



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

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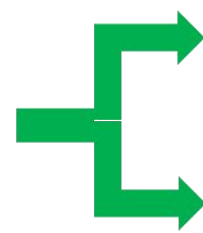
**LE BIOENERGIE E
LA RICERCA DI SISTEMA ELETTRICO**

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



Produzione di metano da biomasse

Biomassa Umide



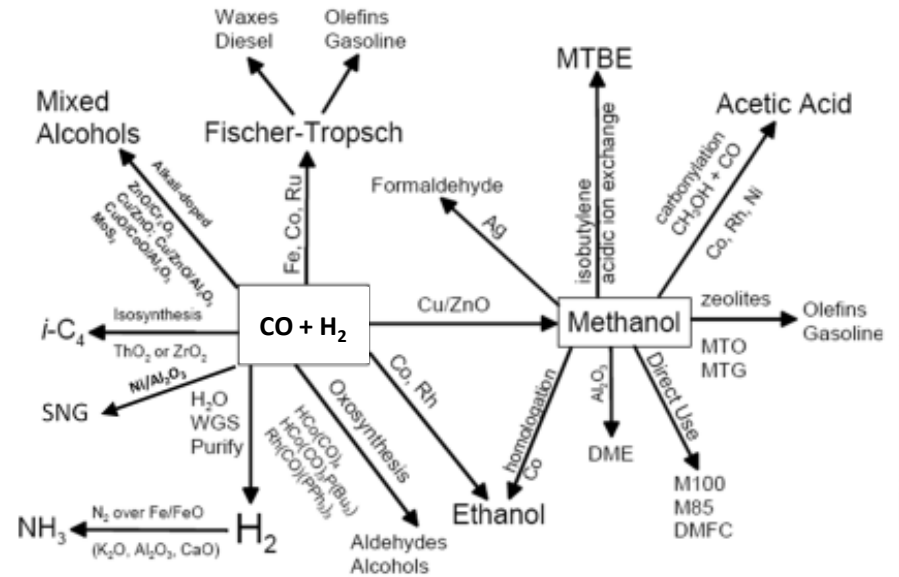
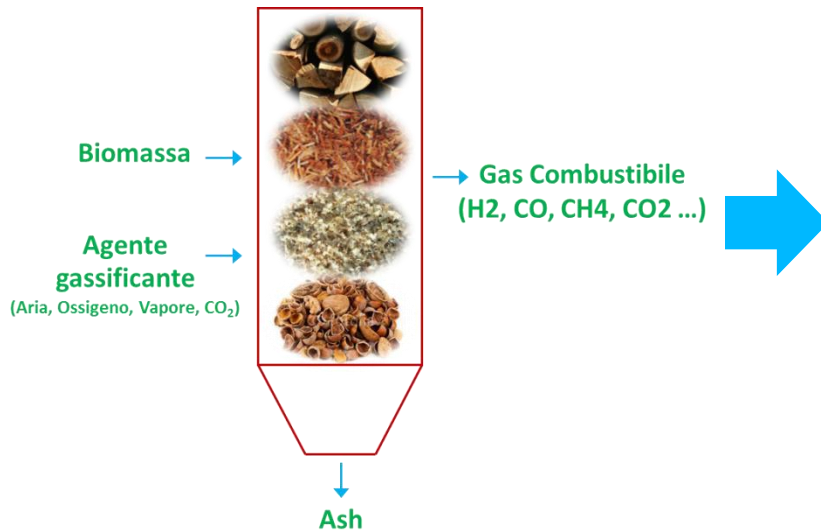
Digestione anaerobica

Gassificazione in acqua supercritica

Biomassa Secche



Gassificazione a «Secco»



Sintesi di biocombustibili liquidi e gassosi

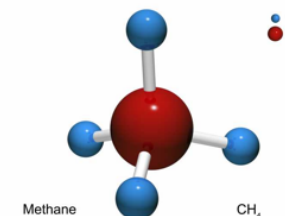
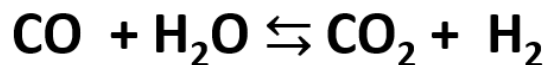
| BioFuels | H ₂ /CO | Calizzatore | P (atm) | T (°C) | η _{en} (LHV-Biom) |
|-----------------|--------------------|--------------|---------|---------|----------------------------|
| Metanolo | 2:1 | Zn/Cr, Cu/Zn | 50-300 | 300-450 | 40-50 |
| Fischer-Tropsch | 2:1 | Fe, Co | 20-30 | 250-300 | 40-50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



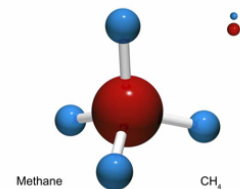
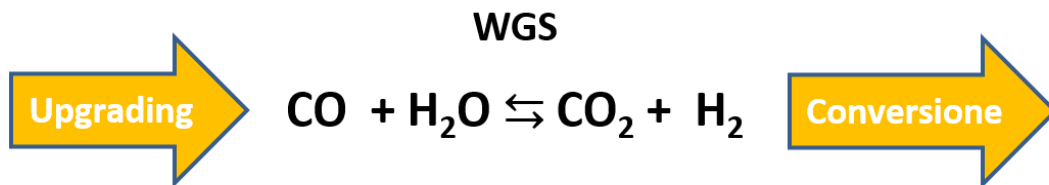
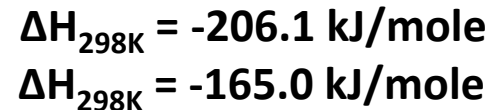
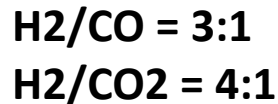
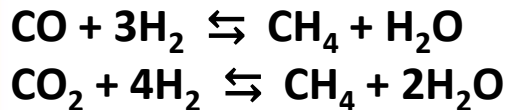
| Gassificante Agente | Composizione Gas Secco (% v) | | | | | | PCI (MJ/Nm ³) | H ₂ /CO |
|------------------------|------------------------------|-------|-----------------|-----------------|----------------|-------------------------------|------------------------------|--------------------|
| | H ₂ | CO | CO ₂ | CH ₄ | N ₂ | C ₂ H ₄ | | |
| 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 ₂ | 30-33 | 28-32 | 22-27 | 9-11 | 2-5 | 1-2 | 11-12 | 1.10 |



WGS



Necessità di aggiustare la composizione del gas: H₂/CO



- 1- stechiometria ⇒ massimizzare la conversione del gas in CH₄
- 2- evitare la disattivazione del catalizzatore per formazione di depositi di carbonio
 $2\text{CO} = \text{C} + \text{CO}_2$

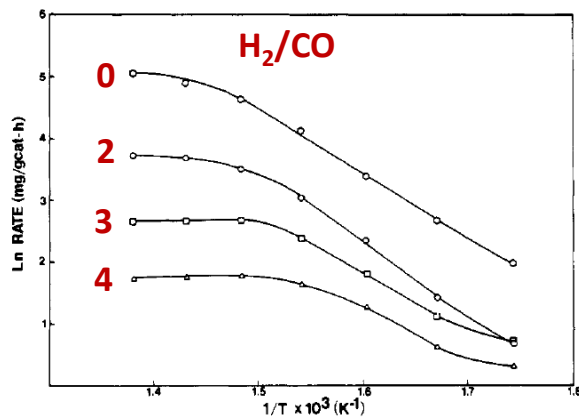


Figure 5. Arrhenius plot of carbon accumulation on 14% Ni/Al₂O₃ at $T = 573\text{--}723 \text{ K}$, P_{CO} of 9.0 kPa, and various H₂/CO ratios: ○, H₂/CO = 0; ○, H₂/CO = 2; □, H₂/CO = 3; Δ, H₂/CO = 4.

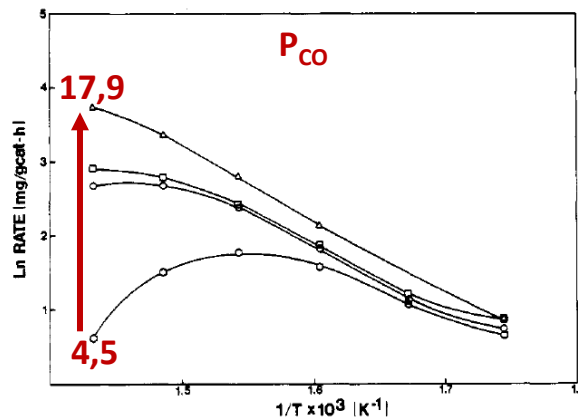


Figure 6. Arrhenius plot of carbon accumulation during methanation at a H₂/CO ratio = 3, $P_{\text{CO}} = 4.5\text{--}17.9 \text{ kPa}$, $T = 573\text{--}698 \text{ K}$: ○, $P_{\text{CO}} = 4.5 \text{ kPa}$; ○, $P_{\text{CO}} = 9.0 \text{ kPa}$; □, $P_{\text{CO}} = 13.4 \text{ kPa}$; Δ, $P_{\text{CO}} = 17.9 \text{ kPa}$.

