

# Biogas upgrading by wood combustion ash accelerated carbonation

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# **Outline**



- Introduction
- Previous experiences
- Materials and experimental facility
- **Results of experimental tests**
- Conclusions



# Introduction



Composition		UNITS	RANGE
Main components	CH4	[% v/v]	40-75
	CO2	[% v/v]	15-60
	H2O	[% v/v]	5-10
Trace components	H2S	[% v/v]	0.05-2
	NH3	[% v/v]	<1
	VOC	[% v/v]	< 0.6
	СО	[% v/v]	0.6
	O2	[% v/v]	< 1
	N2	[% v/v]	< 2

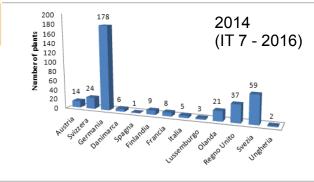
#### Anaerobic biological degradation of biodegradable substrates

- $\rightarrow$  landfill
- → Industrial anaerobic digesters (wastewater sludge, energy crop, livestock residues)

LHV ~ 18-24 MJ/Nm3 (CH4 content)

#### Biogas use:

- Thermal energy production
- Cogeneration with ICE
- Biomethane





### Introduction



- Conventional processes for CO₂ removal → size/economy
- (HPWS, Chemical/amine absorption, PSA, membranes)
- Accelerated carbonation:

$$Ca(OH)_2(s) + CO_2(g) --> CaCO_3(s) + H_2O$$

- Innovative process to capture and <u>store</u> CO<sub>2</sub>
- Natural rocks / industrial alkaline residues
- Bottom Ash (BA) from waste incineration
- Wood ash (WA) from wood combustion (large availability in alpine regions)





#### UPGAS-LOWCO2 Project (LIFE08/ENV/IT/000429) www.upgas.eu (Gen2010-Giu2012)

Programma Life Environment

Dipartimento di Energetica "Sergio Stecco" – Università degli Studi di Firenze – Italy (coordinatore)

Dipartimento di Ingegneria Civile - Università di Roma "Tor Vergata" – Italy (partner)

Centro Servizi Ambiente Impianti S.p.A. – Italy (partner)

Chemical Engineering Department – Universitat Autonoma de Barcelona – Spain (partner)

Institute of Waste Management – Department of Water, Atmosphere and Environment – University of Natural Resources and Applied Life Sciences, Vienna – Austria (partner)

#### TECGAS - TEChologie innovative per l'up-grading del bioGAS (Lug2011-Lug2013)

MATTM - Finanziamento di progetti di ricerca finalizzati ad interventi di efficienza energetica e all'utilizzo delle fonti di energia rinnovabile in aree urbane

Centro Servizi Ambiente Impianti S.p.A. – Italy (coordinatore)

ICAD (International Consortium for Advanced Design) - Università degli Studi di Firenze (partner) Scarlino Energia S.r.l. (partner)

#### BI.R (Biogas Repowering) (Ago2013 – Ago2015)

Bando Regione Toscana POR CReO 2007-2013 – Bando Unico R&S anno 2012.

Cavalzani Inox s.r.l. (coordinatore)

PIN s.c.r.l.. (partner)



## **Materials**



#### Wood ash from the combustion of wood chips

#### Inert:

0.20 % FIR (abete/conifere)

0.65 % BEECH (faggio)

1.43 % POPLAR (pioppo)

Non-hazardous industrial waste CER 10.01.01

- brick production
- road construction / environmental restoring
- composting
- fertilizer production

Landfill

Central heating boiler	
Temperature out [°C]	85
Temperature in [°C]	68
Thermal power [kW]	3.300
Exhaust temperature [°C]	176
Water mass flow rate [kg/h]	166.653

Fondazione Edmund Mach

Trento (IT)

