Carbon dioxide utilisation for methane production by renewable energy sources

V. Barbarossa[1], A. Capriccioli[2], B. Sardella[1], S. Tosti[2]

[1]ENEA, Dip. TER, C.R. ENEA Casaccia, Via Anguillarese 301, S. Maria di Galeria, Roma I-00123, Italy
[2]ENEA, Dip. FPN, C.R. ENEA Frascati, Via E. Fermi 45, Frascati, Roma I-00044, Italy

Overview

- **Introduction**
- **Use of renewable energy for CO_2 capture: recent studies**
- **Methanation of CO_2: the process**
- **Experimental tests**
- **Preliminary costs assessment**

Introduction: CO_2 to methane 1/2

- **Control of the CO_2 emissions (CO_2 capture, transport and segregation):**
  - Because of the great thermodynamic stability of CO_2 (high oxidized status) a high energy reducing compound (hydrogen) could be required to activate the carbon dioxide molecule.
  - Hydrogen (from renewables) + CO_2 could be used to produce chemicals or fuels (methanol, methane, etc.)
  - The process is alternative to the CO_2 segregation methods and permits the storage of renewable sources

- **Italy 1990 CO_2 emissions > 500 Mtonn/y: a reduction of 20% (100 Mtonn/y) could lead to the production of 36 Mtonn/y of methane**

Introduction: CO_2 to methane 2/2

- **Storage of energy from renewable sources:**
  - A criticism of some renewable sources is their variable nature
  - Several storage systems are available (grid integration, pumped-storage hydro systems, batteries, hydrogen-fuel cells, etc.) but they have limitations

- **Methane vs. hydrogen:**
  - Hydrogen is considered a clean energy vector for future but presently there are no wide applications (problems: technology, safety, infrastructures, etc.)
  - Conversely, methane (or hydro-methane) is widely used and for short-middle term applications can be considered as an alternative to hydrogen

Recent studies

- **GREEN-FREDOM™ - A Concept for producing carbon-neutral synthetic fuels and chemicals (F. Jeffrey Martin, William L. Kubic Jr. – Los Alamos National Laboratory):**
  - capture and recover carbon dioxide from the atmosphere (air)
  - split water into hydrogen and oxygen, and convert hydrogen and carbon dioxide into synthetic fuels and organic chemicals

- **At Institute of Membrane Technology (ITM-CNR), Basile et al. developed a process for capturing CO_2 from the emissions of power plants and producing methanol via reaction with hydrogen:**
  - $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\quad (\Delta H_{298K} = -50 \text{ kJ mol}^{-1})$
  - methanol is a liquid used both as a fuel and reactant of chemical synthesis
  - advantages: high density, large market - drawbacks: toxicity

- **At Penn State Univ., Craig Grimes et al. produced methane from CO_2 by using the sun energy:**
  - 160 μL of methane per hour per gram of nanotubes

