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This is an **author produced version** of a paper published in:

Renewable Energy 148 (2020): 889-896

DOI: <https://doi.org/10.1016/j.renene.2019.10.173>

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1 **Effect of basicity in the aqueous phase reforming of brewery**
2 **wastewater for H₂ production**

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8 **Abstract**

9 Real (RBW) and synthetic brewery wastewater (SBW) were treated by aqueous phase
10 reforming (APR) with different 3%Pt/C catalysts for H₂ production from the biomass-
11 derived organic load. APR enabled simultaneous treatment of the wastewater and
12 valorisation to H₂ and alkanes of the biomass-derived organic load. In the catalytic APR
13 of SBW, TOC and COD removal was higher than 60% after reaction time of the
14 experiments. The addition of KOH or NaOH to SBW resulted in a slightly lower TOC
15 and COD removal, however higher yields to H₂ and percentage of valuable gases were
16 obtained in those cases where KOH was added. Catalyst with basic support and low
17 contribution of micropores showed the best performance in the APR of SBW+KOH
18 (~50% of H₂ and 8.9 mmol H₂/g COD). The concentration of anions detected in the
19 liquid effluents varied with the catalysts tested and with the concentration of base,
20 suggesting different reaction pathways. Increasing the concentration of KOH led to
21 CO₂-free H₂ without significant changes in H₂ yield. The results obtained with RBW
22 were in good agreement with those from SBW, although the significantly different
23 behaviour of some catalysts suggests the need of tuning their properties according to the
24 composition of the wastewater.

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27 **Keywords:** hydrogen, brewery wastewater, aqueous phase reforming, basicity

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1. Introduction

The circular economy approach has attracted much interest in the last few years, given the current scenario of high dependence on fossil fuels and human-borne climate change. This approach involves, among others aspects, transitioning from fossil-based to renewable energy sources and a more efficient use of raw materials and products, aimed to minimize waste and pollution. In this context, aqueous phase reforming (APR) has gained an increasing attention since the pioneering work of Cortright *et al.* [1], where the production of valuable gases, such as H₂, from biomass-derived compounds was reported. The APR process can be described by the overall reforming reaction shown in Eq. (1), although other reactions, such as the water-gas shift reaction (WGS), methanation, Fischer-Tropsch, dehydrogenation or dehydration/hydrogenation also occur in different extent [1].

(1)

Oxygenated organic species, such as sorbitol, xylitol, glycerol, galactitol, ethanol, 1-propanol or ethylene glycol, among others, have been extensively studied as substrates for APR [2–7], showing promising results in terms of carbon conversion into gases and valuable gas products. On the other hand, a diversity of catalytic systems, mainly based on VIII group metals, have been described in the literature for APR of oxygenated hydrocarbons [8,9]. Ru and Re catalyst exhibited a higher selectivity to alkanes [10], while Pt-based catalysts showed to be the most active and selective toward H₂ among monometallic catalysts [11]. Nickle has been considered as an economic alternative leading to high selectivity to alkanes, although low stability was observed for this type of catalysts [12]. While bimetallic catalysts were shown to have better performance in selected applications [11,13,14]. The effect of the support on the performance of the catalysts was also investigated in literature, where a large number of studies were

1 conducted using Pt supported on Al₂O₃ [11]. Due to the limited stability of Al₂O₃ under
2 APR conditions, carbon-based catalysts have also been studied [13–15]. Some authors
3 have reported a higher H₂ yield and catalytic activity using basic supports, while higher
4 alkanes production was achieved using neutral and acids supports [4]. However, in our
5 previous work on brewery wastewater APR we observed that, in addition to basic
6 character, texture properties of the support were also important and the best catalytic
7 performance was observed for catalysts supported on mesoporous carbon black with
8 virtually no microporosity and basic pH slurry [16].

9 Concerning the feasibility of the process, techno-economical studies on APR have
10 shown that the cost of the substrate has an important impact on the economy of the
11 process [17]. Therefore, feeding APR processes with waste materials is worthwhile to
12 investigate. With this perspective, the APR process could be extended to new
13 applications such as the treatment of wastewater. Some exploratory works on the
14 potential of APR for the treatment of different wastewaters have been reported by our
15 group [16,18]. However, regarding potential applications, more knowledge is needed on
16 the effect of complex matrices in the catalysts performance, a crucial issue scarcely
17 studied in the literature so far. Most of the works are related to synthetic matrices,
18 which mainly consisting in of mixtures of compounds (methanol, acetic and phosphoric
19 acids, NaOH, etc.) with glycerol as main ingredient, emulating the aqueous fraction
20 from biodiesel production in biorefineries [19,20]. In spite of the experience gathered,
21 the role of bases (i.e KOH, NaOH) in the reaction medium is not well addressed.

22 Several authors have reported positive effects of a basic medium on the APR
23 process due to favoured WGS reaction [21,22], in-situ removal of CO₂ [21–23], or
24 increased gas production [19]. However, some authors indicated a negative effect on
25 catalyst deactivation [20]. For instance, in the case of glycerol using Ni-La/Al₂O₃

1 catalysts, some authors [19] reported that the presence of acetic acid decreased gas
2 production, while KOH increased it. In another related study [20] using similar
3 catalysts, the effect of different acids (phosphoric, sulphuric and acetic) and bases
4 (KOH and NaOH) on the APR of glycerol was investigated, concluding that these
5 compounds affected to catalyst deactivation, particularly in the case of phosphoric acid
6 and KOH.

7 Regarding the application of APR to wastewater treatment, bases are relevant since
8 they are present in a number of industrial wastewaters due to the cleaning-in-place
9 (CIP) operations commonly used in industries such as processing food, beverages,
10 brewing or pharmaceuticals, among others. In general, the CIP cycle involves several
11 water-consuming steps, above ambient temperatures and the use of caustic solutions,
12 leading to basic wastewaters that cannot be treated by conventional biological methods
13 without previous neutralization.

14 In a recent work [16], we explored the application of APR for the treatment of a
15 synthetic brewery wastewater with an initial pH of about 7 and obtained fairly good
16 results in terms of TOC and COD removal (up to 99%) and valuable gases yield (up to
17 12.2 mmol H₂/g COD_{initial}), showing the potential of APR for the treatment of this sort of
18 effluents. In the current work, the effect of NaOH and KOH concentration on the
19 catalysts performance in APR of synthetic brewery wastewater is analysed. **NaOH and**
20 **KOH are commonly found in the formulation of detergents for CIP systems used in**
21 **breweries, therefore, they were the bases selected for this study.** Likewise, a real
22 brewery wastewater has been tested to learn on the potential of application APR to these
23 effluents.

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2 **2. Experimental**

3 *2.1. Materials*

4 Malt extract, yeast extract, peptone, maltose (D-(+)-Maltose monohydrate from
5 potato, $\geq 99\%$), ammonium sulfate ($\geq 99\%$), NaOH ($\geq 99\%$) and KOH ($\geq 99\%$)
6 hexachloroplatinic acid solution (H_2PtCl_6 , 8% wt. in H_2O) were purchased from Sigma-
7 Aldrich. Ethanol ($\geq 99.5\%$) was supplied by Panreac AppliChem. Commercial activated
8 carbons Norit®CAPSUPER (CAP) and Merck (MER) were supplied by Norit and
9 Merck, respectively. Commercial carbon black ENSACO 250G (ENS) and Ketjenblack
10 EC-600JD (KJB) were purchased by Timcal and Akzonobel, respectively.

11 *2.2. Preparation and characterization of supports and catalysts*

12 Pt/C (3 wt. % Pt, carbon basis) catalysts were prepared by incipient wetness
13 impregnation using two commercial activated carbons (CAP and MER) and two carbon
14 blacks (ENS and KJB) as supports. After impregnation, the samples were dried at 333 K
15 overnight in an oven. Finally, the catalysts were calcined at 473 K (2 h) and reduced
16 with 25 N mL/min H_2 flow at 573 K (2 h). **The Pt concentration used was selected in**
17 **preliminary experiments and was already tested in previous works [16,18]. The use of a**
18 **higher load was not considered because it may lead to nanoparticles agglomeration in**
19 **supports with low surface area, as in the case of ENS. Previous works also showed a**
20 **good stability of Pt/C catalyst under simulated and real APR conditions, with low**
21 **significance changes in nanoparticles size, metal oxidation state and catalytic activity**
22 **[16,24].**

23 The catalysts were characterized by scanning transmission electron microscopy
24 (STEM) using a JEOL - 3000F at 300 kV microscope. The mean size of the Pt
25 nanoparticles (NPs) and the size distribution were calculated by averaging more than

1 200 NPs randomly distributed in digital STEM images using the software ‘ImageJ
2 1.51k’. The porous texture of the supports and catalysts was characterized by nitrogen
3 adsorption-desorption at 77 K (TriStar II, Micromeritics). Also, pH slurry
4 measurements were carried out by measuring the pH of an aqueous suspension in
5 distilled water (1 g of solid per 10 ml of water).

6 *2.3. APR experiments and analytical procedures*

7 Synthetic and real brewery wastewater were used as substrates. Synthetic brewery
8 wastewater (SBW) was prepared using malt extract (1 g/L), yeast extract (0.5 g/L),
9 peptone (0.15 g/L), maltose (0.86 g/L), ammonium sulfate (1 g/L) and ethanol (2.8
10 mL/L) based on typical compositions found in brewery wastewater according to the
11 literature [25]. NaOH and KOH were added to adjust the pH of SBW in order to
12 evaluate the effect of these bases and their concentration on the catalysts performance in
13 APR. The pH of SBW was 7, and was adjusted to 11 for some experiments since this is
14 the pH value for the real brewery wastewater (RBW) studied. This last was collected
15 from the plant of an international brewing company based nearby Madrid (Spain).

16 APR runs were performed in stainless steel batch reactors (BR100, Berghoff) at 493
17 K and 24 - 28 bar (initial Ar pressure set at 5 bar) during 4 h, using 0.3 g of catalysts in
18 15 mL of reaction volume under Ar atmosphere. The reactors were purged with Ar
19 several times before each run. The gases were collected in multilayer foil sample bags
20 (Supelco) and the volume was measured by a gas burette and expressed in normal
21 conditions (NTP). The aqueous phase was characterized by Total Organic Carbon
22 (TOC) measured in a TOC-VCSH apparatus (Shimadzu), Chemical Oxygen Demand
23 (COD) determined according to the standard method (ASTM D1252), and ionic
24 chromatography (883 Basic IC Plus, Metrohm). The gas phase was analyzed by a

1 GC/FID/TCD (7820A, Agilent) using 2 packed columns and a molecular sieve allowing
2 to detect H₂, CO, CO₂, CH₄, C₂H₆ and C₃H₈.

3 The TOC and COD removal (%) were determined as the difference between the
4 initial and final TOC or COD values divided by the initial value (mg/L). Carbon
5 conversion to gases (*CC gas* (%)) was calculated from the ratio between C content (g)
6 in the gaseous products and C content (g) in the initial wastewater. H₂ yield (*Y_{H2}*) was
7 defined as the amount of H₂ produced (mmol) divided by the initial COD (g).

8 3. Results and Discussion

9 3.1. Catalysts and supports characterization

10 Table 1 shows the specific surface area (*S_{BET}*), micropore and mesopore volume,
11 and pH slurry of the supports and catalysts prepared. The supports used covered in a
12 wide range of *S_{BET}* (65 - 1750 m²/g), micropore (< 0.001 - 0.66 cm³/g) and mesopore
13 volumes (0.09 - 1.67 cm³/g) and pH slurry (2.9 - 10.6). The carbon black supports (ENS
14 and KJB) showed basic pH slurry and did not present significant micropore volume (<
15 0.001 cm³/g), whereas the activated carbons yielded either acid or basic pH slurry and a
16 significant contribution of micropore volume (0.38 - 0.48 cm³/g). The catalysts prepared
17 presented slightly lower values of *S_{BET}* and pore volume than the corresponding
18 supports due to partial pore blockage by the Pt NPs. The pH slurry of the catalysts did
19 not present any significant difference in comparison to the supports.

