Movable Modular Plant Operation on Synthetic Methane production from CO_2 and Hydrogen from Renewables Sources

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Abstract

Renewables are steadily growing becoming a significant part of the global energy mix, in particular in the power sector. An attractive solution could be represented by Power to Gas (P2G), an energy storage strategy. In the P2G process renewable or excess electric energy is used for water electrolysis to produce hydrogen that is then combined with CO_2 and converted into methane (synthetic or substitute natural gas, SNG) through the Sabatier reaction. SNG is particularly interesting because leads to an easily transportable (in the existing infrastructures) fuel with a wide proven market for power, thermal and mobility final use applications.

The key issue consist on putting together green hydrogen produced by electrolysis fed by Renewables with high content CO/CO_2 gases supplied from different sources (e.g. syngas from gasification, biogas, geothermic fields, soil gas and gas wells).

In this work the CO_2 hydrogenation process, coupled with renewables, has been study in a modular, moveable, skidable plant, in the scale of 0.5-1 Nm^3/h of produced SNG.

The paper reports the results of first experimental activities related to SNG production with Ru based supported catalyst. The experimental activity was carried out in order to check the operability of all components and to improve the knowledge on methanation process in different conditions relevant to Power-to-Gas applications.

Different space velocity, temperature and pressure conditions have been investigated. Results indicate high CO_2 per pass conversion with CO_2/H_2 concentrate feed.

1 Introduction

The increasing penetration of vRES (variable Renewable Energy Sources), essential for the achievement of the ambitious objectives set by the recent Paris agreement (COP21-2015), poses significant challenges for the sustainability of the electricity grid, due to non-programmability of the Renewable Energy Sources. In the Renewables 2017 report [1], the International Energy Agency (IEA) predicts that on global scenario RES generation will reach 8,000 TWh by 2022, an amount equivalent to the combined consumption of China, India and Germany. EU's energy and climate goals for 2030 introduce a new renewable energy target of at least 27% of final energy consumption in the EU by 2030. In Europe is recently evident that large deployments of renewable power resources often produce excess power that out strips demand so the need for grid scale energy storage is necessary to manage renewable energy intermittency and over generation. Energy Storage Technologies can contribute in renewable energy peak shaving avoiding temporal fluctuation that can cause shortage or surplus in energy supply.

For managing renewable power intermittency and over generation Power to Gas (P2G) technology represents one potential tool. Power-to-gas (P2G) is considered to be an enabling technology, to support the integration of renewables with the electrical energy system [2]. The key issue consist on

putting together green hydrogen produced by electrolysis fed by renewables with high content CO_2 gases supplied from different sources.

Synthetic natural gas has got the possibility of being used in widely available means on the market and has favorable chance to be introduced into existing transport / storage infrastructures.

However, the production of synthetic natural gas requires the presence of a CO_2 source which therefore limits the location of the plant. Possible CO_2 feedings come from syngas from: captured CO_2 in energy intensive industry, gasification, biogas, geothermic fields, soil gas and gas wells.

This concept allows storing exceeding renewable power production balancing offer and demand over time on the grid.

