

# Single-step biogas conversion to bio-hydrogen: sorption enhanced catalytic reforming

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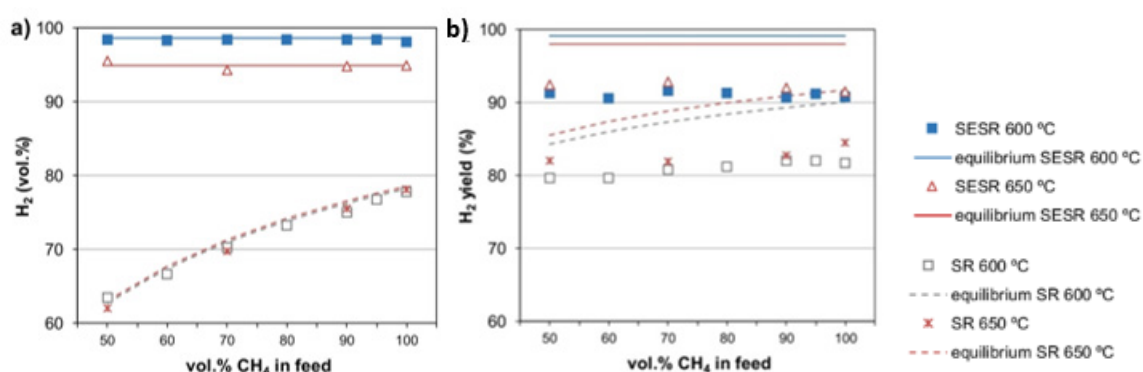
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## Objectives and novelty

The importance of hydrogen as a future clean and renewable energy source has become more prominent as climate change and global warming have attracted increasing attention worldwide. However, most of the hydrogen produced comes from the steam reforming (SR) of fossil resources. Therefore, advanced technologies have been developed to implement CO<sub>2</sub> capture in the process and replace fossil resources with renewables.

This thesis focuses on the production of renewable high-purity hydrogen from biogas using Sorption Enhanced Steam Reforming (SESR), an intensified SR process. This process combines the reforming reaction for H<sub>2</sub> production with in situ CO<sub>2</sub> separation and it is based on Le Chatelier's principle. As a result, the H<sub>2</sub> purity and yield are significantly increased.

The main objective is to produce high-purity, low-carbon hydrogen from biogas, regardless of the composition of the biogas. The influence of CH<sub>4</sub> and CO<sub>2</sub> concentrations (vol.%) in the biogas on the process performance was evaluated experimentally, together with a thermodynamic analysis of the process by simulation. Thus, the effect of biogas H<sub>2</sub>S content on hydrogen production by the SESR process was studied experimentally. The energy efficiency of the biogas SESR process was studied for different process configurations being one of the main important aspects of the study the heat integration to minimize the external utilities. Additionally, a preliminary techno-economic assessment was done. Finally, the efficiency of bio-DME production (as hydrogen carrier) from biogas was studied by simulation integrating the biogas SESR and SEDMES processes to take advantage of their existing synergies.



**Figure 1.** Effect of methane content in biogas on the H<sub>2</sub> concentration (a) and H<sub>2</sub> yield during SESR and SR at 600 and 650 °C. Reaction conditions: steam/CH<sub>4</sub> = 6 mol/mol, GHSV<sub>CH<sub>4</sub></sub> = 1969 mL CH<sub>4,gcat</sub><sup>-1</sup>h<sup>-1</sup>, sorbent/catalyst ratio = 20 g/g, Pd/Ni-Co HT catalyst and dolomite sorbent.

