THE HELMETH PROJECT: CARBON DIOXIDE METHANATION COUPLED WITH HIGH TEMPERATURE ELECTROLYSIS FOR SYNTHETIC NATURAL GAS PRODUCTION

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Abstract
Hydrogenation of carbon dioxide for synthetic natural gas (SNG) production has been investigated in an integrated process. The attention has been focused on the coupling between high temperature (SOEC-based) electrolysis and a methanation section with two isothermal reactors operating at 300°C and 15 bar. Such integration is very promising because the vaporization heat required for the high-T electrolysis can be supplied by the exothermal methanation. The experimental activity has been carried out by testing two inlet mixtures (reproducing the two reactors). A commercial catalyst available at pellet size has been used for the activity test. The experimentally obtained high conversion (up to 93% and 83% for the first and the second reactor, respectively) enables the production of a SNG that could be directly injected in the natural gas distribution grid. Through the thermal integration between hot and cold streams an achievable electricity-to-SNG conversion efficiency equal to 84% (on HHV basis) has been calculated.

Introduction
The intermittency of electricity production from RES (e.g., wind and solar) is one of the key challenges that should be solved in order to drive their widespread diffusion. The electric power production from RES does not often coincide with end-users demand, implying a potential unbalance of the electricity network. Thus, large (and possibly dynamic) electric storage is a relevant topic to be investigated and for which solutions must be created. Currently pumped hydroelectricity is the dominant way for electricity storage. However, the potential of this technology is limited by the topography of the region where it is installed. Compressed-air storage seems to be a viable solution; however it would require large volumes to store energy. Electrochemical storage through batteries represents a possible alternative, but this latter solution suffers from several drawbacks as the devices degradation and the limited storage capacity [1].

The use of synthetic fuels made from CO₂ as carriers for excess renewable electricity offers a potential solution in order to manage fluctuating output of renewable energy and mitigating CO₂ emissions at the same time [2].

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Power-to-gas (PtG) represents a possible pathway for long-term and high-capacity renewable electricity storage. Excess electricity can be used for hydrogen production through water/steam electrolysis. However, H₂ direct use is limited by safety issues (large flammability interval) and storage/transport challenges (e.g., low energy density, steel embrittlement). Hydrogen can react with carbon dioxide according the following exothermal reaction (also known as Sabatier reaction):

\[ 4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O \quad (\Delta h_{298K} = -165 \text{ kJ/mol}) \]  

This reaction enables the production of a synthetic (or substitute) natural gas (SNG) that could be directly injected in an already existing infrastructure as the natural gas distribution grid. In addition, natural gas is used in several sectors (power plants for electricity production, household heating, automotive, etc.) through mature devices and technologies.

Sabatier reaction is catalytically activated: several active metals and supports have been investigated, as nickel, rhodium or ruthenium supported on γ-Al₂O₃, ZrO₂ and CeO₂ [3]. Nickel-based catalysts seem to represent the most suitable technology due to their better trade-off between activity and production cost (nickel is cheaper than other transition metal as rhodium and ruthenium). Recently, Ni-Al hydrotalcite-like catalysts gained interest for carbon dioxide methanation due to their high nickel content [4].

Water electrolysis can take place at low or high temperature. In the first case alkaline (operating at 60-90 °C) or proton exchange membrane (PEM) electrolyzers (operating at 40-80 °C) can be used. In the second case, as an alternative, a promising technology involves solid oxide electrolysis cells (SOEC) for steam (instead of liquid water) electrolysis (operating temperature: 700-900 °C). The coupling between SOEC and methanation is interesting due to the potentially optimal thermal match between the heat requirement for water vaporization and the heat produced by the exothermal reaction. This thermal coupling can lead to superior electricity-to-SNG efficiency, because the vaporization heat is internally provided and not electrically-driven (as in the low temperature electrolysis case). Figure 1 summarizes the aforementioned thermal integration. Concerning the methanation section, several combinations of adiabatic and isothermal/cooled reactors could be exploited. Adiabatic reactor is simpler, but methanation reaction is strongly exothermic: a too high outlet temperature can damage the catalyst leading to its deactivation. In addition, Sabatier reaction is favored at low temperature and a cooled/isothermal reactor can lead to superior methane yield, ensuring the injection of the produced SNG into the gas distribution grid respecting the pipeline prescription on natural gas composition and heating value). In this work we focused on a configuration based on two isothermal reactors (operating at 15 bar) with a water inter-condensation. Clearly, the catalysts activity should be checked at low temperature in order to verify the feasibility of the chosen configuration.
Integration between SOEC and isothermal/cooled methanation has been developed within the HELMETH project, under the European Union's Seventh Framework Programme for the Fuel Cells and Hydrogen Joint Technology Initiative. The main targets of the project are the identification of best catalyst(s) for CO$_2$ methanation and to demonstrate the technical and economic feasibility of the chosen concept through experimental activity, process modeling and the installation of a 30 kW pilot plant.