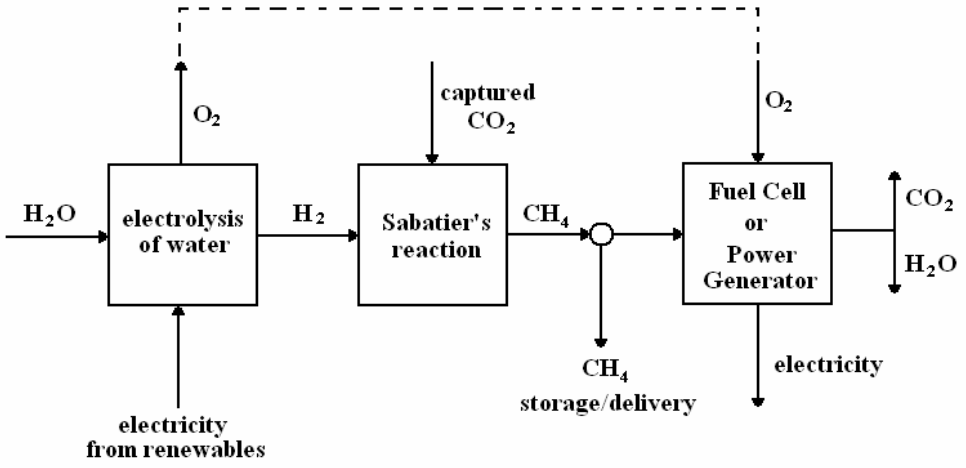
Methanation of CO_2: the process

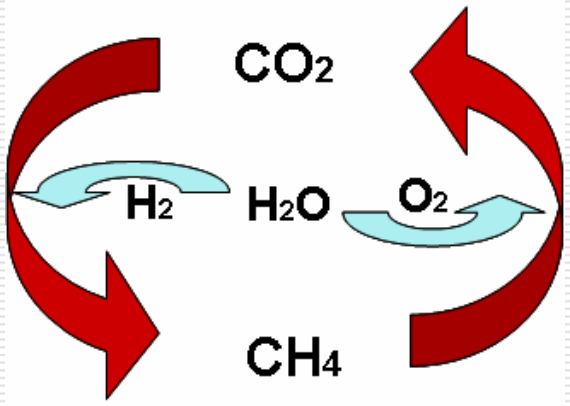
The ENEA process (*) main phases:

- electrolysis to produce hydrogen from water and renewable energy

- methanation reaction to produce methane

- methane storage or power generation

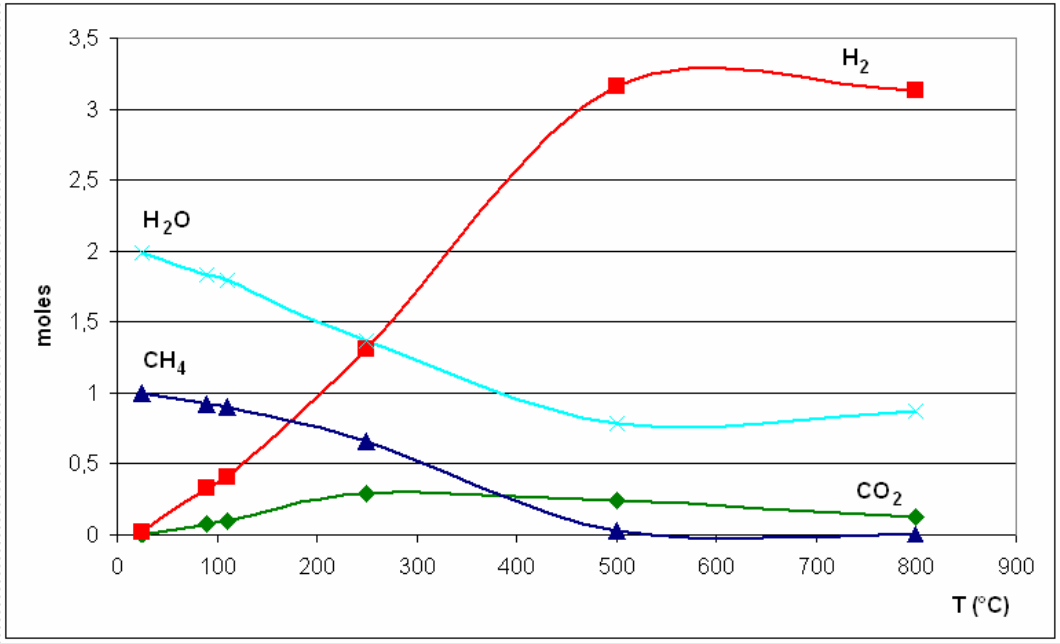




(*) A. Capriccioli, S. Tosti, "Processo per l'utilizzazione di fonti energetiche rinnovabili mediante conversione di anidride carbonica in metano" Italian Patent n. RM2007A000433