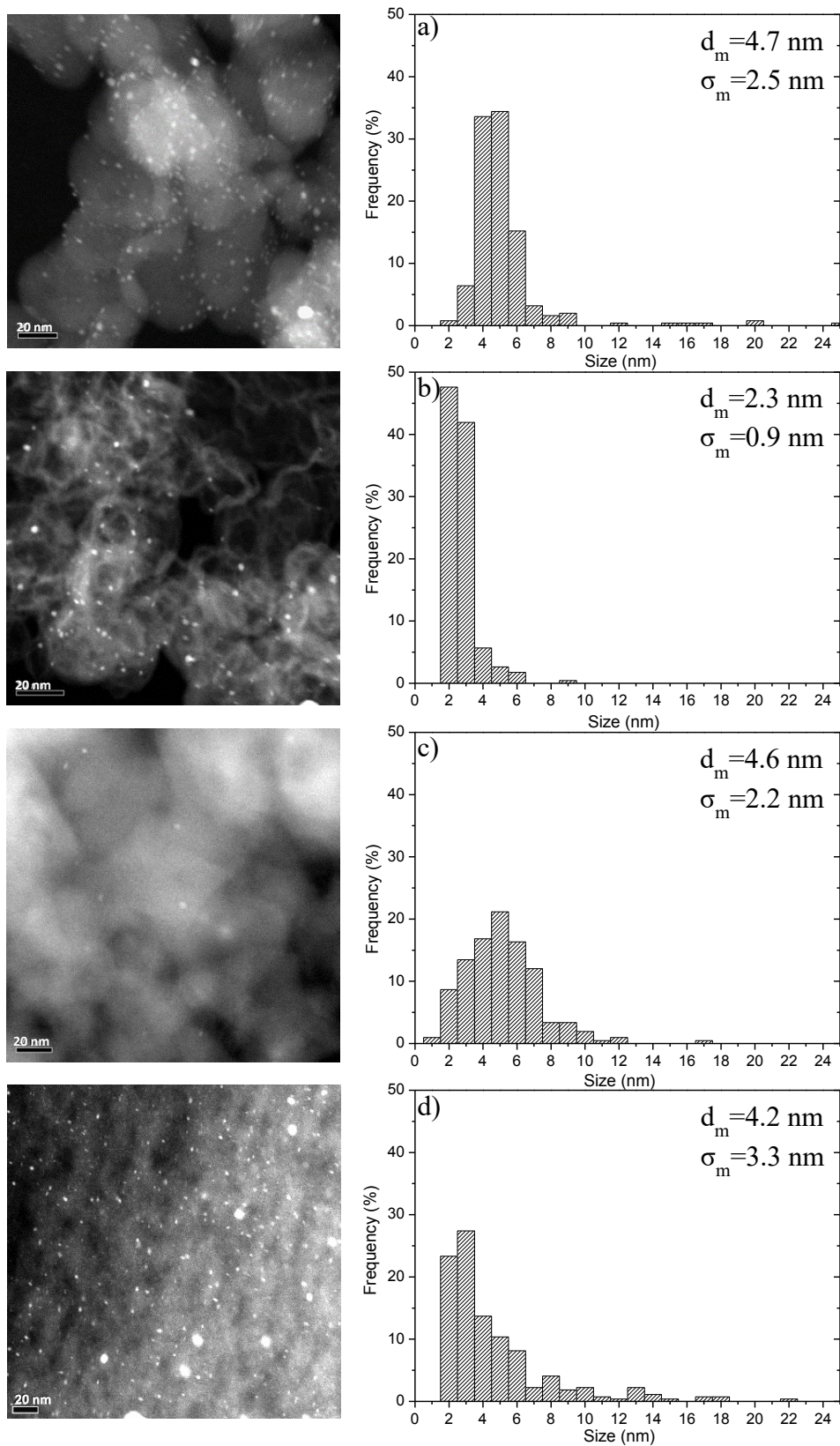
20
21 Table 1. *S_{BET}*, micropore and mesopore volume, and pH slurry of the supports and
22 catalysts

Support/ catalyst	<i>S_{BET}</i> (m ² /g)	Micropore Volume (cm ³ /g)	Mesopore Volume (cm ³ /g)	pH slurry
ENS	65	< 0.001	0.09	8.9
KJB	1415	< 0.001	1.67	10.6
MER	930	0.38	0.15	8.3
CAP	1750	0.48	0.75	2.6

Pt/ENS	65	< 0.001	0.09	8.6
Pt/KJB	1350	< 0.001	1.59	10.2
Pt/MER	910	0.38	0.14	8.5
Pt/CAP	1360	0.31	0.75	2.9

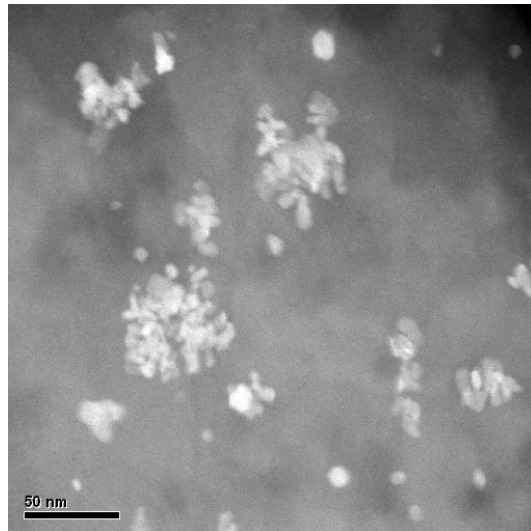
1 Figure 1 shows STEM images and the corresponding size distribution of the Pt NPs
2 in the catalysts. The mean NPs size and size distribution for the Pt/ENS, Pt/MER and
3 Pt/CAP catalysts were quite similar, in the 4.2 - 4.7 nm range, while the Pt/KJB one
4 gave a smaller value of mean NPs size (2.3 nm). In addition, it should mention that the
5 Pt NPs of the Pt/MER catalyst, in some STEM images, showed a higher agglomeration
6 than in the other catalysts (Figure 2).

7



1

2 Figure 1. STEM images of a) Pt/ENS, b) Pt/KJB, c) Pt/MER and d) Pt/CAP catalysts



1
2 Figure 2. STEM image of agglomeration of Pt NPs in the Pt/MER catalysts

3
4 *3.2. Synthetic and real brewery wastewater characterization*

5 The characterization of the SBW and RBW, including TOC, COD, pH and main
6 anions analysed, is summarized in Table 2. The RBW showed TOC and COD values of
7 1646 and 4674 mg/L, respectively. The pH of RBW was basic (pH 11) since it contains
8 significant amounts of the NaOH commonly used in the CIP operations carried out in
9 the food processing and beverages industry. The main organic anions detected
10 correspond to short chain organic acids, which are commonly present in malt extract
11 [26]. The SBW was prepared with a TOC and COD of 1871 and 5846 mg/L,
12 respectively, which are close to above values for RBW and in good agreement with the
13 range of TOC and COD reported for this type of wastewater [25]. The starting pH of
14 SBW was neutral. The main differences found between SBW and RBW in terms of
15 anions composition were relative to acetate and sulfate, which were in significantly
16 higher and lower concentration, respectively, in the case of RBW.

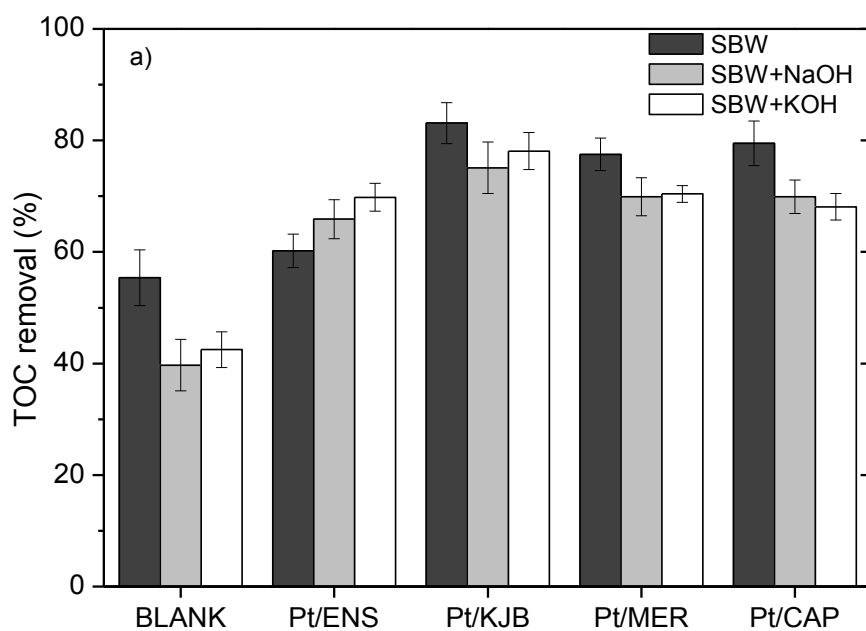
1 Table 2. Characterization of the SBW and RBW

Wastewater	TOC (mg/L)	COD (mg/L)	pH _i	Acetate (mg/L)	Formate (mg/L)	Glycolate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Maleate (mg/L)
SBW	1871 ± 79	5846 ± 331	7	2 ± 1	1 ± 1	8 ± 1	18 ± 3	678 ± 78	-
RBW	1646 ± 230	4764 ± 586	11	172 ± 10	37 ± 3	39 ± 3	15 ± 1	41 ± 4	4 ± 1

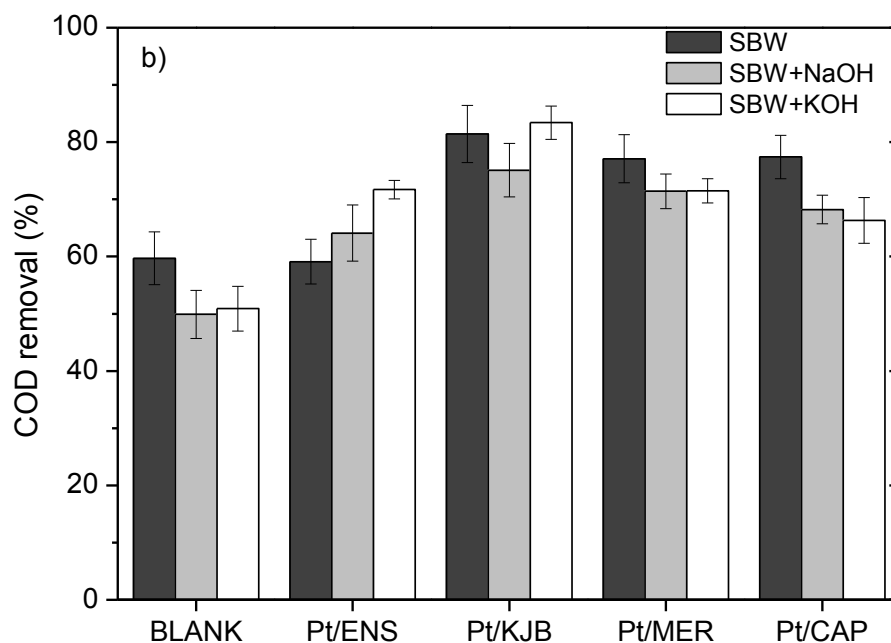
2

3 *3.3. APR of synthetic brewery wastewater*

4 Figure 3 depicts the TOC and COD removal in the blank (without catalyst) and
5 catalysed APR experiments with SBW. Likewise, the results of the experiments with
6 SBW modified with NaOH (SBW+NaOH) or KOH (SBW+KOH) up to a pH value of
7 11 are included. The lowest TOC and COD removal (40 - 60%) corresponded to the
8 blank and can be ascribed mostly to hydrothermal carbonization (HTC) of the organic
9 substrates, which is favoured under the operating conditions used [27]. In general, the
10 TOC and COD removal were higher when catalysts were used, particularly in the case
11 of Pt/KJB, Pt/MER and Pt/CAP, which reached removal values close to 70%. **The**
12 **addition of KOH and NaOH to SBW provoked a slight decrease in TOC and COD**
13 **removal in all experiments, except with Pt/ENS catalyst. Base addition increased the**
14 **selectivity towards liquid phase products, probably through base-catalysed dehydration**
15 **followed by hydrogenation reactions [28], thus reducing the TOC and COD removal.**
16 No significant differences in TOC and COD removal were found by using NaOH or
17 KOH in the experiments with SBW.



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4 Figure 3. a) TOC and b) COD removal in APR runs for SBW ($pH_i = 7$), and for
5 SBW+NaOH and SBW+KOH ($pH_i = 11$)*

6 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
7 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

1
2 Table 3 shows the concentration of short chain carboxylic anions and the pH values
3 measured before and after APR runs. Acetate, formate and glycolate were the most
4 representative in the initial SBW. These three anions significantly increased their
5 concentration in experiments without catalyst (blank), especially in the case of
6 SBW+NaOH and SBW+KOH. During the HTC process organics acids such as formic,
7 acetic and levulinic acids are produced from biomass-derived organic compounds.
8 Some authors [29] have reported that basic conditions significantly affect the
9 decomposition pathway of **hydroxymethylfurfural (HMF)**, which is converted to
10 levulinic or formic acid, increasing the concentration of these acids. In the catalytic
11 APR test, the concentration of these anions decreased in general, particularly in the case
12 of formate, indicating that conversion of the initial substrates takes place upon APR
13 reactions through mechanisms different from those of HTC. Acetate concentration was
14 barely affected by the operating conditions, indicating its refractory character, whereas
15 the glycolate concentration was very sensitive to the type of catalyst, being higher in the
16 SBW+NaOH and SBW+KOH experiments. The carboxylic anions from the blank
17 experiments amounted 9 - 19% of the final TOC, this increasing to 13 - 24% with bases
18 addition. Moreover, the Pt/MER and Pt/CAP catalysts yielded in general effluents with
19 higher glycolate concentration and percentage of short chain carboxylic anions in the
20 final liquid phase of TOC (20 - 24%). A similar observation was made by King *et al.*
21 [28] in the APR of glycerol, who found a higher production of acids with the addition of
22 a base to the reaction medium. They suggested that KOH could promote the Cannizzaro
23 reaction, facilitating the production of acids. Another study using in situ X-ray
24 absorption spectroscopy reported a higher selectivity to acids (four-fold) upon addition
25 of KOH ($\text{pH}_i = 11.8$) in the APR of glycerol [30]. This effect was explained through the

1 interaction between KOH and adsorbed reaction intermediates, especially aldehydes, on
 2 the surface of Pt. The final pH of the effluents was 3 - 4 in the APR runs with SBW
 3 (starting pH = 7), whereas it ranged between 6 and 8 in the SBW+NaOH and
 4 SBW+KOH experiments, when amounts of acids were produced, giving rise to base
 5 neutralization.

