

Energy Production by Hydrothermal Treatment of Liquid and Solid Waste from Industrial Olive Oil Production

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Abstract: This work studies the use of olive oil mill waste (OMW) treated as subcritical or supercritical water to produce both, a biofuel by liquefaction and a gas fuel by gasification. The increasing amount of OMW, both liquid and solid, is becoming a serious environmental problem. This wastewater is highly resistant to biodegradation and contains a wide variety of compounds such as polyphenols, polyols, organic acids, etc, that require depuration treatments to remove the odour and pollutant load before being discharged.

This work studies both, liquefaction and gasification of OMW streams in subcritical and supercritical water in different batch reactors at temperatures between 200 and 530 °C and pressures between 150 and 250 bar. This study also tests the effectiveness of various types of homogeneous (KOH 0.01 g/g_{sample dry}) and heterogeneous catalysts (TiO₂, V₂O₅ and Au-Pd 0.1-0.5 g/g_{sample dry}) for supercritical water gasification (SCWG) and studied the way they affect biomass conversion yields. It also covers the effect that the use of different organic compound concentrations (23, 35, and 80 g O₂/l of chemical oxygen demand concentration (COD)) and compositions (mixtures of solid and liquid OMW) has on energy production results. A maximum of 82% oil yield was obtained from the hydrothermal liquefaction of OMW under optimum conditions (330 °C, 150 bar, 23 g O₂/l as initial concentration and 30 minutes reaction time). Meanwhile, a yield of 88.6 mol H₂/kg_{OMW dry} was obtained when Au-Pd was used as a catalyst for the gasification of OMW supercritical water.

Keywords: Gasification, liquefaction, supercritical water, subcritical water, olive mill wastewater, biofuel, gas fuel.

I. INTRODUCTION

Biomass as a source of energy has a growing interest to reduce both CO₂ emissions and consumption of fossil energy. The conventional processes of pyrolysis, gasification and combustion are thermochemical processes suitable for dry biomass with a water content below 10 wt%. For wet biomass, a previous drying process is required. In the case of wet biomass, such as sewage sludge, cattle manure or food industry waste, which often have a water content over 80 wt%, anaerobic digestion processes are applied successfully. Nevertheless, anaerobic digestion presents some disadvantages, such as a slow rate reaction as well as long typical residence times in the range of 2-4 weeks. Furthermore, fermentation sludge and wastewater obtained from the reactors must be further treated. Therefore, hydrothermal processes have attracted worldwide attention because of the fascinating characteristics of water as a reaction medium under high temperature and pressure conditions [1]. Both hydrothermal liquefaction (HTL)

and supercritical water gasification (SCWG) stand out among other hydrothermal processes. They take place without dissolved oxygen. Moreover, these procedures can be applied without any previous drying processes and, what is more, they present a faster reaction rate of just a few minutes. Water near or above its critical point (T_c = 374 °C and P_c = 221 bar) presents many advantages when used as a reaction media. Under subcritical conditions (water near its critical point), the ionic medium may encourage the formation during the liquid phase of furfurals and phenols, that generate highly valuable products for biofuel production. At supercritical conditions, water becomes completely miscible with non-polar compounds and gases [2]. Hence, the reaction that occurs at SCW environments provides the opportunity to conduct the reaction in a single fluid phase i.e. without any interphase mass transport processes. Furthermore, water density is much lower than that at subcritical conditions, and therefore, it inhibits ionic reactions while facilitates free-radical reactions. Both of these conditions are necessary to form gases such as H₂ or CH₄ which are suitable for gasification reactions.

Several studies have been carried out to produce a high-energy dense liquid from wet biomass by means of hydrothermal liquefaction (HTL) [3-5]. HTL is

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generally carried out in a range of temperatures between 250 and 400 °C and under pressure between 100 and 300 bar. At subcritical conditions water is still in a liquid state and the macromolecules in the biomass are subjected to many degradation and condensation pathways. Several products are obtained, including liquid fuel, called "biocrude" or "bio-oil" with a relatively high heating value that reaches up to 35-40 MJ/kg, a solid residue called "char", water-soluble substances and a CO₂-rich gas [6]. One of the advantages of this process is that the biocrude oil produced by liquefaction is not miscible with water and has lower oxygen content. Therefore, this biocrude presents higher energy contents than pyrolysis-derived oils [7]. Many studies report HTL applied to algae [3, 8-12], forestry and agricultural wastes [13-17], municipal wastes [18-20], manure [12, 21-23], sewage sludge [24-27], and food processing residues [28-32]. Most of these studies have been carried out at batch reactors. The properties and yield of bio-oils depend both on the initial feed (composition and the structure of the biomass) and on operating conditions (mainly temperature and residence time). Generally, with most feed studied, temperatures under 300 °C produced an incomplete depolymerisation. Therefore, a temperature of 300 °C or slightly higher leads to a complete depolymerisation and then, the fragmentations and condensations that produce the typical compounds generally found in the oil phase (heavy hydrophobic compounds). Meanwhile, higher temperatures as well as longer reaction times allow a higher production of solid residue and gas, while oil yield goes down.

On the other hand, supercritical water gasification process (SCWG) is an alternative for the conversion of wet biomass to both, conventional gasification and anaerobic digestion processes. Since, in the case of SCWG, biomass does not need to be dried, costs are reduced. Residence times are also shorter; no more than a few minutes [33, 34]. Therefore, SCWG is a promising technology for the efficient conversion of wet biomass into a gas product that should have great heating power thanks to its high content in hydrogen and light hydrocarbons. Moreover, this gas, after upgrading, can be used as a substitute for natural gas. The composition of the gas obtained depends on the feed used and the operating conditions. If hydrogen is the target product to be obtained, temperatures near 600 °C are required for thermodynamic reasons. Under these conditions, biomass reacts with water, and this leads to a large hydrogen production.

