

BIOGAS CONVERSION TO GREEN HYDROGEN BY CATALYTIC SORPTION ENHANCED STEAM REFORMING (SESR): THE FEASIBILITY STUDY

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ABSTRACT: Clean energy technologies will play a decisive role in power generation and energy mix short-term scenarios to mitigate the environmental problems derived from increasing global energy consumption. In this context, green hydrogen will foreseeably become a clean and environmentally friendly energy carrier for sustainable development. Biogas is a valuable source of renewable energy and a secondary energy carrier produced from biodegradable organic materials via anaerobic digestion. It is mainly composed of CH₄ (35-75 vol.%) and CO₂ (15-55 vol.%). The present work proposes utilizing biogas for green hydrogen production by the sorption enhanced steam reforming (SESR) process. SESR has recently emerged as a novel promising method to improve hydrogen production efficiency. It combines, in a single unit, hydrogen production and carbon dioxide separation by a solid CO₂ acceptor. The objective of the present work is to prove the feasibility of the SESR of biogas to produce high-purity and high-yield hydrogen. To this aim, a comprehensive assessment of the process was carried out by evaluating the effect of the operating conditions on biogas SESR to optimize hydrogen production.

Keywords: Biogas, Catalytic conversion, CO₂ capture, Landfill gas, Hydrogen, Reforming

1 INTRODUCTION

Global warming and climate change are two serious concerns for our society in the coming years. Nowadays, there is still a high dependence on fossil fuels, which cause high greenhouse gas emissions during their combustion [1]. This issue is expected to continue growing in the near future, as it is associated with industrialization and population growth. Therefore, the use of renewable energy sources and clean energy technologies are encouraged in order to reduce greenhouse gas emissions to the atmosphere.

Among the available clean and environmentally friendly energy carriers, green hydrogen, obtained from renewable sources, presents a promising future as it can be used for power and fuel generation, both in transport and industry. Currently, hydrogen is obtained from fossil fuels, mainly by methane steam reforming from natural gas [2].

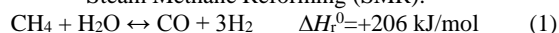
Biogas is a valuable source of renewable energy. It is a secondary energy carrier that can be obtained via anaerobic degradation of organic materials from landfills, sewage sludge, and biowaste digesters [3]. It is mainly composed of methane (35-75%), carbon dioxide (15-55%), and nitrogen (1-25%) in varying proportions depending on its origin [1]. Other minor compounds, such as O₂, H₂, H₂S, H₂O, CO, NH₃, siloxanes, aromatics, and dust can also be present.

Its high CO₂ content limits the direct use of biogas in thermal conversion, as it decreases flame stability and higher heating value (HHV) [4]. Therefore, its transformation in a green energy carrier such as hydrogen by catalytic sorption enhanced steam reforming (SESR) is an interesting option.

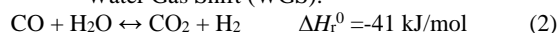
This technology has acquired high relevance during the last years to produce high-quality hydrogen, as it combines the catalytic reforming reaction of the methane contained in biogas and the in-situ CO₂ capture in a single reactor with a bed composed of a catalyst (normally Ni-based) and sorbent particles.

The main reactions that govern this process are shown in Eqs. (1)-(3):

- Steam Methane Reforming (SMR):



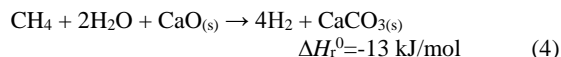
- Water Gas Shift (WGS):



- CO₂ capture:



The overall reaction of SESR process is shown in Eq. (4):



SMR (Eq. (1)) permits obtaining CO and H₂ from biogas' CH₄ oxidation with steam. CO produced during SMR reacts with the remaining steam to produce an additional mole of H₂ while converting CO to CO₂ through WGS (Eq. (2)). At the same time, CO₂ produced during WGS reacts with CaO to produce calcium carbonate (Eq. (3)). The CO₂ capture shifts the equilibrium of SMR and WGS towards H₂ production by Le Chatelier's principle. It allows reforming at lower temperatures (550-650 °C) than in conventional SMR while achieving high H₂ purities [5]. The overall SESR reaction is slightly exothermic (Eq. (4)), as CO₂ capture and WGS enthalpies compensate for the energy required by methane reforming.

