crushing olives, kneading the mass with heat, and separating the oil using a decanter centrifuge [7]. Traditional pneumatic presses are still used in some areas. The decanter separates oil, pomace, and wastewater (alpechín), with the 3-phase method requiring significant water addition. To mitigate environmental issues, the 2-phase process, which generates only oil and a pomace-water mix, is predominantly used in Spain.

In 2015, PIERALISI MAIP introduced the Leopard decanter with Multi-phase (DMF) technology, combining the benefits of 2- and 3-phase systems, reducing water use, and producing stone-free pâté suitable for various applications [8]. This study aims to evaluate the methanogenic capacity of pomace from a two-phase system versus pâté from a multi-phase system on a laboratory scale.

2 Materials and methods.

The trials were conducted by one of the authors at METANOGENIA, SL (Badajoz, Spain). On 20 January 2022, personnel from PIERALISI ESPAÑA, SLU collected representative samples of pâté and destoned pomace and sent them to METANOGENIA on the same day to prevent substrate fermentation, which could alter the trial results. The pâté samples were obtained from a Leopard DMF decanter (PIERALISI MAIP, SpA, Jesi, Italy) at OLIVARERA SOR ANGELA DE LA CRUZ SCA (Estepa, Sevilla, Spain), and the pomace samples were obtained from a two-phase decanter (GEA Group, Düsseldorf, Germany) at SAT SANTA TERESA (Osuna, Sevilla, Spain). The pomace was destoned at the owner’s premises using industrial stone removal equipment (GONZALEZ Y PARIS, SL, La Roda de Andalucía, Sevilla, Spain)). The pâté sample did not include stone parts, as stones contain high lignin content, which retards the methanation process.

Upon receipt, the pâté and pomace dilutions were prepared in duplicate and subjected to a complete physico-chemical characterization. The results are shown in Tables 1 and 2, with values expressed as the average of two determinations. Pomace exhibited a higher Chemical Oxygen Demand (COD) than pâté, which, along with a higher percentage of Volatile Solids (VS), indicates greater biodegradability. Although both by-products had acidic pH values, the pH of pomace was slightly higher, favoring anaerobic treatment. Additionally, the concentration of polyphenols, which inhibit biomethanation, was lower in pomace, and the Carbon/Nitrogen (C/N) ratio was higher. These parameters support the hypothesis that pomace has a higher energy potential than pâté.

Table 3 presents the Hydraulic Retention Time (HRT) required on an industrial scale to avoid inhibition by organic load and polyphenol concentration for each mixture of by-products. Given the recommended daily organic load, pomace mixtures required longer treatment times. Both by-products are rich in polyphenols, so extending the treatment time ensures that the daily dose does not exceed inhibitory limits. Pâté requires a longer treatment time due to its higher polyphenol concentration.

Table 1. Physico-chemical characterization of dilution 70 % pâté 30 % water.

Parameter	Method	Unit	Value
Chemical oxygen demand (COD)	Spectrophotometry	g/L	235.20
pH	Electrometry		4.68
Alkalinity	Potentiometry	g CaCO3/L	3.30
Volatile fatty acids (VFA)	Volumetry	g CH3COOH/L	0.50
Polyphenols	Spectrophotometry	g/L	11.48
Moisture	Gravimetry	%	80.39
Total solids (TS)	Gravimetry	g/kg of sample	196.06
Volatile solids (VS)	Gravimetry	g/kg of sample	167.68
		% of TS	85.52
Mineral solids (MS)	Gravimetry	g/kg of sample	28.38
		% of TS	14.48
Carbon	Elemental analysis	%	10.35
Nitrogen	Elemental analysis	%	0.25
Hydrogen	Elemental analysis	%	10.46
Sulphur	Elemental analysis	%	0.02

The chosen technique for this study was to perform batch tests. In these tests, the total amount of by-product to be treated is introduced into the reactor at the start of the process, and control parameters and biogas production are monitored periodically until production ceases. The same organic load was applied to both by-products to compare their energy potential, incorporating 0.5 g VS of the substrate per g VS of high-quality anaerobic inoculum.