Olive mill waste (*OMW*) is the residue obtained from olive processing plants, which are very common in Mediterranean countries such as Spain. Regular annual *OMW* production is estimated around 10 to 30 million m³. Production levels may vary depending on olive oil extraction method, cultivation soil, use of pesticides and fertilizers, olive harvesting time, degree of ripening, duration of aging, olive variety and weather conditions [35, 36]. Typical *OMW* composition by weight is 83-96% water, 3.5-15% organic compounds and 0.5-2% mineral salts. Such composition comes from olive fruit water content, from the water used to wash and process the olives, the soft tissues from the olive pulp and from a very stable oil emulsion. The polyphenol contents of the organic fraction are responsible for several biological effects, since phenolic compounds of low molecular weight show toxicity that affect seed germination, aquatic organisms and bacteria. Waste appears in two phases: olive mill solid waste (*OMWS*) and liquid effluents (Olive Mill Wastewater, *OMWW*). These two types of *OMW* have a different organic compound concentration: the liquid phase (*OMWW*) has an approximate chemical oxygen demand concentration (COD) of 30 g O₂/l, and the solid phase (*OMWS*) has a COD of 200 g O₂/l, therefore the latter one is highly pollutant. In addition, the COD value for *OMWS* can be around 200-400 times higher than those of typical municipal sewage [36]. While these values are generally an important disadvantage for conventional treatments, it becomes an advantage when processed by SCWG, where high efficiency is correlated with high organic concentrations. Besides, a mixture of *OMWW* and *OMWS* can be used to obtain the ideal concentration and water content to apply SCWG processes [37]. However, only Kipçak *et al.*, 2011 [36], studied non catalytic gasification of *OMWW* in supercritical water. On the other hand, HTL of *OMWW* has been recently studied by Handhoum *et al.*, 2016 [38] a maximum production of bio-oil of 58 wt% at 280 °C was reported.

In this study, two hydrothermal treatments (HTL and SCWG) have been applied to *OMW* with the main purpose of studying the different products formed during those processes and to determine the best conditions to produce gas or liquid fuel. On the other hand, the experiments have also been carried out with cellulose as a model compound in order to enable a comparison between the results obtained from cellulose and from *OMW*. Furthermore, different concentrations of *OMWW* and a mixture of both types of *OMW* (solid and liquid) have been prepared to study

the effect of different feed concentrations on these processes.

Furthermore, this work includes the study of the effect of several kinds of catalysts [39, 40] on the treatment of biomass by SCWG, since the effect of homogeneous and heterogeneous catalysts on *OMW* treatment by SCWG had not been previously studied. Therefore, this study analyses the effect of KOH (homogeneous catalyst) and V_2O_5 , TiO_2 and Au-Pd (heterogeneous catalysts) on the treatment of *OMW* by SCWG.

II. EXPERIMENTAL

Materials

In this study, the experiments were carried out with Olive Mill Waste (*OMW*) as a real wastewater with 21% cellulose content as well as with cellulose as a model compound. In this way, the *OMW* used for the experiments was the by-product obtained from an olive oil production plant in Cordoba (Spain). Microcrystalline cellulose powder was purchased from Merck, while TiO_2 and V_2O_5 were purchased from Panreac. On the other hand, Au-Pd was synthesized at the University of Cadiz own laboratories.

OMW has been prepared at different organic compound concentration levels: undiluted *OMW* at an approximate COD of 35 g O_2/l . *OMW* was diluted to a COD of 21-23 g O_2/l (named *diluted OMW*). In addition, a cellulose aqueous dilution was prepared to the same COD as *diluted OMW* to allow their comparison. *OMW* and *OMWS* were mixed to obtain a new dilution with a COD of 80 g O_2/l .

Equipment and Procedures

The tests were carried out in three different batch reactors. The first batch reactor (Figure 1a) was made of 316 stainless steel; 300 ml autoclave manufactured by Autoclave Engineers. This equipment was used to carry out liquefaction experiments with subcritical water, since it only reaches 330 °C and 200 bar simultaneously. This apparatus is fitted with a variable speed "Magnedrive" stirrer and an electric furnace. The temperature controller (PID) maintained the temperature within ± 2 °C of the set point. The gas inlet, pressure gauge and safety head port are on the top head.

The second reactor was used to carry out liquefaction experiments under supercritical conditions

and reached a temperature of 525 °C and a pressure of 240 bar simultaneously. This reactor (Figure 1b) is similar to the previous one, but it is a 1000 ml batch reactor manufactured by Parr Instrument Company. As a homogenous phase is obtained in this reactor at supercritical condition, this instrument does not need propeller. The main sections in the equipment were connected to a data acquisition unit controlled by the ParrCom application.

The same experiment procedures were applied to both reactors as follows: first, the reaction vessel was loaded with the desired amount of feed and closed. Then, the reactors were purged with N_2 to replace oxygen in gas phase, so there would be no oxidant in the reactor. Then, an initial N_2 pressure was set inside the reactor. The reaction vessels were then heated by means of an external heater to the desired temperature and that temperature was measured by means of a thermocouple. The time required to reach the desired temperature in both equipment was around one hour. After the reaction was completed, the reactors were cooled down to room temperature. The gas obtained was sampled and analysed in a gas chromatographer. Then, the autoclaves were dismantled, and the reaction mixture was recuperated for separation.

On the other hand, SCWG tests were carried out in a small reactor of 47 ml volume (Figure 2). A known mass of the sample and catalyst with a desired load were added to the reactor. Later, the reactors were purged with Helium and closed. This reactor was introduced in a sand bath during 10 and 20 minutes. In this case, the time required reaching 530 °C and 250 bar of temperature and pressure respectively was less than 3 minutes.

Separation and Extraction Procedure

The solid and liquid products obtained from HTL experiments were rinsed off the autoclave by means of acetone. The resulted suspension was filtered through a pre-weighed filter paper under vacuum conditions. The solid filtrate on the filter paper was dried for 24 hours in an oven at 105 °C before weighing according to the Standard Methods for the determination of solids [41]. This solid was defined as solid residue. The filtrate was evaporated under reduced pressure at 50 °C to remove the solvent (acetone) and 90 °C to remove water. The liquid product obtained was defined as oil. Oil and char yields are expressed in wt% of the dry organic matter.

