

# Hydrogen Production by Catalytic Conversion of Olive Mill Wastewater in Supercritical Water

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## Abstract

Hydrothermal gasification is considered to be a promising technology for the efficient conversion of wet biomass residues into fuel gas. Unlike conventional gasification methods, such as methane fermentation or thermal gasification, Supercritical Water Gasification (SCWG) produce a gas fuel, it does not require a previous drying process and it has many advantages from the energy, environmental and financial point of view.

This work is particularly valuable since it studies the use of real biomass residues; i.e. Olive Mill Wastewater (OMW) treated with both catalytic and non-catalytic SCWG to produce hydrogen. The increasing amount of OMW is becoming a serious environmental problem in olive oil-producing countries. SCWG process of OMW in a batch reactor at 530°C and 250 bar was studied, and the effect of the catalysts on the process was evaluated in terms of biomass conversion (COD removal), gases yields (H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and CO) and H<sub>2</sub> selectivity.

## Keywords

Hydrogen, Supercritical water gasification, Catalytic, Olive mill wastewater, Biomass waste

## 1. Introduction

Supercritical water gasification (SCWG) is considered a promising technology for the efficient conversion of wet biomass residues into fuel gas ( $H_2$  and  $CH_4$ ). This process has many advantages from the energy, environmental and economic point of view when compared to conventional processes. Unlike conventional gasification and pyrolysis, SCWG can achieve higher energy efficiency, especially for biomass with high organic matter content, since no drying process is required. Moreover, the reaction temperature of SCWG ( $600^\circ C$ ) is much lower than that in pyrolysis and conventional gasification (above  $1000^\circ C$ ) [1]. From the environmental point of view, SCWG does not generate  $NO_x$  and  $SO_x$  and other polluting gases, unlike fossil fuel combustion, pyrolysis and conventional gasification processes [1,2]. In addition, unlike anaerobic digestion, SCWG takes place in a much shorter residence time lapse [3], this contributes to elude environmental problems associated to waste storage and disposal. With regards to the economic aspects, SCWG is a cost-effective process. García-Jarana et al. [2] showed a study on sewage sludge in a 5 t/h capacity plant. In that study, it was concluded that the SCWG process is more profitable when compared to the production of hydrogen either through the reform of natural gas or through an electrolytic process, at least, when the revenues obtained through gas reforming amounted to more than  $211 \text{ €/t}_{\text{dry matter}}$  in the former process and when such revenues exceeded  $62 \text{ €/t}_{\text{dry matter}}$  in the latter. Therefore, SCWG can be an alternative to conventional processes.

Organic compounds can be treated by supercritical water (SCW) at high temperature and pressure, that is, above pure water's critical point,  $374^\circ C$  and 221 bar, respectively. However, when the objective is the conversion of organic feedstock into fuel gas by supercritical water, then, temperatures around  $500^\circ C$  (if a catalyst is used) or temperatures above  $600^\circ C$  (if a catalyst is not used) are necessary [4,5].

Olive Mill Wastewater (OMW) is a residue from the production of olive oil. It contains several elements: water from fruit and from fruit washing process, soft tissue from pulp and a very stable oil emulsion [6,7]. This type of wastewater presents high resistance to biodegradation and contains a wide variety of compounds such as polyphenols, polyols, organic acids, etc. that require depuration treatment to remove the odour and pollutants before being disposed.

It is estimated that oil extraction at Mediterranean countries generate around  $3 \times 10^7$  m<sup>3</sup> per year of that effluent. In addition, the number of small scale olive oil factories has increased significantly, especially in Andalucía (South of Spain). For this reason, the amount of OMW generated is becoming a serious environmental issue, since the conventional anaerobic digestion that is used at present cannot eliminate so much waste due to the long residence periods required. Both catalytic and non-catalytic supercritical water gasification processes can, therefore, become an alternative to the treatment of OMW and its conversion into fuel gas.

## **2. Materials and methods**

### **2.1. Materials**

Olive Mill Wastewater (OMW) was supplied by an olive oil industrial plant in Cordoba (Spain). OMW was used at two different organic compound concentrations: undiluted OMW with an approximate chemical oxygen demand concentration (COD) of  $30 \pm 2.67$  g O<sub>2</sub>/l; and diluted OMW, mixed with deionised water to a COD value of  $23 \pm 2.56$  g O<sub>2</sub>/l. The main characteristics of the OMW used for this work as total organic carbon concentration (COT), solid concentrations, pH and conductivity are shown in Table 1. In addition, the catalysts KOH, K<sub>2</sub>CO<sub>3</sub>, NaOH and Na<sub>2</sub>CO<sub>3</sub> were purchased from Panreac.

