Renewable hydrogen production from biogas by sorption enhanced steam reforming (SESR): A parametric study

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Abstract

H₂ production from biogas (60%CH₄ + 40%CO₂) by sorption enhanced steam reforming (SESR) was thermodynamically and experimentally studied in a fluidized bed reactor. Biogas is an interesting renewable biomass resource for hydrogen production due to its sustainable nature. SESR combines the catalytic reforming reaction of biogas with simultaneous CO₂ removal in a single step. A Pd/Ni-Co hydrotalcite-like material (HT) was used as catalyst and dolomite as CO₂ sorbent. The effects of temperature (550-800 °C), steam/CH₄ molar ratio (2-6) and gas hourly space velocity (GHSV) (492-3937 mL CH₄ g⁻¹ cat⁻¹ h⁻¹) on the process performance were evaluated. CO₂ in biogas was effectively removed by the sorbent from the gas phase at 550-700 °C, without influencing the reforming process. H₂ yield increased with temperature from 550 to 650 °C, but H₂ concentration decreased at temperatures higher than 600 °C, requiring a tradeoff between both parameters to select an optimum operating temperature. H₂ purity of 98.4 vol.% was obtained at 550-600 °C and H₂ yield

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of 92.7% was reached at 650 °C. Higher steam/CH₄ ratios enhance the process, whereas higher space velocities decrease H₂ yield. Results demonstrate that high-purity high-yield biohydrogen can be produced by the SESR of a renewable biomass resource as biogas.

**Keywords:** Biogas; Hydrogen; Sorption enhanced steam reforming; Pd/Ni-Co catalyst; Dolomite

1. Introduction

Fossil fuels, such as oil, natural gas and coal, are nowadays the main sources for energy production. The use of these resources is undeniably associated with CO₂ emissions, global warming, and climate change issues. To mitigate the environmental impact derived from increasing global energy consumption, clean energy technologies such as solar cells, wind turbines and hydrogen fuel cells will play a greater role in the short-term power generation and energy mix [1]. Thus, hydrogen is regarded as one of the cleanest future energy carrier that can be generated from renewable sources and will give rise to a reduction of CO₂ emissions and environmental problems related to the use of fossil fuels [2]. The worldwide demand for renewable hydrogen as a fuel is expected to increase shortly with the parallel advances in the field of hydrogen-based fuel cells. Nevertheless, conventional hydrogen production is still mostly obtained from natural gas by the endothermic steam methane reforming (SMR) reaction, which is a highly energy-demanding process since it is performed at high temperatures (700-1000 °C). Moreover, its product stream is usually a mixture of H₂, CO and CO₂, and the conversion of CH₄ is limited by equilibrium [3].
Recently, the sorption enhanced steam reforming (SESR) process has emerged as a novel promising method to improve the hydrogen production efficiency. This process can be applied to the conversion of biomass, in line with the widespread interest in developing new technologies to produce hydrogen from renewable sources in a high-energy efficient, cost-competitive and environmentally friendly manner. The SESR process combines hydrogen production with carbon dioxide separation. The CO\(_2\) removal is mostly carried out by high-temperature CaO-based sorbents. Thus, the highly endothermic methane steam reforming (SR) (Eq. (1)), the water-gas shift (WGS) (Eq. (2)) and the exothermic CO\(_2\) sorption (Eq. (3)) reactions are coupled in a single unit, which reduces the total enthalpy change of the process and hence the energy demand in the reforming stage. The overall SESR reaction of methane is shown by Eq. (4).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 & \Delta H^0_r = +206 \text{ kJ mol}^{-1} \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 & \Delta H^0_r = -41 \text{ kJ mol}^{-1} \\
\text{CaO}_{(s)} + \text{CO}_2 & \leftrightarrow \text{CaCO}_3(s) & \Delta H^0_r = -178 \text{ kJ mol}^{-1} \\
\text{CH}_4 + 2\text{H}_2\text{O} + \text{CaO}_{(s)} & \rightarrow 4\text{H}_2 + \text{CaCO}_3(s) & \Delta H^0_r = -13 \text{ kJ mol}^{-1}
\end{align*}
\]

Due to the CO\(_2\) removal, the thermodynamic equilibrium of the SR (Eq. (1)) and WGS (Eq. (2)) reactions is shifted towards the production of H\(_2\) according to the Le Chatelier’s principle, which in turn enhances the hydrogen yield and purity. It allows the use of lower reaction temperatures (typically 550-650 °C) than in conventional steam reforming processes whilst still achieving high H\(_2\) purities.

Production of hydrogen by the SESR process has been proposed in literature using different raw biomass materials, such as glycerol [4-6], ethanol [7-9], bio-oil derived from biomass fast-pyrolysis [10-15] or solid biomass [16]. Similarly, biogas is a biomass resource that may also be an interesting renewable source for hydrogen.
production due to its sustainable nature, since it is produced by the anaerobic digestion process of the biodegradable residual biomass from several origins, such as animal waste, sewage sludge in wastewater treatment plants, and municipal waste in landfills. Biogas is mainly composed of CH4 (55-70 vol.%) and CO2 (27-44 vol.%), with smaller quantities of other gases such as H2S (<3 vol.%) and H2 (<1 vol.%), and traces of NH3 [17]. NH3 would have little effect on catalyst activity, whereas H2S should be removed before the reforming process to avoid the poisoning of the catalyst. Commercial processes to achieve low H2S concentrations in the feed to reformers are widely deployed because the usual feed (i.e., natural gas) also contains some H2S [18].