6

7 Table 3. Short chain carboxylic anions in the effluents from the SBW, SBW+NaOH and
 8 SBW+KOH APR experiments*

Sample	Wastewater	Short chain carboxylic anions (mg/L)			Initial pH	Final pH
		Acetate	Formate	Glycolate		
Initial	SBW	2 ± 1	1 ± 1	8 ± 2	7	-
BLANK	SBW	74 ± 9	66 ± 7	105 ± 9	7	3
	SBW+NaOH	123 ± 11	118 ± 14	221 ± 12	11	8
	SBW+KOH	126 ± 12	121 ± 13	209 ± 10	11	7
Pt/ENS	SBW	98 ± 6	2 ± 1	64 ± 5	7	4
	SBW+NaOH	104 ± 9	10 ± 4	103 ± 8	11	8
	SBW+KOH	106 ± 7	6 ± 3	82 ± 9	11	8
Pt/KJB	SBW	61 ± 5	1 ± 1	34 ± 2	7	3
	SBW+NaOH	80 ± 4	6 ± 1	111 ± 6	11	8
	SBW+KOH	89 ± 5	7 ± 1	91 ± 8	11	8
Pt/MER	SBW	79 ± 5	4 ± 1	102 ± 8	7	3
	SBW+NaOH	71 ± 3	12 ± 2	199 ± 10	11	8
	SBW+KOH	73 ± 6	14 ± 1	200 ± 12	11	7
Pt/CAP	SBW	117 ± 8	1 ± 1	67 ± 3	7	3
	SBW+NaOH	72 ± 4	19 ± 3	249 ± 11	11	6
	SBW+KOH	100 ± 6	11 ± 2	256 ± 12	11	6

9 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 10 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

11

12 Table 4 summarizes the gas volume produced, gas composition, *CC gas* and H₂
 13 yield in the APR experiments. The volume of gas produced varied within a wide range
 14 (1.0 - 40.1 mL), with the blanks showing the lowest production (1.0 - 2.2 mL). The
 15 blanks gave *CC gas* between 1.7 - 3.8%, consisting mainly of CO₂ (50 - 87%) with low
 16 H₂ yields (< 0.03 mmol H₂/g COD). CO was only detected in the blank experiments,
 17 representing 9% of the gas fraction from the APR of SBW and reaching more than 30%

1 from SBW+NaOH and SBW+KOH. The catalysts supported on carbon blacks showed a
2 gas production between 12.2 and 40.1 mL, with *CC gas* in the 15.8 – 41.3% range and
3 H₂ yields between 1.4 and 8.9 mmol H₂/g COD. These values were significantly higher
4 than the obtained with the activated carbon supported catalysts (gas volume: 2.9 - 8.4
5 mL; *CC gas*: 3.7 - 15.1%; H₂ yield: 0.05 - 0.15 mmol H₂/g COD). This frankly higher
6 production of H₂ can be attributed to the fact that the ENS and KJB carbon blacks are
7 basic supports that can enhance the WGS reaction. Some authors [21] have suggested
8 that the basic medium can favors the polarization and dissociation of H₂O, providing
9 hydroxyl anions that can be adsorbed on the catalysts surface, enhancing the WGS
10 reaction [31]. However, the Pt/MER catalyst yielded basic pH slurry while giving low
11 amounts of H₂ and other gases. This behavior of the Pt/MER catalyst can be related to
12 its porous texture, since the MER support has a high contribution of micropores
13 opposite to ENS and KJB. That would determine severe mass transfer limitations of
14 reactants and products, resulting in low gas production, H₂ selectivity and yield [32–34].
15 The Pt/CAP catalyst has an important contribution of mesopores, but both the presence
16 of micropores and the low pH slurry of the support may causes the low H₂ production
17 observed, similar to that of Pt/MER.

18 Regarding the effect of the addition of bases to the wastewater, it has been reported
19 [21,22] that CaO or KOH can favour the WGS reaction by gas withdrawal through the
20 in-situ removal of CO₂, displacing the reactions towards H₂ production. In the current
21 work the addition of bases led to lower percentages of CO₂ in the gas fraction with all
22 the catalysts tested, particularly in the experiments with SBW+KOH, indicating that the
23 addition of a base was effective for the removal of CO₂. However, the Y_{H_2} in the
24 SBW+KOH and SBW+NaOH experiments was higher than in the SBW ones only with
25 the Pt/KJB catalyst. King *et al.* [28] studied the effect of KOH addition in the APR of

1 glycerol using 3%Pt/C and 3%Pt-Re/C catalysts and found a dramatic increase of
2 glycerol conversion. However, they reported a higher production of liquids, being the
3 gas product, and H₂ yield barely affected. Likewise, they suggested that the addition of
4 KOH favoured the C-O bond cleavage, compared to C-C bond cleavage, by base-
5 catalysed dehydration followed by hydrogenation that reduces the H₂ production. Karim
6 *et al.* [30] also found similar results in the APR of glycerol with Pt/C catalysts. The
7 addition of KOH did not affect the gas phase products, while a higher glycerol
8 conversion was observed. These authors also attributed the results to a higher selectivity
9 toward dehydration reactions, which was reflected in a higher C-O/C-C ratio and lower
10 H₂ and CO₂ selectivities in the presence of that base.

11 Comparing the bases used, the highest percentage of H₂ was obtained with KOH.
12 The experiments carried out with SBW+KOH also led to higher gas production, *CC*
13 *gas*, Y_{H_2} , and in some cases a lower percentage of alkanes in the gas fraction. This can
14 be better appreciated for the catalysts that yielded higher amounts of gases (Pt/ENS and
15 Pt/KJB). Similar results were obtained by Liu *et al.* [21] in the APR of ethylene glycol
16 using Ni catalysts with different potassium salts and NaOH. The authors concluded that
17 KOH leads to higher *CC gas* and Y_{H_2} and lower alkanes yields, probably due to
18 blockage of active sites enabling CO methanation. The addition of K to Pt/hydrotalcite
19 catalysts was studied in the APR of glycerol [35] and the results showed that it
20 enhanced the basicity of the catalysts and increased the glycerol conversion and H₂
21 selectivity, although an excess of K loading blocked the active sites of Pt NPs, having
22 the opposite effect.

23 In the SBW+KOH experiments the Pt/ENS catalyst gave the highest percentage of
24 valuable gases (H₂ and alkanes) in the gas fraction (~ 75%) and H₂ yield (8.9 mmol H₂/g
25 COD ≈ 213.6 mL H₂/g COD). This production of gas is higher than the reported in the

1 literature from the anaerobic biological treatment of an equivalent brewery wastewater
 2 (initial COD ca. 6000 mg/L, 149.6 mL H₂/g COD) [36], thus showing the potential of
 3 APR as way of valorisation of brewery wastewater.

4

5 Table 4. Gas volume produced, composition of the gas fraction, *CC gas* and *Y_{H2}* in the
 6 APR of SBW (pH_i = 7), SBW+NaOH (pH_i = 11) and SBW+KOH (pH_i = 11)*

Sample	Wastewater	Gas Volume (mL)	Gas composition (% mol)			CC gas (%)	Y _{H2} (mmol H ₂ / g COD)
			H ₂	CO ₂	Alkanes		
BLANK	SBW	2.2 ± 0.3	1.8 ± 0.3	86.8 ± 6.1	2.2 ± 0.3	3.8 ± 0.4	<0.1
	SBW+NaOH	1.0 ± 0.4	6.6 ± 1.0	50.4 ± 6.4	7.5 ± 3.5	1.7 ± 0.7	<0.1
	SBW+KOH	1.4 ± 0.4	4.2 ± 0.1	58.8 ± 7.0	6.7 ± 2.1	2.5 ± 0.7	<0.1
Pt/ENS	SBW	40.1 ± 0.5	46.7 ± 0.5	32.0 ± 0.8	21.3 ± 0.3	41.3 ± 0.9	8.9 ± 0.1
	SBW+NaOH	23.7 ± 7.1	51.4 ± 2.0	25.6 ± 1.7	23.0 ± 3.7	21.8 ± 7.5	5.8 ± 1.5
	SBW+KOH	35.5 ± 6.9	52.7 ± 0.4	25.1 ± 0.1	22.2 ± 0.4	31.8 ± 6.1	8.9 ± 1.7
Pt/KJB	SBW	12.2 ± 0.5	23.5 ± 0.6	56.9 ± 1.4	19.6 ± 0.9	17.5 ± 0.9	1.4 ± 0.1
	SBW+NaOH	12.5 ± 0.5	32.7 ± 1.0	44.5 ± 1.9	22.8 ± 1.0	15.8 ± 0.9	1.9 ± 0.1
	SBW+KOH	19.3 ± 3.5	38.6 ± 3.4	39.7 ± 2.3	21.7 ± 1.1	22.3 ± 3.1	3.5 ± 0.9
Pt/MER	SBW	4.3 ± 0.4	3.2 ± 0.8	87.4 ± 0.2	9.4 ± 0.9	7.5 ± 0.7	0.1 ± 0.1
	SBW+NaOH	2.2 ± 0.4	4.4 ± 1.3	89.6 ± 0.1	6.0 ± 1.2	3.7 ± 0.7	0.1 ± 0.1
	SBW+KOH	2.8 ± 0.4	9.5 ± 0.2	76.4 ± 1.6	14.1 ± 1.8	4.7 ± 0.6	0.1 ± 0.1
Pt/CAP	SBW	8.4 ± 0.4	1.6 ± 0.4	72.1 ± 0.7	26.3 ± 1.1	15.1 ± 0.6	0.1 ± 0.1
	SBW+NaOH	2.9 ± 0.4	5.6 ± 0.6	86.2 ± 0.4	8.2 ± 1.0	4.9 ± 0.6	0.1 ± 0.1
	SBW+KOH	2.9 ± 0.4	10.6 ± 0.1	80.3 ± 1.2	9.1 ± 1.2	4.7 ± 0.6	0.1 ± 0.1

7 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 8 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

9

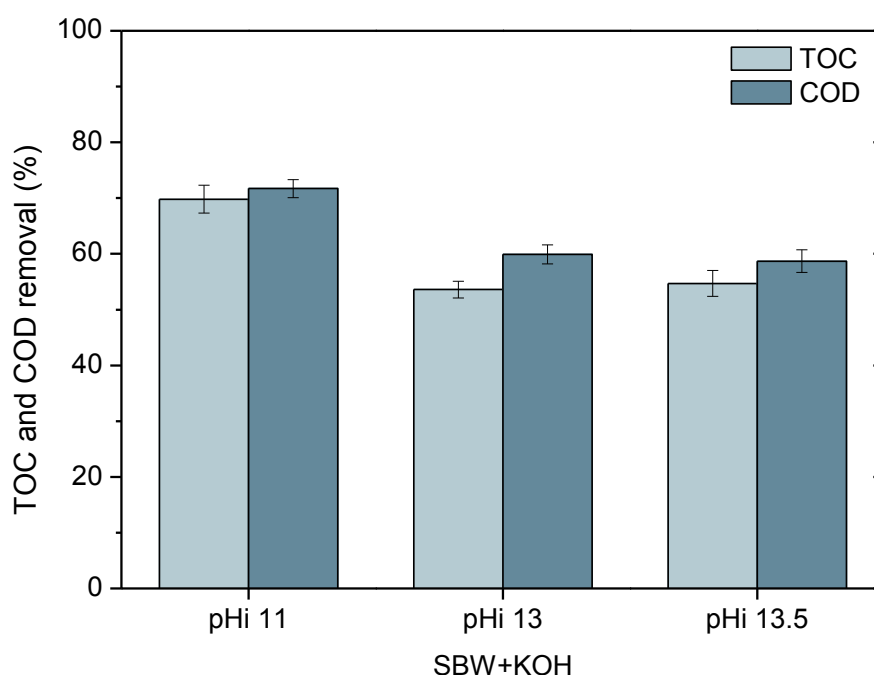
10 3.4. Effect of the pH on the catalyst performance

11 Given the good results obtained with the Pt/ENS catalyst it was selected to assess
 12 the effect of the pH in the APR of SBW+KOH. The pH values tested were selected
 13 taking into account the previous results of CO₂ production in the corresponding
 14 experiments at an initial pH value of 11. An initial pH value of 13.0 was calculated as
 15 the one providing the stoichiometric amount of KOH needed to convert all the CO₂
 16 produced, according to Eq. (2). Initial pH values below and above that value (11 and
 17 13.5, respectively) were selected.

