

# Enriched methane production by solar steam reformer: process evaluation

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## ABSTRACT

The aim of this work is to present a novel hybrid plant for the production of a mixture of methane and hydrogen from a steam reforming reactor whose heat duty is supplied by a molten salt stream heated up by the innovative concentrating solar power plant developed by ENEA. By this way, a hydrogen stream, mixed with natural gas, is produced from solar energy by a consolidated production method as the steam reforming process and by a widely tested and pre-commercial technology as molten salts parabolic mirrors solar plant. After the hydrogen production plant, the residual heat stored in the molten salt stream is used to produce electricity.

A module of the plant requires 1.5 hectares and can supply electricity and gas to 3000 domestic Italian users. A 4-tubes-and-shell reactor 0.5 m long and with packed bed tubular reactor with diameter of 3” is able to produce up to 350 Nm<sup>3</sup>/h of enriched methane.

**Keywords:** enriched methane, hydrogen, solar energy, clean electricity production.

## 1 INTRODUCTION

The energetic matter, due to the growing energy worldwide consumption gone with the reduction of oil and gas availability and to environmental effects of the indiscriminate fossil fuel use in our economies, leads to an increasing interest about the hydrogen as energy carrier. But, the hydrogen technology is not ready for a real commercial breakthrough. Surely, the transition towards hydrogen economy will pass through the use of hybrid technologies, immediately applicable and which lead to important benefits in terms of reduction of GHG emissions and of partial use of renewable energy sources.

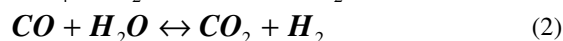
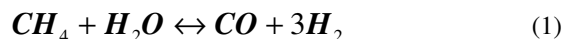
The aim of this work is to present a novel hybrid plant for the production of enriched natural gas (HCNG), with a content of hydrogen of 17%vol, here referred as HCNG-17.

HCNG-17 can be transported, stored and used by means of the actual gas infrastructure. Accordingly, HCNG-17 can be sent into the medium or low-pressure NG grid, immediately after the pressure-reduction stations [1]. In fact, no compressors are used in the medium or low-pressure distribution grid, which facilitates the use of the pipeline infrastructure for hydrogen transport. Furthermore, using HCNG-17 the well-known hydrogen storage problems are overcome since standard storage systems for compressed NG are adaptable to the “enriched” NG at low hydrogen content.

HCNG-17 mixtures can also supply natural gas powered internal combustion engines (NG-ICE), reducing BSFC, BSCO<sub>2</sub>, BSCO, BSHC and improving engine efficiency [2-5]. Only NO<sub>x</sub> emissions increase for higher flame temperature and a catalytic converter may be required.

The proposed technology for HCNG production is based on a consolidated production method such as steam methane reforming (SMR), powered by solar heat by means of a promising, widely tested and pre-commercial technology that makes use of molten salts as heat transfer fluid.

The SMR process is today the most important commercial massive hydrogen production route; it is based on the following two reactions:



Steam reforming reaction (1) is very fast over Ni-based catalyst, so that equilibrium conditions are quickly reached; a significant hydrogen yield is achieved only at high temperatures (850–900°C). This is the reason why SMR reactors are usually placed inside furnaces that supply the high heat flux required to get high methane conversion.

If 17 %vol content of hydrogen is requested, a lower operating temperature is needed to limit methane conversion. This leads to the possibility of efficiently match the steam reforming process with solar-derived heat available at temperatures lower than 600°C.

The concentrating solar power (CSP) plant basically consists of a solar collector field, a receiver, a heat transfer fluid loop; a suitable heat storage system is also required to maximize the “capacity factor” (i.e. productivity) of the solar plant, and to provide solar heat at the desired rate regardless the instantaneous solar radiation availability and fluctuations [6, 7]. The mirrors of the solar field concentrate the direct solar radiation on the solar receiver set at the focal point (if point concentrators are adopted) or at the focal line (if linear concentrators are used). The heat transfer fluid removes the high temperature solar heat from the receiver and it is afterwards collected into an insulated heat storage tank to be pumped, on demand, to the heat users where it releases its sensible heat. Finally, the heat carrier fluid is stored into a lower temperature tank ready to restart the solar heat collection loop. A proper dimensioning of the heat storage system allows to drive the process 24 h/24 h in continuous at the designed working conditions.

