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Treatment and valorisation of fruit juice wastewater by aqueous phase reforming: effect of pH, organic load and salinity

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Abstract

This work analyses the application of aqueous phase reforming as a treatment and valorisation method for fruit juice wastewater enabling production of H₂ and alkanes from renewable source. The variables considered were pH, organic load and salinity of wastewater, since they are fluctuant and can affect the performance of biological treatments most commonly used. The experiments were carried out in batchwise, at 493 K and 24-28 bar for 4 h using a 3 % Pt/C catalyst. Single compounds (glucose, fructose, citric acid, ascorbic acid, galacturonic acid) and fruit juice wastewater were tested as feedstocks. Organic carbon removal from wastewater was higher in the reforming of glucose and fructose within 7-10 pH range, while for organic acids and fruit juice wastewater a higher removal was obtained at pH 2. H₂ yield and selectivity increased at increasing pH, due to better conditions for water-gas shift reaction and abstraction of CO₂. H₂ production by aqueous phase reforming of fruit juice wastewater was little affected by pH, yielding around 6.6 mmol H₂/g initial chemical oxygen demand, in the pH range tested. Alkanes were also produced, with higher proportion of CH₄ than other alkanes at high pH (10-12). A wide operation window was observed regarding organic load of fruit juice wastewater, although organic carbon removal declined slightly at the highest loads tested. Salinity did not affect organic carbon removal, while H₂ yield decreased from 7.8 to 4.2 mmol H₂/g initial chemical oxygen demand at high salinity, probably due to catalyst deactivation. Aqueous phase reforming is proved to be an alternative to biological treatment methods with low sensibility to fluctuations in the characteristics of wastewater.

Keywords: aqueous phase reforming, fruit juice wastewater, hydrogen, wastewater treatment, biomass

1. Introduction

Aqueous phase reforming (APR) is a catalytic process for the valorisation of organic oxygenated compounds to valuable gases (mainly H_2 and alkanes) as well as other chemicals. This process takes place in the liquid phase under conditions (473-523 K and 15-50 bar) at which water-gas shift (WGS) reaction is thermodynamically favoured, generating also H_2 -rich gases with low CO content (Davda et al., 2005). In addition, APR has some advantages compared with conventional steam reforming, mainly because a lower reaction temperature is used and feedstock vaporization is not required, which significantly decreases energy input (Davda et al., 2005) and eliminates undesirable side reactions occurring at high temperatures (Larimi et al., 2016).

Different metal supported catalysts have been tested for APR, such as Pt, Pd and Ru, with Pt being one the most active and selective to H_2 (Davda et al., 2003). Pt allows C-C bond cleavage with low C-O cleavage rates and enhances WGS reaction (Davda et al., 2005). Regarding the supports, different supports have been tested in APR, including oxides, like Al_2O_3 (Duarte et al., 2017), SiO_2 (Davda et al., 2003), or CeO_2 - ZrO_2 (Stekrova et al., 2018), but their stability is limited under the operating conditions commonly used in APR (Luo et al., 2008) and they have lower catalytic performance compared to carbon supports, which also showed higher hydrothermal stability (Kim et al., 2016). Support's surface chemistry has also considerable influence in APR, since basic supports facilitates H_2 production by favouring WGS reaction (Guo et al., 2012).

Most of the studies on APR in literature are focused on individual oxygenated hydrocarbons such as ethylene glycol (Davda et al., 2003; Shabaker et al., 2003), sorbitol (Kirilin et al., 2012), glucose (Davda and Dumesic, 2004; Kaya et al., 2015) or glycerol (Schwengber et al., 2016), among others, while, studies with more complex feedstocks or mixture of simple compounds are scarce (Pipitone et al., 2019a). On the other hand, a recent and promising application for APR is treatment and valorisation of biomass-derived wastewaters, such as those from fish cooking industry (Oliveira et

al., 2018) or breweries (Oliveira et al., 2019). So far, interesting results have been obtained with brewery wastewater, where the main component is maltose (Oliveira et al., 2019). In this context, wastewaters from juice industry could be also a suitable feedstock for APR, since they contain relatively high organic load, consisting mainly of monosaccharides, such as glucose and fructose (González del Campo et al., 2014, 2013), and organic acids, such as citric, ascorbic and galacturonic (from pectin) acids (Viuda-Martos et al., 2011), which could be appropriate substrates for that process. Moreover, fruit juice industry produces large amounts of wastewater (10 L wastewater/L juice) (Akbay et al., 2018) with high organic load, which requires treatment before disposal. Traditionally, biological processes have been proposed for treating and/or valorising this type of wastewater (El-Kamah et al., 2010; Tawfik and El-Kamah, 2012). However, large fluctuations in organic load, salinity, pH and suspended solids, can be a drawback for biological treatment, because the microbial biomass involved usually requires large acclimation periods, as well as stable salinity and pH values in order to maintain a good performance. Large fluctuations of these parameters are common in the fruit juice wastewater due to seasonal production and the various operations involved (Gonzalez del Campo et al., 2012). Likewise, clean-in-place processes are widely extended in food industry, which can lead to wastewater with high alkalinity.

Previous studies on APR of glucose (Davda and Dumesic, 2004) and fructose (Tanksale et al., 2006), which are typically contained in fruit juice wastewater, have shown promising results in terms of carbon conversion to gases and selectivity to H_2 . Nevertheless, these studies with model compounds do not consider problems associated to complex mixtures and fluctuating conditions of real wastewater from industrial processes. Different studies have shown that impurities in feedstocks can cause catalyst deactivation, possibly due to the poisoning of active sites mainly by inorganic salts (Lehnert and Claus, 2008). Boga et al. (2016) studied the influence of impurities on catalyst performance in the APR of crude glycerol using 1 wt. % Pt/ Mg-(Al)O, 1 wt. % Pt/ Al_2O_3 , 5 wt. % Pt/ Al_2O_3 and 5 wt. % Pt/C catalysts, showing that the presence of NaCl and inorganic salts greatly

inhibits H₂ formation. Stearic acid, long chain aliphatics and olefins were formed, giving rise to catalyst deactivation. In a previous work it was reported that production of gases in the APR of fish-canning wastewater with Pt/C catalysts was negatively affected by high salt concentrations (Oliveira et al., 2018). On the other hand, Remón et al. (2016b) reported that feedstock pH has a high effect on gas production. The presence of KOH increased gas yield and decreased H₂ consumption in hydrogenation reactions, while addition of acetic acid decreased gas production and led to catalyst deactivation due to metal leaching. Finally, Kirilin et al. (2010) showed that the organic load of starting feedstock has a strong influence on APR decreasing gas yield as it increases. In a previous work (Oliveira et al., 2019) it was also found a gradual decrease of carbon conversion to gas when feedstock organic load was increased. Accordingly, the effect of parameters such as pH, salinity and organic load on catalytic performance during treatment and valorisation of wastewater by APR should be evaluated.