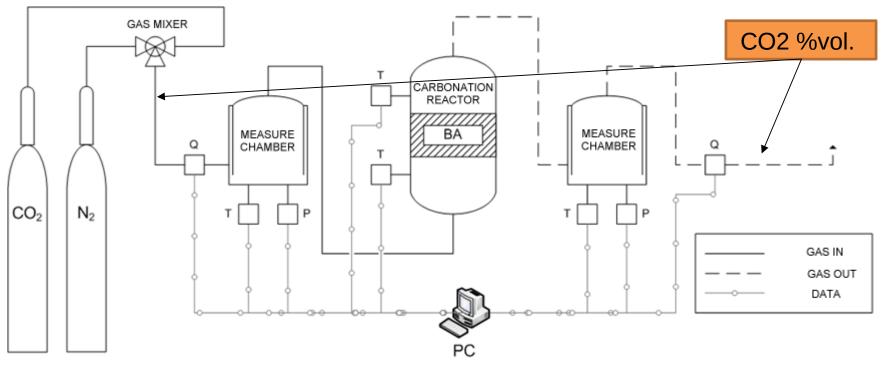
Pilot plant

PARAMETER	METHOD	Unit.	Result
Colore	IS 08.03/062 rev 0 2011		grigio
Odore	IS 08.03/062 rev 0 2011	-	assente
Stato fisico	IS 08.03/062 rev 0 2011		Solido polverulento
Solidi totali (residuo secco a 105°C)	CNR IRSA 2 Q 64 Vol 2 1984	%	99
Solidi totali fissi (residuo a 550°C)	CNR IRSA 2 Q 64 Vol 2 1984	% s.s.	98
ph	CNR IRSA 1 Q 64 Vol 3 1985	U.pH	13.2
Antimonio	EPA 6010C 2007 + UNI EN 13567:2004	mg/kg	1
Arsenico	EPA 6010C 2007 + UNI EN 13567:2004	mg/kg	2
Cadmio	EPA 6010C 2007 + UNI EN 13567:2004	mg/kg	2.4
Cromo totale	EPA 6010C 2007 + UNI EN 13567:2004	mg/kg	41.2
Cromo esavalente	CNR IRSA 16 Q 64 Vol 3 1985	mg/kg	<5
Rame	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	136
Piombo	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	5.1
Mercurio	UNI EN 1483:2008 + UNI EN 13657:2004	mg/kg	<0.2
Nichel	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	17.1
Selenio	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	<1
Stagno	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	<5
Tellurio	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	<1
Tallio	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	<10
Zinco	EPA 6010C 2007 + UNI EN 13657:2004	mg/kg	130
Carbonio organico totale (TOC)	UNI EN 13137:2002	mg/kg	14000



### **Experimental facility - lab**





- → CO2/N2 cylinders/ gas mixer
- → Measurement chambers
- → Acquisition system
  - $\rightarrow$  PC
  - $\rightarrow$  Volumetric flow rate (Q)
  - $\rightarrow$  Temperature (T)
  - $\rightarrow$  Pressure (P)

N2 was used as substitute of CH4 in the laboratory tests for safety reasons.



### **Experimental facility - lab**

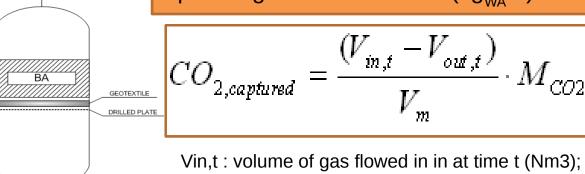
INLET GAS





Test	Gas composition	Gas composition	WA	Moisture	Gas flow rate
	CO <sub>2</sub> [% v/v]	N <sub>2</sub> [% v/v]	[kg]	[%]	[NI/h]
WA_m20_i WA_m20_ii	40	60	6	20	24
WA_30_i WA_30_ii	40	60	6	30	24

### Specific gas flow rate: 4 NI/(kg<sub>wa</sub>·h)



Vin,t: volume of gas flowed in in at time t (Nm3); Vout,t: volume of gas flowed out at time t (Nm3);

Vm : 22,414 (Nm3/kmol), molar volume at normal

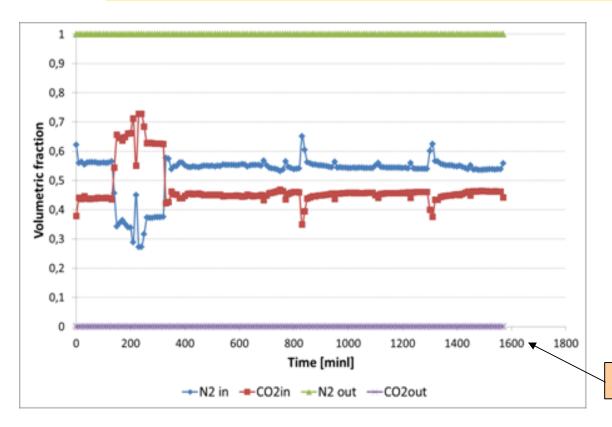
conditions;

MCO2: 44 kg/kmol, CO2 molar weight



### **Results - lab**





#### Preliminary test

When the test was stopped, the volumetric concentration of CO<sub>2</sub> in the exiting stream was still below 0.5% in vol.

