Solar enriched methane production: Assessment of plant potentialities and applications

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The crucial environmental issue due to fossil fuel use in our society and industries and more and more perceived by the communities is stimulating the development of innovative technologies with the scope of reducing GHGs and pollutants emissions, improving plants efficiency and exploiting renewable energy sources.

The idea proposed in the present work links this context: a novel hybrid plant for the production of a mixture of methane and hydrogen (20%vol), called enriched-methane, from a steam reforming reactor whose heat duty is supplied by a concentrating solar power (CSP) plant by means of a molten salt stream is here conceived, modelled and assessed. The enriched-methane mixture can be applied in methane internal combustion engines (ICE) reducing CO, CO2, unburned emissions and improving engine efficiency. Moreover, the residual sensible heat of solar-heated molten salt stream can be used to generate medium-pressure steam and to produce electricity by a steam-turbine. Therefore, the plant proposed is co-generative, producing both hydrogen and electricity from a solar source.

The behaviour of methane steam reforming reactor is simulated by means of a 2D mathematical model and the design of a cogenerative solar plant is proposed, evaluating its potentialities in terms of MWh of electricity produced and number of vehicles fed by enriched-methane. A single CSP module (surface requirement = 1.5 hectares) coupled with a 4-tubes-and-shell shaped reactor is able to produce 686 tons/year of hydrogen, equivalent to 3.430 tons/year of 20%vol H2-CH4 mixture and 3.097 MWh/year of clean electricity.

Keywords: Enriched methane, solar energy, hydrogen production, CSP plant, molten salt.

Introduction

Hydrogen can be produced from renewable energy sources and it can fed fuel cells for generating electricity without local air pollutants or greenhouse gas (GHG) emissions. Therefore it has the potentiality of re-shaping the entire energy worldwide system as renewable energy vector. But, the hydrogen technology is not yet ready for a real commercial breakthrough since production methods, storage and end-use technologies suffer for high cost and low efficiency. As a consequence, it is a worth assessment that the transition towards a hydrogen economy will pass through the development and application of hybrid technologies, immediately applicable and leading to important benefits in terms of reduction of GHG emissions thanks to a partial use of renewable energy sources.

Enriched-methane (EM) is a hybrid mixture, composed by a fossil fuel (methane) and hydrogen produced by renewable energy sources. If hydrogen content is limited at value lower than 20%, EM can be sent into the medium or low-pressure natural gas (NG) grid, immediately after the pressure-reduction stations, as stated by Haeseldonckx (2007). In fact, no compressors are integrated in the medium or low-pressure distribution grid, facilitating the use of the pipeline infrastructure for hydrogen transport. Furthermore:

1. using EM the well-known hydrogen storage drawbacks are avoided since standard and currently available storage systems for compressed NG are adaptable to the “enriched” NG at low hydrogen content;

2. EM can feed natural gas powered internal combustion engines (NG-ICE). A number of papers, appeared in the scientific literature, claims that increasing hydrogen content in the NG engine allows BSFC, BSCO2, BSCO, BSHC to be reduced, improving the engine efficiency and reducing the pollutants emissions (Bauer, 2001; Akansu, 2004; Ortenzi, 2008).

From these considerations, it appears evident that a wide application of EM would be a first step towards the diffusion of hydrogen as energy carrier for automotive.
The proposed technology for EM 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 Concentrating Solar Power (CSP) technology that makes use of molten salts as heat transfer fluid (Figure 1).

**Figure 1. CSP plant at Priolo (Italy) in construction phase:**
Collectors streaks (a,b), molten salt storage system (c)

CSP plant basically consists of a solar collector field, a receiver, a heat transfer fluid loop. A heat storage system is 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, as reported by Winter (1991) and Mills (2004). The mirrors of the solar field concentrate the direct solar radiation on the solar receiver set 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 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 driving 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 heat transfer fluid and storage medium for CSP plants, as reported by Herrmann (2002), Pacheco (2002) and Kearney (2003).

Normally, the molten salt sensible heat is used to generate water 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. Moreover, the continuous operation, assured by the proper dimensioning of heat storage system, makes easier the coupling of CSP with a chemical plant.

SMR process is the most important commercial massive hydrogen production route; it is based on the following two reactions:
Steam reforming reactions are endothermic and 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) for thermodynamics issues.