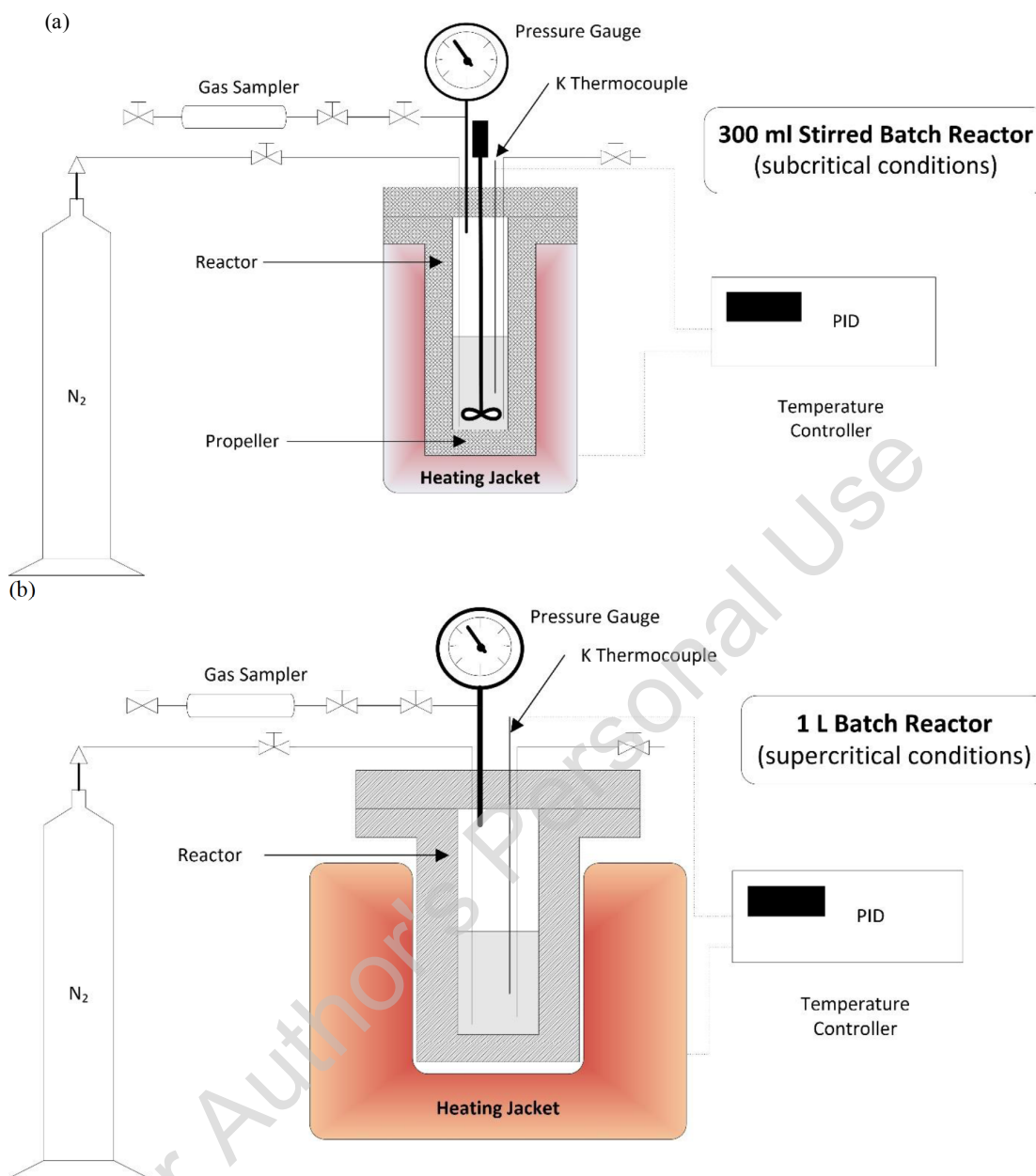


Figure 1: Schematic diagram of the stirred batch reactor used for liquefaction experiments at subcritical conditions (a) and schematic diagram of the autoclave used at supercritical conditions (b).

Analytical Methods

Gas samples were analysed using an HP 6890 Series gas chromatograph with a Thermal Conductivity Detector (TCD). Two in-series columns were used to separate H_2 , O_2 , N_2 , CO_2 , and CH_4 gases where the second one was used to separate CO from CO_2 . The system was calibrated by means of a standard mixture of these gases.

COD determination was carried out by the Standard Methods for the examination of water and wastewater [41].

Evaluation of the Results

In order to establish the mass balance in HTL experiments, the yields of the different products were determined by the following formulae:

$$\text{Oil yield (\%)} = \frac{W_{oil}}{W_{sample\ dry}} \times 100 \quad (1)$$

$$\text{SR yield (\%)} = \frac{W_{solid\ residue}}{W_{sample\ dry}} \times 100 \quad (2)$$

$$\text{Gas yield (\%)} = \frac{W_{gas}}{W_{sample\ dry}} \times 100 \quad (3)$$

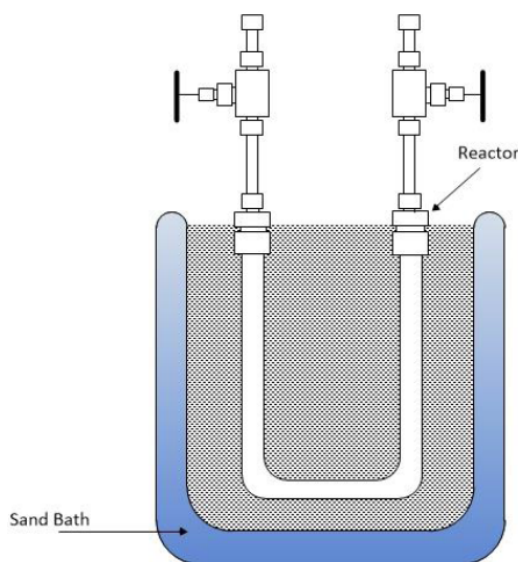


Figure 2: Batch reactor and sand bath schematic diagram.

where W_{oil} , $W_{solid\ residue}$ and W_{gas} are the masses of oil, solid residue, and gas respectively. $W_{sample\ dry}$ is the mass of the sample on a dry basis. Moreover, the aqueous organic products and water were included together as WSP and their yield was calculated as follows:

$$WSP\ yield\ (\%) = 100\% - (Oli\ yield + SR\ yield + Gas\ yield) \quad (4)$$

On the other hand, the results from SCWG experiments were evaluated as follows:

$$Gas\ yields\ (Y_i): Y_i \left(\frac{mol}{Kg\ sample\ dry} \right) = \frac{n_i}{m_{sample\ dry}} \quad (5)$$

$$Hydrogen\ efficiency\ (HE): Y_i\ (\%) = \frac{4n_{CH_4} + 2n_{H_2}}{n_{H, sample\ dry}} \times 100 \quad (6)$$

$$Hydrogen\ selectivity\ (S_{H_2}): S_{H_2} = \frac{n_{H_2}}{2n_{CH_4}} \quad (7)$$

where n_i is mol of each individual gas, being n_{CH_4} and n_{H_2} is mol of methane and hydrogen respectively. Moreover, $m_{sample\ dry}$ is the mass of the sample on a dry basis and $n_{H, sample}$ is mol of hydrogen from sample.