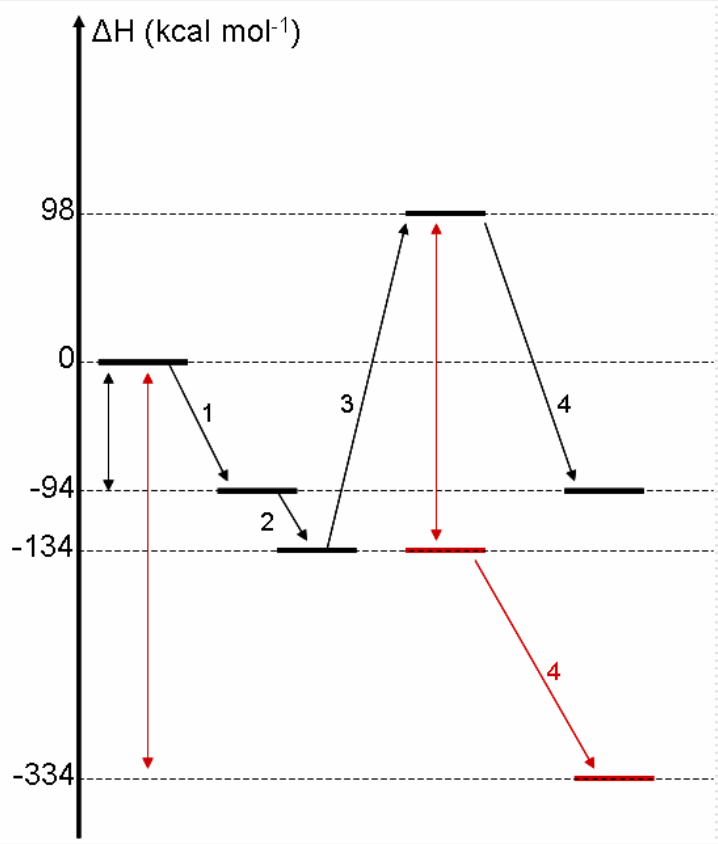
Methanation of CO_2: the process

- The Sabatier's reaction:
  - $CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O$ $\Delta H_{298K} = -164{,}9$ kJ mol^{-1}
  - several catalysts have been studied: Ni-La_2O_3-Ru, Cu-Zn-Cr, Fe-Cu



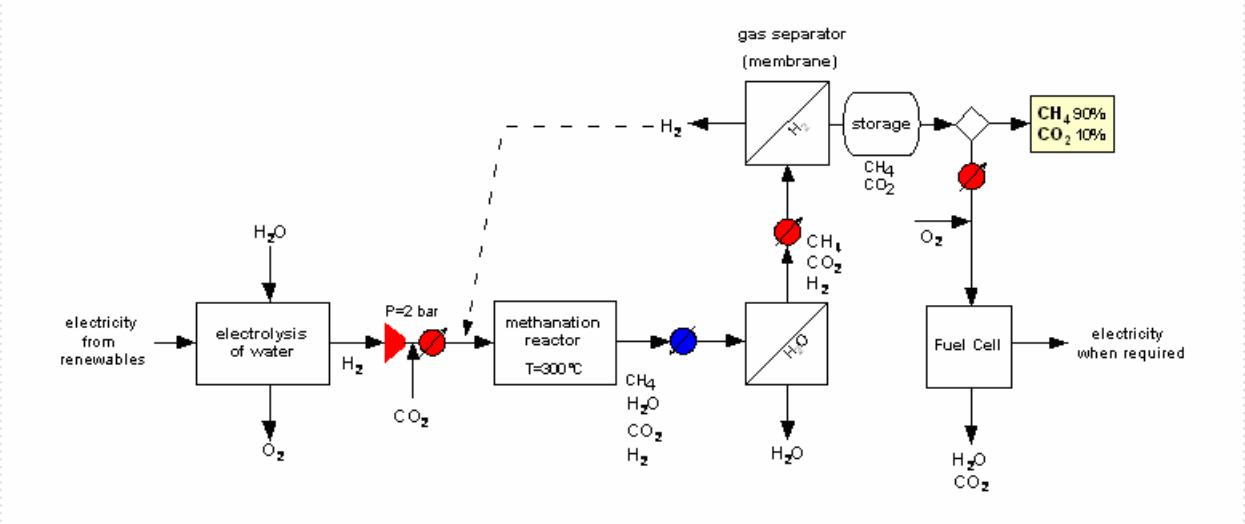
Methanation of CO_2: the process

1. $C + O_2 = CO_2$
2. $CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$
3. $4\ H_2O = 4\ H_2 + 2\ O_2$
4. $CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$



