



# AUTOTHERMAL REFORMING OF OLIVE MILL WASTEWATER: ENERGY BALANCE

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**Abstract:** In this paper, the autothermal reforming (ATR) of olive mill wastewater was experimentally performed for the first time and compared to the traditional reforming (TR) of the same effluent. The tests were conducted with the use of a bimetallic ruthenium-nickel catalyst, with  $\text{La}_2\text{O}_3$  and supported on  $\text{SiO}_2$ . Different operating conditions were tested (temperature range of 400 – 700 °C and oxygen-to-carbon molar ratio ( $\text{O}_2/\text{C}$ ) of 0.0-0.5), with the objective of assessing their effect on the hydrogen yield. Characterisation of fresh and spent catalysts was also conducted, namely temperature programmed oxidation (TPO) and inductively coupled plasma - optical emission spectroscopy (ICP-OES), to correlate changes in the catalysts with their performance.

**Introduction:** Olive mill wastewater (OMW) is a high organic load effluent of the olive oil production industry. It is pollutant to the ground and water, and produced in high volumes, with some estimates suggesting that 30 million cubic meters are produced yearly [1]. In this work, the autothermal reforming of said waste product is performed. The steam reforming is an endothermic reaction, which would produce renewable hydrogen by decomposing the organic oxygenated compounds present in the effluent into syngas –  $\text{H}_2$  and  $\text{CO}$  (Eq. 1) [2]. However, this process can be improved by adding a sub-stoichiometric amount of  $\text{O}_2$  at the reaction inlet, which would promote the partial oxidation of OMW (Eq. 2). The partial oxidation reaction still produces hydrogen, and is exothermic, making it possible to achieve thermally neutral operation, in the so-called autothermal reforming [3].

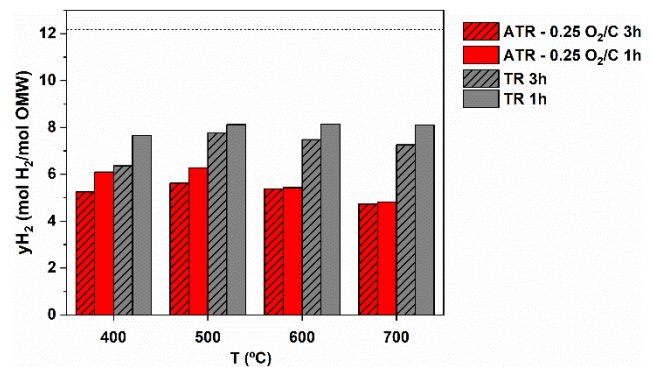
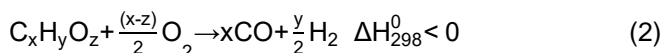
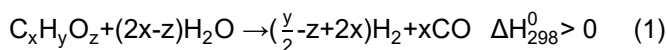


Figure 1- Hydrogen yield for the two reactor configurations (TR and ATR) after 1 h and 3 h of reaction for different temperatures. P = 1 bar.

**Conclusions:** The catalytic tests showed that hydrogen production is larger for low oxygen-to-carbon molar ratios (0.25), whilst high  $\text{O}_2/\text{C}$  values will cause the production of hydrogen to practically disappear. Hydrogen yield was higher for the TR configuration for all temperatures tested (Figure 1), but catalyst deactivation was reduced for the ATR. On the other hand, higher oxygen-to-carbon means higher amounts of heat released, crucial to carry out the endothermal reforming process. The results were compared also in terms of the amount of heat released during the reaction and the net calorific value of the hydrogen produced; it was found that the ATR at 500 °C with 0.25 oxygen-to-carbon ratio was the optimal configuration tested in terms of energetic efficiency.

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