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# Thermodynamic analysis of Glycerol Steam Reforming for hydrogen production with in situ hydrogen and carbon dioxide separation

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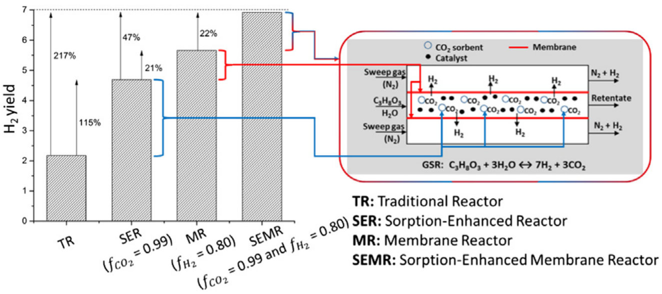
## HIGHLIGHTS

- A thermodynamic analysis of a SEMR for Glycerol Steam Reforming was performed.
- Thermodynamically, higher temperatures, WGFRs and lower pressures are better.
- The SEMR produces 217% more hydrogen than a traditional reactor.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A thermodynamic study of Glycerol Steam Reforming (GSR) for hydrogen production with in situ carbon dioxide and hydrogen (reaction products) simultaneous removal was performed. The sorption-enhanced membrane reactor (SEMR) was divided into multiple sub-Gibbs reactors and the Gibbs free energy minimization method was employed. The effects of temperature (600–800 K), molar water-to-glycerol feed ratio (WGFR) (3–9), pressure (1–5 atm) and fraction of hydrogen and carbon dioxide removal (*f*, 0–0.99) on the GSR process were target of investigation. A hydrogen yield (total moles of hydrogen produced/mole of reacted glycerol) very close to the stoichiometric value of 7 was obtained at 700 K, WGFR of 9, 1 atm and for $f_{CO_2} = 0.99$ and $f_{H_2} = 0.80$. This corresponds to an enhancement of 217%, 47% and 22% in terms of hydrogen yield comparatively to the traditional reactor (TR), sorption-enhanced reactor (SER) with carbon dioxide capture ($f_{CO_2} = 0.99$) and membrane reactor (MR) with hydrogen separation ($f_{H_2} = 0.80$), respectively. In terms of coke, its formation was only observed under WGFRs below the stoichiometric value of 3.

## 1. Introduction

The use of glycerol, the main by-product of the biodiesel manufacture process, for hydrogen production is not only environmentally more attractive than fossil-based routes, but also valorizes glycerol itself thus making biodiesel more competitive. The Glycerol Steam Reforming (GSR) is an endothermic and equilibrium-limited process that requires high operating temperatures (Eq. (1) – cf. Table 1). The GSR process involves the decomposition of glycerol (Eq. (2) – cf. Table 1) followed by the water-gas shift (WGS, Eq. (3) – cf. Table 1) reaction (multiplied by a factor of 3).

Even though a theoretical production of 7 mol of hydrogen per mole of consumed glycerol should be observed, the existence of

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**Notation and glossary**

*List of acronyms*

| | |
|---|---|
| GSR | Glycerol Steam Reforming |
| MR | membrane reactor |
| RWGS | reverse water-gas-shift |
| SER | sorption-enhanced reactor |
| SEMR | sorption-enhanced membrane reactor |
| SRM | steam reforming of methane |
| TR | traditional reactor |
| WGFR | water-to-glycerol feed ratio |
| WGS | water-gas shift |

side reactions (e.g. methanation) leads to a decrease in hydrogen production. Theoretical studies on new reactor configurations that combine GSR and carbon dioxide [1,2] or hydrogen [3] selective removal (reaction products in Eq. (1)) have allowed to conclude that such intensified processes permit to enhance the hydrogen production and decrease the production of both methane and carbon monoxide by-products by shifting the thermodynamic equilibrium. Moreover, such processes allow the attainment of similar or even better performance than in a traditional reactor (TR) while operating at milder operating conditions. However, the effect of the selective removal of both products simultaneously during GSR has never been studied. Such a process could be achieved with a multifunctional Sorption Enhanced Membrane Reactor (SEMR), which would simultaneously carry out the GSR reaction and remove pure hydrogen and carbon dioxide from the reaction zone by means of a hydrogen selective membrane and a carbon dioxide selective sorbent, respectively (Fig. 1). The continuous use of such reactor configuration would require two parallel reactors, being that while one of them is producing pure $H_2$ through GSR (which exits in the permeate stream and is not mixed with any other species, apart from the inert carrier gas, due to membrane selective permeation - left side of Fig. 1), the other is being regenerated, i.e., carbon dioxide is being removed and exits in the retentate stream (again $N_2$ can be used as purge gas - right side of Fig. 1). In other words, each reactor has two operation modes being that along time each of them goes through the reaction–regeneration cycle repeatedly. Since the goal is to shift the thermodynamic equilibrium of GSR during reaction mode by retaining $CO_2$ in the sorbent, once the sorbent gets saturated and $CO_2$ starts breaking through the column the reaction is ended (Fig. 1(a)). At this point, the set of valves moves this reactor feed (glycerol and steam) to e.g. $N_2$ so that the sorbent bed can be regenerated (Fig. 1(b)). During this last step no $H_2$ is produced in this reactor, being produced in the other reactor that is now in the reaction stage. Moreover, although $CO_2$ might affect membrane permeability towards $H_2$, this is not very pronounced as, for instance, it occurs with CO, and such effect is reversible (thus, as long as $CO_2$ is removed, high permeability towards $H_2$ is restored) [4]. The main requirement is that operating conditions, namely in terms of temperature, are compatible for the GSR catalyst, $CO_2$ sorbent and $H_2$-selective membrane, which is the case [5].