Recently, some molten nitrate mixtures at temperatures up to 550°C have been positively tested as convenient, cost-effective and environmental friendly heat transfer fluid and storage medium for CSP plants [7-9].

Normally, the molten salt sensible heat is used to generate high pressure steam to be sent to a steam turbine Rankine cycle for the production of electrical energy.

However, the molten salt temperature of 550°C seems to be suitable for the enrichment of a methane stream by producing the hydrogen through the SMR process. The proposed process scheme is shown in Figure 1. Solar energy stored in the molten salt can power the hydrogen production process (reformer heat duty, reactant steam generation, pre-heating of the reactants), and the residual heat can be used for the electrical energy production. By this way, a co-generation plant can be developed, able to produce a HCNG stream (to be sent in the NG pipeline or to be stored for the NG-ICE application), and clean electrical energy.

In the present paper, the behaviour of such a plant is simulated by modelling the SMR reactor and the heat exchange phenomena between the molten salt stream and the packed bed reactor. A reformer able to produce a HCNG-17 stream is designed, and the electrical power output by the plant is evaluated.

## 2 PROCESS DESCRIPTION

Figure 2 shows a scheme of the solar SMR plant for the production of enriched methane.

The reactant mixture, essentially composed by methane and steam, is the feedstock of a heat-exchanger shaped steam reforming reactor (Figure 3), in which the 550°C molten salt stream, heated up by solar energy in the CSP plant, is sent into the shell. Reactions (1-2) generate a gas mixture composed of CH<sub>4</sub>, H<sub>2</sub>O, H<sub>2</sub>, CO and CO<sub>2</sub>. The CO is converted into CO<sub>2</sub> and H<sub>2</sub> in a WGS reactor operating in two-steps (high and low temperature), and the final abatement of the residual CO traces is made by

methanation. The steam is separated by condensation, while the CO<sub>2</sub> content is eliminated by absorption in a typical regenerative MDEA unit. The final stream leaving the process is a methane-hydrogen mixture, whose composition depends on reformer performance and CH<sub>4</sub> stream added at the plant outlet line.

The molten salt stream supplies the heat required by reforming reactions, process steam generation and reactants pre-heating; the residual sensible heat is used to generate further steam to be sent to a steam turbine for electricity production.

The core of the process is the steam reforming reactor heated up by the molten salt. The physical-chemical phenomena inside the reaction environment and the heat exchange between the molten salt stream and the reactant mixture are taken into account in the two-dimensional mathematical model described in [10,11].

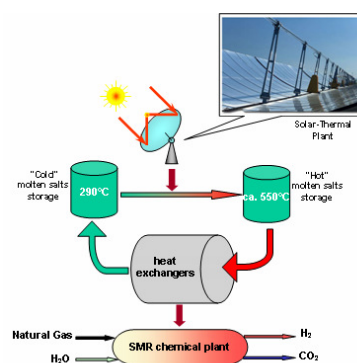


Figure 1 : Simplified scheme of parabolic trough power plant with two-tank molten salt storage

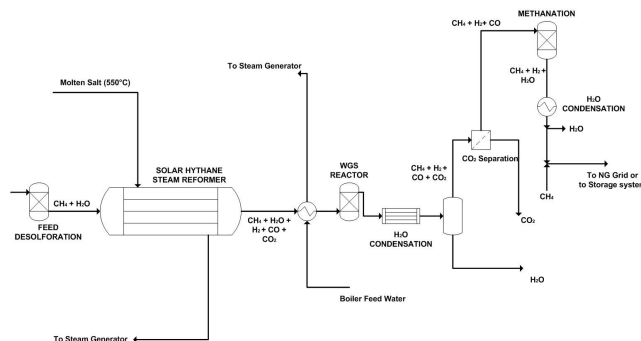


Figure 2 : Process scheme

## 3 RESULTS AND COMMENTS

Reactor conditions assumed in the following simulations are reported in Table 1. Catalyst pellets and packed bed properties are typical for industrial steam reformers, while length and diameter of the reactor are lower, considering that traditional reactors are 10 -15 m long and with an internal diameter of about 10-13 cm. The higher compactness of the reformer applied in this work is

