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

MINISTERO DELLO SVILUPPO ECONOMICO

Comunicazione e diffusione dei risultati sulle attività ENEA sul P2G/L nell'ambito del WP3 - Allegato

E.Giacomazzi, F.R. Picchia

Allegato al
Report RdS/PTR2019/136

COMUNICAZIONE E DIFFUSIONE DEI RISULTATI SULLE ATTIVITÀ ENEA SUL P2G/L NELL'AMBITO DEL WP3 - ALLEGATO

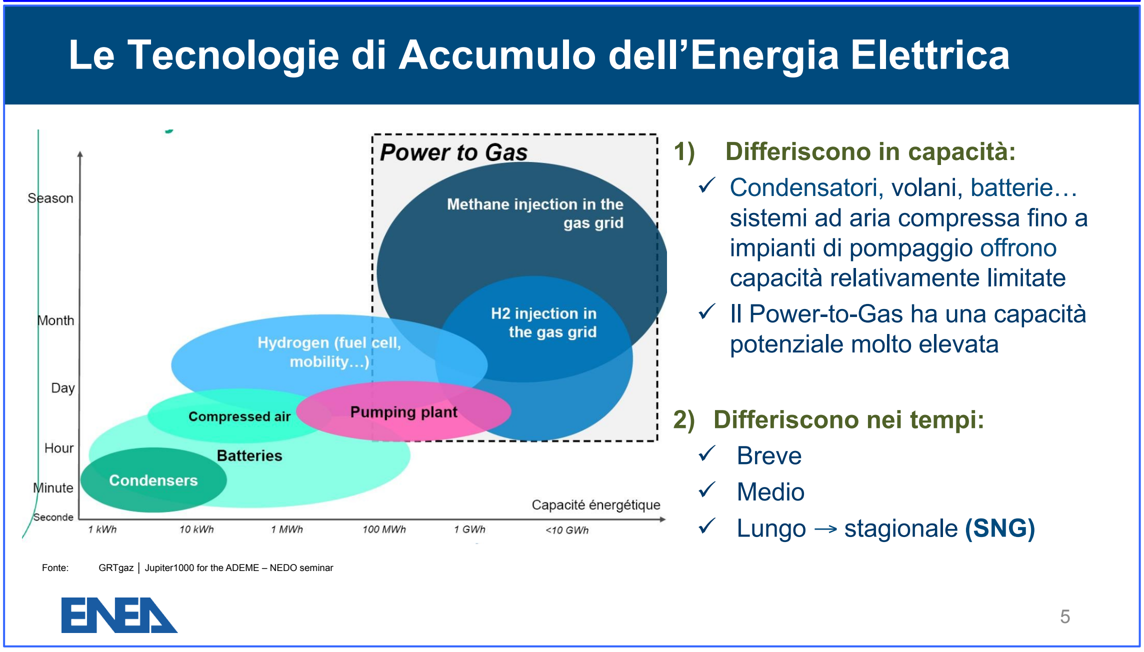
E.Giacomazzi, F.R. Picchia – DTE-PCU-IPSE, ENEA

Dicembre 2019

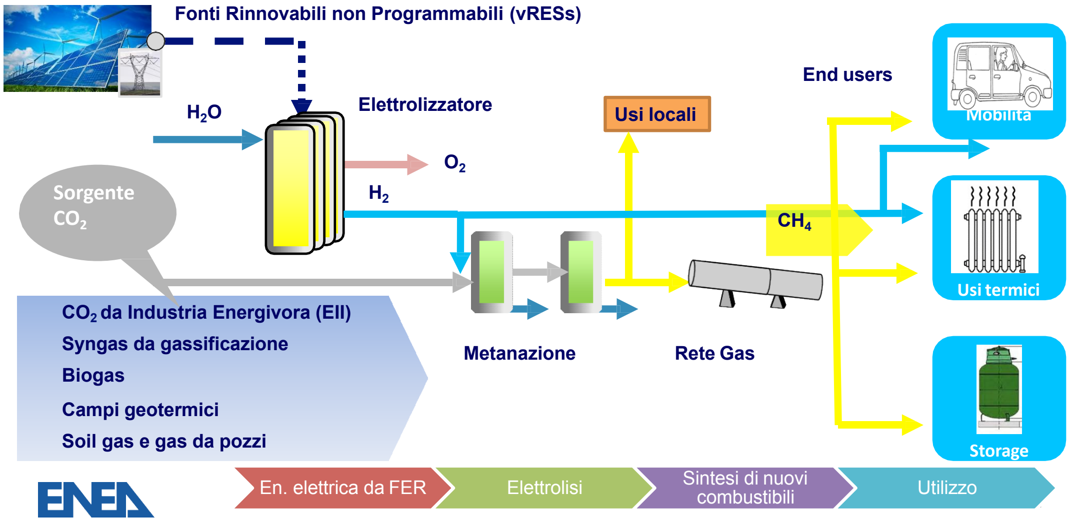
Report Ricerca di Sistema Elettrico

Accordo di Programma Ministero dello Sviluppo Economico - ENEA
Piano Triennale di Realizzazione 2019-2021 - I annualità
Obiettivo: *Tecnologie*
Progetto: Tema 1.2 "Sistemi di accumulo, compresi elettrochimico e power to gas, e relative interfacce con le reti"
Work package: WP3 "Power-to-Gas"
Linea di attività: LA3.34 Comunicazione, diffusione dei risultati e coordinamento sulle attività ENEA su P2G/L e integrazione con sistemi generazione elettrica innovativi - I Anno
Responsabile del Progetto: Giulia Monteleone ENEA
Responsabile del Work Package: Eugenio Giacomazzi ENEA

Si riportano alcune slide di presentazioni e poster realizzati nell'ambito del progetto.



Il Power To Gas (P2G)



La produzione di H2: Elettrolisi dell'acqua

	Alkaline electrolysis	PEM electrolysis	SOEC Solid oxide electrolysis
State of development	Commercial	Commercial	Laboratory
Electrolyte	OH-	Solid polymer membrane (Nafion)	ZrO_2 ceramic doped with $Y_2O_3O^{2-}$
Power consumption $kWhe/Nm^3H_2$	4.5-7	4.5-7	3
Efficiency	67-70 %	60-80 %	90 %
Investment cost €/kWe	800-1000	1400-2100	>2000[a]

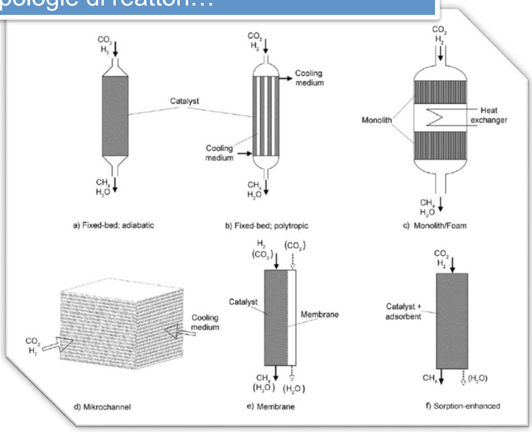
[a] High uncertainty due to pre-commercial status of SOEL
Source: Renewable and Sustainable Energy Reviews 82 (2018) 2440–2454

HySTAT™ Cell Stack

12

Metanazione catalitica: i reattori

Diverse tipologie di reattori…



Source: Renewable and Sustainable Energy Reviews 81 (2018) 433–446

Reazione altamente esotermica

Lo smaltimento del calore e il controllo della temperature sono fondamentali per la progettazione dei reattori

16

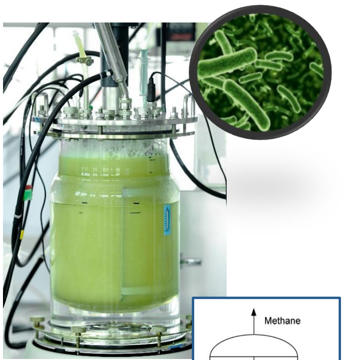
Metanazione biologica

La produzione di metano a partire da CO2 è attuata da microorganismi di diverse famiglie (p.es. : **archea**).