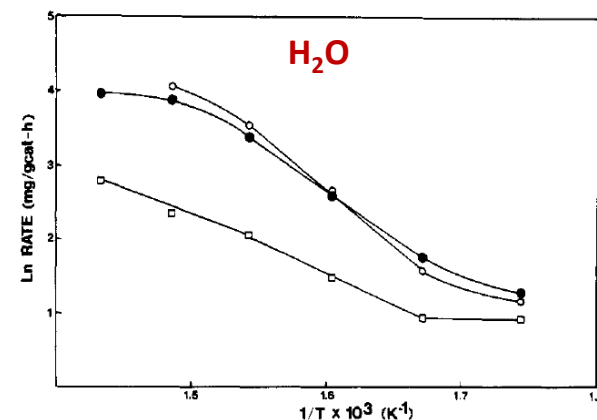


Figure 7. Arrhenius plot of carbon accumulation during methanation with $P_{\text{CO}} = 13.4 \text{ kPa}$, H₂/CO = 2 with and without 2.7 kPa of H₂O added to the feed stream: ○, before, and ●, after addition of water; □, in the presence of water.

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 CO₂



Biomassa



Gassificazione

Purificazione gas
e reforming

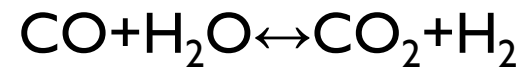
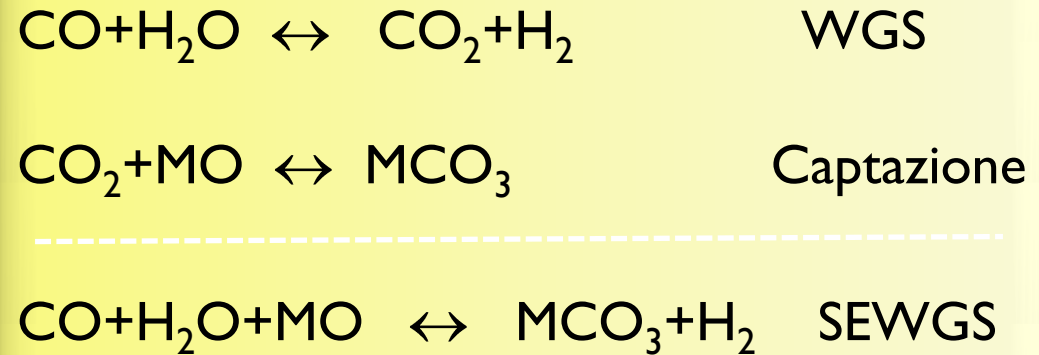
Water Gas Shift
HT

Water Gas Shift
LT

Rimozione CO₂

Metanazione

Rimozione CO₂



Gas → WGS + captazione → H₂, H₂O, ...

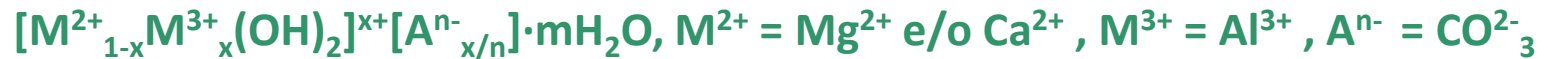
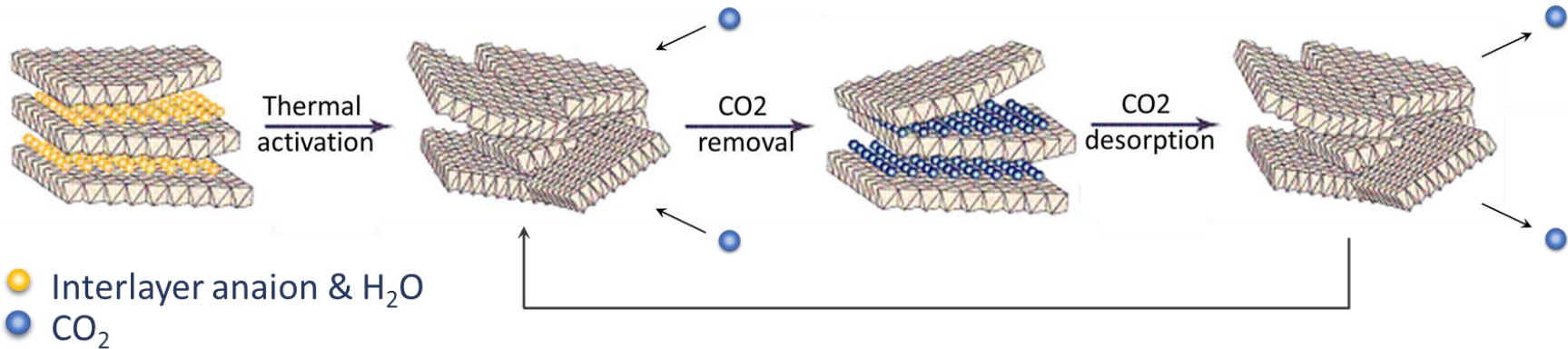
Steam + CO₂ ← rigenerazione ← Steam

✓ **Intensificazione di processo**

(riduzione costi di investimento, prestazioni di processo)



Sorbenti per la rimozione di CO2

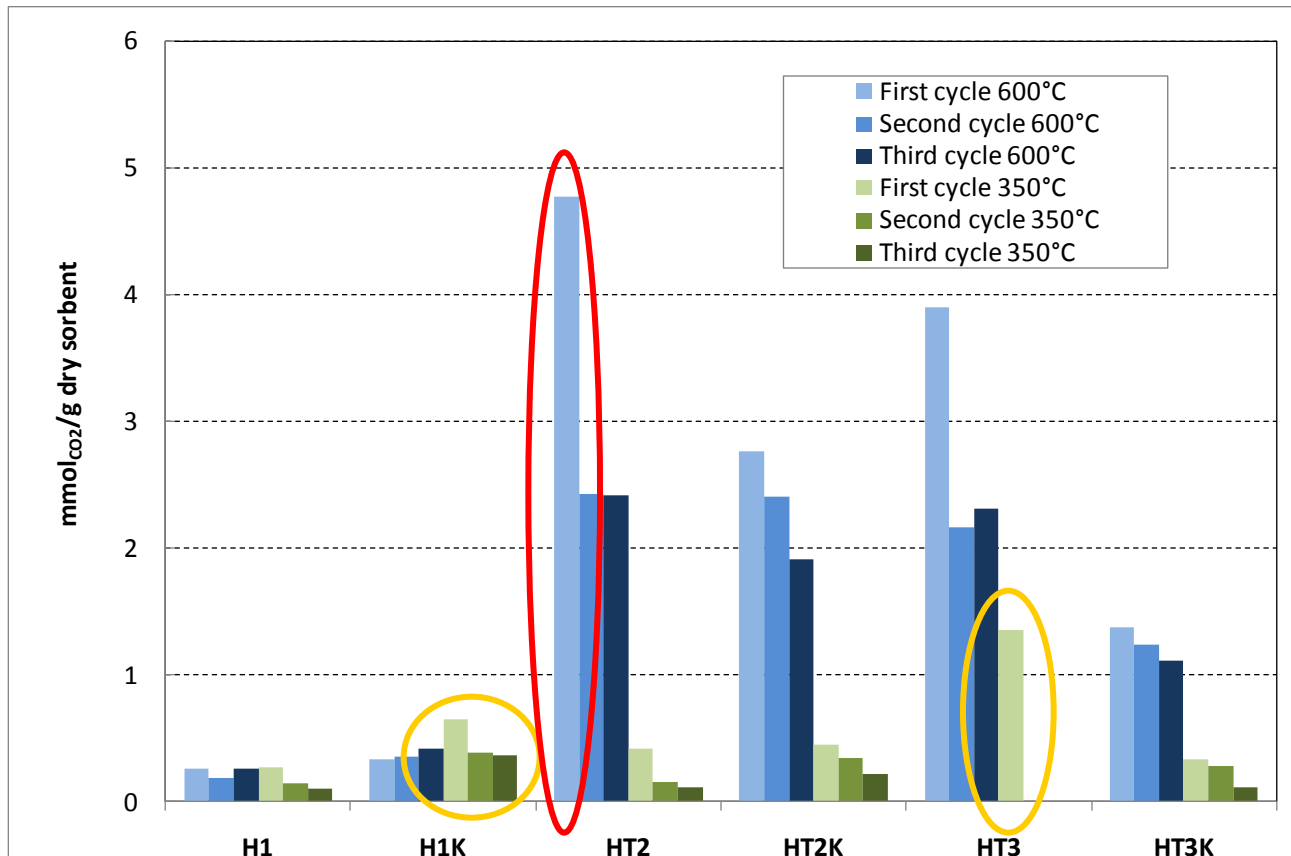


| Acronimo | Sorbente | M ⁺⁺ /M ⁺⁺⁺ |
|----------|--|-----------------------------------|
| HT1 | Mg/Al Idrotalcite | Mg/Al=2/1 |
| HT1K | Mg/Al Idrotalcite + 20%p K ₂ CO ₃ | Mg/Al=2/1 |
| HT2 | Ca/Al Idrocalumite | Ca/Al=2/1 |
| HT2K | Ca/Al Idrocalumite + 20%p K ₂ CO ₃ | Ca/Al=2/1 |
| HT3 | Mg/Ca/Al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