III. RESULTS AND DISCUSSION

Different tests for the liquefaction and gasification of Olive Mill Waste (OMW) stream have been carried out in subcritical and supercritical water at temperatures between 200 and 530 °C and pressures between 150 and 250 bar. In addition, different organic compound concentrations of OMW have been studied: OMWW, diluted OMWW and OMW mixture.

III.I. Effect of Variable Operating Conditions on Hydrothermal Biomass Liquefaction

Operating conditions such as temperature or reaction time may have an effect on the many competitive reaction pathways which can be produced in the liquefaction process [42]. Generally, temperature promotes biomass fragmentations, which increases the yield of liquids. Hydrolysis, fragmentation and repolymerization reactions have a specific extension depending on the temperature during the process. Initially, depolymerization of biomass is a dominant reaction. Later in the process, repolymerization reactions become more active and this leads to the formation of char. When temperature reaches 330-350 °C, the gasification is enhanced and some oily products can be decomposed. Therefore, in general, higher amounts of oil are produced at an intermediate temperature range (250–330 °C) [43-45]. However, the optimum temperature for oil yield depends on the kind of biomass. Therefore, a study on the effect of HTL operating conditions on actual waste should be carried out.

a) Effect of Temperature

The effect of temperature on the oil yields of solid residue, gas, and liquid (aqueous organic products + water) was investigated for a range of temperatures between 200 and 330 °C. Other conditions remained invariable i.e. 60 minutes reaction time and 150 bar pressure (under this pressure the reaction always takes place in a liquid water phase). All the tests were carried out with olive mill wastewater diluted to 23 g O₂/l COD (dilute OMWW). The data obtained are shown in Figure 3. It can be seen that the oil yield increased as temperature went up (from 200 to 330 °C) and reached a maximum value of 80.3 wt% at 330 °C. At the same time, as temperature increased, solid residue went down from 5.87 to 2.25 wt%. The gas yield increased with temperature increment, while the WSP yield decreased as temperature rose. Similar effect was obtained in a previous study where bagasse liquefaction yielded [14] a maximum of 59% of oil at 330 °C (the highest temperature studied). In another previous study, HTL of secondary pulp/paper-mill sludge and waste newspaper [46] showed an increment of both, oil and WPS yields as temperature went up from 250 to 350 °C, while SR yield dropped accordingly. Zhou *et al.*, 2010 [47] also obtained an increment of oil yield (9.6 to 20.4 wt%) within the 220-300 °C temperature range, while there was a reduction of oil yield at 320 °C when HTL was applied to macroalgae. Handhoun *et al.*, 2016 [38] also studied

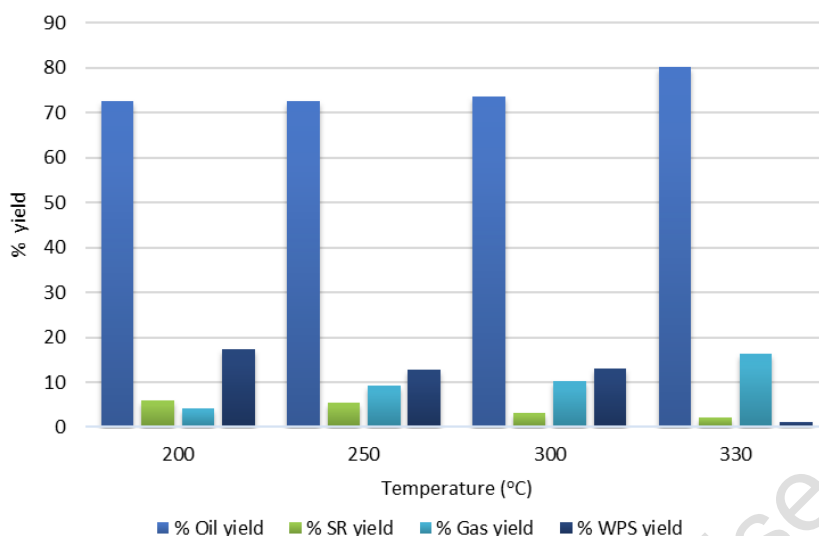


Figure 3: Effect of temperature on *diluted OMWW* liquefaction for 60 minute reaction time, under 150 bar and using a stirred batch reactor.

OMWW and obtained an increment of oil production as temperature climbed to 280 °C and then, a reduction when temperature reached 300 °C. The differences, when compared to the data obtained in the present study, could be due to the use of a stirred batch reactor, where the reaction occurs in a homogeneous medium, and also to the fact of using a higher water content.

b) Effect of Reaction Time

The experiments with *diluted OMWW* liquefaction were carried out in a stirred batch reactor at 330 °C and 150 bar and with two different reaction times: 30 and 60 minutes. The results obtained are shown in Figure 4. As can be seen, similar results were obtained from both reaction times. Thus, it is not necessary to apply longer reaction times, since there are no significant differences. Moreover, an optimum reaction time of 30 minutes for hydrothermal liquefaction of *E. Prolifera* (macroalgae) is presented by Zhou *et al.*, 2010 [47].

c) Effect of Initial Concentration

Different liquefaction tests were carried out with different initial organic concentration and composition at subcritical conditions (330 °C and 150 bar) and at supercritical conditions (400 °C and 250 bar) with 30 minutes reaction time. In both cases, under subcritical and supercritical conditions, the samples of *OMWW* were studied with and without dilution (named *diluted OMWW* and *OMWW*, respectively). The concentration's COD of the *diluted OMWW* was 23 g O₂/l, while *OMWW* had a concentration with a COD of