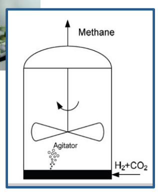
Il processo ha luogo in soluzione acquosa a temperature dell'ordine dei 40 -70 °C.

Lo stadio limitante è il trasferimento di massa dell'idrogeno nella fase liquida.

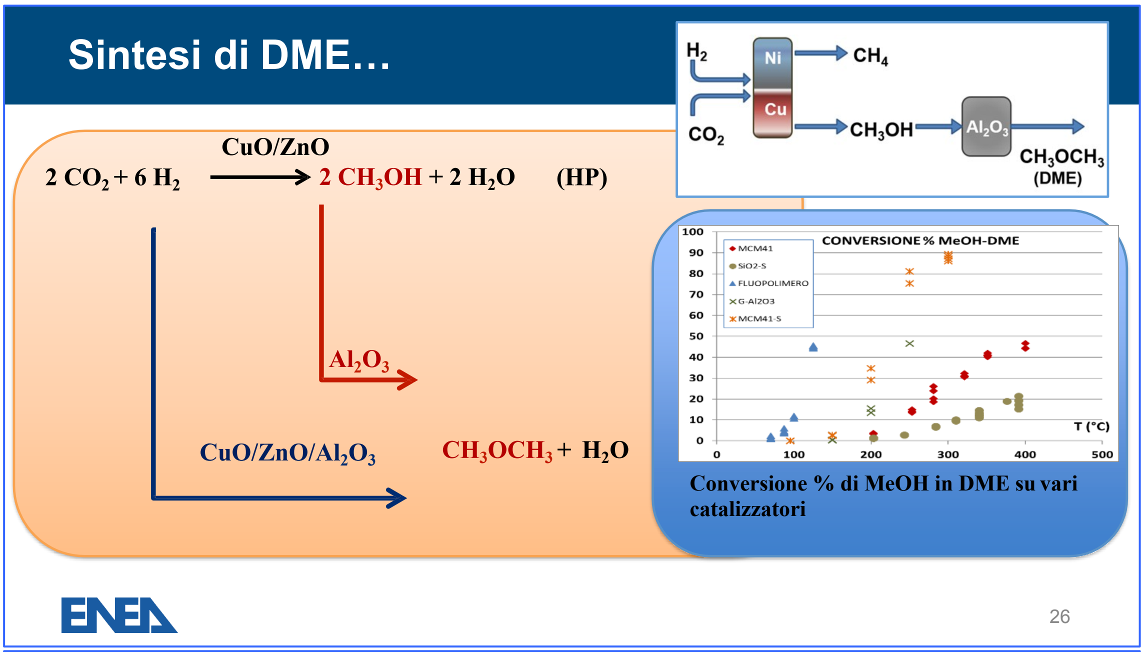
Reattori CSTR o a bolle sono quelli più utilizzati.

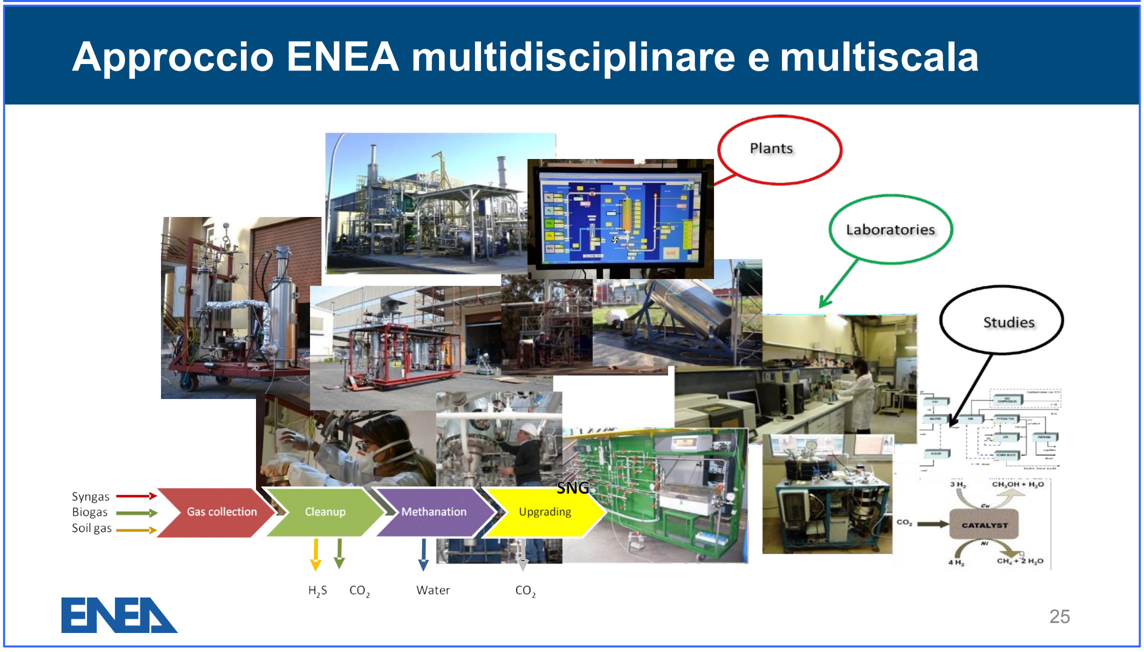


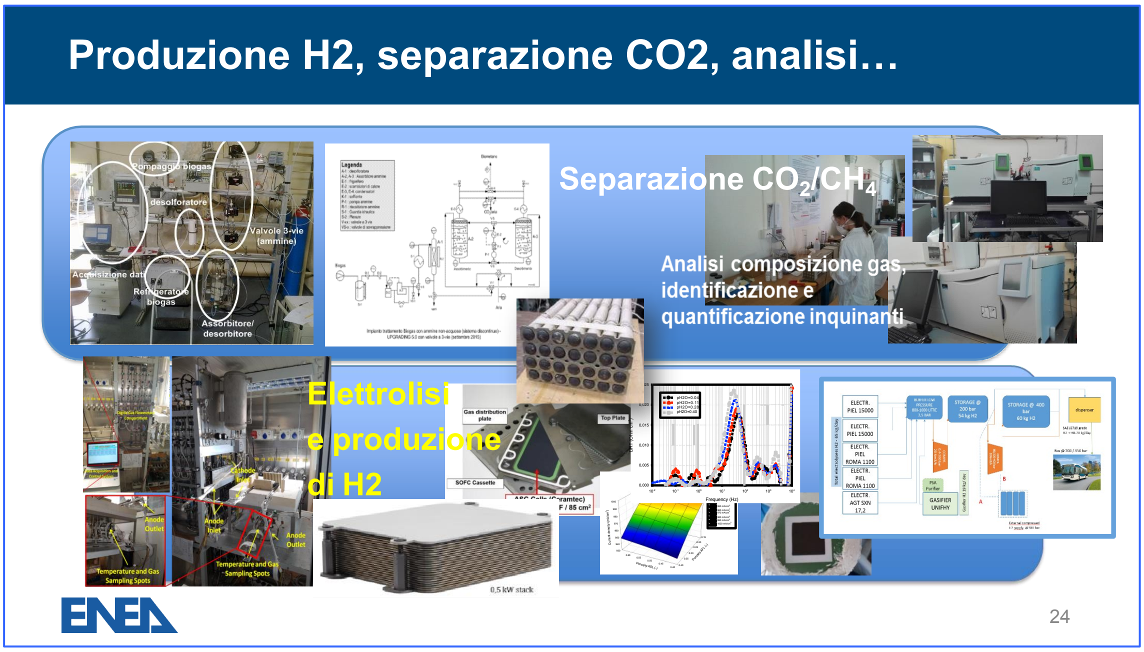
©Electrochaea GmbH



18


Sintesi di DME…
H2
Ni
CH4
Cu
CO2
CH3OH
Al2O3
CH3OCH3
(DME)
CuO/ZnO
2 CO2 + 6 H2 → 2 CH3OH + 2 H2O (HP)
Al2O3
CuO/ZnO/Al2O3
CH3OCH3 + H2O
CONVERSIONE % MeOH-DME
MCM41
SiO2-S
FLUOPOLIMERO
G-Al2O3
MCM41-S
T (°C)
Conversione % di MeOH in DME su vari catalizzatori
ENEA
26


