Hydrogen Production Through Glycerol Steam Reforming in Different Reactor Configurations – From Conventional to Sorption-Enhanced Membrane Reactor

Joel Silva[1], Miguel Soria[1], Silvano Tosti[2], Luis Madeira[1*]

[1] LEPABE, Department of Chemical Engineering, Faculty of Engineering - University of Porto, Rua Dr. Roberto Frias, s/n 4200-465, Porto, Portugal; 2 Dipartimento FSN - ENEA C. R. Frascati - via E. Fermi 45, 00044 Frascati (Rome), Italy

**Corresponding author: mmadeira@fe.up.pt*

Highlights

- A Ga substituted, microwave aged K impregnated hydrotalcites was prepared.
- An astonishing CO_2 sorption capacity of 2.09 mol/kg was obtained at 300 ºC (p_{CO2} = 3.1 bar).
- Steam enhanced the hydrotalcite's performance during breakthrough experiments.
- Full glycerol conversion was obtained in the packed bed reactor at 400 ºC.

1. Introduction

Using the main by-product of biodiesel manufacture, glycerol, for H_2 production is environmentally advantageous and makes biodiesel more competitive due to glycerol valorization. This can be achieved by glycerol steam reforming (GSR), which is an endothermic equilibrium-limited process (equation 1).

$$C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2 \qquad \Delta H_{298K} = 128 \text{ kJ/mol} \qquad (1)$$

From the stoichiometry of reaction (1), a maximum production of 7 moles of H_2/mole of consumed glycerol should be observed if no side reactions occur. Thermodynamic studies on different hybrid reactor configurations that combine GSR and CO_2 [1] or H_2 [2] or both products [3] removal allowed concluding that such processes enhance the H_2 production by shifting the thermodynamic equilibrium, being that only in the case of removal of both products the maximum (theoretical) H_2 yield has been reached. On the other hand, a previous modeling study of GSR under realistic conditions in a packed bed reactor has shown that besides the H_2 yield keeping far from such limit, the glycerol conversion itself is limited (below 100%), unless very drastic conditions are employed [4]. Therefore, several reactor concepts will be experimentally tested: traditional packed bed reactor (PBR), sorption-enhanced reactor (SER) using a CO_2-selective sorbent, membrane reactor (MR) with and H_2-permselective membrane, and sorption-enhanced membrane reactor (SEMR) combining the previous ones. The main goal of this work is to experimentally assess the actual impact that the removal of CO_2 and/or H_2 from the reaction medium has on both glycerol conversion (total and into gaseous products) and H_2 yield.

2. Methods

In order to better understand how the capture of CO_2 occurs over a hydrotalcite-like material, an extended preliminary assessment was done using a Mg-Al hydrotalcite with CO_3^{2-} as the charge compensating anion in which Al is partially substituted with Ga, aged under microwave irradiation and impregnated with 20 wt.% of potassium (selected from a group of 4 hydrotalcites) [5]. Furthermore, with the aim of characterizing the permeation of H_2 through a 100 μm thick Pd-Ag membrane, pure H_2 permeation tests under different driving forces and temperatures will be performed. Finally, a catalyst supplied by Johnson Matthey will be used during the catalytic tests, either in the PBR or in the SER, MR and SEMR.

3. Results and discussion

The CO_2 sorption isotherm of the modified hydrotalcite was obtained at 300 ºC under dry conditions. The results obtained so far are very promising, with outstanding capacities as compared to literature values, being that a sorption equilibrium value of 2.09 mol/kg at 3.10 bar of CO_2 was obtained (Fig.1) [5]. Moreover, breakthrough experiments under dry conditions were performed and the effect of temperature (300-400 ºC), total pressure (1.3-6.0 bar) and CO_2 concentration (5-15 vol.% CO_2) was analyzed. As expected, higher CO_2 concentrations and total pressures allow the attainment of higher sorption capacities. On the other hand, temperature didn't have any significant effect on the working sorption capacity. Finally, tests under wet conditions (5-15 vol.% H_2O) were performed and an enhancement of the sorption capacities was observed, which makes this sorbent highly suitable to be used in steam reforming or water-gas shift reactions, where steam is always present. The reactor configurations testing for GSR under different conditions are still under way, being that glycerol conversions above 99% have already been observed for the PBR at only 400 ºC. However, both conversion of glycerol into gaseous products (CO_2, CO and CH_4) and H_2 yield are still far (around 50% and 2, respectively) from their limits, under similar conditions, opening the path for the reactor configurations mentioned above.

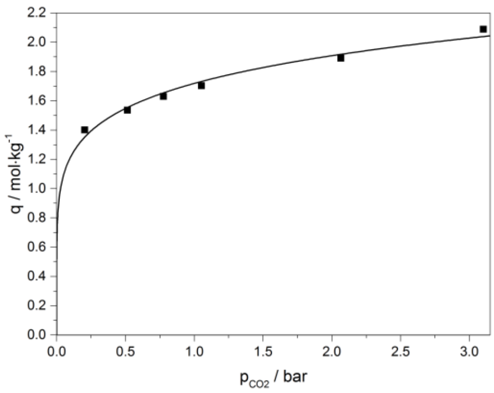

Figure 1. CO_2 sorption equilibrium isotherm at 300 ºC of the modified hydrotalcite; adapted from [5].

4. Conclusions

Preliminary sorption tests allowed to observe outstanding equilibrium CO_2 sorption capacities with the modified hydrotalcite, higher than those normally reported in the literature for similar materials and well above the minimum value of 0.3 mol/kg considered for their application in pre-combustion capture applications. Moreover, it was observed that the presence of H_2O highly enhances the sorption capacity of the hydrotalcite. Such material is thus expected to provide an important enhancement effect in either the SER or SEMR for the glycerol conversion and H_2 yield. In fact, preliminary PBR tests have shown that even though full glycerol conversions are attained, there are still significant improvements that can be achieved, in terms of glycerol conversion into gaseous products and H_2 yield, when the hybrid reaction systems are used.

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