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Figure 4 shows the TOC and COD removal achieved at these three initial pH values. Around 70% of TOC and COD removal reached at $\text{pH}_i = 11$, while lower percentages were achieved at higher pH. Similar results were found in the APR of glycerol with 3%Pt/C upon the addition of KOH ($\text{pH}_i = 12$) [28]. Therefore, this base may change the reaction pathway, increasing the production of liquids without increasing significantly the H_2 yield, due to competitive reactions involving base-catalysed dehydration followed by subsequent hydrogenation.



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Figure 4. TOC and COD removal in the APR of SBW+KOH with Pt/ENS at different initial pH*

*Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

Table 5 shows the concentration of representative anions from the APR runs of SBW+KOH at different initial pH values. In all cases the pH decreased along the APR due to the generation of organic acids. Acetate, formate and glycolate concentration

1 was much lower at the lowest starting pH ($\text{pH}_i = 11$). The amount of these anions
 2 corresponded to 14% of the final TOC, while increasing up to 30 and 36% at 13 and
 3 13.5 initial pH, respectively. Thus confirming that organic acids formation is favoured
 4 at increased pH [28,30].

5

6 Table 5. Short chain carboxylic anions the APR of SBW+KOH with Pt/ENS at different
 7 initial pH*

Sample	Initial pH	Short chain carboxylic anions (mg/L)			Final pH
		Acetate	Formate	Glycolate	
Pt/ENS	11	106 ± 7	6 ± 3	82 ± 9	8
	13	235 ± 11	33 ± 4	392 ± 12	10
	13.5	330 ± 16	30 ± 4	419 ± 14	12

8 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 9 of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

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11 Table 6 shows the gas volume produced, the composition of the gas fraction, *CC gas*
 12 and Y_{H_2} at the different values of initial pH tested. The *CC gas* significantly decreased
 13 from around 32%, for an initial pH of 11, to around 15% for 13 and 13.5 initial pH, due
 14 to the in-situ removal of the CO_2 giving rise to potassium carbonate. Table 6 also shows
 15 that for those initial pH values no CO_2 was found in the gas fraction. A *corrected-CC*
 16 *gas* was estimated for the reactions performed under those conditions by adding the
 17 amount of CO_2 produced in the experiment at pH 11. No significant differences were
 18 found between the *CC gas* of the reaction carried out at initial pH 11 and the *corrected-*
 19 *CC gas* at 13 and 13.5. Therefore, the in-situ removal of CO_2 did not affect to the total
 20 carbon conversion to gases. The volume of gas produced decreased from 35.5 mL, for
 21 an initial pH 11, to 25.8 - 27.1 mL at 13 and 13.5. The Y_{H_2} did not change significantly
 22 with the initial pH of the wastewater (8.7 - 9.0 mmol $\text{H}_2/\text{g COD}$) and the amount of
 23 alkanes was similar in all the experiments (0.31 - 0.34 mmol). However, looking at the
 24 results in more detail, it can be seen that the molar fraction of C_2H_6 and C_3H_8 of the total

1 alkanes $((C_2H_6 + C_3H_8) / (CH_4 + C_2H_6 + C_3H_8))$ decreased from 10% at initial pH 11, to 3
 2 and 2 % at 13 and 13.5, respectively. This indicates that the addition of KOH reduce the
 3 formation of C_2^+ , probably because the dehydration-hydrogenation of alcohols is
 4 hindered [28].

5

6 Table 6. Gas volume produced, composition of the gas fraction and Y_{H_2} in the APR of
 7 SBW+KOH with Pt/ENS at different initial pH*

Initial pH	Gas produced (mL)	Gas composition (% mol)			CC gas (%)	Corrected-CC gas (%)	Y_{H_2} (mmol H ₂ /g COD)
		H ₂	CO ₂	Alkanes			
11	35.5 ± 6.9	52.7 ± 0.4	25.1 ± 0.1	22.2 ± 1.7	31.8 ± 6.1	-	8.9 ± 1.7
13	27.1 ± 1.9	70.2 ± 2.0	0	29.8 ± 2.0	15.0 ± 0.1	30.9	9.0 ± 0.9
13.5	25.8 ± 1.4	71.0 ± 1.5	0	29.0 ± 1.4	13.8 ± 0.1	29.6	8.7 ± 0.7

8 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 9 of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

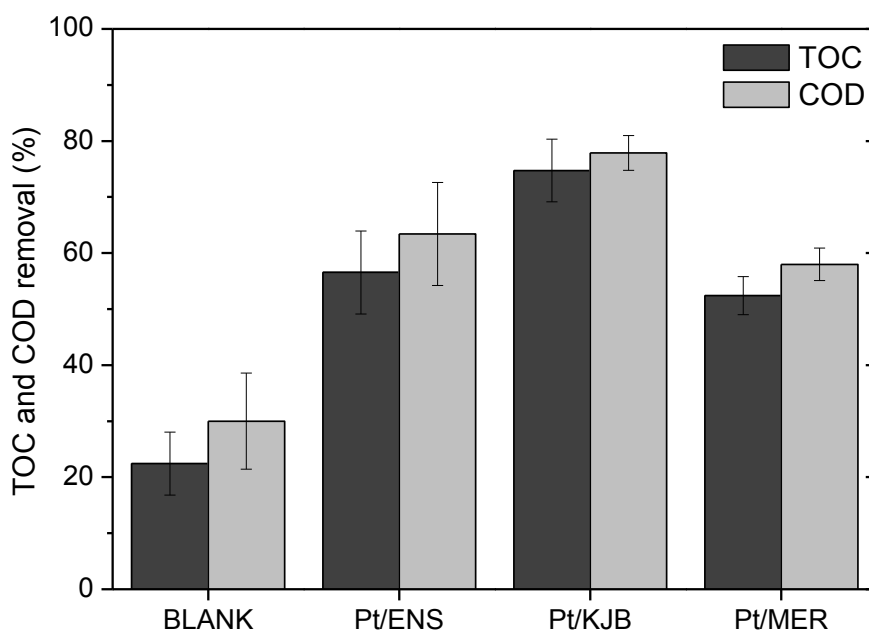
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11 3.5. APR of real brewery wastewater

12 The study of the treatment by APR of RBW was carried out with a sample of pH_i
 13 11, from a brewing plant. However, as indicated above, RBW with pH values even
 14 higher can be generated depending on the dosage of alkali used in the CIP operations
 15 and could contribute to total or partial removal of CO₂ from the resulting gas without
 16 affecting significantly the production of valuable gases. The percentages of TOC and
 17 COD removal upon APR of that RBW are depicted in Figure 5. They ranged between
 18 22 - 75% and 30 - 78%, respectively. The lowest values corresponded to the blank
 19 which undergoes basically HTC at a lower than the SBW previously tested. The results
 20 show that minor components of RBW are determining in the case of blank experiments,
 21 as observed in other works showing that complex carbohydrates contribute largely to
 22 the formation of hydrochar [37]. The removal of TOC and COD from SBW and RBW
 23 was equivalent with Pt/ENS and Pt/KJB and slightly lower with Pt/MER.

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3 Figure 5. TOC and COD removal after APR runs with different catalysts

4 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
5 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

6

7 Table 7 shows the concentration of short chain carboxylic anions and the pH values
8 measured before and after APR of RBW. The concentrations of acetate, formate and
9 glycolate significantly increased in the blank experiments. The amount of those species
10 in the starting RBW corresponded to 6% of the TOC and this proportion increased to
11 34% in the blank experiment, being two-fold the percentage achieved in the blank
12 experiments previously conducted with SBW. In the catalysed APR reactions the
13 formate concentration hardly changed, while the concentration of acetate, glycolate and
14 maleate increased significantly, leading to final pH values between 7 and 8. Moreover,
15 the Pt/MER catalyst yielded higher glycolate concentration than the other catalysts, as
16 observed in the APR of SBW as well. In the APR of RBW, in contrast to SBW, the

1 proportion of carboxylic anions in the remaining TOC was higher with the Pt/KJB
 2 catalyst (60% of final TOC) than with the Pt/MER one (44%).

3

4 Table 7. Short chain carboxylic anions and final pH upon APR of RBW by APR with
 5 different catalysts ($\text{pH}_i = 11$)*

Initial	172 ± 10	37 ± 3	39 ± 3	4 ± 1	-
BLANK	449 ± 13	260 ± 3	463 ± 3	0	7
Pt/ENS	481 ± 13	44 ± 7	242 ± 7	25 ± 3	8
Pt/KJB	420 ± 8	30 ± 2	109 ± 2	12 ± 4	8
Pt/MER	386 ± 17	31 ± 2	504 ± 7	26 ± 1	8

6 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 7 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

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9 Table 8 shows the volume and composition of the gas fraction, *CC gas* and Y_{H_2} from
 10 the APR of RBW. The lowest *CC gas* (3%) was obtained in the blank experiments. The
 11 carbon-black catalyst (Pt/ENS and Pt/KJB), yielded *CC gas* between 27 and 40%,
 12 significantly higher than the obtained with Pt/MER. Likewise, those catalysts gave the
 13 highest *CC gas* from both SBW and RBW, being similar with Pt/ENS and significantly
 14 higher from the real wastewater with the Pt/KJB catalyst. The H_2 yield in the last case
 15 reached 12.9 mmol H_2/g COD (≈ 309.1 mL H_2/g COD), which is equivalent to the
 16 highest H_2 yield found in our previous work with SBW but at higher temperature (498
 17 K, 12.2 mmol H_2/g COD) [16]. This H_2 yield achieved doubles the optimized value
 18 reported from anaerobic biological treatment (149.6 mL H_2/g COD) [36].

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1 Table 8. Gas volume produced, composition of the gas fraction, *CC gas* and Y_{H_2} in the
 2 APR of RBW

Sample	Gas produced (mL)	Gas composition (% mol)			<i>CC gas</i> (%)	Y_{H_2} (mmol H ₂ /g COD)
		H ₂	CO ₂	Alkanes		
BLANK	1.6 ± 0.1	0.9 ± 0.6	94.2 ± 2.1	3.6 ± 0.2	3.3 ± 0.1	< 0.1
Pt/ENS	26.3 ± 4.1	51.1 ± 3.2	28.8 ± 2.1	20.1 ± 1.1	27.0 ± 4.0	7.8 ± 1.4
Pt/KJB	41.2 ± 2.4	53.6 ± 6.3	26.5 ± 5.6	19.9 ± 0.7	40.0 ± 2.9	12.9 ± 2.3
Pt/MER	4.7 ± 0.9	11.7 ± 6.9	78.9 ± 7.6	9.4 ± 0.7	8.5 ± 1.0	0.3 ± 0.3

3 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 4 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

5

6 4. Conclusions

7 The APR of brewery wastewater was studied using different Pt/C catalysts (3 wt. %) and alkaline agents (NaOH, KOH) in order to assess the influence of the basicity conferred to wastewaters by CIP operations. TOC and COD removal in blank experiments was between 40 - 60%, mainly ascribable to hydrothermal carbonization of organic substrates, while removal values were higher when catalysts were used (up to 83%). The addition of NaOH or KOH to SBW resulted in slightly lower TOC and COD removal, although an increase in the percentage of valuable gases (H₂ and alkanes) and H₂ yield was observed, mainly when KOH was added. Catalysts supported on carbon blacks showed better performance in the APR of SBW in terms of gas production, carbon conversion to gas and H₂ yields, respect to activated carbons due to higher basicity. Pt/ENS yielded the highest percentage of valuable gases in the gas fraction (~75%) and the highest H₂ yield (8.9 mmol H₂/g COD) in the APR of SBW+KOH with an initial pH of 11. Increasing the initial pH of SBW+KOH up to pH 13 and 13.5, led to CO₂-free H₂ without modifying the H₂ yield. Virtually CO free H₂ was also obtained, which relevant in applications such as fuel cells. The results obtained with SBW or RBW were relatively similar, indicating that SBW is a good representative of RBW for testing as a wastewater treatment and valorisation approach. However, the different H₂

1 yields obtained with Pt/KJB from SBW and RBW suggest that the composition of the
2 wastewater needs to be considered for the sake of optimization.

3 **Acknowledgements**

4 The authors greatly appreciate financial support from Spanish AEI (CTQ2015-
5 65491-R). A. S. Oliveira thanks the Spanish AEI a research grant (BES-2016-077244)
6 and B. Saenz de Miera thanks the Regional Government of Madrid a predoctoral grant
7 (PEJD-2017-PRE/AMB-3670).