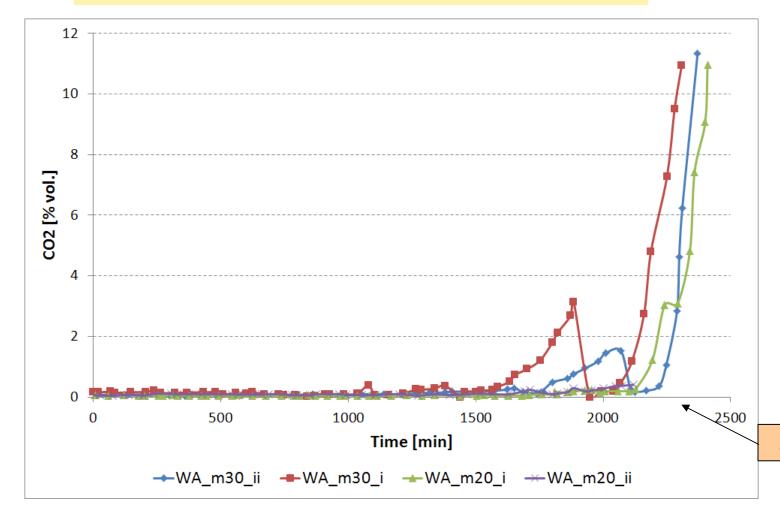
26-27 hours

Volumetric fraction of CO<sub>2</sub> and N<sub>2</sub> in the entering and exiting gas flow, registered during the first 26 hours of the second laboratory test.



### **Results - lab**



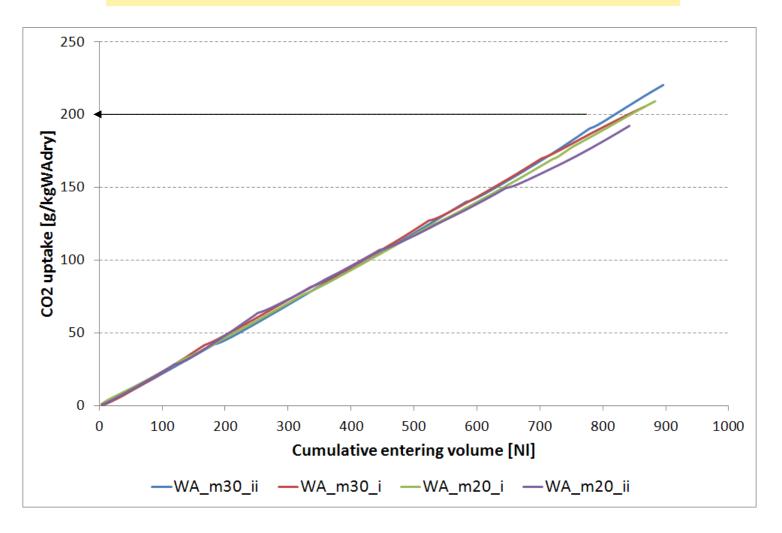


37-38 hours



### **Results - lab**





BA case:

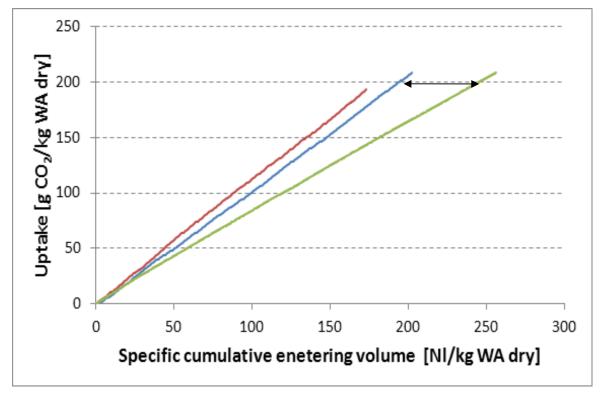
pilot reactor fed with real landfill gas

 $CO_2$  specific uptake = 10– 22 g  $CO_2/kg_{BA}$ 



### **Results - comparison**





27 I vs. 700 I

Lab – 30% moisture

Lab – 20% moisture

pilot



### **Conclusions**



- Simple process of direct contact in a fixed bed reactor between wood ash and biogas
- Capture the CO, to produce biomethane
- The process is able to completely capture the CO<sub>2</sub>, in its starting phase. After about 30 hours the CO<sub>2</sub> starts to appear again in the exiting stream and rapidly increases.
- Specific uptake was about 200 g/kg of dry WA (much higher than bottom ash, specific CO<sub>2</sub> uptake was in the range of 10-20 g/kg).
- Results were confirmed by pilot tests (real biogas).

