ANAEROBIC DIGESTION OF OME IN AN ABR AND BIOMETHANE PRODUCTION BY VSA ON NATURAL ZEOLITES FROM TUFFS

Valerio Paolini[1], Francesco Petracchini[1],
Ettore Guerriero[1], Ilaria Bientinesi[2],

[1] CNR - Institute of Atmospheric Pollution Research, Via Salaria Km 29,300 Monterotondo (RM);
[2] AZZERO CO2 srl, via Genova 23, Roma (RM).

OLIVE MILL EFFLUENTS

Olive mill effluents (OME) management: to exploit its energy and nutrients potential.

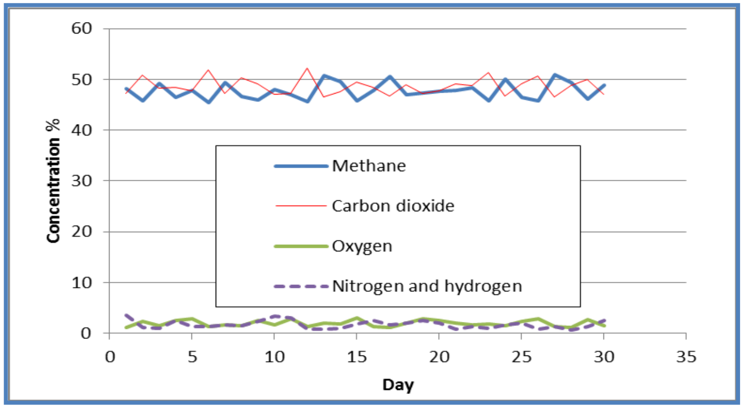
- **Spreading** (olive mill wastewaters) → growndwater/soil contamination (phenolic substances, nitrates); N_2O, NH_3 and odorous emissions; no energy recovery.
- **Combustion** (olive mill solid wastes) → air pollution, wet olive pomaces from «two phases olive mills»; difficult nutrients recovery.

Anaerobic digestion allows both energy and nutrients recovery, but is hampered by lipides (foams), low C/N ratio, phenolic substances. Possible approaches:

- Oxidative pretreatments
- Physical removal of phenolic substances
- Specific inocula
- Codigestion
- A more efficient digester?

ANAEROBIC BAFFLED REACTOR

- 5 digestion tanks
- Total volume 1 m^3
- Feed composition: olive cake (50%) and bovine manure (50%).
- Feed rate: 0.35 m^3 per week
- Mesophilic conditions (30 °C)
- Biogas production: 75 L h^{-1}



Biogas composition		
	Average	min and max
Methane	47.7 %	45.3 - 51.5 %
Carbon dioxide	48.6 %	46.7 - 53.2 %
Oxygen	2.0 %	1.2 - 3.1 %
Other (N_2, H_2 etc)	1.7 %	0.9 - 3.5 %

CNR - Institute of Atmospheric Pollution Research
Valerio Paolini
v.paolini@iia.cnr.it
www.iia.cnr.it
www.biogame.it

BIOGAS UPGRADING TO BIOMETHANE

The high stability of the ABR biogas stream allowed us to evaluate a new approach to biogas upgrading: a vacuum swing adsorption on natural zeolites.

Tuffs:

- building materials, available in large amounts
- composed of natural zeolites (Chabazite, Phillipsite, Clinoptilolite)
- commonly used in ion exchange, slow release of water
- possible uses in AD: nitrogen removal, digestate treatments
- selective CO_2 and H_2S adsorption (Paolini et al., 22th EU BC&E Proceedings, 2014)

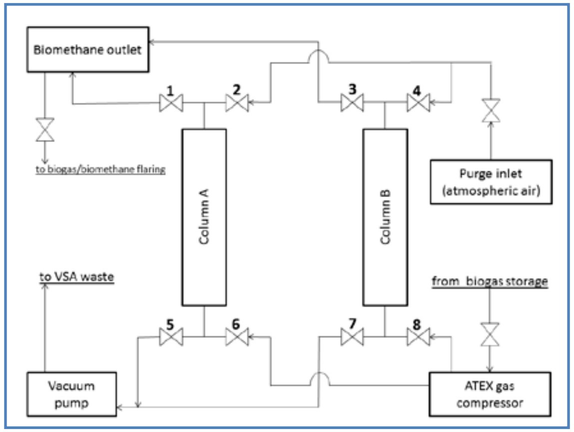
VSA ON NATURAL ZEOLITES

Vacuum swing adsorption

- Advantages: efficiency, biomethane purity, total costs and scalability
- Commonly used adsorbents: synthetic zeolites and activated carbon
- Alternative natural adsorbents (lower costs)

