Carbon dioxide utilisation for methane production by renewable energy sources

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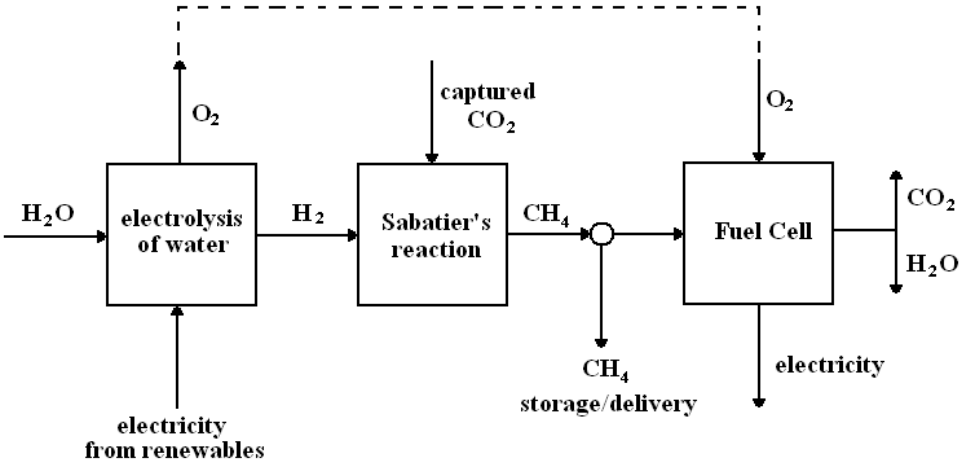
Carbon capture and storage (CCS) is a well stabilized route to reduce the concentration of the greenhouse gas (CO_2) from atmosphere. However, the introduction of CCS processes always requires additional costs which can be economically withstood when governamental laws would rule the CO_2 emissions. On the other hand, the geological storage of a given amount of CO_2 avoids the possible energetic use of C for about 27% wt.: consequently, more efforts should be dedicated to the possible utilization of CO_2 in chemicals and fuels synthesis.

The aim of this work is to propose an alternative way to treat CO_2 in order to achieve both the CO_2 segregation and its energetic use.

Because of the great thermodynamic stability of CO_2 and its high oxidized status, a high energy reducing compound is required to activate the carbon dioxide molecule. Hydrogen is a suitable substance for reaction with carbon dioxide. According to the Sabatier's reaction, one mole of methane can be obtained by the reaction of one mole of carbon dioxide and four moles of hydrogen:

$$CO_2 + 4\ H_2 == CH_4 + 2\ H_2O \qquad \Delta H = -\ 164.9\ KJ/mol$$

If hydrogen is produced by renewable energy, this reaction could be inserted in a carbon free emission cycle for power generation. In the following Figure 1 we report a description of the whole proposed process that consists of 3 main phases:
i- electrolysis to produce hydrogen from water and renewable energy (oxygen is also given as a by-product);
ii- methanation reaction to produce methane;
iii- methane storage or power generation.



i- The electrolytic cells actually can reach efficiency of more than 70 %, but the high temperature/high pressure electrolytic cells can greatly improve this efficiency
ii- The methane conversion factor depends on the temperature and on the H_2/CO_2 molar ratio, and almost total conversion of CO_2 to CH_4 are easily achieved.
iii- The methane could be used in an electric energy production unit like a fuel cell or oxicombustion using the O_2 generated by the electrolytic cell.

The methanation reaction is a slightly exothermic reaction that takes places at relatively low temperature. In fact, thermodynamic calculation shows a complete conversion to methane at room temperature.
We have carried out some experimental measurements using a quartz tubular reactor filled with powder Ni as catalyst. Preliminarily results show a low kinetic barrier as it can be seen in the Figure 2, where we report the CO_2 to CH_4 conversion yield vs. the reaction temperature for three different CO_2/H_2 feed molar ratios by operating at 1 atm.

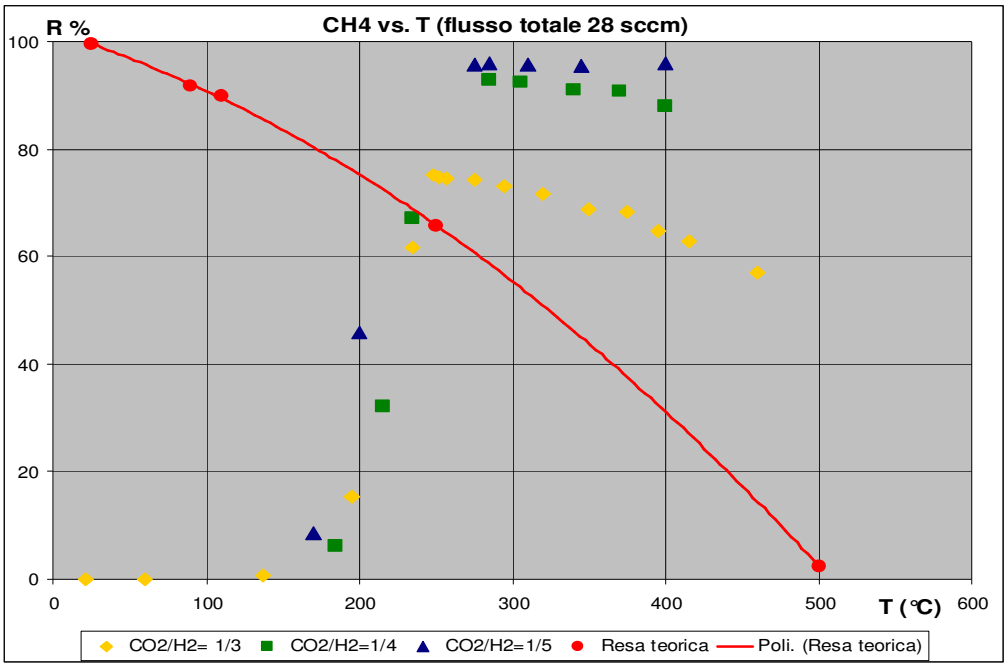


Figure 2
As can be seen, we obtain total CO2 to CH4 conversion with CO2/H2 molar ratio of 1/4 and 1/5 at temperature of 300 °C.