## 2.2. Equipment and procedures

A 47 ml reactor made of 316 stainless steel was built by the University of Cadiz (Figure 1). All of the experiments were carried out according to the same experimental procedure. In the first place, a known concentration and mass of OMW with an amount of catalyst were added into the reactor (see Table 2). Then, the reactor was purged with Helium (supplied by Linde) for 2 minutes in order to replace the air in the gas phase and then the system was closed. Later on, the reactor was introduced in a previously preheated fluidized sand bath (PID controlled at 550°C) and maintained in the bath for 20 minutes. The time lapse to reach 530°C and 250 bar inside the reactor was less than 3 minutes, as can be seen in Figure 2. The temperature and pressure inside the reactor increased at the same time. The total amount of liquid phase injected into the reactor was previously calculated to obtain a final pressure of around 250 bar when a temperature of 530°C was reached. When the reaction time was over, the reactor was removed from the sand bath and quickly submerged into water to stop the reaction. Then, by means of a specific device manufactured by our team (see Figure 3), the pressure inside the reactor was measured. In a first step, the helium bottle and valves (V1-V3) were opened to purge the system and remove the air. Subsequently, the helium bottle and valve (V1) were closed and valve (V2) was opened, to create a vacuum inside the system by means of a Millipore vacuum/pressure pump (4). Then, valve (V2) was closed to maintain the vacuum condition in the system. Finally, valve (V4) of the reactor (5) was opened and the pressure was measured by means of a U-shaped mercury pressure gauge (2). A syringe was used to take samples from the vial (3).

### 2.3. Analytical methods

The composition of the gas produced during the OMW degradation was analysed using an HP 6890 Series gas chromatograph with a Thermal Conductivity Detector (TCD) and Helium as carrier gas. Two in-series columns were used to separate the different gases obtained from the experiments. The first column separate H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> gases and the second one was used to separate CO from CO<sub>2</sub>. The system was calibrated by means of a standard mixture of these gases that was purchased from Linde (Spain).

Chemical Oxygen Demand (COD) and total solids were calculated following the standard methods for the examination of water and wastewater [8]. COD was analysed with a photometer PF-11 (MACHEREY-NAGEL) by closed reflux colorimetric method (5220D). While total solids were analyzed by the standard method (2540B), also known as *total solids dried at 103-105 °C*. pH and conductivity values were obtained using a pH-meter Basic 20+ Crison and a conductimeter Crison CM35, respectively.

### 2.4. Evaluation of the results

According to literature, many parameters can be used to evaluate SCWG processes. Some of them are gas yield, molar fraction of product gas, gasification efficiency and carbon gasification efficiency [9–13]. Gas yield (Y<sub>i</sub>) is the most important parameter for the evaluation of the SCWG process [13]. Therefore, the gas yield and the reduction of the COD concentration were calculated for the SCWG experiments according to the following equations (1-3).

$$\text{Gas yields (Y}_i\text{): } Y_i \left( \frac{\text{mol}}{\text{Kg}_{\text{sample dry}}} \right) = \frac{n_i}{m_{\text{sample dry}}} \quad (1)$$

$$\text{Percentage of COD reduction: COD removal(\%)} = \frac{COD_{in} - COD_{out}}{COD_{in}} \times 100 \quad (2)$$

$$\text{Hydrogen selectivity (SH}_2\text{): } S_{H_2} = \frac{n_{H_2}}{2n_{CH_4}} \quad (3)$$

Where  $n_i$  is mol of each individual gas and  $m_{sample\ dry}$  is the mass of the OMW sample on a dry basis.  $COD_{in}$  and  $COD_{out}$  represent the COD values of the initial feed and the final residue of the SCWO experiments, respectively. Moreover,  $n_{CH_4}$  and  $n_{H_2}$  is mol of methane and hydrogen respectively.

In each experiment, hydrogen ( $Y_{H_2}$ ), methane ( $Y_{CH_4}$ ), carbon dioxide ( $Y_{CO_2}$ ) and carbon monoxide ( $Y_{CO}$ ) yields have been calculated.