35 g O₂/l. In addition, olive mill wastewater was mixed with olive mill solid waste (COD = 200 g O₂/l) to obtain the sample named *OMW mixture* with a COD of 80 g O₂/l. The results obtained from these experiments can be seen in Figure 5. In general, when higher initial concentration is used, lower oil yield is obtained, while there is an increment in the solid residue in both situations, subcritical and supercritical conditions. Similar results were obtained from the previous study where HTL was applied to *OMWW* [38] and water content was reduced. These authors suggested that a lower water content with a higher biomass concentration enhances the secondary reactions and produces higher SR yields and lower oil yields. In the present study, the best results were obtained at

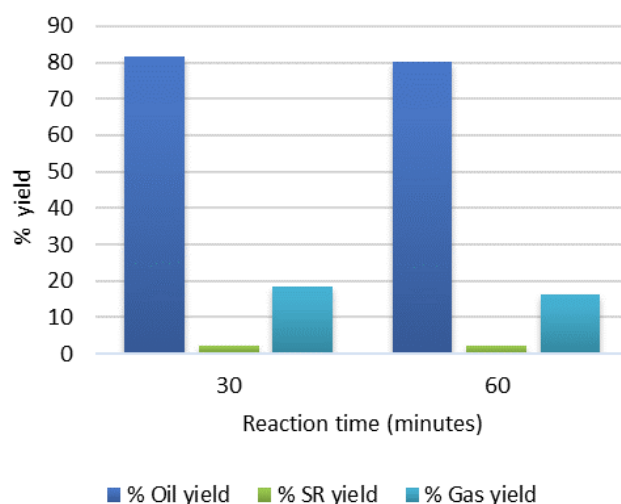


Figure 4: Effect of reaction time on *diluted OMWW* liquefaction in the stirred batch reactor at 330 °C and 150 bar.

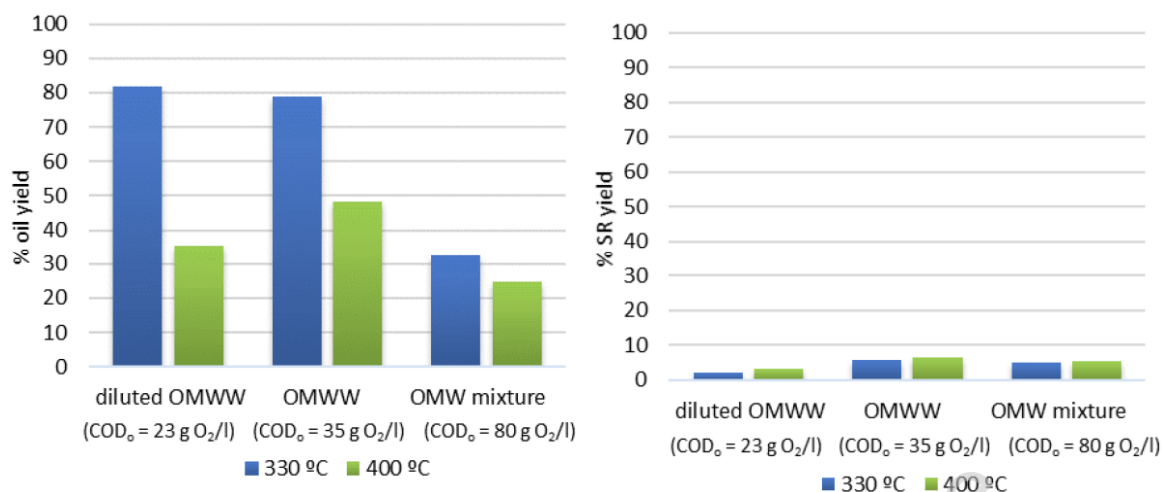


Figure 5: Effect of the initial concentration on OMW liquefaction at 330 and 400 °C for 30 minutes reaction time.

subcritical conditions, where 81.8 wt% of oil yield was obtained when OMWW was used. This is a higher value than the results presented in the previous paper, and this may be caused by a higher water content (98%) of the OMWW studied compared to the water content (88%) used by Handhoum *et al.*, 2016 [38]. Moreover, as previously mentioned, a stirred batch reactor was used in the present study for subcritical conditions.

In the present study, the treatment of OMW by HTL produced its best results at 330 °C, 150 bar and with an initial COD of 23 g/l. Under these conditions, SR yield was the lowest and oil production was 81.8 wt%. Moreover, a reaction time of 30 minutes was enough to liquefy the OMWW.

III.2. Supercritical Water Gasification Experiments

According to literature [48], all of the organic molecules are not transformed into hydrogen or carbon dioxide in the case of real wastewaters. As a result, tar and char can be formed during supercritical water gasification processes. Therefore, this char and tar sedimentation usually plugs the reactor after several hours running. Moreover, they limit the amount of hydrogen that can be formed. The amount of these materials can be effectively reduced by the use of a catalyst in the SCWG process. Different catalysts (homogeneous and heterogeneous) have been studied. Garcia-Jarana *et al.*, 2008 [34] showed that the addition of KOH increases the production of H₂. Watanabe *et al.*, 2003 [49] studied the effects of NaOH and ZrO₂ as catalysts on the partial oxidative gasification of n-hexadecane and lignin in supercritical water. They showed that zirconia doubles H₂ production and that NaOH production was almost 4

times greater than that produced without the use of a catalyst at 400 °C and 260 bar. On the other hand, different supported catalysts (Al₂O₃, TiO₂, MgO, ZrO₂, etc.) [39, 50], mainly nickel and ruthenium have also been studied and proved higher efficiency for SCWG.

