



Accordo di Programma MSE-ENEA

  
MINISTERO DELLO SVILUPPO ECONOMICO

**RICERCA DI SISTEMA ELETTRICO**



**Area: Produzione di energia elettrica e protezione dell'ambiente**

**Progetto B.1.1 - Sviluppo di sistemi per la produzione di energia elettrica da biomasse e l'upgrading dei biocombustibili**

# Upgrading del syngas a bio-SNG

Donatella Barisano

ENEA, Unità Tecnica Tecnologie Trisaia

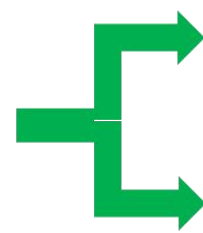
**LE BIOENERGIE E  
LA RICERCA DI SISTEMA ELETTRICO**

**Roma, 25 giugno 2015 - ENEA Sede Legale - Via Giulio Romano, 41**



# Produzione di metano da biomasse

**Biomassa  
Umide**



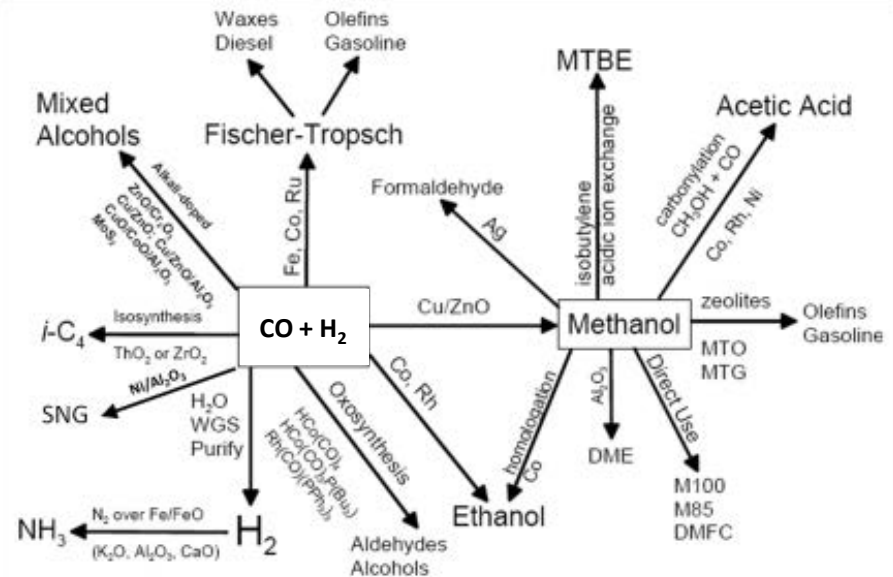
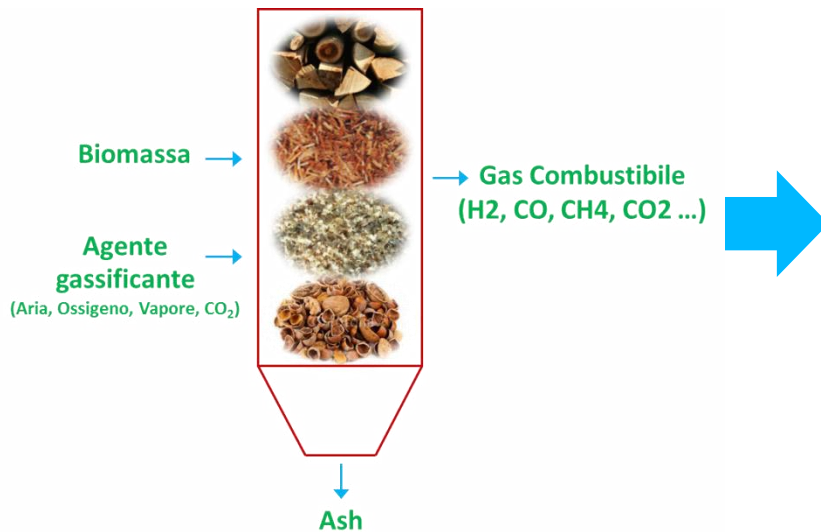
**Digestione  
anaerobica**

**Gassificazione in  
acqua supercritica**

**Biomassa  
Secche**



**Gassificazione  
a «Secco»**



# Sintesi di biocombustibili liquidi e gassosi

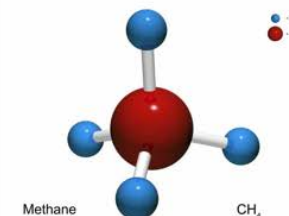
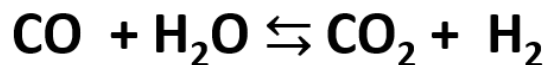
BioFuels	H <sub>2</sub> /CO	Calizzatore	P (atm)	T (°C)	η <sub>en</sub> (LHV-Biom)
Metanolo	2:1	Zn/Cr, Cu/Zn	50-300	300-450	40-50
Fischer-Tropsch	2:1	Fe, Co	20-30	250-300	40-50
Metano	3:1	Ni	5-30	300-450	65-70



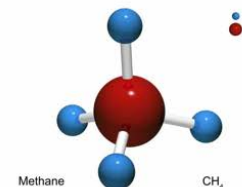
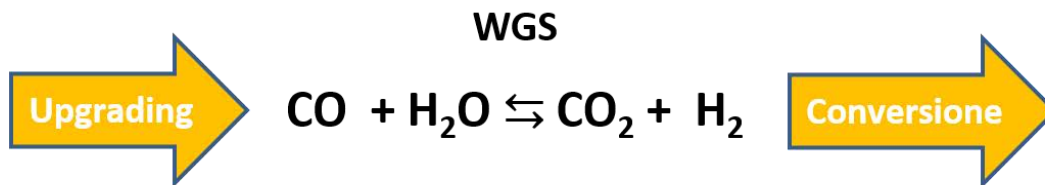
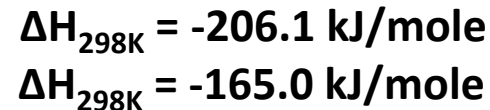
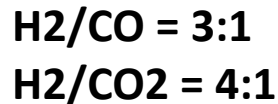
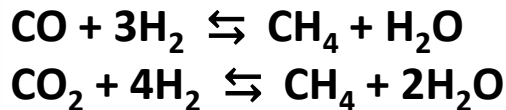
Gassificante Agente	Composizione Gas Secco (% v)						PCI (MJ/Nm <sup>3</sup> )	H <sub>2</sub> /CO
	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>		
Aria	9-10	12-15	14-17	2-4	56-59	< 1	3.8-4.6	0.70
Ossigeno	30-34	30-37	25-29	4-6	2-5	< 1	9-10	0.96
Vapore	32-41	24-26	20-22	10-12	2-5	2-3	12-13	1.46
Vapore/O <sub>2</sub>	30-33	28-32	22-27	9-11	2-5	1-2	11-12	1.10



WGS



# Necessità di aggiustare la composizione del gas: H<sub>2</sub>/CO



- 1- stechiometria ⇒ massimizzare la conversione del gas in CH<sub>4</sub>
- 2- evitare la disattivazione del catalizzatore per formazione di depositi di carbonio  
 $2\text{CO} = \text{C} + \text{CO}_2$

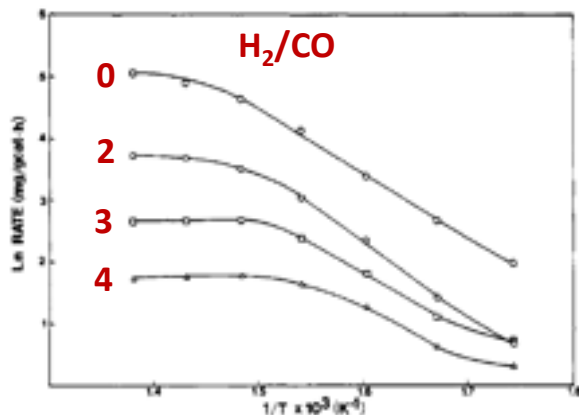


Figure 5. Arrhenius plot of carbon accumulation on 14% Ni/Al<sub>2</sub>O<sub>3</sub> at T = 573–723 K, P<sub>CO</sub> of 9.0 kPa, and various H<sub>2</sub>/CO ratios: ○, H<sub>2</sub>/CO = 0; ◐, H<sub>2</sub>/CO = 2; ◑, H<sub>2</sub>/CO = 3; △, H<sub>2</sub>/CO = 4.

