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Experimental and Theoretical Studies of Solar Steam Reforming Assisted by Molten Salts

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1 Introduction

Steam reforming of methane is today the mostly used industrial process for hydrogen production, covering about 48 % of hydrogen demand. The process is based on two catalytic reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1) \qquad (\text{SMR}, \Delta H_{298\,K} = +206\ \text{kJ/mol})$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2) \qquad (\text{WGS}, \Delta H_{298\,K} = -41\ \text{kJ/mol})$$

Reaction (1) is usually carried out at 800-1000 °C in a tubular catalytic reactor placed in an industrial furnace. Hydrogen yield is afterwards maximized in one or two water-gas-shift (WGS) (2) reactors operating at lower temperatures (200-500 °C).

The whole process requires heat to power the highly endothermic SMR reaction (1), generate reactant steam, and drive purification units (e.g. CO_2 separation). This process heat is usually provided burning a fraction of the natural gas (NG) supply [1].

Alternatively, high-temperature carbon-free heat sources, like solar or nuclear, can be used to power the whole thermochemical process: in this way environmental benefits in terms of reduction of CO_2 emissions can be achieved, together with a corresponding reduction of methane consumption, as represented in Figure 1.

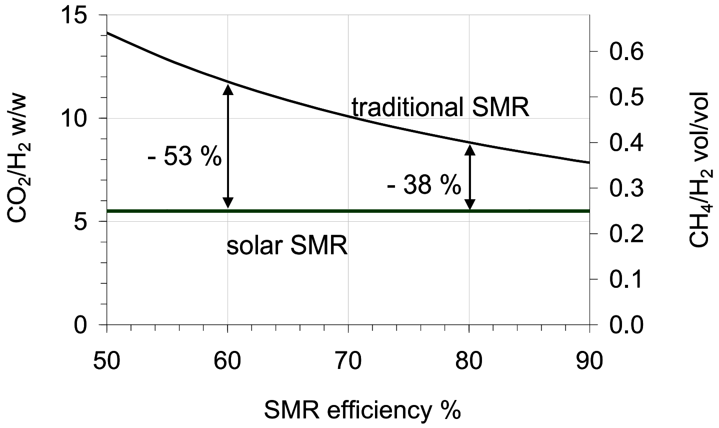

Figure 1: **Comparison between conventional and solar SMR in terms of specific CO_2 emissions related to overall process thermal efficiency.**

Given the lower NG demand, the solar (or nuclear) route is less sensible to NG price and availability. Therefore, due to possible increase of NG price, we can expect for the near future a hydrogen production cost from solar SMR competitive with the traditional process [2].

Solar SMR can be directly carried out in a high-temperature solar receiver reactor set on a tower [2]. This technology enables reactor operation at suitable temperature levels for the SMR reaction (1), but effectiveness is strictly linked to instant solar radiation fluctuations and night/day cycles.

In this paper it is presented an alternative solar SMR technology, studied by ENEA in the framework of the “Solar Thermodynamic Project”. This innovative route makes use of a molten salts stream as heat transfer fluid and storage medium to drive the SMR process under steady state and designed conditions. Main R&D issues deal with the lower operating temperatures (450-550 °C) than the conventional route (800-1000 °C): this results in thermodynamic limits of SMR reaction (1), but also allows to lower material concerns and to drive SMR (1) and WGS reactions simultaneously.

Preliminary theoretical analysis and experimental programs are overviewed.

2 Process Description

Molten nitrate mixtures ($NaNO_3/KNO_3$ 60/40 w/w) up to 565 °C have been proved as suitable heat carriers and storage medium for concentrating solar power (CSP) plants. Particularly, ENEA has recently demonstrated their use in an innovative solar trough technology (a 5 MW_e demonstration plant has been built in Sicily, and will be started in the next months).

This system is also suitable to steadily power themochemical processes up to 550 °C [3], and steam reforming of methane (from NG or biogas) is an interesting option.

In Figure 2 is shown a general process scheme. During solar radiation hours the molten salts (MS), flowed through the solar receiver of the CSP plant, are heated up to about 550 °C and stored in a “hot” tank. The CSP plant with heat storage tanks is dimensioned to supply 24 h/24 h heat at constant rate to the thermochemical plant; a back up heater (powered by an auxiliary fuel, e.g. biomass or biogas) is often integrated in the MS loop to ensure constant heat supply even after long cloudy periods. MS are first sent to the SMR + WGS reactor, consisting of a shell and tube heat exchanger with the inner tubes packed with the catalyst (Figure 3). Residual sensible heat of MS is used to power the feed gas pre-heater (Pr-Htr), steam generator (Steam-Gn), and downstream separation units. Due to thermodynamic limits resulting from reaction temperatures lower than 550 °C, a CH_4/H_2 gas mixture will be obtained after cooling and water removal by condensation (GL-Sep) and CO_x removal (e.g. methanation and CO_2 adsorption in regenerative amine solution cycles).