VSA prototype:

- 2 PE columns 6 cm x 1 m length
- 7 Kg natural zeolites TGVT (chabasite 65 ± 5 %)
- Feed: 2 L min^{-1} biogas ($1.00 \cdot 10^5$ Pa) for 6 minutes
- Biogas was dehydrated and desulfurized
- Desulfurization with iron oxide pellets (95 - 140 to 4 - 8 ppm)
- Regeneration: 5 min, $3.00 \cdot 10^4$ Pa, 4 L min^{-1} (atmospheric air)
- Monitoring period : 3 months
- Compliance with 94/9/CE directive



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Valerio Paolini
v.paolini@iia.cnr.it
www.iia.cnr.it
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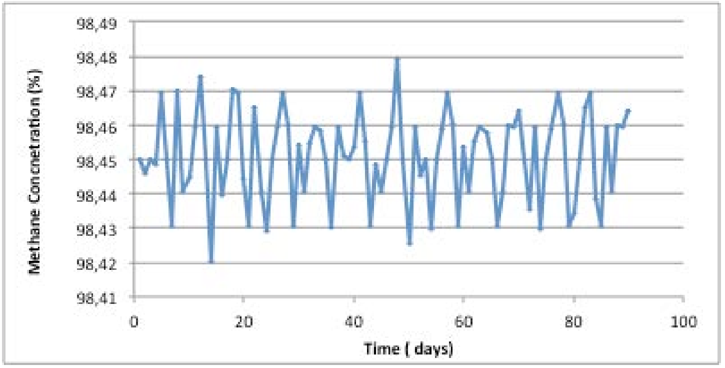
BIOMETHANE PRODUCTION

Biomethane production: 0.85 - 1.1 L min^{-1}
Methane losses < 5%

	Average	Min and max
Methane	98.4 %	95.4% - 99.2 %
Carbon dioxide	0.06 %	<0.1 - 0.3 %
Oxygen	0.5 %	0.2 - 1.5 %
Other (N_2, H_2 etc)	0.9 %	0.5 - 2.8 %

- Methane purity >95%: compliance with national standards?
- Carbon dioxide <0.3% (removal efficiency > 99%)
- High O_2 concentration due to biogas composition and atmospheric air recirculation



Biomethane temporal stability (R^2 = 0.0003 and RSD = 0.013% for CH_4 concentration during 3 months), due to biogas feed stability and to dehydration/desulfurization

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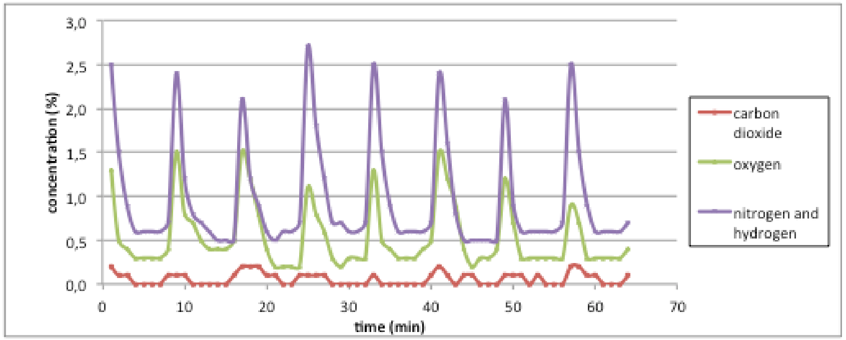
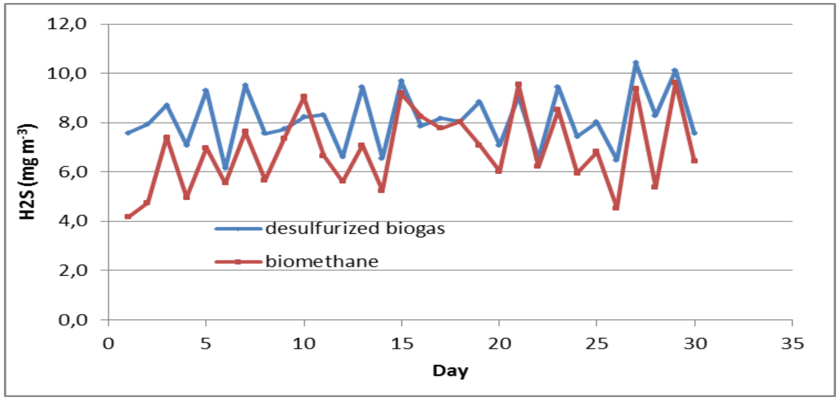
COMPLIANCE WITH NATIONAL STANDARDS?