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22

1 **Effect of basicity in the aqueous phase reforming of brewery**
2 **wastewater for H₂ production**

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8 **Abstract**

9 Real (RBW) and synthetic brewery wastewater (SBW) were treated by aqueous phase
10 reforming (APR) with different 3%Pt/C catalysts for H₂ production from the biomass-
11 derived organic load. APR enabled simultaneous treatment of the wastewater and
12 valorisation to H₂ and alkanes of the biomass-derived organic load. In the catalytic APR
13 of SBW, TOC and COD removal was higher than 60% after reaction time of the
14 experiments. The addition of KOH or NaOH to SBW resulted in a slightly lower TOC
15 and COD removal, however higher yields to H₂ and percentage of valuable gases were
16 obtained in those cases where KOH was added. Catalyst with basic support and low
17 contribution of micropores showed the best performance in the APR of SBW+KOH
18 (~50% of H₂ and 8.9 mmol H₂/g COD). The concentration of anions detected in the
19 liquid effluents varied with the catalysts tested and with the concentration of base,
20 suggesting different reaction pathways. Increasing the concentration of KOH led to
21 CO₂-free H₂ without significant changes in H₂ yield. The results obtained with RBW
22 were in good agreement with those from SBW, although the significantly different
23 behaviour of some catalysts suggests the need of tuning their properties according to the
24 composition of the wastewater.

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26 **Keywords:** hydrogen, brewery wastewater, aqueous phase reforming, basicity

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1. Introduction

The circular economy approach has attracted much interest in the last few years, given the current scenario of high dependence on fossil fuels and human-borne climate change. This approach involves, among others aspects, transitioning from fossil-based to renewable energy sources and a more efficient use of raw materials and products, aimed to minimize waste and pollution. In this context, aqueous phase reforming (APR) has gained an increasing attention since the pioneering work of Cortright *et al.* [1], where the production of valuable gases, such as H₂, from biomass-derived compounds was reported. The APR process can be described by the overall reforming reaction shown in Eq. (1), although other reactions, such as the water-gas shift reaction (WGS), methanation, Fischer-Tropsch, dehydrogenation or dehydration/hydrogenation also occur in different extent [1].

(1)

Oxygenated organic species, such as sorbitol, xylitol, glycerol, galactitol, ethanol, 1-propanol or ethylene glycol, among others, have been extensively studied as substrates for APR [2–7], showing promising results in terms of carbon conversion into gases and valuable gas products. On the other hand, a diversity of catalytic systems, mainly based on VIII group metals, have been described in the literature for APR of oxygenated hydrocarbons [8,9]. Ru and Re catalyst exhibited a higher selectivity to alkanes [10], while Pt-based catalysts showed to be the most active and selective toward H₂ among monometallic catalysts [11]. Nickle has been considered as an economic alternative leading to high selectivity to alkanes, although low stability was observed for this type of catalysts [12]. While bimetallic catalysts were shown to have better performance in selected applications [11,13,14]. The effect of the support on the performance of the catalysts was also investigated in literature, where a large number of studies were

1 conducted using Pt supported on Al₂O₃ [11]. Due to the limited stability of Al₂O₃ under
2 APR conditions, carbon-based catalysts have also been studied [13–15]. Some authors
3 have reported a higher H₂ yield and catalytic activity using basic supports, while higher
4 alkanes production was achieved using neutral and acids supports [4]. However, in our
5 previous work on brewery wastewater APR we observed that, in addition to basic
6 character, texture properties of the support were also important and the best catalytic
7 performance was observed for catalysts supported on mesoporous carbon black with
8 virtually no microporosity and basic pH slurry [16].

9 Concerning the feasibility of the process, techno-economical studies on APR have
10 shown that the cost of the substrate has an important impact on the economy of the
11 process [17]. Therefore, feeding APR processes with waste materials is worthwhile to
12 investigate. With this perspective, the APR process could be extended to new
13 applications such as the treatment of wastewater. Some exploratory works on the
14 potential of APR for the treatment of different wastewaters have been reported by our
15 group [16,18]. However, regarding potential applications, more knowledge is needed on
16 the effect of complex matrices in the catalysts performance, a crucial issue scarcely
17 studied in the literature so far. Most of the works are related to synthetic matrices,
18 which mainly consisting in of mixtures of compounds (methanol, acetic and phosphoric
19 acids, NaOH, etc.) with glycerol as main ingredient, emulating the aqueous fraction
20 from biodiesel production in biorefineries [19,20]. In spite of the experience gathered,
21 the role of bases (i.e KOH, NaOH) in the reaction medium is not well addressed.

22 Several authors have reported positive effects of a basic medium on the APR
23 process due to favoured WGS reaction [21,22], in-situ removal of CO₂ [21–23], or
24 increased gas production [19]. However, some authors indicated a negative effect on
25 catalyst deactivation [20]. For instance, in the case of glycerol using Ni-La/Al₂O₃

1 catalysts, some authors [19] reported that the presence of acetic acid decreased gas
2 production, while KOH increased it. In another related study [20] using similar
3 catalysts, the effect of different acids (phosphoric, sulphuric and acetic) and bases
4 (KOH and NaOH) on the APR of glycerol was investigated, concluding that these
5 compounds affected to catalyst deactivation, particularly in the case of phosphoric acid
6 and KOH.

7 Regarding the application of APR to wastewater treatment, bases are relevant since
8 they are present in a number of industrial wastewaters due to the cleaning-in-place
9 (CIP) operations commonly used in industries such as processing food, beverages,
10 brewing or pharmaceuticals, among others. In general, the CIP cycle involves several
11 water-consuming steps, above ambient temperatures and the use of caustic solutions,
12 leading to basic wastewaters that cannot be treated by conventional biological methods
13 without previous neutralization.

14 In a recent work [16], we explored the application of APR for the treatment of a
15 synthetic brewery wastewater with an initial pH of about 7 and obtained fairly good
16 results in terms of TOC and COD removal (up to 99%) and valuable gases yield (up to
17 12.2 mmol H₂/g COD_{initial}), showing the potential of APR for the treatment of this sort of
18 effluents. In the current work, the effect of NaOH and KOH concentration on the
19 catalysts performance in APR of synthetic brewery wastewater is analysed. NaOH and
20 KOH are commonly found in the formulation of detergents for CIP systems used in
21 breweries, therefore, they were the bases selected for this study. Likewise, a real
22 brewery wastewater has been tested to learn on the potential of application APR to these
23 effluents.

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2 **2. Experimental**

3 *2.1. Materials*

4 Malt extract, yeast extract, peptone, maltose (D-(+)-Maltose monohydrate from
5 potato, $\geq 99\%$), ammonium sulfate ($\geq 99\%$), NaOH ($\geq 99\%$) and KOH ($\geq 99\%$)
6 hexachloroplatinic acid solution (H_2PtCl_6 , 8% wt. in H_2O) were purchased from Sigma-
7 Aldrich. Ethanol ($\geq 99.5\%$) was supplied by Panreac AppliChem. Commercial activated
8 carbons Norit®CAPSUPER (CAP) and Merck (MER) were supplied by Norit and
9 Merck, respectively. Commercial carbon black ENSACO 250G (ENS) and Ketjenblack
10 EC-600JD (KJB) were purchased by Timcal and Akzonobel, respectively.

11 *2.2. Preparation and characterization of supports and catalysts*

12 Pt/C (3 wt. % Pt, carbon basis) catalysts were prepared by incipient wetness
13 impregnation using two commercial activated carbons (CAP and MER) and two carbon
14 blacks (ENS and KJB) as supports. After impregnation, the samples were dried at 333 K
15 overnight in an oven. Finally, the catalysts were calcined at 473 K (2 h) and reduced
16 with 25 N mL/min H_2 flow at 573 K (2 h). The Pt concentration used was selected in
17 preliminary experiments and was already tested in previous works [16,18]. The use of a
18 higher load was not considered because it may lead to nanoparticles agglomeration in
19 supports with low surface area, as in the case of ENS. Previous works also showed a
20 good stability of Pt/C catalyst under simulated and real APR conditions, with low
21 significance changes in nanoparticles size, metal oxidation state and catalytic activity
22 [16,24].

23 The catalysts were characterized by scanning transmission electron microscopy
24 (STEM) using a JEOL - 3000F at 300 kV microscope. The mean size of the Pt
25 nanoparticles (NPs) and the size distribution were calculated by averaging more than

1 200 NPs randomly distributed in digital STEM images using the software ‘ImageJ
2 1.51k’. The porous texture of the supports and catalysts was characterized by nitrogen
3 adsorption-desorption at 77 K (TriStar II, Micromeritics). Also, pH slurry
4 measurements were carried out by measuring the pH of an aqueous suspension in
5 distilled water (1 g of solid per 10 ml of water).

6 *2.3. APR experiments and analytical procedures*

7 Synthetic and real brewery wastewater were used as substrates. Synthetic brewery
8 wastewater (SBW) was prepared using malt extract (1 g/L), yeast extract (0.5 g/L),
9 peptone (0.15 g/L), maltose (0.86 g/L), ammonium sulfate (1 g/L) and ethanol (2.8
10 mL/L) based on typical compositions found in brewery wastewater according to the
11 literature [25]. NaOH and KOH were added to adjust the pH of SBW in order to
12 evaluate the effect of these bases and their concentration on the catalysts performance in
13 APR. The pH of SBW was 7, and was adjusted to 11 for some experiments since this is
14 the pH value for the real brewery wastewater (RBW) studied. This last was collected
15 from the plant of an international brewing company based nearby Madrid (Spain).

16 APR runs were performed in stainless steel batch reactors (BR100, Berghoff) at 493
17 K and 24 - 28 bar (initial Ar pressure set at 5 bar) during 4 h, using 0.3 g of catalysts in
18 15 mL of reaction volume under Ar atmosphere. The reactors were purged with Ar
19 several times before each run. The gases were collected in multilayer foil sample bags
20 (Supelco) and the volume was measured by a gas burette and expressed in normal
21 conditions (NTP). The aqueous phase was characterized by Total Organic Carbon
22 (TOC) measured in a TOC-VCSH apparatus (Shimadzu), Chemical Oxygen Demand
23 (COD) determined according to the standard method (ASTM D1252), and ionic
24 chromatography (883 Basic IC Plus, Metrohm). The gas phase was analyzed by a

1 GC/FID/TCD (7820A, Agilent) using 2 packed columns and a molecular sieve allowing
2 to detect H₂, CO, CO₂, CH₄, C₂H₆ and C₃H₈.

3 The TOC and COD removal (%) were determined as the difference between the
4 initial and final TOC or COD values divided by the initial value (mg/L). Carbon
5 conversion to gases (*CC gas* (%)) was calculated from the ratio between C content (g)
6 in the gaseous products and C content (g) in the initial wastewater. H₂ yield (*Y_{H2}*) was
7 defined as the amount of H₂ produced (mmol) divided by the initial COD (g).

8 3. Results and Discussion

9 3.1. Catalysts and supports characterization

10 Table 1 shows the specific surface area (*S_{BET}*), micropore and mesopore volume,
11 and pH slurry of the supports and catalysts prepared. The supports used covered in a
12 wide range of *S_{BET}* (65 - 1750 m²/g), micropore (< 0.001 - 0.66 cm³/g) and mesopore
13 volumes (0.09 - 1.67 cm³/g) and pH slurry (2.9 - 10.6). The carbon black supports (ENS
14 and KJB) showed basic pH slurry and did not present significant micropore volume (<
15 0.001 cm³/g), whereas the activated carbons yielded either acid or basic pH slurry and a
16 significant contribution of micropore volume (0.38 - 0.48 cm³/g). The catalysts prepared
17 presented slightly lower values of *S_{BET}* and pore volume than the corresponding
18 supports due to partial pore blockage by the Pt NPs. The pH slurry of the catalysts did
19 not present any significant difference in comparison to the supports.