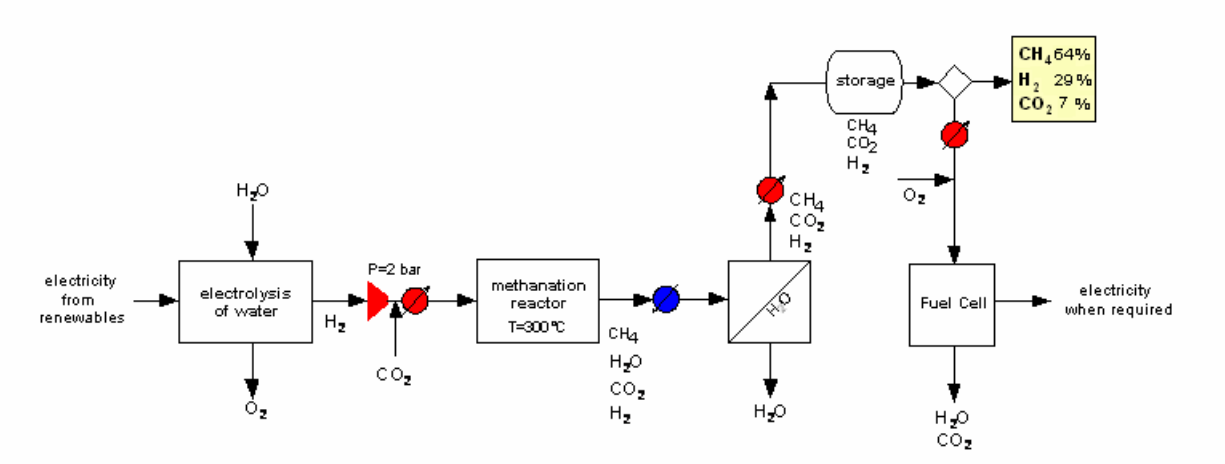
Methanation of CO_2: the process

- The Sabatier's reaction at 300 °C and 2 atm can be carried out on Ru catalysts with a conversion of about 90 %
- after separating water and hydrogen (recycled), a mixture of metahne (90 %) and CO_2 (10 %) is obtained



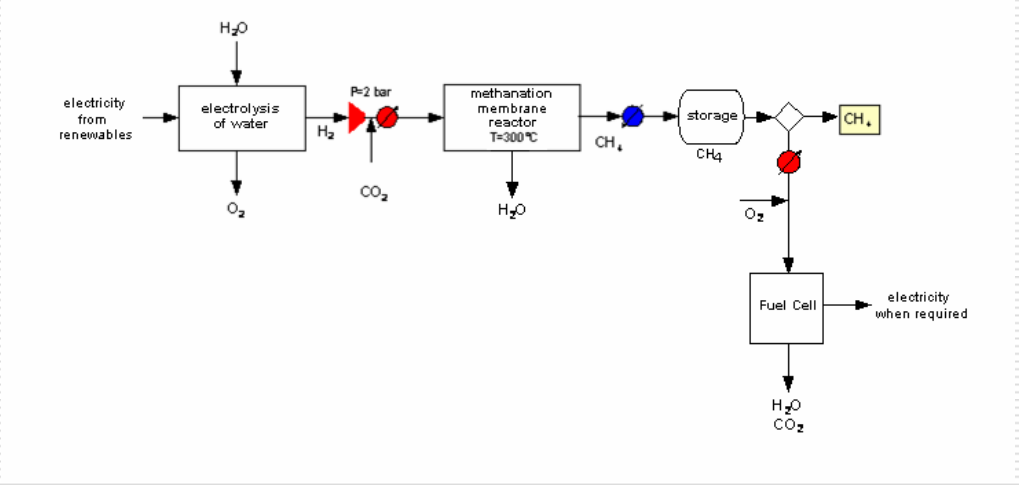
Methanation of CO_2: the process

- semplified process scheme: only water is separated
- a gas mixture containing methane + hydrogen (hydro-methane) and CO_2 is produced



Methanation of CO_2: the process

- when a membrane (ceramic perm-selective for water vapor) reactor (*) is used the reaction conversion is close to 100 %
- the process is semplified and methane close to purity is directly produced