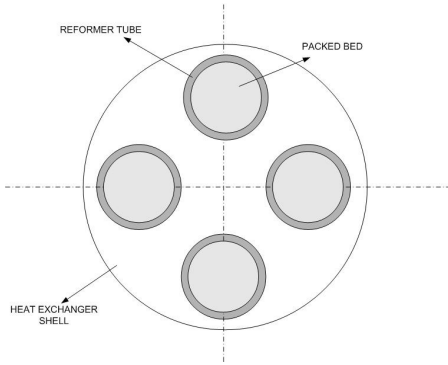


Figure 3 : Heat-exchanger shaped steam reformer reactor

due to the lower methane conversion required in the process. As design point, a flow-rate of 4 kg/s for the molten salt stream at 550°C sent to the shell (Figure 3) is assumed. A co-current configuration of heating fluid and reactant gas stream is assumed.

For each simulation, methane conversion

$$X_{CH_4} = \frac{F_{CH_4,0} - F_{CH_4,ex}}{F_{CH_4,0}} \quad (3)$$

is calculated and the amount of methane to be added to reach the hydrogen content specification of 17 %vol is evaluated. Then, the HCNG-17 production rate and the electric power obtained exploiting the molten salt residual sensible heat are assessed.

Reactor length	0.5 m
Internal radius	0.0381 m
Catalyst particle diameter	0.011 m
Catalyst bed density	1016 kg/m <sup>3</sup>
Bed void	0.5
Gas inlet temperature	773 K
H <sub>2</sub> O/CH <sub>4</sub> molar ratio	2.5

Table 1 : Reactor conditions assumed

### 3.1 Effect of residence time

Residence time is calculated as the ratio between the mass of catalyst in the packed bed and the total inlet molar flow-rate. Therefore, the higher the total inlet molar flow-rate, the lower the resulting residence time.

Figure 4 shows the effect of the residence time on methane conversion. Increasing residence time has a positive effect on the methane conversion because of the longer contact time of the gas mixture with the catalyst packed bed; moreover, reformer outlet gas mixture temperature increases (T=737.9 K at 1 kg<sub>cat</sub>/s/mol, T=740.4

K at 10 kg<sub>cat</sub>/s/mol). On the other hand, the lower feed flow-rate leads to lower amounts of hydrogen produced. As shown in Figure 5, the total flow-rate of enriched methane produced is strongly affected by the residence time, being reduced to lower than one-fifth increasing the residence time from 1 to 10 kg<sub>cat</sub> s/mol. As a consequence, by increasing the residence time, the steam to be generated for the reaction and the total thermal duty required to the molten salt stream are reduced; in fact, the temperature of the molten salt leaving the chemical plant is higher at longer residence times (T=781.6 K at 1 kg<sub>cat</sub>/s/mol, T=818.4 K at 10 kg<sub>cat</sub>/s/mol) and the electrical power generated by the steam turbine exploiting the residue molten salt sensible heat increases (see Figure 5).

In conclusion, increasing the gas residence time leads to a higher methane conversion in the steam reformer and to a higher electrical power output, but reduces the enriched methane production rate. The optimal residence time has to be fixed on the basis of the amounts of enriched methane and electrical power required by the users and of plant design optimization.

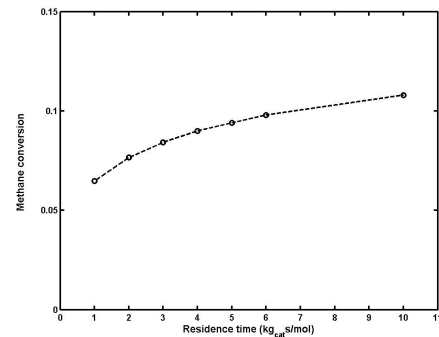


Figure 4 : methane conversion vs. residence time at operating pressure of 10 bar

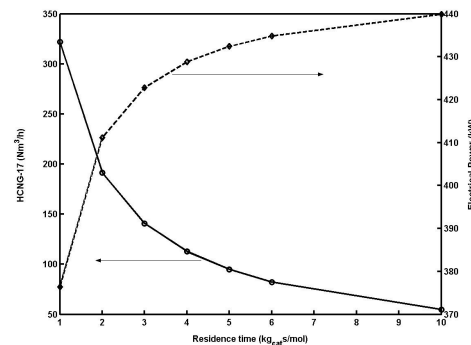


Figure 5 : HCNG-17 and electrical power produced by the 4-tubes heat exchange shaped reactor at various residence times and at 10 bar