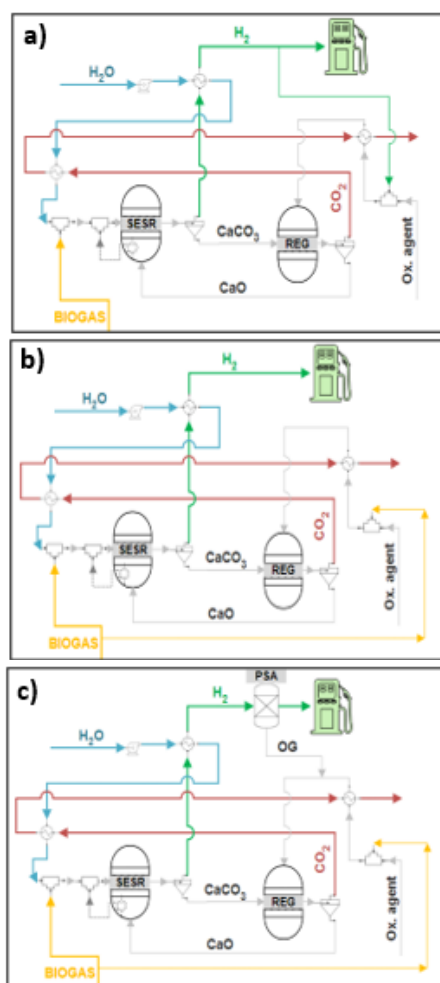
## Main results

Regarding the effect of biogas composition (concerning CH<sub>4</sub> content) H<sub>2</sub> yield, H<sub>2</sub> selectivity, CH<sub>4</sub> conversion, H<sub>2</sub> purity, and concentrations of CH<sub>4</sub>, CO, and CO<sub>2</sub> in the effluent gas were analysed for different CH<sub>4</sub> and CO<sub>2</sub> compositions (vol.%) of the biogas. The results were compared with the biogas steam reforming (SR) process without CO<sub>2</sub> capture. High-purity (98.4 vol.%) and high-yield (91%) H<sub>2</sub> can be obtained by SESR of biogas (CH<sub>4</sub>+CO<sub>2</sub>) over a Pd/Ni-Co catalyst and using Arctic dolomite as carbon dioxide sorbent.

The effect of H<sub>2</sub>S concentration (150, 350, 500, and 1000 ppm) in the biogas (60 CH<sub>4</sub>/40 CO<sub>2</sub> vol./vol.%) on the performance of the SESR process was also studied. No catalyst deactivation due to H<sub>2</sub>S poisoning was detected during cyclic SESR of biogas at 600 °C for H<sub>2</sub>S concentrations of 150 and

350 ppm (five cycles). However, for 1000 ppm H<sub>2</sub>S, a slight decrease in H<sub>2</sub> yield (between 4.5% and 10.8% points) and H<sub>2</sub> purity (between 2% and 3% points) was found.

In addition, different process flowsheets were designed in AspenPlus software and the economic analysis of the most promising one was carried out using biogas as feedstock. Natural gas was also used for comparison purposes. In the case of biogas, the lowest value of the levelised cost of hydrogen (LCOH) was obtained when the heat was supplied to the calciner by indirect air combustion in an external burner (2.8 €/kg H<sub>2</sub> including CO<sub>2</sub> storage). In the case of natural gas using an indirectly heated calciner, the LCOH was only slightly lower (2.6 €/kg H<sub>2</sub> including CO<sub>2</sub> storage), indicating that biogas could be a potential substitute for natural gas, being renewable and economically competitive.



**Figure 2.** Simplified flow diagrams of the process configurations proposed for the biogas SESR; a fraction of the produced H<sub>2</sub> is used as fuel for the sorbent regeneration (a) or biogas is utilized as fuel for the sorbent regeneration or biogas is used as fuel for the sorbent regeneration, and a PSA unit is included (c).

Finally, the integration of the biogas SESR process with the Sorption Enhanced Dimethyl Ether (DME) Synthesis (SEDMES) process is studied. SEDMES is a novel process to synthesize DME in which water is removed in situ with a solid adsorbent, following the same concept based on Le Chatelier's principle as the SESR process. This work evaluated the production of bio-DME from biogas by efficiently integrating the SESR and SEDMES processes, achieving a final Cold Gas Efficiency (CGE) of 74%.

