

Alternative use of CO₂

This paper describes the CO₂ conversion to methane by reduction with hydrogen on a Ni catalyst. When compared to geological sequestration, the conversion of CO₂ to methane represents an interesting alternative to the common treatment of the CO₂ problem. CO₂/CH₄ conversion process is a good way to chemically store energy, provided that hydrogen is generated from a renewable energy source

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Usò alternativo della CO₂

Nel presente articolo è discussa la conversione della anidride carbonica in metano, via riduzione con idrogeno. La proposta rappresenta un modo alternativo, rispetto al sequestro geologico, di trattare l'eccesso del gas serra. Se l'idrogeno è ottenuto da fonte rinnovabile, la conversione CO₂/CH₄, risulta essere un buon metodo per accumulare chimicamente l'energia rinnovabile

Introduction

The growing use of fossil fuels (solid, liquid and gas) as the main primary energy sources, inevitably leads to an increasing amount of carbon dioxide released into the atmosphere.

All estimates converge in indicating the contribution of coal, oil and gas estimated at about 80% of our energy portfolio until at least 2050.

On the other hand, the increasing CO₂ concentration in the atmosphere is indicated as the main cause of the greenhouse effect on the planet with consequent climate change. These reasons motivated in recent years growing efforts, from both technical-scientific and political communities, to control the accumulation of the atmospheric CO₂. Carbon capture technologies are a well stabilized route to reduce the concentration of the greenhouse gas (CO₂) from the atmosphere. However, the introduction of these capture processes always requires additional costs regardless of the adopted technology (post-combustion capture, pre-combustion capture or oxy-combustion).

Despite higher costs, the adoption of efficient technologies for capturing CO₂ is essential for the preservation of the environment. For this reason, legislation in developed countries is directed towards increasing restrictions on the amount of carbon dioxide emitted into the atmosphere.

Besides the capture of CO₂, its final sequestration in geologically stable sites is currently proposed for storing enormous quantities of gas involved. However, the geological storage of a given amount of CO₂ avoids the possible use of C for about 27% wt. Therefore it seems reasonable to question if we can take advantage of this huge amount of carbon (1 ppm CO₂, all over the Earth corresponds to ~ 1.4 10⁹ metric tons of carbon!).

The answer is, of course, positive and there are numerous examples of technological uses of CO₂ and synthetic processes using this gas^(1,2,3). Among its technological utilization we can remember carbon dioxide used as an additive in beverages and food, as a refrigerant, in fire extinguishers and as a solvent in supercritical conditions. Moreover, CO₂ finds wide application in the natural oils' extraction process from vegetables as well as, at an even higher quantitative extent, in the pressurization of fossil fuel deposits for enhanced oil recovery (EOR).

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These technological processes do not contribute to the emission limitation of CO₂ since the gas is largely released into the atmosphere; they are nevertheless interesting because the CO₂ often replaces toxic or more expensive chemicals.

The CO₂ is also an important source of carbon for the synthesis of organic and inorganic compounds. Unfortunately, carbon dioxide is a very stable molecule that needs high-energy reducing substances for its conversion into useful compounds. The high amount of energy required for its activation has so far limited its use on a large scale. The most widespread use of CO₂ in the industrial processes is the urea synthesis:



In pharmaceuticals the CO₂ is used for the synthesis of salicylic acid, precursor of acetyl-salicylic acid (Aspirin). Another example is provided by dimethyl carbonate (DMC) which is conventionally synthesized from methanol and phosgene:



The carbon dioxide is an interesting alternative to highly toxic phosgene, according to the simple reaction:

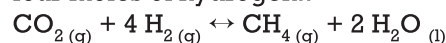


The DMC is used as a precursor of several important industrial products such as polycarbonates.

The hydrogenation of CO₂

Given the enormous amount of CO₂ discharged into the atmosphere, none of the uses discussed above is able to significantly contribute to reducing emissions of greenhouse gases. The only product consumable at the same rate generating the CO₂ is a fuel. There is, in fact, a growing interest around the possibility to treat the CO₂ in a reducing environment to convert it to methanol^(4,5) or methane^(6,7,8). This option is an alternative to the well documented reduction of CO₂ to carbon monoxide. In the latter case reduction can be achieved with hydrogen or water vapour using heat or radiation^(9,10,11). The obtained CO/H₂ mixture can be used as fuel or for subsequent FT synthesis of hydrocarbons⁽¹²⁾. More recently, decomposition of CO₂ has been achieved by applying the same thermochemical cycles' approach used for the water splitting^(13,14).

Among all possible reduction products of CO₂, our interest⁽¹⁵⁾ is focused on the conversion to methane, for reasons that will be better clarified later. We will discuss in more details the carbon dioxide reduction by hydrogen according to the Sabatier's reaction, in which one mole of methane can be obtained by the reaction of one mole of carbon dioxide and four moles of hydrogen::



This equilibrium reaction has been deeply investigated mainly in the direction of the formation of H₂ and CO₂: the methane reforming with superheated steam is commonly used for hydrogen production. The temperature is the main parameter affecting the equilibrium. The methanation reaction is exothermic and spontaneous at room temperature: ΔH = -165 KJ/mole e ΔG = -113.5 KJ/mole. The ΔH and G behaviours with the temperature are shown in Figure 1 below.