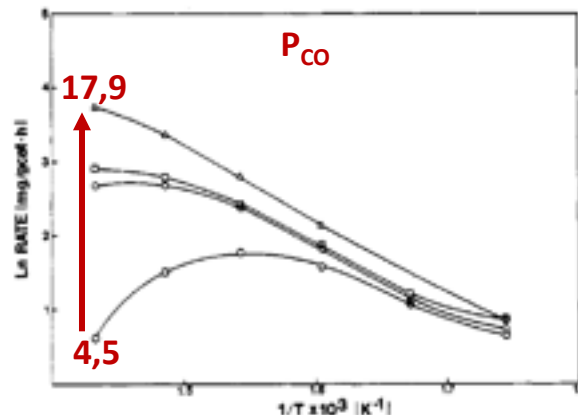


Figure 6. Arrhenius plot of carbon accumulation during methanation at a H<sub>2</sub>/CO ratio = 3, P<sub>CO</sub> = 4.5–17.9 kPa, T = 573–698 K: ○, P<sub>CO</sub> = 4.5 kPa; ◐, P<sub>CO</sub> = 9.0 kPa; ◑, P<sub>CO</sub> = 13.4 kPa; △, P<sub>CO</sub> = 17.9 kPa.

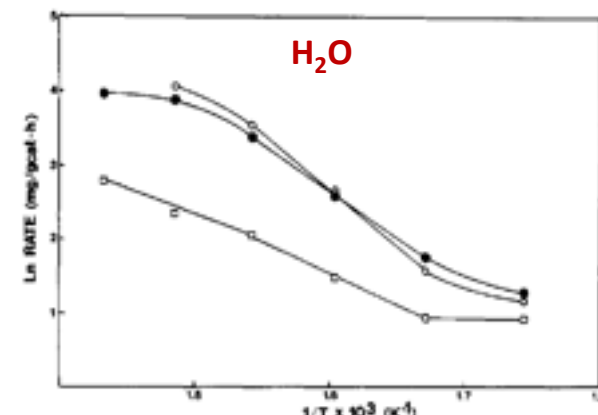


Figure 7. Arrhenius plot of carbon accumulation during methanation with P<sub>CO</sub> = 13.4 kPa, H<sub>2</sub>/CO = 2 with and without 2.7 kPa of H<sub>2</sub>O added to the feed stream: ○, before, and ●, after addition of water; ◑, in the presence of water.

# Accordo di Programma MSE-ENEA sulla Ricerca di Sistema Elettrico



Progetto B.1.1 “ Sviluppo di sistemi per la produzione di energia elettrica da biomasse e l’upgrading dei biocombustibili

“b.3 Ottimizzazione del processo di produzione di biometano a partire da syngas sull’impianto pilota di metanazione BIOSNG”



Agenzia nazionale per le nuove tecnologie, l’energia e lo sviluppo economico sostenibile

- ***Arricchimento di syngas nel contenuto di  $H_2$  attraverso l’impiego di sorbenti SEWGS per la cattura di  $CO_2$  (Sorbenti Mg/Al, Ca/Al e Mg/Ca/Al)***
- ***Sviluppo e caratterizzazione di catalizzatore di metanazione Ni/Mg/Al***



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# SEWGS: la reazione di WGS assistita da sorbenti per la CO<sub>2</sub>



Biomassa



Gassificazione

Purificazione gas  
e reforming

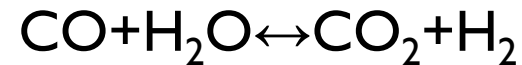
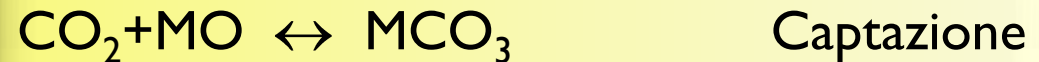
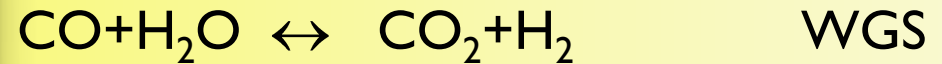
Water Gas Shift  
HT

Water Gas Shift  
LT

Rimozione CO<sub>2</sub>

Metanazione

Rimozione CO<sub>2</sub>



Gas → WGS + captazione → H<sub>2</sub>, H<sub>2</sub>O, ...

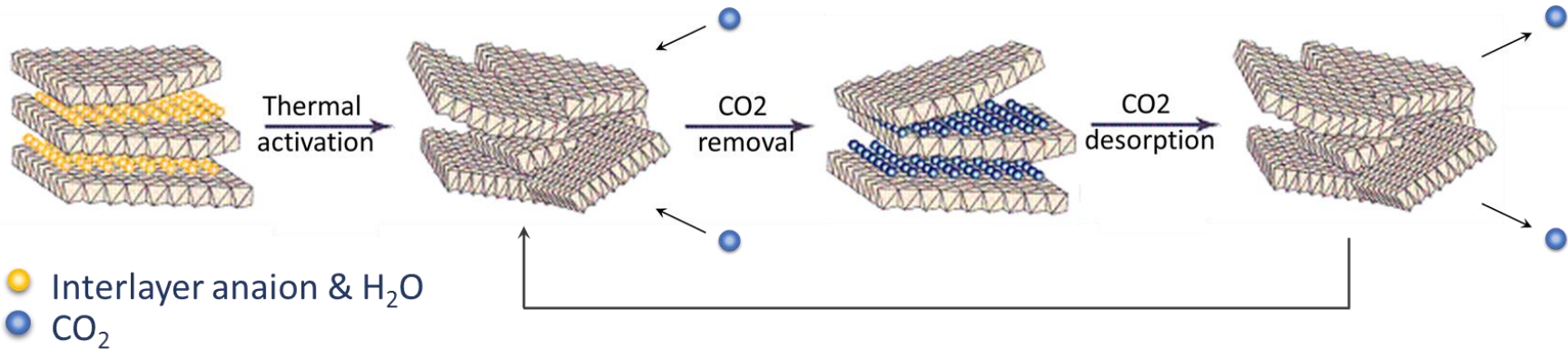
Steam + CO<sub>2</sub> ← rigenerazione ← Steam

✓ **Intensificazione di processo**

(riduzione costi di investimento, prestazioni di processo)



# Sorbenti per la rimozione di CO2

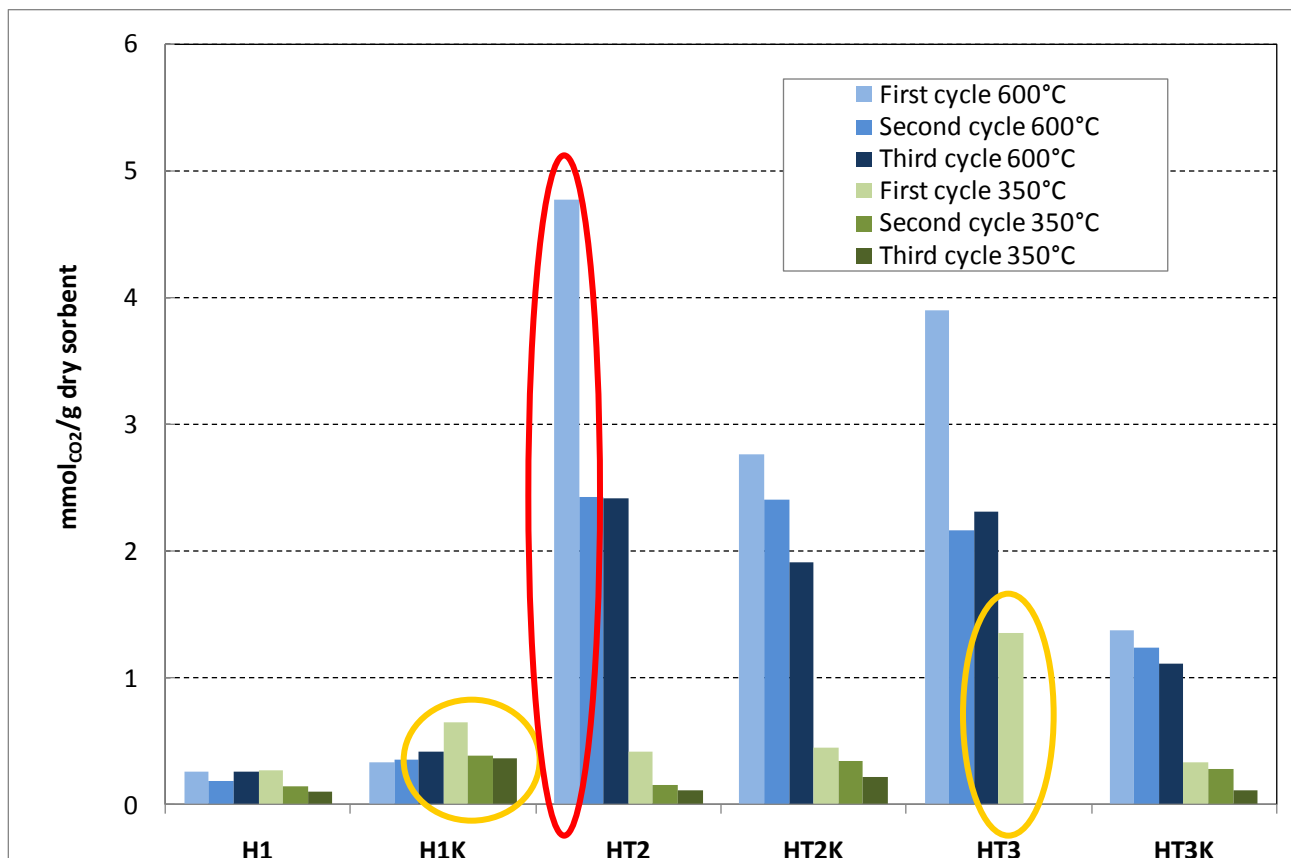


Acronimo	Sorbente	M <sup>++</sup> /M <sup>+++</sup>
HT1	Mg/Al Idrotalcite	Mg/Al=2/1
HT1K	Mg/Al Idrotalcite + 20%p K <sub>2</sub> CO <sub>3</sub>	Mg/Al=2/1
HT2	Ca/Al Idrocalumite	Ca/Al=2/1
HT2K	Ca/Al Idrocalumite + 20%p K <sub>2</sub> CO <sub>3</sub>	Ca/Al=2/1
HT3	Mg/Ca/Al Idrotalcite	Mg/Ca/Al=1/1/1
HT3K	Mg/Ca/Al Idrotalcite + 20%p K <sub>2</sub> CO <sub>3</sub>	Mg/Ca/Al=1/1/1
PMG70/K	Mg/Al Idrotalcite com. + 20%p K <sub>2</sub> CO <sub>3</sub>	Mg/Al=3/1