### 3. Results and Discussion

The hydrothermal gasification experiments have been carried out at around 530°C and 250 bar for an invariable reaction time interval of 20 min. Two different initial feed concentrations of the OMW, measure in terms of COD concentration, were studied and four alkali metal catalysts (KOH,  $K_2CO_3$ , NaOH and  $Na_2CO_3$ ) with several concentrations were used. As described in detail in Table 2, a total of 13 experiments were carried out. Some of them were performed in triplicate to establish the reproducibility of their results. A result confidence level of 95% was obtained from the triplicate experiments.

#### 3.1. Variations in hydrogen yield according to catalyst type and its concentration

To examine the effect of the type of catalyst and its concentration on  $H_2$  production by SCWG, a series of experiments have been performed with a low concentration of the homogeneous catalysts and the real concentration of the OMW, i.e. a COD value of  $30 \pm 2.67$  g  $O_2/l$  (Figure 4). Under the actual operating conditions studied, the  $H_2$  yield without catalyst was of 32.95 mol/kg  $OMW_{dry}$ , a much higher yield than any

results obtained by other authors [14–18] from other compounds or waste in supercritical water gasification processes. In the literature there is only one study of the gas yield for the SCWG of OMW without a catalyst and it was conducted by Kipçak et al. [7]. The maximum amount of gas obtained was 7.71 ml/ml OMW at 550°C and with a reaction time of 30 sec. The gas obtained contained 9.23% hydrogen, which is equivalent to producing 0.047 mol/kg<sub>OMW dry</sub>. This result obtained in the previous paper is less than the yield obtained in the present study, possibly due to the shorter reaction time used in that study.

If the economic aspects of the SCWG process is to be improved, the gasification efficiency level should be considered. Using a catalyst is a possible way to improve such efficiency, since it enables the production of hydrogen at a relatively lower temperature but within the range of a supercritical gasification process. Catalysts to be used for SCWG need to be different to the ones used for conventional gasification, since the particular operating conditions, such as the high pressure, the type of feedstock and the particular characteristics of the supercritical medium may affect the efficiency level of the catalyst [19]. Several authors claim that potassium additions may not influence the gasification yield [20–22]. According to that, similar results were obtained in the present work, since the experiments carried out with concentrations below 14 wt% of the different catalysts used (KOH, K<sub>2</sub>CO<sub>3</sub>, NaOH and Na<sub>2</sub>CO<sub>3</sub>) showed than no improvement in performance was obtained (Figure 4). Nevertheless, when the amount of catalyst was incremented to 41-58 wt%, an increase in hydrogen yield was achieved (Figure 5). In addition, hydroxide catalysts (NaOH and KOH) obtained a higher yield in hydrogen production than carbonate catalysts (Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>). The best hydrogen yield was obtained when using KOH catalyst (58 wt%) with 76.73 mol H<sub>2</sub>/kg<sub>OMW dry</sub>, followed by NaOH catalyst

(58 wt%) with 74.26 mol H<sub>2</sub>/kg<sub>OMW dry</sub>. For carbonate catalysts, using a 58 wt% concentration of both catalysts K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, 25.24 and 24.10 mol H<sub>2</sub>/kg<sub>OMW dry</sub> were obtained respectively. i.e., around a third of the yield. These results are promising for OMW residue, when compared with other studies in the literature in which the same catalysts are used with different residues or raw materials. Louw et al. obtained 7.47 mol H<sub>2</sub>/kg in a study with 10 wt% paper waste sludge (PWS) at 450°C, with a reaction time of 60 min and using 1g of K<sub>2</sub>CO<sub>3</sub> per gram of PWS [14]. Another work with the K<sub>2</sub>CO<sub>3</sub> catalyst (10 wt%) carried out by Madenoğlu et al. [23] to study a SCWG process with mannose (8 wt%) at 700°C and with 1 hour reaction time, obtained a yield of 57.39 mol H<sub>2</sub>/kg<sub>mannose</sub>. Some authors used KOH catalyst and/or catalysts with Na. Ding et al. [15] carried out a study with pinewood at 550°C with 30 minute reaction time and 0.42 g of KOH, the result was 5.55 mol H<sub>2</sub>/g<sub>feed</sub>. In another study, Guan et al. [24] obtained 8.2 and 5.5 mol/kg H<sub>2</sub> approximately, using algae with 1 g/g of NaOH and KOH as catalysts respectively, in 40 min reaction time at 450°C, with water density 0.09 g/cm<sup>3</sup> and 4.8 wt% load. Finally, Ge et al. [25] carried out some SCWG experiments with coal (5 wt%) at 700°C, with a 5 minute reaction time and NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and KOH as catalysts at 1/1 catalyst/coal ratio. Their respective yields were 37, 24, 38 and 39 mol H<sub>2</sub>/kg<sub>coal</sub>.