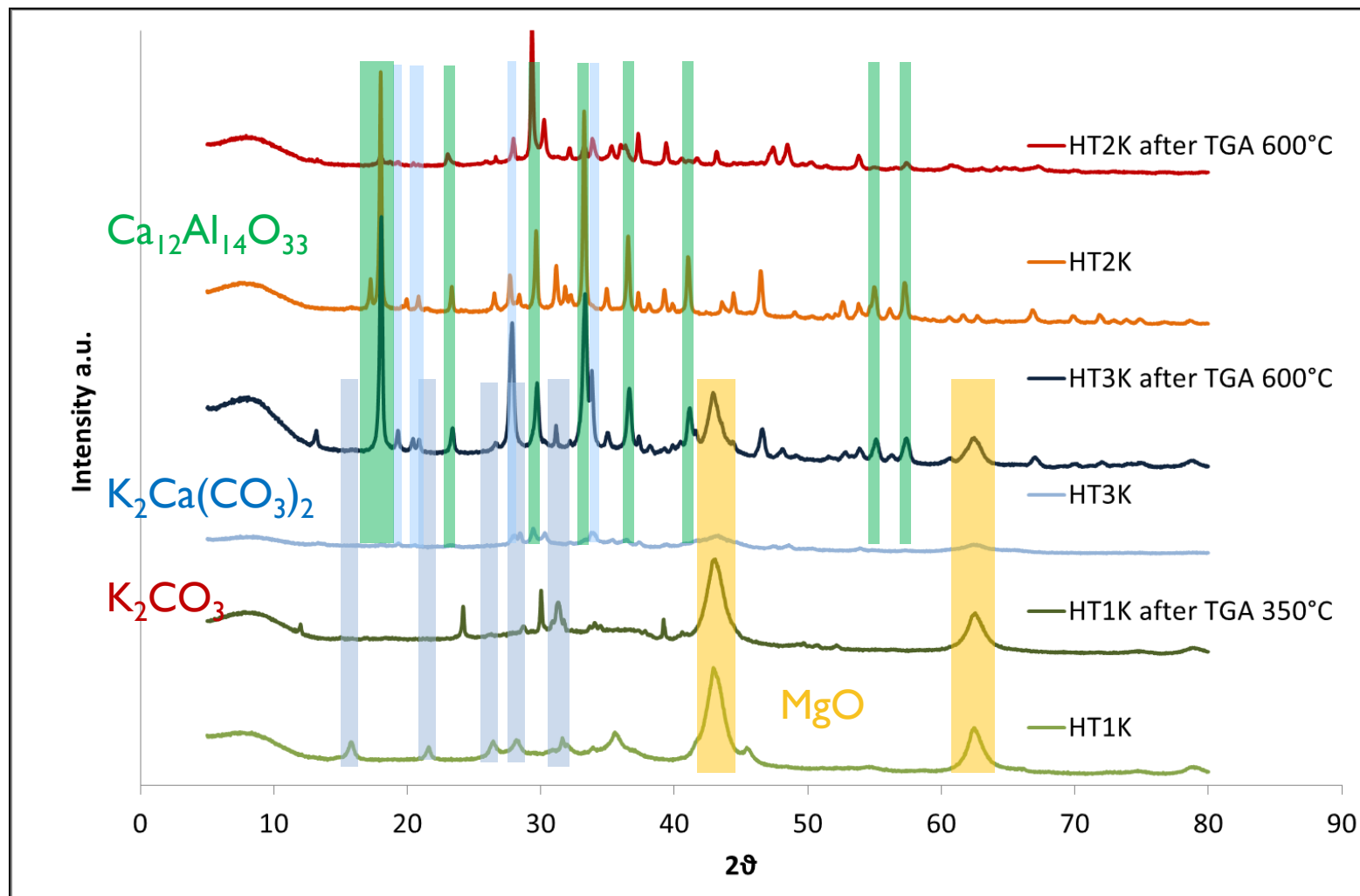
Test in TGA: $P_{CO_2}=1$ bar; $T_{ads\ Low}=350^\circ C$; $T_{ads\ High}=600^\circ C$



| | | |
|-----------------------|--|---|
| Test a bassa T | HT3 migliore performance (1.36 mmolCO ₂ /g _{sorbente}) | HT1K migliore performance tra i sorbenti impregnati con K (0.66 mmolCO ₂ /g _{sorbente}) |
| Test a alta T | HT2 migliore performance (4.78 mmolCO ₂ /g _{sorbente}) | Campioni impregnati con K Effetto non rilevante |