Test in TGA:  $P_{CO_2}=1$  bar;  $T_{ads\ Low}=350^\circ C$ ;  $T_{ads\ High}=600^\circ C$

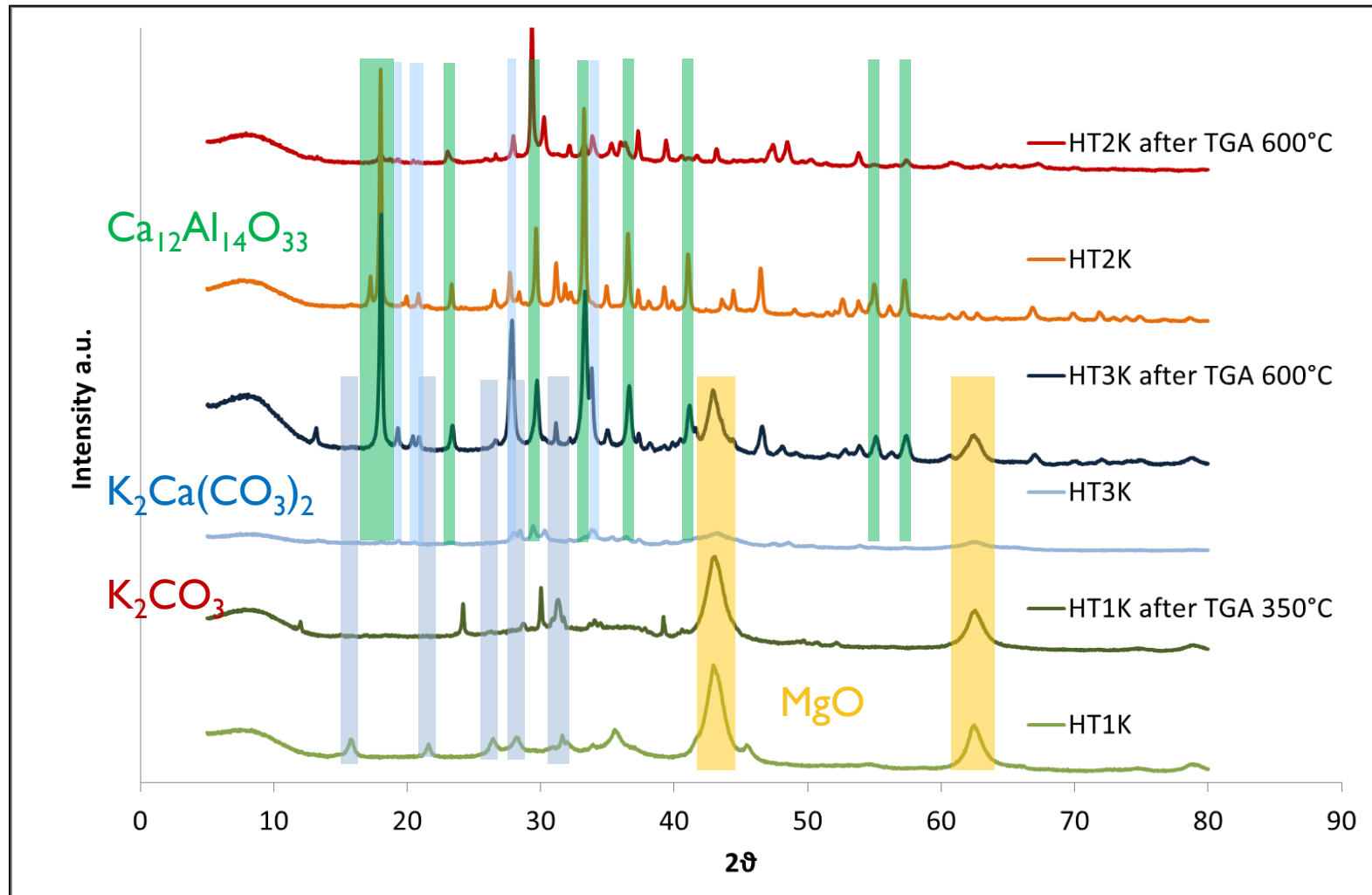


<b>Test a bassa T</b>	<b>HT3</b> migliore performance (1.36 mmolCO <sub>2</sub> /g <sub>sorbente</sub> )	<b>HT1K</b> migliore performance tra i sorbenti impregnati con K (0.66 mmolCO <sub>2</sub> /g <sub>sorbente</sub> )
<b>Test a alta T</b>	<b>HT2</b> migliore performance (4.78 mmolCO <sub>2</sub> /g <sub>sorbente</sub> )	<b>Campioni impregnati con K</b> Effetto non rilevante



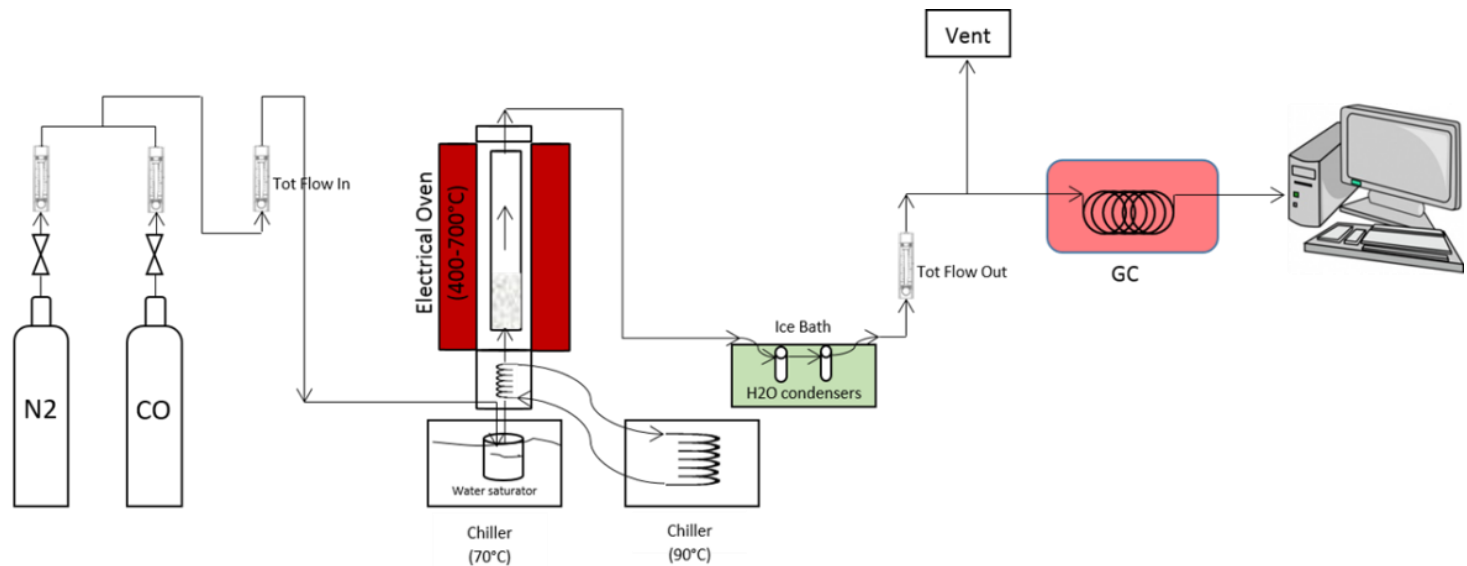


# Caratterizzazioni XRD



La riduzione della capacità sorbente osservata in HT2 e HT3 dopo il primo ciclo, è rispettivamente dovuta alla formazione di fasi stabili  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  (Mayenite) e  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  (Fairchildite)