Approccio ENEA multidisciplinare e multiscala
Plants
Laboratories
Studies
Syngas
Biogas
Soil gas
Gas collection
Cleanup
Methanation
Upgrading
SNG
H2S
CO2
Water
CO2
CATALYST
ENEA
25


Produzione H2, separazione CO2, analisi…
Separazione CO2/CH4
Analisi composizione gas, identificazione e quantificazione inquinanti
Elettrolisi e produzione di H2
desolforatore
Valvole 3-vie (ammine)
Acquisizione dati
Assorbitore/ desorbitore
0,5 kW stack
24

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

ALMA · UNIVERSITAS · STUDIORUM · PARMENSIS · A.D. 962

P2G: From Hydrogen To Oxygenated Fuels

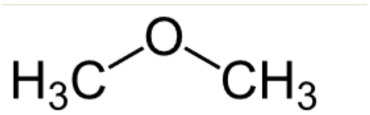
First Italian Conference on Carbon Dioxide Capture and Utilization
Bari, 6/12/2019

Francesco Pancrazzi, **Vincenzo Barbarossa, Raimondo Maggi e Rosanna Viscardi**

DME as an Alternative Fuel

	DME	Methane	Methanol	Ethanol	FTD	LPG	Gasoline	Diesel	Hydrogen
Molecular Weight (g mol^{-1})	46.07	16.04	32.04	46.07		44.1	114	198.4	2.016
Density (g cm^{-3})	0.67^{c}	0.00072^{b}	0.792^{b}	0.785^{b}	0.76-0.79^{e}	0.54^{e}	0.71-0.77^{e}	0.80-0.86^{b}	0.00089^{e}
Normal boiling point (°C)	-24.9	-162	64	78	180-320^{e}	-30^{e}	0-210^{e}	125-400	-253^{e}
Octane Number (RON)	-	122	110	110	-	90-96	90-100	-	>125
Cetane Number	55-60	-	5	-	55-75	-	-	40-55	-
Energy content^{e} (MJ/kg)	28,43	50	19.5	28,4	44	46.3	42.7	43.1	119.9
Carbon Content^{f} (wt%)	52.2	74	37.5	52.2	85^{e}	82^{e}	85.5	87	0
Sulfur Content^{f} (ppm^{g})	0	~7-25	0	0		10-50	~200	~250	0

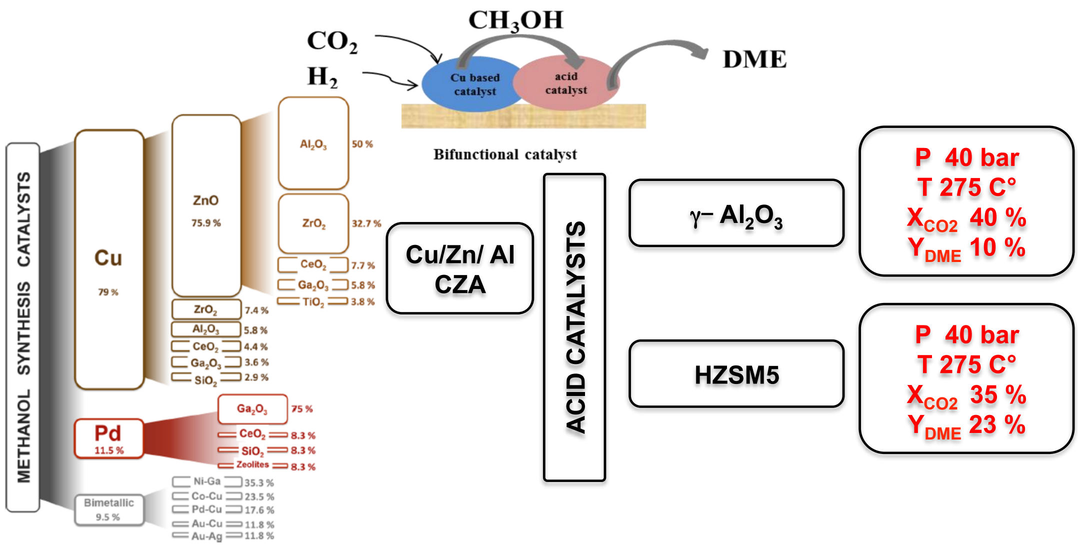
- ❖ High cetane number
- ❖ High oxygen content
- ❖ Low particulate emissions



Università degli Studi di Parma

3

Direct DME synthesis



Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO_2 Hydrogenation Processes, *Chem. Rev.* 2017, 117, 14, 9804-9838

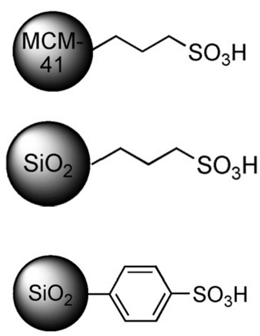
Università degli Studi di Parma 4

A new class of unconventional acid catalysts

- Sulfonic catalysts are materials composed of an inorganic support such as mesoporous silica or amorphous silica functionalyzed with a sulfonic acid groups

- They own acidic strenght similar to sulfuric acid

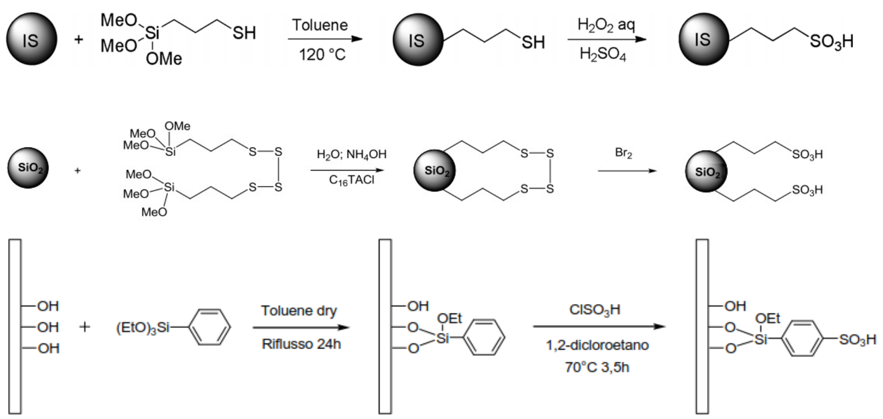
- Chep materials, easy to work with and easy to recycle.



