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Catalytic reforming of olive mill wastewater and methane in a Pd-membrane reactor

Silvano Tosti ^{a,*}, Massimiliano Fabbricino ^b, Ludovico Pontoni ^b,
Vincenzo Palma ^c, Concetta Ruocco ^c

^a ENEA, Dip. Fusione e Tecnologie per la Sicurezza Nucleare, C.R. ENEA Frascati, Via E. Fermi 45, Frascati (RM) I-00044, Italy

^b Dept. of Civil, Architectural and Environmental Engineering, Univ. of Naples Federico II, Via Claudio 21, Naples I-80125, Italy

^c Dept. of Chemical Engineering, Univ. of Salerno, Via Giovanni Paolo II 132, Fisciano (SA) I-84084, Italy

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ABSTRACT

Olive mill wastewater (OMW) is a biomass by-product of the olive oil industry. To treat this waste, reforming has been studied as a means of both producing hydrogen/syngas and reducing the pollution resulting from OMW.

This study investigated a process in which OMW was added to methane and fed into a membrane reformer. The goal was to use the large water excess in OMW for reforming the methane.

The results of the experiment showed that the combined reforming of methane and OMW is characterized by high hydrogen yields, with all the organic matter (the total organic carbon of both the OMW and the methane) reacting to produce hydrogen. Particularly, at 450 °C and 500 kPa with a space velocity of 0.17 mol h⁻¹ g_{CAT}⁻¹ and a steam-to-carbon ratio of 16.6, hydrogen yields around 45 g per 100 g of TOC fed were measured. This corresponds to the production of 12.3 kg of ultra-pure hydrogen per ton of treated OMW. Also, it was demonstrated that adding methane to OMW does not affect the ability of the reforming process to reduce the pollution from the wastewater.

Finally, the optimum operating conditions of the membrane reformer were defined by analyzing the effect of the space velocity and steam-to-carbon ratio on hydrogen production.

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Introduction

Olive oil production is concentrated in Mediterranean regions, and more than 9 million ha are devoted to olive tree cultivation [1]. The worldwide production of olive oil is around 2.5 Mt,

corresponding to a market value of about 9 G€. Olive mill wastewater (OMW) is an important byproduct of olive oil milling. As a biomass, it is characterized by the presence of phenolic compounds and long-chain fatty acids [2,3]; thus, OMW exhibits high resistance to biodegradation and the usual processes for water treatment are not applicable [4–7].

* Corresponding author.

E-mail address: silvano.tosti@enea.it (S. Tosti).

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At present, most Mediterranean countries commonly use land disposal of OMW, which threatens water bodies and ecosystems. The pollution caused by OMW has been estimated to be 200 times higher than that from urban wastewater [8], so land disposal has a strong impact on the environment. Furthermore, land disposal is expensive for the small-medium enterprises that compose the majority of olive oil milling operations.

Recently, catalytic reforming of OMW has been studied in both traditional [9] and membrane [10–12] reactors, with the aim of valorizing this wastewater by producing a syngas consisting mainly of hydrogen, CO₂, and methane. Membrane reactors consisting of Pd–Ag permeators have been used in several experiments for producing ultrapure hydrogen from dehydrogenation reactions [13–15].

In general, the high water content of biomass is problematic in the production of syngas via reforming, and much work on the steam reforming of bio-ethanol has verified that the energy efficiency and economy of these processes is negatively affected by water removal after fermentation [16,17]. In previous work on OMW reforming, the OMW was distilled before the reaction tests in order to increase the concentration of organic matter up to some tens of g L⁻¹ of total organic carbon (TOC). However, this organic content of the water is still not enough to make the process convenient considering an energy point of view.

The need to concentrate the liquid biomass could be avoided by adding methane to the feed stream of the reformer. As an example, combined steam reforming of dilute ethanol mixtures and methane was tested in a Pd-membrane reactor by verifying that high hydrogen yields (close to 50%) can be achieved with an EtOH/methane feed molar ratio of 4/1 operating at 500 kPa [18]. Based on this experience, the present work studies the combined reforming of OMW and methane. In particular, before the reforming the fraction of OMW rich in water and the semi-solid residue have been removed via distillation. Such an approach does not correspond to the best practice from the energy efficiency point of view, but it allowed comparing the results of these experiments with those of previous tests in which a Pd-membrane reactor using the same catalyst was fed only with distilled OMW [12].