Each test was conducted in a reactor consisting of a 2-liter glass jar with a movable lid containing a plastic part with two outlets. One outlet was kept closed, and the other was used to evacuate the produced gas. The gas was conveyed through silicone tubing to a 10-liter gas hood. This hood comprised two PVC cylinders: the lower cylinder, open at the top and filled with water, contained a stainless-steel pipe connected to the reactor and protruding above the water level. The upper cylinder, open at the bottom, was inserted into the lower cylinder. When biogas was generated in the reactor, it was channeled through the stainless-steel pipe and released above the water, accumulating inside the upper cylinder and causing it to rise. This cylinder was calibrated to measure the volume of accumulated biogas.

Table 2. Physico-chemical characterization of dilution 70 % pomace 30 % water.

Parameter	Method	Unit	Value
Chemical oxygen demand (COD)	Spectrophotometry	g/L	293.25

pH	Electrometry		5.15
Alkalinity	Potentiometry	g CaCO3/L	4.25
Volatile fatty acids (VFA)	Volumetry	g CH3COOH/L	0.37
Polyphenols	Spectrophotometry	g/L	8.61
Moisture	Gravimetry	%	74.81
Total solids (TS)	Gravimetry	g/kg of sample	251.90
Volatile solids (VS)	Gravimetry	g/kg of sample	224.25
		% of TS	89.02
Mineral solids (MS)	Gravimetry	g/kg of sample	27.66
		% of TS	10.98
Carbon	Elemental analysis	%	15.88
Nitrogen	Elemental analysis	%	0.25
Hydrogen	Elemental analysis	%	10.09
Sulphur	Elemental analysis	%	0.02

The reaction medium was maintained at 38°C by immersing the reactors in an electrically heated water bath. The contents of the reactors were homogenized using a magnetic stirrer and a magnet. The methane content in the biogas was analyzed using the BIOGAS5000 gas analyzer (Fonotest SL, Madrid, Spain), which employs the infrared absorption method to determine methane concentration.

After filling each reactor with 1.5 L of inoculum, the reactors were hermetically sealed, heated to 38°C, and connected to their gas hoods. Biogas production from the inoculum was monitored for several days to ensure no leaks, homogeneous biogas production, and exhaustion of the inoculum, indicating that all detected biogas production was due to the incorporated substrates. After these checks, the same amount of inoculum was removed as the amount of substrate incorporated, and the test began.

Biogas production and methane quality were measured periodically, with representative samples taken weekly from each reactor to determine physico-chemical parameters such as pH, Volatile Fatty Acids (VFA), polyphenol concentration, alkalinity, COD, moisture, total solids concentration, minerals, and volatiles [9, 10]. The trial concluded when no biogas production was observed from any reactor for several days.

Table 3. Time of Hydraulic Retention (HRT) according to organic load and polyphenols content.

Substrate	HRT organic load (days)	HRT polyphenols (days)
70 % pate / 30 % water	80	150
70 % pomace / 30 % water	100	115

3 Results and discussion

Three consecutive experiments with a total of 9 batch trials were carried out.

In the first Experiment, 4 trials were carried out simultaneously, in which the following mixtures of by-products were tested:

- Trial 1: 70% pâté/30% water.
- Trial 2: 50% pâté/50% water.
- Trial 3: 70% pomace/30% water.
- Trial 4: 50% pomace/50% water.

At the end of this experiment, to corroborate the results obtained and to consolidate the conclusions, trials 1 and 3 were repeated:

- In Experiment 2, 2 reactors were loaded, one fed with 70% pate and the other with 70% pomace.
- In Experiment 3, 2 reactors were loaded with 70% pâté and one with 70% pomace.