On the basis of above considerations, the current work analyses the behaviour of different feedstocks varying from single compounds to mixtures usually found in fruit juice wastewaters (FJW) in order to assess the potential application of APR for the treatment and valorisation of these effluents. Likewise, the influence of pH, organic load and salinity is also addressed.

2. Experimental

This section describes the materials used, the preparation and characterization of the catalysts and feedstocks, and the reaction setup together with the analytical determination for both gases and liquid effluent. Likewise, the equations used to obtain the parameters used in the discussion are listed.

2.1. Materials

Hexachloroplatinic acid solution (8 wt. % in H₂O), fructose (FRU), ascorbic acid (ASC), D-galacturonic acid (GAL) and ammonium sulphate were purchased from Sigma Aldrich. Glucose

monohydrate (purity >99.9 %) (GLU) was supplied by Guinama S.L.U. Citric acid (>99 %) (CIT), potassium hydroxide, hydrochloric acid and sodium chloride (NaCl >99 %) were purchased from Panreac. ENSACO 250G carbon black were supplied by TIMCAL Canada Inc (Canada).

2.2. Preparation and characterization of support and catalyst

Pt catalyst (3 wt. %) supported on carbon black (ENSACO 250G) was prepared by incipient wetness impregnation method using hexachloroplatinic acid solution as Pt precursor. Following impregnation, the catalyst was dried at 333K for 1 h, calcined in air at 473 K during 2 h and then reduced under 25 N mL/min H₂ flow at 573 K for 2 h. The carbon support and the catalyst were characterized by N₂ adsorption-desorption at 77 K (Micromeritics TriStar II) and pH slurry measurements, as determined from aqueous suspensions in water using 1 g of solid per 10 mL of water. BET surface area of carbon black support was 65 m²/g, without significant microporosity and its pH slurry was 8.9. No significant differences were found between porous texture and pH slurry of the support and the final catalyst.

2.3. Preparation and characterization of feedstocks

Single compounds typically present in a real FJW (GLU, FRU, CIT, ASC and GAL) and a synthetic FJW were tested as feedstock for APR experiments. In the case of single compounds, 1 wt. % aqueous solutions were used. FJW was prepared based on typical chemical oxygen demand (COD) values (El-Kamah et al., 2010) and concentrations of individual components found in these type of wastewaters (González del Campo et al., 2014, 2013; Viuda-Martos et al., 2011). The standard FJW feedstock contained 2.18 g/L GLU, 1.98 g/L FRU, 0.77 g/L CIT, 0.32 g/L ASC and 0.35 g/L GAL. Feedstocks were characterized by total organic carbon (TOC), measured in a TOC-VCSH apparatus (Shimadzu), and COD, determined according to standard method ASTM D1252. TOC of the single model feedstocks varied between 3,500 and 4,200 mg/L and COD between 8,300 and 12,800 mg/L. TOC of FJW was 2,317 mg/L and COD value was 5,925 mg/L. Feedstocks pH was adjusted to 2, 7,

10 and 12, using HCl or KOH. Three different COD values (2,873, 5,925 and 11,592 mg/L) of FJW were prepared, diluting or concentrating the standard FJW, within the usual range for this type of wastewater (El-Kamah et al., 2010) and keeping the same proportion of individual components. Salinity effect was evaluated by adding to feedstock the most representative inorganic compounds reported in FJW literature (Can, 2014; El-Kamah et al., 2010; Gonzalez del Campo et al., 2012), where a high variability is reported. The feedstock with high salt concentration, denoted as FJW-HSC, contained 300 mg/L $(\text{NH}_4)_2\text{SO}_4$, 27 mg/L KH_2PO_4 and 640 mg/L NaCl and the feedstock with low salt concentration, denoted as FJW-LSC, contained 150 mg/L $(\text{NH}_4)_2\text{SO}_4$, 13 mg/L KH_2PO_4 and 320 mg/L NaCl.

2.4. Aqueous phase reforming experiments

APR experiments were performed in batch using a 50 mL stainless steel stoppered reactor (BR100, Berghoff) provided with magnetic stirring (500 rpm). The reaction was carried out at 493 K and 24-28 bar. The reaction time was set at 4 h, using 15 mL of feedstock and 0.3 g of catalyst. These conditions were selected in preliminary experiments and were already tested in previous works (Oliveira et al., 2019, 2018). The reactor was purged several times with Ar before running the reaction. After cooling down reactor to room temperature, the gases produced were collected in multilayer foil sample bags (Supelco, USA). The gas volume produced is expressed under normal conditions (NTP) and it was measured using a gas burette. The gases were analysed by GC/FID/TCD (7820A, Agilent) allowing quantification of H_2 , CO_2 , CO, CH_4 , C_2H_6 and C_3H_8 . Each experiment was performed at least by duplicate.

Effluent from APR reaction was filtered and characterized by TOC and COD. TOC and COD removal was calculated according to Eq. (1) and carbon conversion to gas (CC_{gas}) according to Eq. (2).

$$TOC \text{ or } COD \text{ Removal (\%)} = \frac{X_{initial}(\frac{mg}{L}) - X_{final}(\frac{mg}{L})}{X_{initial}(\frac{mg}{L})} \times 100 \quad (1)$$

where X is the TOC or COD value,

$$CC \text{ gas (\%)} = \frac{C_{gas(g)}}{C_{initial(g)}} \times 100 \quad (2)$$

The carbon conversion to liquid ($CC \text{ liq}$), including unreacted compounds, was calculated according to Eq. (3) and the carbon conversion to solid ($CC \text{ sol}$) was estimated according to Eq. (4).

$$CC \text{ liq (\%)} = \frac{C_{liq(g)}}{C_{initial(g)}} \times 100 \quad (3)$$

$$CC \text{ sol (\%)} = 100 - CC \text{ liq (\%)} - CC \text{ gas (\%)} \quad (4)$$

In the experiments carried out with single compound feedstocks H_2 selectivity (S_{H_2}), H_2 yield (Y_{H_2}) and CH_4 selectivity (S_{CH_4}) were calculated by Eq. (5), Eq. (6) and Eq. (7), respectively.

$$S_{H_2} (\%) = \frac{H_{2gas} (mol)}{C_{gas} (mol)} \times \frac{1}{R} \times 100 \quad (5)$$

where R is the H_2/CO_2 stoichiometric reforming ratio ($R = 12/6$ for GLU, $12/6$ for FRU, $9/6$ for CIT, $10/6$ for ASC and $10/6$ for GAL).

$$Y_{H_2} (\%) = \frac{H_{2gas} (mol)}{H_{2stoichiometric} (mol)} \times 100$$

(6)

$$S_{CH_4} (\%) = \frac{CH_{4gas} (mol)}{C_{gas} (mol)} \times 100 \quad (7)$$

For APR experiments with FJW, H_2 yield (Y_{H_2}) and CH_4 yield (Y_{CH_4}) were calculated according to Eq. (8) and Eq. (9), respectively.

$$Y_{H_2} (mmol/g_{COD i}) = \frac{mmol_{H_2}}{COD_{initial(g)}} \times 100 \quad (8)$$

$$Y_{CH_4} (mmol/g_{COD i}) = \frac{mmol_{CH_4}}{COD_{initial(g)}} \times 100 \quad (9)$$

3. Results and discussion

This study investigates the behaviour in APR of different feedstocks varying from single compounds to mixtures usually found in FJW, in order to assess their role in the treatment and valorisation of effluents. The influence of pH, organic load and salinity is also addressed.