The features of this technology allow the connection of electrical and gas networks in a single energy system introducing high flexibility in the balance of the grid [3]. The advantage of this approach is that it is relatively easy to store large quantities of gas as consequence of the large storage capacity of the natural gas network and the connected gas storage systems. For example in Germany the natural gas grid has a storage capacity of about 220 TWh while the German electricity grid has a storage capacity of about 0.4 TWh [4] .
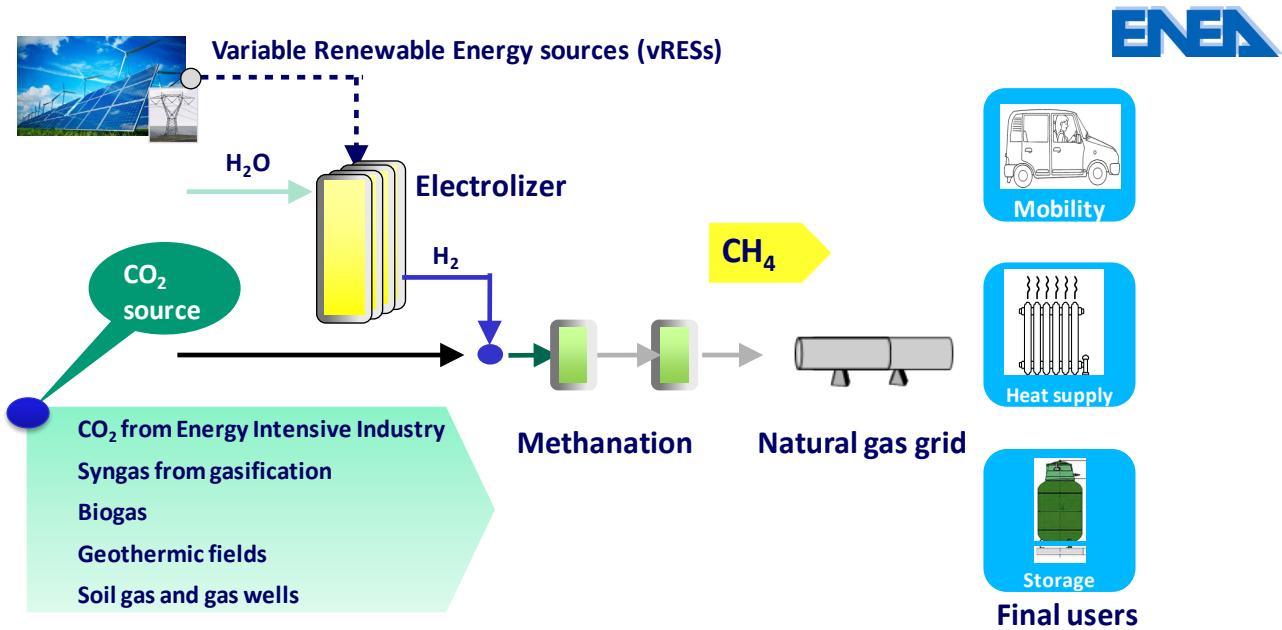

Figure 1: Power to Gas concept simplified scheme

The yields of the process are of the order of 30-60% according to [5], whether one wants to convert the gaseous vector obtained into electrical energy or to use the thermal energy of the same.

Generally, the efficiency of Power to Gas systems with production of SNG increases when the released heat is used, for example for district heating or in nearby industrial plants for the regeneration of amines.

Further R&I efforts are required to reduce technology and non-technology costs, improve performances and promote technology deployment to market.

The Power to Gas process has some critical aspects that can be outlined as follows:

1. Technology for the production of hydrogen.

88   2. Technologies for CO_2 separation, absorption and purification.

89   3. Catalyst performance in terms of catalytic efficiency, durability and poisoning sensitivity.

90   The reduction of carbon dioxide with hydrogen is a subject studied by Sabatier since the beginning
91   of the last century. The CO_2 hydrogenation reaction requires for each mole of carbon dioxide four
92   moles of hydrogen to produce one mole of methane (Eq. 1):

93    $$CO_2 + 4H_2 \rightarrow +CH_4 + 2H_2O \qquad \Delta H°_{298} = \text{- 165 kJ/mol} \qquad (1)$$

94   CO_2 methanation is an equilibrium highly exothermic reaction. Thermodynamically, the CO_2
95   conversion decreases with increasing temperature and increases with the pressure, at temperatures
96   below 600 °C [6]. In theory, the hydrogenation of methane CO_2 is favored at low temperatures,
97   where the conversion of CO_2 and selectivity CH_4 can reach almost 100%. Conversely, the kinetics
98   and therefore the reaction rate increase with the temperature. Furthermore, temperatures higher than
99   500 ° C favor the RWGS reaction and therefore the reaction is not investigated above
100   500÷600°C [7]. In the typical temperature range of 200-500 ° C, the increase in pressure is
101   effective up to a certain point and the further increase in pressure is less effective, consequently a
102   pressure of 10 to 30 atm is considered the most suitable in terms of stress on the catalyst.

103   However, the electron reduction of CO_2 to CH_4 by hydrogen is characterized by a high kinetic
104   barrier, consequently to proceed at acceptable rate a suitable heterogeneous catalysts with a high
105   activity is necessary especially at low temperature.

106   Several metals for CO_2 methanation may be used as catalyst, their catalytic activities follow the
107   order Ru > Ni > Co > Fe > Mo and noble metal proportions might increase the productivity [8].

108   The CO_2 methanation is a highly exothermic reaction as a consequence an important issue in the
109   design of a methanation reactor is to realize a good temperature control in order to avoid
110   temperature increase inside the catalyst bed. Improper heat removal can cause hot spots,
111   construction material stress, sintering of the catalyst and formation of carbon particles.