3.1 Experiment 1

The results of the weekly monitoring of pH, volatile fatty acids (VFA), polyphenol concentration, alkalinity, Chemical Oxygen Demand (COD), moisture, total solids concentration, minerals, and volatiles are reported in Table 4. The anaerobic degradation of both pomace and pâté was carried out successfully in all experimental reactors. However, the reactors fed with pomace exhibited different behaviors compared to those treating pâté.

In the reactors operating with pomace, a slight increase in pH was observed, which was associated with a gradual reduction in the concentration of VFA to very low values. This behavior indicates that the methanogenic bacteria efficiently transformed the VFAs into biogas, thus preventing their accumulation and the acidification of the medium. The alkalinity remained constant, and the concentration of polyphenols decreased slightly. In contrast, the concentration of organic matter, as indicated by COD, decreased by 32% and 24%, and the volatile solids concentration decreased by 19% and 17% for 50% and 70% pomace, respectively. This evolution of organic matter concentration shows that all the microorganisms involved in the anaerobic degradation worked in a coordinated manner.

In the reactors fed with pâté, a slight increase in pH was also observed. However, in this case, the increase was due to the high alkalinity of the medium, which prevented acidification despite the increase in VFA concentration observed during the first two weeks of experimentation. This accumulation of acids indicates that the methanogenic bacteria transformed them into biogas at a slower rate than the acetogenic bacteria generated them, suggesting that the activity of methanogenic bacteria may have been affected by the higher concentration of polyphenols in these reactors. By the end of the test, a significant reduction in the concentration of VFAs was observed, although it was lower than that achieved when treating pomace.

Table 4. Physico-chemical characterization of digestate in Experiment 1: substrate 70/30 pâtè/water, pomace/water.

Parameter (unit)	70 % pâtè / 30 % water				70 % pomace / 30 % water		
	Start	Week 1	Week 2	End	Start	Week 1	End
pH	7.23	7.70	8.26	7.73	7.50	8.24	8.07
VFA (g CH3COOH/L)	1.13	2.67	1.73	0.93	1.07	0.60	0.27
Alkalinity (g CaCO3/L)	11.30	10.50	11.70	12.40	11.80	11.40	11.40
Polyphenols (g/L)	2.05	2.08	1.85	1.96	1.60	1.51	1.52
CDO (g/L)	47.05	45.65	38.88	35.10	46.08	34.35	35.20
Moisture (g/kg)	94.69	94.90	95.29	95.52	94.98	95.32	95.63
TS (g/kg)	53.08	51.04	47.15	44.76	50.23	46.85	43.74
VS (g/kg)	36.89	34.38	30.06	27.77	33.79	29.34	27.94
MS (g/kg)	16.19	16.66	17.09	16.99	16.45	17.51	15.79

Regarding the degradation of organic matter, the reduction in COD was lower in the reactors treating pâté, with decreases of 26% and 25% for 50% and 70% pâté, respectively. However, the degradation of volatile solids was higher than in the reactors treating pomace, with reductions of 33% and 25% for 50% and 70% pâté, respectively. Therefore, it can be concluded that pâté is more biodegradable than pomace, as the concentration of volatile solids is a more direct measure of organic matter than COD.

Table 5. Physico-chemical characterization of digestate in Experiment 1: substrate 50/50 pâtè/water, pomace/water.

Parameter (unit)	50 % pâtè / 50 % water				50 % pomace / 50 % water		
	Start	Week 1	Week 2	End	Start	Week 1	End
pH	7.45	7.78	7.82	7.75	7.65	8.07	8.19
VFA (g CH3COOH/L)	1.07	1.53	2.13	0.67	1.20	0.47	0.33
Alkalinity (g CaCO3/L)	11.20	10.40	12.10	12.10	11.70	11.30	11.80
Polyphenols (g/L)	2.05	1.99	1.89	1.85	1.73	1.56	1.57
CDO							