3.1. Effect of pH on the aqueous phase reforming

The effect of pH on the APR experiments was evaluated using single compounds typically present in FJW, therefore a synthetic FJW feedstock was prepared as mixture of these simple compounds. In the experiments, pH values of 2, 7, 10 and 12 were selected and HCl and KOH were used to adjust the pH of the feedstocks.

3.1.1. Aqueous phase reforming of single compounds

TOC and COD removal in APR experiments carried out with single compounds at different feedstock pH values is shown in Fig.1. A significant influence of pH can be observed, with different trends for the single compounds tested. Low TOC and COD removal values were achieved for GLU and FRU at acidic pH (pH 2), these values increasing with pH and peaking between pH 7 and 10. APR of GLU achieved higher removal values, compared to the FRU, with 94.1 % of TOC removal at pH 7 and 81.3 % of COD removal at pH 10. In the literature, some authors (Irmak and Öztürk, 2010) reported a similar TOC removal (starting solution 4,400 mg/L) at neutral feedstock pH in the APR of glucose at 523 K using a Pt (5 wt. %) catalyst supported on activated carbon.

TOC and COD removal values with organic acid substrates (CIT, ASC and GAL) at acidic pH were higher than for GLU and FRU, decreasing gradually at increasing pH. The highest TOC and COD removal values (94.9 and 79.7 %, respectively) were obtained with CIT at pH 2. King et al. (2010) also observed a higher selectivity towards liquid phase products in the APR of glycerol a pH 12 with a 3 % Pt/C catalyst when KOH was added to the feedstock, although glycerol conversion was higher

at this pH. They suggested that the C-O bond cleavage was more favoured than C-C in the presence of KOH, possibly through base-catalysed dehydration reactions of aldehydic intermediates followed by hydrogenation reactions, which could justify the lower removal values at very high pH (pH 12). In the case of GLU and FRU, the addition of HCl in the reactions a pH 2 also could favours C-O bond cleavage through dehydration reactions catalysed by protons in the liquid phase (Cortright et al., 2002), which could justify a lower TOC and COD removal at this pH.

During APR, in addition to the reforming reaction, several other reactions take place, such as WGS, cracking, Fischer-Tropsch, dehydrogenation/hydrogenation, dehydration, deoxygenation, thermal decomposition, hydrogenolysis, as well as condensation and cyclization reactions (Cortright et al., 2002; Huber and Dumesic, 2006). Gas and liquid products or carbon deposits can result from these reactions, involving not only the starting compounds but also liquid phase intermediates. In the current work, in addition to gas products (H_2 , CO_2 , CO , CH_4 , C_2H_6 and C_3H_8), some acids, such as acetic, formic and oxalic, were also identified in the liquid phase (not shown). However, the analysis of the liquid phase could not be used to reveal the reaction mechanism at different pH values, since the identified compounds represented less than 30 % of the C remaining in the liquid. On the other hand, although an APR mechanism has been proposed for GRU (Davda and Dumesic, 2004) and FRU (Tanksale et al., 2006), other reactions that compete with the reforming may be favoured with the change of pH (Yang et al., 1996). Likewise, Kirilin et al. (2010) reported the identification of over 260 compounds involved in the APR of sorbitol, showing the complexity of the mechanisms involved.

Regarding the gas products, Table 1 shows the gas production and composition from APR of single compounds, while Table 2 shows the CC_{liq} , CC_{gas} , CC_{sol} , C_2^+ , Y_{H_2} , SH_2 and SCH_4 values from APR of single compounds. As a general trend the gas volume produced increased when pH increased within the range tested (2-12), except in the case of CIT, where the opposite trend was observed (Table 1), possibly, because the reforming may not be the main decomposition mechanism for this

compound. Similar trends were observed for *CC gas* accordingly, although this parameter was also affected by CO₂ abstraction of the gas fraction by the addition of the KOH (Table 2).

For all the single compounds, at pH 2, the gas fraction was composed majorly of CO₂ (Table 1), and its percentage decreased significantly at increasing pH, due to formation of carbonate in the liquid phase (Liu et al., 2010; Xu et al., 2006). This reduction of CO₂ percentage was quite significant even at neutral pH, confirming that the addition of base is responsible for the removal of CO₂ from the gas fraction. CO was only detected in the experiments at acidic and neutral pH, which indicates that CO₂ abstraction at high pH favours WGS reaction, displacing reaction towards H₂ formation. Liu et al. (2010) suggested that KOH addition could influence WGS reaction, through the direct provision of hydroxyl anions and/or inducing water polarization and dissociation. Moreover, these authors showed that CO_x-free H₂ could be produced by combination of APR of ethylene glycol with KOH-carbonation, where addition of KOH could favour APR process by hindering methanation, promotion of WGS reaction and abstraction of CO₂.

In general, S_{H_2} and Y_{H_2} increased at increasing pH (Table 2). As mentioned above, the addition of a base to APR feedstock could favour WGS reaction thus improving H₂ yield (Liu et al., 2010; Xu et al., 2006). However, King et al. (2010) and Karim et al. (2012) reported a decrease in both H₂ and CO₂ selectivity upon KOH addition (pH 12) in APR of glycerol with 3 % Pt/C catalyst, while a higher production of liquid phase products was observed. In the current work, the base addition also led to higher production of liquid phase products, possibly via dehydration reactions catalysed by the base, especially a pH 12, where all compounds showed a higher *CC liq* than a pH 10 (Table 2). Although it is important to highlight that the *CC liq* showed also includes the unreacted components.

Under APR conditions, processes such as hydrothermal carbonization (HTC) can also take place, leading to the formation of solids that contribute to lack of carbon balance closure. For this reason, *CC sol* was estimated from *CC liq* and *CC gas* (Table 2). All compounds showed higher *CC sol* at

pH values closer to original pH of the feedstock, pH 2 in the case of acids and pH 7 in the case of monosaccharides. When HCl or KOH were added to achieve extreme pH values a decrease in *CC sol* and an increase in *CC liq* was observed. Former works also reported lower solid yields with the addition of acidic and basic solutions (H₂SO₄ and NaOH) to feedstock in the HTC of sucrose, which was attributed to reaction shift towards the formation of liquid products (Latham et al., 2014).