Different functionalizations are possible due to different organic functions

Università degli Studi di Parma 7

Sulfonic catalysts synthesis

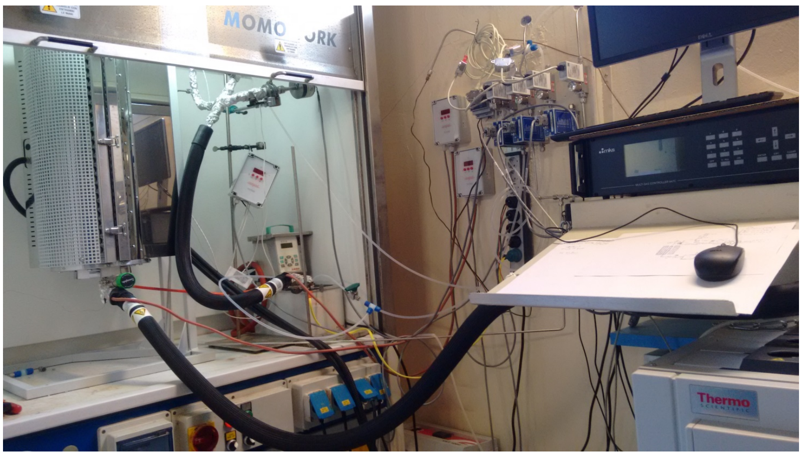


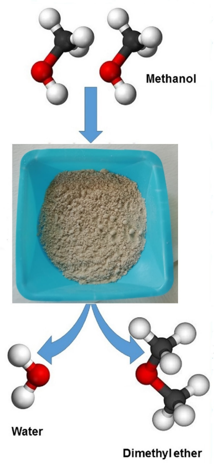
Safe reaction conditions and simple work-up

Università degli Studi di Parma

8

Experimental apparatus for DME synthesis





Temperatura reazione (°C)	Pressione (atm)	Flusso di N_2 (mL/min)	Flusso MeOH(g) (mL/min)
100-450	1	10	0.9-1.7

Y_{DME} = 2 mol DME / (mol MeOH)°

Università degli Studi di Parma

11

RICERCA DI SISTEMA ELETTRICO

CATALYTIC CONVERSION OF METHANOL TO DIMETHYL ETHER (DME) OVER SUPPORTED SULFONIC ACIDS CATALYSTS

Rosanna VISCARDI*[1], Vincenzo BARBAROSSA[1], Daniele MIRABILE GATTIA[1], Raimondo MAGGI[2], Giovanni MAESTRI[2], Emanuele PARIS[2]

[1]Casaccia Research Center, ENEA, Italy , [2]University of Parma, Italy

*rosanna.viscardi@enea.it

3rd International Conference on Applied Surface Science
Pisa June 17-20 , 2019

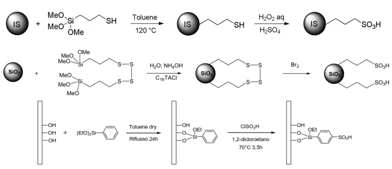
Italian National Agency for New Technologies, Energy and Sustainable Economic Development

1. Background and objectives

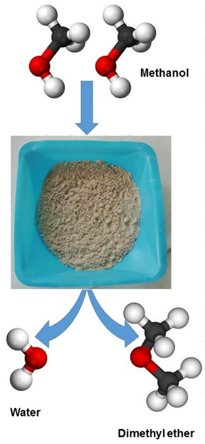
Dimethyl ether (DME) is a promising multisource and multipurpose clean fuel and value-added chemical synthesized from syngas. This process can be either performed in a single stage (direct process) using a dual catalysis system or a two stage (indirect process) where syngas is first converted into methanol and then dehydrated to produce DME. Despite tremendous efforts, catalytic synthesis of DME via a high efficient route remains a great challenge. Catalyst design is at the heart of enhancing the catalytic efficiency of DME synthesis The selection of an appropriate catalyst for methanol dehydration is dependent on a number of factors as acid strength and characteristics, pore size and morphology, temperature resistance and active temperature range, and toxicity and coking resistance. These factors must be weighted with the cost effectiveness of a given catalytic material. It is expected that the ideal catalyst will possess adjustable acid strength, structure, and promising mechanical and hydrothermal stability. Even though **modified alumina** and **zeolite** are the more obvious choices, they do not satisfy all these criteria. **Alumina** is an inexpensive and active catalyst for DME synthesis with a promising mechanical strength; however, its hydrophilicity is one of the major drawbacks. **Zeolites**, on the other hand, offer a high hydrothermal stability but the presence of strong acid sites which lead to the formation of by-products and coke is their most common challenge. We propose a new class of SO_3H-functionalized materials with tunable Lewis and Brønsted acid sites, as efficient catalysts to perform the methanol dehydration process.

2. The catalysts

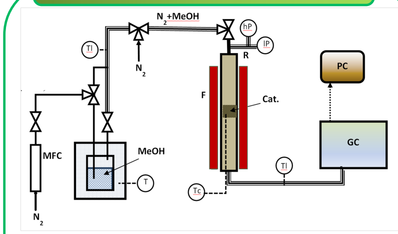
The catalysts tested are **sulfonic acids** grafted on inorganic support such as SiO_2 and MCM-41.



- Cheap materials, safe to handle, and easy to recycle
- Tunable acid strength with the support's functionalization
- Mild reaction conditions
- Work-up steps very easy



3. Experimental set-up



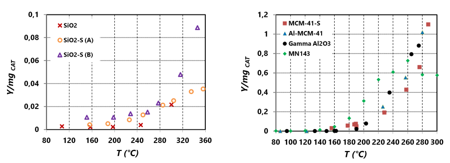
A flow of nitrogen saturated with **methanol at 20°C** was fed to the reactor operating at temperatures between **100°C and 450°C and 1 bar** .

4.Physico-chemical properties

Catalyst	Surface Area (m^2/g)	Surface Acidity (meq H^+ /g)
$\gamma - Al_2O_3$	250	-
SiO_2	540	-
MCM-41	1240	-
Al-MCM-41	940	-
MCM-41-$(CH_2)_3$-SO_3H	970	2.53
SiO_2-$(CH_2)_3$-SO_3H (A)	510	0.23
SiO_2-$(CH_2)_3$-SO_3H (B)	490	0.60
SiO_2-Al_2O_3 – C_6H_4 –SO_3 H (MN143)	371	0.90

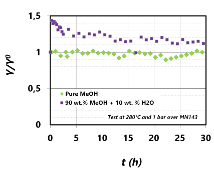
- Increase of acidity for the functionalized catalysts
- Lower surface area for the MCM-41 supported sulfonic acid

5. MeOH Conversion



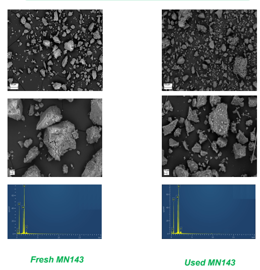
- The functionalization with sulfonic groups increases the dehydration activity of inorganic supports.
- At lower temperatures MN143 is more active than commercial catalysts.

6. Stability Test



- High stability of MN143 catalyst
- Very slow deactivation with H_2O

7. SEM Analysis



The presence of sulfur confirmes that the organic moiety containing the sulfonic groups have not been removed during the process ⟶ high thermal stability

8. Conclusion

- The new class of supported sulfonic acids is very interisting and promising as catalysts for the methanol dehydration.
- The introduction of sulfonic groups results in a simple and powerful way to modulate the catalytic activity in inorganic materials.
- These materials are very active, selective and stable catalysts for this process.
- The catalytic activity of MN143 was higher than those of the reference commercial catalysts.

Italian National Agency for New Technologies, Energy and Sustainable Economic Development

Le Tecnologie Power to Gas per l’Utilizzo Innovativo delle Reti Energetiche

Ing. Paolo Deiana

Dipartimento Tecnologie Energetiche – PCU – IPSE

Centro Congressi Fondazione CARIPLO – Auditorium Giacomo Manzù – Milano, 12-13 giugno 2019

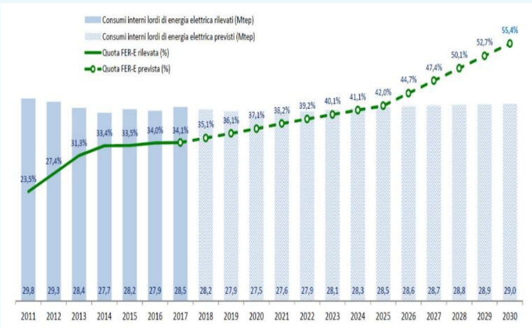
UNI-CIG 2019 FORUM

IL SISTEMA GAS-EUROPA

UNA VISTA POLIEDRICA SUL SISTEMA MULTI-GAS

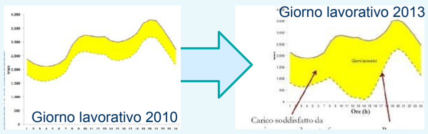
Le FER e l’Accumulo Energetico

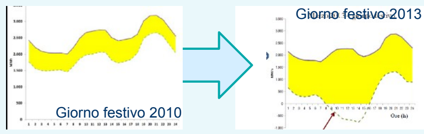
2019 PNIEC FER nei consumi elettrici 55% al 2030 (34% al 2017)



Le Tecnologie di Accumulo dell’Energia possono contribuire al peak shaving delle FER variabili (eolico e solare) evitando le fluttuazioni temporali che possono causare surplus o deficit nella fornitura di energia.