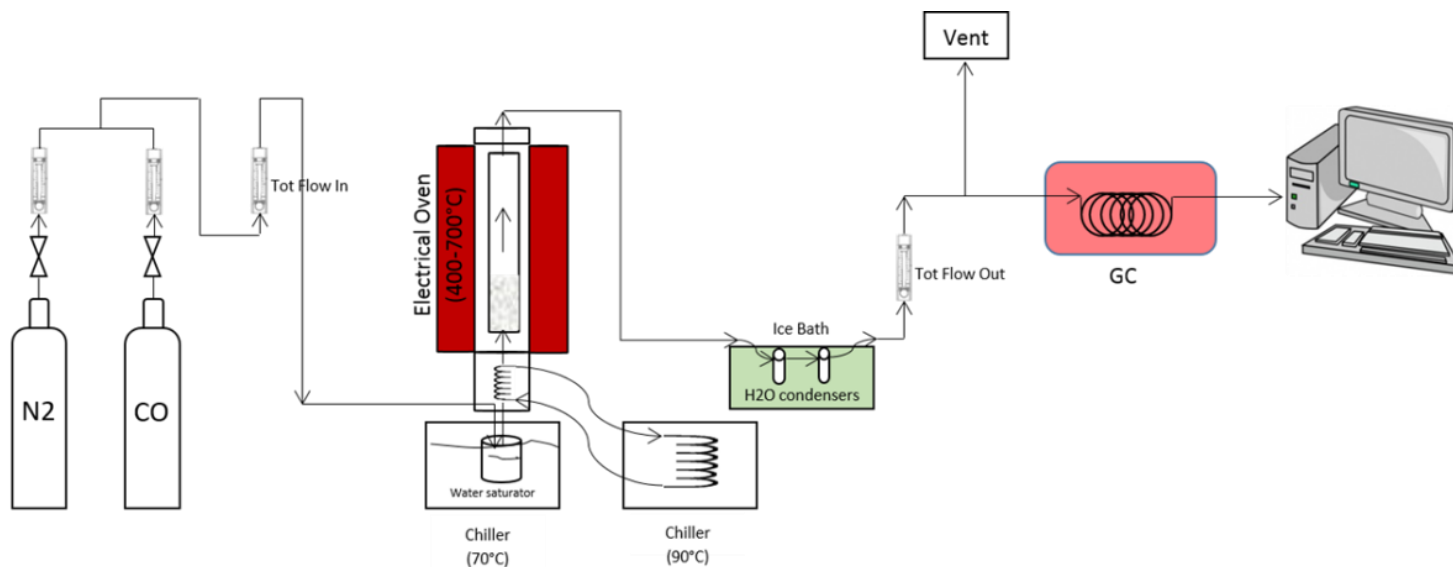


Caratterizzazioni XRD



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/H₂O



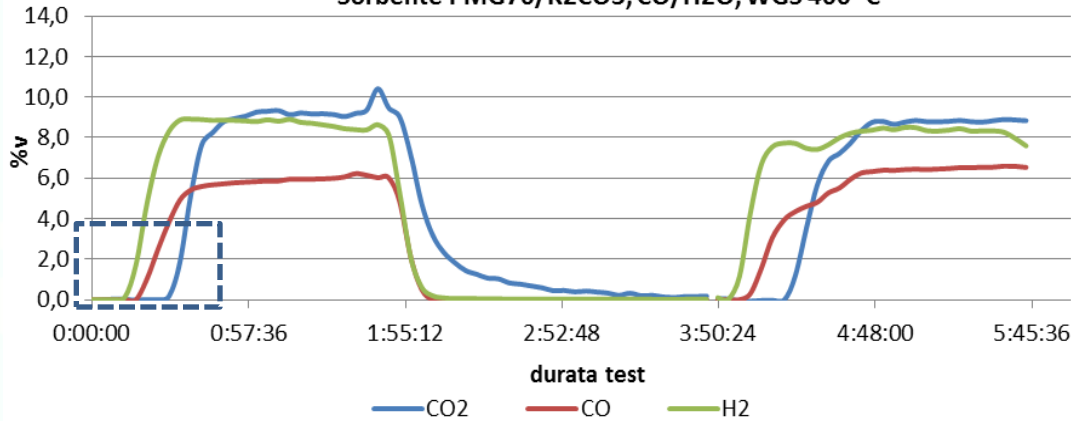
| Composizione Gas | % _{v, secco} |
|-------------------------------|-----------------------|
| N ₂ | 70-73 |
| CO | 16-18 |
| Ar | 10-13 |
| H ₂ O (%-v, umido) | 30 |
| Pressione (atm) | 1 |
| Temperatura (° C) | 400, 600 |



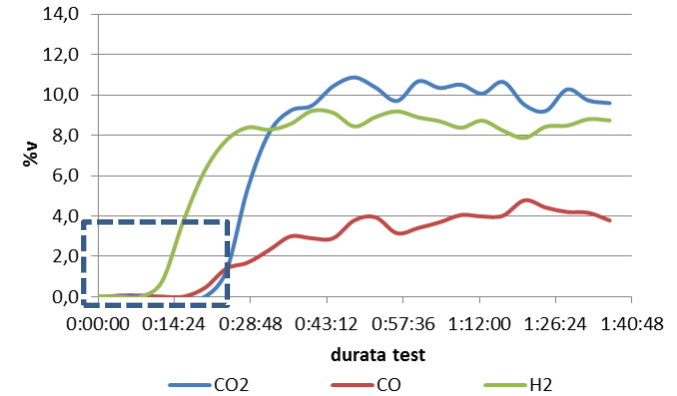
Per tener conto dell'ottimizzazione del processo complessivo anche rispetto all'efficienza energetica, sono state condotte prove di WGS e simultanea rimozione CO₂ a bassa (400 °C) ed alta temperatura (600 °C).

Test di SEWGS con miscela CO/H₂O

Sorbente PMG70/K₂CO₃, CO/H₂O, WGS 400 °C

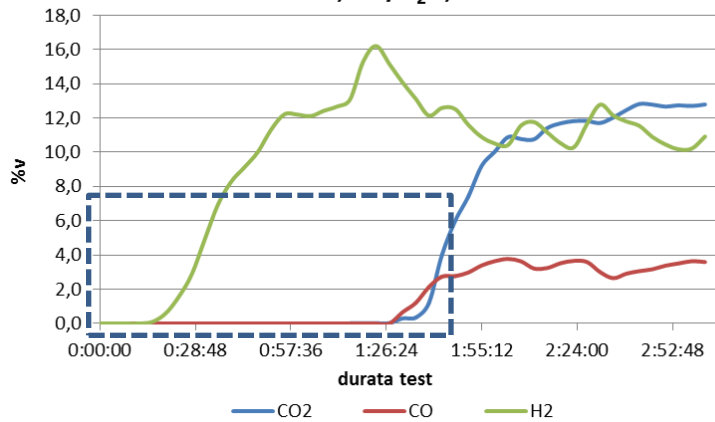


Sorbente HT1K, CO/H₂O, WGS 400 °C

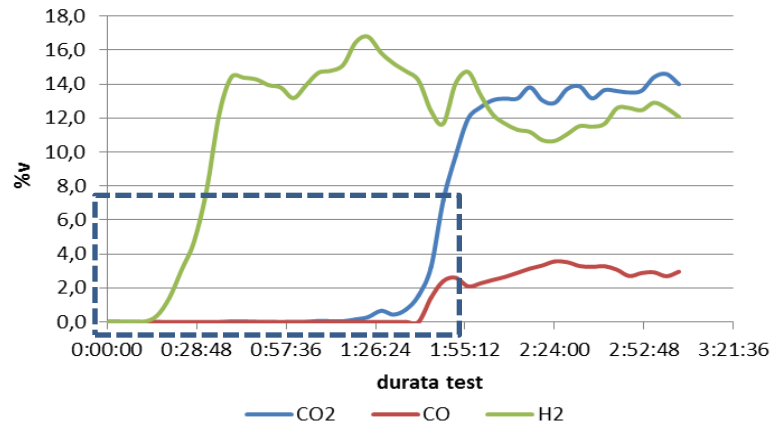


Capacità sorbente Mg/Al impregnato: 0.15-0.20 mmol_{CO₂}/g_{sorbente}

Sorbente HT2, CO/H₂O, WGS 600 °C



Sorbente HT3, CO/H₂O, WGS 600 °C



Capacità sorbente (Mg/Ca/Al): 1.0-1.5 mmol_{CO₂}/g_{sorbente}

➔ **Sperimentazione su gas reale**

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



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- *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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Test di metanazione al BioSNG di Trisaia

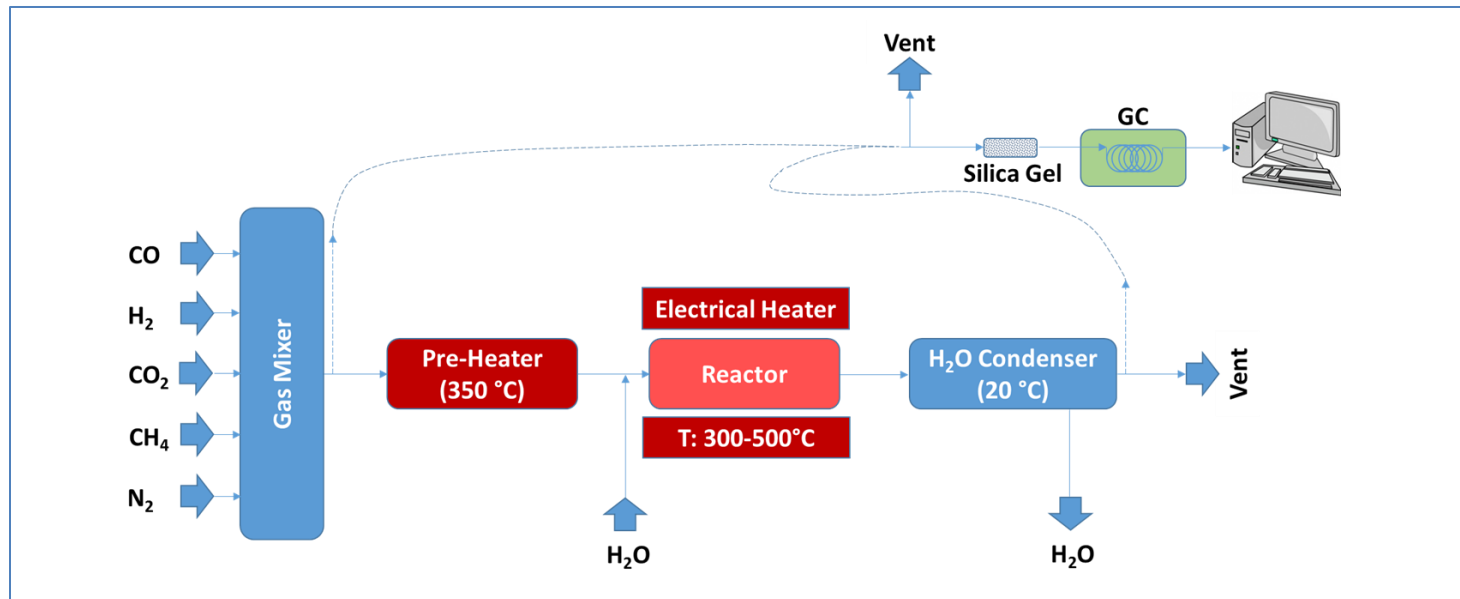


A)