Biogas is receiving increased attention as a renewable energy source due to its potential to replace fossil fuels for power and heat generation [19, 20]. In 2015, the European Union produced 181 TWh of biogas energy, but its potential is higher and the production can rise up to 472 TWh by 2030 [21]. Up to now, it has mainly been used for power production and as transportation fuel after an upgrading step, but biogas is not a common energy source due to its high CO2 content [22] that decreases the heating value and flame stability of the gas mixture [23]. However, it has recently been considered as a viable alternative for introducing significant amounts of renewable hydrogen on the market by reforming processes [24], since it can be used as an alternative CH4 source [25]. Some studies in the literature have reported the synthesis gas production from biogas by conventional steam reforming [26-29]. However, the biogas SESR has been hardly reported in the literature. If biogas is subjected to reforming using a carbon dioxide sorbent, the process would theoretically be more exothermic than the sorption enhanced reforming of pure methane, due to the large amount of CO2 included in the biogas, which would also foreseeably be removed from
the gas phase by the carbonation reaction providing additional heat to the system. It would supply an additional advantage to the process.

In literature, thermodynamic analyses of the sorption enhanced hydrogen production from combined CO₂ and steam reforming together with partial oxidation of biogas [30], as well as from SESR of biogas [31], have shown that the use of CaO clearly enhances the production of hydrogen. Phromprasit et al. [32] studied bed arrangements of catalyst and sorbent for the biogas SESR in a fixed bed reactor and demonstrated that the best results are obtained when the catalyst (12.5 wt.% Ni/Al₂O₃) is physically mixed with the sorbent (CaO). Preliminary batch tests on a small sorption enhanced reforming dual bubbling fluidized bed reactor system have been performed using upgraded biogas and a hydrogen concentration of 94 vol.% has been obtained [24]. Moreover, Phromprasit et al. [1, 3] compared the activity of different multifunctional catalysts based on Ni and CaO for hydrogen production from SESR of biogas.

Taking into account the scarce number of published works on this topic, an exhaustive assessment of the process operating conditions for the SESR of biogas to optimize the production of hydrogen is still lacking. Therefore, the objective of the present work is to experimentally assess the effect of temperature, steam/CH₄ molar ratio and gas hourly space velocity (GHSV) on the biogas SESR performance, as well as to compare the results with the conventional steam reforming of biogas. Experiments with pure methane will also be performed for comparison purposes. The optimum values of the operating variables will be set according to the results achieved for the main characteristic parameters of the process, i.e., H₂ yield, CH₄ conversion, H₂ purity, and CH₄, CO and CO₂ concentrations in the effluent gas. The thermodynamic analysis
of the process will also be carried out to determine the theoretical feasibility of the SESR process under the selected reaction conditions and to compare the equilibrium values with the experimental results.

2. Materials and Methods

2.1. Catalyst

A Pd/Ni-Co hydrotalcite-like material (HT) was used as catalyst in the present work due to the promising results obtained in previous studies of the research group during the SESR of biomass materials [10, 12, 13]. A 20%Ni-20%Co hydrotalcite-like material precursor was firstly prepared by the co-precipitation method as reported by He et al. [33]. Then, the Pd/Ni-Co HT catalyst was prepared by the incipient wetness impregnation method with 1% (w/w) load of Pd and characterized as described in detail by Fermoso et al. [10]. It was reduced at 670 °C (heating rate of 2 °C min⁻¹) for 10 h in a mixed flow of H₂ (50 NmL min⁻¹) and N₂ (50 NmL min⁻¹) before use. The particle size of the catalyst used was 250-500 μm.

2.2. CO₂ sorbent

Arctic dolomite, supplied by Franefoss Miljøkalk As (Norway), has a purity of approximately 98.5 wt.% CaMg(CO₃)₂ and no sulfur according to X-ray fluorescence analysis. The initial maximum CO₂ capture capacity of the dolomite was 0.46 g CO₂/g sorbent. It was calcined in airflow of 200 NmL min⁻¹ at 800 °C for 4 h before its use.

2.3. Experimental procedure

Fig. 1 shows a schematic flow diagram of the experimental setup used for the
biogas SESR experiments. It consists of an updraft bubbling fluidized bed quartz reactor (i.d., 27 mm) located inside a tubular electric furnace. The reactor was loaded with a 12 g mixture of calcined dolomite and Pd/Ni-Co HT catalyst, at a sorbent-to-catalyst ratio of 5 g/g, for the study of temperature and steam/CH₄ molar ratio effects. The study of the GHSV effect was performed on a bed of 10.5 g with a sorbent-to-catalyst ratio of 20 g/g to assure sufficient duration of the pre-breakthrough stage at high values of space velocity. The reactor is not operating under adiabatic conditions during the experiments, and the reaction temperature is controlled by a K-type thermocouple connected to a temperature controller and data recorder. Gases are delivered by Bronkhorst® mass flow controllers, while water is fed in with a Gilson® high-performance liquid chromatography (HPLC) pump.

Fig. 1. Schematic flow diagram of the experimental setup.