Profili di produzione giornaliera Sud Italia





Una maggiore penetrazione nel mercato di sistemi di produzione di energia elettrica da fonte rinnovabile comporta il contestuale <u>sviluppo di sistemi di accumulo</u>, giornaliero e stagionale, dell’energia prodotta.

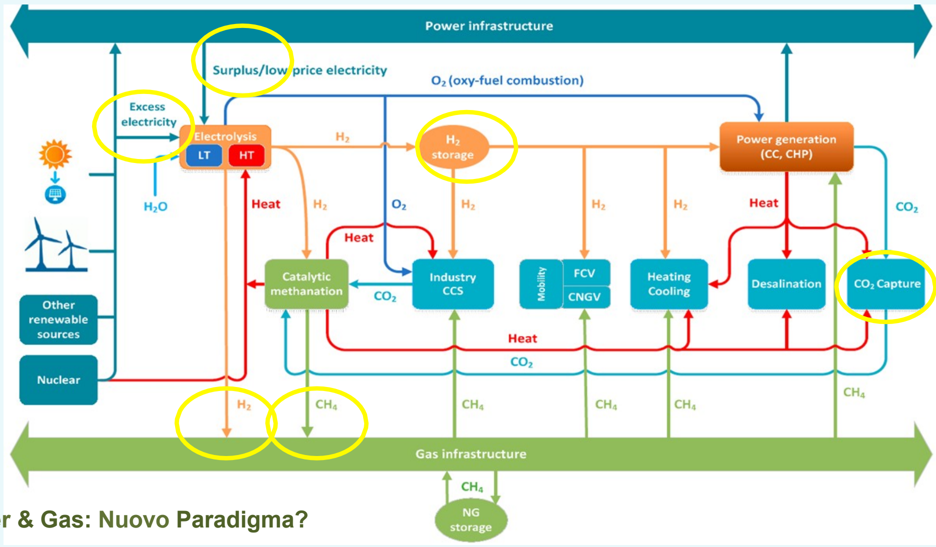
4/18

UNI-CIG 2019 FORUM

IL SISTEMA GAS-EUROPA

UNA VISTA POLIEDRICA SUL SISTEMA MULTI-GAS

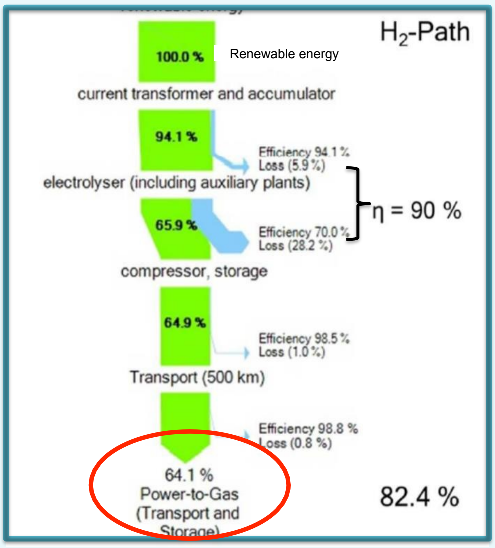
Le Reti Energetiche verso Utilizzi Innovativi

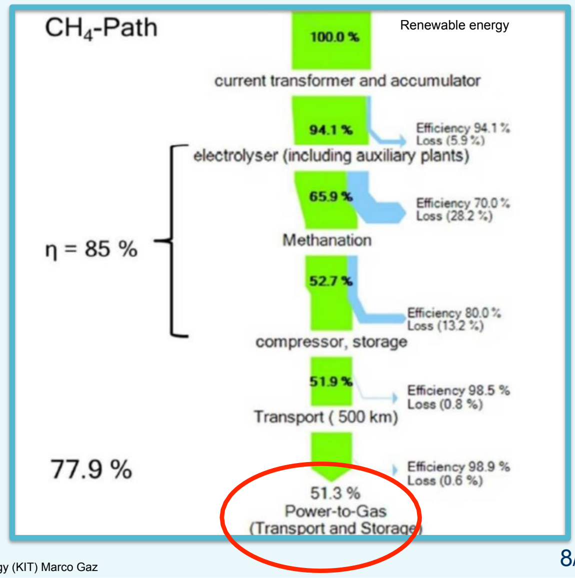


Reti Power & Gas: Nuovo Paradigma?

6/18

Efficienza dei processi P2H e P2M





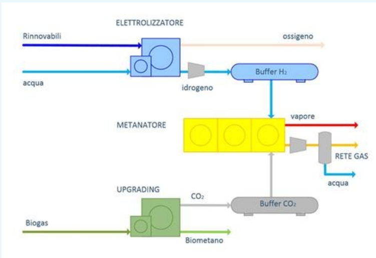
Source DVGW Research Center at Engler-Bunte-Institut of Karlsruhe Institute of Technology (KIT) Marco Gaz

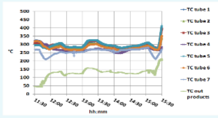
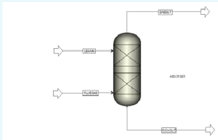
8/18

Background sulle tecnologie P2G

- Testing su sistemi e componenti in taglia significativa (elettrolisi, metanazione…)
- Sperimentazione su catalizzatori Ni/Ru commerciali su scala lab/pilota
- Modellazione di sistema, analisi di sostenibilità ambientale/economica
- Coordinamento di progetti di R&I, collaborazioni con Industria/Università
- Technology transfer, brevetti, supporto A.P. e Policy Maker



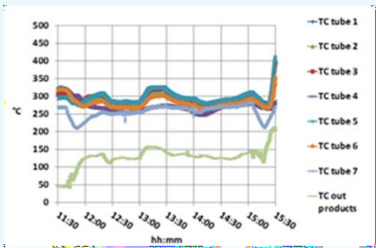
15/18

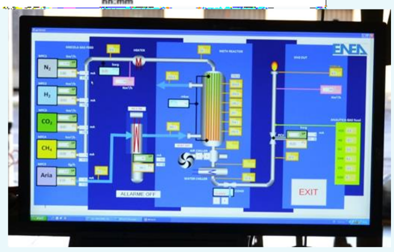
UNI-CIG 2019 FORUM

IL SISTEMA GAS-EUROPA
UNA VISTA POLIEDRICA
SUL SISTEMA MULTI-GAS

Elettrolizzatore e Metanatore in linea

Source: ENEA Casaccia Research Center





16/18

UNI-CIG 2019 FORUM

IL SISTEMA GAS-EUROPA
UNA VISTA POLIEDRICA
SUL SISTEMA MULTI-GAS

Italian National Agency for New Technologies, Energy and Sustainable Economic Development