112   For this reason, to remedy this issue different plant configuration and reactors concept have been
113   developed, in a way that can be summarized as follows: cascades of fixed bed reactors with
114   intercooler, isothermal fixed-bed reactors, fluidized-bed, three-phase and structured reactors (Gotz,
115   2014).

116   The fixed-bed reactors, that can operate in adiabatic or isothermal condition, are mainly used.
117   Catalytic methanation reactors are typically operated at temperatures between 200 and 550 °C and
118   at pressures ranging from 1 to 20 bar. Considering a simple one-stage process, elevated conversions
119   can only be achieved at lower temperatures or elevated pressures. Carbon dioxide conversions of
120   about 93% are achieved by increasing the pressure to 20 barg and maintaining the temperature at
121   450 ° C. [11]

122   The maximum operating GHSV of adiabatic fixed-bed reactors, assumed for technical plants, is
123   normally in the range of 2000 e 5000 h^{-1} as reported in [12].

124   The process of methanation is currently applied in the industrial production of ammonia and, after
125   the oil crises in the 1970s, for the production of SNG from synthesis gas [8].

126   However, the application in the Power to Gas process is more complex, due to small size of the
127   plant and intermittent or dynamic operation [12].

128

2. Moveable plant description

130   A pilot scale experimental facility dedicated to study and test the methanation process has been
131   built at ENEA Casaccia Research Center. The pilot plant is equipped with a methanation unit

constituted by a multi-tubular fixed bed reactor able to work in isothermal or adiabatic conditions. The reactor is of the "shell-and-tube" type to guarantee the correct heat transfer between the reagent gas and the refrigerant; the catalyst bed consists of tubes filled with pellets and inert material, while in the shell the coolant circulation takes place.

The system is able to work in the range of 1-5 bar using a back pressure valve. The feed gas is obtained by mixing pure gas from cylinders with the help of four mass flow controllers (MFC) to emulate different gas mixtures entering into reactive section. The inlet gas is heated up to 250 °C before entering into the reactor in a electric heater. The temperature is set up to better address the operating start up conditions necessary for the methanation reaction. All auxiliaries are included in the facility.
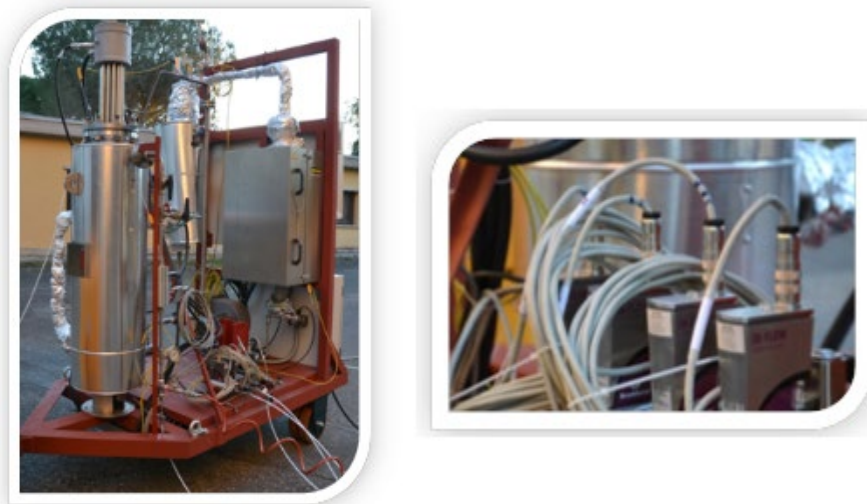
Figure 2. Pilot plant details at ENEA Research Center.