But, if only a small amount of hydrogen is required (<20% vol), the methane conversion required is much lower (5-10%) and a lower thermal level is required. Coupling the SMR with a CSP plant seems to be a good solution to assure the proper process thermal level, supplying the reforming heat duty by a solar source.

In the following, the potentialities of a solar SMR process to produce clean electricity and a stream of enriched-methane (H2 20% vol) are assessed via simulations.

**Process description**

Figure 2 shows the flow diagram of process proposed. Molten salt stream are heated up 550°C by solar collector, then it is stored in hot storage tank. Immediately after the hot storage, SMR plant is placed, in order to exploit the molten salt at highest temperature, producing enriched methane (H2 20% vol). Then, molten salt is sent to a steam generator where it is cooled to 290°C (minimum thermal level), generating the steam for the electricity production. At the end, molten salt streams is stored in cold storage tank and sent again towards solar collectors.

\[
\begin{align*}
CH_4 + H_2O &\leftrightarrow CO + 3H_2 & \Delta H_{298K}^0 &= 206 \text{kJ/mol} \\
CO + H_2O &\leftrightarrow CO_2 + H_2 & \Delta H_{298K}^0 &= -41 \text{kJ/mol} \\
CH_4 + 2H_2O &\leftrightarrow CO_2 + 4H_2 & \Delta H_{298K}^0 &= 165 \text{kJ/mol}
\end{align*}
\]

which, together, yield:

\[
CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2
\]

STEAM GENERATOR AND POWER BLOCK

FIGURE 2. CSP + SOLAR SMR PLANT FLOW DIAGRAM
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 a 2D mathematical model described by De Falco (2009) and suitable to evaluate both axial and radial profiles of components concentrations, reactants and molten salt temperatures and reaction pressure.

By the simulation tool, methane conversion, hydrogen production and consequently enriched methane output flow and output molten salt temperature, needed to calculate the electricity generation, can be assessed varying operating conditions as inlet temperatures, molten salt flowrate, reaction pressure and reactant feedstock compositions. De Falco (2009) collects many results, making clear the reactor behavior and particularly:

- increasing residence time improves methane conversion but negatively affects the total enriched methane production;
- reaction pressure has a negative effect on reactor performance;
- inlet reactant temperature positively affects the reactor behavior;
- steam-to-carbon ratio, i.e. the ratio between reactant steam and methane flowrates in the feedstock, has a negative effect on reactor performance since increases methane conversion but reduces the global process efficiency for the greater amount of steam to be produced for the reactions.

From these results, an optimized operating conditions set has been found, and reported in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Optimal reformer operating conditions (De Falco, 2009)</th>
</tr>
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<tbody>
<tr>
<td>( W / F ) *</td>
</tr>
<tr>
<td>steam to carbon ratio</td>
</tr>
<tr>
<td>operating pressure</td>
</tr>
<tr>
<td>inlet gas mixture temperature</td>
</tr>
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Note: *Residence time is calculated dividing the total catalyst mass packed in the reactor by the total inlet reactant flowrate.

In the next paragraph, some figures are reported in order to show reactor behavior and production at optimal operating conditions.

The most meaningful simulation outputs are:
1. EM production;
2. Exit molten salt temperature, by which calculating the electricity production by:

\[
P_{el} = \eta_{t} \cdot w_{MS} \cdot c_{P,MS} \cdot (T_{MS,ex} - 290) \tag{4}
\]

where \( P_{el} \) is the total electrical power produced (kW), \( w_{MS} \) is the molten salt mass flowrate, assumed equal to 4 kg/s which is a mean value for CSP modules, \( c_{P,MS} \) the molten salt specific heat, \( T_{MS,ex} \) the exit molten salt temperature and 290°C the minimum molten salt temperature. The term is the steam-turbine electrical efficiency, taken equal to 28% for small size turbines (< 1MWel).

**Plant design**

In the present paragraph, a CSP + EM plant is dimensioned. It is assumed that plant outputs are used to satisfy domestic electrical users and to feed methane ICE.