### 3.2 Effect of operating pressure

Since the steam reforming reaction (1) occurs with an increase of the gas volume, the pressure affects negatively

the equilibrium conversion, so that both methane conversion ( $X_{\text{CH}_4}=0.093$  at 5 bar,  $X_{\text{CH}_4}=0.074$  at 20 bar) and the enriched methane production (see Figure 6) result unfavourable at high pressure levels.

On the other hand, increasing the operating pressure leads to a slight enhancement of the electrical power production. The main reason is that the latent heat required to generate the reactant steam slightly decreases as the pressure increases (37.8 MJ/kmol at 5 bar vs. 34 MJ/kmol at 20 bar).

Altogether, a convenient solution appears to be setting the inlet pressure as low as possible consistently with the pressure drops which, however, are always small in the ranges of operating conditions assumed.

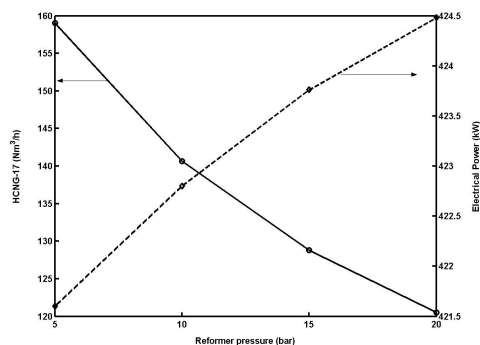


Figure 6 : HCNG-17 and electrical power produced by the 4-tubes heat exchange shaped reactor at various operating pressure and with a residence time of 3 kg<sub>cat</sub>/mol

### 3.3 Plant design

The main design features of a solar enriched methane plant for supplying the enriched methane and the electrical energy required by a small Italian municipality are assessed.

The yearly *pro-capite* household consumption of electricity and methane, according to the Italian Statistics Institute (ISTAT) are 1228.7 kWh<sub>el</sub>/y and 429.1 Nm<sup>3</sup>/y, value corrected at 486.9 Nm<sup>3</sup>/y to consider the different lower heating value of HCNG-17.

According to the results of simulations performed, the operating pressure is imposed equal to 5 bar.

It can be noticed from Figure 7 that 3000 Italian domestic gas and electricity users can be supplied by the 4 tubes heat exchanger shaped reactor shown in Figure 3 and imposing a residence time of 2.9 kg<sub>cat</sub>/mol, installed in a solar field which requires 1.5 hectares about.

## 4 CONCLUSIONS

The performance of a novel hybrid plant for the production of a 17%vol H<sub>2</sub>-CH<sub>4</sub> gas mixture has been assessed. The steam reforming heat duty is supplied by a

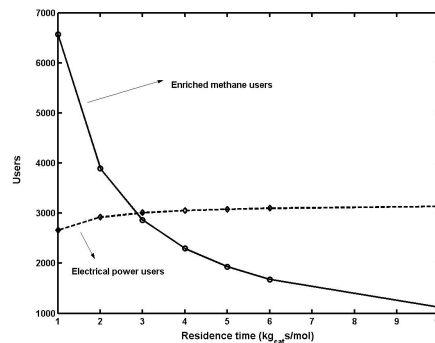


Figure 7 : HCNG-17 and electricity users

molten salt stream heated up by a concentrating solar power (CSP) plant.

Simulation results show that a CSP plant with an active area of about 15,000 m<sup>2</sup> coupled with a 4 tubes-and-shell reactor is able to supply the electricity and enriched methane to about 3000 Italian domestic users.

However, some important issues have to be faced yet, mainly dealing with technical-economy assessment of this novel co-generative plant design.

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