# Test di SEWGS con miscela CO/H<sub>2</sub>O

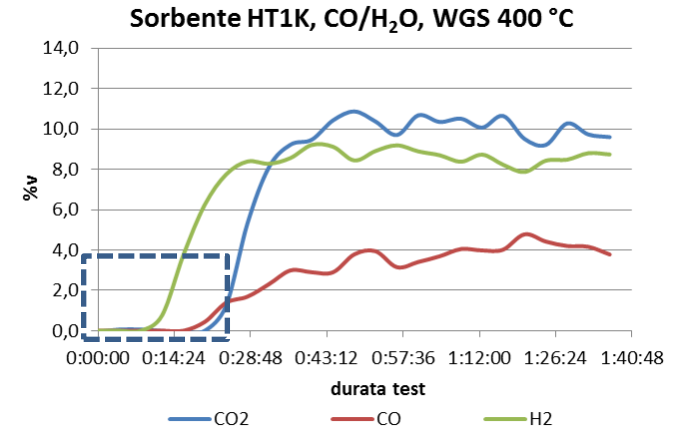
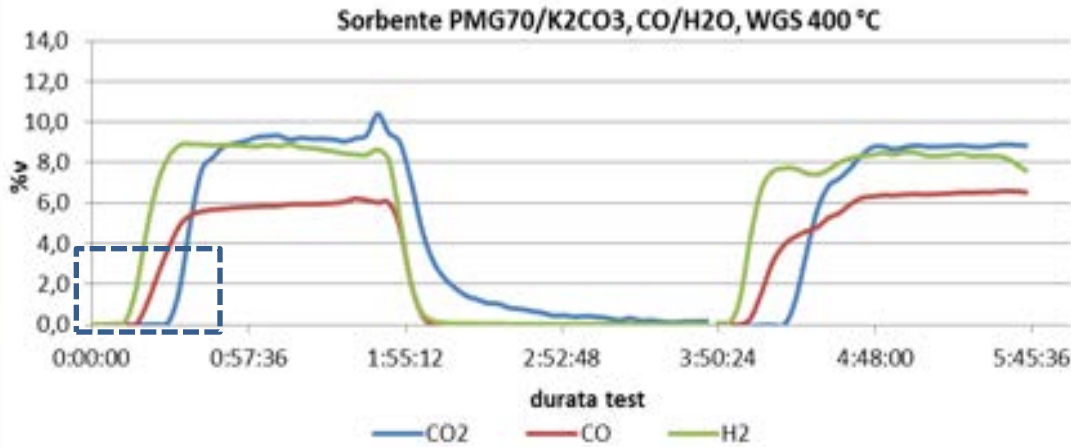


Composizione Gas	% <sub>v, secco</sub>
N <sub>2</sub>	70-73
CO	16-18
Ar	10-13
H <sub>2</sub> O (%-v, umido)	30
Pressione (atm)	1
Temperatura (° C)	400, 600

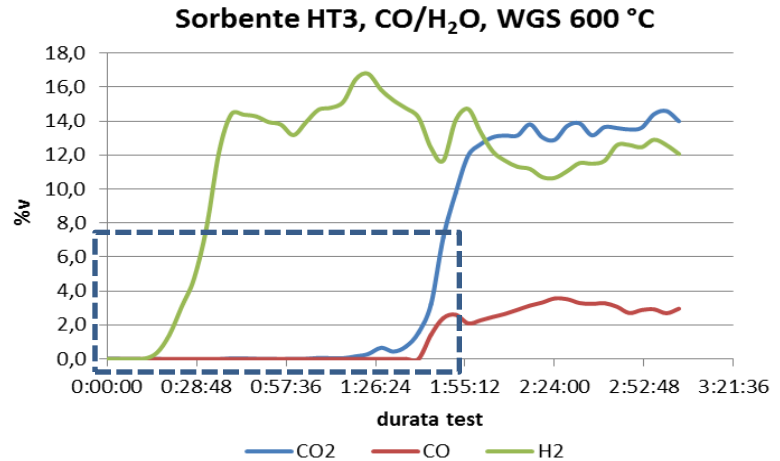
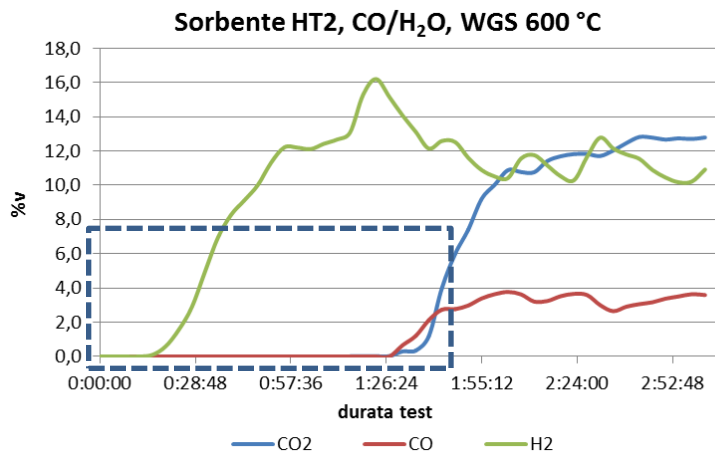


Per tener conto dell'ottimizzazione del processo complessivo anche rispetto all'efficienza energetica, sono state condotte prove di WGS e simultanea rimozione CO<sub>2</sub> a bassa (400 °C) ed alta temperatura (600 °C).

# Test di SEWGS con miscela CO/H<sub>2</sub>O



Capacità sorbente Mg/Al impregnato: 0.15-0.20 mmol<sub>CO<sub>2</sub></sub>/g<sub>sorbente</sub>



Capacità sorbente (Mg/Ca/Al): 1.0-1.5 mmol<sub>CO<sub>2</sub></sub>/g<sub>sorbente</sub>

➔ **Sperimentazione su gas reale**

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- **Sviluppo e caratterizzazione di catalizzatore di metanazione Ni/Mg/Al**



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# Test di metanazione al BioSNG di Trisaia

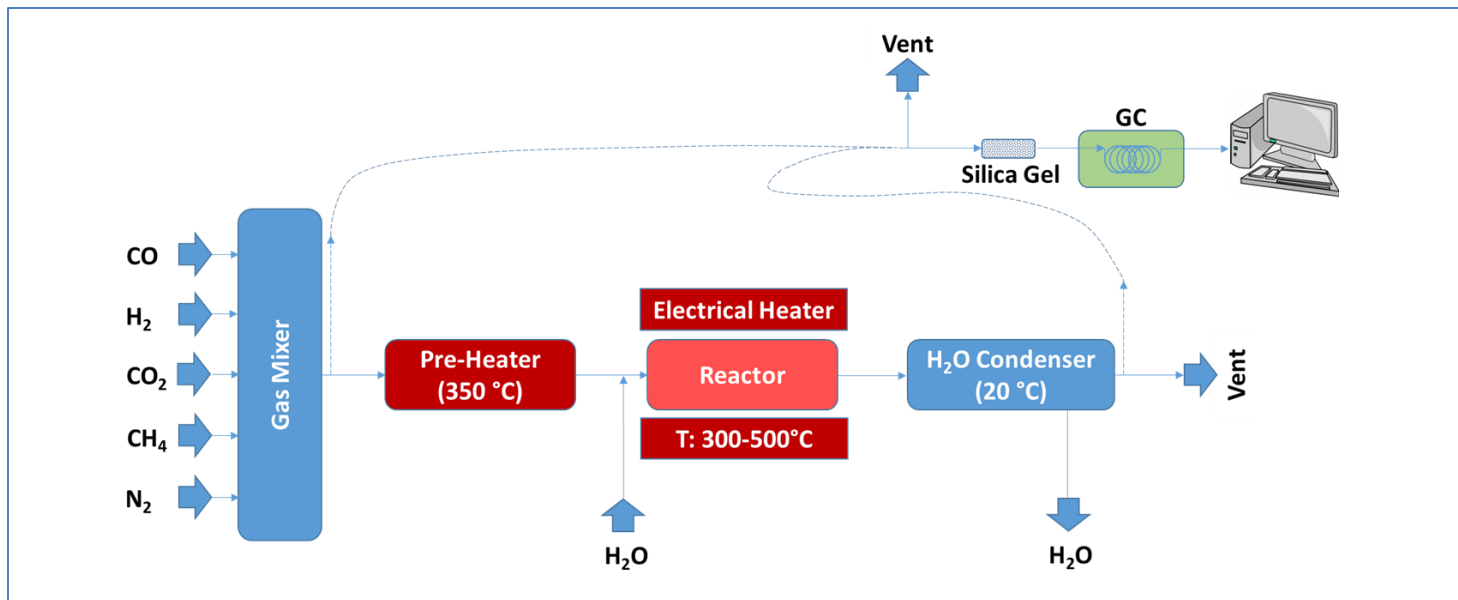


A)



B)