Moreover, the effect of different feedstock concentration levels has been studied. A fall in the concentration of the feedstock dry biomass is associate to a climb in H<sub>2</sub> production [26]. Similar results have been obtained by reducing the initial OMW concentration from 30 ± 2.67 g O<sub>2</sub>/l to 23 ± 2.56 g O<sub>2</sub>/l, where an increment in hydrogen yield of 3.21 mol/kg<sub>OMW dry</sub> was obtained. However, this fact does not necessarily imply that a dilution of the waste is better for supercritical gasification. An economic analysis of the whole process should be done. Such analysis should determine whether the increase



in the economic benefits of a higher hydrogen yield would compensate for the increase in the costs associated with a higher volume of waste to be treated.

### **3.2. Reduction of CO<sub>2</sub> and CO in the presence of a catalyst.**

Figure 6 shows the results of CO<sub>2</sub> and CO production from OMW processed by SCWG in the absence and in the presence of alkali metal catalysts (KOH, K<sub>2</sub>CO<sub>3</sub>, NaOH and Na<sub>2</sub>CO<sub>3</sub>). As can be seen from Figure 5, very low yields of carbon monoxide are obtained when a catalyst is used. This is because the main function of the catalyst is to improve the water-gas shift reaction [27]. A higher concentration of catalyst is related to a greater reduction of CO, where hydroxide catalysts are the ones that obtain the best results.

According to several authors, including a catalyst should result in an increment in both CO<sub>2</sub> and H<sub>2</sub> concentrations [28,29]. However, a decrease in the production of CO<sub>2</sub> is observed (Figure 5). The same result is reported by Yanik et al. [20] in a SCWG study on sunflower stalk with K<sub>2</sub>CO<sub>3</sub>, which concluded that the fall in CO<sub>2</sub> production might be associated to the dissolution of CO<sub>2</sub> in an aqueous medium that would form carbonate salts and/or carbonic acids.

### **3.3. H<sub>2</sub> selectivity and COD removal.**

Experimental results from Hydrogen selectivity (SH<sub>2</sub>) and Chemical Oxygen Demand removal (COD removal) are shown in Table 2. Experiments were carried out with a low concentration alkali metal catalyst and with a real COD from OMW at 30 ± 2.67 g O<sub>2</sub>/l, where a drop in SH<sub>2</sub> was observed. This fall in hydrogen selectivity might be associated to a reduction in the water gas shift reaction greater than the reduction in the methanation. However, there is an increment in SH<sub>2</sub> when the COD concentration of

OMW was reduced to  $23 \pm 2.56$  g O<sub>2</sub>/l and increase the concentration of the catalysts used. This is due to an increment in the difference between two competitive reactions: water gas shift and methanation.

COD removal in all the experiments completed has also been studied (Table 2). The percentage of COD removal was in the range 75-89 % for almost all of the experiments. This is a much higher result than those obtained by García Jarana et al. [29] with SCWG on cutting oil waste and vinasses. In addition, it should be noted that a higher COD removal has been obtained by means of carbonate catalysts.

#### **4. Conclusions**

This study has successfully studied the gasification of olive mill waste by catalytic supercritical water processes. The effect of different alkali metal catalyst types at different concentrations has been tested. The tests proved that low concentrations of alkali metal catalysts did not increase hydrogen yield, but also that an increment in catalyst concentration would improve hydrogen yield. In addition, it should be noted that hydroxide catalysts obtained a higher hydrogen yield than carbonate catalysts. The most favourable experimental condition was at 530°C temperature, 230 bar pressure, 20 minute reaction time, with 58 wt% of KOH and  $23 \pm 2.56$  g O<sub>2</sub>/l initial COD from OMW, which would obtain 76.73 mol H<sub>2</sub>/kg<sub>OMW dry</sub>. A higher concentration of catalyst is related to a greater reduction of CO, where hydroxide catalysts are the ones to obtain the best results. Furthermore, a decrease in the production of CO<sub>2</sub> was observed that might be associated to a dissolution of CO<sub>2</sub> in water to form carbonate salts and/or carbonic acids.