SESR experiments were carried out feeding simulated biogas with a composition of 60/40 CH₄/CO₂ (vol.%), and 100% CH₄ for comparison purposes. The experiments
were performed at atmospheric pressure and isothermally, at temperatures between 550 and 800 ºC. The reactor was heated to the desired experimental reaction temperature under N₂ atmosphere (100 NmL min⁻¹). Then, CH₄ or the CH₄/CO₂ mixture, together with steam and N₂ (25 NmL min⁻¹ of N₂ flow used as internal standard), was introduced updraft to the reactor through the catalyst/sorbent bed. Liquid H₂O was firstly evaporated in an evaporator and mixed with the gas stream, and the mixture was heated to 200 ºC in a preheating zone before being fed to the reactor. The steam/CH₄ molar ratio was evaluated between 2 and 6, while the GHSV was assessed between 492 and 3937 mL CH₄ gₗcum⁻¹ h⁻¹. During the experiments, the SESR process proceeded until the calcined dolomite became saturated (pre-breakthrough), which is experimentally indicated by an increase in the CO₂ concentration in the outlet gas due to the loss of CO₂ capture capacity of the calcined dolomite. When the CO₂ capture by the sorbent was negligible (post-breakthrough), conventional catalytic steam reforming was assumed to occur, which was allowed to reach steady-state for comparison purposes.

The effluent gas from the reactor was cleaned of solid particles that may have been elutriated from the bed using a cyclone. The excess steam and other liquids that could have formed were separated from the exiting gas by condensation in a thermoelectric cooling tank. The dried gas was analyzed using an on-line dual-channel Varian® CP-4900 Micro GC, equipped with Molsieve 5 Å and PPQ columns, and with a thermal conductivity detector (TCD). Helium was used as the carrier gas. The species detected were H₂, CH₄, CO, and CO₂. The gas composition was calculated on nitrogen-free and dry bases. Through a nitrogen balance, the flow rates of the products were calculated.
H₂ yield, CH₄ conversion, H₂ purity, and CH₄, CO, and CO₂ concentrations were calculated from Eqs. (5)-(8), respectively:

\[
\text{H₂ yield (\%)} = 100\% \cdot \left( \frac{F_{\text{H₂, out}}}{4 \cdot F_{\text{CH₄, in}}} \right) \quad (5)
\]

\[
\text{CH₄ conversion (\%)} = 100\% \cdot \left( \frac{(F_{\text{CH₄, in}} - F_{\text{CH₄, out}})}{F_{\text{CH₄, in}}} \right) \quad (6)
\]

\[
\text{H₂ purity (vol.\%)} = 100\% \cdot \left( \frac{y_{\text{H₂}}}{\Sigma y_i} \right) \quad (7)
\]

\[
\text{CH₄/CO/CO₂ (vol.\%)} = 100\% \cdot \left( \frac{y_{\text{CH₄/CO/CO₂}}}{\Sigma y_i} \right) \quad (8)
\]

where \(F_{\text{H₂, out}}\) is the molar flow rate of H₂ produced (mol min⁻¹), \(F_{\text{CH₄, in}}\) is the molar flow rate of methane fed in (mol min⁻¹), \(y_i\) is the molar fraction (N₂ free and on a dry basis) of each species \(i\) (H₂, CH₄, CO and CO₂) in the outlet gas, and \(F_{\text{CH₄, out}}\) is the molar flow rate of CH₄ produced (mol min⁻¹).

The gas hourly space velocity (GHSV) is defined as the ratio of the methane volumetric flow rate to the mass of catalyst, according to Eq. (10):

\[
\text{GHSV (mL CH₄ g⁻¹ cat h⁻¹)} = \frac{\text{Volumetric flow rate of inlet methane (mL CH₄ h⁻¹)}}{\text{Mass of catalyst (g)}} \quad (10)
\]

2.4. Thermodynamic equilibrium calculations

Thermodynamic analysis of the SESR process was conducted taking into account the reaction conditions used in the experimental study to compare the equilibrium and experimental results. The equilibrium composition was estimated using Aspen Plus V10 software (AspenTech) by minimizing the Gibbs free energy of the system [34]. Peng-Robinson thermodynamic package was used as property method. The species considered were H₂, CH₄, CO, CO₂, H₂O, CaO and CaCO₃. C₂H₄, C₂H₆ and C (graphite as solid carbon) were also included in the product pool, but their concentrations in the equilibrium stream were negligible to be considered as significant products [7].
3. Results and Discussion