Moreover the plant is equipped with several sensors and a data acquisition system. The composition of flowing gas, in each section, is measured by online gas analysis system. The nominal methane flow is in the range of 0.25 to 1 Nm^3/h.
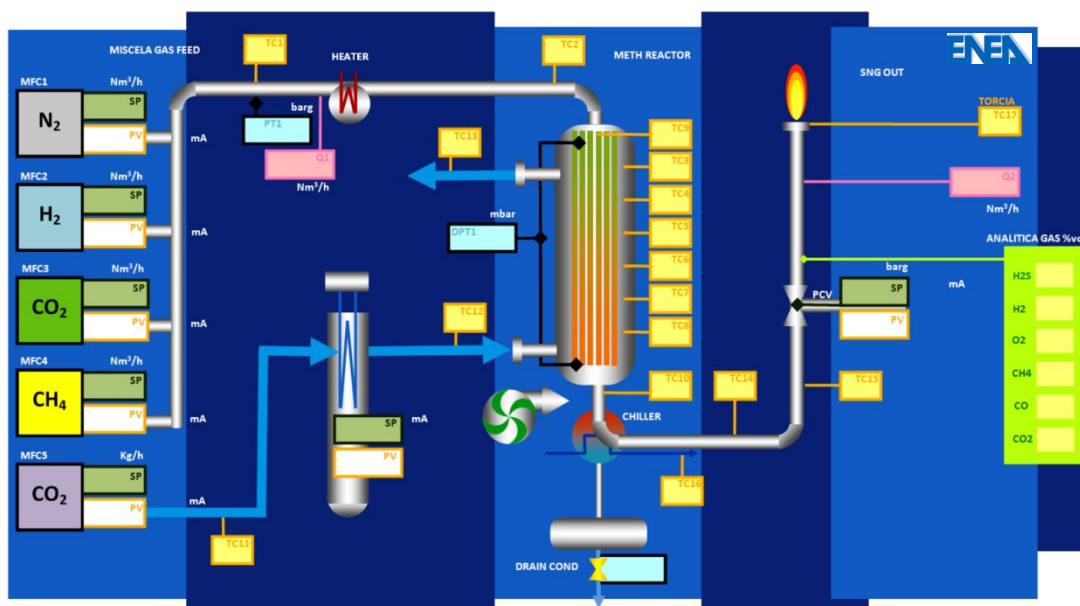
Figure 3. Pilot plant scheme at ENEA R.C.

Downstream water is separated by a condenser and the dry gas is sent to a flare. Water is collected and measured. The reactor was equipped with different K-type thermocouples inserted on the reactor shell and in the middle high of each tube filled with catalyst. In this way it's possible to acquire temperature values inside the reactor during the test.

The pilot plant is equipped with a data acquisition system to monitor the main operating parameters and control the process. Input and output variables are elaborated by a PLC (programmable logic control) system. The software architecture allows controlling the parameters of interest and permits the application of appropriate adjustments in both manual and automatic way during the pilot plant activities, the start up and the shut-down phase. The data acquisition system is also equipped with alarms to block the process in case of malfunctions.

The whole system is installed on a skid that is movable on site. In this research facility is possible: to test different real or mixed gas, to test different methanation catalysts and intensified reactors and finally is possible also to test SNG upgrading methodologies (e.g. membranes).

3. Methodology and experimental activities

The experimental activity was carried out in order to check the operability of all components and to improve the knowledge on methanation process in different conditions relevant to Power-to Gas applications. The experimental tests were carried out considering all the problems related to the process.

The test procedure includes: a heating phase of the catalytic bed, a hydrogen reduction step at atmospheric pressure, experimental tests and finally a shutdown phase in an inert environment. Different space velocity (GHSV), gas inlet composition, reagent mixture, H_2/CO_2 ratio, temperature and pressure conditions have been investigated.

In this study flow rates and GHSV data are calculated as:

$$GHSV \left(\frac{Nm^3}{g * h}\right) = \frac{Normalised\ volumeric\ gas\ flow\ \left(\frac{Nm^3}{h}\right)}{catalyst\ bed\ weight\ (g)} \qquad (2)$$

In order to prevent hot spot phenomena and to distribute the heat produced by the reaction along the reactor axis and to facilitate the disposal of heat, a 1 to 1 volumetric dilution with inert glass was selected

Catalysts	Ru 0.5% wt.
Support	Al_2O_3 pellets
Temperature range	250-350 °C
Pressure range	1-5 bar
Feed gas mix T in	250°C
GHSV $Ncm^3/(g*h)$	3000-11000
Reactor condition	Isothermal /Adiabatic multitube

Table 1: Main Test Parameters

A commercial methanation catalyst (Ru 0.5% wt on Al_2O_3) was used in the present work.

This choice is alternative to the most common used cheaper Ni based catalyst. The basic idea is to overcome the main disadvantage of Ni and its high tendency to oxidize like the other non-noble metals (Fe and Co). Another reason is to avoid nickel carbonyl formation that is very toxic to the human organism. Moreover Ru is a noble metals and offers positive characteristics such as high activity, CH_4 selectivity (also at low temperatures) and high resistance to oxidizing atmospheres [13].