**Impianto pilota BioSNG: A) unità controllo gas, B) reattore**

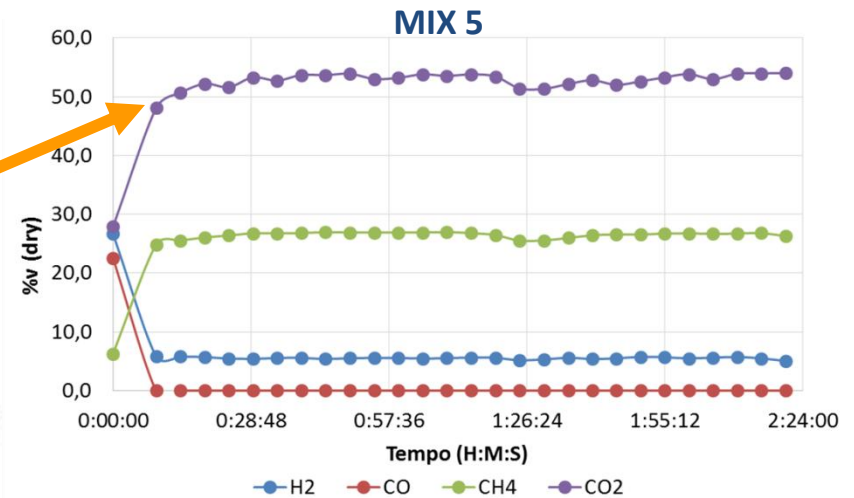
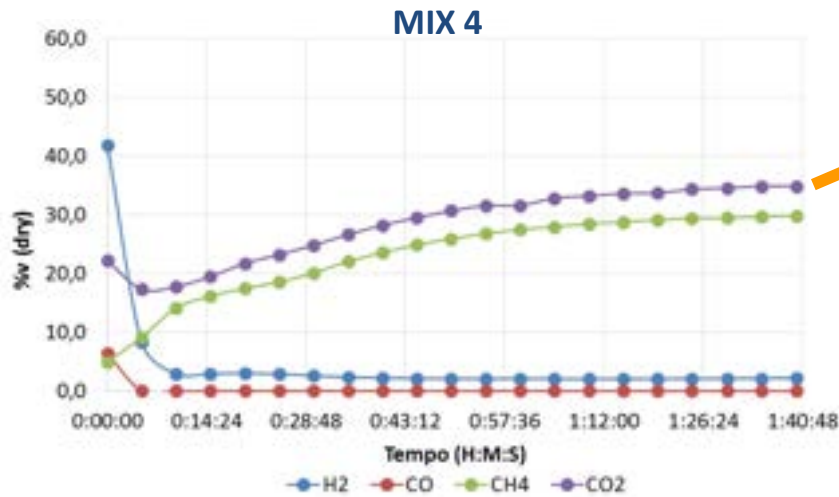


# Test su catalizzatore commerciale (G1-85, BASF)



Mix	%v						H <sub>2</sub> /CO
	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	H <sub>2</sub> O	
1	56.5	13.5	--	--	30.0	--	4.2
2	49.8	20.6	--	--	29.6	--	2.4
3	25.2	18.1	--	--	56.7	--	1.4
4	32.2	5.0	17.1	3.8	18.9	23.0	6.5
5	18.3	15.4	19.2	4.3	11.6	31.2	1.2

Condizioni operative	
T (°C)	330 -380
P (bar <sub>a</sub> )	20-25
GHSV (h <sup>-1</sup> )	1000



A)



B)



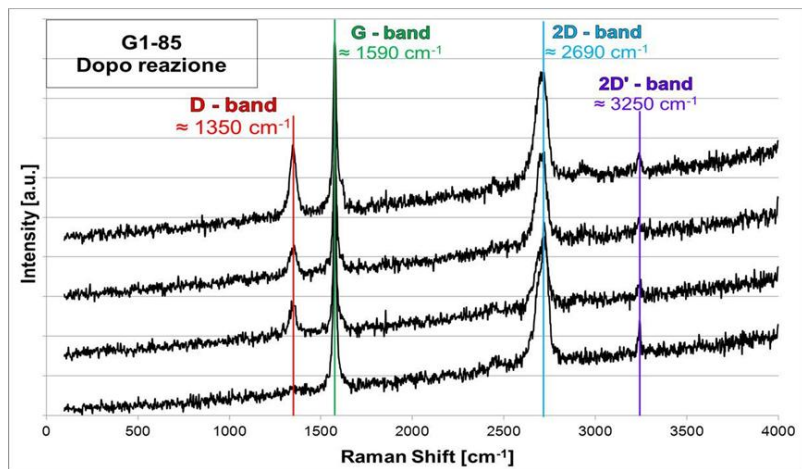
C)



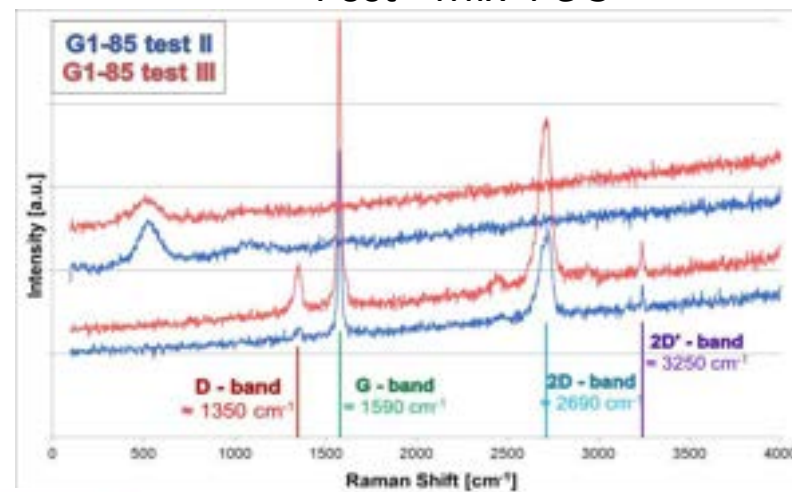
D)

A) pellet TQ, B) fine prova mix 3, C) fine prova mix 4, D) fine prova mix 5

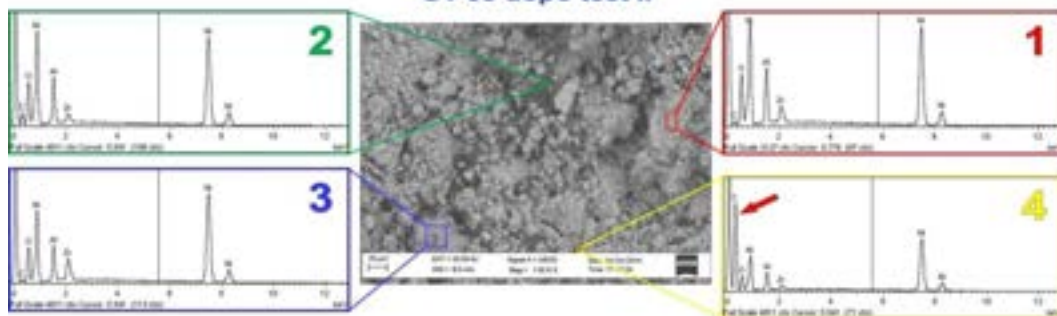
Post - Mix 3



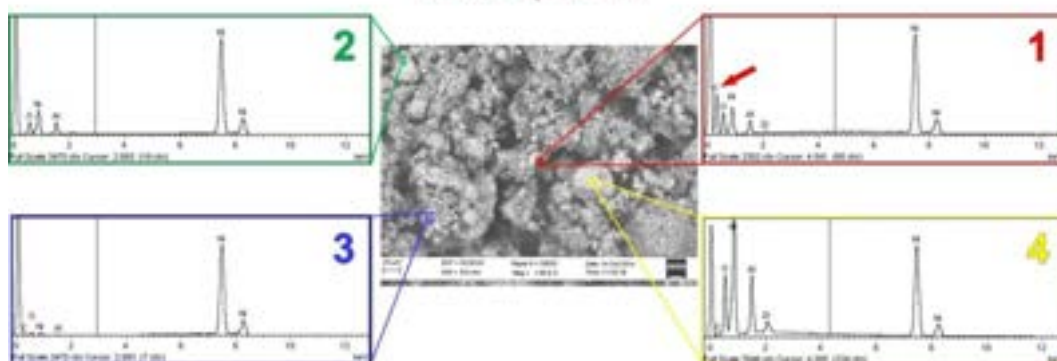
Post - Mix 4 e 5



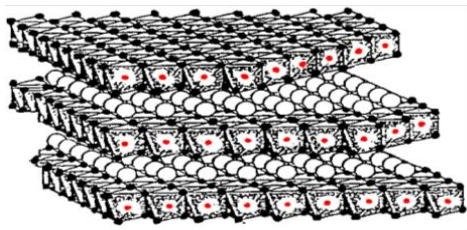
G1-85 dopo test II



G1-85 dopo test III



Su tutti i campioni di catalizzatore, le caratterizzazioni post-test rivelano segnali dovuti a depositi di carbonio



- $Mg^{2+}$ ,  $Al^{3+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$
- $OH^-$   $OCO_3^{2-}$

