

HYDROGEN AND METHANE PRODUCTION FROM ORANGE PROCESSING WASTE "PASTAZZO" IN TWO STAGE ANAEROBIC PROCESS



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BACKGROUND

Anaerobic Digestion (AD) for biogas production offers a sustainable, carbon neutral and eco-friendly alternative for energy generation. This process produces a mixture of gases, primarily methane (CH₄) and carbon dioxide (CO₂) through four main metabolic steps (hydrolysis, acidogenesis, acetogenesis and methanogenesis) and involves several groups of microorganisms. The acidogenic phase of AD corresponds to Dark Fermentation (DF), an anaerobic process that produces hydrogen (H₂) and soluble metabolic products. It is possible to develop a two-stage process, by physical separation of the acidogenesis phase producing H₂, and the methanogenesis phase producing CH₄ for increasing the stability and overall performance of the process.

In Italy 340 thousand tons of orange processing waste, named Pastazzo, are produced every year and the cost associated with the disposal of large quantities of this residue is excessively burdensome for the companies. Due to its biochemical composition, it is considered possible to use the pastazzo as a substrate for the anaerobic fermentation for biogas production. However, the rapid acidification of this waste and the presence of limonene can inhibit the activity of methanogenic bacteria.

PURPOSE OF THE WORK

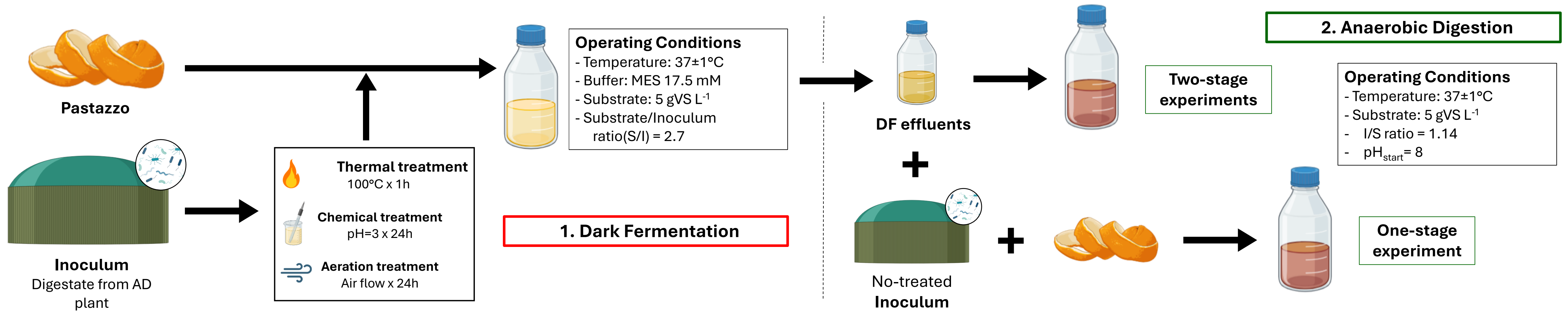
Pastazzo is characterized by high organic content, however, the rapid acidification due to the production of large quantities of VFAs, and the presence of D-limonene can inhibit the activity of methanogenic bacteria. A physical separation of the hydrolysis and acidogenesis phase from the methanogenesis phase could help to overcome these issues, increasing the CH₄ production performance and at the same time allowing simultaneous production of bioH₂ and bioCH₄.

This work proposes the energetic valorisation of orange processing waste "pastazzo" through the development of a two-stage anaerobic process, for simultaneous production of bio-H₂, and bio-CH₄, by optimising energy conversion efficiency and the synergy of the integrated process.

Research activities were conducted to evaluate a pre-treatment of the inoculum for the first stage of the process, Dark Fermentation (DF). The aim was selecting performant microbial consortium enriched in hydrogen producing microorganisms. Three different pretreatments: thermal, chemical and aeration, were tested and compared.