However Ru is more expensive than Ni and actually it is not used for industrial-scale SNG production. In perspective, ruthenium could be more used because the high cost would be offset by high yields in methane especially at low temperatures [10]. One of the most representative scientific work related to the kinetics of Sabatier's reaction on Ru-based catalysts is the one of Peter Lunde and Frank Kester [16]. The work describes the experimental tests carried out in a cooled tube reactor without dilution at atmospheric pressure and in isothermal conditions on a ruthenium-based catalyst (0.5% by weight of Ru supported on γ-alumina) with different inlet H_2/CO_2 ratio gas mixtures. Result indicate a CO_2 conversion rate of 86% with a low GHSV of 526 h^{-1} at a pressure of 0.1 MPa.,

Results are reported as carbon dioxide conversion X_{CO_2} calculated as follows:

$$X_{CO_2} = \frac{n_{CO_2\,(in)} - n_{CO_2\,(out)}}{n_{CO_2\,(in)}}$$
(3)

Where n_{CO_2} is inlet and outlet carbon dioxide mole stream.

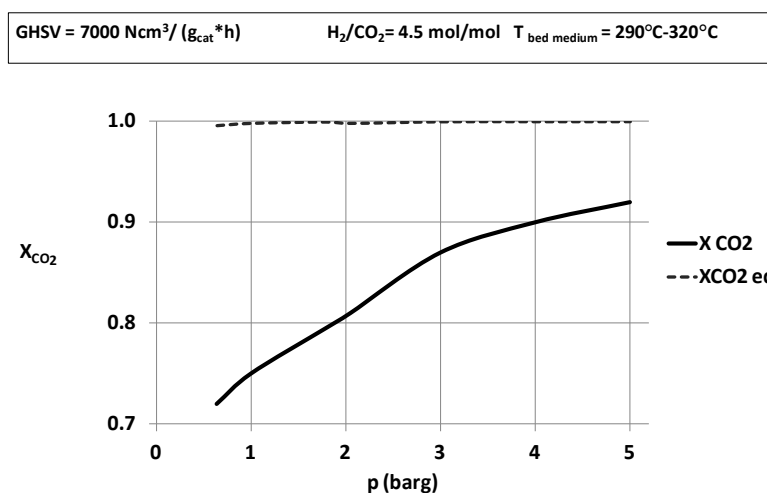**4. Results**

Effect of pressure

Sabatier's reaction is favoured by pressure, so the effect of pressure on the process, in the range 1-5 bar, was studied. Falbo….Considering the Peffect on thermodynamics, it is reported that the performance of PtG technology may be optimized if the CO_2 methanation reactor is operated with a pressure in the 5–20 ata range.

Figure 4 Thermodynamic yield in function of pressure

Figure 4 shows the effect of pressure on catalyst activity, the effect of pressure on X_{CO_2} is evident because at 290°C-320°C the catalyst works far from the thermodynamic equilibrium conditions.

Effect of GHSV

Typical GHSV for adiabatic fixed bed reactor is in the range of 2000-5000 h^{-1} for technical plant. Generally in the laboratory tests are performed with GHSV values higher than those used in the plants [12].

The effect of GHSV on CO_2 conversion has been investigated (Figure 5) . Results show that by increasing GHSV from 6000 to 11000 $Ncm^3/(h*gcat)$, X_{CO2} decreases from 0.95 to 0.87. This results are in line with what reported in the literature: Lange et al. [14] investigated the carbon dioxide to methane hydrogenation using RuNi bimetallic catalysts, in this study the catalyst containing ruthenium, increasing space velocities, showed only a small decline in carbon dioxide conversion. Also Janke et al. [15] investigated the CO_2 hydrogenation at 1 bar and $H_2/CO_2 = 4$ over a 10% $Ru/\gamma-Al_2O_3$ catalyst and demonstrates an excellent selectivity to methane and CO_2 conversions under low space-velocity conditions.

| GHSV	$Ncm^3/(g*h)$	6500	7200	11500
H_2/CO_2	-	4.3	4.3	4.3
p	barg	5	5	5
T internal medium value	°C	290	280	290
CO_2 conversion	X_{CO2}	0.94	0.92	0.89