CIT was the single compound leading to the highest S_{CH_4} (59.6 %) at pH 12, while low S_{H_2} and Y_{H_2} were obtained at all pH values tested. The presence of a higher percentage of C₃H₈ in the gas fraction at pH 2, compared to the other single compounds, could indicate consecutive decarboxylations leading to the formation of C₃H₈, as reported by Verduyckt and De Vos (2017). On the other hand, the difficulty to reform CIT could be associated to the presence of C not activated by hydroxyl groups and/or by direct fragmentation of CIT in recalcitrant compounds such as acetic acid. The proposed reforming mechanisms (Cortright et al., 2002) may change for compounds with a C:O ratio different than 1:1 (Wei et al., 2014) and some authors also suggest that C activated by O-binding would weaken the C-C bonds favouring the production of H₂ and CO (Tokarev et al., 2010). In addition, Verduyckt and De Vos (2017) also reported that under similar reaction conditions (Pt/C catalysts, 498 K) the formation of CIT degradation products (acetic and pyruvic acids and acetone) could be promoted by addition of a base. This could justify the higher S_{CH_4} here observed in comparison to other single compounds, especially when KOH was added, since the APR of acetic acid (Gutiérrez Ortiz et al., 2016) or compounds with recalcitrant groups, such as ketone or carboxyl (Pipitone et al., 2019a), mainly lead to production of CH₄ and CO₂

ASC yielded the highest selectivity to H₂ (58.8 %) at pH 12, however, the highest Y_{H_2} was obtained with GLU (12.4 %) at the same pH (Table 2). Cortright et al. (2002) studied H₂ production by APR of glucose under similar reaction conditions (1 wt. % glucose, 498 K and 29 bar) and observed *CC gas* and S_{H_2} values around 50 %. These differences could be due to the use 3 % Pt/Al₂O₃ catalyst, which exhibits high *CC gas* and S_{H_2} and low alkanes production (Shabaker et al., 2003), and also to a

1 reactor configuration (continuous fixed bed) that leads to a different residence time. On the other
2 hand, Kaya et al. (2015) reported a lower percentage of H₂ in the gas fraction (20 %) in the APR of a
3 glucose feedstock of similar initial concentration with a 10 % Pt/C catalyst at 523 K using a batch
4 reactor. This observation could be due to a lower dispersion of Pt nanoparticles because of the high
5 Pt load used, which can result in lower catalytic activity and H₂ production (Kim et al., 2014), and/or
6 the differences in residence time during the reaction experiments (2 versus 4 h).
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15 In all the experiments, the ratio between C₂⁺ (C₂H₆ + C₃H₈) and total alkanes (CH₄ + C₂H₆ + C₃H₈)
16 was higher at acidic pH than at neutral and basic (Table 2). With organic acid feedstocks, less C₂⁺
17 were produced when pH increased to 7, especially in the case of CIT, when that ratio decreased from
18 90.2 to 5.0 %. For ASC and GAL the ratio decreased from 74.9 to 18.3 % and 88.5 % to 25.2 %, respectively,
19 when the pH increased from 2 to 7. For the monosaccharides, the highest decrease in
20 C₂⁺ occurred at pH values between 10 and 12, with GLU yielding the highest amount of C₂⁺.
21 Therefore, the addition of a base provoked a clear reduction of relative amount of C₂⁺ in the gas
22 fraction. Similar conclusions were reported by King et al. (2010) in the APR of glycerol, suggesting
23 that the pathway to C₂⁺ formation was hindered at high pH, possibly due to a lower contribution of
24 dehydration-hydrogenation of alcohols. Some authors have also reported that the selectivity to
25 heavier alkanes increases by increasing acidity of the feedstock (Davda et al., 2005).
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42 **3.1.2. Aqueous phase reforming of fruit juice wastewater**

43 FJW was subjected to APR under different initial pH values to compare the behaviour of single
44 compounds and complex matrices. TOC and COD removal was shown in Figure 2. Although FJW
45 was composed mainly of GLU and FRU (80 wt. %), TOC and COD removal showed a trend closer
46 to the one observed for organic acids in the single compounds experiments. Thus, when pH increased
47 TOC and COD removal decreased significantly. At pH 2, removal values of up 91.7 % were
48 achieved and these values were reduced to a minimum of 48.9 % at pH 12.
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As can be seen in Table 3, the gas volume produced remained almost constant in the pH range tested, except at pH 12, where a decline was observed, although CO₂ abstraction at high pH contributes to lower gas production. The *CC gas* decreased monotonically at increasing pH, while the *CC liq* increased and the *CC sol* decreased with the addition of KOH to the mixture, as observed in the APR of the simple compounds (Table 4). The Y_{H_2} increased until pH 10, which can be attributed to enhanced WGS reaction, as it was observed for single compounds. A maximum Y_{H_2} of 7.8 mmol H₂/g COD_i was obtained at pH 10, then decreasing to 6.6 mmol H₂/g COD_i at pH 12. This can be due to a higher contribution of base-catalysed dehydration reactions at pH 12, which are followed by hydrogenation (Karim et al., 2012; King et al., 2010) decreasing H₂ production. Y_{CH_4} was relatively low in comparison to Y_{H_2} , with values between 0.8 and 2.3 mmol CH₄/g COD_i. As observed in the APR of single compounds, addition of base provokes decrease of C₂⁺ alkanes, especially when the pH increased from 2 to 7. The H₂ yield (7.8 mmol H₂/g COD_i at pH 10) was similar to that reported for acidogenic fermentation of FJW (González del Campo et al., 2014). It is worthy to mention that relatively low changes in Y_{H_2} were observed in APR of FJW at different pH, therefore this treatment can be a good alternative to overcome the drawbacks of acidogenic fermentation derived from the variability of pH, such as the need of longer retention times or acclimatization (Gonzalez del Campo et al., 2012).

3.2. Effect of organic load on the aqueous phase reforming of fruit juice wastewater

The effect of organic load was investigated at pH 10, since the highest Y_{H_2} was obtained at this pH. Moreover, basic pH values are common in the wastewater from industries such as processing food, beverages or brewing due to the cleaning-in-place (CIP) operations performed, where basic cleaning solution are used. TOC and COD removal values at different initial organic load are shown in Figure 3. The percentage of COD removal remained almost unchanged, while a small variation was observed for TOC removal. This is a relevant finding with regard to the potential application of APR

to these wastewater since with other type of effluents (e.g. brewery wastewater) a substantial decline in TOC and COD removal was observed when increasing the initial organic load within a similar range of COD_i (Oliveira et al., 2019).

Table 5 shows the gas volume and composition from APR of JFW with different organic load, and Table 6 summarizes the results obtained from the APR at different organic loads. The increase of the organic load of FJW affected the composition of the resulting gas, as showed in the Table 5. At the lowest COD_i tested the gas fraction showed the highest percentage of alkanes (22.1 %), and the lowest of H₂ (25.2 %). This last increased significantly with the organic load of the feedstock, showing the highest value at intermediated COD_i and then decreasing at the highest organic load tested, where the higher contribution of HTC increased the generation of CO₂.