B)

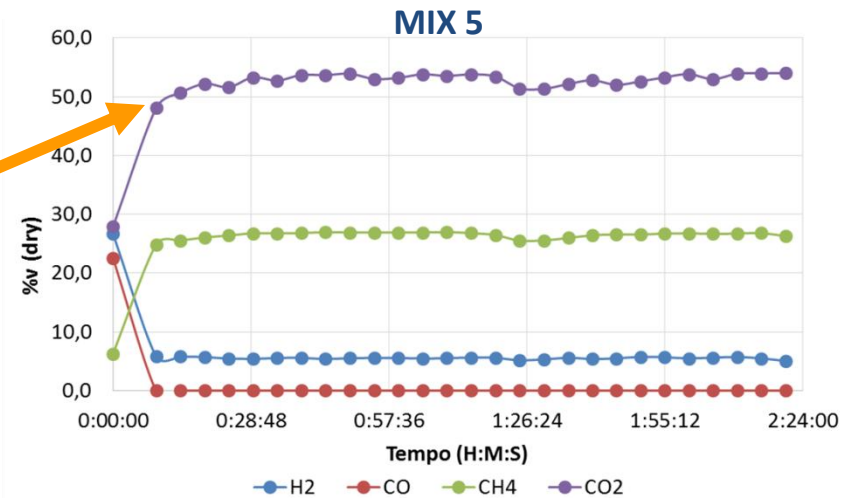
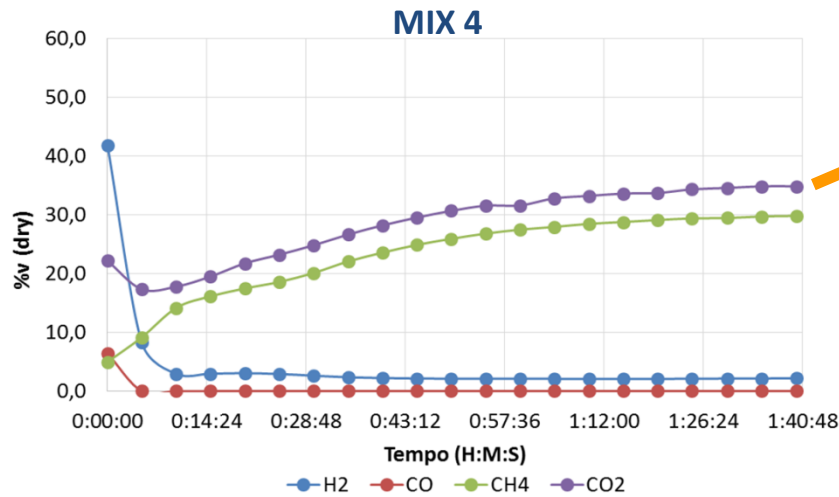
Impianto pilota BioSNG: A) unità controllo gas, B) reattore



Test su catalizzatore commerciale (G1-85, BASF)

| Mix | %v | | | | | | H ₂ /CO |
|-----|----------------|------|-----------------|-----------------|----------------|------------------|--------------------|
| | H ₂ | CO | CO ₂ | CH ₄ | N ₂ | H ₂ 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 _a) | 20-25 |
| GHSV (h ⁻¹) | 1000 |



A)



B)



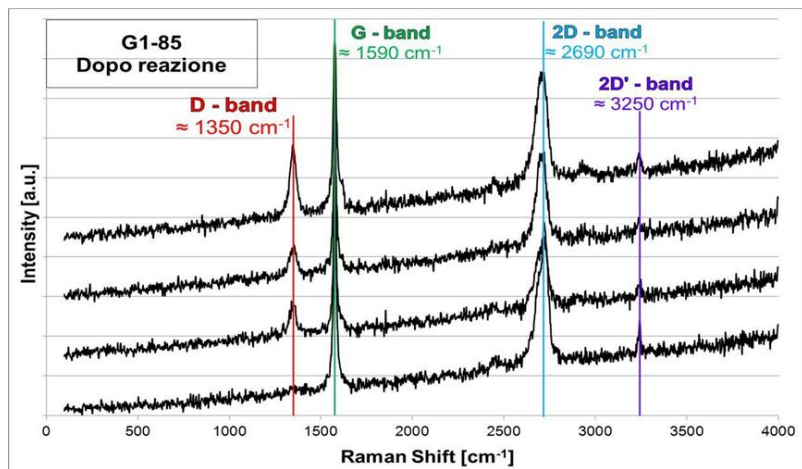
C)



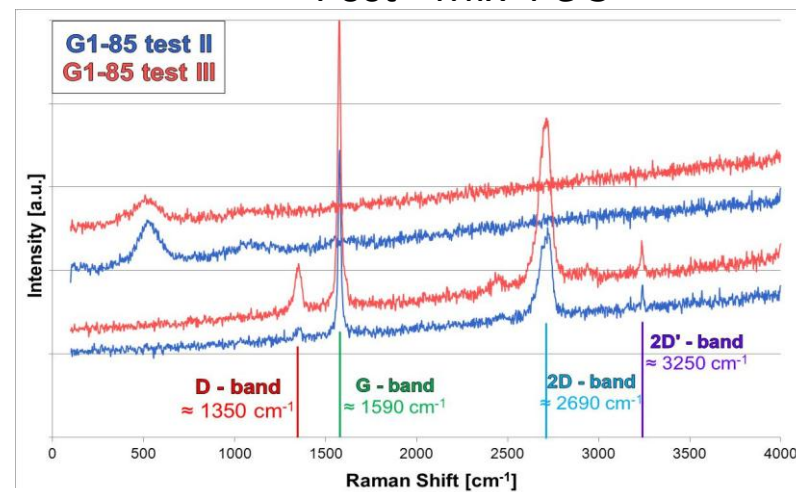
D)