(g/L)	45.70	42.13	36.03	33.95	49.25	38.45	33.55
Moisture (g/kg)	94.83	95.11	95.43	95.58	95.02	95.50	95.77
TS (g/kg)	51.69	48.85	45.68	44.18	49.84	45.00	42.26
VS (g/kg)	40.57	32.13	29.04	27.21	33.13	27.82	26.78
MS (g/kg)	11.12	16.73	16.64	16.96	16.71	17.18	15.48

Experiment 1. Energy performance. Biogas production and methane content were periodically recorded, with results summarized in Table 6. Reactors treating pomace exhibited different behaviors compared to those treating pâté.

In pomace reactors, maximum daily biogas production occurred on the first day, followed by a significant reduction and a gradual decrease over the next five days, with no production in the last ten days. This typical batch trial behavior is due to the initial high nutrient availability, which activates the bacterial population, leading to rapid organic matter degradation. As resources diminish, biogas production decreases until the biodegradable matter is exhausted.

In pâté reactors, biogas production was delayed due to the accumulation of fatty acids (Tables 4, 5). Maximum production was reached within 24 hours, followed by a sharp decrease over seven days and a significant increase over the next eight days, during which most energy production was recorded. The trial continued for an additional five days with no further biogas production.

The highest energy yield was obtained from the anaerobic treatment of 70% pâté, followed by 70% pomace. Substrates with 50% by-product had similar cumulative biogas and methane yields.

Table 6. Batch Experiment 1. Energy potential of treated substrates.

Parameter	70% pâtè /30 % water	50% pâtè /50 % water	70% pomace /30 % water	50% pomace /50 % water
Biogas L/ kg of VS	271.7	157.1	185.2	154.3
Methane L/kg of VS	135.9	63.1	92.8	74.0
Biogas L/ kg of diluted substrate	45.6	18.6	41.5	28.6
Methane L/ kg of diluted substrate	22.8	7.5	20.8	13.7
Biogas L/ kg of substrate	65.1	37.3	59.3	57.2
Methane L/ kg of substrate	32.6	15.0	29.7	27.4

3.2 Experiment 2.

In Experiment 2, two reactors were loaded with 70% pâté and 70% pomace, respectively. The reactor fed with pomace exhibited different behavior compared to the one treating pâté, particularly in the degradation of volatile fatty acids (VFAs). Similar to

Experiment 1, there was a higher accumulation of VFAs in the first week, which subsequently decreased. Other observed parameters behaved similarly in both reactors.
However, in terms of energy yield, both cumulative biogas and methane production were higher when treating pomace, which contrasts with the results from Experiment 1. This consistent behavior was observed in both reactors, regardless of the substrate used. To validate these findings, a new experiment was conducted.

3.3 Experiment 3.

In this experiment, two reactors were loaded with 70% pâté and one with 70% pomace. The pH increased in all reactors, along with the concentration of volatile fatty acids (VFAs) during the first weeks. In reactors fed with 70% pâté, the reduction in VFAs occurred after reaching maximum biogas production. Alkalinity, humidity, and polyphenol concentration remained constant, indicating that these compounds do not significantly degrade anaerobically. This could lead to their accumulation in continuous operations when treating by-products rich in these compounds, such as pâté or pomace.

Regarding the degree of degradation, similar to Experiment 1, pâté resulted in a greater reduction in volatile solids concentration (30%) compared to pomace (26%).

Experiment 3. Energy performance. Results are reported in Table 7. It can be observed that, although there are differences between the two reactors fed with pâté, both achieve a higher volumetric production of biogas and methane than pomace. As in Experiment 1, a different behavior of the reactors treating pâté is again observed, as both reactors start energy production with a delay compared to the reactor fed with pomace. In other words, they need more time to start generating biogas and therefore also more time to completely degrade the substrate and stop producing biogas.

Table 7. Batch Experiment 1. Energy potential of treated substrates.