The Gibbs free energy increases rapidly with temperature, and becomes positive over 500 °C, making the spontaneous reaction opposite to that of methanation, which is the reforming of methane.

A simple numerical simulation of the Sabatier's equilibrium is shown in Figure 2 for the total pressure of 1 bar and starting from 2 moles of water and 1 mole of methane. As it can be seen, we have a complete conversion to methane at room temperature, whereas over 300 °C the methane reforming takes places.

Therefore temperature is the main experimental parameter. The Sabatier's reaction has been experimentally tested at ENEA Casaccia labs. We have carried out some experimental measurements using a quartz tubular reactor for three different CO₂/H₂ feed molar ratios by operating at 1 atm. Due to the kinetic barrier in this reaction, it is necessary to introduce a catalyst that increases the reaction rate. The catalysts commonly used are metals such as Ru, Rh and Ni: in our study we filled the quartz reactor with Ni powder (average particle size 43 nm). In Figure 3, we report the CO₂ to CH₄ conversion yield vs. the reaction temperature, ranging from 25 °C to 500 °C, when the feed gas is composed only of carbon dioxide and hydrogen in the ratio of 1:3, 1:4 and 1:5.

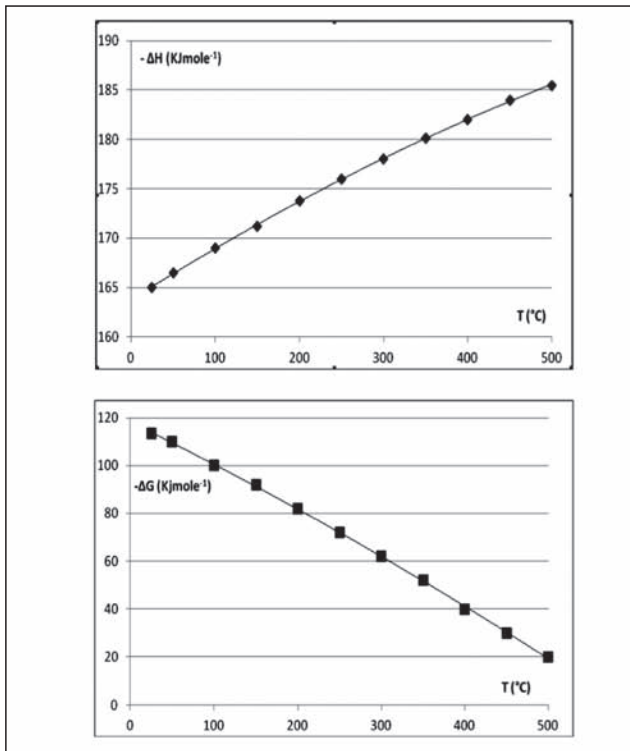


FIGURE 1 Molar enthalpy and molar Gibbs free energy for Sabatier reaction in the temperature range 25 °C - 500 °C
Source: ENEA

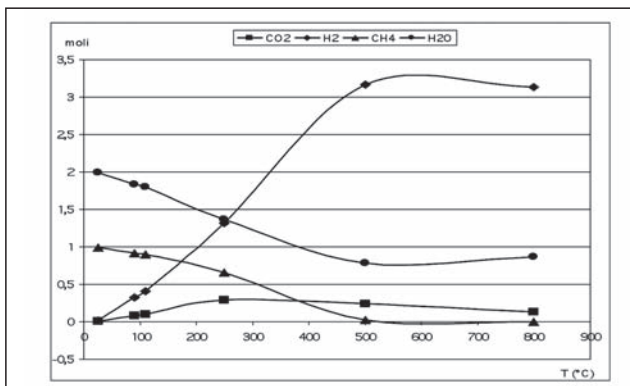


FIGURE 2 Numerical simulation for Sabatier equilibrium
Source: ENEA

As it can be seen from the figure, there is a threshold around 200 °C, then the yield increases rapidly and reaches a maximum value just before 300 °C. When the CO_2/H_2 ratio is 1/4 and 1/5 the maximum