Presently additional laboratory tests are ongoing. Detailed analysis of the leaching behaviour of A before and after the carbonation are ongoing. At the same time a preliminary sizing for a hypothetical industrial plant is under development, with the aim of performing an economic analysis of the treatment cost, in order to compare with conventional upgrading technologies. Life cycle assessment of the process and its comparison with conventional processes is under development as well.









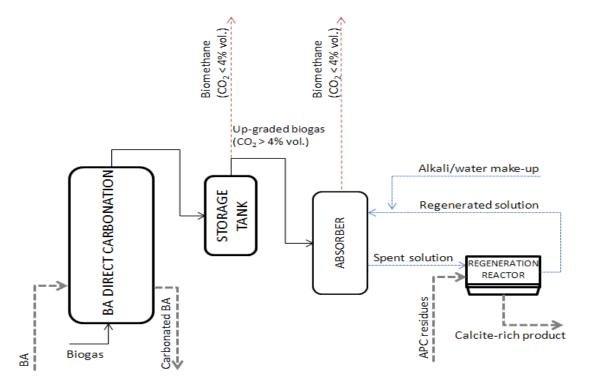




UPGAS-LOWCO2 Project (LIFE08/ENV/IT/000429)









TECGAS - TECnologie innovative per l'up-grading del bioGAS





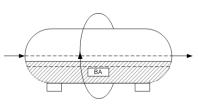
#### **BI.R** (Biogas Repowering)

















# **Project on-going**



Up-Ash (Dec2015 – Aug2017)

Co-funded by Servizio Sviluppo Sostenibile e Aree Protette della Provincia Autonoma di Trento

Fondazione Edmund Mach (coordinator)

In collaboration with:

Università degli Studi Niccolò Cusano

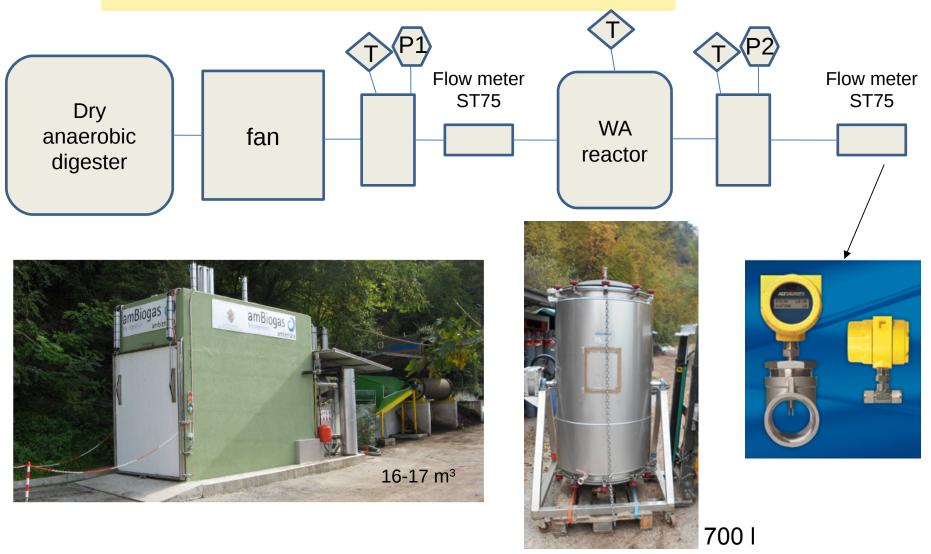
Università degli Studi di Firenze – Dipartimento di Ingegneria Industriale

- → Experimental tests on pilot plant of a biogas upgrading process by accelerated carbonation of wood ash
- → laboratory tests (unifi/unicusano)
- → pilot tests (at Fondazione Mach)



## **Experimental facility - pilot**







## **Results - pilot**



CH₄	59-61	[%]
CO <sub>2</sub>	39-41	[%]
WA	137	[kg]
Average biogas flow rate	0.3	[m³/h]
Time	4740	[min]
Final uptake CO <sub>2</sub>	181.13	[g/kgW <sub>Adrytte</sub> ]
Starting moisture of WA	34.09	[%]
Final moisture of WA	32.83	[%]
pH before	12.38	-
pH after	11.08	-
110		