20

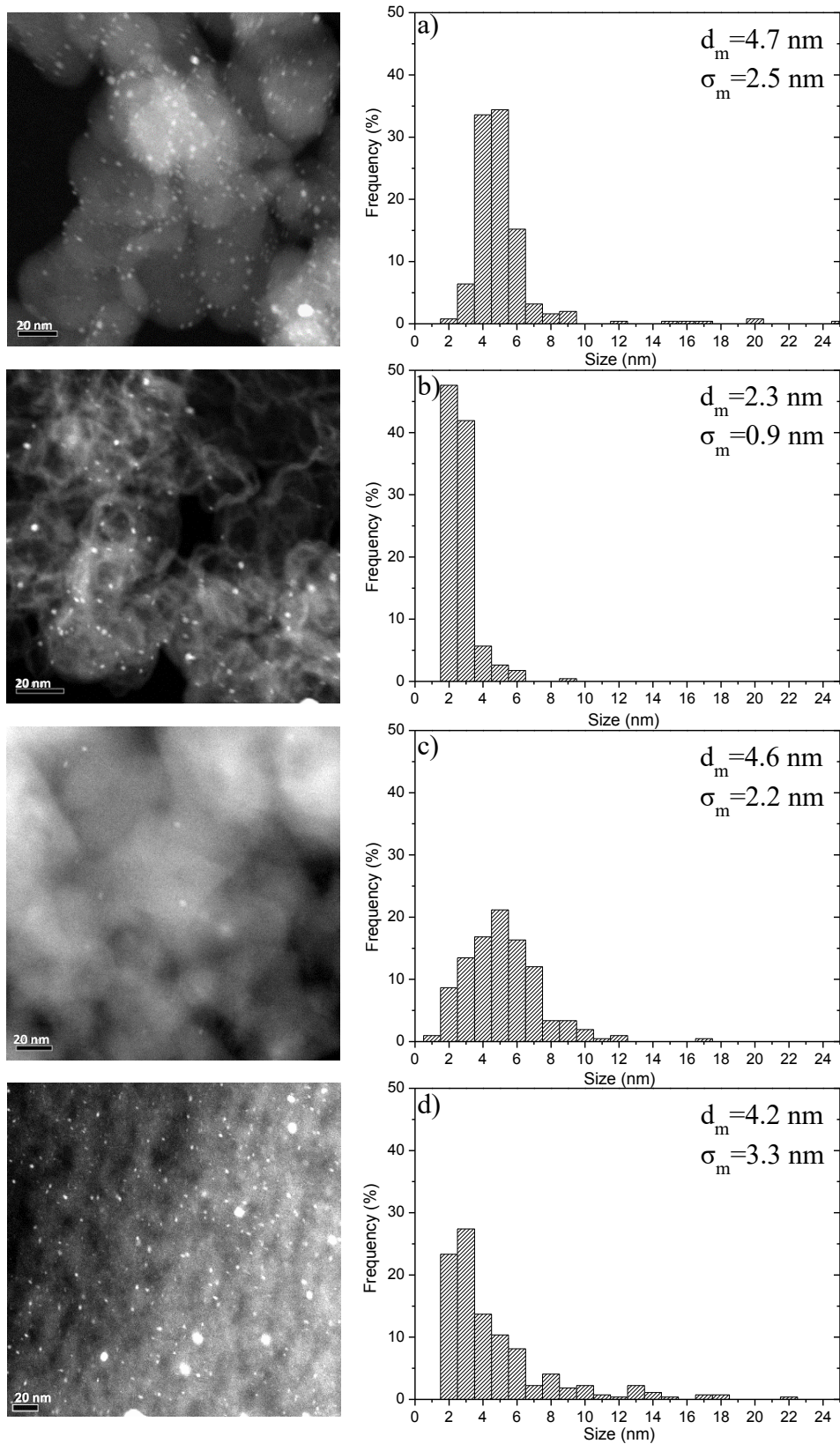
21 Table 1. *S_{BET}*, micropore and mesopore volume, and pH slurry of the supports and
22 catalysts

Support/ catalyst	<i>S_{BET}</i> (m ² /g)	Micropore Volume (cm ³ /g)	Mesopore Volume (cm ³ /g)	pH slurry
ENS	65	< 0.001	0.09	8.9
KJB	1415	< 0.001	1.67	10.6
MER	930	0.38	0.15	8.3
CAP	1750	0.48	0.75	2.6

Pt/ENS	65	< 0.001	0.09	8.6
Pt/KJB	1350	< 0.001	1.59	10.2
Pt/MER	910	0.38	0.14	8.5
Pt/CAP	1360	0.31	0.75	2.9

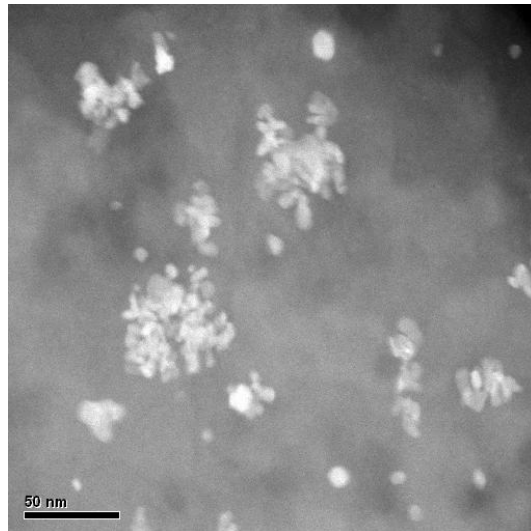
1 Figure 1 shows STEM images and the corresponding size distribution of the Pt NPs
2 in the catalysts. The mean NPs size and size distribution for the Pt/ENS, Pt/MER and
3 Pt/CAP catalysts were quite similar, in the 4.2 - 4.7 nm range, while the Pt/KJB one
4 gave a smaller value of mean NPs size (2.3 nm). In addition, it should mention that the
5 Pt NPs of the Pt/MER catalyst, in some STEM images, showed a higher agglomeration
6 than in the other catalysts (Figure 2).

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2 Figure 1. STEM images of a) Pt/ENS, b) Pt/KJB, c) Pt/MER and d) Pt/CAP catalysts



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2 Figure 2. STEM image of agglomeration of Pt NPs in the Pt/MER catalysts

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4 *3.2. Synthetic and real brewery wastewater characterization*

5 The characterization of the SBW and RBW, including TOC, COD, pH and main
6 anions analysed, is summarized in Table 2. The RBW showed TOC and COD values of
7 1646 and 4674 mg/L, respectively. The pH of RBW was basic (pH 11) since it contains
8 significant amounts of the NaOH commonly used in the CIP operations carried out in
9 the food processing and beverages industry. The main organic anions detected
10 correspond to short chain organic acids, which are commonly present in malt extract
11 [26]. The SBW was prepared with a TOC and COD of 1871 and 5846 mg/L,
12 respectively, which are close to above values for RBW and in good agreement with the
13 range of TOC and COD reported for this type of wastewater [25]. The starting pH of
14 SBW was neutral. The main differences found between SBW and RBW in terms of
15 anions composition were relative to acetate and sulfate, which were in significantly
16 higher and lower concentration, respectively, in the case of RBW.

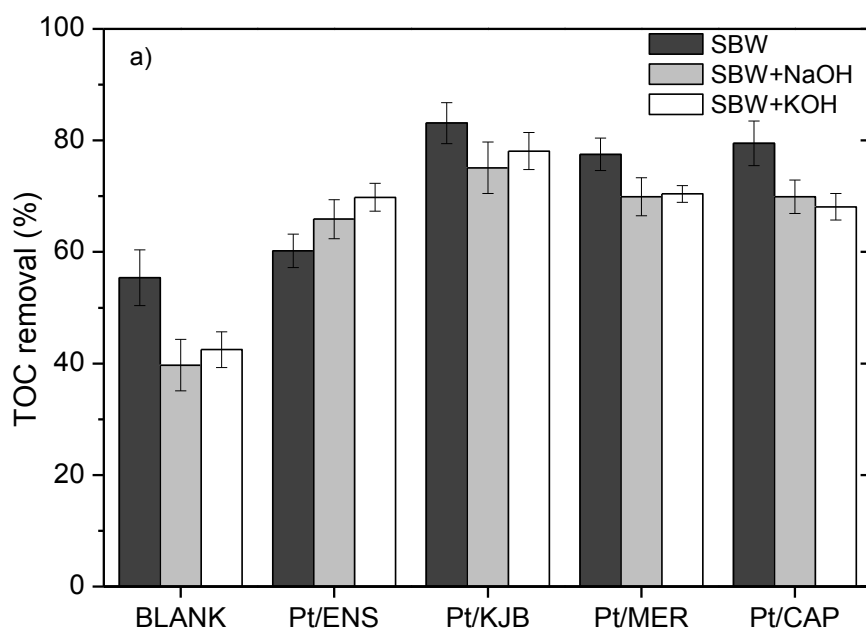
1 Table 2. Characterization of the SBW and RBW

Wastewater	TOC (mg/L)	COD (mg/L)	pH_i	Acetate (mg/L)	Formate (mg/L)	Glycolate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Maleate (mg/L)
SBW	1871 ± 79	5846 ± 331	7	2 ± 1	1 ± 1	8 ± 1	18 ± 3	678 ± 78	-
RBW	1646 ± 230	4764 ± 586	11	172 ± 10	37 ± 3	39 ± 3	15 ± 1	41 ± 4	4 ± 1

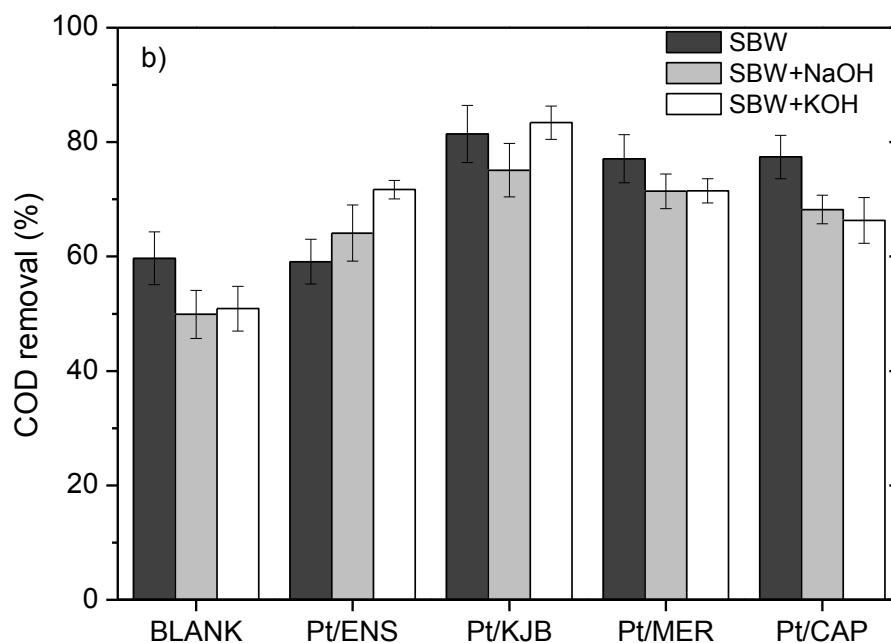
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3 *3.3. APR of synthetic brewery wastewater*

4 Figure 3 depicts the TOC and COD removal in the blank (without catalyst) and
5 catalysed APR experiments with SBW. Likewise, the results of the experiments with
6 SBW modified with NaOH (SBW+NaOH) or KOH (SBW+KOH) up to a pH value of
7 11 are included. The lowest TOC and COD removal (40 - 60%) corresponded to the
8 blank and can be ascribed mostly to hydrothermal carbonization (HTC) of the organic
9 substrates, which is favoured under the operating conditions used [27]. In general, the
10 TOC and COD removal were higher when catalysts were used, particularly in the case
11 of Pt/KJB, Pt/MER and Pt/CAP, which reached removal values close to 70%. The
12 addition of KOH and NaOH to SBW provoked a slight decrease in TOC and COD
13 removal in all experiments, except with Pt/ENS catalyst. Base addition increased the
14 selectivity towards liquid phase products, probably through base-catalysed dehydration
15 followed by hydrogenation reactions [28], thus reducing the TOC and COD removal.
16 No significant differences in TOC and COD removal were found by using NaOH or
17 KOH in the experiments with SBW.



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4 Figure 3. a) TOC and b) COD removal in APR runs for SBW ($pH_i = 7$), and for
5 SBW+NaOH and SBW+KOH ($pH_i = 11$)*

6 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
7 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

1
2 Table 3 shows the concentration of short chain carboxylic anions and the pH values
3 measured before and after APR runs. Acetate, formate and glycolate were the most
4 representative in the initial SBW. These three anions significantly increased their
5 concentration in experiments without catalyst (blank), especially in the case of
6 SBW+NaOH and SBW+KOH. During the HTC process organics acids such as formic,
7 acetic and levulinic acids are produced from biomass-derived organic compounds.
8 Some authors [29] have reported that basic conditions significantly affect the
9 decomposition pathway of hydroxymethylfurfural (HMF), which is converted to
10 levulinic or formic acid, increasing the concentration of these acids. In the catalytic
11 APR test, the concentration of these anions decreased in general, particularly in the case
12 of formate, indicating that conversion of the initial substrates takes place upon APR
13 reactions through mechanisms different from those of HTC. Acetate concentration was
14 barely affected by the operating conditions, indicating its refractory character, whereas
15 the glycolate concentration was very sensitive to the type of catalyst, being higher in the
16 SBW+NaOH and SBW+KOH experiments. The carboxylic anions from the blank
17 experiments amounted 9 - 19% of the final TOC, this increasing to 13 - 24% with bases
18 addition. Moreover, the Pt/MER and Pt/CAP catalysts yielded in general effluents with
19 higher glycolate concentration and percentage of short chain carboxylic anions in the
20 final liquid phase of TOC (20 - 24%). A similar observation was made by King *et al.*
21 [28] in the APR of glycerol, who found a higher production of acids with the addition of
22 a base to the reaction medium. They suggested that KOH could promote the Cannizzaro
23 reaction, facilitating the production of acids. Another study using in situ X-ray
24 absorption spectroscopy reported a higher selectivity to acids (four-fold) upon addition
25 of KOH ($\text{pH}_i = 11.8$) in the APR of glycerol [30]. This effect was explained through the

1 interaction between KOH and adsorbed reaction intermediates, especially aldehydes, on
 2 the surface of Pt. The final pH of the effluents was 3 - 4 in the APR runs with SBW
 3 (starting pH = 7), whereas it ranged between 6 and 8 in the SBW+NaOH and
 4 SBW+KOH experiments, when amounts of acids were produced, giving rise to base
 5 neutralization.