Precursore tipo idrotalcite



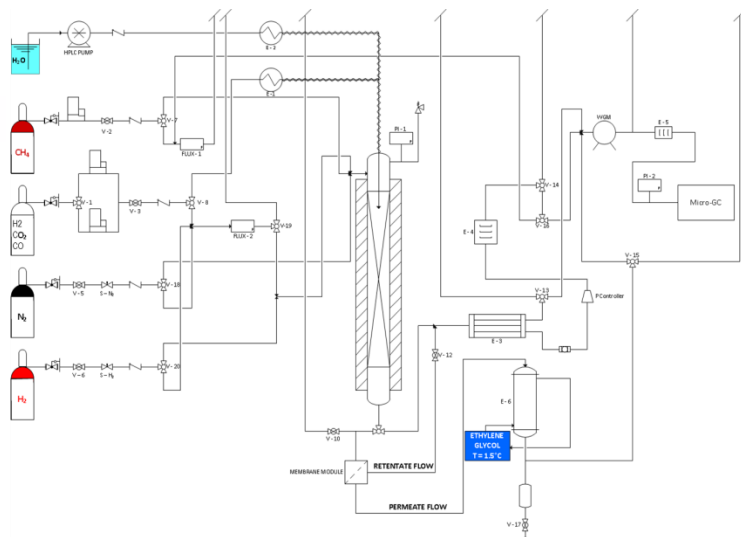
Ossido misto da preattivare

Rapporti atomici Ni/Mg/Al /Fe				
	Campione 1	Campione 2	Campione 3	Campione 4
Ni	24,5	33,33	24	26,66
Mg	42,2	33,33	51	40
Al	33,3	33,33	25	20
Fe	0	0	0	13,33
% of NiO	35,0	45,0	35,0	35,0
% of Ni°	27,1	34,8	27,1	33,33

Campione 3 prestazioni migliori  
(attività catalitica e stabilità nel tempo)



Ottimizzazione del rapporto Mg/Al



Rapporti atomici Ni/Mg/Al			
Ni	24.0	24.0	24.0
Mg	51.0	56.0	47.0
Al	25.0	20.0	29.0
TOTALE	100.0	100.0	100.0
% p/p NiO	35.0	35.0	35.0
% p/p Ni°	27.5	27.5	27.5
$M^{2+}/M^{3+}$	3.0	4.0	2.5

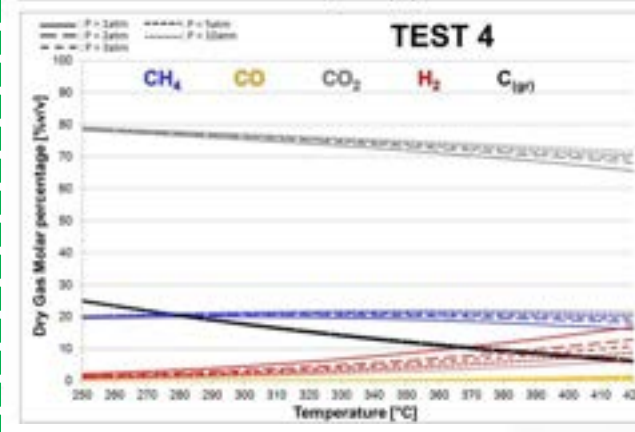
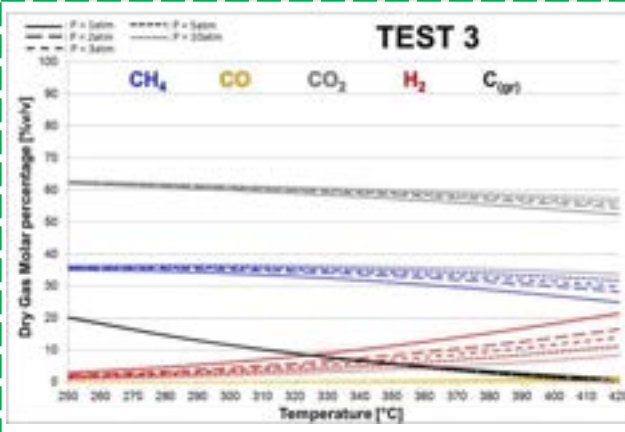
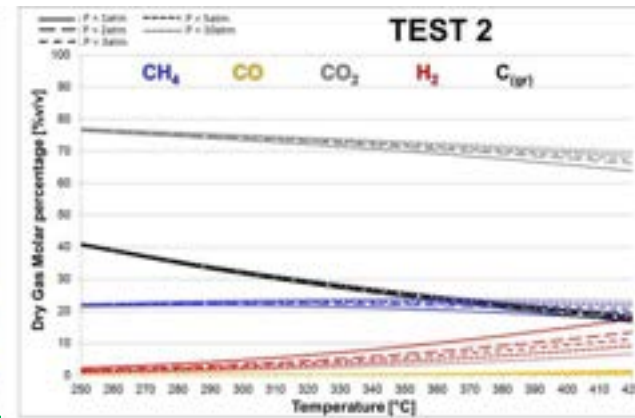
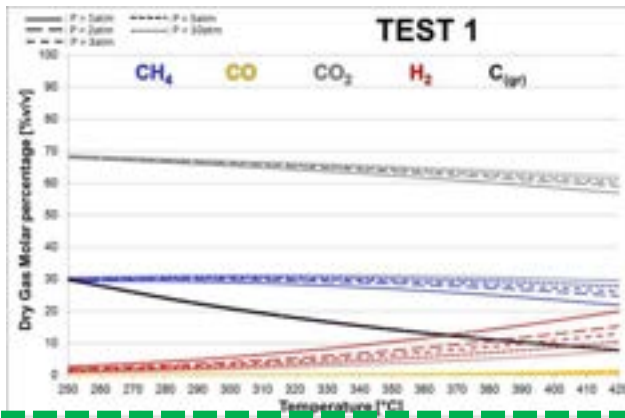


# Test di Metanazione – I fase

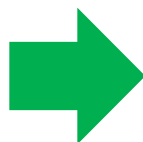
	TEST 1	TEST 2	TEST 3	TEST 4
$T_{oven}$ [°C]	300			
GHSV [h <sup>-1</sup> ]	20000			
$\tau$ [ms]	180			
$H_2/CO$	4.1			
Composizione miscela entrante [%v/v]				
H <sub>2</sub>	32.88	32.56	32.58	26.69
CO	8.03	8.12	8.05	6.67
CH <sub>4</sub>	3.98	4.02	3.99	3.31
CO <sub>2</sub>	28.14	34.22	24.14	34.04
C <sub>2</sub> H <sub>6</sub>	1.07	1.07	1.07	0.87
H <sub>2</sub> O(v)	25.90	20.01	30.17	28.47



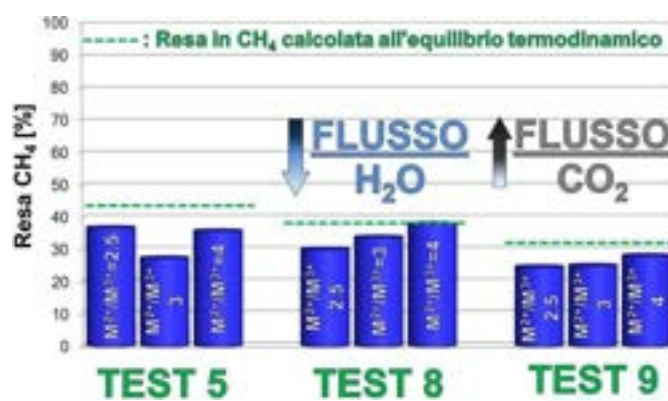
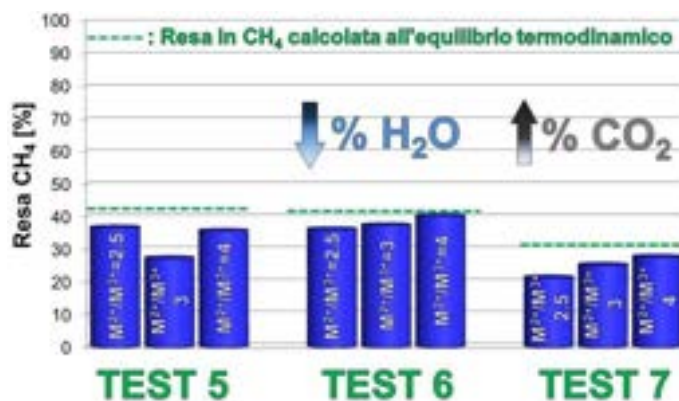
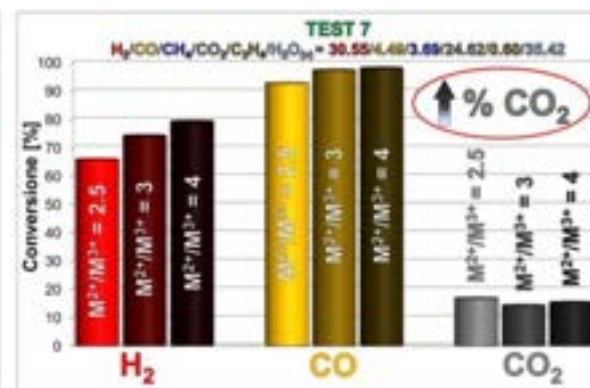
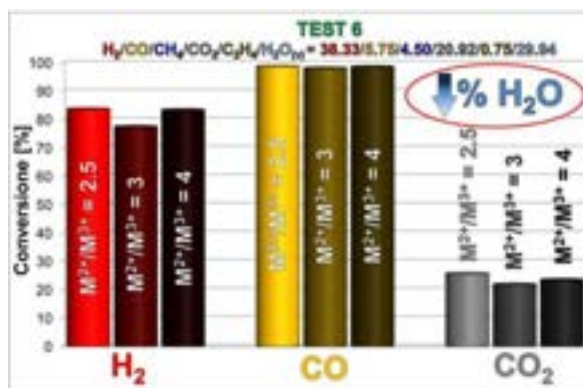
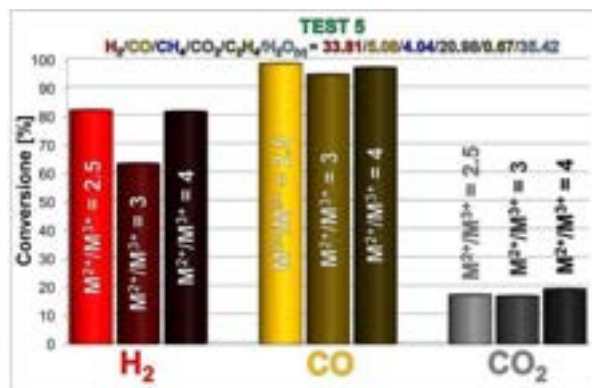
Basse rese in CH<sub>4</sub> e lacuna nella chiusura del bilancio al carbonio (- 20/30%p)