On the other hand, it has been proved that OMW initial COD and the concentration level of homogeneous alkali metal catalysts may affect hydrogen selectivity. SCWG is considered a promising technology for the removal of COD from OMW. The percentage

of COD removal was 75-89 % in almost all the experiments. Moreover, carbonate catalysts obtained the highest percentage of COD elimination.

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Figure Legend:

- Figure 1: Batch reactor and sand bath schematic diagram.
- Figure 2: Heating curve.
- Figure 3: Scheme of the system to measure pressure inside the reactor. (1) Helium bottle. (2) U-shaped mercury pressure gauge. (3) Ampoule to take gases samples by means of a syringe. (4) Vacuum/Pressure Pump. (5) Reactor. (V1-V3) valves. (V4) Needle valve.
- Figure 4: H<sub>2</sub> Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of  $30 \pm 2.67$  g O<sub>2</sub>/l.
- Figure 5: H<sub>2</sub> Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of  $23 \pm 2.56$  g O<sub>2</sub>/l.
- Figure 6: CO<sub>2</sub> and CO Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of  $23 \pm 2.56$  g O<sub>2</sub>/l.

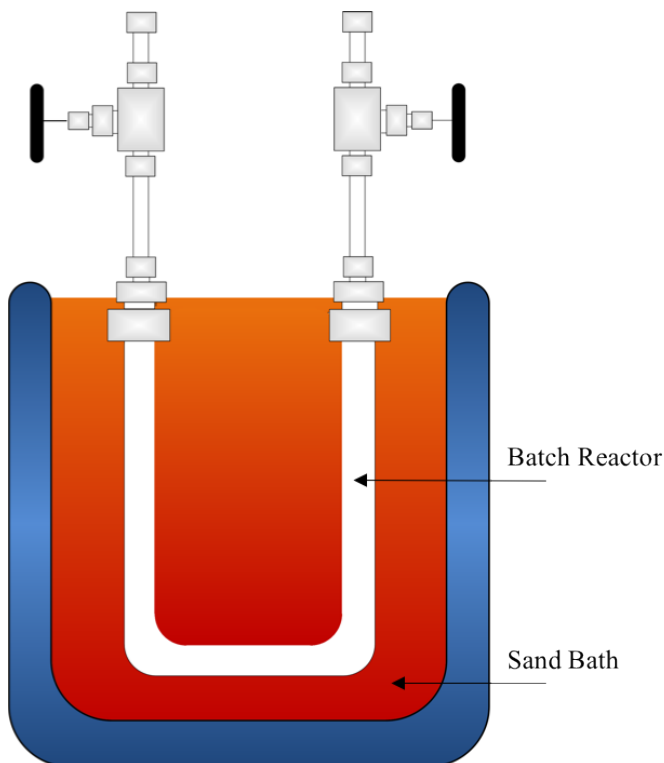


Fig.1. Batch reactor and sand bath schematic diagram.