## Conclusions

According to the experimental results obtained, the production of renewable H<sub>2</sub> by the sorption enhanced steam reforming (SESR) of biogas has been demonstrated both thermodynamic and experimentally. High-purity (98.4 vol.%) and high-yield (91%) hydrogen can be obtained by SESR of biogas (CH<sub>4</sub>+CO<sub>2</sub>) on a Pd/Ni-Co catalyst and using Arctic dolomite as carbon dioxide sorbent. Additionally, the catalyst did not deactivate due to H<sub>2</sub>S poisoning during cyclic SESR of biogas for H<sub>2</sub>S concentrations of 150 and 350 ppm at 600 °C. However, a H<sub>2</sub>S concentration of 1000 ppm slightly reduced H<sub>2</sub> yield and H<sub>2</sub> purity.

On the other hand, regarding the simulation work did, it was observed that a flowsheet configuration

that includes regeneration using biogas as fuel and a PSA for the purification of the H<sub>2</sub> can produce ~100 vol.% H<sub>2</sub> purity at 675 °C, 5 bar, and S/CH<sub>4</sub> = 5, with a CGE of 77.3% and zero carbon emissions if air-fired calciner is applied. However, potentially negative emissions and ~100% captured CO<sub>2</sub> are feasible if regeneration is performed in an oxy-fuel combustion atmosphere. Partial negative emissions could also be feasible if the air combustion is performed in an external burner.

Regarding the techno-economic analysis comparing biogas and natural gas SESR, the lowest levelised cost of hydrogen (LCOH) is obtained when using natural gas (2.6 €/kg H<sub>2</sub> including CO<sub>2</sub> storage), but this is also the only case with CO<sub>2</sub> emissions (2.8 kgCO<sub>2</sub>/kg H<sub>2</sub>). The lowest LCOH when using biogas is 2.8 €/kg H<sub>2</sub> with CO<sub>2</sub> storage suggesting that biogas could be a potential substitute for natural gas and economically competitive.

Finally, from the integration of biogas SESR and DME production by SEDMES, it can be concluded that it could be possible to convert biogas into DME efficiently following a net zero approach integrating biogas SESR and SEDMES technologies. By exploiting the synergies between the two processes, it was possible to leverage the overall CGE to 74 from 63.8%.

## Related publications

The work presented in this thesis dissertation results from three published papers and two international collaborations. The main related publications are as follows:

- [1] Effect of H<sub>2</sub>S on biogas sorption enhanced steam reforming using a Pd/Ni-Co catalyst and dolomite as a sorbent. A. Capa, M. P. González-Vázquez, D. Chen, F. Rubiera, C. Pevida, and M. V. Gil. *Chem. Eng. J.*, vol. 476, no. July, 2023, <https://doi.org/10.1016/j.cej.2023.146803> (Q1)
- [2] Process simulations of high-purity and renewable clean H<sub>2</sub> production by sorption enhanced steam reforming (SESR) of biogas. Capa, A., Yongliang, Y., Rubiera, F., Pevida, C., Gil, M.V., Clough, P.T., 2023. 1. *ACS Sustain. Chem. Eng.* <https://doi:10.1021/acssuschemeng.2c07316>. Article in press.
- [3] Biogas, a renewable source of methane and hydrogen. Capa, A., Durán, I., Gil, M.V., Rubiera, F., Pevida, C., 2022. *Boletín Ciencia y Tecnología RIDEA*, n°56: 43-60.
- [4] Blends of bio-oil/biogas model compounds for high-purity H<sub>2</sub> production by sorption enhanced steam reforming (SESR): Experimental study and energy analysis. Rodríguez, S., Capa, A., García, R., Chen, D., Rubiera, F., Pevida, C., Gil, M.V., 2021. *Chem. Eng. J.* 432, 134396. <https://doi.org/10.1016/j.cej.2021.134396> (Q1).
- [5] On the effect of biogas composition on the H<sub>2</sub> production by sorption enhanced steam reforming (SESR). Capa, A., García, R., Chen, D., Rubiera, F., Pevida, C., Gil, M. V., 2020. *Renew. Energy* 160, 575–583. <https://doi.org/10.1016/j.renene.2020.06.122> (Q1).

Full thesis can be downloaded from: <https://digibuo.uniovi.es/dspace/handle/10651/72585>