3.1. Thermodynamic equilibrium results

Fig. 2 shows the thermodynamic equilibrium results for the SESR and SR of methane (100% CH4) and biogas (60%CH4 + 40%CO2) at reaction temperatures between 550 and 800 °C. In the case of methane (blue lines), the SESR and SR concentrations of H2, CH4, CO and CO2 differ at temperatures between 550 and 725 °C but at higher temperatures a good agreement is observed. This means that CO2 removal by the reaction represented in Eq. (3) occurs in the range 550-725 °C, and that the CO2 produced is not captured between 725 and 800 °C. However, in the case of biogas (red lines), the SESR and SR concentration profiles of H2, CH4, CO and CO2 differ between 550 and 750 °C but concur at higher temperatures, meaning that the CO2 removal takes place up to 750 °C. The effective CO2 removal at 725-750 °C for biogas could be due to the higher CO2 partial pressure in the gas phase which shifts the CO2 capture to a slightly higher temperature. The CO2 adsorption by the carbonation reaction relies on the difference between the CO2 partial pressure in the gas phase and the partial pressure of CO2 at equilibrium, the last one dependent on the temperature. Thus, the carbonation reaction at higher temperatures requires higher CO2 partial pressure in the gas phase to occur. The equilibrium results in Fig. 2 show that the CO2 removal by the carbonation reaction occurs up to 725-750°C, while at higher temperature CO2 is not captured by the sorbent. The carbonation reaction on CaO sorbents is achieved by increasing the partial pressure of CO2 in the gas phase above that of the CaO-CaCO3 equilibrium, which is temperature-dependent. A CO2 partial pressure in the gaseous stream higher than the CO2 equilibrium pressure for a given temperature is the driving force of the removal of CO2 by reaction with the sorbent [35].
Fig. 2. Thermodynamic equilibrium results for the SESR and SR of methane (CH$_4$) and biogas (60%CH$_4$ + 40%CO$_2$) as a function of temperature: (a) H$_2$, (b) CH$_4$, (c) CO and (d) CO$_2$ concentrations. Reaction conditions: 1 bar; steam/CH$_4$ = 6 mol/mol.

On the other hand, when the SESR results for methane and biogas are compared (continuous lines), it can be observed that the concentrations of H$_2$, CH$_4$, CO and CO$_2$ are exactly alike for both cases in the temperature range of 550-700 ºC; this indicates that all the extra CO$_2$ introduced with the biogas is removed from the gas phase by reaction with the sorbent at these conditions. The carbonation reaction (Eq. (3)) occurs below 700 ºC during the SESR of biogas and proceeds until the complete removal of the CO$_2$ in the gas phase. As mentioned above, the carbonation reaction also takes place between 700 and 750 ºC for biogas, but the extra CO$_2$ contained in the biogas stream would not be completely removed by the sorbent since the CO$_2$ concentration in the gas
phase is higher for the biogas case than for the methane case under such conditions (Fig. 2d). According to the thermodynamic equilibrium, these results indicate that the CO\(_2\) contained in biogas does not affect the SESR performance at conditions where CO\(_2\) is removed by the carbonation reaction. At temperatures higher than 750 °C, no carbonation reaction occurs, and conventional SR takes places since there is not CO\(_2\) removal by the sorbent.

As can be seen in Fig. 2, under SR conditions at all the evaluated temperatures (dashed lines), higher concentrations of CO\(_2\) and CO and lower concentrations of H\(_2\) are attained for the biogas case than for methane. CH\(_4\) concentration profiles are only slightly higher for biogas than for methane. The CO\(_2\) added with the biogas prompts higher concentrations of CO\(_2\) which cannot be removed under SR conditions due to the absence of the sorbent. The higher CO content is related to the higher CO\(_2\) concentration in the gas phase for the biogas case that hinders the WGS reaction (Eq. (2)), which in turn explains the lower H\(_2\) concentration. Likewise, a higher CO content in the gas phase may decrease the steam reforming of methane (Eq. (1)) and reduce its conversion.

3.2. Effect of temperature on the SESR of biogas

The effect of reaction temperature on the SESR process was evaluated in the 550-800 °C temperature range. The experiments were performed using a steam/CH\(_4\) molar ratio of 6 (i.e., three times higher than the stoichiometric steam/CH\(_4\) molar ratio) and a GHSV of 492 mL CH\(_4\) g\(_{\text{cat}}\)\(^{-1}\) h\(^{-1}\). Fig. 3 shows the results of the SESR process as a function of temperature for the experiments with biogas (60%CH\(_4\) + 40%CO\(_2\)). Experiments feeding methane solely (100% CH\(_4\)) have also been conducted for
comparison purposes. Bars represent the experimental results, while lines show the equilibrium values from the thermodynamic analysis.

Fig. 3a shows the H\(_2\) concentration in the effluent gas as a function of the reaction temperature during the SESR of methane and biogas. In both cases, H\(_2\) purity reaches an approximately constant value (around 98.4 vol.\%) in the 550-600 \(^\circ\)C temperature range and then gradually decreases with the increase in the reaction temperature. On the other hand, the H\(_2\) concentration is very similar after 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 \(^\circ\)C.

Fig. 3b shows the CH\(_4\) concentration as a function of temperature during the SESR of methane and biogas. CH\(_4\) concentration in the effluent gas decreases with the reaction temperature. The steam methane reforming reaction is thermodynamic and kinetically enhanced at high temperatures. Besides, the methanation reaction is thermodynamically favored at low temperatures and hindered with the temperature increase. Therefore, lower CH\(_4\) concentrations are attained at higher temperatures. Sorption enhanced reforming experiments in literature with ethanol [7], glucose and sorbitol [36] also showed high CH\(_4\) concentrations at low temperatures. The low CH\(_4\) concentrations found at high temperatures showed that the Pd/Co-Ni HT catalyst successfully catalyzed the methane steam reforming reaction during the SESR of biogas.
Fig. 3. Effect of temperature on the H₂ (a), CH₄ (b), CO (c) and CO₂ (d) concentrations, as well as on H₂ yield (e) and CH₄ conversion (f), during SESR of methane (CH₄) and biogas (60%CH₄ + 40%CO₂). Reaction conditions: steam/CH₄=6 mol/mol, GHSV=492 mL CH₄ gcat⁻¹ h⁻¹, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite sorbent.
It can be seen in Fig. 3b that the experimental CH₄ contents are above the equilibrium values at low temperatures, which agrees with the small differences observed between the experimental H₂ concentrations and those of the equilibrium at 550 and 575 °C (Fig. 3a). On the other hand, CH₄ concentration is slightly higher for biogas than for methane at low temperatures, particularly at 550-575 °C, and decreases as the temperature increases. This can be ascribed to slower CO₂ sorption kinetics at low temperatures and its important effect on the process enhancement by sorption, which could have slightly decreased the CH₄ conversion in the case of biogas where higher CO₂ concentrations in the gas phase are present.