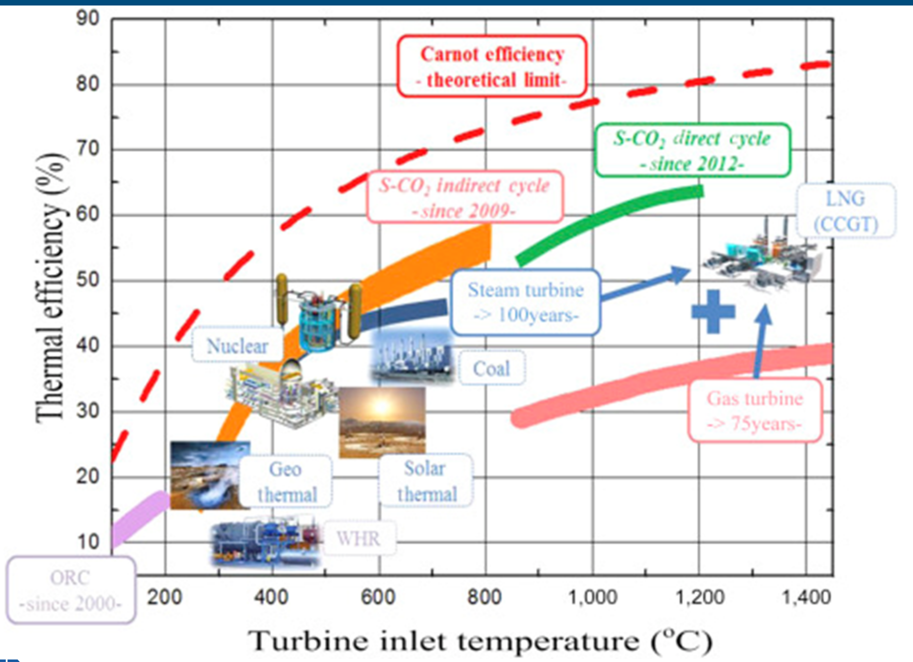
Supercritical CO_2 Power Cycles …a jump in the future

CO_2 Club Italy Open Forum

Rome, 16 April 2019

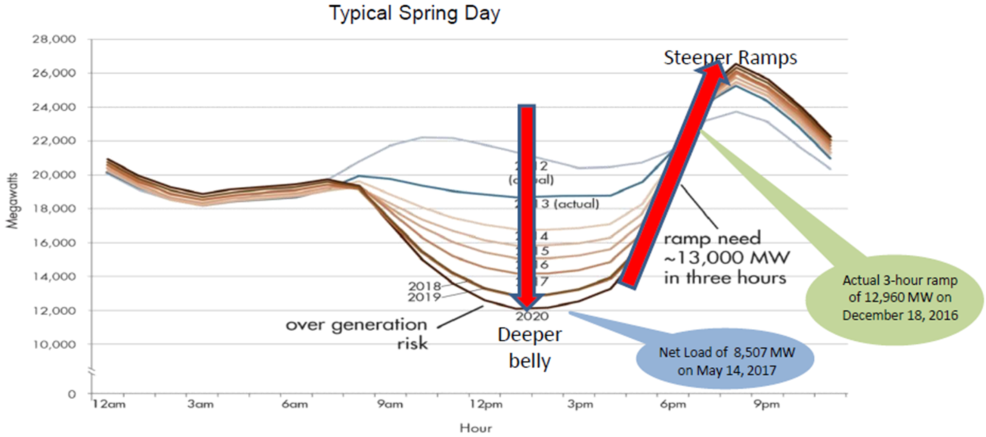
Giuseppe Messina
Process and Energy Systems Engineering Laboratory

Supercritical CO_2 Power Cycles: what are they?



Supercritical CO_2 Power Cycles: why care?

Actual net-load and 3-hour ramps are approximately four years ahead of ISO's original estimate



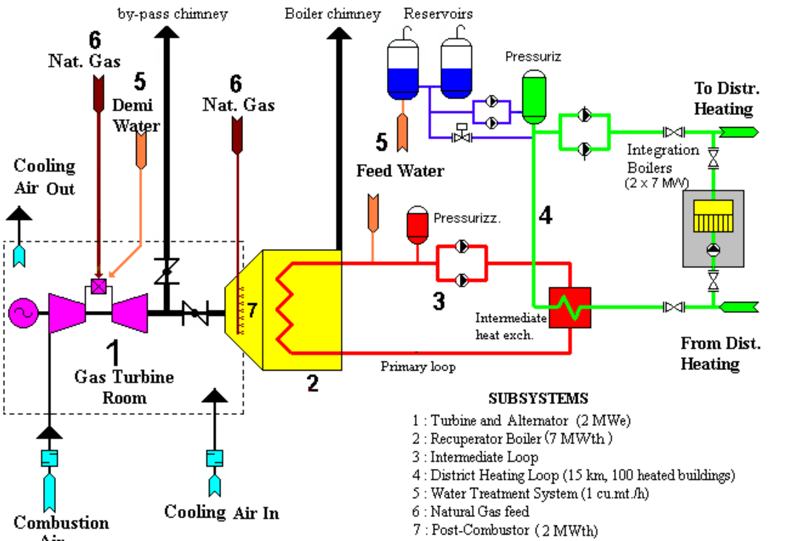
ISO Public 9 Terna

ENEA 9

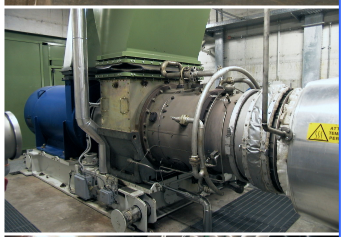
Supercritical CO2 Power Cycles …a jump in the future - CO_2 Club Italy Open Forum – Rome – 16 April 2019

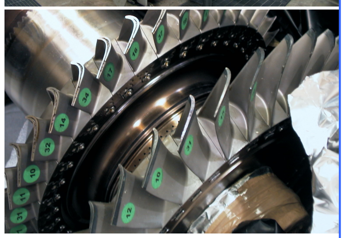
Supercritical CO_2 Power Cycles: how is it going?