The present work studies the influence of different operating parameters (temperature, steam/CH₄ ratio, gas hourly space velocity (GHSV), and biogas composition) on the sorption enhanced steam reforming (SESR) of biogas. The results are also compared with thermodynamic equilibrium predictions.

2 EXPERIMENTAL

2.1 Materials and methods

The experiments were performed in a commercial laboratory-scale device (PID EngTech Microactivity Reference). This versatile equipment can accurately

perform different chemical processes and reactions.

SESR experiments were performed at atmospheric pressure and isothermally in a heated updraft bubbling fluidized bed reactor. When the operating temperature was reached, pure methane or biogas (mixture of CH_4+CO_2) together with steam and N_2 (used as internal standard) were introduced into the reaction zone through the catalyst/sorbent bed. Water required to produce steam is provided using a Gilson High-Performance Liquid Chromatography (HPLC) pump. Outlet gas is cleaned before analysis in a Varian CP-4900 MicroGC equipped with two columns (5 Armstrong MolSieve and PPQ) and a thermal conductivity detector: solid particles dragged by the gaseous flow are eliminated in a cyclone, and water is condensed in a Peltier trap. A schematic diagram of the experimental set-up is provided in Figure 1.

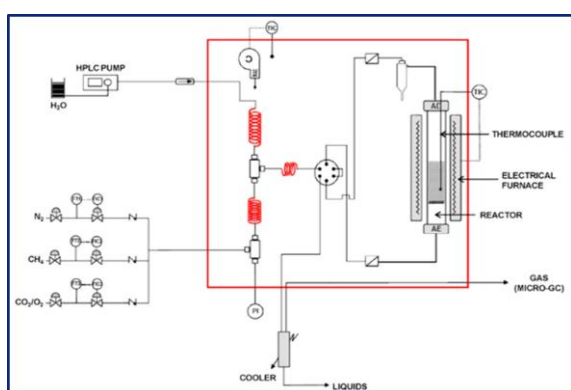


Figure 1. Schematic representation of the experimental set-up used in this work.

The catalyst used was a 1%Pd/20%Ni-20%Co hydrotalcite-like material (Pd/Ni-Co HT) synthesized in the laboratory. The preparation of the precursor [6] and catalyst [7] have been detailed elsewhere.

Arctic dolomite was used as CaO-based material for CO_2 sorption. It was provided by Franefoss Miljøkalk A/S, Norway. It presents a $\text{CaMg}(\text{CO}_3)_2$ purity of 98.5 wt.% and no sulfur according to X-ray fluorescence analysis. Its maximum CO_2 capture was estimated as 0.46 g $\text{CO}_2/\text{g}_{\text{sorbent}}$. BET surface area and pore volume of the calcined dolomite were 11.0 m^2/g and 0.16 cm^3/g , respectively [8].

The effect of temperature (550 to 800 °C), steam/ CH_4 molar ratio (2 to 6, i.e., 1 to 3 times the stoichiometric value), gas hourly space velocity (GHSV, from 492 to 3937 $\text{mL}_{\text{CH}_4}/(\text{g}_{\text{cat}}\cdot\text{h})$) and CH_4/CO_2 composition in the inlet biogas (50 to 95 vol.% CH_4) on the performance of the biogas SESR was evaluated.

Thermodynamic analysis of the SESR process was also conducted for comparison purposes taking into account the reaction conditions tested in the experimental study. The thermodynamic equilibrium results were determined using the Aspen Plus V10[®] software (AspenTech) by minimizing the Gibbs free energy of the system [9].

3 RESULTS AND DISCUSSION

3.1 Influence of temperature

The effect of temperature on pure methane (CH_4) and biogas (CH_4+CO_2) SESR is shown in Figure 2, including

experimental results and thermodynamic predictions.