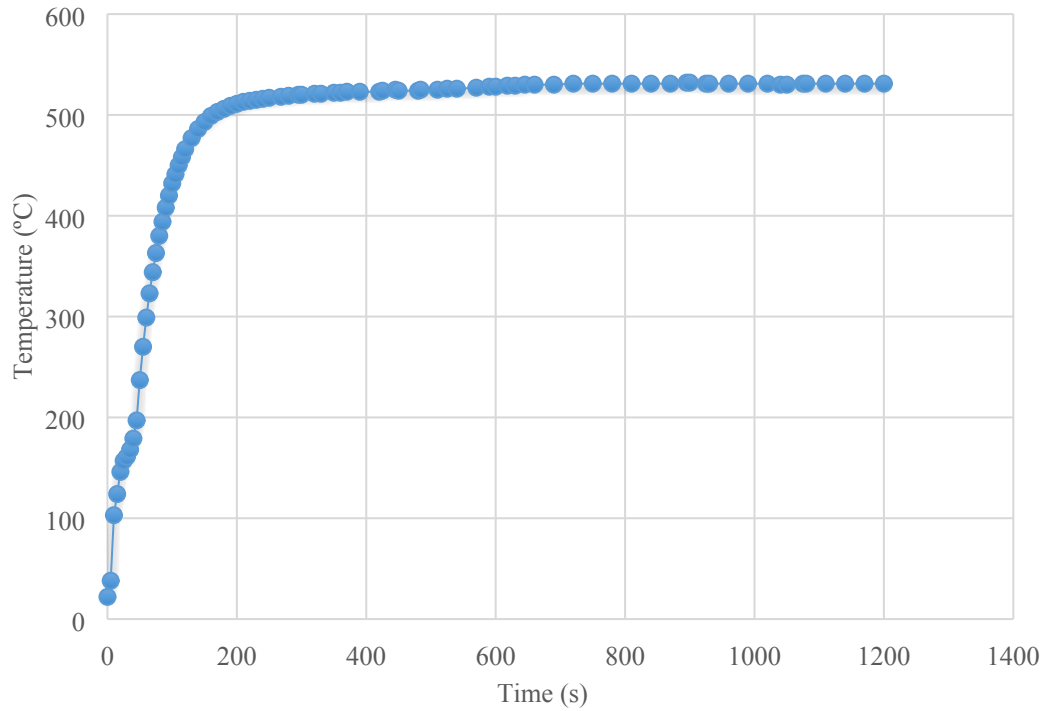


Fig. 2. Heating curve

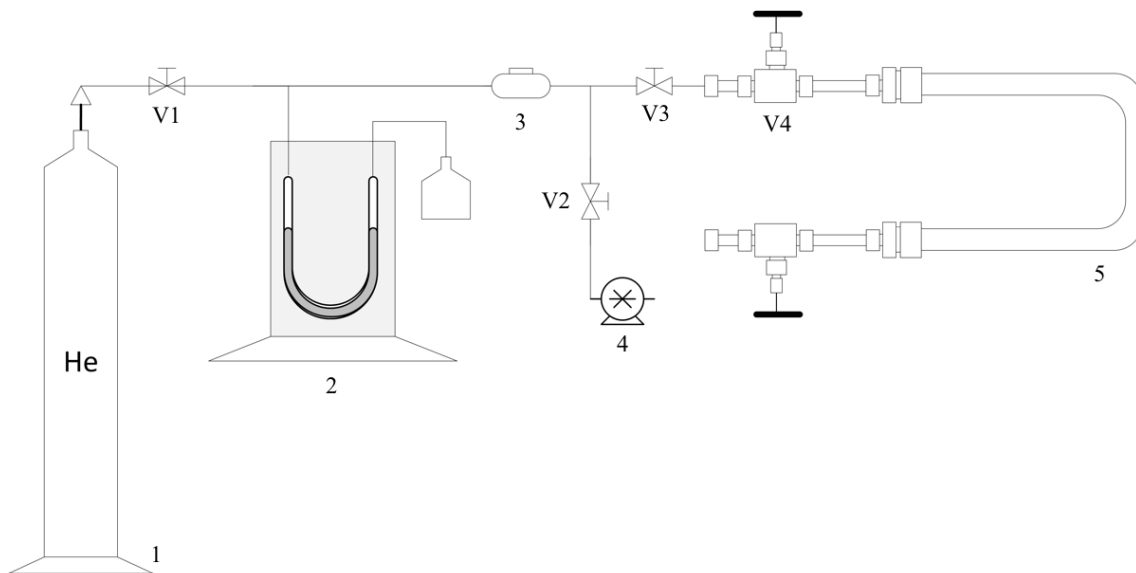


Fig. 3. Scheme of the system to measure pressure inside the reactor. (1) Helium bottle. (2) U-shaped mercury pressure gauge. (3) Ampoule to take gases samples by means of a syringe. (4) Vacuum/Pressure Pump. (5) Reactor. (V1-V3) valves. (V4) Needle valve.