**Table 1**
Reactions in equilibrium considered during the GSR thermodynamic simulations.

| Reaction | $\Delta H_r^{298\ K}$ (kJ mol$^{-1}$) | Reaction number |
|---|---|---|
| $C_3H_8O_3 + 3H_2O \rightleftharpoons 7H_2 + 3CO_2$<br>(GSR – Glycerol Steam Reforming) | 128 | (1) |
| $C_3H_8O_3 \rightleftharpoons 3CO + 4H_2$<br>(decomposition of glycerol) | 251 | (2) |
| $CO + H_2O \rightleftharpoons H_2 + CO_2$<br>(WGS – water-gas shift) | −41 | (3) |
| $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$<br>(methanation) | −206 | (4) |
| $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$[a] | −165 | (5) |
| $2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$[b]<br>(dry reforming of methane) | −247 | (6) |
| $2CO \rightleftharpoons CO_2 + C$<br>(Boudouard reaction) | −172 | (7) |
| $CH_4 \rightleftharpoons 2H_2 + C$<br>(methane cracking) | 75 | (8) |
| $CO + H_2 \rightleftharpoons H_2O + C$<br>(carbon monoxide reduction) | −131 | (9) |
| $CO_2 + 2H_2 \rightleftharpoons 2H_2O + C$<br>(carbon dioxide reduction) | −90 | (10) |

[a] Sum of both reverse of Eq. (3) and Eq. (4).
[b] Sum of Eqs. (3) and (4).

In this work an equilibrium thermodynamic analysis of GSR in a SEMR was done, for the first time, with ASPEN PLUS software and the effect of the operating temperature, pressure, water-to-glycerol feed ratio (WGFR) and $H_2$ removal fraction (for constant $CO_2$ removal) on hydrogen production was accessed. Moreover, a comparison between the results obtained under equilibrium conditions for the SEMR and for the other types of reactors (TR, membrane reactor (MR) and sorption enhanced reactor (SER)) was done as well. Finally, the limits in terms of WGFR for avoiding coke formation at different temperatures was discussed. This thermodynamic analysis is crucial as it may indicate the suitability of applying such intensified reaction-separation process for hydrogen production from glycerol. Moreover, and although thermodynamic considerations alone do not provide evidence for the practicability of the design, it provides valuable information about the limits that can be attained in actual operation, and gives indication on how to proceed and which conditions have to be applied in order to achieve maximum performance.

## 2. Methodology

ASPEN PLUS V7.3 was used to perform all the simulations. The Gibbs free energy minimization methodology (nonstoichiometric method), which calculates the equilibrium composition through the minimization of the Gibbs free energy of a specific set of species was applied (a more detailed description of the methodology is available in Supplementary data).

For such simulations, the species included were hydrogen, carbon dioxide, carbon monoxide, methane, glycerol, water and solid carbon. By considering these species, some of the possible reactions that might be in equilibrium together with GSR (Eqs. (2) and (3)), are the ones shown in Table 1. The reaction in Eq. (5), which is the sum of both reverse of Eq. (3) and Eq. (4), is included in Table 1 with the single purpose of facilitating the analysis of the stoichiometric relations in the SEMR.

The modular approach used to simulate the SEMR (Supplementary data, Fig. S1) is represented by $(n + 1)$ sub-reformers and $n$ sub-separators. Each sub-reformer consists on a Gibbs reactor which performs the thermodynamic equilibrium calculations through the method previously explained. The sub-separators consist on component separators that separate chemical species based on specified flows or split fractions, which in practice is related with factors like membrane and sorbent selectivities, membrane area and sorbent quantity, etc. For $n = 0$ a simple Gibbs reactor is simulated; for $n = 1$ a single separator and two sub-reformers are used; and so on. The value of $n$ depends on the values of the global removal fractions of $CO_2$ ($f_{CO_2}$) and $H_2$ ($f_{H_2}$) specified (higher values of $f$ imply higher values of $n$). It is worth