Therefore, different experiments have been carried out in order to determine the effect of different catalysts on the SCWG of OMW. Thus, a 47 ml batch reactor was used at 530 °C and 250 bar simultaneously with a reaction time of 10 and 20 minutes. This study analyses several tests where KOH was used as a homogeneous catalyst and V₂O₅, TiO₂ and Au-Pd as heterogeneous catalysts. V₂O₅ has not been studied previously for SCWG processes but it is a catalyst that is regularly used for oxidation reactions where temperatures reach 600 °C, so it could be a suitable catalyst for the process that we are studying. Table 1 shows the operating conditions and the results obtained from the different tests. The percentage of COD removal was close to 90% in almost all the experiments (Table 1).

a) Effect of Reaction Time and the Use of KOH as a Catalyst on Cellulose

In this case, the SCWG experiments of SCWG were carried out using an aqueous dilution of cellulose (23 g O₂/l of COD_o) and 0.01 g/g cellulose of KOH. This ratio was established based on literature [34]. The effect of KOH on gas yield was tested at reaction times of 10 and 20 minutes on gas yield. As it is shown in Figure 6, when the reaction time increased from 10 to 20 minutes without the presence of catalyst, H₂ yield increased from 11.6 mol/kg_{cellulose} up to 19.3 mol/kg_{cellulose}. Moreover, H₂ and CO₂ yields were higher with the presence of KOH (0.01 g/g cellulose) for both

Table 1: Experimental Conditions and Results

Feed	Catalyst		Experimental conditions				Individual gas yield (mol/kg _{sample dry})					Hydrogen efficiency (HE) (%)			Feed COD ₀ (g O ₂ /l)	COD removal (%)
	Type	Load (g/g _{sample dry})	T _{end} (°C)	P _{end} (bar)	Reaction time (min)	H ₂	CH ₄	CO ₂	CO	Hydrogen efficiency (HE) (%)	SH ₂ (mol H ₂ /mol CH ₄)					
Cellulose	None	-	514	245	10	11.60	8.99	28.04	30.82	95.82	0.65	23.41	70.44			
	KOH	0.01	513	245	10	20.31	8.70	41.51	8.19	122.19	1.17	21.32	58.56			
	None	-	534	257	20	19.26	11.08	40.44	9.58	134.23	0.87	21.63	80.08			
	KOH	0.01	534	254	20	20.60	11.82	48.70	4.99	143.37	0.87	21.63	69.79			
	Au-Pd	0.5	55	257	20	55.06	5.72	36.36	2.34	215.44	4.81	22.86	89.98			
Diluted OMWW	None	-	538	259	20	55.22	21.69	55.60	2.15	261.90	1.27	23.60	85.14			
	KOH	0.01	538	259	20	51.82	17.30	54.54	2.07	229.51	1.50	23.60	81.76			
	Au-Pd	0.1	536	253	20	80.85	17.64	61.12	1.57	308.43	2.29	21.74	88.13			
	Au-Pd	0.5	533	256	20	88.68	12.90	52.15	2.36	304.06	3.44	21.93	88.10			
OMWW	None	-	545	262	20	51.36	12.94	39.01	1.18	205.16	1.98	34.99	89.93			
	KOH	0.01	526	252	20	44.53	12.18	50.09	1.02	183.00	1.83	34.99	85.85			
	Au-Pd	0.5	536	260	20	56.43	8.50	42.26	1.76	195.04	3.32	34.99	87.85			
OMW mixture	None	-	526	252	20	13.04	10.88	24.10	0.67	92.77	0.60	80.16	90.76			
	V ₂ O ₅	0.5	536	254	20	13.67	7.67	23.37	1.24	77.31	0.89	80.16	91.81			
	KOH	0.01	536	268	20	13.97	11.63	26.85	0.86	99.25	0.60	80.16	91.99			
	TiO ₂	0.5	536	258	20	19.71	10.34	28.37	0.85	107.64	0.95	80.16	91.68			
	Au-Pd	0.5	536	259	20	29.89	6.35	21.82	0.66	113.53	2.35	80.16	90.03			

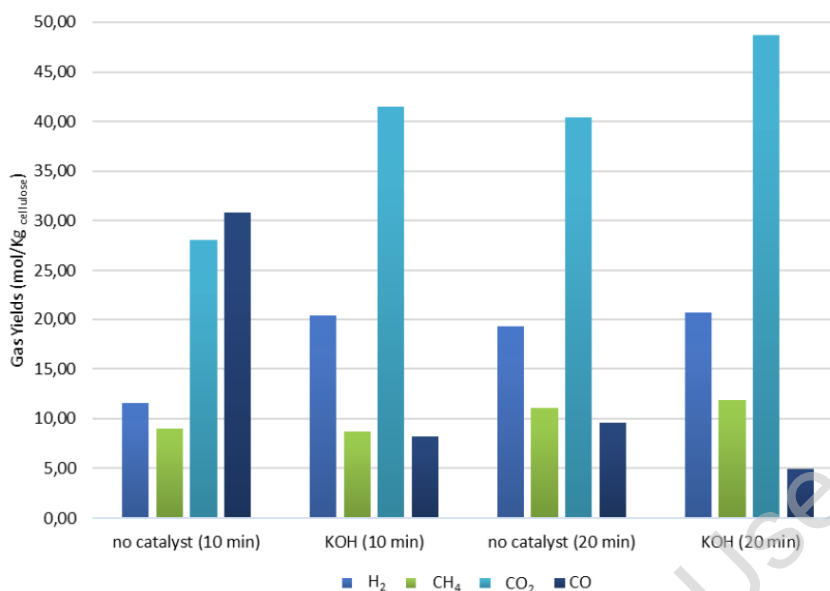


Figure 6: Gas Yield (mol/kg_{cellulose}) from cellulose with and without KOH catalyst (0.1 g/g_{cellulose}) at 530 °C, 250 bar and 10 and 20 minutes reaction time.

reaction times. Similar results were observed by Louw *et al.*, 2015 [50], the consistent H₂ and CO₂ yields achieved with an increment of the reaction time, confirms the fact that the use of a catalyst affects the water-gas shift process, even within relatively short reaction times. Reaction times longer than 20 minutes have not been studied because many authors have shown that H₂ selectivity declined as the reaction time increases. Nanda *et al.*, 2016 [51] found that greater yields of CO₂ and CH₄ lowered H₂ selectivity at reaction times of 30 min and 45 min. Williams and Onwudili, 2005 [52] reported that longer reaction times lower H₂ yield because H₂ molecules are consumed via hydrogenation, appearing in the liquid effluent.

