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Full Length Article

Steam reforming of olive oil mill wastewater with in situ hydrogen and carbon dioxide separation – Thermodynamic analysis

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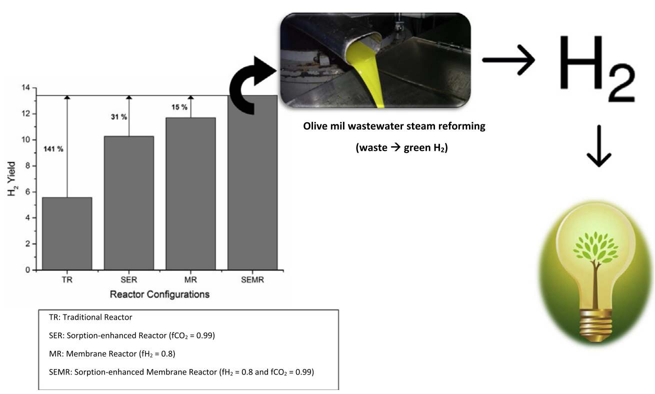
HIGHLIGHTS

- Olive mill wastewater valorization for H_2 production via steam reforming.
- A thermodynamic analysis of a sorption-enhanced membrane reactor was performed.
- Higher temperatures and contents of water and lower pressures increase H_2 yield.
- Higher H_2/CO_2 removal fractions increase H_2 yield.
- Higher water content in the feed inhibits coke formation.

GRAPHICAL ABSTRACT



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ABSTRACT

A thermodynamic analysis of the steam reforming reaction of olive oil mill wastewater (OMW) with in situ carbon dioxide (CO_2) and hydrogen (H_2) simultaneous removal was performed. The idea behind is the integration of the reformer with a H_2-selective membrane and a CO_2-sorbent in a hybrid multifunctional reactor. The simulations were performed at different temperatures (300–500 °C), pressures (1–11 bar), removal fractions of H_2 (0–0.8), removal fractions of CO_2 (0–0.99) and also for different water contents in the feed (20–92 wt.%). The results were compared in terms of performance reached for the different reactor configurations: traditional reactor (TR), membrane reactor (MR) with H_2 separation, sorption-enhanced reactor (SER) with CO_2 capture and sorption-enhanced membrane reactor (SEMR). For the SEMR, the optimum operation conditions were determined. An H_2 yield very close to the stoichiometric value of 13.54 was obtained at 1 bar, 500 °C, water content in the feed of 60–92 wt.% (steam-to-carbon feed ratio, SCFR = 2.1–16.0), fCO_2 = 0.99 and fH_2 = 0.80. The H_2 yield obtained in such optimum conditions corresponds to an enhancement of 141% comparatively to the TR. Moreover, under these operation conditions there is no significant production of CO_2, CO, CH_4 and coke.

1. Introduction

Nowadays, the olive oil industry is very important economically in some parts of the world, namely in Mediterranean countries, although it is a traditional industry. It is estimated that more than 9 million hectares of cultivated olive tree exists in this region [1]. Also, it is reported that 76% of the world's olive oil production is

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Nomenclature

List of Variables

fCO_2	Removal fraction of CO_2 (dimensionless)
fH_2	Removal fraction of H_2 (dimensionless)
G^T	Total Gibbs free energy (kJ)
$m_{i,k}$	Molar flow rate of species *i* in the permeate stream of sub-separator/sub-reformer *k* ($mol \cdot h^{-1}$)
n_i	Number of moles of component *i* in the system (mol)
k	Number of the sub-separator/sub-reformer
Y_i	Yield of species *i* (mol of *i* specie/ mol of OS)
$\Delta H_f^{0^\circ C}$	Enthalpy of formation at standard conditions ($kJ \cdot mol^{-1}$)
$\Delta H_r^{0^\circ C}$	Enthalpy of reaction at standard conditions ($kJ \cdot mol^{-1}$)
η_{SEMR}	Efficiency of the sorption-enhanced membrane reactor (dimensionless)
μ_i	Chemical potential of species *i* ($kJ \cdot mol^{-1}$)
v_i	Stoichiometric coefficient of species *i*

List of Acronyms

MR	Membrane reactor
OMW	Olive mill wastewater
OMWSR	Olive mill wastewater steam reforming
OS	Organic species
RWGS	Reverse water-gas shift
SCFR	Steam-to-carbon feed ratio
SEMR	Sorption-enhanced membrane reactor
SER	Sorption-enhanced reactor
TR	Traditional reactor
WGS	Water-gas shift

localized in Europe, with the Iberian Peninsula being the higher production zone (66% of Europe's total) [1,2]. However, there are other countries with significant olive oil production: Morocco, Tunisia, Syria and United States of America. In this way, it is observed that these countries are considerably affected by the pollution resulting from the olive oil mill wastewater (OMW), representing a major environmental problem, where large quantities of effluents are generated. This environmental concern is accentuated by the increase of the olive oil production [3].