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

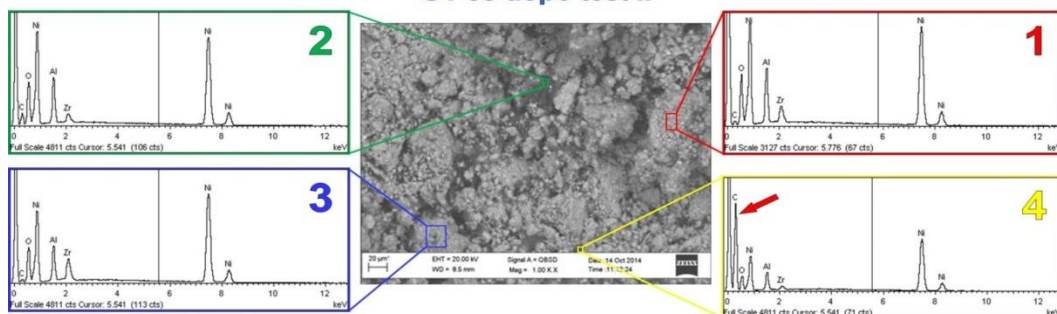
Post - Mix 3



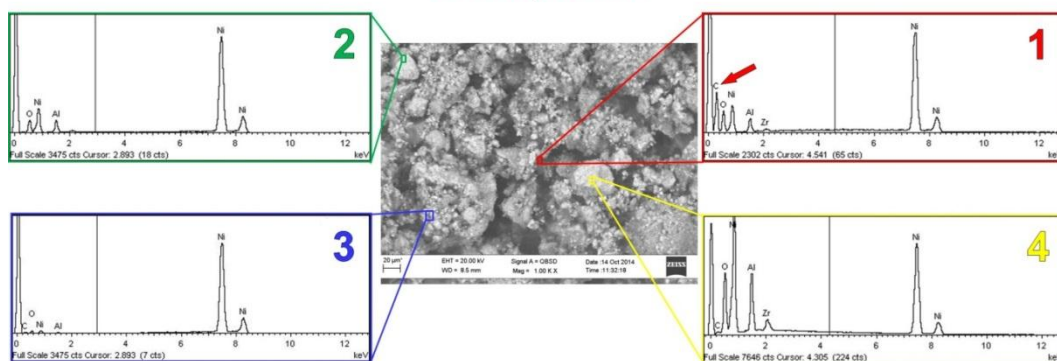
Post - Mix 4 e 5



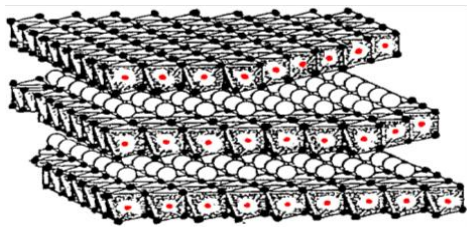
G1-85 dopo test II



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



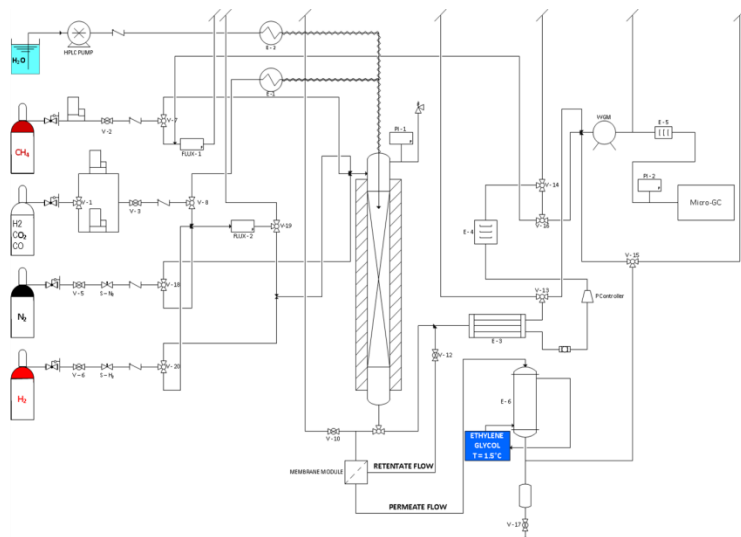
Ossido misto da preattivare

| 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 ^o | 27,1 | 34,8 | 27,1 | 33,33 |

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



Ottimizzazione del rapporto Mg/Al



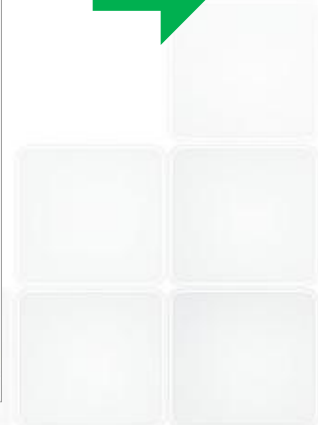
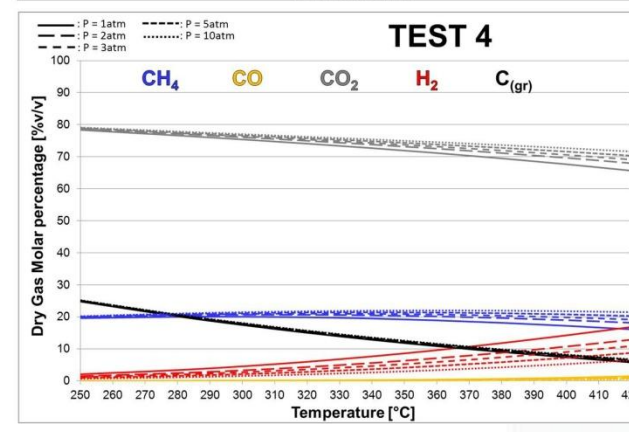
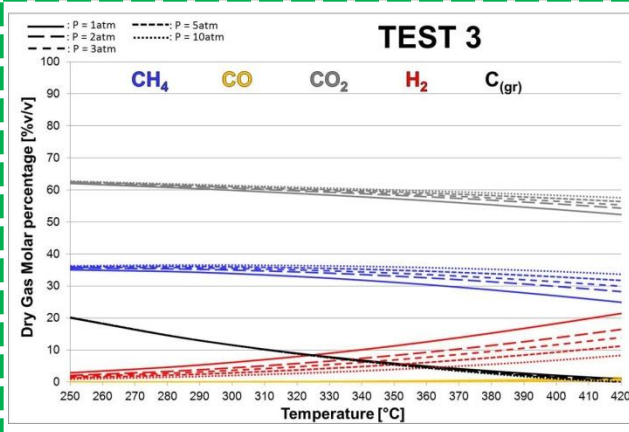
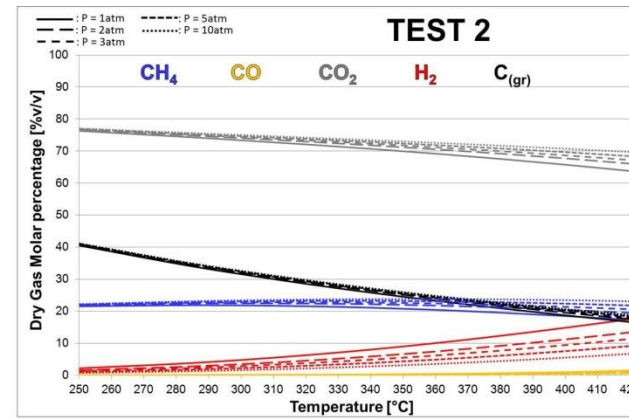
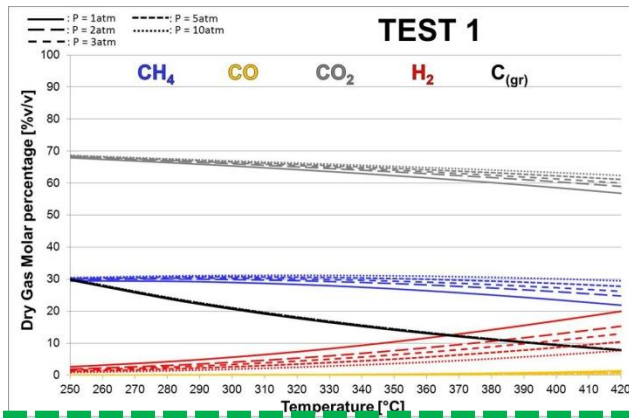
| Rapporti atomici Ni/Mg/Al | | | |
|--------------------------------------|------------|------------|------------|
| Ni | 24.0 | 24.0 | 24.0 |
| Mg | 51.0 | 56.0 | 47.0 |
| Al | 25.0 | 20.0 | 29.0 |
| TOTALE | 100.0 | 100.0 | 100.0 |
| % p/p NiO | 35.0 | 35.0 | 35.0 |
| % p/p Ni ^o | 27.5 | 27.5 | 27.5 |
| M²⁺/M³⁺ | 3.0 | 4.0 | 2.5 |

Test di Metanazione – I fase

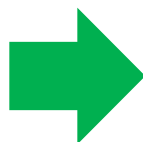
| | TEST 1 | TEST 2 | TEST 3 | TEST 4 |
|--------------------------------------|--------------|--------------|--------------|--------------|
| T_{oven} [°C] | 300 | | | |
| GHSV [h^{-1}] | 20000 | | | |
| τ [ms] | 180 | | | |
| H_2/CO | 4.1 | | | |
| Composizione miscela entrante [%v/v] | | | | |
| H₂ | 32.88 | 32.56 | 32.58 | 26.69 |
| CO | 8.03 | 8.12 | 8.05 | 6.67 |
| CH₄ | 3.98 | 4.02 | 3.99 | 3.31 |
| CO ₂ | 28.14 | 34.22 | 24.14 | 34.04 |
| C ₂ H ₄ | 1.07 | 1.07 | 1.07 | 0.87 |
| H ₂ O(v) | 25.90 | 20.01 | 30.17 | 28.47 |