Fig. 3c shows the CO concentration as a function of temperature during the SESR of methane and biogas. At lower temperatures, very low CO concentrations are found since the WGS reaction equilibrium is shifted towards H₂ production in the presence of a sorbent that carries out the in-situ removal of CO₂. Moreover, CO concentration increases with the reaction temperature due to the exothermic WGS reaction, which is thermodynamically favorable at low temperatures.

Fig. 3d shows the CO₂ concentration as a function of temperature during the SESR of methane and biogas. Overall, the experimental values for the CO and CO₂ concentrations are in good agreement with those predicted by the thermodynamic equilibrium at the temperatures studied. CO₂ concentration also increases with the reaction temperature, which is due to the carbonation reaction being exothermic and thermodynamically favored at low temperatures. However, when temperature increases, the removal of CO₂ from the gas phase decreases, and hence the shift of the equilibrium of the steam reforming and WGS reactions to the side of the products by the sorption enhanced process is reduced. This explains the lower concentrations of H₂ (Fig. 3a) and
higher concentrations of CO (Fig. 3c) at high temperatures. High H₂ concentration with low CO content (<1 vol.%) is required for electricity and heat generation by phosphoric acid fuel cells (PAFC), which are being considered for generating high-energy efficient clean energy [37]. According to the experimental results obtained, the SESR of biogas could produce a hydrogen stream that well suits the requirements of PAFCs when performed at 550-625 °C.

The gas concentrations profiles from the SESR of biogas and methane are very similar under the same experimental conditions, and only small differences have been found, as mentioned above, at 550-575 °C when slightly higher CH₄ concentrations and lower H₂ contents were obtained for biogas.

Fig. 3e shows the H₂ yield as a function of the reaction temperature during the SESR of methane and biogas. H₂ yield increases with the reaction temperature until it reaches a maximum, and then it decreases with temperature. The highest H₂ yield is attained at 650 °C (93.2% for the methane case and 92.7% for biogas). The H₂ yield is only slightly lower for biogas than for methane in the temperature range studied. Moreover, H₂ yield values are below those of the equilibrium at all the temperatures studied, although the differences are more pronounced at lower temperatures.

Fig. 3f shows the CH₄ conversion as a function of the reaction temperature during the SESR of methane and biogas. Conversion of CH₄ increases with the reaction temperature. The lowest values of CH₄ conversion are attained at 550-575 °C, as expected from the observed CH₄ concentration profiles. CH₄ conversion values around 99% are obtained at 600-625 °C, while values higher than 99.5%, very close to the equilibrium, are obtained at temperatures above 650 °C. CH₄ conversion for the biogas case is under that for methane at 550-575 °C, but it reaches similar values at higher
temperatures. The slightly lower CH$_4$ conversion values, and hence slightly higher CH$_4$ concentrations, found at 550-575 ºC for biogas could be ascribed to the slower kinetics of CO$_2$ sorption at such temperatures, as mentioned above. Lower CO$_2$ capture rates at low temperatures limit the process since the SESR reaction is intrinsically dependent on the rate of CO$_2$ removal. Therefore, this could explain the slightly lower CH$_4$ conversion and H$_2$ yield values achieved for biogas.

On the other hand, there is a correspondence between the lower CH$_4$ conversion and the lower H$_2$ yield obtained for biogas at low temperatures compared to methane. Nevertheless, at higher temperatures, the H$_2$ yield is still lower for biogas which indicates the influence, although to a lesser extent, of the presence of CO$_2$ in the biogas in the conversion to H$_2$. Apart from the steam reforming reaction, other reactions could also occur simultaneously during the reforming process. Thus, coke deposition can occur, which may be derived from any gas containing carbon elements by means of side reactions such as decomposition of CH$_4$, disproportionation of CO, or hydrogenation of CO$_2$ and CO. In the case of biogas, the reforming of these compounds could have been slowed down, favoring the formation of carbon deposits, due to the higher concentration of CO$_2$ in the gas phase and/or to a lower number of available catalytic active sites in the bed given the higher amount of CO$_2$ reacting with the sorbent. The tendency towards coke deposition may be related to the ratios of carbon, hydrogen, and oxygen in the raw gas, with lower O/C and H/C ratios leading to higher coke deposition. Thus, coke deposition is more likely to occur in dry reforming (i.e., CO$_2$ reforming) than in steam and partial oxidative reforming [38].
3.3. Effect of temperature on the SR of biogas

The effect of reaction temperature on the conventional steam reforming process, i.e., without CO₂ removal by a sorbent, was also evaluated in the 550-800 °C temperature range. The experiments were also carried out using a steam/CH₄ molar ratio of 6 (i.e., three times higher than the stoichiometric value) and a GHSV of 492 mL CH₄ g₉cat⁻¹ h⁻¹. Fig. 4 shows the results of the SR process as a function of temperature for the experiments with biogas (60%CH₄ + 40%CO₂), and pure methane (100% CH₄) for comparison purposes. Bars represent the experimental results and lines show the equilibrium values obtained from the thermodynamic analysis at similar conditions.