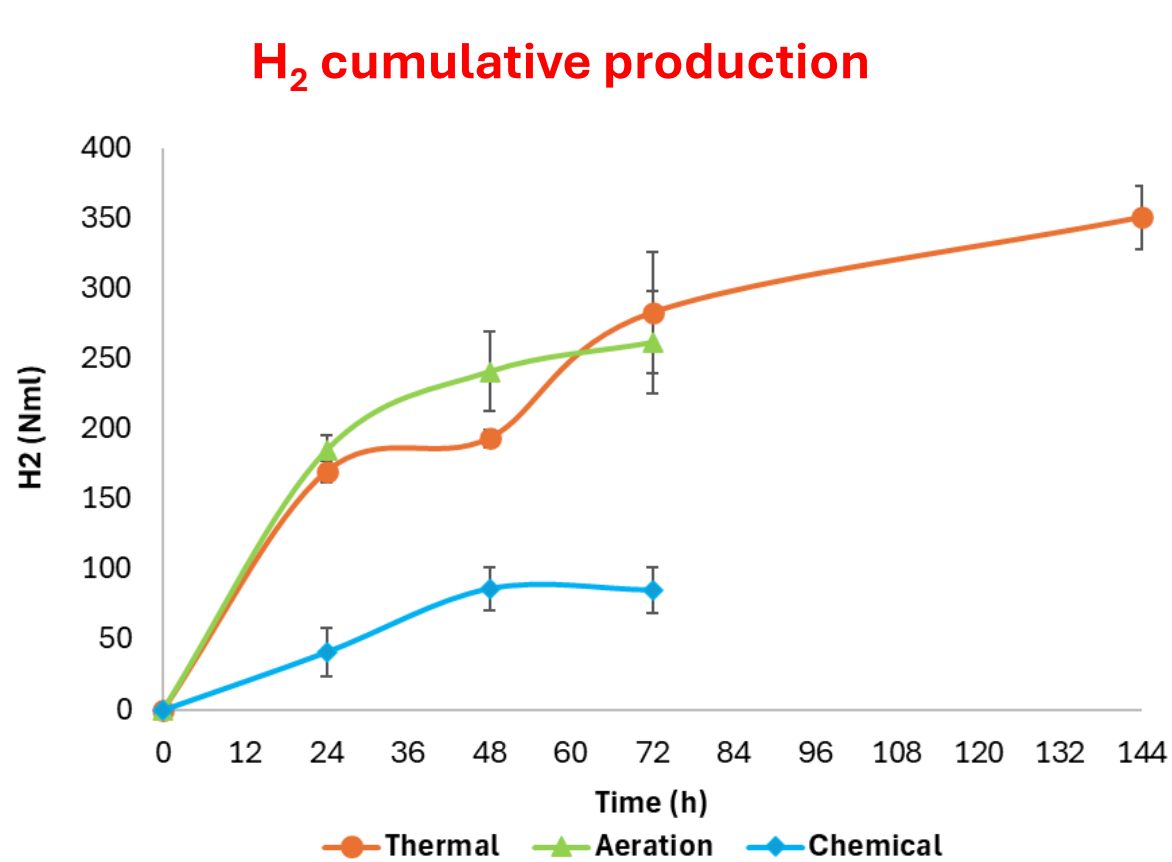
MATERIALS AND METHODS

Two-stage experiments for the bio-H₂ production (DF process) followed by an AD process for the bio-CH₄ production were performed in batch configuration in triplicate. The one-stage AD experiments were also performed in triplicate.