The volume of gas generated increased with organic load (Table 5), but *CC gas* was twice higher for the less concentrated FJW (70.6 versus 35.7 %), while the *CC sol* increased from 1.1 % to 28.7 % with organic load, as shown in Table 6. This may indicate that at higher organic load there is a higher contribution of hydrothermal carbonization (HTC). In previous works in the literature, Kirilin et al. (2010) also reported that reforming more concentrated feedstock resulted in lower transformation of organic matter to gaseous products. Likewise, Pipitone et al. (2019b) reported that APR of glucose and xylose concentrated solutions led to a higher solid phase production due to the formation of high molecular weight compounds by condensation reactions.

3.3. Effect of salinity on the aqueous phase reforming of fruit juice wastewater

The juice industry produces wastewater with variable salt concentration depending on season and batches. Different salt concentrations have been tested to learn on the effect of this variable in APR. As in the previous section, all the experiments were performed at pH 10. Within the salinity range tested (see Section 2.3 of Experimental), salinity did not significantly affect the TOC and COD removal, as can be seen in the Figure 4.

Table 7 shows the gas production and composition from APR of FJW with different salinity, while Table 8 summarizes the results obtained regarding gas production, as well as the *CC liq* and *CC sol*. There were no significant variations in the gas volume and *CC gas* within the low salinity range (FJW and FJW-LSC), while at the highest salinity (FJW-HSC) substantially lower values were obtained. Similarly, Y_{H_2} and the percentage of H_2 in the gas were also significantly lower at the highest salinity. On the other hand, *CC sol* increased from 24.8 %, in the experiment without salts, to 35.2 % at the highest salinity. Boga et al. (2016) reported deactivation of APR catalysts by NaCl, giving rise to decreased glycerol conversion and H_2 selectivity. Lehnert and Claus (2008) also reported that the presence of NaCl was responsible of catalyst deactivation and lower H_2 production. In a previous work (Oliveira et al., 2018) a negative effect of salts on the APR of a fish-canning wastewater was observed, leading to low gas production with a high proportion of CO_2 . Remón et al. (2016a) also reported that the presence of salt in cheese whey negatively affected to the catalyst performance in APR, because the presence of salts promotes the dehydration, condensation and polymerisation reactions increasing the proportion of char and coke precursors favouring catalyst deactivation, which leads to lower gas production and higher solids production. In addition, it was reported that Na salts showed a catalytic effect to accelerate HTC of biomass (Ming et al., 2013) and the presence of $(NH_4)_2SO_4$ considerably increased the yields of hydrochar from sucrose in acidic and basic conditions (Latham et al., 2014). However, for the purpose of the current work it is noteworthy that there is a wide salinity range where no relevant affection is observed in the APR of FJW.

4. Conclusion

APR of wastewater from fruit juice production has been investigated and the effect of pH, organic load and salinity have been addressed. Previous experiments with single components showed that TOC and COD removal was higher for glucose and fructose feedstocks in the 7-10 pH range, whereas with ascorbic, galacturonic and citric acids, the acidic pH led to higher removal. FJW

behaved closer to organic acids feedstocks, even though the main components of those wastewaters are monosaccharides.

In general, H₂ yield and selectivity increased at increasing pH, accompanied by a decrease in percentage of CO₂ in the gas, due to CO₂ abstraction as carbonate. CH₄ selectivity also increased with pH, mostly due to CO₂ abstraction and a lower formation of C₂⁺ alkanes, possibly through lower contribution of dehydration-hydrogenation of alcohols. H₂ yield averaged around 6.6 mmol H₂/g COD_i in the APR of FJW with little influence of initial pH. The highest H₂ yield values were observed with low-medium organic load of FJW. Salinity did not affect the TOC and COD removal within the range tested, while a negative effect was found on the H₂ yield at high salinity, most probably due to the catalyst deactivation giving rise to a higher contribution of hydrothermal carbonization.

APR is a flexible method for the treatment of FJW that makes possible valorisation of the biomass-derived component of the wastewater to H₂ and alkanes within a wide operation window regarding pH, organic load and salinity.

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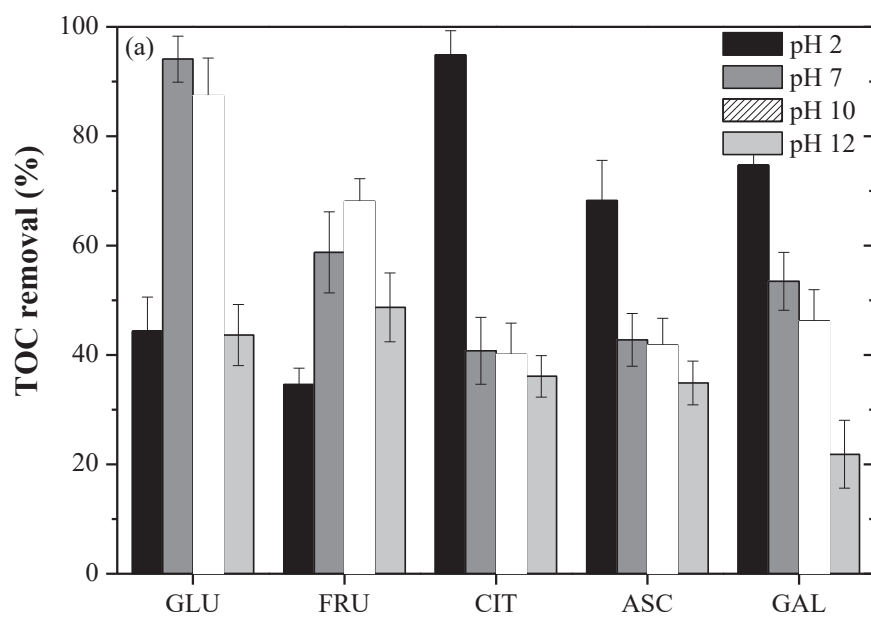
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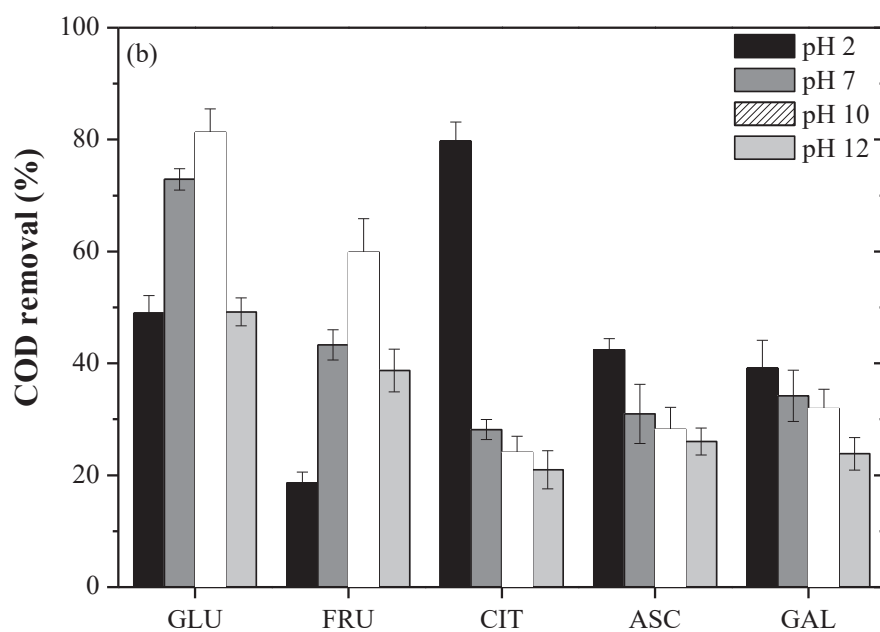