Experimental

Tests were conducted on samples of OMW obtained in previous works [11,12]. This wastewater was collected from a traditional olive mill located in Frascati (Italy) during Autumn 2013, and it was preserved at –20 °C. Similar to the previous experimental investigations, the OMW was filtered and distilled prior to the reforming tests.

OMW distillate

After filtration, OMW of pH 5.47 was distilled at ambient pressure by controlling the temperature of the liquid phase. A first fraction (A) was separated below the temperature of about 101 °C, a second fraction rich in water (B) below 104 °C, a third fraction (C) below 120 °C, while a semi-solid residue (D) was collected in the still pot. The distillate used in the

reforming experiment has been obtained by mixing the fraction A and C. The semi-solid residue is rich in inorganic compounds and, therefore, it has not been treated together with the fractions A and C in the reformer where could form deposits over the catalytic bed.

The distillate was characterized in terms of pH, total phenols, chemical oxygen demand (COD), and total organic carbon (TOC). Table 1 reports the characteristics of the OMW distillates used in this work as well as those from a previous study [12]. Analyses were conducted according to the Standard Methods for the Examination of Water and Wastewater [19]. Total phenol and COD were measured by spectrometry, using a Photolab 6600 UV–Vis spectrophotometer. In detail, the total phenols were measured following the methodology associated with the Folin-Ciocalteu reagent, while COD was obtained following closed reflux standard methods. TOC was calculated as the difference between the total carbon and the total inorganic carbon, and these latter values were determined using an OI Analytical AURORA 1030W TOC Analyzer set in TC-TIC mode. All used reagents were of laboratory grade. Only ultrapure water was used for the dilutions.

Pd-membrane reformer and catalyst

The membrane module was manufactured at the ENEA Frascati laboratories by using a dense Pd–Ag (with Ag 23 wt%) membrane tube of diameter 10 mm, length 152 mm, and wall thickness 0.150 mm. The membrane module configuration used to ensure the long life of the Pd-membranes is described elsewhere [20].

The Pd–Ag tube was filled with 4.6 g of glass spheres of diameter 2 mm mixed with 5.0 g of a catalyst developed by the University of Salerno. According to the preparation procedure, Al₂O₃ pellets (2 mm) were washcoated with a ceria-zirconia layer and, then, active metals (platinum, rhodium and palladium) were impregnated on mixed metal (CeO₂–ZrO₂) oxides support. In particular, Al₂O₃ pellets (supplied by Sigma–Aldrich) after preliminary calcination at 600 °C for 3 h (heating rate of 10 °C min⁻¹) were dipped into a slurry prepared by dispersing CeO₂–ZrO₂ powder (supplied by Rhodia) in a colloidal solution. The colloidal solution was prepared by acidifying a suspension (CeO₂–ZrO₂/AlOOH = 5/1), containing also methyl cellulose (1 wt %), with HNO₃ at pH = 4–5. Then, the pellets were dried overnight at 120 °C and calcined at the same conditions reported above. The metals were deposited by co-impregnating the washcoated pellets with an aqueous solution of the three corresponding metal salts: platinum, rhodium and palladium chlorides (supplied by Sigma–Aldrich). The loading of every noble metal was 1 wt% while the CeO₂–ZrO₂/Al₂O₃ weight ratio was equal to 0.08. In order to evaluate the carbon formation tendency of the system

Table 1 – Analysis of the OMW distillate used for feeding the Pd-membrane reactor.

| pH | Total phenols (mg L ⁻¹) | COD (mg L ⁻¹) | TOC (mg L ⁻¹) | Ref. |
|-----|-------------------------------------|---------------------------|---------------------------|-----------|
| 4 | 123.7 | 50,951 | 9050 | This work |
| 3.6 | 153.3 | 42,173 | 8694 | [12] |

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