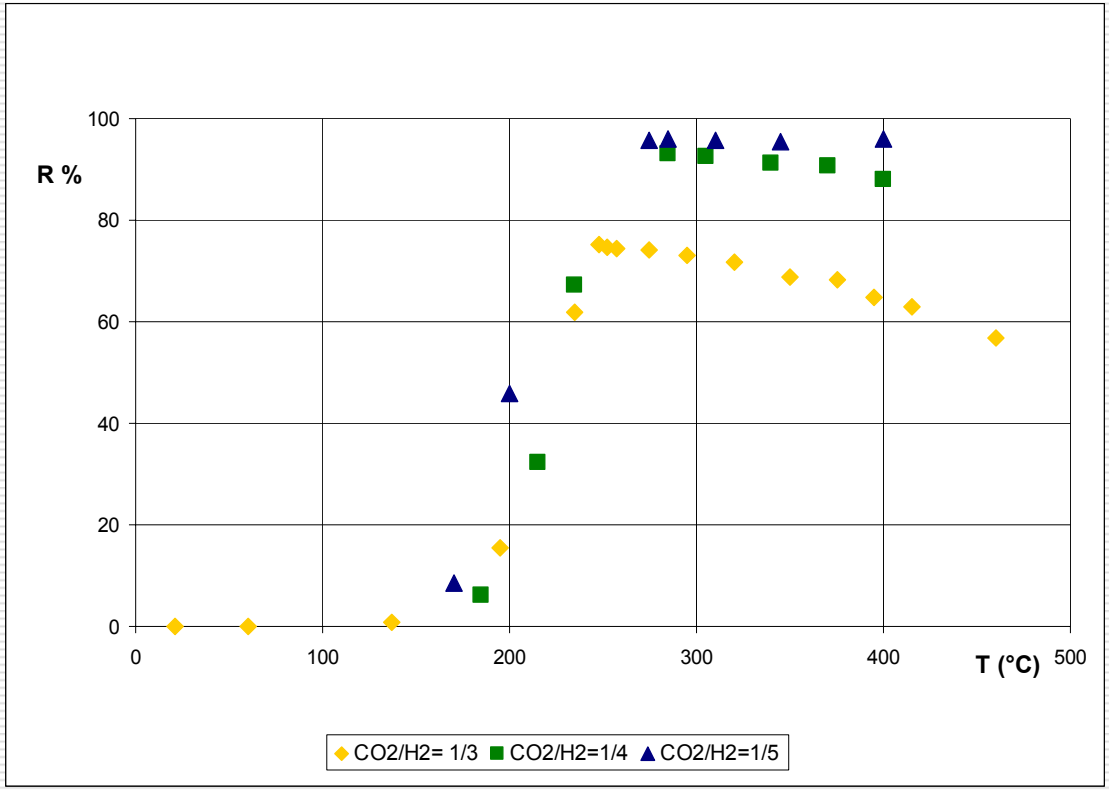
*Haruhiko Ohya et al., Methanation of carbon dioxide by using membrane reactor integrated with water vapor permselective membrane and its analysis, J. of Membrane Science 131 (1997) 237-247

Experimental tests

- The Sabatier's reaction has been tested at ENEA Casaccia labs
- A quartz tubular reactor filled with powder Ni (average size 43 nm) as catalyst has been used
- Feed streams of different CO_2/H_2 molar ratios have been tested (1/3, 1/4, 1/5)
- Temperature range T_{amb} – 500 °C

Experimental tests

- A kinetic barrier has been observed when operating below 200-250 °C
- Over such temperatures, reaction conversion close to 100 % have been measured



Preliminary costs assessment

- Cost of the methane from hydrogen produced via electrical energy

- Main assumptions:
  - Methane produced at 10 atm
  - CO_2 feed concentration of 20 %
  - Avoided cost for CO_2 transportation and segregation of 6 €/tonn*
  - Income from selling oxygen of 1c€/kg
  - Max price of electricity 15 c€/kWh**
  - Market price of methane 3.6 c€/kWh***

*Castor Project, www.encapco2.org/CECD/castor_wildenborg.pdf

**Italian Energy Authority (end 2006)

***Gas prices in the EU25 in January 2006, Eurostat News Release, 90/2006 - 6 July 2006

Preliminary costs assessment

- The cost of methane produced is strongly affected by the price of the electricity
- By using electricity at 2,4 c€/kWh the methane gas price becomes close to the market one (3,6 c€/kWh)

Electricity price, c€/kWh	2.4	5	15
Cost of the methane produced, c€/kWh	3.98	8.29	24.88
Cost of the methane produced[1], c€/kWh	3.87	8.18	24.77
Cost of the methane produced[2], c€/kWh	3.30	7.61	24.20

[1] by considering the avoided costs for CO_2 trans. and segregation

[2] as (1) + income from selling oxygen

Summary/Conclusions

- A process of CO_2 methanation has been studied by ENEA labs
- The process permits the storage of both CO_2 and renewable energy
- The process uses well established and reliable technologies (water hydrolysis, methanation reactors, fuel cells, etc.)
- Presently, for methane safe-reliable technologies and infrastructures are available (rather than hydrogen)
- The assessment of the cost of the methane produced should take into account:
  - the use of low cost energy coming from renewable sources (i.e. solar, wind) when not required by the grid
  - the avoided costs of CO_2 segregation
  - the costs of by-products (i.e. oxygen)
- Preliminary cost evaluation showed that the cost of methane produced is strongly affected by the electricity one
- Important promotion of these applications is expected by Governmental policy (i.e. green certificates)

THANK YOU

FOR YOUR ATTENTION