Figure 1. (a) TOC and (b) COD removal upon APR of single compounds at different initial pH (T = 493 K, t = 4 h)

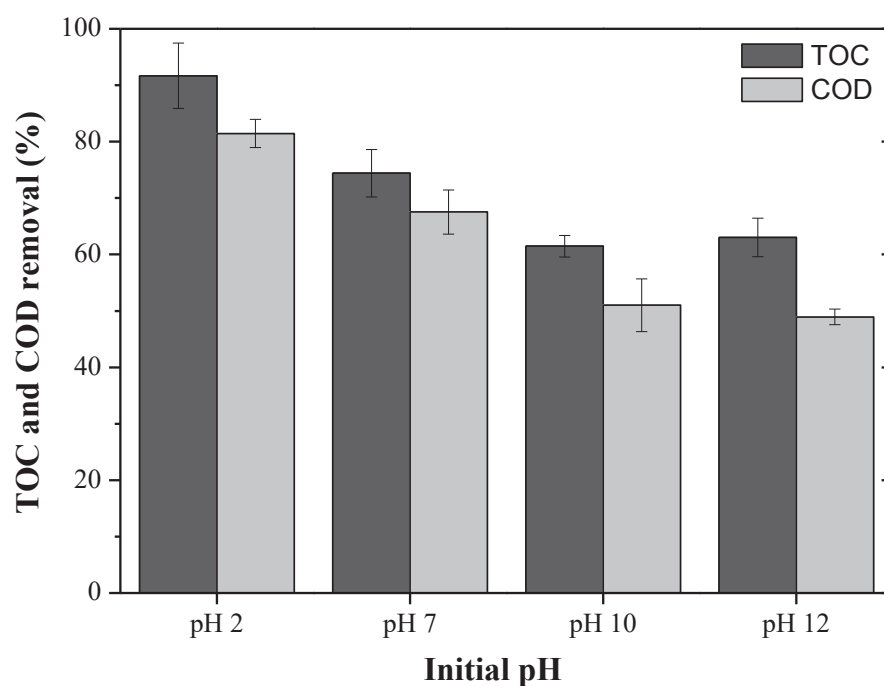


Figure 2. TOC and COD removal upon APR of FJW at different initial pH ($T = 493\text{ K}$; $t = 4\text{ h}$)

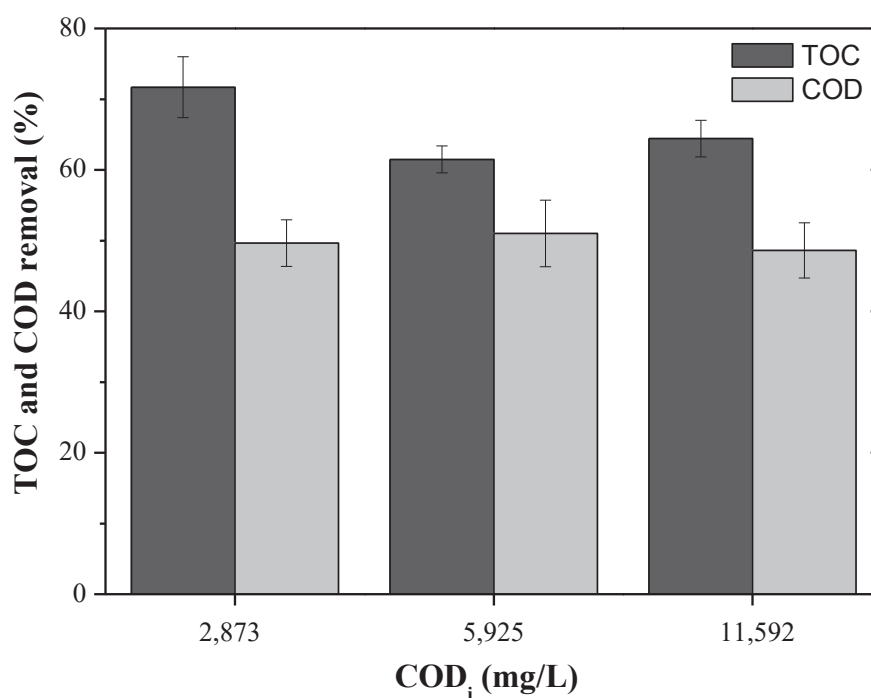


Figure 3. TOC and COD removal upon APR of FJW with different organic load ($T = 493\text{ K}$; $t = 4\text{ h}$)

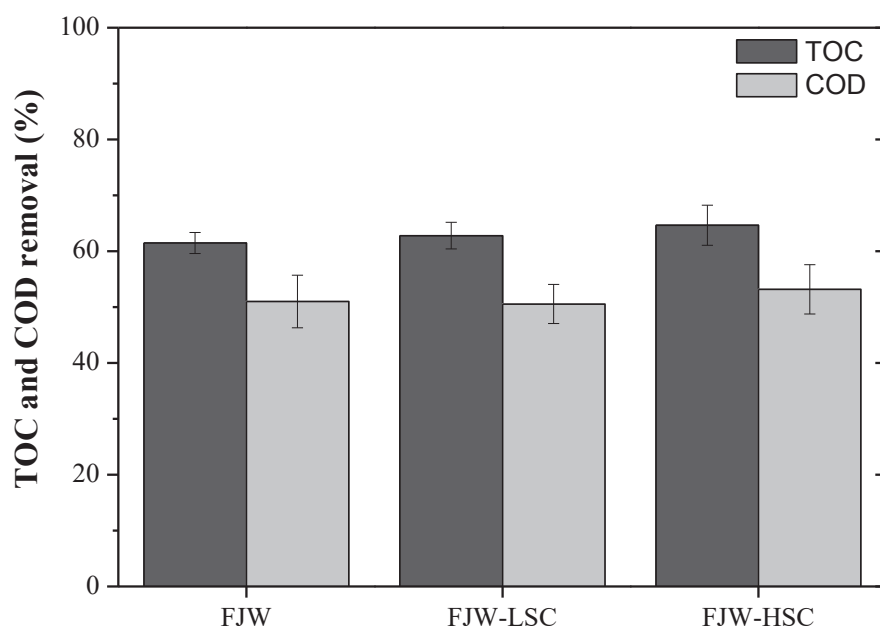


Figure 4. TOC and COD removal upon APR of FJW with different salinity ($T = 493\text{ K}$; $t = 4\text{ h}$)

Table 1. Gas composition and volume obtained from APR of single compound feedstocks (T = 493 K; t = 4 h)