ENEA facilities ready to involve in a H2020 demonstration project



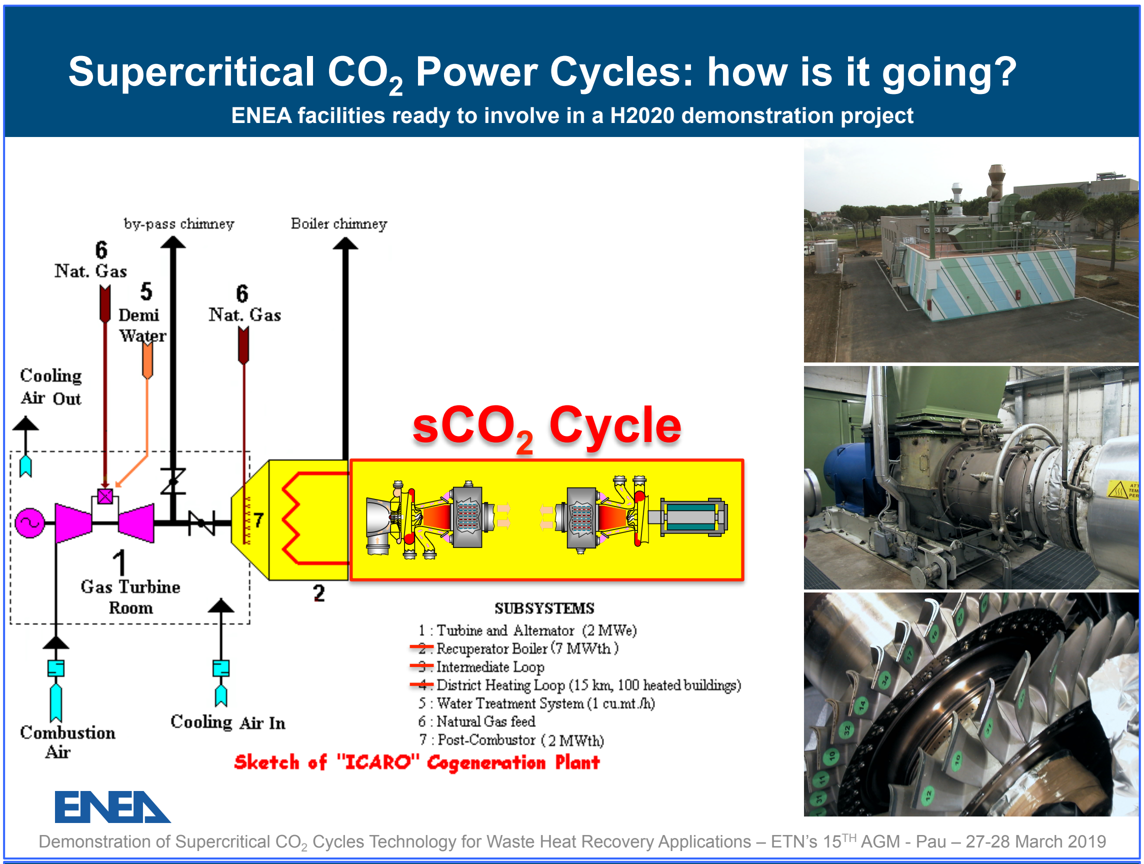
Sketch of "ICARO" Cogeneration Plant

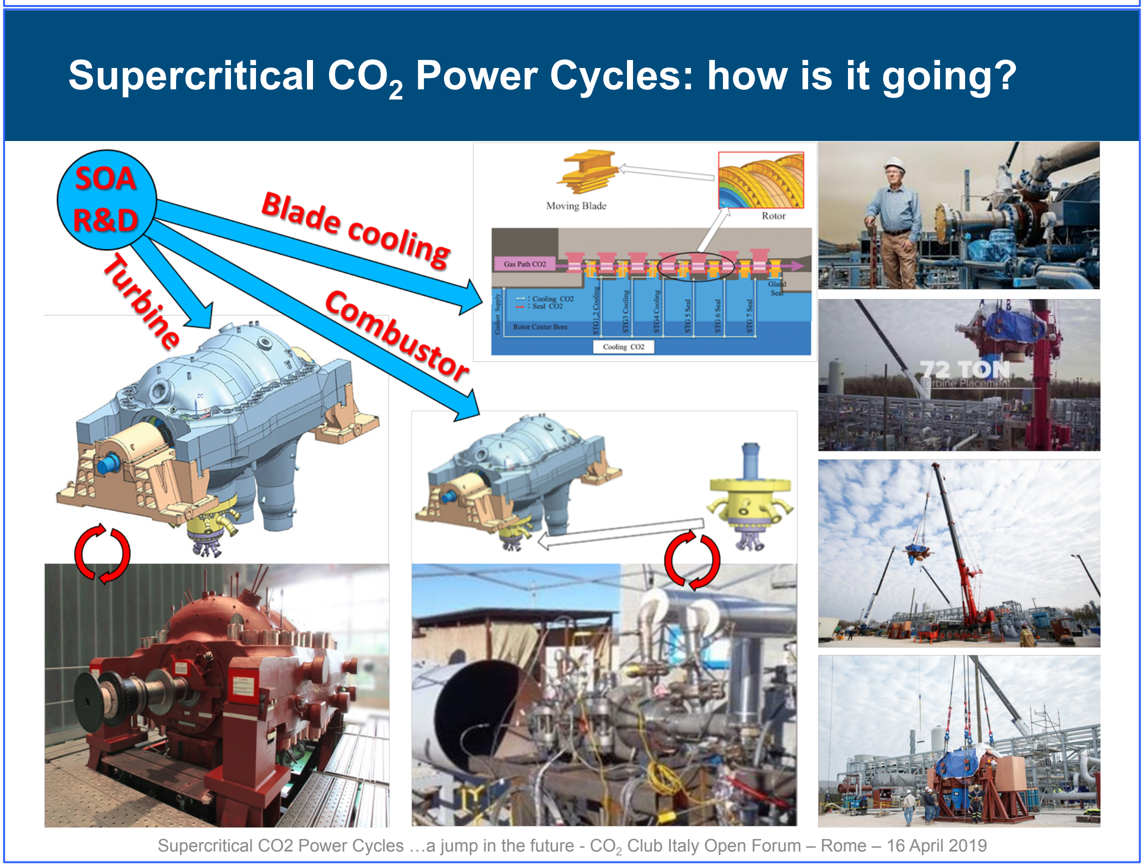




ENEA

Demonstration of Supercritical CO_2 Cycles Technology for Waste Heat Recovery Applications – ETN's 15[TH] AGM - Pau – 27-28 March 2019


Supercritical CO2 Power Cycles: how is it going?
ENEA facilities ready to involve in a H2020 demonstration project
by-pass chimney
Boiler chimney
6
Nat. Gas
5
Demi Water
6
Nat. Gas
Cooling Air Out
sCO2 Cycle
7
1
Gas Turbine Room
2
Combustion Air
Cooling Air In
SUBSYSTEMS
1 : Turbine and Alternator (2 MWe)
2 : Recuperator Boiler (7 MWth)
3 : Intermediate Loop
4 : District Heating Loop (15 km, 100 heated buildings)
5 : Water Treatment System (1 cu.mt./h)
6 : Natural Gas feed
7 : Post-Combustor (2 MWth)
Sketch of "ICARO" Cogeneration Plant
ENEA
Demonstration of Supercritical CO2 Cycles Technology for Waste Heat Recovery Applications – ETN's 15TH AGM - Pau – 27-28 March 2019


Supercritical CO2 Power Cycles: how is it going?
SOA
R&D
Blade cooling
Turbine
Combustor
Moving Blade
Rotor
Cooling CO2
72 TON
Supercritical CO2 Power Cycles …a jump in the future - CO2 Club Italy Open Forum – Rome – 16 April 2019

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

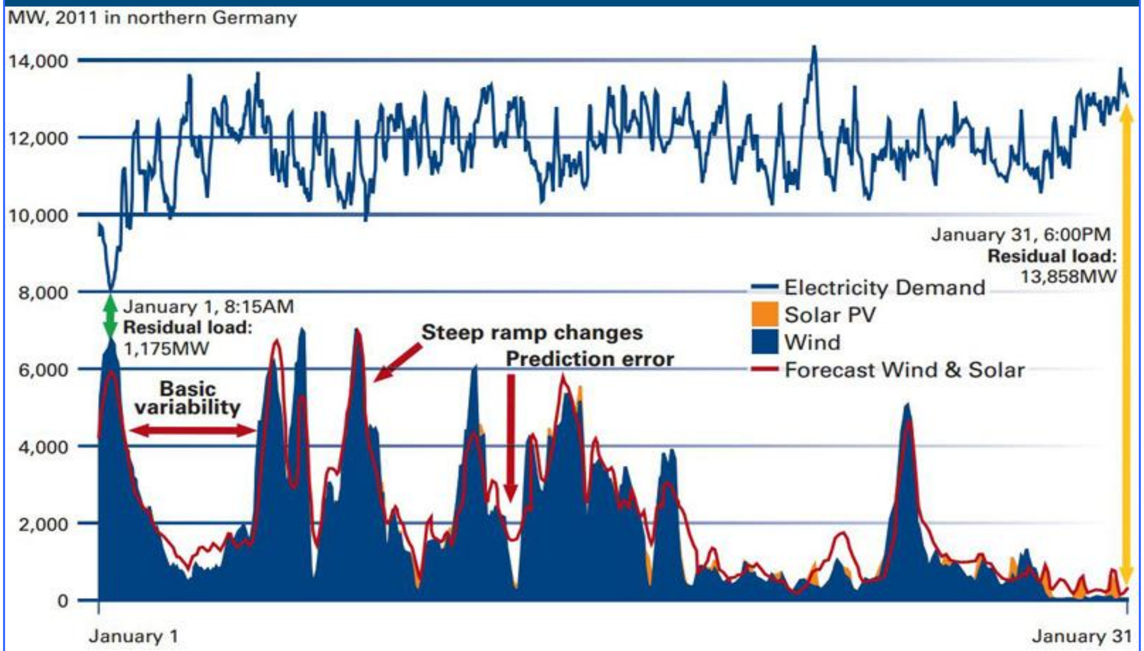
I problemi di rete, gli accumuli e la gestione delle FER ELETTRICHE

Piano Nazionale Energia e Clima
Seminario FILCTEM - CGIL

Roma, 24 ottobre 2019

Giuseppe Messina
Laboratorio Ingegneria dei Processi e dei Sistemi per l'Energia

Incremento della penetrazione delle FER variabili
flessibilità e adeguatezza del sistema elettrico

