

# Steam Reforming of the Olive Mill Wastewater in Multifunctional Reactors

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Olive oil production is one of the agro-industrial sectors with major critical environmental impacts: the olive oil mill wastewater (OMW) is a pollutant by-product of this process [1]. In this way, it was suggested the application of the OMW steam reforming (OMWSR), which can economically valorize this waste ( $H_2$  production). A hybrid reactor configuration combining the OMWSR with  $H_2$  and  $CO_2$  selective removal is proposed herein for the 1<sup>st</sup> time, due to its potential to overcome the restrictions of the reversible reactions. It was compared the performance of a traditional reactor (TR), a sorption-enhanced reactor (SER - with  $CO_2$  sorbent), a membrane reactor (MR - with an  $H_2$ -selective membrane) and the sorption-enhanced membrane reactor (SEMR - integrating both separations).

The best operating conditions for the OMWSR in a SEMR were determined in a thermodynamics analysis [2]. The  $H_2$  yield increases with the  $H_2$  and/or  $CO_2$  removal. It was also verified that the advantages of the SEMR are more perceptible at lower temperatures, and so this reactor configuration can be operated under milder conditions, which favor  $CO_2$  sorption and membrane stability. Among the prepared hydrotalcites, the one modified with gallium and with potassium, presents the highest  $CO_2$  sorption capacity in comparison with the other synthesized and even commercial sorbents [3]. About 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 them, the Rh/ $Al_2O_3$  and Ni/ $SiO_2$ - $Al_2O_3$  catalysts presented a high and stable  $H_2$  yield during 24 h of time-on-stream [4].

The removal of  $H_2$  and  $CO_2$  allowed reaching higher and stable  $H_2$  yields in the SEMR during the pre- and post-breakthrough time in comparison with the TR (see Fig. 1 a-b)) [5]. This allows the simultaneous production of highly pure  $H_2$  in the retentate and permeate sides. A higher improvement in terms of  $H_2$  yield was observed when the MR and particularly the SEMR was applied (see Fig. 1 c) -  $H_2$  yield enhancement of  $\approx 44\%$  was noted compared to the TR). It was also demonstrated that the steam reforming process, when implemented in a SEMR, can efficiently handle real OMW effluents, with high productions of  $H_2$ .

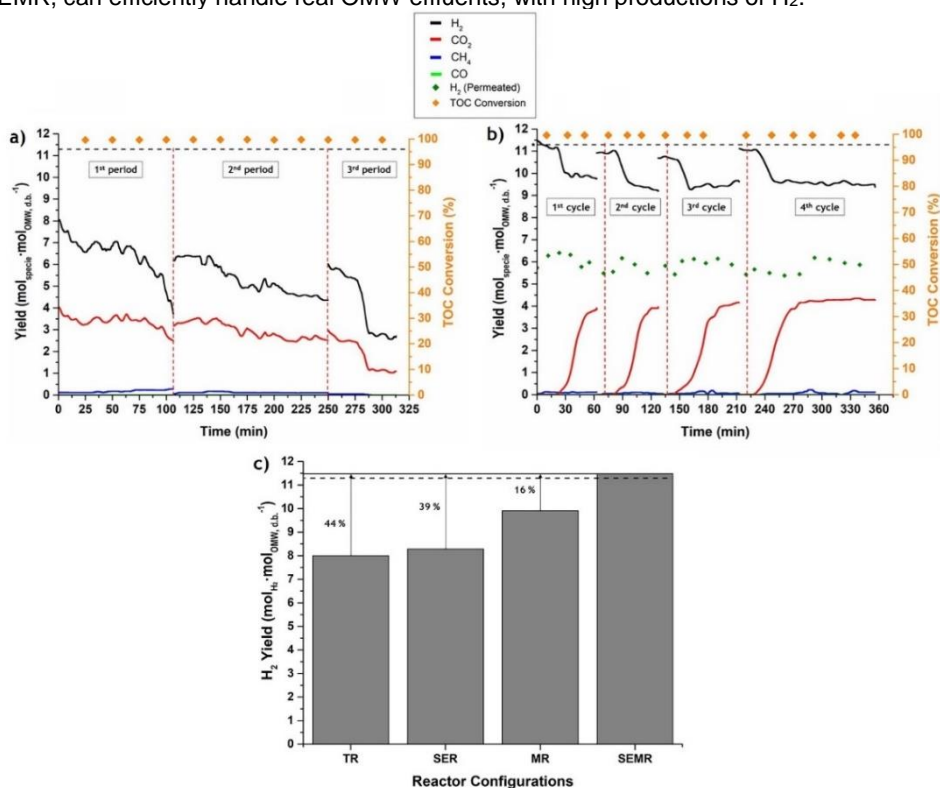


Fig. 1. Gaseous species yield and TOC conversion in a) TR or b) SEMR at 400 °C/4 bar. c)  $H_2$  yield with different reactor configurations at 400 °C/4 bar.

## ACKNOWLEDGEMENTS

This work was financially supported by: LA/P/0045/2020 (ALiCE), UIDB/00511/2020 and UIDP/00511/2020 (LEPABE) funded by National Funds through FCT/MCTES (PIDDAC); project HyGreen&LowEmissions (NORTE-01-0145-FEDER-000077), supported by NORTE 2020, under the PORTUGAL 2020 Partnership Agreement, through the ERDF; and project NORTE-01-0247-FEDER-39789, funded by ERDF, through NORTE 2020. M. Soria thanks FCT for the financial support of his work contract through the Scientific Employment Support Program (Norma Transitória DL 57/2017).

## REFERENCES

- [1] Dermeche S, Nadour M, Larroche C, Moulti-Mati F and Michaud P. 2013. Olive mill wastes: Biochemical characterizations and valorization strategies. *Process Biochemistry* 48 (10): p. 1532-1552.
- [2] Rocha C, Soria MA, Madeira LM. 2017. Steam reforming of olive oil mill wastewater with in situ hydrogen and carbon dioxide separation – Thermodynamic analysis. *Fuel* 207: p. 449-460.
- [3] Rocha C, Soria MA, Madeira LM. 2020. Doping of hydrotalcite-based sorbents with different interlayer anions for  $CO_2$  capture. *Separation and Purification Technology* 235: p. 116140.
- [4] Rocha C, Soria MA, Madeira LM. 2021. Screening of commercial catalysts for steam reforming of olive mill wastewater. *Renewable Energy* 169: p. 765-779.
- [5] Rocha C, Soria MA, Madeira LM. 2022. Olive mill wastewater valorization through steam reforming using hybrid multifunctional reactors for high-purity  $H_2$  production. *Chemical Engineering Journal* 430: p. 132651.