Compound	Initial pH	Gas composition (% mol)					Gas volume (mL)	
		H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₃ H ₈	
GLU	pH 2	0.7 ± 0.1	92.6 ± 0.7	2.3 ± 0.7	1.5 ± 0.1	2.0 ± 0.1	1.0 ± 0.1	15.5 ± 0.6
	pH 7	28.5 ± 0.6	61.3 ± 0.5	0.0 ± 0.0	3.6 ± 0.1	3.5 ± 0.1	3.2 ± 0.1	54.5 ± 1.4
	pH 10	23.7 ± 2.7	58.4 ± 2.3	0.0 ± 0.0	7.1 ± 0.4	8.6 ± 5.8	2.3 ± 0.3	55.2 ± 1.3
	pH 12	45.6 ± 1.6	45.7 ± 0.1	0.0 ± 0.0	6.6 ± 1.2	1.5 ± 0.3	0.6 ± 0.1	64.9 ± 11.1
FRU	pH 2	2.4 ± 0.1	92.7 ± 0.2	0.4 ± 0.1	2.4 ± 0.1	0.7 ± 0.1	1.4 ± 0.1	14.0 ± 0.1
	pH 7	3.6 ± 3.5	87.6 ± 6.1	3.3 ± 0.1	3.0 ± 2.0	1.1 ± 0.2	1.4 ± 0.6	20.7 ± 9.5
	pH 10	22.8 ± 0.4	62.2 ± 0.3	0.0 ± 0.0	10.3 ± 0.1	3.5 ± 0.1	1.2 ± 0.1	42.5 ± 0.4
	pH 12	42.1 ± 0.4	47.3 ± 0.6	0.0 ± 0.0	8.9 ± 0.1	1.2 ± 0.1	0.5 ± 0.1	53.1 ± 0.8
CIT	pH 2	1.9 ± 0.1	75.2 ± 7.4	0.0 ± 0.0	2.2 ± 0.2	9.0 ± 0.1	11.7 ± 1.2	55.4 ± 2.9
	pH 7	1.5 ± 0.1	45.0 ± 0.2	0.0 ± 0.0	50.8 ± 0.2	1.7 ± 0.1	0.9 ± 0.1	20.9 ± 0.1
	pH 10	0.2 ± 0.1	40.3 ± 0.5	0.0 ± 0.0	57.6 ± 0.6	1.4 ± 0.1	0.5 ± 0.1	19.9 ± 0.2
	pH 12	1.7 ± 1.4	38.1 ± 7.6	0.0 ± 0.0	58.3 ± 9.3	1.3 ± 0.2	0.6 ± 0.1	18.9 ± 5.6
ASC	pH 2	0.2 ± 0.1	91.7 ± 0.1	0.2 ± 0.1	2.0 ± 0.1	3.2 ± 0.1	2.7 ± 0.1	38.3 ± 0.3
	pH 7	30.7 ± 0.2	61.3 ± 0.3	0.0 ± 0.0	6.5 ± 0.1	1.0 ± 0.1	0.4 ± 0.1	45.8 ± 0.5
	pH 10	32.4 ± 0.2	57.0 ± 0.3	0.0 ± 0.0	9.1 ± 0.1	1.1 ± 0.1	0.4 ± 0.1	55.8 ± 0.5
	pH 12	50.2 ± 0.6	41.6 ± 0.7	0.0 ± 0.0	7.0 ± 0.1	0.9 ± 0.1	0.3 ± 0.1	41.4 ± 0.6
GAL	pH 2	5.8 ± 5.7	86.6 ± 12.1	0.8 ± 0.8	0.8 ± 0.5	4.4 ± 0.3	1.6 ± 1.6	22.6 ± 12.9
	pH 7	27.2 ± 0.6	62.3 ± 0.9	0.0 ± 0.0	7.9 ± 0.3	2.2 ± 0.1	0.4 ± 0.1	39.4 ± 1.4
	pH 10	32.1 ± 0.9	58.3 ± 0.4	0.0 ± 0.0	7.2 ± 0.6	1.9 ± 0.1	0.5 ± 0.2	43.5 ± 1.3
	pH 12	23.0 ± 8.3	69.1 ± 9.1	0.0 ± 0.0	5.6 ± 3.0	1.3 ± 0.6	1.0 ± 0.4	18.4 ± 6.1

Table 2. Results obtained from APR of single compound feedstocks (T = 493 K; t = 4 h)

Compound	Initial pH	CC liq (%)	CC gas (%)	CC sol (%)	C ₂ ⁺ (% mol)	Y _{H2} (%)	S _{H2} (%)	S _{CH4} (%)
GLU	pH 2	55.6 ± 6.2	15.3 ± 0.7	29.1 ± 5.5	65.7 ± 0.7	<0.1	0.3 ± 0.1	1.5 ± 0.1
	pH 7	5.9 ± 4.2	42.7 ± 0.8	51.4 ± 3.4	66.7 ± 0.5	6.5 ± 0.3	17.5 ± 0.5	4.4 ± 0.1
	pH 10	12.6 ± 6.9	47.5 ± 5.3	39.9 ± 1.6	58.4 ± 13.9	5.4 ± 0.5	13.2 ± 2.7	7.9 ± 1.1
	pH 12	56.3 ± 5.6	35.4 ± 4.9	8.0 ± 0.7	23.7 ± 0.5	12.4 ± 2.5	40.1 ± 2.8	11.6 ± 1.7
FRU	pH 2	65.4 ± 3.0	10.7 ± 0.1	23.9 ± 2.9	46.5 ± 1.2	0.1 ± 0.1	1.2 ± 0.1	2.4 ± 0.1
	pH 7	41.2 ± 7.4	17.7 ± 9.4	41.1 ± 16.8	48.1 ± 10.1	0.4 ± 0.4	1.8 ± 1.8	3.0 ± 2.0
	pH 10	31.9 ± 4.1	27.3 ± 0.2	40.8 ± 3.9	31.1 ± 0.1	4.0 ± 0.1	13.8 ± 0.3	12.5 ± 0.1
	pH 12	51.3 ± 6.3	28.7 ± 0.6	20.0 ± 5.7	16.0 ± 0.1	9.3 ± 0.1	35.0 ± 0.6	14.8 ± 0.3
CIT	pH 2	5.1 ± 4.4	64.5 ± 4.6	30.4 ± 9.0	90.2 ± 0.5	0.6 ± 0.1	0.9 ± 0.1	1.7 ± 0.2
	pH 7	59.2 ± 6.1	20.1 ± 0.1	20.7 ± 6.0	5.0 ± 0.1	0.2 ± 0.1	1.0 ± 0.1	49.8 ± 0.2
	pH 10	59.9 ± 5.7	18.1 ± 0.2	22.0 ± 5.5	3.3 ± 0.1	<0.1	0.1 ± 0.1	56.3 ± 0.5
	pH 12	63.9 ± 3.8	17.2 ± 5.6	18.9 ± 9.4	2.5 ± 0.9	0.3 ± 0.3	2.0 ± 1.0	59.6 ± 8.8
ASC	pH 2	31.7 ± 7.3	34.4 ± 0.2	33.9 ± 7.1	74.9 ± 0.1	<0.1	0.1 ± 0.1	1.8 ± 0.1
	pH 7	57.2 ± 4.8	27.0 ± 0.3	15.8 ± 4.5	18.3 ± 0.1	6.9 ± 0.1	25.9 ± 0.2	9.1 ± 0.1
	pH 10	58.2 ± 4.9	32.1 ± 0.4	9.7 ± 4.5	14.0 ± 0.1	8.8 ± 0.1	28.0 ± 0.2	13.1 ± 0.1
	pH 12	65.1 ± 4.0	17.5 ± 0.4	17.4 ± 3.6	14.4 ± 0.1	10.1 ± 0.1	58.8 ± 1.3	13.6 ± 0.3
GAL	pH 2	25.3 ± 5.0	22.3 ± 11.5	52.4 ± 16.5	88.5 ± 16.5	0.7 ± 0.6	3.4 ± 3.3	0.8 ± 0.5
	pH 7	46.5 ± 5.3	29.7 ± 1.2	23.8 ± 4.1	25.2 ± 0.1	5.8 ± 0.1	21.5 ± 0.6	10.4 ± 0.4
	pH 10	53.8 ± 5.7	31.5 ± 0.1	14.7 ± 5.6	25.4 ± 2.5	7.5 ± 0.1	27.1 ± 1.0	10.1 ± 0.8
	pH 12	78.2 ± 6.2	14.6 ± 5.5	7.2 ± 0.7	28.6 ± 8.2	2.3 ± 1.3	17.2 ± 8.3	7.0 ± 3.8