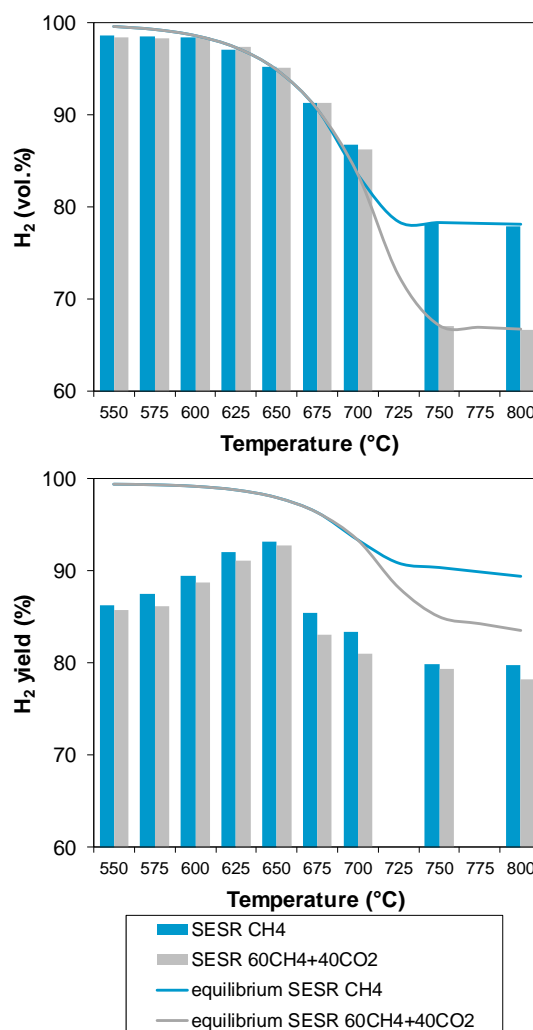


Figure 2. Effect of temperature on the H_2 concentration and H_2 yield during SESR of methane (CH_4) and biogas (60% $\text{CH}_4+40\%\text{CO}_2$). Reaction conditions: steam/ $\text{CH}_4=6$ mol/mol, $\text{GHSV}=492$ $\text{mL}_{\text{CH}_4}/(\text{g}_{\text{cat}}\cdot\text{h})$, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT was used as catalyst and Arctic dolomite as sorbent.

Figure 2 shows H_2 concentration and H_2 yield during SESR. As it can be observed, H_2 purity reaches a maximum, nearly constant value, around 98.4 vol.% in the 550-600 °C temperature range, and then gradually decreases with the increase in temperature. H_2 concentration is very similar for the SESR of both methane and biogas. Overall, the H_2 concentration values are close to those of the equilibrium under the studied conditions and only small differences were detected at 550-575 °C. On the other hand, H_2 yield increases with the reaction temperature until it reaches a maximum value at 650 °C (93.2% for methane and 92.7% for biogas), and then it decreases. H_2 yield values are below those determined by the equilibrium in the whole studied temperature range, although the differences are more pronounced at lower temperatures.

H_2 yield and purity during the SESR process presented different tendencies with temperature, so a compromise between those parameters should be taken when selecting an optimum operating temperature, which

could be around 625 °C.

For comparison purposes, conventional steam reforming (SR) was also tested. Figure 3 shows H₂ yield and H₂ concentration evolution with temperature during SR. H₂ concentration slightly increases with temperature up to 600 °C when it reaches an approximately constant value (around 78 vol.% for methane and 66.5 vol.% for biogas) that is maintained in the 600-800 °C temperature range. H₂ yield increases as the reaction temperature increases until it reaches a maximum value, and then it decreases. The highest value for the H₂ yield is obtained at 650 °C (83.7% for methane and 82.4% for biogas). Experimentally obtained values are lower than those expected from equilibrium in all the cases.