Country	Required composition	Reference
Austria	CO_2 < 2.0%; O_2 < 0.5% (Upper Wobbe index 13.3 - 15.7 kWh m^{-3})	Directives OVGW G31 (2001) and G33 (2006)
France	CO_2 < 2%; O_2 < 0.01% (Higher Wobbe index: 48.24 - 56,52 MJ/Nm^3 for H gas, 42.48 - 46.8 MJ/Nm^3 for L gas)	Decree no. 555 of June 15th 2004; AFG specifications B562-1 (2010) and B562-2 (2011)
Germany	CO_2 < 6%; O_2 < 3% (Wobbe index 10.5 - 13.0 kWh m^{-3} for L gas, 12.8 - 15.7 kWh m^{-3} for H gas)	Standards DVGW G260 (2008) and G262 (2004)
Italy	CO_2 < 3%; O_2 < 0.6% (Wobbe index 47.31 - 52.33 MJ m^{-3})	Standard UNI/TR 11537
Netherlands	CO_2 < 2.5%; O_2 < 0.5% (Wobbe index 49.9 - 55.7 MJ Nm^{-3})	Decree no. WJZ/13196684
Sweden	CH_4 > 97.0%; O_2 < 1% (Lower Wobbe index 12.2 - 13.1 kWh m^{-3})	Standard SS 155438
Switzerland	CH_4 > 96.0%; CO_2 < 6%; O_2 < 0.5% (Wobbe indexes not specified)	Directive SVGW G13
United Kingdom	O_2 < 0.2 % (Wobbe index: 51.41 - 47.20 MJ m^{-3})	GSMR 1996
California	CO_2 < 3%; O_2 < 0.2% (Upper Wobbe index 47.6 - 51.6 MJ Nm^{-3})	(Danish Technological Institute Report on Biogas and bio-syngas upgrading, 2012)
Michigan	CH_4 > 93.5%; CO_2 < 2%; O_2 < 3% (Wobbe indexes not specified)	(Danish Technological Institute Report on Biogas and bio-syngas upgrading, 2012)

FURTHER CONSIDERATIONS



- Column switching: atmospheric air contamination confirmed, while CO_2 remains below 0.3%
- An improvement is expected from biomethane recirculation
- Light desulfurization effect (4-8 to 2-7 ppm)
- VSA waste : low CH_4 (and significant CO_2)



VSA waste composition	
Flow rate	34.5 - 36.0 L min^{-1}
Methane	< 0.1 %
Carbon dioxide	1.5 - 3.0 %
Hydrogen sulfide	< 2 mg m^{-3}
Oxygen	19.5 - 20.5 %
Nitrogen	75.5 - 77.5 %

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CONCLUSIONS AND REMARKS

- The feasibility of biomethane from OME was demonstrated
- A valuable biofuel was prouced using two wastes (OME and tuff)

- Using an ABR resulted in a very stable biogas stream
- Natural zeolites compatibility with real biogas conditions: small temporal variations
- Natural zeolites CO_2 selectivity: high purity biomethane

- Oxygen contamination can be a key point in VSA
- An improvement is expected with biomethane recirculation
- Compliance with national standards needs to be defined

- Biogas desulfurization/dehydration on natural zeolites is also possible
- VSA can be scaled to the suitable size, depending on the application

CNR - Institute of Atmospheric Pollution Research
Valerio Paolini
v.paolini@iia.cnr.it

Thank you for your attention

www.biogame.it

www.iia.cnr.it
www.azzeroco2.it

v.paolini@iia.cnr.it