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Initial pH	Gas composition (% mol)				Gas volume (mL)	
	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₃ H ₈
pH 2	27.8 ± 3.6	60.1 ± 3.0	0.3 ± 0.1	4.0 ± 0.3	3.6 ± 0.5	4.3 ± 0.4
pH 7	34.9 ± 1.4	49.3 ± 1.4	0.2 ± 0.2	11.9 ± 0.1	2.9 ± 0.2	0.9 ± 0.1
pH 10	40.8 ± 1.7	45.1 ± 0.1	0.0 ± 0.0	11.3 ± 1.4	2.0 ± 0.4	0.8 ± 0.1
pH 12	40.0 ± 0.4	48.2 ± 0.1	0.0 ± 0.0	9.5 ± 0.6	1.7 ± 0.1	0.6 ± 0.3

Table 3. Gas composition and volume from APR of FJW at different initial pH (T = 493 K; t = 4 h)

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Initial pH	<i>CC liq</i> (%)	<i>CC gas</i> (%)	<i>CC sol</i> (%)	C_2^+ (% mol)	Y_{H_2} (mmol H ₂ /g COD _i)	Y_{CH_4} (mmol CH ₄ /g COD _i)
pH 2	8.3 ± 5.8	48.8 ± 0.2	42.9 ± 5.6	66.0 ± 4.3	5.3 ± 1.0	0.8 ± 0.1
pH 7	25.6 ± 4.2	41.6 ± 3.0	32.8 ± 1.2	24.2 ± 1.3	6.8 ± 0.9	2.3 ± 0.2
pH 10	38.5 ± 1.9	36.7 ± 3.2	24.8 ± 5.1	20.0 ± 0.1	7.8 ± 0.1	2.2 ± 0.4
pH 12	37.0 ± 3.4	31.9 ± 0.4	31.1 ± 3.0	19.8 ± 2.5	6.6 ± 0.1	1.6 ± 0.1

Table 4. Results obtained from APR of FJW at different initial pH (T = 493 K; t = 4 h)

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COD _i (mg/L)	Gas composition (% mol)				Gas volume (mL)	
	H ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₃ H ₈
2,873	25.2 ± 0.7	52.7 ± 1.7	0.0 ± 0.0	15.8 ± 0.7	4.9 ± 0.2	1.4 ± 0.1
5,925	40.8 ± 1.7	45.1 ± 0.1	0.0 ± 0.0	11.3 ± 1.4	2.0 ± 0.4	0.8 ± 0.1
11,592	33.4 ± 0.3	51.8 ± 0.6	0.0 ± 0.0	11.7 ± 0.2	2.5 ± 0.1	0.7 ± 0.1

Table 5. Gas composition and volume from the APR of FJW with different organic load (T = 493 K; t = 4 h)

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COD_i (mg/L)	<i>CC liq</i> (%)	<i>CC gas</i> (%)	<i>CC sol</i> (%)	C₂⁺ (% mol)	<i>Y_{H2}</i> (mmol H₂ /g COD_i)	<i>Y_{CH4}</i> (mmol CH₄ /g COD_i)
2,873	28.3 ± 4.3	70.6 ± 3.6	1.1 ± 0.7	28.7 ± 0.1	3.9 ± 0.1	2.5 ± 0.1
5,925	38.5 ± 1.9	36.7 ± 3.2	24.8 ± 5.1	20.0 ± 0.1	7.8 ± 0.1	2.2 ± 0.4
11,592	35.6 ± 2.6	35.7 ± 0.7	28.7 ± 1.9	21.2 ± 0.1	4.9 ± 0.1	1.7 ± 0.1

Table 6. Results obtained from the APR of FJW with different organic load (T = 493 K; t = 4 h)

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Wastewater	Gas composition (% mol)						Gas volume (mL)
	H ₂	CO ₂	CO	C	CH ₄	C	
FJW	40.8 ± 1.7	45.1 ± 0.1	0.0 ± 0.0		11.3 ± 1.4	2.0 ± 0.4	40.6 ± 2.3
FJW-LSC	38.1 ± 0.9	46.4 ± 1.4	0.0 ± 0.0		12.3 ± 0.4	2.7 ± 0.1	42.9 ± 1.4
FJW-HSC	35.1 ± 1.4	48.6 ± 1.6	0.0 ± 0.0		13.3 ± 0.1	2.3 ± 0.1	29.9 ± 3.7

Table 7. Gas composition and volume from the APR of FJW with different salinity (T = 493 K; t = 4 h)

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Wastewater	CC_{liq} (%)	CC_{gas} (%)	CC_{sol} (%)	C_2^+ (% mol)	Y_{H_2} (mmol H_2 /g COD _i)	Y_{CH_4} (mmol CH_4 /g COD _i)
FJW	38.5 ± 1.9	36.7 ± 3.2	24.8 ± 5.1	20.0 ± 0.1	7.8 ± 0.1	2.2 ± 0.4
FJW-LSC	37.2 ± 2.4	40.6 ± 1.8	22.2 ± 0.6	21.0 ± 0.1	6.5 ± 0.1	2.1 ± 0.1
FJW-HSC	35.4 ± 3.6	29.4 ± 3.1	35.2 ± 0.5	18.4 ± 0.3	4.2 ± 0.7	1.6 ± 0.2

Table 8. Results obtained from the APR of FJW with different salinity (T = 493 K; t = 4 h)