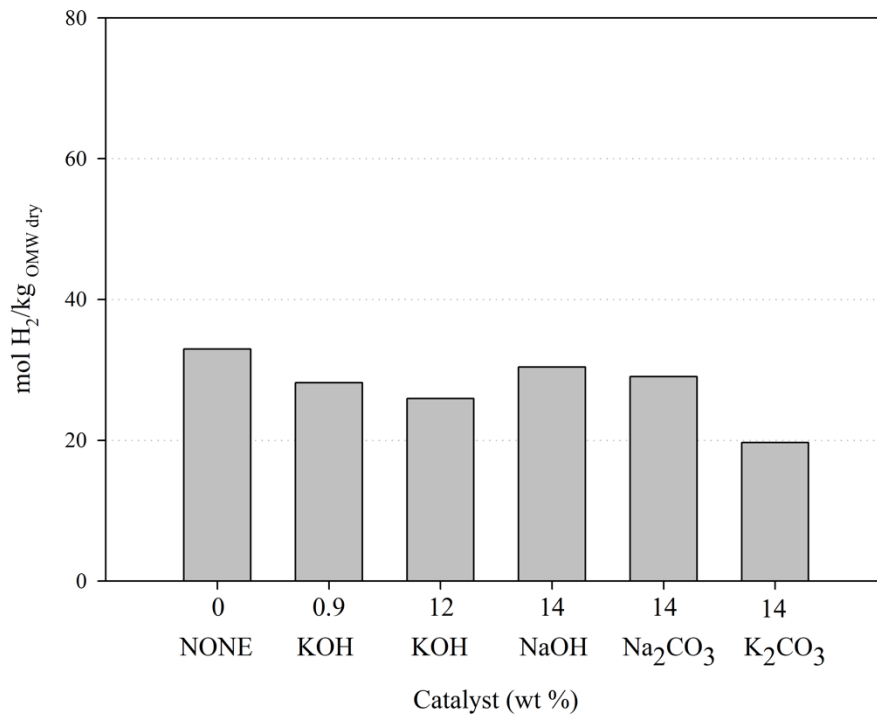


Fig. 4. H<sub>2</sub> Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of  $30 \pm 2.67$  g O<sub>2</sub>/l.

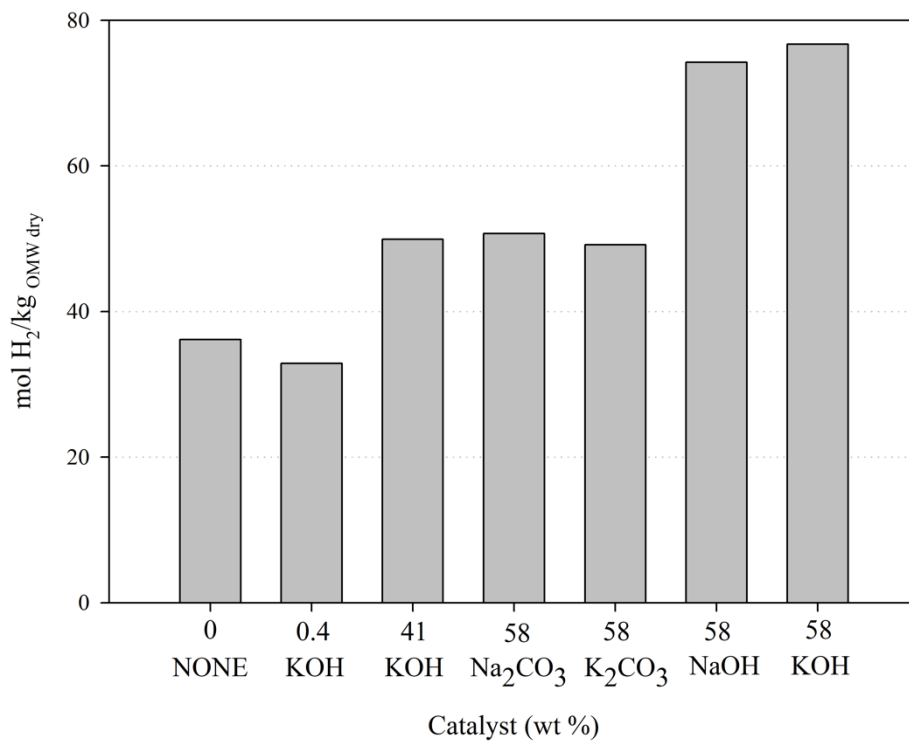


Fig. 5. H<sub>2</sub> Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of  $23 \pm 2.56$  g O<sub>2</sub>/l