RISULTATI

1. Dark Fermentation - H₂ production

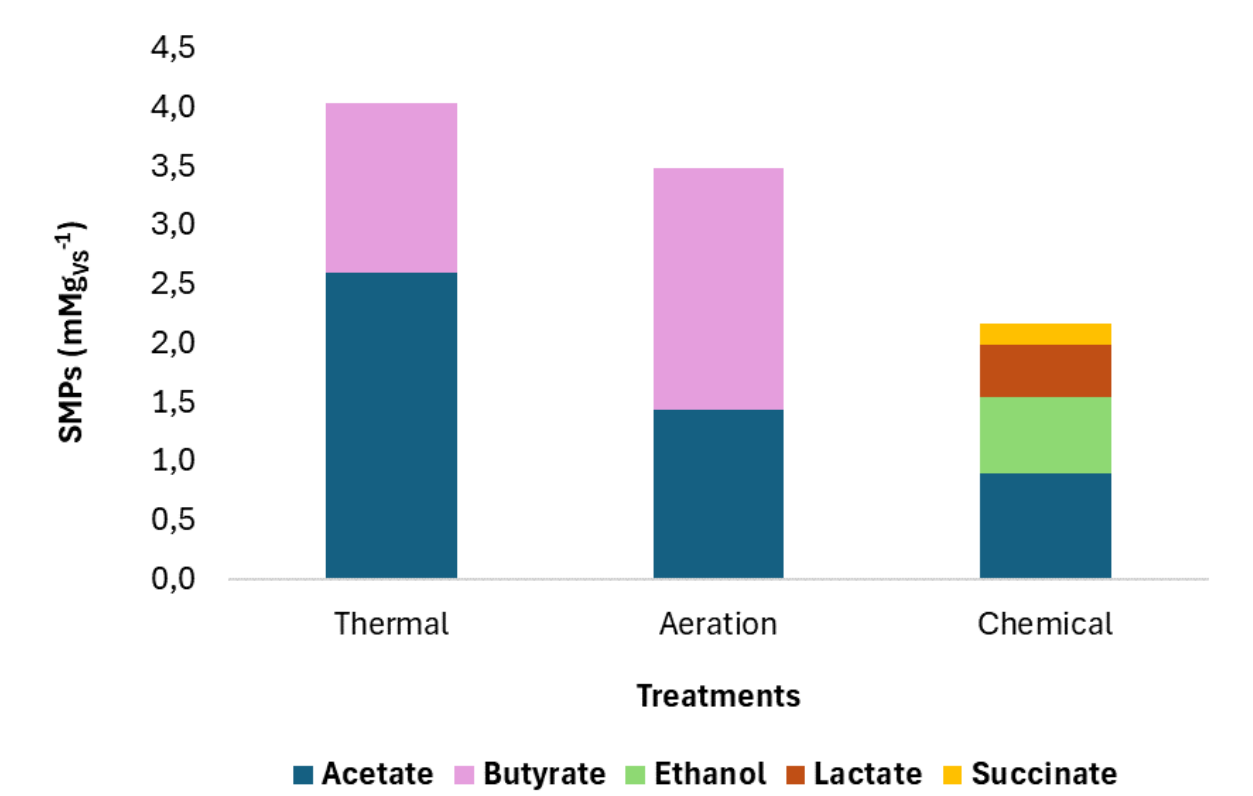


H₂ performances and production kinetics

Inoculum Treatments	Modified Gompertz Parameters				Experimental data		
	H ₂ (Nml)	r (Nml h ⁻¹)	λ (h)	R ²	H ₂ yield (Nml gVS ⁻¹)	H ₂ max (%)	pH end
Thermal	178.8 ± 11.6 176.9 ± 38.4	9.6 ± 1.7 4.9 ± 2.6	0.7 ± 0.5 50.9 ± 2.3	1.00 ± 0.00	186.7 ± 7.8	52.1 ± 0.3	4.1 ± 0.1
Aeration	259.7 ± 36.8	8.3 ± 0.6	0.0 ± 0.0	0.99 ± 0.01	145.6 ± 20.1	42.5 ± 3.5	4.4 ± 0.1
Chemical	86.4 ± 16.0	8.6 ± 1.3	18.9 ± 2.9	1.00 ± 0.00	46.6 ± 10.8	24.4 ± 2.4	3.9 ± 0.0