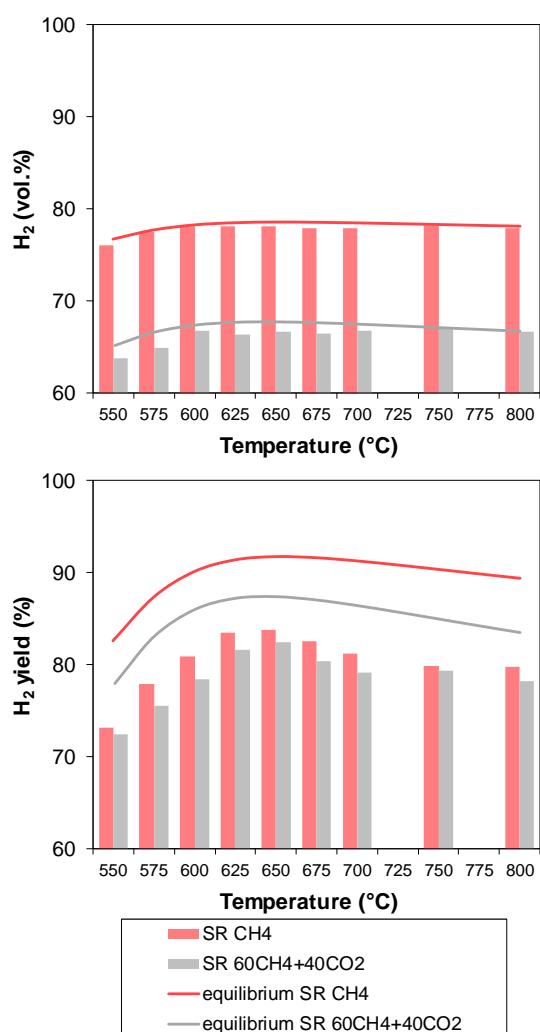


Figure 3. Effect of temperature on the H₂ yield and H₂ concentration during conventional steam reforming (SR) of methane (CH₄) and biogas (60% CH₄+40% CO₂). Reaction conditions: steam/CH₄=6 mol/mol, GHSV=492 mL_{CH₄}/(g_{cat}·h), sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT was used as catalyst and Arctic dolomite as sorbent.

3.2 Influence of steam/CH₄ ratio

Results presented in Figure 4 indicate that higher steam/CH₄ molar ratios increase both H₂ concentration and yield. This enhancement is more noticeable when the steam/CH₄ molar ratio increases from 2 to 4. This is explained because a higher concentration of steam promotes the SMR and WGS reactions, increasing the H₂

production.

In both cases, values obtained for SESR are higher than those obtained for SR. The equilibrium results for H₂ purity are similar to the experimentally obtained values for both SESR and SR, while the equilibrium values for H₂ yield are higher than those obtained experimentally.

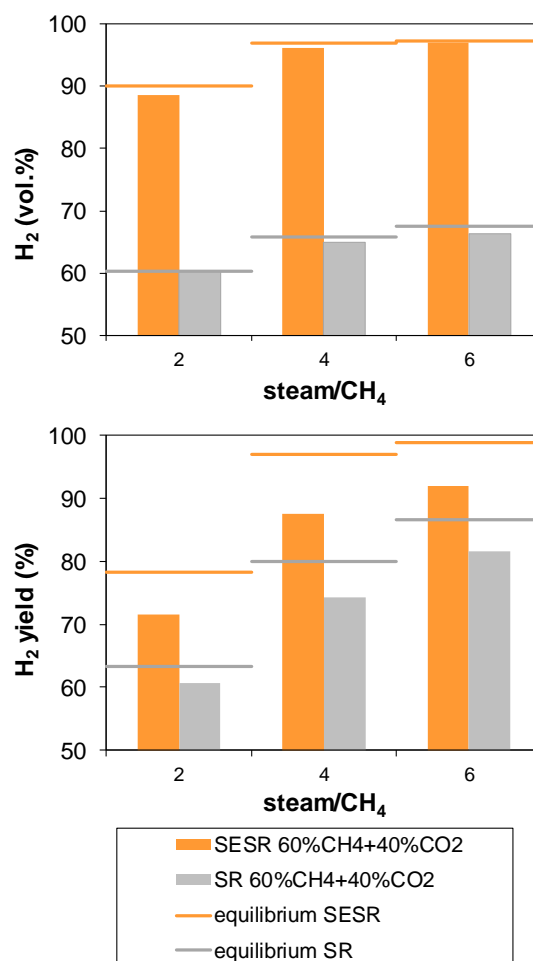


Figure 4. Effect of steam/methane ratio on the H₂ concentration and H₂ yield during SESR and SR of biogas (60% CH₄+40% CO₂). Reaction conditions: GHSV=492 mL_{CH₄}/(g_{cat}·h), sorbent/catalyst ratio=5 g/g, temperature 625 °C, Pd/Ni-Co HT was used as catalyst and Arctic dolomite as sorbent.