In addition, CO production decreased with the use of KOH, just as Kruse *et al.*, 2000 [53] reported that CO gas production went down when the concentration of KOH increased from 0 to 5%. All of these data allowed validating the equipment and experimental procedures used in the present study. On the other hand, it should be noted that the test with cellulose and KOH as a catalyst with a reaction time of 20 minutes achieved the highest H₂ yield. Therefore, 20 minutes reaction time was used for the rest of the tests.

b) Effect of Heterogeneous and Homogeneous Catalysts on Olive Mill Waste Mixture (OMW Mixture)

Once the reaction time was established at 20 minutes, the effect of different heterogeneous (V₂O₅, TiO₂ and Au-Pd with a load of 0.5 g/g_{OMW dry}) and homogeneous catalysts (KOH with a load of 0.01

g/g_{OMW dry}) on *OMW mixture* was studied (Figure 7a). The gas yields were not significantly different from those obtained without a catalyst for both catalysts tested: V₂O₅ and KOH. H₂ gas production increased with the use of V₂O₅, TiO₂ and Au-Pd to 13.7, 19.7 and 29.9 mol/kg_{OMW mixture dry} respectively. Although, *OMW mixture* had a high organic concentration (COD of 80 g/l), the results from these tests have been similar to those reported by others authors [39, 50].

Since Au-Pd rendered the best results, a decision was made to study KOH as a homogeneous catalyst and Au-Pd as a heterogeneous catalyst for different concentrations of *OMW* and, as explained above, to study the effect of different feedstock concentrations on SCWG processes.

c) Effect of the Use of KOH and Au-Pd as Catalysts on Different Concentration of Olive Mill Wastewater and Cellulose

Several tests on *dilute OMWW* with KOH catalyst (0.01 g/g_{OMW dry}) and different loads of Au-Pd (0.5 and 0.1 g/g_{OMW dry}) catalyst were conducted. Figure 7b shows the variations in gas yields at each one of the experiments with and without a catalyst. H₂ yield did not improve with the addition of KOH, however, when Au-Pd was added, the improvement was significant. The test where Au-Pd (0.5 g/g_{OMW dry}) was used as a catalyst obtained the greatest H₂ production, therefore, that amount of Au-Pd was used for the rest of the experiments with cellulose (Figure 7c) and *OMWW* (Figure 7d).

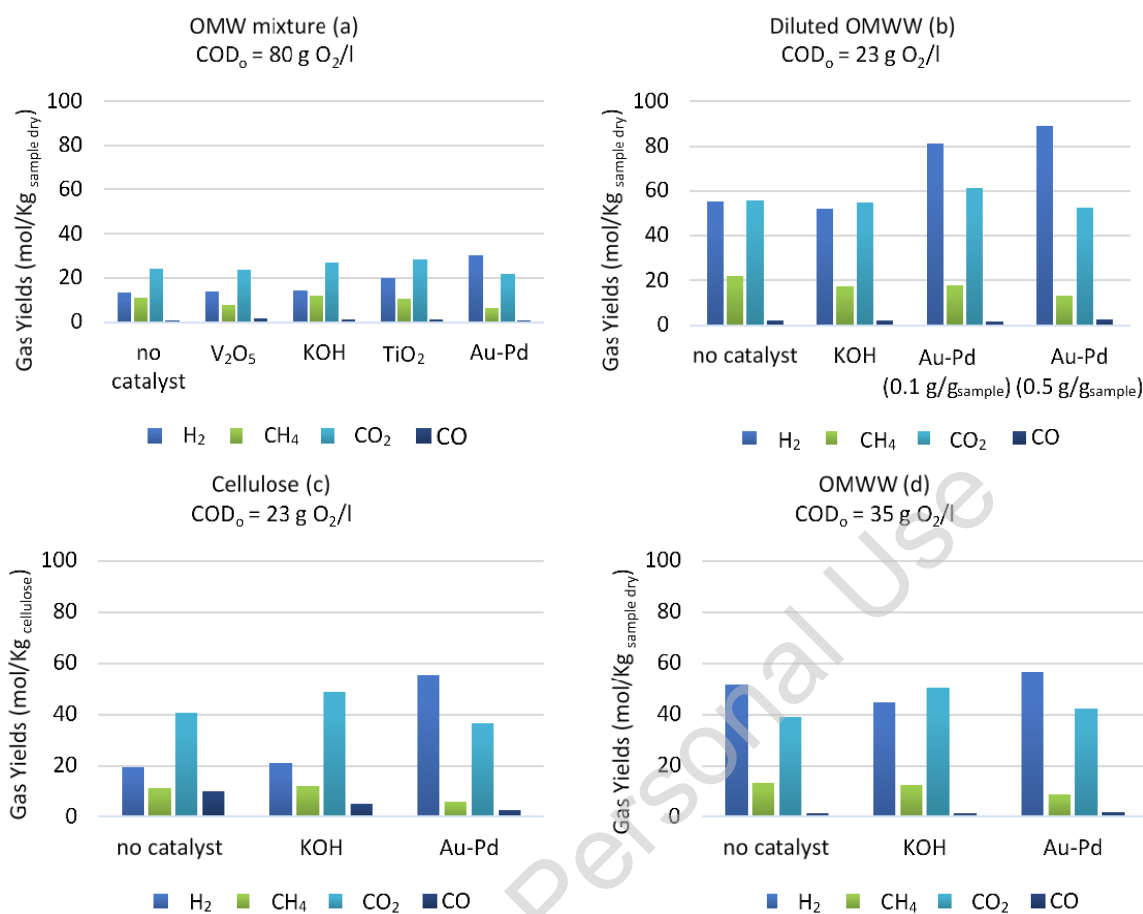


Figure 7: Effect of catalysts on the composition of the gaseous phase from SCWG experiments of *OMW mixture* (a), *diluted OMWW* (b), *cellulose* (c) and *OMWW* (d) at 530 °C, 250 bar and 20 minutes reaction time.

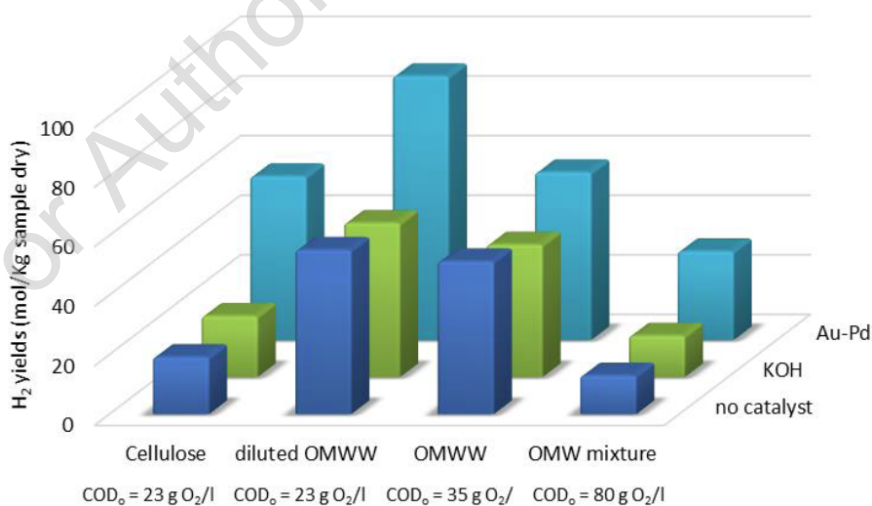


Figure 8: Comparison of H₂ yield (mol/kg_{sample dry}) obtained from SCWG from cellulose, *diluted OMWW*, *OMWW* and *OMW mixture* without or with KOH (0.01 g/g_{sample dry}) and Au-Pd (0.5 g/g_{sample dry}) as catalysts at 530 °C, 250 bar and 20 minutes reaction time.

