Olive Mil Wastewater Valorisation through Steam Reforming using a Hybrid Sorption-Enhanced Membrane Reactor

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1. Introduction

Olive mill wastewater (OMW) is a pollutant by-product of the olive oil production [1]. This effluent has a high pollutant organic load, namely polyphenols, sugars and fatty acids, among others. In order to mitigate the environmental impact of this agro-industrial sector, it was proposed the application of the OMW steam reforming (OMWSR), which enables valorising this waste while producing green H_2. A new multifunctional reactor configuration combining the OMWSR with H_2 and/or CO_2 selective removal is proposed herein for the 1st time, due to its potential to overcome some restrictions like the thermodynamic limitation of the reversible reaction(s) and the avoidance of several undesired side reactions. In this work, it will be studied and compared the performance of a traditional reactor (TR), a Sorption-Enhanced Reactor (SER – with a CO_2-selective sorbent), a Membrane Reactor (MR – with an H_2-selective membrane) and the Sorption-Enhanced Membrane Reactor (SEMR – integrating both separations in the same device).

2. Methods

The thermodynamic analysis of OMWSR was done employing the Aspen Plus V8.8® software [2]. The simulations were made at different temperatures, pressures and removal fractions of H_2 and CO_2 to identify the best operational conditions and performance limits. Also, CO_2 equilibrium isotherms and breakthrough curves were obtained through static and dynamic tests, respectively, with commercial sorbents and home-prepared doped-hydrotalcites (HTCs with different interlayer anions) at 300 ºC [3]. Further, a catalytic screening (@ 350/400 ºC; 1 bar) was performed with commercial and home-prepared catalysts in a TR with synthetic OMW. After that, stability tests (24 h of time-on-stream) were performed with the best catalysts to be subsequently used in the above-mentioned multifunctional reactors. The physicochemical characterization of all the samples was realized through several techniques (XRD, TPO, TPD-CO_2, etc.).

3. Results and discussion

The optimum operation conditions for the OMWSR in a SEMR were determined in the thermodynamics analysis [2]. The H_2 yield increases with the H_2 and/or CO_2 removals – see Figure 1a). It was also verified that the advantages of the SEMR are more perceptible at lower temperatures (300-400 ºC), and so this reactor configuration can be operated under milder conditions, which favor CO_2 sorption by the HTCs.

Among the prepared HTCs, the one modified with gallium and doped with potassium (HTC-CO_3(Ga)_K) presents the highest CO_2 sorption capacity (1.45 $mmol \cdot g^{-1}$, @ p_{CO2}= 1 bar and 300 ºC) in comparison with the other synthesized HTCs and commercial sorbents – see Figure 1b) [3].

Regarding the catalysts screening, the Rh-based, as well as the Ni/SiO_2-Al_2O_3 and Ni-Ru/SiO_2 samples reached the highest values of H_2 yield among the 10 commercial and 5 prepared catalysts tested (materials with different active phases/support and distinct metal loadings) – see Figure 1c). Among them, the catalysts Rh/Al_2O_3 and 0.5 wt.% Rh/Al_2O_3 presented a high and relative stable H_2 yield (ca. 9 mol_{H2}/mol_{OMW}) during 24 h of time-on-stream.

The ongoing work consists in the application of the best catalysts in a MR with a Pd-Ag perm-selective membrane (supplied by Tecnalia) and in a SER with a promising CO_2 sorbent. Subsequently, the catalyst, sorbent and membrane will be employed in the multifunctional SEMR.

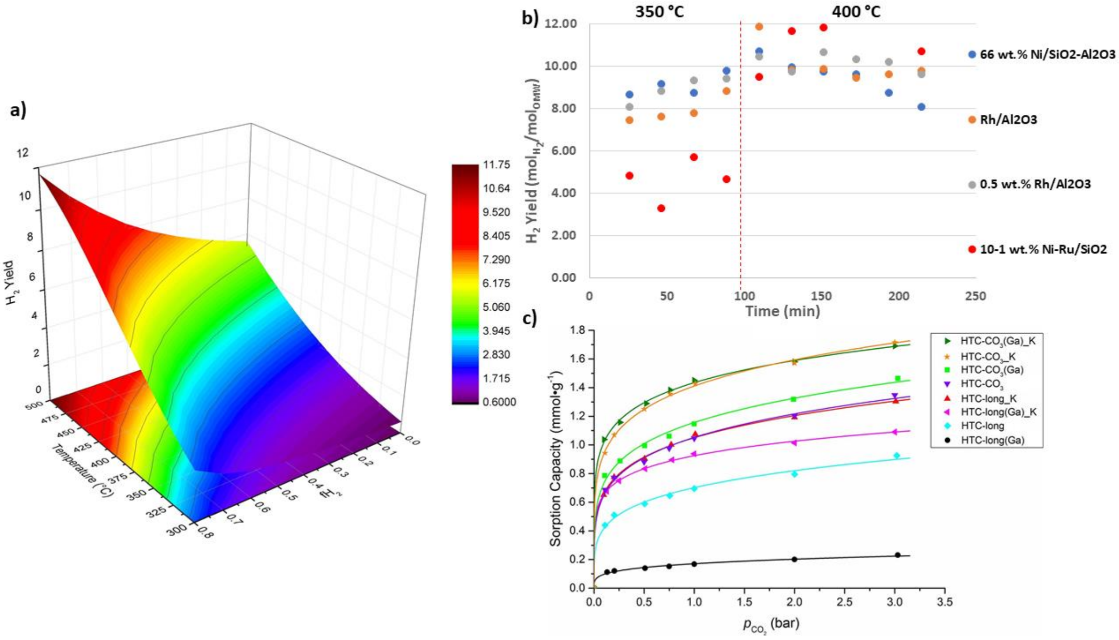

Figure 1. (a) Yield of H_2 as function of temperature and H_2 removal fraction at 1 bar in a MR – thermodynamic analysis. (b) H_2 yield obtained using commercial and prepared catalysts. (c) CO_2 equilibrium isotherms of prepared hydrotalcites at 300 ºC.

4. Conclusions

Thermodynamic analysis showed that the SEMR has several advantages in comparison with other reactor configurations. A modified HTC was prepared (HTC-CO_3(Ga)_K) revealing high CO_2 sorption capacity under conditions suitable for a SER. Several commercial and new catalysts have shown high catalytic performance for OMWSR, some of them with high stability during 24 h of reaction (Rh/Al_2O_3 and 0.5 wt.% Rh/Al_2O_3). Some of the most promising materials will be integrated in a SEMR.

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