Table 2: Effect of GHSV Variation on CO_2 Conversion
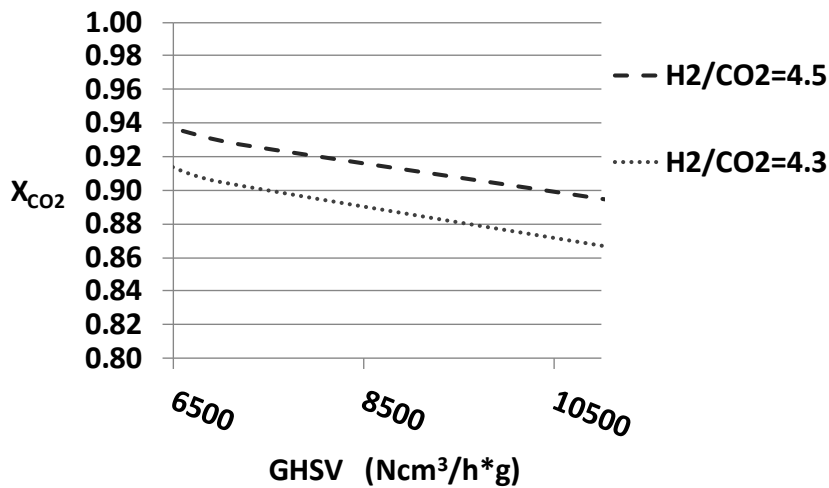
Figure 5. Effect of GHSV and H_2/CO_2 inlet ratio on CO_2 conversion

A decreasing trend is also observed changing the H2/CO2 molar inlet ratio. According to that experimental results indicate a slight increase in the CO_2 conversion when H2/CO2 ratio varies from 4.3 to 4.5

Figure 6 indicates SNG composition and GHSV trend during a test.
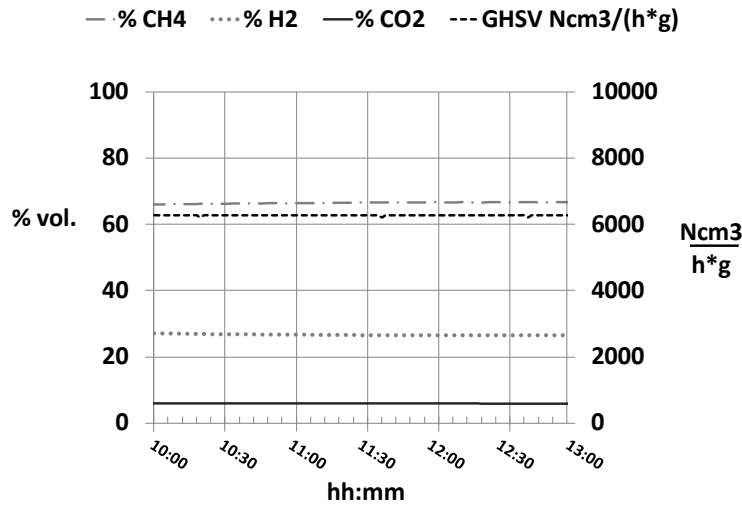
Figure 6 SNG composition and GHSV trend during a test

High methane concentration values (up to 67%) have been achieved in once through configuration with temperatures in the range of 300-330 °C and pressure of 5 barg. During this experimental test temperatures on reactor tube side remain quite constant meaning good thermal distribution for a better control of the process.
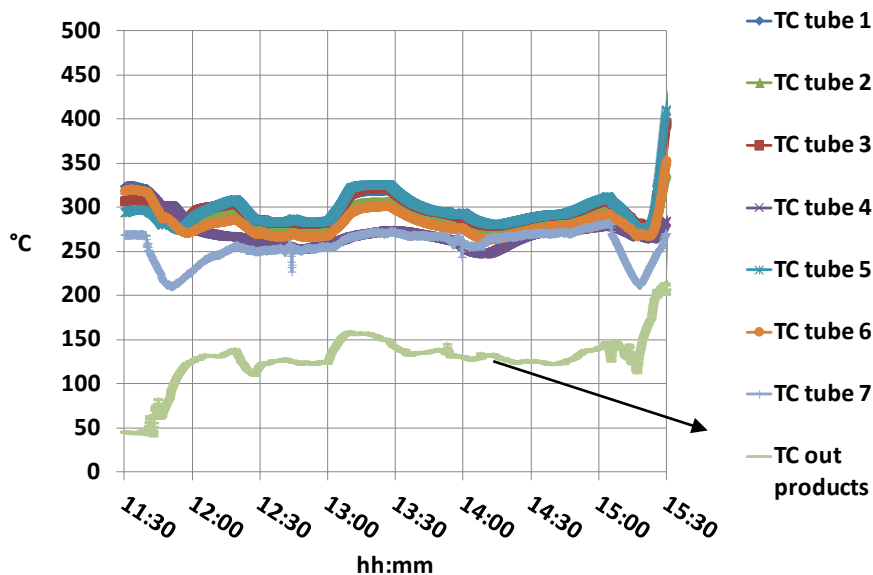
Figure7: Temperature trend on reactor tube side