3.3 Influence of GHSV

As can be observed in Figure 5, the H₂ yield remains practically constant with space velocity during SESR, although a slight decrease occurs for the highest GHSV value tested. However, during biogas SR, a gradual decrease for H₂ yield as space velocity increases is observed. High space velocities result in a lower fuel conversion due to a shorter contact time of gas and solid phases.

Thermodynamically, neither H₂ yield nor H₂ concentration in the outlet gaseous stream are influenced by GHSV, as expected. Experimental H₂ purity matches the thermodynamic equilibrium, while H₂ yield is lower than the theoretical equilibrium one.

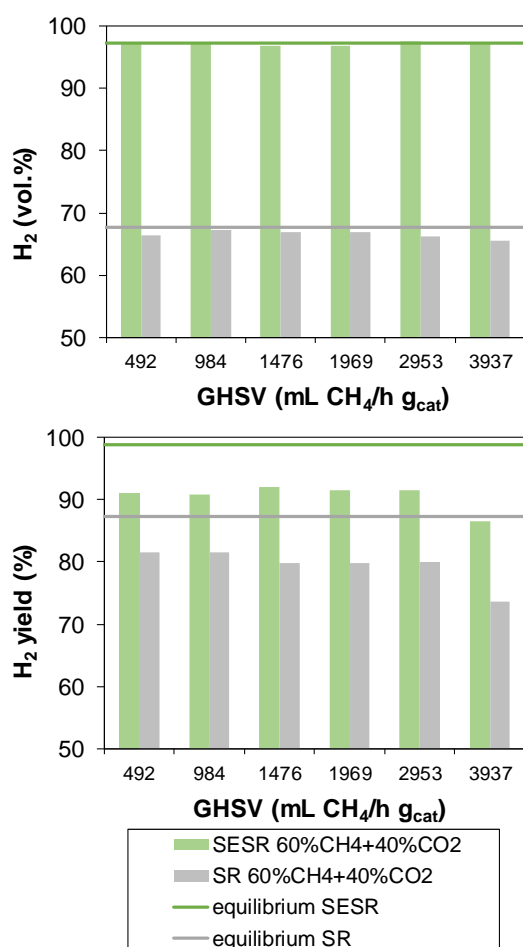


Figure 5. Effect of gas hourly space velocity (GHSV) on the H₂ concentration and H₂ yield during SESR and SR of biogas (60% CH₄+40% CO₂). Reaction conditions: temperature 625 °C, steam/CH₄ = 6 mol/mol, sorbent/catalyst ratio=20 g/g, Pd/Ni-Co HT as catalyst and Arctic dolomite as sorbent.

3.4 Influence of biogas composition

The influence of biogas composition was evaluated at 600 and 650 °C. As it can be observed in Figure 6, H₂ concentration in SESR presents an approximately constant value for all the biogas compositions studied (50 to 100 CH₄ vol.%, CO₂ balance), which is also similar to that obtained for pure methane (100 vol.% CH₄ in the plots).

Besides, the experimental values are close to the equilibrium at both temperatures and in all the range of CH₄ concentrations in biogas. Thermodynamic analysis proves no effect on the SESR performance of the CO₂ contained in the biogas compared to pure methane. It indicates that CO₂, both provided with biogas and generated during WGS, is effectively removed from the gaseous product stream by the carbonation reaction (Eq. (3)). It provides the SESR process great flexibility since it would be possible to use biogas with different compositions derived from a wide range of biosources. Furthermore, it should be noted that the presence of CO₂ in the feed gas could be positive from the energy efficiency point of view since the carbonation reaction to remove CO₂ is exothermic.