6

7 Table 3. Short chain carboxylic anions in the effluents from the SBW, SBW+NaOH and
 8 SBW+KOH APR experiments*

Sample	Wastewater	Short chain carboxylic anions (mg/L)			Initial pH	Final pH
		Acetate	Formate	Glycolate		
Initial	SBW	2 ± 1	1 ± 1	8 ± 2	7	-
BLANK	SBW	74 ± 9	66 ± 7	105 ± 9	7	3
	SBW+NaOH	123 ± 11	118 ± 14	221 ± 12	11	8
Pt/ENS	SBW	126 ± 12	121 ± 13	209 ± 10	11	7
	SBW+NaOH	98 ± 6	2 ± 1	64 ± 5	7	4
Pt/KJB	SBW+NaOH	104 ± 9	10 ± 4	103 ± 8	11	8
	SBW+KOH	106 ± 7	6 ± 3	82 ± 9	11	8
Pt/MER	SBW	61 ± 5	1 ± 1	34 ± 2	7	3
	SBW+NaOH	80 ± 4	6 ± 1	111 ± 6	11	8
Pt/CAP	SBW+KOH	89 ± 5	7 ± 1	91 ± 8	11	8
	SBW	79 ± 5	4 ± 1	102 ± 8	7	3
Pt/CAP	SBW+NaOH	71 ± 3	12 ± 2	199 ± 10	11	8
	SBW+KOH	73 ± 6	14 ± 1	200 ± 12	11	7
Pt/CAP	SBW	117 ± 8	1 ± 1	67 ± 3	7	3
	SBW+NaOH	72 ± 4	19 ± 3	249 ± 11	11	6
	SBW+KOH	100 ± 6	11 ± 2	256 ± 12	11	6

9 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 10 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

11

12 Table 4 summarizes the gas volume produced, gas composition, *CC gas* and H₂
 13 yield in the APR experiments. The volume of gas produced varied within a wide range
 14 (1.0 - 40.1 mL), with the blanks showing the lowest production (1.0 - 2.2 mL). The
 15 blanks gave *CC gas* between 1.7 - 3.8%, consisting mainly of CO₂ (50 - 87%) with low
 16 H₂ yields (< 0.03 mmol H₂/g COD). CO was only detected in the blank experiments,
 17 representing 9% of the gas fraction from the APR of SBW and reaching more than 30%

1 from SBW+NaOH and SBW+KOH. The catalysts supported on carbon blacks showed a
2 gas production between 12.2 and 40.1 mL, with *CC gas* in the 15.8 – 41.3% range and
3 H₂ yields between 1.4 and 8.9 mmol H₂/g COD. These values were significantly higher
4 than the obtained with the activated carbon supported catalysts (gas volume: 2.9 - 8.4
5 mL; *CC gas*: 3.7 - 15.1%; H₂ yield: 0.05 - 0.15 mmol H₂/g COD). This frankly higher
6 production of H₂ can be attributed to the fact that the ENS and KJB carbon blacks are
7 basic supports that can enhance the WGS reaction. Some authors [21] have suggested
8 that the basic medium can favors the polarization and dissociation of H₂O, providing
9 hydroxyl anions that can be adsorbed on the catalysts surface, enhancing the WGS
10 reaction [31]. However, the Pt/MER catalyst yielded basic pH slurry while giving low
11 amounts of H₂ and other gases. This behavior of the Pt/MER catalyst can be related to
12 its porous texture, since the MER support has a high contribution of micropores
13 opposite to ENS and KJB. That would determine severe mass transfer limitations of
14 reactants and products, resulting in low gas production, H₂ selectivity and yield [32–34].
15 The Pt/CAP catalyst has an important contribution of mesopores, but both the presence
16 of micropores and the low pH slurry of the support may causes the low H₂ production
17 observed, similar to that of Pt/MER.

18 Regarding the effect of the addition of bases to the wastewater, it has been reported
19 [21,22] that CaO or KOH can favour the WGS reaction by gas withdrawal through the
20 in-situ removal of CO₂, displacing the reactions towards H₂ production. In the current
21 work the addition of bases led to lower percentages of CO₂ in the gas fraction with all
22 the catalysts tested, particularly in the experiments with SBW+KOH, indicating that the
23 addition of a base was effective for the removal of CO₂. However, the Y_{H_2} in the
24 SBW+KOH and SBW+NaOH experiments was higher than in the SBW ones only with
25 the Pt/KJB catalyst. King *et al.* [28] studied the effect of KOH addition in the APR of

1 glycerol using 3%Pt/C and 3%Pt-Re/C catalysts and found a dramatic increase of
2 glycerol conversion. However, they reported a higher production of liquids, being the
3 gas product, and H₂ yield barely affected. Likewise, they suggested that the addition of
4 KOH favoured the C-O bond cleavage, compared to C-C bond cleavage, by base-
5 catalysed dehydration followed by hydrogenation that reduces the H₂ production. Karim
6 *et al.* [30] also found similar results in the APR of glycerol with Pt/C catalysts. The
7 addition of KOH did not affect the gas phase products, while a higher glycerol
8 conversion was observed. These authors also attributed the results to a higher selectivity
9 toward dehydration reactions, which was reflected in a higher C-O/C-C ratio and lower
10 H₂ and CO₂ selectivities in the presence of that base.

11 Comparing the bases used, the highest percentage of H₂ was obtained with KOH.
12 The experiments carried out with SBW+KOH also led to higher gas production, *CC*
13 *gas*, Y_{H_2} , and in some cases a lower percentage of alkanes in the gas fraction. This can
14 be better appreciated for the catalysts that yielded higher amounts of gases (Pt/ENS and
15 Pt/KJB). Similar results were obtained by Liu *et al.* [21] in the APR of ethylene glycol
16 using Ni catalysts with different potassium salts and NaOH. The authors concluded that
17 KOH leads to higher *CC gas* and Y_{H_2} and lower alkanes yields, probably due to
18 blockage of active sites enabling CO methanation. The addition of K to Pt/hydrotalcite
19 catalysts was studied in the APR of glycerol [35] and the results showed that it
20 enhanced the basicity of the catalysts and increased the glycerol conversion and H₂
21 selectivity, although an excess of K loading blocked the active sites of Pt NPs, having
22 the opposite effect.

23 In the SBW+KOH experiments the Pt/ENS catalyst gave the highest percentage of
24 valuable gases (H₂ and alkanes) in the gas fraction (~ 75%) and H₂ yield (8.9 mmol H₂/g
25 COD ≈ 213.6 mL H₂/g COD). This production of gas is higher than the reported in the

1 literature from the anaerobic biological treatment of an equivalent brewery wastewater
 2 (initial COD ca. 6000 mg/L, 149.6 mL H₂/g COD) [36], thus showing the potential of
 3 APR as way of valorisation of brewery wastewater.

4

5 Table 4. Gas volume produced, composition of the gas fraction, *CC gas* and Y_{H_2} in the
 6 APR of SBW (pH_i = 7), SBW+NaOH (pH_i = 11) and SBW+KOH (pH_i = 11)*

Sample	Wastewater	Gas Volume (mL)	Gas composition (% mol)			CC gas (%)	Y_{H_2} (mmol H ₂ / g COD)
			H ₂	CO ₂	Alkanes		
BLANK	SBW	2.2 ± 0.3	1.8 ± 0.3	86.8 ± 6.1	2.2 ± 0.3	3.8 ± 0.4	<0.1
	SBW+NaOH	1.0 ± 0.4	6.6 ± 1.0	50.4 ± 6.4	7.5 ± 3.5	1.7 ± 0.7	<0.1
	SBW+KOH	1.4 ± 0.4	4.2 ± 0.1	58.8 ± 7.0	6.7 ± 2.1	2.5 ± 0.7	<0.1
Pt/ENS	SBW	40.1 ± 0.5	46.7 ± 0.5	32.0 ± 0.8	21.3 ± 0.3	41.3 ± 0.9	8.9 ± 0.1
	SBW+NaOH	23.7 ± 7.1	51.4 ± 2.0	25.6 ± 1.7	23.0 ± 3.7	21.8 ± 7.5	5.8 ± 1.5
	SBW+KOH	35.5 ± 6.9	52.7 ± 0.4	25.1 ± 0.1	22.2 ± 0.4	31.8 ± 6.1	8.9 ± 1.7
Pt/KJB	SBW	12.2 ± 0.5	23.5 ± 0.6	56.9 ± 1.4	19.6 ± 0.9	17.5 ± 0.9	1.4 ± 0.1
	SBW+NaOH	12.5 ± 0.5	32.7 ± 1.0	44.5 ± 1.9	22.8 ± 1.0	15.8 ± 0.9	1.9 ± 0.1
	SBW+KOH	19.3 ± 3.5	38.6 ± 3.4	39.7 ± 2.3	21.7 ± 1.1	22.3 ± 3.1	3.5 ± 0.9
Pt/MER	SBW	4.3 ± 0.4	3.2 ± 0.8	87.4 ± 0.2	9.4 ± 0.9	7.5 ± 0.7	0.1 ± 0.1
	SBW+NaOH	2.2 ± 0.4	4.4 ± 1.3	89.6 ± 0.1	6.0 ± 1.2	3.7 ± 0.7	0.1 ± 0.1
	SBW+KOH	2.8 ± 0.4	9.5 ± 0.2	76.4 ± 1.6	14.1 ± 1.8	4.7 ± 0.6	0.1 ± 0.1
Pt/CAP	SBW	8.4 ± 0.4	1.6 ± 0.4	72.1 ± 0.7	26.3 ± 1.1	15.1 ± 0.6	0.1 ± 0.1
	SBW+NaOH	2.9 ± 0.4	5.6 ± 0.6	86.2 ± 0.4	8.2 ± 1.0	4.9 ± 0.6	0.1 ± 0.1
	SBW+KOH	2.9 ± 0.4	10.6 ± 0.1	80.3 ± 1.2	9.1 ± 1.2	4.7 ± 0.6	0.1 ± 0.1

7 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 8 of wastewater; 0.3 g catalyst; 500 rpm, 4 h.

9

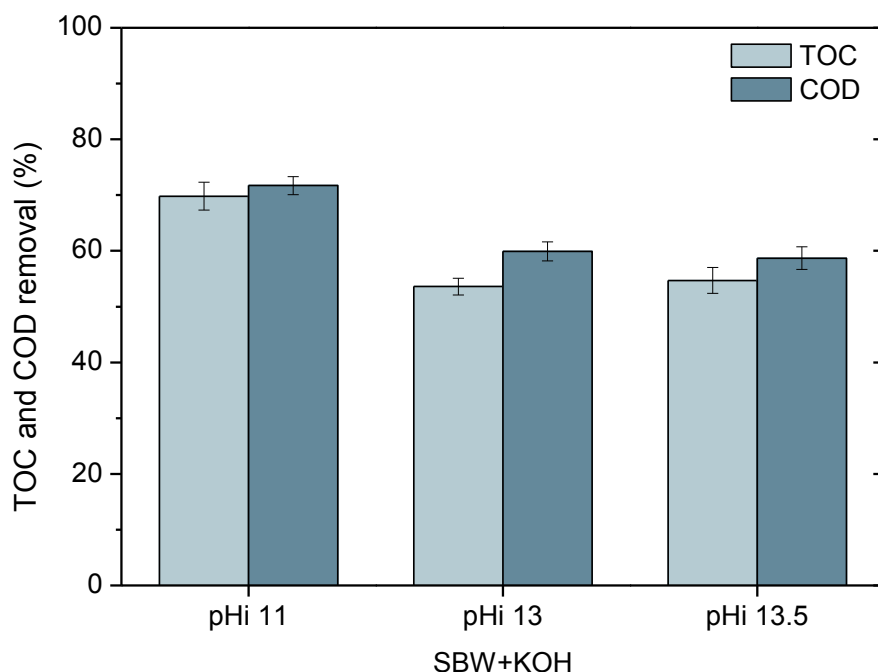
10 3.4. Effect of the pH on the catalyst performance

11 Given the good results obtained with the Pt/ENS catalyst it was selected to assess
 12 the effect of the pH in the APR of SBW+KOH. The pH values tested were selected
 13 taking into account the previous results of CO₂ production in the corresponding
 14 experiments at an initial pH value of 11. An initial pH value of 13.0 was calculated as
 15 the one providing the stoichiometric amount of KOH needed to convert all the CO₂
 16 produced, according to Eq. (2). Initial pH values below and above that value (11 and
 17 13.5, respectively) were selected.

