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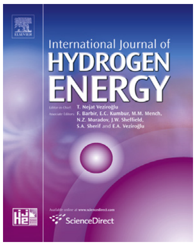

Solar steam reforming for enriched methane production: Reactor configurations modeling and comparison

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ABSTRACT

A solar low-temperature steam reforming process for the production of an Enriched Methane (EM) mixture composed by CH_4 and H_2 (20%vol) exploiting the solar energy stored in a Molten Salt stream heated up by a Concentrating Solar Plant (MS-CSP) is presented and simulated through a two-dimensional steam reforming reactor model.

Two configurations are considered and compared: the Integrated Heat Exchanging (IHE) configuration, where the steam reformers are tubes-and-shell reactors continuously heated up by the hot MS stream, and the External Heat Exchanging (EHE) configuration composed by a series of heat exchangers and insulated reformers where the reactions are adiabatically driven.

The effect of the main operating conditions as Gas Hourly Space Velocity (GHSV), inlet reactor temperature and reactant mixture composition is assessed for both the configurations, demonstrating the process feasibility. Furthermore, in order to increase the process performance, an electrical power generation unit is also included, exploiting the sensible heat of the residual MS stream after the EM production unit: in this case, with a feed of 2000 Nm^3/h of natural gas, about 6130 Nm^3/h of enriched methane and 475 kW_{el} are produced with the EHE configuration, while 3720 Nm^3/h and 585 kW_{el} are obtained with IHE configuration.

Introduction

Enriched methane (EM) is a gas mixture composed by hydrogen (10–30% vol) and methane, able to be used as feedstock in the traditional natural gas internal combustion engines (NG-ICE) without the need of expensive technical modifications and leading to an improvement of the engine efficiency and to a reduction of CO, CO_2 and un-burned emissions [1–6]. Therefore, the EM is a hybrid fuel composed by an amount of fossil fuel (natural gas) and a share of hydrogen, produced by exploiting renewable energy as solar

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energy, wind, hydroelectric energy or biomass: its combustion leads to the emission of pollutants and Green House Gases (GHGs) for the fossil fuel share, while hydrogen combustion produces only water. Consequently, the greater the amount of hydrogen in EM composition, the greater the emission reduction, as shown in Fig. 1 where the mass reduction of CO_2 emission is depicted in function of H_2 volumetric composition.

Moreover, EM can be stored in the standard compressed natural gas storage systems and, if the H_2 content is limited at 17%, the mixture can be distributed by means of the medium pressure NG grid, immediately after the pressure reduction stations [7].

Basically, EM solves the main technological problems (production, storage, distribution and use) which are hindering the hydrogen diffusion as energy vector: EM can be considered as a first technological steps towards the "hydrogen economy" development [8] since it can be applied in the next years using all the infrastructure already available for the natural gas, with immediate environmental and energetic benefits.

Many processes are proposed in the literature to produce EM exploiting renewable energies [9–13]. Here, a solar-driven steam reforming process [12] is modeled and assessed. Since the steam reforming is the most important massive H_2 production route [14] and a wide industrial experience on the technology is already available, the solar reforming seems to be the most competitive process to produce large amount of EM mixture.

Steam reforming is based on the following reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298K} = 206\,\frac{kJ}{mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -41\,\frac{kJ}{mol} \tag{2}$$

The first one is the Steam Reforming reaction (SR), strongly endothermic and very fast over Ni-based catalyst, so that equilibrium conditions are quickly approached; the second one is the exothermic Water Gas Shift (WGS) reaction, that produces a further amount of hydrogen converting CO into CO_2.

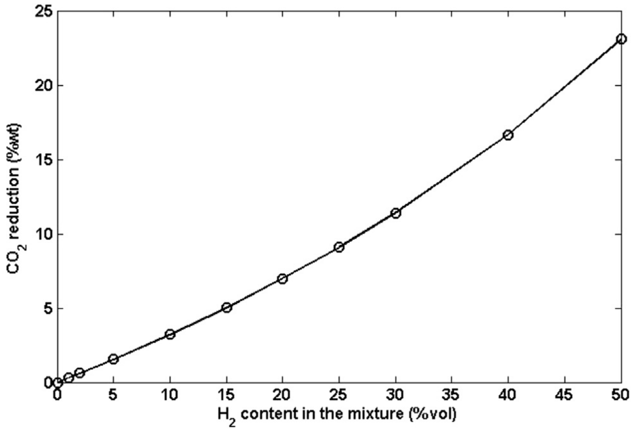

Fig. 1 – CO_2 reduction (%wt) vs. EM H_2 volumetric content during EM combustion in NG-ICE.

In the industrial reforming plants for hydrogen production, the reactors operate at high temperature (850–1000 °C) in order to achieve high hydrogen yield (methane conversion > 90%); to reach these temperatures, reactors are heated inside furnaces. Then, H_2 is separated from the outlet stream by using standard separation processes (Pressure Swing Adsorption, ammine absorption, etc).

If an EM stream has to be produced instead of pure hydrogen, the traditional process unit is modified as follow:

1. the operating temperature is reduced (~500 °C) since a low methane conversion is required (<35%);
2. the H_2 produced through the reforming process has not to be separated from CH_4, avoiding the installation of expensive separation units. On the contrary, a separation unit to remove carbon dioxide may be required.

From these considerations, it has been proposed to produce EM by coupling a low-temperature steam reforming with a MS-CSP (Molten Salt based Concentrating Solar Power) plant [12,13], by which a molten salt stream is heated up to 550 °C (a temperature suitable for the low temperature steam reforming) thanks to parabolic mirrors able to concentrate solar rays on a receiver tube.

The hot molten salt stream is stored in hot storage systems, properly designed in order to maximize the "capacity factor" (i.e. productivity) of the solar plant and to dump the effects of the instantaneous solar radiation availability and fluctuations [15–17]. Then, the hot stream provides all the process heat duties (endothermic reactions thermal duty, steam generation, feedstock pre-heating). Fig. 2 shows a plant conceptual layout.

The core of the chemical process is the low-temperature steam reforming reactor (LTSRR), which has to be properly modeled. In the present paper two different reactor configurations are proposed and compared:

- Internal Heat Exchanging (IHE) configuration, where the reactants, preheated in an external heat exchanger, are fed to a tubes-and-shell reactor heated up by the hot molten salt stream, fed to the shell;
- External Heat Exchanging (EHE) configuration, composed by a series of heat exchanger + reformer modules. The feedstock is firstly heated in an external heat exchanger by

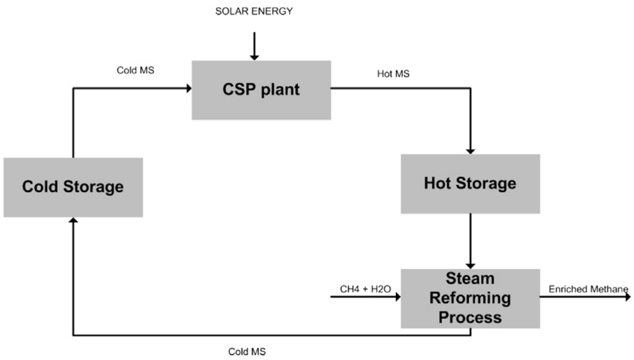

Fig. 2 – Steam reforming coupled with MS-CSP plant conceptual layout.