The effect of KOH and Au-Pd catalysts on cellulose (23 g O₂/l of COD), with the same feed concentration as *diluted OMWW* dilute, were studied (Figure 7c). There by, the experiments with *diluted OMWW* and

cellulose would be comparable. Such tests confirmed the benefits obtained from Au-Pd as a catalyst in both experiments, with cellulose and with *diluted OMWW*, because the H₂ yield almost tripled the results obtained

without a catalyst. On the other hand, the CH₄ yield decreased, which may be due to the effect caused by Au-Pd on the water-gas shift reaction, while it did not significantly affect the formation of CH₄ (methanation reaction) [54].

Furthermore, the effect of KOH and Au-Pd on *OMWW* was studied (Figure 7d). Higher COD concentration, such as *OMW mixture* and *OMWW*, could yield less H₂ than that obtained from *diluted OMWW*. Nevertheless, even though a higher concentration of biomass has a negative impact on SCWG processes

Table 2: Selection of Results from Studies on the Use of SCWG Catalysts

Feedstock	Operating conditions			Catalyst	H ₂ yield (mmol H ₂ /g feed)	Reference
	Temperature (°C)	Feed Concentration	Reaction time			
Cellulose	550	Water-to-biomass 7:1	30 min	--	1.16	57
				0.65 g Ni/CeO ₂ /Al ₂ O ₃	1.63	
				0.65 g Dolomite	1.69	
				0.42 g KOH	9.09	
Pinewood	550	Water-to-biomass 7:1	30 min	--	0.83	57
				0.65 g Ni/CeO ₂ /Al ₂ O ₃	1.3	
				0.65 g Dolomite	0.99	
Mannose	700	8 wt%	1 h	0.42 g KOH	5.55	58
				--	32.30	
Fructose	700	4 wt%	60 s	10 wt% K ₂ CO ₃	57.39	58
				--	18.71	
Phenol	600	0.55-3.5 g/15mL	1 h	0.8 wt% KOH	59.23	59
				0.8 wt% NaOH	54.73	
Lactose	550	2.5 wt%	30 min	--	18.70	60
				K ₂ CO ₃	19.30	
Sugarcanne Bagasse	400	0.25 g /10 cc water	15 min	--	1.19	61
				0,1wt% NaOH	8.12	
				0,1wt% KOH	6.22	
Paper waste sludge	450	10 wt%	60 min	0,1wt% Na ₂ CO ₃	11.71	62
				Cu 20% on γ-Al ₂ O ₃	11	
Hydrochar (product of hydrothermal carbonization process)	400	15 wt%	16 h	--	1.04	50
				1g Ni /g _{PWS}	5.79	
Bassage	400	0.05g/ 4g water	15 min	1g K ₂ CO ₃ /g _{PWS}	7.47	63
				--	0.0004	
				K ₂ CO ₃	0.0007	
				--	7.13	
Indole	500	0.3 mol/l	30 min	5 wt% Ru/γ-Al ₂ O ₃ (impregnation)	13.00	64
				5 wt% Ru/γ-Al ₂ O ₃ (microemulsion)	15.60	
				5 wt% Ru/γ-Al ₂ O ₃ with 1,5 wt% Zinc (microemulsion)	18.00	
Indole	500	0.3 mol/l	30 min	25.08 wt% of 30 wt% Ni-0.1Ru/CeO ₂	2.99	65

[55], better results were obtained from these experiments than those reported by others authors [39, 50]. In addition, even though the H₂ yield increased with respect to the experiment without a catalyst at the same concentration level (51.4 mol/kg_{sample dry}), the effect of Au-Pd was slightly lower (56.4 mol/kg_{sample dry}) than that obtained with a lower concentration level. On the contrary, the use of KOH as a catalyst did not increase H₂ production.

Figure 8 shows and compares the H₂ yield from previous experiments carried out with and without catalysts (KOH and Au-Pd) for each sample (cellulose, *diluted OMWW*, *OMWW* and *OMW mixture*). In all the tests, the use of Au-Pd as a catalyst improved hydrogen production, where *diluted OMWW* was the best waste option, with a yield of 88.6 mol/kg_{sample dry}. It should be noted that *diluted OMWW* resulted in a higher H₂ yield than cellulose with the same initial COD. Nevertheless, the production of H₂ with the use of Au-Pd in all feedstock was better than that obtained by others authors who used other heterogeneous catalysts [39, 50, 56]. On the other hand, the results obtained from the use of KOH for all feed stocks were better than those reported by Ding *et al.*, 2014 [57] who obtained 9 mol/kg of biomass at 550 °C. Some of the results from SCWG catalysts in the literature are showed in Table 2.

IV. CONCLUSIONS

Oil mill wastewater can be successfully used to produce gas or liquid fuel without a previous drying process. Hydrothermal liquefaction of oil mill wastewater has been carried out in subcritical and supercritical water. The results from this study highlight the interesting possibility of using *OMWW* without a previous drying process to obtain liquid fuel as well as bio-crude. When no catalyst was used, a maximum yield of 82% was reached at 330 °C, 150 bar of pressure and 30 minutes reaction time. On the other hand, when Au-Pd is used as a catalyst for the supercritical water gasification of oil mill waste water, a significant improvement of hydrogen production was obtained in all the tests carried out, where *diluted OMWW* was the best feed option with a yield of 88.6 mol H₂/kg_{sample dry}.

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