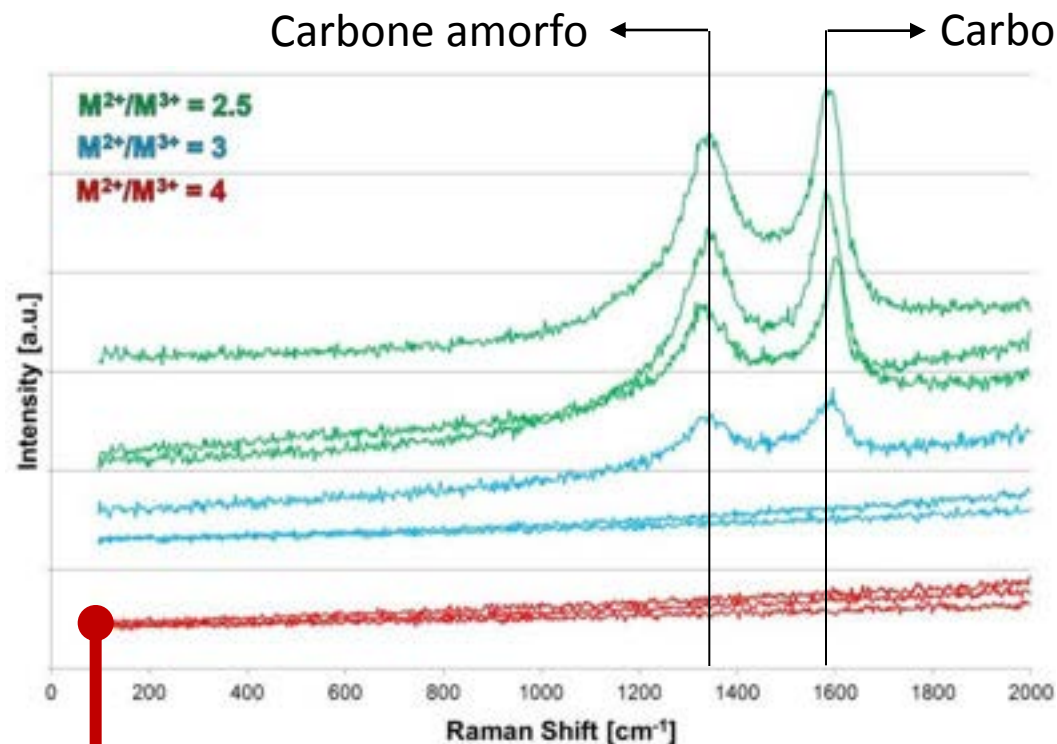
Incrementando  $H_2/CO$  e contenuto di  $H_2O$  e  $CO_2$  tale da essere al di fuori dal limite di formazione di C.



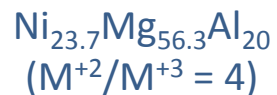
	TEST 5	TEST 6	TEST 7	TEST 8	TEST 9
STD.		% $H_2O$ ↑	% $CO_2$ ↑	FLUSSO $H_2O$ ↓	FLUSSO $CO_2$ ↑
$T_{over}$ [°C]	300				
GHSV [ $h^{-1}$ ]	20000	20000	20000	18392	21170
$\tau$ [ms]	180	180	180	195	170
$H_2/CO$	6.8	6.8	6.8	6.8	6.8
Composizione miscela entrante [%v/v]					
$H_2$	33.81	38.33	30.55	36.82	31.42
$CO$	5.68	5.75	4.49	5.58	4.79
$CH_4$	4.04	4.50	3.69	4.40	3.79
$CO_2$	20.98	20.92	24.62	22.84	25.95
$C_2H_6$	0.67	0.75	0.60	0.73	0.63
$H_2O(v)$	35.42	29.94	35.42	29.81	33.81



Il catalizzatore a rapporto  $M(II)/M(III) = 4$  risulta il più attivo in tutte le condizioni



Spettri Raman ottenuti su 3 zone di campioni Ni/Mg/Al



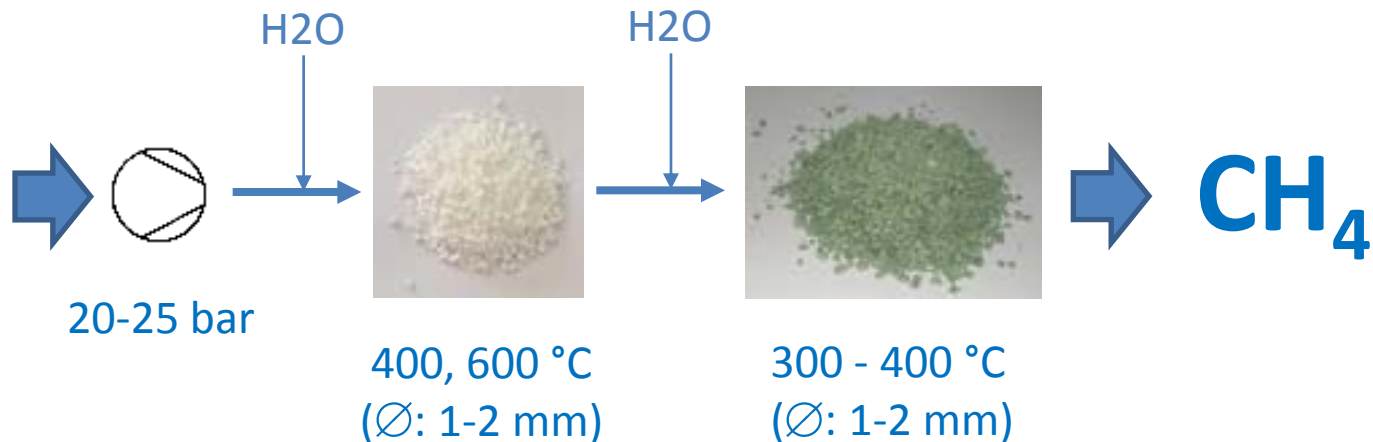
Sperimentazione su  
gas reale

Catalizzatore	(Ni + Mg)/Al ( $M^{+2}/M^{+3}$ )	%Ni
$\text{Ni}_{24.3}\text{Mg}_{46.7}\text{Al}_{29}$	2,5	27.5 % <sub>p</sub>
$\text{Ni}_{24}\text{Mg}_{51}\text{Al}_{25}$	3	27.5 % <sub>p</sub>
$\text{Ni}_{23.7}\text{Mg}_{56.3}\text{Al}_{20}$	4	27.5 % <sub>p</sub>

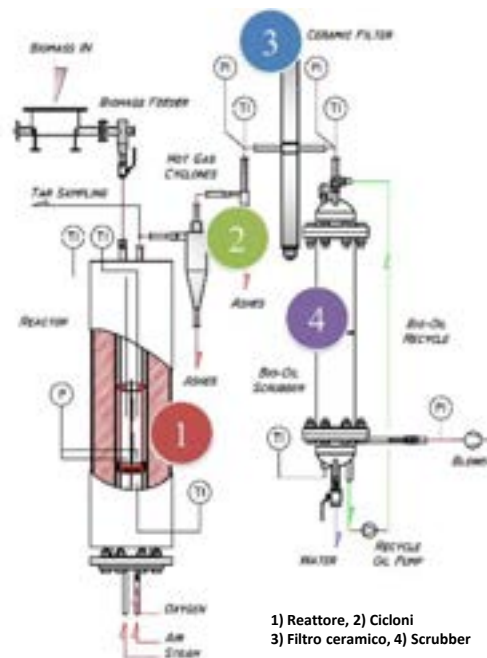
# Set-up sperimentale prove con gas reale