As shown in Fig. 4a, after the SR of both methane and biogas, 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. At higher temperatures, the endothermic nature of the steam methane reforming reaction thermodynamically favors this reaction. CH₄ concentration in the effluent gas decreases with the reaction temperature (Fig. 4b) because, as aforementioned, the steam methane reforming prevails over the methanation reaction at high temperatures. CO concentration increases with the reaction temperature (Fig. 4c), since the exothermic WGS reaction is thermodynamically unfavorable at high temperatures, which leads to higher concentrations of CO and lower concentrations of CO₂. Thus, CO₂ concentration decreases with the reaction temperature (Fig. 4d). Overall, the experimental concentrations of the gases are very close to those of the equilibrium in the range of temperatures studied.
Fig. 4. Effect of temperature on the H$_2$ (a), CH$_4$ (b), CO (c) and CO$_2$ (d) concentrations, as well as on H$_2$ yield (e) and CH$_4$ conversion (f), during SR of methane (CH$_4$) and biogas (60%CH$_4$ + 40%CO$_2$). Reaction conditions: steam/CH$_4$=6 mol/mol, GHSV=492 mL CH$_4$ g$_{\text{cat}}$^{-1} h$^{-1}$, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite sorbent.
On the other hand, a much lower concentration of H\(_2\) is obtained for the biogas case than for methane (Fig. 4a), following the higher concentrations of CO\(_2\), CO, and CH\(_4\). The higher concentration of CO\(_2\) in the gas phase in the case of biogas prevents the WGS reaction, resulting in higher CO content, and in turn lower H\(_2\) concentration. These results are also predicted by the equilibrium and it can then be confirmed that the excess CO produced from biogas SR compared to methane SR is related to the lack of CO\(_2\) and H\(_2\) that would be obtained by the WGS and steam methane reforming reactions. It could, therefore, be assumed that all the CH\(_4\) converted produces CO and H\(_2\) by Eq. (1) and that any excess CO is due to the CO\(_2\) in biogas that prevents WGS from occurring to a greater extent.

Fig. 4e shows the H\(_2\) yield as a function of the reaction temperature during the SR of methane and biogas. H\(_2\) yield increases as the reaction temperature increases until it reaches a maximum value, and then it decreases. The highest value for H\(_2\) yield is obtained at 650 °C (83.7% for methane and 82.4% for biogas). H\(_2\) yield follows the tendency shown by the equilibrium prediction, but with lower values for all the temperatures studied. On the other hand, the equilibrium predicted H\(_2\) yield is lower for biogas than for methane for all the temperatures studied.

Fig. 4f shows the CH\(_4\) conversion as a function of the reaction temperature during the SR of methane and biogas. CH\(_4\) conversion increases with the reaction temperature up to values higher than 98% from 650 °C, following the equilibrium results. Higher temperatures favor the conversion due to the endothermic nature of the steam methane reforming reaction. CH\(_4\) conversion values are slightly lower for biogas than for methane between 550 and 600 °C but, as predicted by equilibrium, they approach at higher temperatures.
During biogas steam reforming, a combination of steam reforming of methane (Eq. (1)) and dry methane reforming (Eq. (11)) could occur:

\[
\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_r^0 = +247 \text{ kJ mol}^{-1}
\] (11)

However, the dry methane reforming reaction is a highly endothermic reaction that occurs at high temperatures (>700 °C) [39] and plays a minor role when enough H\textsubscript{2}O is available [17]. In the present work, the absence of dry methane reforming can be assumed because the conversion of CH\textsubscript{4} after the SR of biogas is not higher than that of the pure methane case. It has been shown in literature that the steam methane reforming and WGS reactions are predominant when using a relatively high steam/C ratio and this results in the production of CO\textsubscript{2} and H\textsubscript{2} [26, 40].

3.4. Optimum temperature conditions for the SESR and SR of biogas

\( \text{H}_2 \) yield and H\textsubscript{2} concentration showed different trends with temperature after the SESR and SR processes (Figs. 3 and 4, respectively). Thus, for the SESR process, H\textsubscript{2} yield increased with temperature from 550 to 650 °C, but H\textsubscript{2} concentration decreased at temperatures higher than 600 °C. This means that for selecting an optimum temperature for the SESR and SR of biogas, a compromise between these parameters needs to be taken. In the case of the SESR of biogas (Fig. 3), the highest H\textsubscript{2} yield is 92.72% at 650 °C. At this temperature, a high value of CH\textsubscript{4} conversion (99.32%) is obtained but the concentration of H\textsubscript{2} is limited to 95.12 vol.%. On the other hand, the highest H\textsubscript{2} concentration during the SESR of biogas, 99.4 vol.%, is obtained in the 550-600 °C temperature range. Under such conditions, the H\textsubscript{2} yield values are below 90% (85.8-88.9%). Similar trends are observed in the conventional SR of biogas (Fig. 4). This means that keeping the temperature below 650 °C would increase the H\textsubscript{2} concentration,
and decrease the CO and CO₂ concentrations but would also considerably increase the CH₄ content which in turn would reduce the H₂ yield. Therefore, both variables will need to be balanced to comply with the objectives of the process in each particular case. In the present work, an intermediate temperature has been selected to study the effect of other process parameters, such as steam/CH₄ molar ratio and space velocity. Thus, a reaction temperature of 625 °C was used in the subsequent experiments. For the SESR of biogas at 625 °C the H₂ concentration reaches 97.4 vol.%, with a H₂ yield of 91.1% and CH₄ conversion of 98.8%, while the CH₄, CO and CO₂ concentrations obtained are 0.3, 0.9 and 1.5 vol.%, respectively.