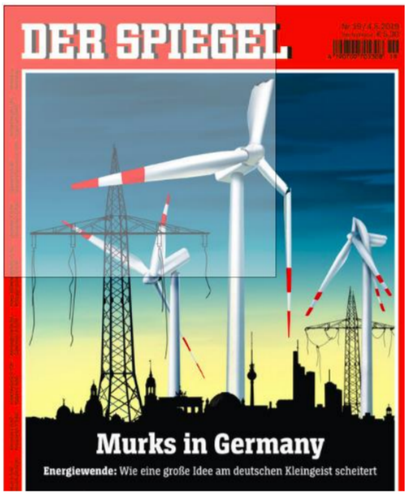


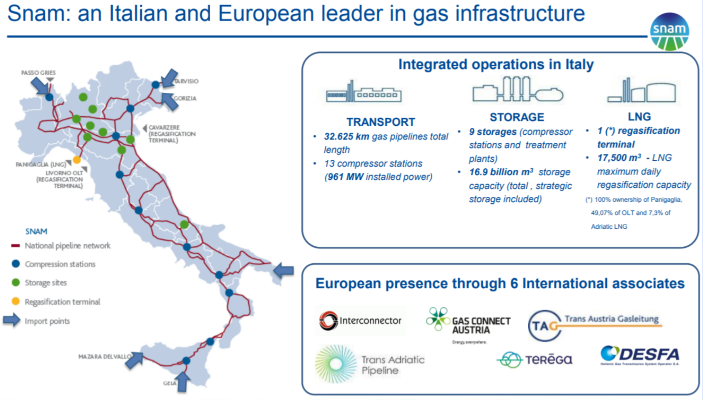
ENEA 8

Piano Nazionale Energia e Clima - Seminario FILCTEM – CGIL – Roma 24 ottobre 2019

Incremento della penetrazione delle FER variabili

accoppiamento delle reti elettrica e gas





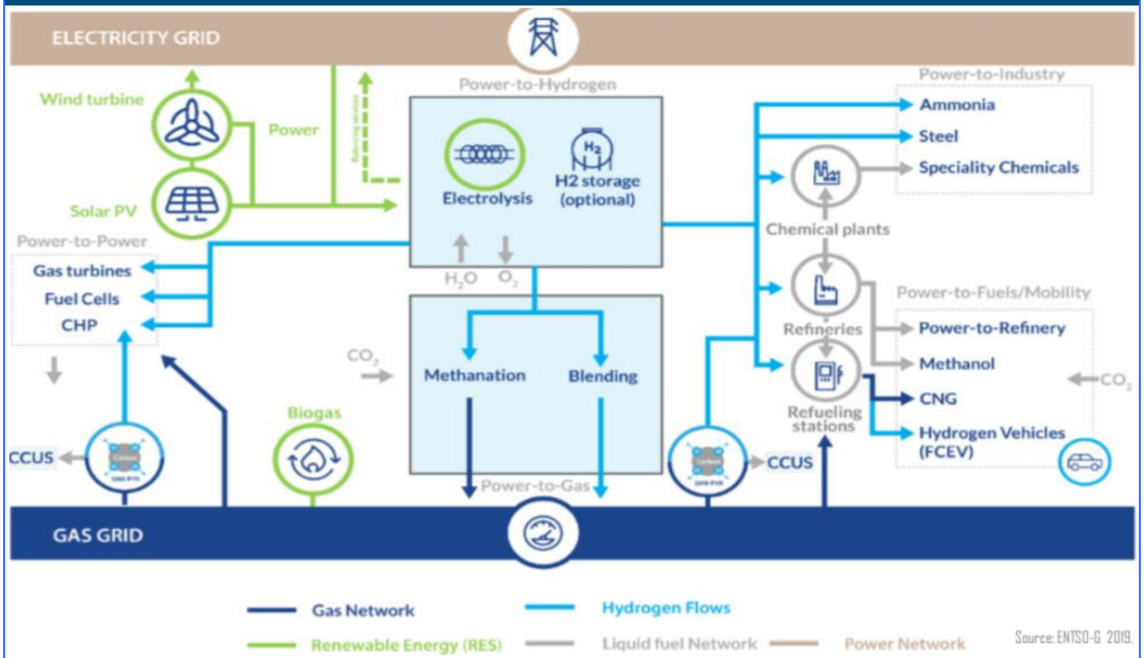
10 anni fa la Germania ha deciso di ampliare la rete elettrica

Pianificati:	7700 km
Realizzati:	950 km
Realizzati nel 2017:	30 km

Gas pipeline Φ 120 = 8 x 3GW elettrodotti

Incremento della penetrazione delle FER variabili

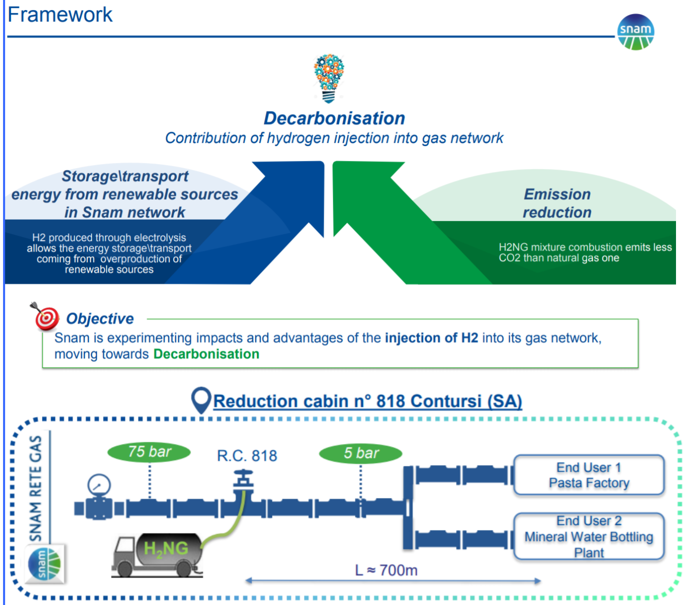
accoppiamento delle reti elettrica e gas – accumulo e decarbonizzazione: Power-to-Gas



Source: ENTSO-G 2019.

Incremento della penetrazione delle FER variabili

accoppiamento delle reti elettrica e gas – accumulo e decarbonizzazione: Power-to-Gas



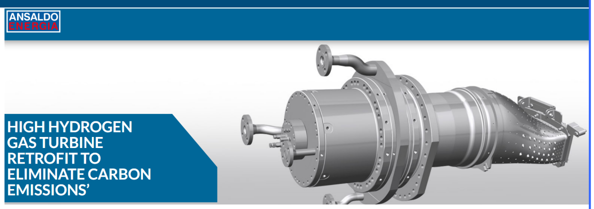
SNAM ha completato con successo la sperimentazione dell'iniezione di H2 al 5% in volume in una porzione di gasdotto asservito a due utenze industriali

ENEA 13

Piano Nazionale Energia e Clima - Seminario FILCTEM – CGIL – Roma 24 ottobre 2019

Incremento della penetrazione delle FER variabili

accoppiamento delle reti elettrica e gas:
incremento della flessibilità di combustibile nelle turbine a gas



L'obiettivo principale del progetto High Hydrogen Retrofit è quello di sviluppare un retrofit di sistema di combustione a emissioni ultra-basse (sotto 9ppm NOx e CO) a basso costo per le turbine a gas esistenti nell'intervallo di potenza compreso tra 1 MW e 300 MW. **La flessibilità di combustibile e il funzionamento stabile dal 100% di gas naturale al 100% di idrogeno e qualsiasi loro miscela sono requisiti chiave.** Questa è una sfida chiave poiché i cambiamenti estremi nella reattività del combustibile che passano dal gas naturale all'idrogeno possono provocare un drammatico spostamento del rilascio di calore all'interno del combustore, che può essere fisicamente distruttivo se non ben controllato.

ENEA 14

Piano Nazionale Energia e Clima - Seminario FILCTEM – CGIL – Roma 24 ottobre 2019