The yearly pro-capite household consumption of electricity, according to the Italian Statistics Institute - ISTAT (2006), is:

\[
Q_{E.E.} = 1228.7 \frac{kWh}{y}
\]
while, assuming a specific ICE methane consumption of 17 km/kg\textsubscript{methane} and considering that 1 kg of EM at 20% vol. of hydrogen (equal to 3.03% wt) has a lower heating value (LHV) of 52.16 MJ/kg (versus 50 MJ/kg of methane), the specific EM consumption for a ICE is 17.8 km/kg\textsubscript{EM}. Therefore, assuming a mean yearly vehicle path of 10,000 km, the yearly EM vehicle consumption can be imposed equal to 562 kg.

Molten salts CSP plants fabricated by ENEA are composed by single modules which can be replicated in parallel to reach the potentialities required by the application. One module is able to heat up a molten salt stream within the range 2 - 6 kg/s (1 MW\textsubscript{th}) and requires a surface of about 1.5 hectares. In the following, the simulations are made considering one CSP module, a mean molten salt stream of 4 kg/s and an operation of 8760 hours/year, thanks to the use of a properly dimensioned molten salt hot storage (550°C) tank.

**Reactor behavior**

The reactor assumed in the following simulations is a four-tubes-and-shell shaped reactor (Figure 3), with the sizes summarized in Table 2.

![Figure 3. Solar enriched methane reactor configuration](image)

**Table 2. Reactor parameters**

<table>
<thead>
<tr>
<th>Reactor parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Reactor length</td>
<td>3.5 m</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>0.0508 m (2&quot;)</td>
</tr>
<tr>
<td>Catalyst density</td>
<td>1990.6 kg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Void fraction</td>
<td>0.5</td>
</tr>
<tr>
<td>Catalyst particle diameter</td>
<td>0.011 m</td>
</tr>
</tbody>
</table>

The next figures show the temperature distribution inside the reactor. It has to be noticed:

- the cold spot in the first part of the reactor, due to the fast reactions kinetics rate;
- the strong radial gradient (up to 20 K between axis and wall reformer) due to the scarce thermal conductivity of catalyst packed bed;
- molten salt temperature profile from Figure 5. The molten salt temperature is reduced of 13 K about to heat up the reactors.

Figure 6 reports methane conversion profile (a) and pressure drops (b). The final methane conversion is equal to 14.5% about, much higher than the conversion required since the hydrogen concentration in the exit stream (after CO, CO\textsubscript{2} and steam separation) is 41%. In order to reduce hydrogen content at 20%, it is assumed to add a methane stream before storing EM mixture.

The pressure drop is about 5 bar along the 3.5 m long reactor.
Figure 4. Temperature map inside EM reformer

Figure 5. Axial temperature profiles
Plant dimensioning

Imposing the operating conditions and parameters reported in Tables 1 and 2, the single CSP module coupled with the EM chemical plant is able to produce:
- 686 tons/year of hydrogen, equivalent to 3.430 tons/year of EM (H2 20%vol);
- 3.097 MWh/year of clean electrical energy.

These outputs can feed:
- 6.104 EM ICE based vehicles;
- 2.521 Italian domestic electrical users.

Table 3. CSP + EM Plant Potentialities

<table>
<thead>
<tr>
<th>CSP Modules</th>
<th>Surface required (hectares)</th>
<th>H₂ production (tons/year)</th>
<th>EM vehicles fed</th>
<th>Electrical used fed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>686</td>
<td>6.104</td>
<td>2.521</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>2.058</td>
<td>18.312</td>
<td>7.563</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>4.116</td>
<td>36.624</td>
<td>15.126</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>6860</td>
<td>61.040</td>
<td>25.210</td>
</tr>
</tbody>
</table>

Assembling more CSP modules in parallel, the number of users satisfied by plant outputs increases proportionally. Table 3 shows the potentiality of the proposed technology.

Conclusions

A novel hybrid plant for the production of a mixture of methane and hydrogen (20%vol), called enriched-methane, from a steam reforming reactor whose heat duty is supplied by a concentrating solar power (CSP) plant by means of a molten salt stream has been presented and evaluated. The behavior of a 4-tubes-and-shell shaped reactor has been simulated by a 2D mathematical model able to calculate axial and radial profile.

The potentiality of the plant in terms of EM production and clean electricity generation has been reported: a plant which requires a surface of about 1.5 hectares is able to produce the electricity needed by 2.521 Italian domestic users and the EM for 6.104 methane ICE based vehicles.

The wide application of EM in the place of methane in automotive sector would be a first step in the short-term for the conversion of our economies according to more sustainable criteria.
References