![Diagram of methanation process]

**Figure 1.** Thermal integration between high-T electrolysis and methanation.

**Experimental**
A test rig has been designed and set up in order to perform tests at high pressure. All involved gases are bottled. Three pressure reduction sections progressively decrease the gas pressure before the mass flow controllers (MFCs) panel. The MFCs have been checked and calibrated by using an electronic flowmeter. The stainless steel tube reactor has a metallic grid for catalyst support and is surrounded by a ceramic blanket equipped with electric resistances for the heat up and thermal control. A vertical atmospheric well is vertically placed in the reactor center, reaching the catalyst support grid in order to read the proper reaction temperature. Downstream the reactor a tube-in-tube condenser and a steel tank allow the produced water separation. A back pressure controller regulates the system pressure. Then the gas flows through a multi-channel gas analyzer able to measure CO, CO$_2$, CH$_4$, H$_2$ and O$_2$. The gas analyzer is equipped with non-dispersive infrared (NDIR) sensors for CO, CO$_2$ and CH$_4$ measurement, a thermal conductivity (TCD) detector for H$_2$ and a paramagnetic sensor for O$_2$. A system of three pneumatic valves enables the bypass of reacting and condensing section in
order to analyze also the reacting mixture (as a cross check of the MFCs correct functioning). Safety devices stop the gas feeding and discharge the gas in the test rig while unusual temperature and/or pressure values are read by thermocouples and/or pressure indicators. A sketch of the test unit with the main devices is shown in Figure 2.

Figure 2. Test rig for methane synthesis. The main devices have been indicated.

In order to simulate the isothermal reactors a test campaign has been carried out at 15 bar and 300 °C. The reactor has been fed with two reacting mixtures: ‘Reactor 1’ and ‘Reactor 2’, both containing a low nitrogen dilution (10%, only for analytical reasons) and a stoichiometric ratio between hydrogen and carbon dioxide (H₂/CO₂=4). In order to reproduce the chosen methanation configuration, ‘Reactor 2’ inlet mixture presents high methane content (60%). The involved inlet mixtures are summarized in Table 1.

Table 1. Composition of the inlet streams.

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>( y_{H_2} )</th>
<th>( y_{CO_2} )</th>
<th>( y_{CH_4} )</th>
<th>( y_{N_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Reactor 1’</td>
<td>72%</td>
<td>18%</td>
<td>0%</td>
<td>10%</td>
</tr>
<tr>
<td>‘Reactor 2’</td>
<td>24%</td>
<td>6%</td>
<td>60%</td>
<td>10%</td>
</tr>
</tbody>
</table>

The reactor has been filled with 3.7 g of a Ni/γ-Al₂O₃ commercial catalyst (“CRG-F” from British Gas) available at pellet size (diameter≈3mm, length≈3mm). Four different flow rates have been tested for each inlet mixture in order to verify the
residence time effect on the yield/conversion.

**Results and discussion**

Figure 3 presents the experimentally obtained methane yield (at 300 °C and 15 bar) as a function of the gas hourly space velocity. As expected, an increase of inlet flow/space velocity (i.e., a reduction of the residence time) results in a decrease of conversion both for ‘Reactor 1’ and ‘Reactor 2’ inlet streams.

![Figure 3](image)

**Figure 3.** Result of experimental activity on commercial catalyst pellets. R1 and R2 stay for ‘Reactor 1’ and ‘Reactor 2’, respectively.

A maximum methane yield of ≈93% and ≈83% has been obtained for Reactor 1 and Reactor 2 inlet mixture, respectively. These values has been used in a model simulating the coupling between SOEC and isothermal methanation built using Aspen plus™. As said, the chosen methanation concept is characterized by two isothermal reactors with an inter-condensation between the two reactors and a final condensation in order to separate the produced water. In addition, the required heat for the water vaporization has been considered equal to the heat produced within the methanation section: the equivalence has been “forced” in the model by adjusting the water conversion (into hydrogen) within the SOEC electrolysis unit.

The as produced synthetic natural gas must fulfill some prescription for pipeline injection. Due to the different legislation across European countries, averaged values have been considered for SNG acceptable composition and energy content. In particular, hydrogen content should be lower than 5% (molar basis), higher heating value (HHV) must be higher than 35 MJ/Sm$^3$ and Wobbe index (WI) must be greater than 47 MJ/Sm$^3$.

If the first and the second reactor have a conversion equal to 93% and 83% respectively, the produced SNG has the following composition: $y_{\text{CH}_4} = 94.1\%$;
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\(y_{\text{H}_2}=4.5\%\); \(y_{\text{CO}_2}=1.1\%\). In addition, HHV=36.1 MJ/Sm\(^3\) and WI=48.9 MJ/Sm\(^3\). Thus, it can be injected in the natural gas distribution grid. A thermal integration through the Pinch Analysis has been considered in order to minimize the external heat requirement (i.e., to maximize the efficiency). By considering a minimum temperature difference between hot and cold fluids equal to 10 °C, the needed external heat resulted equal to 6% of the overall electrolysis electric requirement. If the external heat is considered electrically provided, an overall electricity-to-SNG efficiency (LHV based) equal to 75% (84% if HHV based) has been calculated. The main efficiency results are summarized in Table 2.

Table 2. Efficiency results. The overall conversion efficiency can be obtained by multiplying the SNG productivity and LHV (or HHV). SNG productivity takes into account also the required electricity for pumps and compressors (CO\(_2\) has been considered available at atmospheric pressure).

| SNG productivity [kg\(_{\text{SNG}}\)/MWh\(_{\text{el}}\)] | 55.6 |
| LHV [kWh/kg\(_{\text{SNG}}\)] | 13.5 (32.5 MJ/Sm\(^3\)) |
| Efficiency (LHV basis) | \(\approx 75\%\) |
| HHV [kWh/kg\(_{\text{SNG}}\)] | 15.1 (36.1 MJ/Sm\(^3\)) |
| Efficiency (HHV basis) | \(\approx 84\%\) |

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