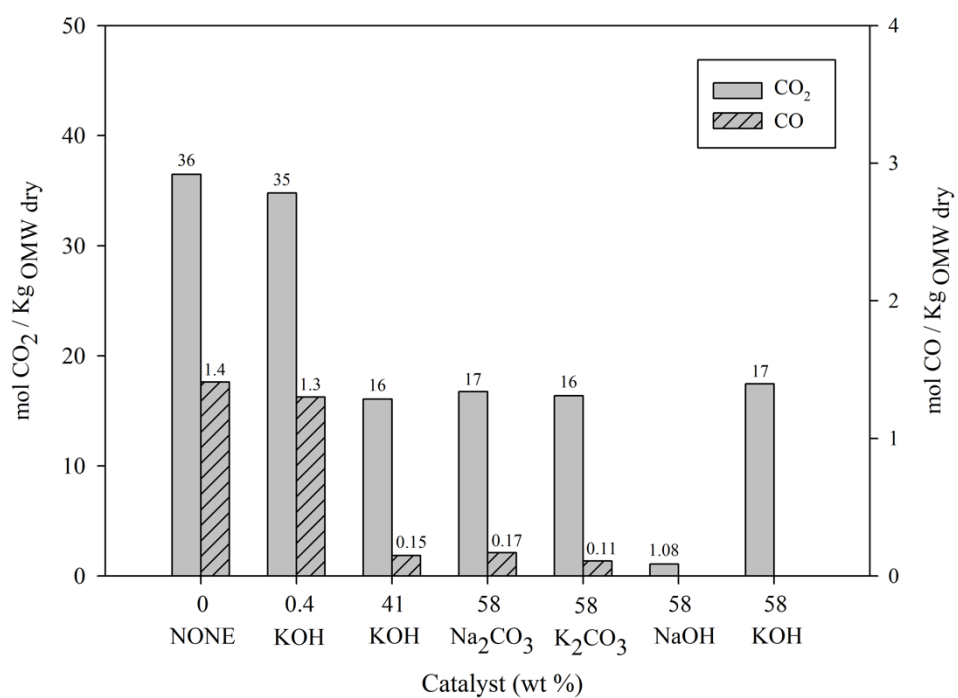


Fig. 6. CO<sub>2</sub> and CO Yield (mol/kg OMW dry) with different catalysts concentrations and an initial COD value of 23± 2.56 g O<sub>2</sub>/l.

Table legend:

- Table 1: The characteristics of the olive mill wastewater.
- Table 2: Experimental conditions and results.

**Table 1**

The characteristics of the olive mill wastewater.

Parameters	Value
Chemical Oxygen Demand. COD (g O <sub>2</sub> /L)	32.5
Total Organic Carbon. TOC (ppm)	6314
pH	5.66
Solids Concentration (g/L)	7.43
Conductivity (mS/cm)	1.7

**Table 2**  
Experimental conditions and results.

Temperature (°C)	Pressure (bar)	Reaction time (min)	Catalyst	Catalyst concentration (wt %)	COD <sub>0</sub> (g O <sub>2</sub> /L)	Gas Yield (mol/kg <sub>OMW dry</sub> )				Hydrogen selectivity (SH <sub>2</sub> ) (mol H <sub>2</sub> /mol CH <sub>4</sub> )	COD removal (%)
						H <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	CO		
539	258	20	NONE	0	32.02	32.95	32.48	10.98	0.74	5.20	84.33
526	252	20	KOH	0.9	34.89	28.19	32.71	7.71	0.64	3.24	82.27
542	259	20	KOH	12	29.81	25.91	18.54	6.87	0.21	4.96	85.85
529	255	20	NaOH	14	27.60	30.41	25.41	12.33	0.50	4.03	77.47
529	256	20	Na <sub>2</sub> CO <sub>3</sub>	14	28.77	29.06	15.72	4.52	0.47	3.97	81.11
529	253	20	K <sub>2</sub> CO <sub>3</sub>	14	28.95	19.68	17.07	5.32	0.35	3.32	84.87
538	259	20	NONE	0	23.60	36.16	36.48	14.24	1.41	2.58	75.75
530	250	20	KOH	0.4	23.60	32.87	34.79	11.12	1.30	3.16	77.62
542	260	20	KOH	41	25.31	49.92	16.06	12.38	0.15	4.03	77.47
544	264	20	Na <sub>2</sub> CO <sub>3</sub>	58	24.10	50.72	16.74	12.76	0.17	3.70	89.14
544	264	20	K <sub>2</sub> CO <sub>3</sub>	58	25.24	49.19	16.37	14.84	0.11	2.47	85.32
530	256	20	NaOH	58	18.41	74.26	1.08	22.95	0.00	6.42	66.97
530	256	20	KOH	58	20.55	76.73	17.47	15.09	0.00	3.66	84.63