Hydrogen can be recovered and purified from the outlet CH_4/H_2 mixture (e.g. by PSA) and methane recycled. Otherwise, the hydrogen-containing methane (often referred as HCNG) is a valuable energetic product for several applications [4]: it was demonstrated that, within certain composition limits (5-30 $\%_{vol}$ of H_2), pure NG replacement with HCNG in internal combustion engines (ICE) has some environmental benefits in terms of local pollution; the use of a renewable source for hydrogen generation leads to additional environmental benefits even to the global level. Residual MS sensible heat (to 290 °C) can be used for the co-generation of solar electricity by steam cycles [5].

It is noteworthy that the gas fueled industrial SMR furnace of the industrial process is replaced by more compact and modular heat exchangers with improved scale down capabilities. This makes the SMR process more efficient at the small-medium scale, and eliminates flue gas emissions of the chemical plant.

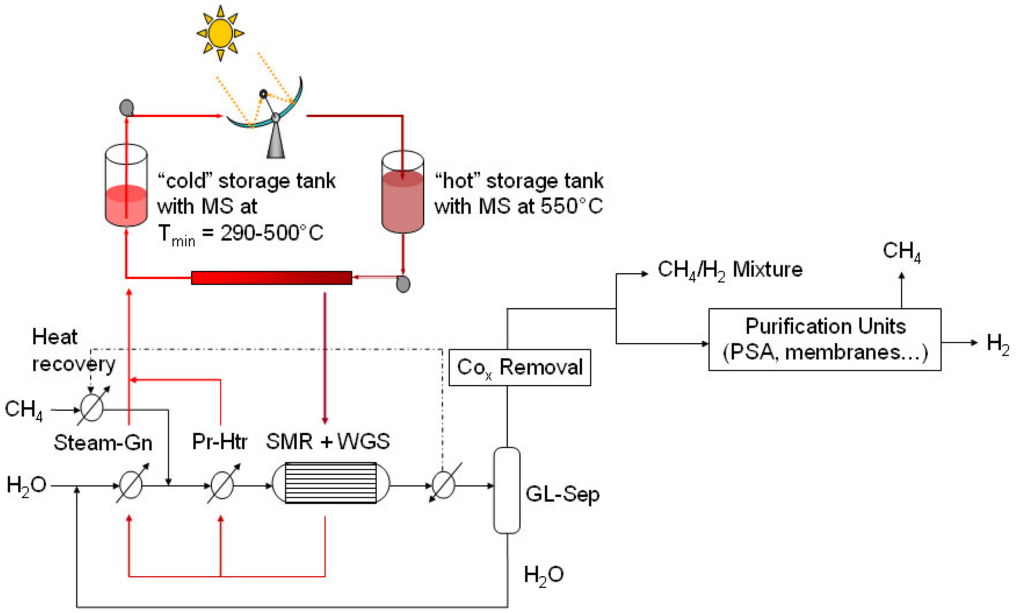

Figure 2: **Simplified scheme of the SMR process powered by a concentrating solar plant using molten salts (MS) as heat transfer fluid.**

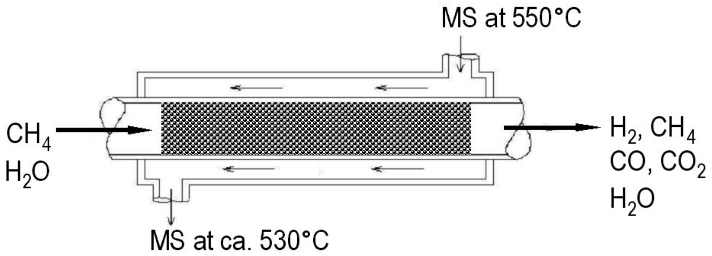

Figure 3: **Methane steam reforming packed-bed reactor using molten salts (MS) as heat transfer fluid.**

3 Preliminary Results and Application

MS assisted solar SMR has been analyzed by means of suitable mathematical models for catalytic steam reformers (specifically developed by the University "La Sapienza" - Rome), and the ASPEN Plus process simulator for flowsheet development with mass and energy balances. A parametrical analysis of several chemical process configurations was carried out at nominal pressures of 10 and 20 bar, and 2.2 mol/mol steam-to-carbon ratio into SMR reactor inlet.

In order to shift methane conversion above the thermodynamic limits, H_2 selective membranes or CO_2 Sorption Enhanced Reforming Process (SERP) can be applied. Particularly, we first considered a process configuration involving a single reactor followed by conventional CH_4/H_2 separation units (e.g. PSA). This benchmark configuration was compared with advanced process scheme consisting of SMR reactors set in series with intermediate membrane units for H_2 removal. Permeated hydrogen was assumed extracted by a vacuum pump whose duty was accounted in the energy balance. In Figure 4 is represented the overall thermal energy demanded to the CSP plant with the number of reaction/membrane stages in series: by increasing single-pass methane conversion and hydrogen output rate, membrane exploitation leads to a significant energy efficiency increase of the thermochemical process. Therefore, membranes make the chemical plant more complex but significantly reduce the costs for the CSP plant.