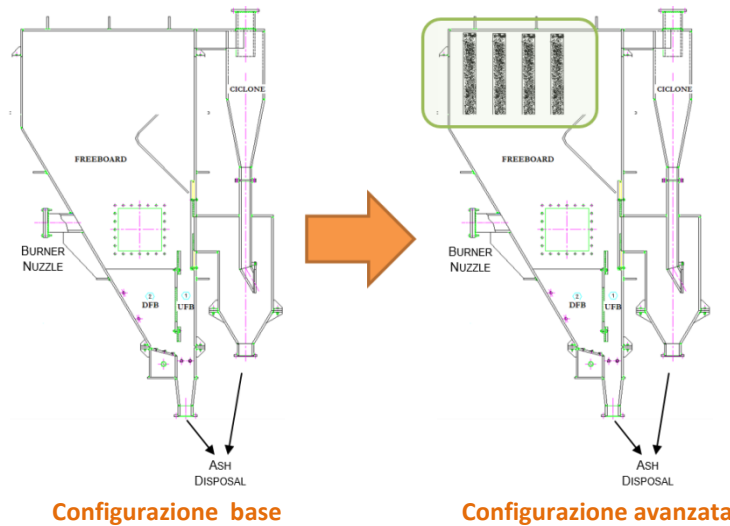
**Impianto ICBFB 10 kWt**



**Reattore ICBFB 10 kWt**



# Impianto pilota di gassificazione ICBFB-1MW<sub>t</sub>



- **Miglioramento efficienza energetica Tot**
- **Semplificazione degli stadi di purificazione gas «a valle»**
- **Riduzione costi Tot di investimento**

[www.unifhy.eu](http://www.unifhy.eu)

Steam/oxygen biomass gasification at pilot scale in an internally circulating bubbling fluidized bed reactor. D. Barisano, G. Canneto, F. Nanna, E. Alvino, G. Pinto, A. Villone, M. Carnevale, V. Valerio, A. Battafarano, G. Braccio. Article in press, Fuel processing technology, 2015.

Steam/oxygen biomass gasification in a 1000 kw<sub>th</sub> ICBFB pilot plant. D. Barisano, G. Canneto, F. Nanna, E. Alvino, G. Pinto, A. Villone, A. Battafarano, M. Corrado, G. Braccio. In Proceedings of the 23rd European Biomass Conference and Exhibition. 1-4 June 2015, Vienna, Austria

# Diffusione risultati

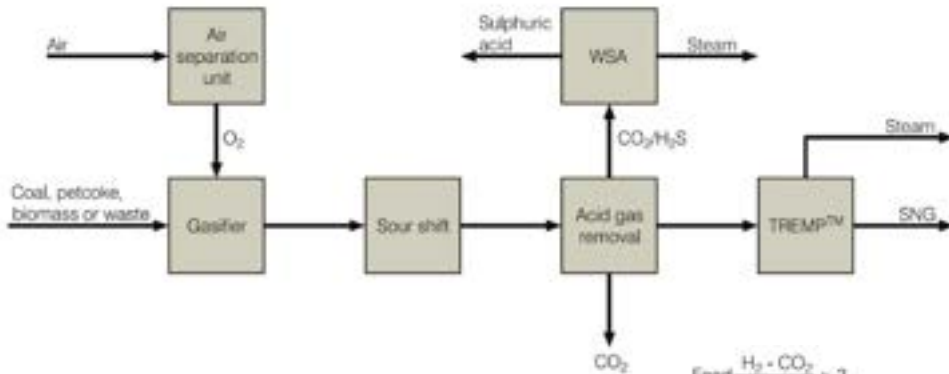


- Development of innovative catalysts for methanation of syngas deriving from biomass gasification. R. Mafessanti, D. Barisano, F. Basile, G. Fornasari, A. Vaccari. XIX Congresso Nazionale della Divisione di Chimica Industriale della Società Chimica Italiana, Salerno, 14-16 Settembre 2015.
- Production of BioMethane from Syngas Experimental Tests at Bench Scale Reactor. F. Nanna, G. Canneto, A. Villone, D. Barisano. EU BC&E 2015 - 23rd European Biomass Conference and Exhibition – Messe Wien, Exhibition and Congress Center. 1 - 4 June 2015, Vienna (Austria).
- Sorbent selection for product gas upgrading via simultaneous CO<sub>2</sub> removal and H<sub>2</sub> enrichment. D. Barisano, A. Villone, K. Gallucci, F. Micheli, P.U. Foscolo. EU BC&E 2015 - 23rd European Biomass Conference and Exhibition – Messe Wien, Exhibition and Congress Center. 1 - 4 June 2015, Vienna (Austria).
- CO<sub>2</sub> Sorption-Enhanced Processes by Hydrotalcite-Like Compounds at Different Temperature Levels. K. Gallucci, F. Micheli, D. Barisano, A. Villone, P. U. Foscolo, L. Rossi. Int. J. Chem. React. Eng. Volume 13, Issue 2, Pages 143–152, ISSN (Online) 1542-6580, ISSN (Print) 2194-5748, DOI: 10.1515/ijcre-2014-0131, April 2015.
- CO<sub>2</sub> Sorption by Hydrotalcite-Like Compounds in Dry and Wet Conditions. K. Gallucci, F. Micheli, A. Poliandri, L. Rossi, P. U. Foscolo. Int. J. Chem. React. Eng. ISSN (Online) 1542-6580, ISSN (Print) 2194-5748, DOI: 10.1515/ijcre-2014-0167, April 2015.
- In situ gas composition adjustment via catalytic activated CO<sub>2</sub> sorbent. A. Villone, F. Nanna, D. Barisano. EU BC&E 2014 - 22nd European Biomass Conference and Exhibition - Setting the course for a biobased economy. 23 - 26 June 2014, CCH Congress Center, Hamburg (Germany).
- Rapporti tecnici scaricabili dal sito: [http://www.enea.it/it/Ricerca\\_sviluppo/ricerca-sistema-elettrico/biomasse](http://www.enea.it/it/Ricerca_sviluppo/ricerca-sistema-elettrico/biomasse)

**Grazie per l'attenzione**



# From solid fuels to substitute natural gas (SNG) using TREMP™



CH <sub>4</sub> , mole-%	94-98
CO <sub>2</sub> , mole-%	0.2-2
H <sub>2</sub> , mole-%	0.05-2
CO, mole-%	<100 ppm
N <sub>2</sub> + Ar, mole-%	2-3
HHV, KJ/Nm <sup>3</sup>	37,380-38,370
HHV, Btu/scf	950-975

Table 1: Typical specification of SNG produced by the TREMP™ technology.

Figure 1: Gasification process – from coal, petcoke, waste or biomass to SNG.

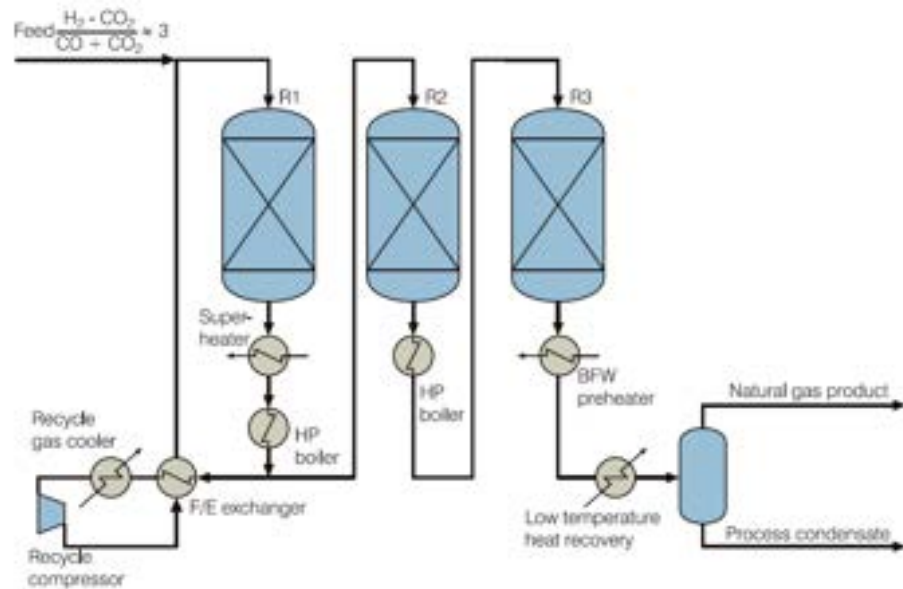


Figure 2: Example of the Topsoe TREMP™ technology.

[http://topsoe.ru/business\\_areas/gasification\\_based/Processes/~media/PDF%20files/SNG/Topsoe\\_TREMP.ashx](http://topsoe.ru/business_areas/gasification_based/Processes/~media/PDF%20files/SNG/Topsoe_TREMP.ashx)