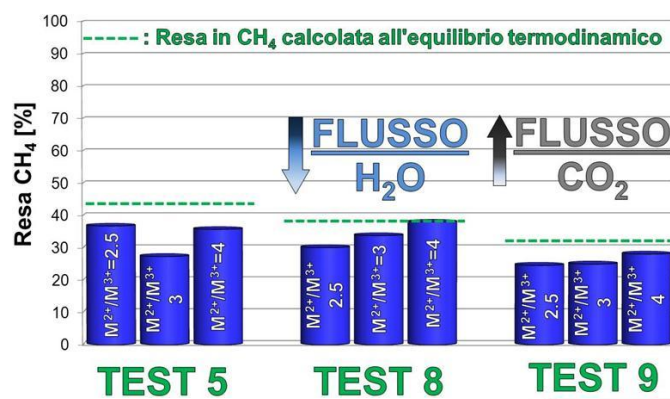
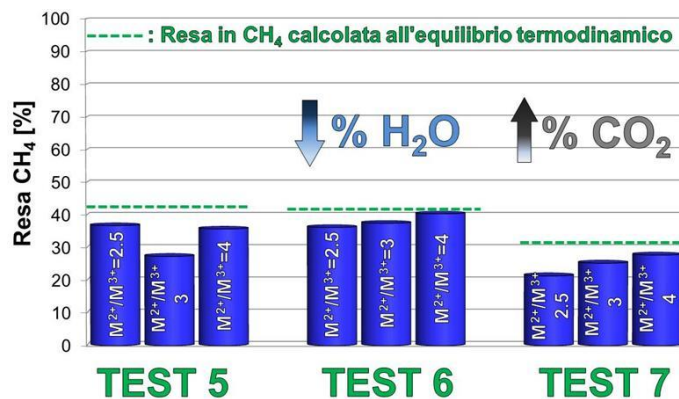
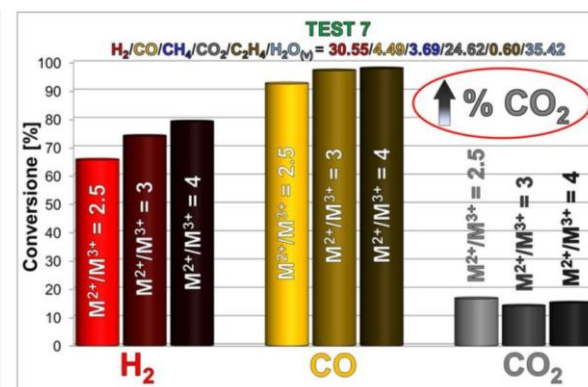
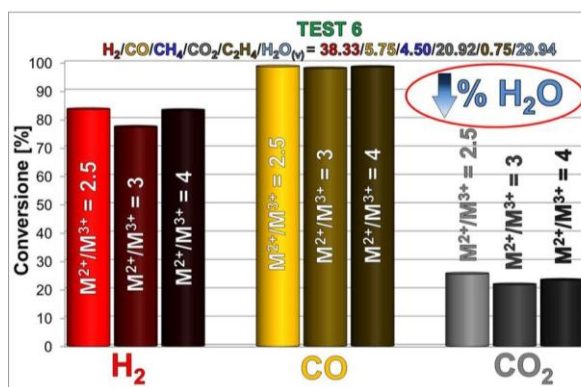
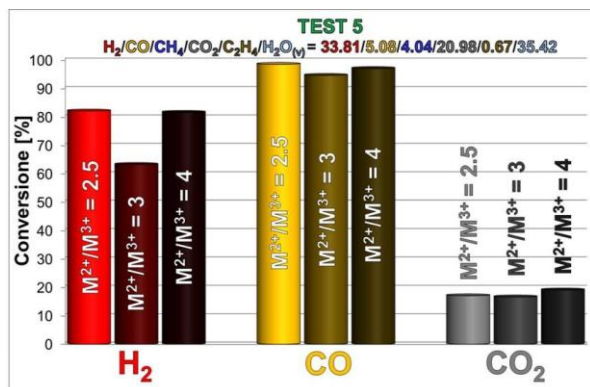
Basse rese in CH₄ e lacuna nella chiusura del bilancio al carbonio (- 20/30%p)



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

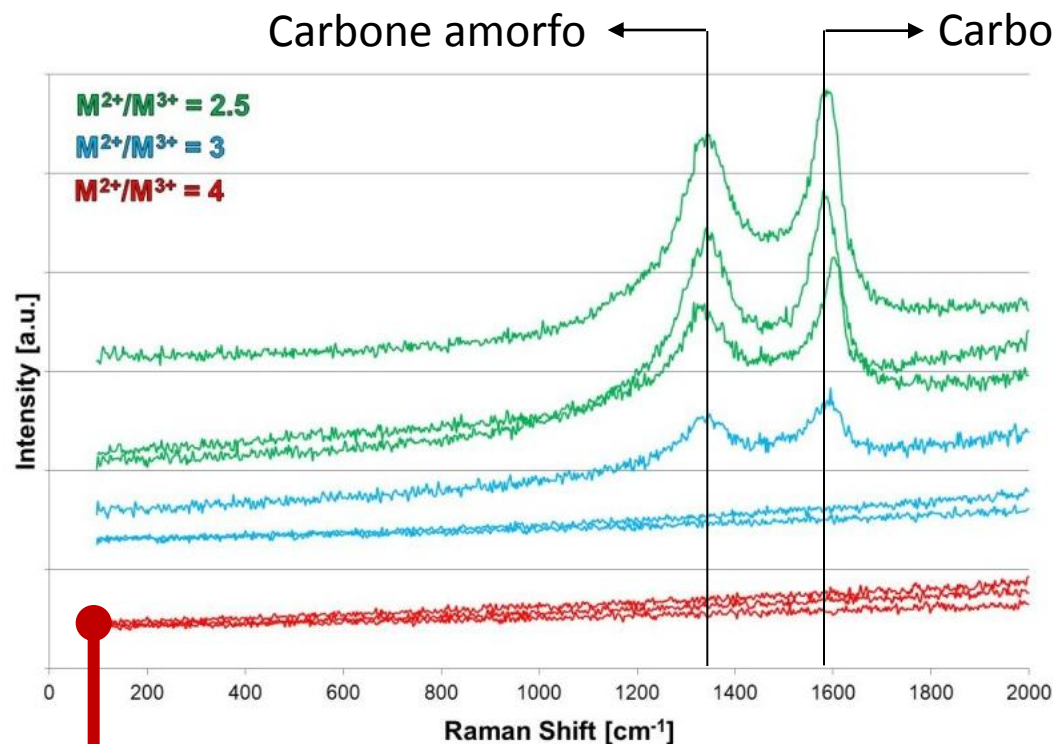


| | TEST 5 | TEST 6 | TEST 7 | TEST 8 | TEST 9 |
|--------------------------------------|--------|------------|------------|-----------------|-----------------|
| STD. | | ↓ % H_2O | ↑ % CO_2 | ↓ FLUSSO H_2O | ↑ FLUSSO CO_2 |
| T_{oven} [°C] | 300 | | | | |
| GHSV [h^{-1}] | 20000 | 20000 | 20000 | 18392 | 21170 |
| τ [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 | 5.08 | 5.75 | 4.49 | 5.56 | 4.79 |
| CH_4 | 4.04 | 4.50 | 3.69 | 4.40 | 3.79 |
| CO_2 | 20.98 | 20.92 | 24.62 | 22.84 | 25.85 |
| C_2H_4 | 0.67 | 0.75 | 0.60 | 0.73 | 0.63 |
| $H_2O(v)$ | 35.42 | 29.94 | 35.42 | 29.81 | 33.61 |



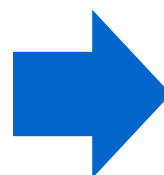
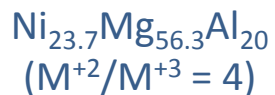
Il catalizzatore a rapporto $M(II)/M(III) = 4$ risulta il più attivo in tutte le condizioni

Formazione depositi di carbonio



| Catalizzatore | (Ni + Mg)/Al (M ²⁺ /M ³⁺) | %Ni |
|--|---|---------------------|
| Ni _{24.3} Mg _{46.7} Al ₂₉ | 2,5 | 27.5 % _p |
| Ni ₂₄ Mg ₅₁ Al ₂₅ | 3 | 27.5 % _p |
| Ni _{23.7} Mg _{56.3} Al ₂₀ | 4 | 27.5 % _p |

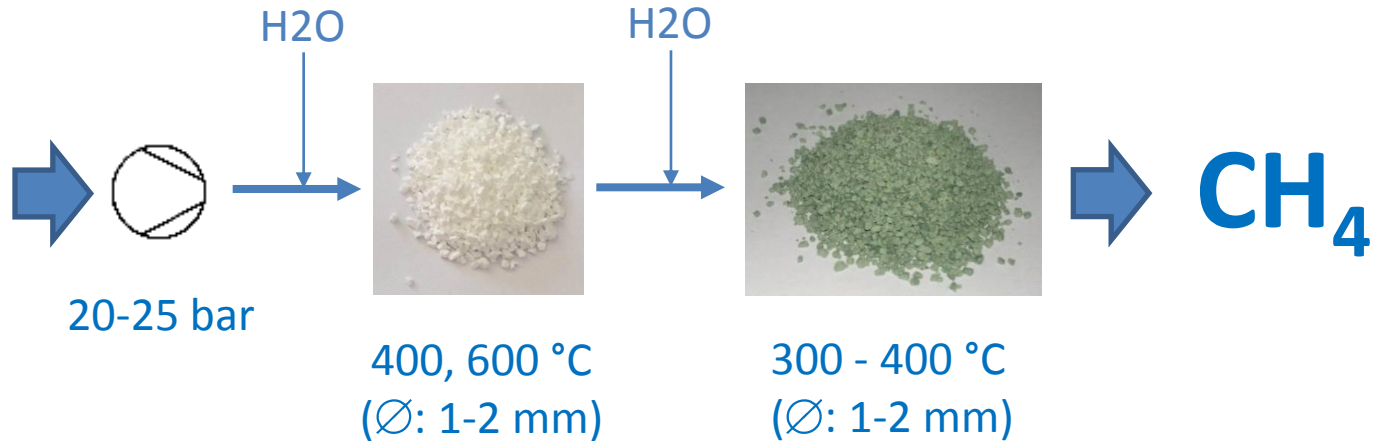
Spettri Raman ottenuti su 3 zone di campioni Ni/Mg/Al