On the other hand, under the studied conditions, a reaction temperature of 650 °C seems optimum for the SR of biogas since at this temperature the H₂ yield reaches its maximum value (82.4%) with an acceptable value of the CH₄ conversion (98.2%). Furthermore, the H₂ concentration reaches 66.6 vol.% and the concentrations of CH₄, CO and CO₂ are 0.4, 8.9 and 24.1 vol.%, respectively.

These results demonstrate the advantages of the sorption enhanced reaction for biogas compared to the conventional catalytic steam reforming process without in situ CO₂ removal. The addition of dolomite to the biogas SESR process results in much higher H₂ purity and H₂ yield in the outlet gas stream under all the studied conditions. Thus, a gas with more than 98 vol.% of hydrogen may be obtained in the SESR outlet stream under the conditions of these experiments. The conventional steam reforming process only reaches values of 78 vol.% of hydrogen.
3.5. Effect of steam/CH$_4$ molar ratio on the SESR and SR of biogas

The effect of steam/CH$_4$ molar ratio on the SESR and SR of biogas (60%CH$_4$ + 40%CO$_2$) was evaluated at 625 °C and a GHSV of 492 mL CH$_4$ g$_{cat}^{-1}$ h$^{-1}$. Steam/CH$_4$ molar ratios of 2, 4 and 6 were studied (i.e., one, two and three times higher than the stoichiometric steam/CH$_4$ molar ratio, respectively). The results are shown in Fig. 5.

The results show that higher steam/CH$_4$ molar ratios increase the H$_2$ concentration (Fig. 5a) while they reduce the CH$_4$ (Fig. 5b) and CO (Fig. 5c) concentrations, mainly when the steam/CH$_4$ molar ratio increases from 2 to 4. The CO$_2$ concentration remains practically unchanged for all the evaluated steam/CH$_4$ molar ratios during the SESR process (Fig. 5d) indicating that the carbonation reaction proceeds normally under these conditions. However, it slightly increases with the steam/CH$_4$ molar ratio during the SR process because the WGS reaction is favored. Low steam/C ratios (and therefore, low steam/CH$_4$ ratios in biogas) enhance methanation whereas a higher concentration of steam promotes both the steam methane reforming and the WGS reactions, reducing the CH$_4$ and CO contents and increasing the H$_2$ and CO$_2$ concentrations in the product gas [41]. Moreover, the H$_2$ purity reduces at low steam/CH$_4$ molar ratios since it is strongly influenced by the higher methane content in the effluent gas. On the other hand, H$_2$ yield (Fig. 5e) and CH$_4$ conversion (Fig. 5f) increase with the steam/CH$_4$ molar ratio, especially when the steam/CH$_4$ molar ratio increases from 2 to 4.
Fig. 5. Effect of steam/CH₄ molar ratio on the H₂ (a), CH₄ (b), CO (c) and CO₂ (d) concentrations, as well as on H₂ yield (e) and CH₄ conversion (f), during SESR and SR of biogas (60%CH₄ + 40%CO₂). Reaction conditions: temperature=625 °C, GHSV=492 mL CH₄ g cat⁻¹ h⁻¹, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite sorbent.

For the SESR process of biogas, when the stoichiometric value of the steam/CH₄ molar ratio is used (i.e., 2), a H₂ concentration of 88.5 vol.% is obtained, with H₂ yield of 71.5% and CH₄ conversion of 82.9%. In reforming processes, steam is usually added
exceeding the stoichiometric value to promote hydrogen production and to prevent coking since carbon deposition by polymerization or thermal decomposition occurs if the gas contains low amounts of the oxidizing component such as H2O. If carbon deposits are formed on the catalyst, the catalyst activity will be reduced, causing an increase in the methane content at the expense of the hydrogen production [42]. Higher steam/C molar ratios (i.e., higher steam/CH4 molar ratios in the present work) are favorable from a thermodynamic point of view, although high steam quantities will reduce the energy efficiency of the process since the evaporation of water is highly energy demanding [5].

With higher values of steam/CH4 molar ratio, such as 4 and 6, much higher H2 concentrations are reached at the expense of the marked decrease in the CH4 and CO concentrations. Moreover, an increase in the steam/CH4 molar ratio is especially important for the H2 yield, which is significantly enhanced for higher values, as was also the case in the SESR of acetic acid in a previous study [11], where it is reported that a higher amount of steam increases the conversion of tars and intermediate compounds contributing to avoid carbon deposits during the reforming process.

Thus, for a steam/CH4 molar ratio of 4, H2 concentration of 96.1 vol.%, H2 yield of 87.5% and CH4 conversion of 97.5% are obtained. Likewise, for a steam/CH4 molar ratio of 6, H2 concentration of 97.1 vol.%, H2 yield of 92.0% and CH4 conversion of 99.5% are reached.