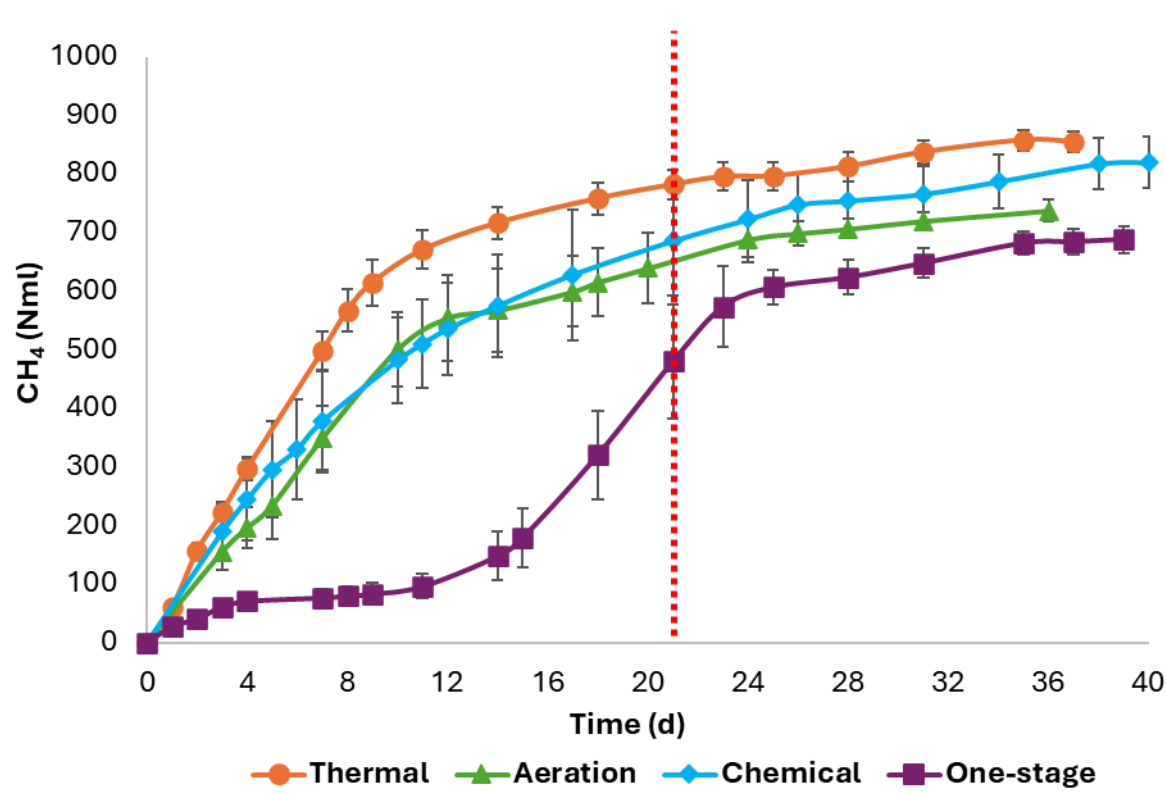
* ° First and second H₂ production steps of Thermal condition (diauxic behavior)

DF pathways - Soluble Metabolic Products (SMPs - end)



2. Anaerobic Digestion - CH₄ production

CH₄ cumulative production



CH₄ performances and production kinetics

Two-stage (DF Effluents)	Modified Gompertz Parameters				Experimental data		
	CH ₄ (Nml)	r (Nml d ⁻¹)	λ (d)	R ²	CH ₄ yield (Nml gVS ⁻¹)	CH ₄ max (%)	SMPs end (mM)
Thermal	811.1 ± 21.2	74.8 ± 6.1	0.1 ± 0.1	1.00 ± 0.00	476.3 ± 9.6	74.2 ± 1.5	0
Aeration	709.2 ± 0.6	47.6 ± 9.3	0.0 ± 0.0	1.00 ± 0.00	409.8 ± 9.9	74.4 ± 1.4	0
Chemical	784.9 ± 33.9	50.2 ± 12.6	0.0 ± 0.0	0.99 ± 0.00	455.4 ± 24.3	71.6 ± 0.4	0
One-stage	720.6 ± 26.2	43.0 ± 1.8	9.8 ± 1.9	0.99 ± 0.00	382.4 ± 12.8	64.0 ± 1.8	2.1 ± 0.7 (Propionate)

Energy recovery (MJ Kg Pastazzo) at day 21 of AD

	DF Treatment	H ₂ (MJ Kg ⁻¹)	CH ₄ (MJ Kg ⁻¹)	Total energy (MJ Kg ⁻¹)
Two-stage	Thermal	0.28 ± 0.01	2.01 ± 0.06	2.29 ± 0.07
	Aeration	0.22 ± 0.03	1.64 ± 0.15	1.86 ± 0.18
	Chemical	0.07 ± 0.01	1.76 ± 0.24	1.84 ± 0.26
One-stage	-	-	1.23 ± 0.25	1.23 ± 0.25

CONCLUSION

CH₄ production was higher in the two-stages process, whatever the inoculum treatment. However, the thermal was the most effective treatment for both DF stage and full two-stage process. This agree with the highest energy recovery of 2.29 ± 0.07 MJ Kg⁻¹ of pastazzo calculated at the day 21 of the two-stage process which was 23% and 24% and 86% higher than the other treatments and the one-stage process, respectively.