The aqueous residues associated with this agro-industrial activity are generated using either the traditional pressing or the centrifugation systems (three- or two-phase systems); the OMW results from both the water contained in the olives (mainly) and the water used in the production process of the olive oil (especially with the centrifugation systems) [1,4]. It can been seen a big quotient between OMW and olive oil production in these processes [5]. It is estimated that 30 Mm^3 of OMW are produced per year worldwide [4].

The composition of OMW is highly variable, depending on several factors like the method of extracting the oil, the region of cultivation, the treatment of the tree, the maturation of the olive, and the weather conditions that the olive was subjected to in the ripening process [6]. OMW consists in liquid and solid matter. The liquid is mainly composed by water, polyphenols, sugars and fatty acids; the compounds most referenced are the following: vanillic acid, caffeic acid, tyrosol, *p*-coumaric acid, cinnamic acid, D-arabinose, D-galactose, D-galacturonic acid, syringe acid, gallic acid, protocatechuic acid, phenol, acetic acid, phenethyl alcohol, guaiacol and benzyl alcohol [1,4–20]. However, it is important to remark that more than 30 polyphenols and sugars have been detected in OMW [21].

The large amounts of OMW produced cause large environmental impacts because of the high values of chemical oxygen demand and biochemical oxygen demand present in such polluted streams [4,22–24]. Pollution from OWM was estimated to be 200 times higher than urban wastewater [1].

Therefore, it is necessary to use efficient technologies for the treatment of these wastes and to enable a sustainable use of resources. Although many different technologies have been attempted [3,9,25], such methods are not used due to economic and technical reasons. In this perspective, the possibility of valorizing such waste has been considered, namely through catalytic steam reforming of OMW (OMWSR). This technology would allow eliminating the organic species presents in the OMW stream while producing hydrogen (H_2), therefore providing added-value. This biofuel is environmentally attractive because it is renewable and reduces the emission of carbon dioxide – CO_2 cycle [26]. The OMWSR would help reducing the pollution level as well as to economically valorize a by-product of the olive oil sector without any value so far.

It was verified that the OMWSR is a thermodynamically viable process [27]. There are however several limitations when the OMWSR occurs in a traditional reactor: formation of large quantities of by-products (particularly CH_4 and coke) and the need of severe operation conditions (typically high temperatures). OMWSR has been also studied experimentally in both traditional [8] and membrane reactors [1], with the co-production of methane (CH_4) and carbon monoxide (CO), apart from H_2 and CO_2. This reaction is endothermic and limited by the equilibrium, thus requiring high operation temperatures. The selective removal of the reaction products (CO_2 and/or H_2) may therefore improve the H_2 yield and decrease both CH_4 and CO production.

To apply this technology with the simultaneous removal of both products, it is necessary to use a H_2-selective membrane (e.g. Pd-Ag) and a CO_2-selective sorbent (e.g. calcium oxide – CaO), that is a sorption-enhanced membrane reactor (SEMR) [28]. To operate in practice, this process would need two parallel reactors: while one of them is producing H_2, the other is being regenerated, i.e., CO_2 is being removed from the sorbent. Since the aim is to shift the thermodynamic equilibrium of OMWSR reaction by sorption of CO_2, once the sorbent gets saturated and CO_2 starts breaking through the column the process is finished in such a column. Then, the feed switches to for example an inert gas, or steam, so that the sorbent bed can be regenerated while the other reactor is now in the producing stage.

Thermodynamic analysis of steam reforming of oxygenates (e.g. ethanol and glycerol) in a traditional reactor [7,26,29–31] or in a membrane reactor [26,29,32] were already performed. The sorption-enhanced reaction concept via CO_2 sorption has also been investigated in previous studies [33–37]. However, only a very limited number of reports addresses the simultaneous removal of both products, and none was focused in the OMWSR.

In this study thermodynamic analysis of the OMWSR in a traditional reactor (TR), in a membrane reactor (MR), in a sorption-enhanced reactor (SER) and also in a SEMR is done for the first time. For this purpose, the effect of the temperature, pressure, content of water in the feed, removal fraction of CO_2 and/or H_2 was assessed. In a parallel way, the study of the coke formation at different conditions was also performed.