Effect of CH₄ in the feed

The effect of CH$_4$ in the feed has been also studied and showed in Figure 8 to better simulate a second and a third reactor. The main conditions were: pressure 5 barg, H$_2$/CO$_2$ ratio 4.5. The resulting temperature inside the seven catalytic bed has been constant in the range of 310-330 °C.
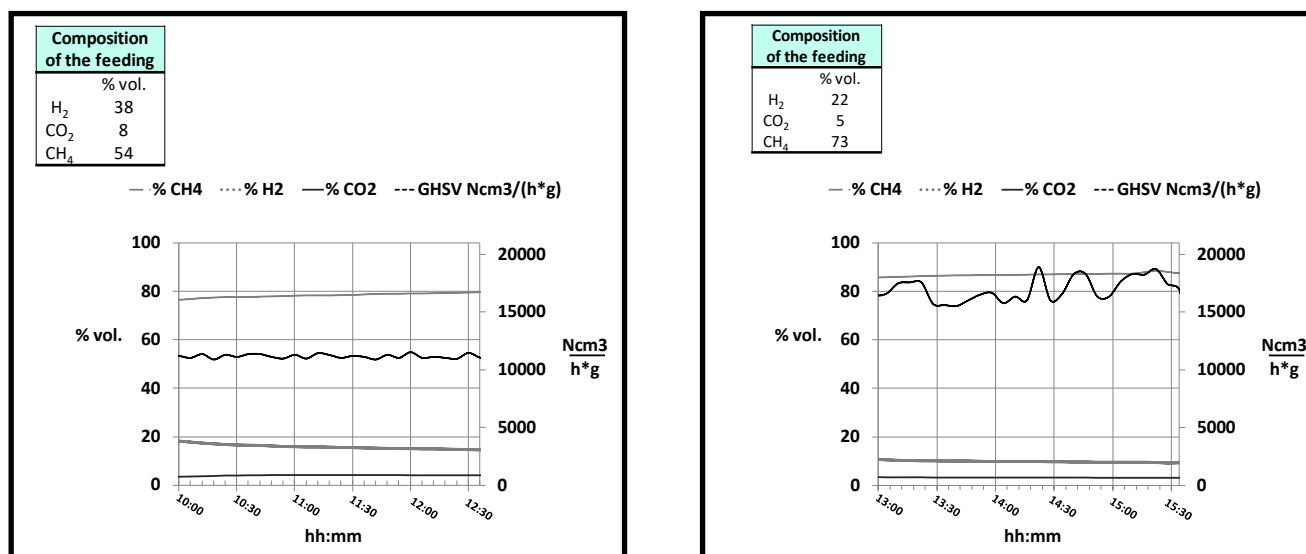

Figure 7: Effect of CH$_4$ in the feed

5. Conclusions

A new Moveable Modular Plant dedicated to CO2 Hydrogenation to CH4 has been designed and built at Enea Casaccia Research Center. A first experimental campain was carried out in order to check the operability of all components and to improve the knowledge on methanation in the different phase of start-up, steady operation and shut down.

A first characterization of the process was performed using a Ru based catalyst and the modalities and key parameters to achieve standard operating conditions were identified. The declared objective of testing the system and assessing the performance was successfully achieved. High methane concentration values (up to 67%) have been achieved in once through configuration with temperatures in the range of 300-330 °C and pressure of 5 barg.

After the first experimental sessions, different ongoing activities are running and many future developments are in progress.

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Acknowledgment

Acronyms

Nomenclature

α oxidant/coal mass ratio

η efficiency

μ steam/coal mass ratio

W   weight fraction (%)