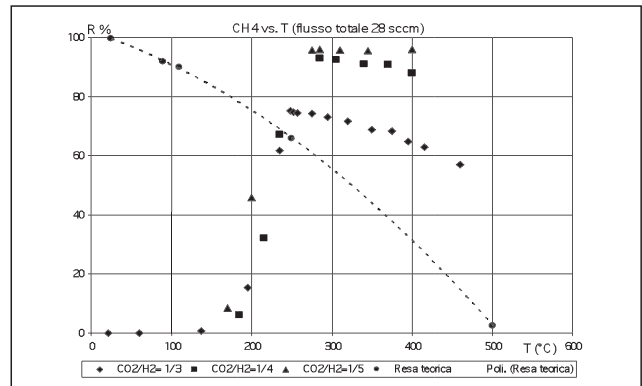


FIGURE 3 Experimental behaviour of the conversion yield as a function of temperature
Source: ENEA

yield is close to 100 %, while when the ratio CO_2/H_2 is less than the stoichiometric ratio, the maximum yield is about 75%. In all the cases a further increase in temperature corresponds to a reduction in yield, that is more remarkable as far as we are away from stoichiometric ratio. The observed behaviour is congruent with expectations: as temperature increases the methanation regresses in favour of the reforming. The kinetic barrier moves the maximum methane yield of nearly 300 degrees. The preliminary experimental results just described demonstrate the simplicity of the methanation reaction and the ability to “exploit” the CO_2 by reduction with hydrogen.

Consider the following reactions:

- 1) $\text{C} + \text{O}_2 \leftrightarrow \text{CO}_2$ $\Delta H = -94.051 \text{ Kcal/mole}$
- 2) $\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$ $\Delta H = -39.439 \text{ Kcal/mole}$
- 3) $4 \text{H}_2\text{O} \leftrightarrow 4 \text{H}_2 + 2 \text{O}_2$ $\Delta H = +231.2 \text{ Kcal/mole}$
- 4) $\text{CH}_4 + 2 \text{O}_2 \leftrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$ $\Delta H = -191.761 \text{ Kcal/mole}$

Reaction (1) represents the combustion of carbon and can be considered the generation phase in a generic thermal plant; reactions (2-3-4) represent a cycle in which CO_2 is continuously transformed into CH_4 that, in turn, is burned by restoring the CO_2 . This is a carbon free emission cycle for power generation that consists of 3 main phases:

- i- electrolysis to produce hydrogen and oxygen from water;
- ii- methanation reaction to produce methane;
- iii- methane storage or power generation.

The cycle is supported by the dissociation of H_2O , which provides H_2 for the methanation and O_2 for the combustion, while both reactions (2, 4) regenerate H_2O . The entire cycle can be represented by the following scheme:

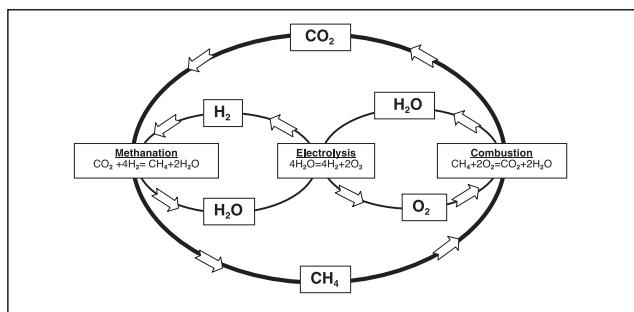


FIGURE 4 Theoretical cycle involving CO_2 , H_2 , O_2 , H_2O and CH_4
Source: ENEA

Looking at this cycle, someone could smile naughtily, as if proposing to bring up the water already fallen by a dam. But if the energy to operate the water dissociation comes from a renewable source (i.e., solar, wind), the cycle is a way to chemically accumulate renewable energy as methane. This occurrence allows us to overcome the problem of renewable sources variability. A project based on this cycle is currently underway in Germany ⁽¹⁶⁾, where a company formed by three different institutions has already set up a working prototype.

Custom-made solution for Italy

Our proposal stands as a possible solution to several problems, some of a general nature, such as the reduction of atmospheric CO_2 , other local, related to the particular Italian situation. The development of renewable sources in Italy is witnessing the peculiar condition of restriction instead of encouragement. According to ANEV (National Association of Wind Energy), 1,300 MW of installed wind power plants are subject to a modulation of their power with a reduction in annual energy capability of 700 GWh ⁽¹⁷⁾. It is as if 30% of the installed wind power capacity was blocked. The serious difficulties renewable energy sources are faced with in Italy can be traced to two main categories: administrative barriers related to the uncertainty of the authorized

standards and technical barriers due to the inadequacy of the electricity distribution network to receive all the power generated by renewable energy plants ⁽¹⁸⁾. Apart from the administrative problems, the technical problem can be solved by significantly reconsidering the structure of our electricity distribution network.

And what if our electricity-producing wind turbines and photovoltaic systems should produce methane? We would save the cost of compliance of the electricity distribution network, remove an obstacle to the diffusion of renewable energy sources, contribute to reducing CO_2 , and finally reduce our dependence on foreign energy supplies.

Conclusions

We have proposed an alternative route to the treatment of CO_2 , which allows the enhancement of carbon in the molecule, through its conversion to methane. The process uses well established and reliable technologies (water hydrolysis, methanation reactors, fuel cells, etc.). The method is a good way to store the electricity generated from renewable sources such as chemical energy; it is easily accessible and transportable thanks to the widespread presence in Italy of methane distribution network. Finally, considering the Italian CO_2 emissions in 1990 (about 500 Mt), a reduction of 20 % (100 Mt) could lead to the production of 36 Mt of methane. At least it's something!

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