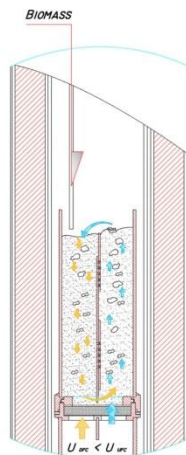
Sperimentazione su
gas reale



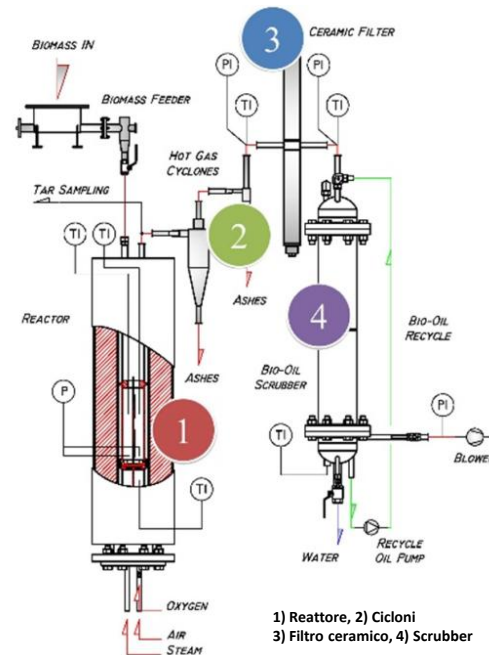
Set-up sperimentale prove con gas reale



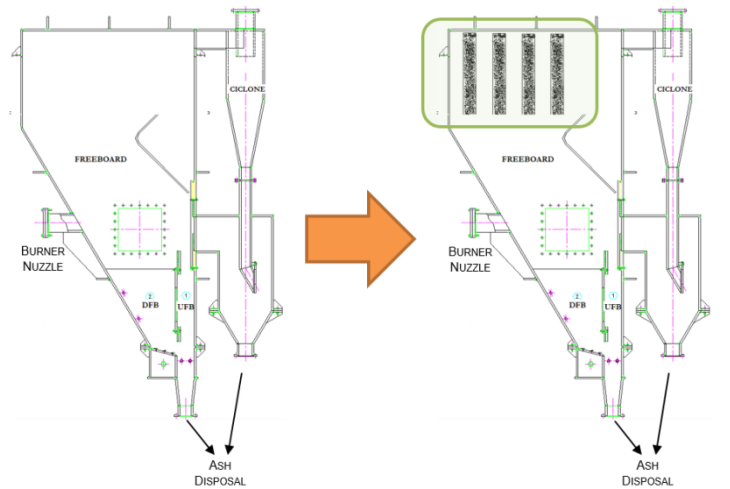
Impianto ICBFB 10 kWt



Reattore ICBFB 10 kWt



Impianto pilota di gassificazione ICBFB-1MW_t



Configurazione base

Configurazione avanzata

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

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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.

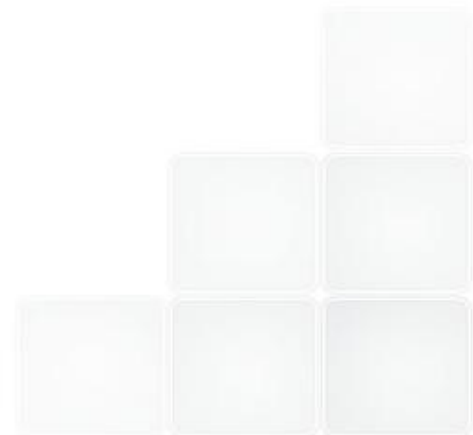
Steam/oxygen biomass gasification in a 1000 kw_{th} ICBFB pilot plant. D. Barisano, G. Canneto, F. Nanna, E. Alvino, G. Pinto, A. Villone, A. Battafarano, M. Corrado, G. Braccio. In Proceedings of the 23rd European Biomass Conference and Exhibition. 1-4 June 2015, Vienna, Austria

Diffusione risultati

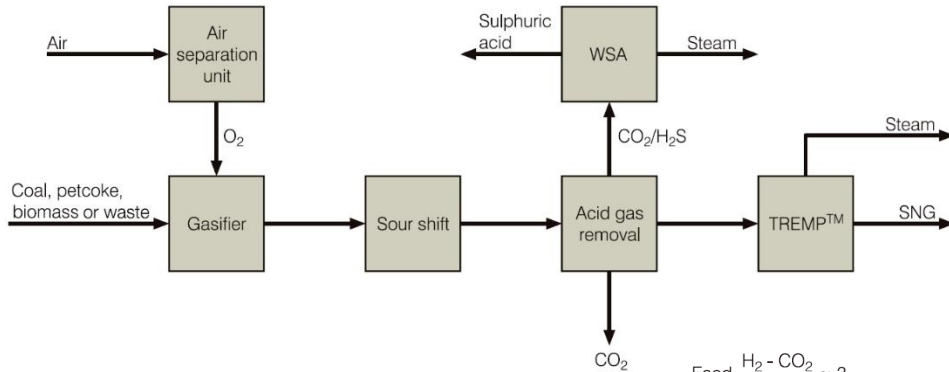


- Development of innovative catalysts for methanation of syngas deriving from biomass gasification. R. Mafessanti, D. Barisano, F. Basile, G. Fornasari, A. Vaccari. XIX Congresso Nazionale della Divisione di Chimica Industriale della Società Chimica Italiana, Salerno, 14-16 Settembre 2015.
- Production 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 CO₂ removal and H₂ 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).
- CO₂ 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.
- CO₂ 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 CO₂ 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

Grazie per l'attenzione



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



| | |
|-----------------------------|---------------|
| CH ₄ , mole-% | 94-98 |
| CO ₂ , mole-% | 0.2-2 |
| H ₂ , mole-% | 0.05-2 |
| CO, mole-% | <100 ppm |
| N ₂ + Ar, mole-% | 2-3 |
| HHV, KJ/Nm ³ | 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.

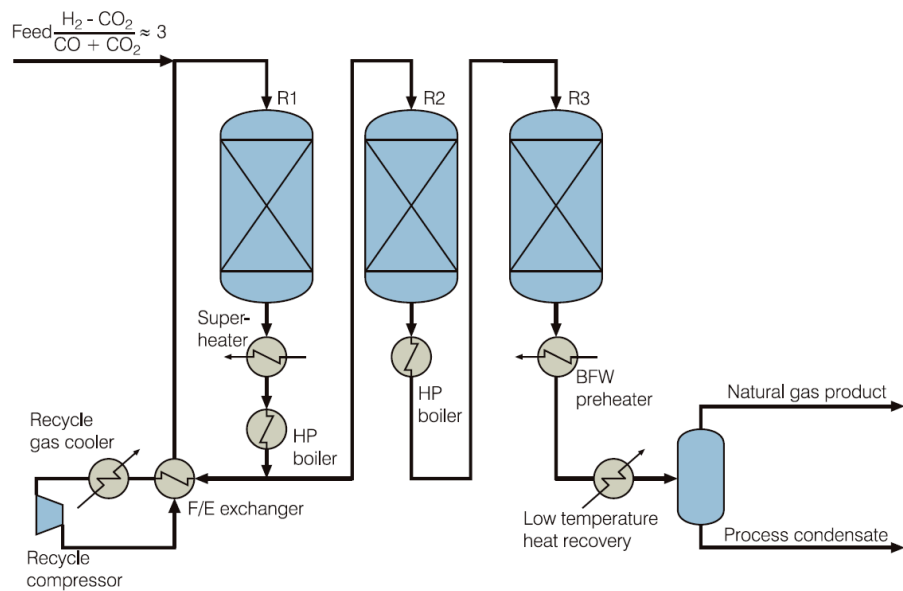


Figure 3: Example of the Topsoe TREMP™ technology.

http://topsoe.ru/business_areas/gasification_based/Processes/~media/PDF%20files/SNG/Topsoe_TREMP.ashx