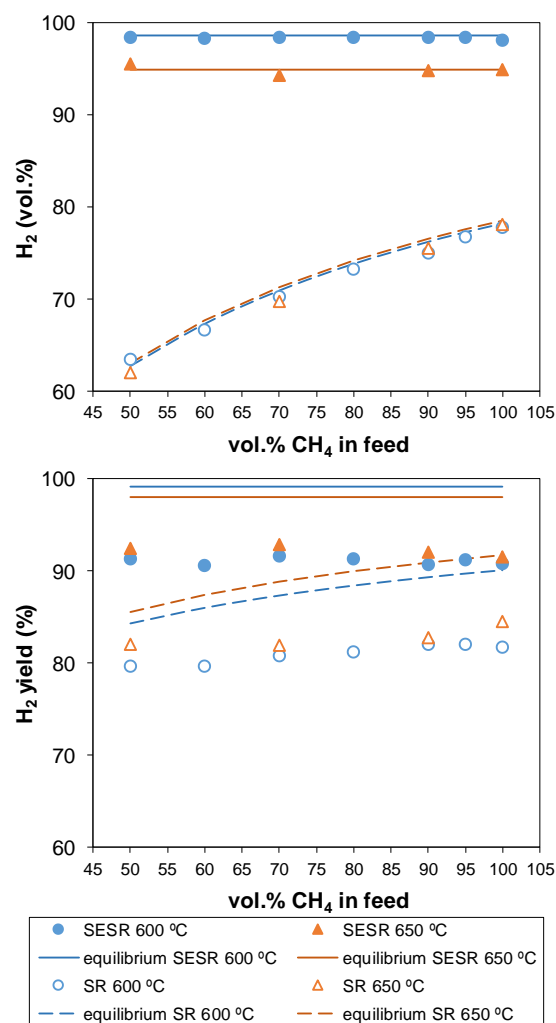


Figure 6. Effect of biogas composition on the H₂ concentration and H₂ yield during SESR and SR. Reaction conditions: temperature 600 and 650 °C, steam/CH₄ = 6 mol/mol, GHSV=1969 mL_{CH₄}/(g_{cat}·h), sorbent/catalyst ratio=20 g/g, Pd/Ni-Co HT as catalyst and Arctic dolomite as sorbent.

On the other hand, when CO₂ is not removed by a sorbent during the SR process, the H₂ concentration gradually increases with the CH₄ concentration in the inlet biogas (i.e., lower CO₂ concentration). These results suggest that higher CO₂ concentrations in the biogas prevent the WGS reaction from occurring to a greater extent (or the equilibrium between CO and CO₂ could tend to favor the reverse WGS), resulting in higher CO contents, and in turn lower H₂ concentrations.

Regarding H₂ yield, the SESR experimentally obtained values are similar independently of the biogas composition. They are lower than those predicted by the thermodynamic equilibrium under all the conditions studied, though.

For SR, a slight increase in the H₂ yield is detected for the higher methane contents in the biogas but still below the equilibrium calculations.

4 CONCLUSIONS

The results of the present study demonstrate the advantages of the sorption enhanced steam reforming (SESR) process compared to the conventional biogas steam reforming (SR) without in situ CO₂ removal.

Biogas SESR delivered high purity (98.4 vol.%) and high-yield (92.7%) green H₂ using Pd/Ni-Co HT as catalyst and Arctic dolomite as CO₂ sorbent in a single step fluidized bed reactor.

The parametric analysis pursued concludes as follows:

- Regarding the temperature influence, the highest H₂ purities were obtained in the 550-600 °C range and maximum H₂ yield at 650 °C. It indicates that optimum SESR temperature for biogas SESR could be close to 625 °C.
- Regarding the Steam/CH₄ influence, higher steam/CH₄ molar ratios increase H₂ concentration and yield since a higher concentration of steam promotes both the SMR and WGS reactions, increasing the production of H₂.
- H₂ yield remains practically constant with space velocity during SESR, although slightly decreases for the highest value tested.
- Regarding the biogas composition, the H₂ concentration in SESR keeps constant for all the biogas compositions studied and similar to that obtained for pure methane.

Finally, it was experimentally proven that CO₂ supplied with biogas is effectively removed by the carbonation reaction during the SESR process at 550-700 °C in the tested concentration ranges (5 to 50 vol.% CO₂), so it does not influence the reforming process when compared to pure CH₄.

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6 ACKNOWLEDGEMENTS

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