As it is shown in Fig. 5, similar tendencies in the results have been found for the SR process of biogas. As mentioned above, the dry methane reforming reaction (Eq. (11)) could occur at low steam/CH4 molar ratios. A slightly higher CH4 conversion is thermodynamically obtained for the SR of biogas compared to pure methane when a
steam/CH$_4$ molar ratio of 2 is used at temperatures higher than 600 °C (data not shown). It suggests that dry reforming (Eq. (11)) could have occurred to a certain extent under SR when a steam/CH$_4$ molar ratio of 2 was used. This would explain the lower CH$_4$ concentration for biogas SR than for biogas SESR under these conditions (Fig. 5b). Likewise, quite similar CH$_4$ conversion was obtained for the SR and SESR of biogas when a steam/CH$_4$ molar ratio of 2 was used (Fig. 5f).

3.6. Effect of gas hourly space velocity (GHSV) on the SESR of biogas

The effect of gas hourly space velocity on the SESR and SR of biogas (60%CH$_4$ + 40%CO$_2$) was evaluated at 625 °C and using a steam/CH$_4$ molar ratio of 6. The GHSV ranged from 492 to 3937 mL CH$_4$ g$_{cat}^{-1}$ h$^{-1}$. The results are shown in Fig. 6. The equilibrium results are also shown in Fig. 6, which present constant values along the GHSV range studied because these results correspond to thermodynamic equilibrium conditions and are not affected by the space velocity.

For SESR of biogas, the concentrations of H$_2$ (Fig. 6a), CH$_4$ (Fig. 6b), CO (Fig. 6c) and CO$_2$ (Fig. 6d) are kept constant in the range of the space velocities studied. In the case of SR of biogas, CO and CO$_2$ concentrations do not vary significantly with the space velocity. However, H$_2$ concentration slightly decreases, while CH$_4$ concentration slightly increases at higher GHSV values.

On the other hand, for SESR of biogas, H$_2$ yield (Fig. 6e) and CH$_4$ conversion (Fig. 6f) remain quite constant with space velocity, although a decrease in the H$_2$ yield is detected at the highest space velocity studied. However, a gradual decrease in these parameters seems to occur during the SR of biogas as space velocity increases.
Fig. 6. Effect of GHSV on the H₂ (a), CH₄ (b), and CO and CO₂ (c) concentrations, as well as on H₂ yield (e) and CH₄ conversion (f), 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 catalyst and dolomite sorbent.

A lower fuel conversion might be expected at high space velocities due to a shorter contact time of gas and solid phases. In the present work, the worsening in the conversion is reflected by the decrease in the H₂ yield at high space velocities.
However, the H₂ purity is not affected by the increase in GHSV for the SESR of biogas, and it only slightly decreases at the highest space velocity values studied for the SR of biogas. It has been reported in the literature that H₂ yield may be more affected by the space velocity than H₂ purity in the case of the sorption enhanced steam reforming of glycerol [43] suggesting that, together with a decrease in the conversion, a higher formation of coke may occur at high space velocities. Although higher space velocity values may decrease the H₂ yield and CH₄ conversion, the space velocity is an important parameter from an economic point of view and has a high impact on the capital cost of the installation. Higher space velocities involve smaller reactor dimensions and hence lower catalyst inventory. In the present work, a worsening of the SESR process performance for biogas was only detected at the highest space velocity value studied.

5. Conclusions

High purity and high yield of hydrogen can be produced from biogas (60%CH₄ + 40%CO₂) in a single-step SESR process on a Pd/Ni-Co catalyst using dolomite as CO₂ sorbent, showing the biogas SESR as a promising process for biohydrogen production. High CH₄ conversion ability of the Pd/Ni-Co catalyst has been demonstrated for the SESR of biogas. The results of the present study prove the advantages of the sorption enhanced reaction over the conventional catalytic biogas steam reforming process.

Under the studied conditions, no effect of the CO₂ contained in the biogas on the SESR process performance occurs due to the ability of the sorbent to remove all the CO₂ from the gas phase at 550-700 °C. For the SESR of biogas, higher temperatures
lead to higher conversion of CH$_4$, whereas the H$_2$ yield reaches maximum values in the 625-650 °C temperature range. However, H$_2$ purity decreases with temperature. H$_2$ purity up to 98.4 vol.% is achieved from the SESR of biogas at 550-600 °C and H$_2$ yields higher than 90% are reached at 625-650 °C. On the other hand, H$_2$ yield, CH$_4$ conversion, and H$_2$ purity increase with the steam/CH$_4$ molar ratio due to the enhancement of the steam reforming and WGS reactions. Moreover, CH$_4$ conversion and H$_2$ purity values are maintained when high space velocities are used for the SESR of biogas, although H$_2$ yield decreases at the highest value studied.

Acknowledgements

The authors thank Franefoss Miljøkalk A/S (Norway) for supplying Arctic dolomite. This work was carried out with financial support from the Spanish MICINN (Project ENE2017-83530-R) and from the Gobierno del Principado de Asturias (PCTI, Ref. IDI/2018/000115), both co-financed by the European Regional Development Fund (ERDF). M.V. Gil acknowledges support from a Ramón y Cajal grant (RYC-2017-21937) of the Spanish Government, co-financed by the European Social Fund (ESF).

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