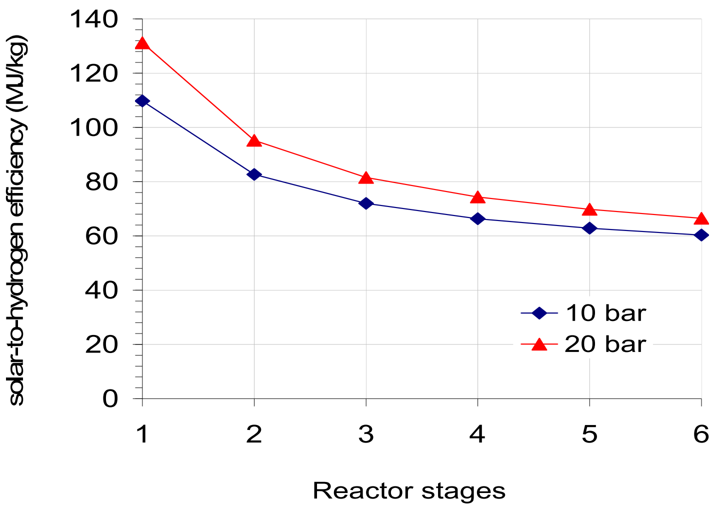

Figure 4: **Thermal energy demand by the thermochemical process per kg of hydrogen produced using different reaction/membrane stages in series.**

It is noteworthy that the reactor/membrane units train is fairly equivalent to a single integrated membrane reactor, i.e. a reactor equipped with the membrane tube set inside the catalytic bed [6]: the use of membranes working at temperatures close to SMR reactor temperatures (530-550 °C) should allow us to design compact membrane reformers powered by molten salts at 550 °C, with results fairly equivalent to those plotted in Figure 4.

Research and development activities in ENEA are now focused on experimental validation of these theoretical results, and engineering studies to process optimization.

First, suitable catalysts must be identified for methane steam reforming in the temperature range of 450-550 °C. Both commercial and home-made supported catalysts are investigated. Catalyst long-term stability (i.e. constant H_2 production rate over at least 200 hours operation), activity and selectivity (WGS reaction effectiveness) is determined under different operating conditions like temperature (450-550 °C), pressure (1-20 bar), steam-to-carbon ratio, space velocity. Besides identification of the most promising catalyst, this preliminary study allows determination of the effect of process parameters for subsequent reactor design.

Moreover, performances of H_2-selective membranes are investigated in terms of selectivity and permeability under representative process conditions.

Afterwards, a MS-heated SMR prototype will be designed, constructed and integrated in the Molten Salts Experimental test facility (MOSE plant) in ENEA-Casaccia research center. In case of an integrated membrane reactor, an engineering challenge is the fitting of the rates of the three controlling physical-chemical mechanisms, i.e. mass transport through the membrane, reaction kinetics, and heat transfer from MS to reacting gas mixture.

Some of these activities will be carried out in the framework of the upcoming MET.I.SOL. project (founded by the Italian Ministry for the Environment), mainly focused on methane/hydrogen mixtures thermochemical production from solar energy, on-board storage and utilization in ICE vehicles. This project will be coordinated by Fiat Motors and several partners from Italian Industries, Regional Energy Agencies, Private Enterprises, Universities, and Research Organizations.

4 Summary

The pathway to hydrogen generation entirely from renewable energy and material sources probably goes by a transitional period with the utilization of hybrid fossil/renewable integrated systems.

Solar steam reforming of methane is set in this context, specifically suited for a country like Italy whose actual energy policy is mainly based on the imported NG, but also characterized by convenient solar radiation levels in the Southern Regions.

A new solar SMR process is being developed by ENEA, using molten nitrates as solar heat carriers and storage medium at about 550 °C. The potential of this process have been proved theoretically by process simulation studies. Engineering and experimental activities aimed to the development of a prototype apparatus are now in progress in ENEA's laboratories.

It is remarkable that the developed technology (MS powered SMR) can find interesting impact in the industrial chemistry wherever it is convenient decoupling the heat demanding reactor from the heat source. For example, this practice allows multi-fuel and power source exploitation (e.g. coupling biomass with solar heat); moreover gas emissions will be avoided at the final user's level. The use of convective heat transfer in place of conventional radiant furnaces, by means of a non-pressurized heat transfer fluid like MS operating at about 550 °C, reduces the material concerns (use of special steel alloys) and the overall plant volume.

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