Parameter	70% pâtè /30 % water (R1)	70% pâtè /30 % water (R2)	70% pomace /30 % water
Biogas L/ kg of VS	455.8	377	283.9
Methane L/kg of VS	222.5	186	101.1
Biogas L/ kg of diluted substrate	76.4	63.2	63.7
Methane L/ kg of diluted substrate	37.3	31.2	22.7
Biogas L/ kg of substrate	109.2	90.3	91
Methane L/ kg of substrate	53.3	44.5	32.4

The maximum methane content in the biogas is also reached later in the pâté reactors, but no significant differences are shown between pâté and pomace (both slightly lower than 70%). Both by-products can generate a biogas with a high methane richness. There are differences between the energy potentials of the two reactors that have treated pâté, but despite this, the energy yield of pâté is always higher than that of pomace, especially when comparing methane production.

Table 8. Energy potential of treated substrates: average ± standard deviation *

Parameter	70% pâtè /30 % water	70% pomace /30 % water
Biogas L/ kg of VS	368.2 ± 92.4	218.4 ± 56.8
Methane L/kg of VS	181.5 ± 43.5	97.2 ± 4.2
Biogas L/ kg of diluted substrate	61.7 ± 15.5	49.0 ± 12.8
Methane L/ kg of diluted substrate	30.4 ± 7.3	21.8 ± 1.0
Biogas L/ kg of substrate	88.2 ± 22.1	70.0 ± 18.2
Methane L/ kg of substrate	43.5 ± 10.4	31.1 ± 1.4

*Statistics have been calculated considering Experiment 1 and 3 for the pâtè and 1, 2 and 3 for the pomace.

Finally, considering the average results obtained from treating the substrate with 70% pomace and 70% pâté (excluding Experiment 2, which is not representative), as shown in Table 8, pâté demonstrates a higher energy potential than pomace. Specifically, pâté yields 43.5 L methane/kg, compared to 31.1 L methane/kg for pomace. However, the limited number of observations precludes a statistical test of this statement.

It is challenging to find articles with comparable results due to several factors:

1. Variability of Olive Mill By-Products: The physico-chemical characteristics depend on the extraction method, olive variety, and harvest. The lack of detailed information on the origin and treatments of by-products further complicates comparisons. For instance, [11] reports 373±4 ml $CH4$/g VS for pomace sieved to 2 mm, while [12] shows 255.20±1.6 ml $CH4$/g VS without detailed substrate information.
2. Different Organic Loadings: Tests with varying organic loadings are not comparable. Our study consistently uses the same organic load for both pâté and pomace. In [13], results range from 124.55 to 255.20±1.6 ml $CH4$/g VS.
3. Test Methods: Results from batch and continuous tests are not comparable. For example, [14] reports 0.20 l $CH4$ STP/g COD with an 80% pomace dilution.
4. Complexity of Biomethanation: The high polyphenol concentration in olive mill by-products complicates finding literature with biomethanation results using these by-products as the sole substrate.

These factors underscore the relevance of our results, which compare pomace and pâté, by-products of olive oil extraction from mills using different extraction systems.

4 Conclusions

1. After carrying out nine batch biomethanation trials, treating pâté and pomace, it can therefore be concluded that the behavior of the pâté is different to that of the pomace, since when subjected to anaerobic treatment under the same conditions the pâté requires more time to reach maximum energy production, generates biogas for a longer time than pomace and needs more time to reach total degradation.
2. On average, the eight batches considered show that pâté yields 26% more biogas and 39% more methane than pomace, both calculated in L/kg of substrate. Specifically, the biogas and methane yield for pâté are 88.2 L/kg and 43.5 L/kg, respectively, while for pomace, they are 70 L/kg and 31.1 L/kg, respectively.
3. One possible reason for this different behavior is the differential rheology of pâté versus pomace. Perhaps the bacteria find a friendlier medium in the pâté, which allows them to move more easily due to its creamier texture.

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