(2)

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Figure 4 shows the TOC and COD removal achieved at these three initial pH values. Around 70% of TOC and COD removal reached at $\text{pH}_i = 11$, while lower percentages were achieved at higher pH. Similar results were found in the APR of glycerol with 3%Pt/C upon the addition of KOH ($\text{pH}_i = 12$) [28]. Therefore, this base may change the reaction pathway, increasing the production of liquids without increasing significantly the H_2 yield, due to competitive reactions involving base-catalysed dehydration followed by subsequent hydrogenation.



9

10 Figure 4. TOC and COD removal in the APR of SBW+KOH with Pt/ENS at different
11 initial pH*

12 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
13 of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

14

15 Table 5 shows the concentration of representative anions from the APR runs of
16 SBW+KOH at different initial pH values. In all cases the pH decreased along the APR
17 due to the generation of organic acids. Acetate, formate and glycolate concentration

1 was much lower at the lowest starting pH ($\text{pH}_i = 11$). The amount of these anions
 2 corresponded to 14% of the final TOC, while increasing up to 30 and 36% at 13 and
 3 13.5 initial pH, respectively. Thus confirming that organic acids formation is favoured
 4 at increased pH [28,30].

5

6 Table 5. Short chain carboxylic anions the APR of SBW+KOH with Pt/ENS at different
 7 initial pH*

Sample	Initial pH	Short chain carboxylic anions (mg/L)			Final pH
		Acetate	Formate	Glycolate	
Pt/ENS	11	106 ± 7	6 ± 3	82 ± 9	8
	13	235 ± 11	33 ± 4	392 ± 12	10
	13.5	330 ± 16	30 ± 4	419 ± 14	12

8 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 9 of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

10

11 Table 6 shows the gas volume produced, the composition of the gas fraction, *CC gas*
 12 and Y_{H_2} at the different values of initial pH tested. The *CC gas* significantly decreased
 13 from around 32%, for an initial pH of 11, to around 15% for 13 and 13.5 initial pH, due
 14 to the in-situ removal of the CO_2 giving rise to potassium carbonate. Table 6 also shows
 15 that for those initial pH values no CO_2 was found in the gas fraction. A *corrected-CC*
 16 *gas* was estimated for the reactions performed under those conditions by adding the
 17 amount of CO_2 produced in the experiment at pH 11. No significant differences were
 18 found between the *CC gas* of the reaction carried out at initial pH 11 and the *corrected-*
 19 *CC gas* at 13 and 13.5. Therefore, the in-situ removal of CO_2 did not affect to the total
 20 carbon conversion to gases. The volume of gas produced decreased from 35.5 mL, for
 21 an initial pH 11, to 25.8 - 27.1 mL at 13 and 13.5. The Y_{H_2} did not change significantly
 22 with the initial pH of the wastewater (8.7 - 9.0 mmol $\text{H}_2/\text{g COD}$) and the amount of
 23 alkanes was similar in all the experiments (0.31 - 0.34 mmol). However, looking at the
 24 results in more detail, it can be seen that the molar fraction of C_2H_6 and C_3H_8 of the total

1 alkanes $((C_2H_6 + C_3H_8) / (CH_4 + C_2H_6 + C_3H_8))$ decreased from 10% at initial pH 11, to 3
 2 and 2 % at 13 and 13.5, respectively. This indicates that the addition of KOH reduce the
 3 formation of C_2^+ , probably because the dehydration-hydrogenation of alcohols is
 4 hindered [28].

5

6 Table 6. Gas volume produced, composition of the gas fraction and Y_{H_2} in the APR of
 7 SBW+KOH with Pt/ENS at different initial pH*

Initial pH	Gas produced (mL)	Gas composition (% mol)			CC gas (%)	Corrected-CC gas (%)	Y_{H_2} (mmol H ₂ /g COD)
		H ₂	CO ₂	Alkanes			
11	35.5 ± 6.9	52.7 ± 0.4	25.1 ± 0.1	22.2 ± 1.7	31.8 ± 6.1	-	8.9 ± 1.7
13	27.1 ± 1.9	70.2 ± 2.0	0	29.8 ± 2.0	15.0 ± 0.1	30.9	9.0 ± 0.9
13.5	25.8 ± 1.4	71.0 ± 1.5	0	29.0 ± 1.4	13.8 ± 0.1	29.6	8.7 ± 0.7

8 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 9 of SBW+KOH; 0.3 g Pt/ENS catalyst; 500 rpm, 4 h.

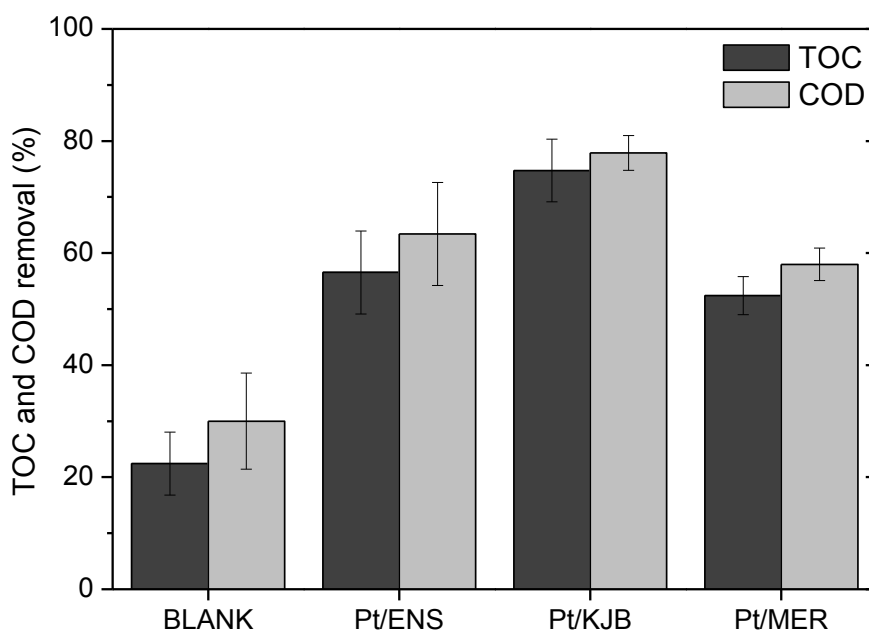
10

11 3.5. APR of real brewery wastewater

12 The study of the treatment by APR of RBW was carried out with a sample of pH_i
 13 11, from a brewing plant. However, as indicated above, RBW with pH values even
 14 higher can be generated depending on the dosage of alkali used in the CIP operations
 15 and could contribute to total or partial removal of CO₂ from the resulting gas without
 16 affecting significantly the production of valuable gases. The percentages of TOC and
 17 COD removal upon APR of that RBW are depicted in Figure 5. They ranged between
 18 22 - 75% and 30 - 78%, respectively. The lowest values corresponded to the blank
 19 which undergoes basically HTC at a lower than the SBW previously tested. The results
 20 show that minor components of RBW are determining in the case of blank experiments,
 21 as observed in other works showing that complex carbohydrates contribute largely to
 22 the formation of hydrochar [37]. The removal of TOC and COD from SBW and RBW
 23 was equivalent with Pt/ENS and Pt/KJB and slightly lower with Pt/MER.

24

1



2

3 Figure 5. TOC and COD removal after APR runs with different catalysts

4 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
5 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

6

7 Table 7 shows the concentration of short chain carboxylic anions and the pH values
8 measured before and after APR of RBW. The concentrations of acetate, formate and
9 glycolate significantly increased in the blank experiments. The amount of those species
10 in the starting RBW corresponded to 6% of the TOC and this proportion increased to
11 34% in the blank experiment, being two-fold the percentage achieved in the blank
12 experiments previously conducted with SBW. In the catalysed APR reactions the
13 formate concentration hardly changed, while the concentration of acetate, glycolate and
14 maleate increased significantly, leading to final pH values between 7 and 8. Moreover,
15 the Pt/MER catalyst yielded higher glycolate concentration than the other catalysts, as
16 observed in the APR of SBW as well. In the APR of RBW, in contrast to SBW, the

1 proportion of carboxylic anions in the remaining TOC was higher with the Pt/KJB
 2 catalyst (60% of final TOC) than with the Pt/MER one (44%).

3

4 Table 7. Short chain carboxylic anions and final pH upon APR of RBW by APR with
 5 different catalysts (pH_i = 11)*

Initial	172 ± 10	37 ± 3	39 ± 3	4 ± 1	-
BLANK	449 ± 13	260 ± 3	463 ± 3	0	7
Pt/ENS	481 ± 13	44 ± 7	242 ± 7	25 ± 3	8
Pt/KJB	420 ± 8	30 ± 2	109 ± 2	12 ± 4	8
Pt/MER	386 ± 17	31 ± 2	504 ± 7	26 ± 1	8

6 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
 7 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

8

9 Table 8 shows the volume and composition of the gas fraction, *CC gas* and Y_{H_2} from
 10 the APR of RBW. The lowest *CC gas* (3%) was obtained in the blank experiments. The
 11 carbon-black catalyst (Pt/ENS and Pt/KJB), yielded *CC gas* between 27 and 40%,
 12 significantly higher than the obtained with Pt/MER. Likewise, those catalysts gave the
 13 highest *CC gas* from both SBW and RBW, being similar with Pt/ENS and significantly
 14 higher from the real wastewater with the Pt/KJB catalyst. The H₂ yield in the last case
 15 reached 12.9 mmol H₂/g COD (\approx 309.1 mL H₂/g COD), which is equivalent to the
 16 highest H₂ yield found in our previous work with SBW but at higher temperature (498
 17 K, 12.2 mmol H₂/g COD) [16]. This H₂ yield achieved doubles the optimized value
 18 reported from anaerobic biological treatment (149.6 mL H₂/g COD) [36].

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23

1 Table 8. Gas volume produced, composition of the gas fraction, *CC gas* and Y_{H_2} in the
2 APR of RBW

Sample	Gas produced (mL)	Gas composition (% mol)			<i>CC gas</i> (%)	Y_{H_2} (mmol H ₂ /g COD)
		H ₂	CO ₂	Alkanes		
BLANK	1.6 ± 0.1	0.9 ± 0.6	94.2 ± 2.1	3.6 ± 0.2	3.3 ± 0.1	< 0.1
Pt/ENS	26.3 ± 4.1	51.1 ± 3.2	28.8 ± 2.1	20.1 ± 1.1	27.0 ± 4.0	7.8 ± 1.4
Pt/KJB	41.2 ± 2.4	53.6 ± 6.3	26.5 ± 5.6	19.9 ± 0.7	40.0 ± 2.9	12.9 ± 2.3
Pt/MER	4.7 ± 0.9	11.7 ± 6.9	78.9 ± 7.6	9.4 ± 0.7	8.5 ± 1.0	0.3 ± 0.3

3 *Reaction conditions: 493 K; total reaction pressure: 24 - 28 bar (initial Ar pressure set at 5 bar); 15 mL
4 of RBW; 0.3 g catalyst; 500 rpm, 4 h.

5

6 4. Conclusions

7 The APR of brewery wastewater was studied using different Pt/C catalysts (3 wt. %) and alkaline agents (NaOH, KOH) in order to assess the influence of the basicity
8 conferred to wastewaters by CIP operations. TOC and COD removal in blank
9 experiments was between 40 - 60%, mainly ascribable to hydrothermal carbonization of
10 organic substrates, while removal values were higher when catalysts were used (up to
11 83%). The addition of NaOH or KOH to SBW resulted in slightly lower TOC and COD
12 removal, although an increase in the percentage of valuable gases (H₂ and alkanes) and
13 H₂ yield was observed, mainly when KOH was added. Catalysts supported on carbon
14 blacks showed better performance in the APR of SBW in terms of gas production,
15 carbon conversion to gas and H₂ yields, respect to activated carbons due to higher
16 basicity. Pt/ENS yielded the highest percentage of valuable gases in the gas fraction (~
17 75%) and the highest H₂ yield (8.9 mmol H₂/g COD) in the APR of SBW+KOH with an
18 initial pH of 11. Increasing the initial pH of SBW+KOH up to pH 13 and 13.5, led to
19 CO₂-free H₂ without modifying the H₂ yield. Virtually CO free H₂ was also obtained,
20 which relevant in applications such as fuel cells. The results obtained with SBW or
21 RBW were relatively similar, indicating that SBW is a good representative of RBW for
22 testing as a wastewater treatment and valorisation approach. However, the different H₂
23

1 yields obtained with Pt/KJB from SBW and RBW suggest that the composition of the
2 wastewater needs to be considered for the sake of optimization.

3 **Acknowledgements**

4 The authors greatly appreciate financial support from Spanish AEI (CTQ2015-
5 65491-R). A. S. Oliveira thanks the Spanish AEI a research grant (BES-2016-077244)
6 and B. Saenz de Miera thanks the Regional Government of Madrid a predoctoral grant
7 (PEJD-2017-PRE/AMB-3670).

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: