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Aqueous phase reforming coupled to catalytic wet air oxidation for the removal and valorisation of phenolic compounds in wastewater

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Abstract

Aqueous phase reforming (APR) coupled to catalytic wet air oxidation (CWAO) has been investigated as an approach to remove phenolic compounds from wastewater, converting them into valuable gases. Partial oxidation of phenol was achieved in the first CWAO stage trying to minimize mineralization so to allow a high yield to valuable gases in the second APR stage. APR runs were carried out with different mixtures of compounds corresponding to phenol oxidation pathway (phenol, quinones, long and short chain acids) and representing different degrees of oxidation in CWAO stage. A range of TOC and COD removal (74 – 90 %) was observed in APR stage for the single compounds, with higher removal for long chain acids. Likewise, long chain acids provided with the highest conversion to gases. APR of mixtures rich in acids gave the highest yield to CH₄ (11.0 mmol CH₄ / g TOC_{initial}). H₂ production was low in all cases, due to competing direct conversion of long and short chain acids into CH₄. TOC and COD removal from wastewater was similar in APR-CWAO and APR, however the conversion to gases and the yield to CH₄ were markedly higher for APR-CWAO, thus overcoming the difficulties previously observed in the direct APR of phenol.

Keywords: aqueous phase reforming, catalytic wet air oxidation, phenol, methane, hydrogen.

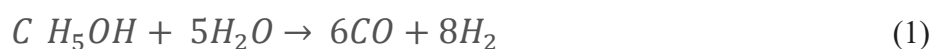
1. Introduction

Phenolic compounds are widely used in chemical, oil, gas, coal, and pesticides industries, among others. They have been considered as priority concern pollutants by several national agencies and institutions, such as the Environmental Protection Agency (USA) or the European Union, because of their proved toxic effects on human health and environment (Mahugo-Santana et al., 2010). Phenol is usually found in the wastewater discharged from the coal tar, petroleum refinery, steel, plastic, disinfectant, pharmaceutical, and rubber plants (Dargahi et al., 2017). Phenols-bearing wastewaters are usually treated by physico-chemical and biological systems, although special acclimatization is required since phenols inhibit biological processes. The physico-chemical treatment of wastewater containing phenolic compounds has gathered much interest in literature. Oxidation processes have shown their ability to remove phenols, including techniques such as wet air oxidation (Joglekar et al., 1991; Kolaczowski et al., 1997), catalytic wet air oxidation (Monteros et al., 2015; Wang et al., 2014), catalytic wet peroxide oxidation (Martin-Martinez et al., 2016; Zazo et al., 2006), Fenton process (Poerschmann et al., 2017; Zazo et al., 2011) or ozone- and or UV-based oxidation (Esplugas et al., 2002), among others. Successful oxidation of phenols allows to remove the hazardous effects but not to valorise the pollutants, while waste valorisation is an essential approach to close the loop and meet the circular economy aims (Kirchherr et al., 2017).

Aqueous phase reforming (APR) is a process converting organic compounds present in aqueous media to valuable gases, mainly H_2 and CH_4 . This process usually takes place at 200 - 250 °C and 15 - 50 bar, where side reactions such as water gas-shift (WGS), methanation, Fischer-Tropsch and hydrothermal carbonization (HTC) are also

thermodynamically favoured (Cortright et al., 2002). Main substrates traditionally studied in APR are oxygenated hydrocarbons model compounds including ethylene glycol, xylitol, sorbitol, etc (Cortright et al., 2002; Kirilin et al., 2012). Studies on more complex matrices are less frequent and works on the application to real industrial wastewaters are recent and still scarce. In our previous works, APR was applied to the treatment and valorisation of wastewater effluents from tuna-canning (Oliveira et al., 2018) and brewing industry (Oliveira et al., 2019). APR of brewery wastewater resulted in high TOC and COD removal and valuable gases production at high yield, showing the potential of this process for simultaneous wastewater treatment and valorisation.

In this context, APR could be used to valorise other types of wastewater, however, in its application to substrates with abundant high-weight molecules and aromatics, condensation and HTC are competing reactions resulting in major drawbacks (Chen et al., 2016; Kang et al., 2012). For example, in the case of lignin HTC, the resulting hydrochar is mainly composed by polyaromatic and phenolic compounds (Zhang et al., 2019). The APR of phenol, for example, could theoretically produce up to 14 mol of H_2 per mol of phenol, according to reactions (1) and (2).



Substrates commonly used in APR, such as oxygenated hydrocarbons, has a balanced ratio between C and O, close or equal to 1:1, which is not the case of phenol, and this could hinder the reforming process. APR reaction may change with the C:O ratio of

substrate (Cortright et al., 2002; Wei et al., 2014) and values of that ratio around 1 are considered as optimum to obtain a high H₂ selectivity (Chheda et al., 2007). Some studies suggested that O atoms bounded to C atoms favour the production of H₂ and CO because of C-C bond weakening, whereas the scission of C-O bonds in these compounds could favour the production of light alkanes (Tokarev et al., 2010). However, previous works on APR of phenolics are quite scarce. Yan *et al.* (Yan et al., 2017) and Li *et al.* (Li et al., 2018) reported APR of phenol using NiCe/ZSM-5 and Ni/ZSM catalysts at 240 - 250 °C and 40 - 70 bar. These studies focus on catalytic activity and some information on performance parameters such as TOC/COD conversion and production of gases is not available.

On the other hand, CWAO can be used to degrade phenolic compounds into intermediates in the oxidation pathway that could be more easily converted to valuable gases by APR process in a further stage. The reaction temperatures and catalysts used in APR and CWAO are compatible and inexpensive air is used for the oxidation process. The intermediates generated by oxidation have lower number of carbon atoms and a C:O ratio closer or equal to 1:1 (Joglekar et al., 1991; Zazo et al., 2005). Thus, APR of feedstocks with a shorter carbon chain has been reported to be more selective to H₂ production (Cortright et al., 2002). Therefore, a partial oxidation of phenolic compounds would generate species that can be converted into valuable gases by APR, avoiding some drawbacks of direct phenol APR.

In the current work, coupling of APR and CWAO is studied as an approach for phenol-bearing wastewater treatment and valorisation. Wastewater was subjected in a first stage

to CWAO and in a second stage to APR. APR of feedstocks consisting mixtures of species representative of phenol oxidation pathway was studied to learn on the contribution of the corresponding individual compounds and assess the potential of the coupled process.

2. Experimental

2.1. Materials

Hexachloroplatinic acid (H_2PtCl_6 , 8 wt. %), phenol (> 99 %), hydroquinone (> 99 %), acetic acid (> 99 %), malonic acid (> 99 %), maleic acid (> 99 %), oxalic acid (> 99 %), fumaric acid (> 99 %) were supplied by Sigma Aldrich. Formic acid (> 98 %) and catechol (99 %) were purchased to Panreac and Alfa Aesar, respectively. Commercial carbon black ENSACO 250G (ENS) was supplied by Timcal and commercial Pt/ Al_2O_3 catalyst (0.5 wt. %) was supplied by Micromeritics.

2.2 Catalyst preparation and characterization

Pt/ Al_2O_3 catalyst (0.5 wt. %) with a Pt dispersion of 30.5 % was used for the CWAO experiments given the good performance of this type of catalysts in CWAO process (Kim and Ihm, 2011). The catalyst was grinded and sieved to powder form (<250 μm) before its use.

An own-made Pt/C (3 wt. %, powder form) catalyst was used for the APR runs and adsorption experiments given the better hydrothermal stability of the carbon materials compared to alumina supports in the APR conditions and the good performance showed in a previous works on APR (Oliveira et al., 2019). The Pt/C catalyst was synthesized using the commercial carbon black ENS, which was characterized by N_2 adsorption-

desorption at 77 K (TriStar II, Micromeritics) and pH slurry measurements (Oliveira et al., 2018), yielding a BET specific surface area of $65 \text{ m}^2 / \text{g}$, negligible micropore volume, $0.1 \text{ cm}^3 / \text{g}$ of mesopore volume, and pH slurry value of 8.9. The Pt/C catalyst was prepared by incipient wetness impregnation of ENS, followed by drying at room temperature during 2 h and overnight oven drying at $60 \text{ }^\circ\text{C}$. Calcination in air at $200 \text{ }^\circ\text{C}$ for 2 h and reduction under $25 \text{ N mL} / \text{min H}_2$ flow at $300 \text{ }^\circ\text{C}$ for 2 h were carried out. The Pt/C catalyst did not present significant differences in pore texture and pH slurry when compared to ENS support. Further characterization of this catalyst can be found elsewhere (Oliveira et al., 2020).

2.3 Feedstock and mixtures preparation

As a first approach, coupling of APR and CWAO was studied subjecting to APR feedstock and mixtures (synthetic solutions) representative of a phenol-bearing wastewater subjected to oxidation.

Table 1 shows the theoretical composition of feedstocks used to study the processability of the different representative compounds identified in the phenol oxidation routes proposed by Zazo et al. (Zazo et al., 2005) and Joglekar et al. (Joglekar et al., 1991). Initial theoretical TOC was $76.5 \text{ mg} / \text{L}$ for all feedstocks. FPhOH feedstock consisted exclusively of phenol, while FAromatic feedstock simulated a first partial oxidation stage in phenol oxidative route leading to compounds where aromatic ring is still preserved. FLargeAcid and FShortAcid feedstocks simulated last oxidation states, being composed entirely of long ($\text{C}_2 - \text{C}_4$) and short ($\text{C} - \text{C}_2$) chain organic acids, respectively.

1

2 Feedstock mixtures were also prepared to study the processability of more complex
 3 matrices containing compounds with different oxidation degree. The composition of the
 4 mixtures is summarized in Table 2. Mixture M-1 simulates oxidation conditions where
 5 phenol is partially oxidized, but only to aromatic intermediates, whereas in M-2, it is
 6 considered that phenol is partially oxidized to organics acids. M-3 is a mixture
 7 containing all the compounds that may be present in phenol partial oxidation route.

8 Table 1. Composition of feedstocks

Feedstock	Compound	Concentration (mg / L)	Concentration* (mg C / L)
FPhOH	Phenol	100	76.5(100)
FAromatic	Hydroquinone	58	38.3(50)
	Catechol	58	38.3(50)
FLargeAcid	Oxalic acid	115	30.6 (40)
	Malonic acid	22	7.7 (10)
	Maleic acid	74	30.6 (40)
	Fumaric acid	19	7.7 (10)
FShortAcid	Oxalic acid	86	23.0 (30)
	Formic acid	59	15.3 (20)
	Acetic acid	96	38.3 (50)

9 *: in brackets percentage of total organic carbon

10 Table 2. Mixtures of feedstocks

Mixture	Feedstock	Percentage (%)	Compounds	Concentration (mg / L)	Concentration* (mg C / L)
M-1	FPhOH	50	Phenol	50	38.3 (50)
	FAromatic	50	Hydroquinone	29	19.1 (25)
			Catechol	29	19.1 (25)
M-2	FPhOH	34	Phenol	34	26.0 (34)
	FLargeAcid	33	Oxalic acid	66	17.7 (23)
	FShortAcid	33	Malonic acid	7	2.5 (3)
			Maleic acid	24	10.1 (13)
			Fumaric acid	6	2.5 (3)
			Formic acid	19	5.0 (7)
			Acetic acid	32	12.6 (17)
M-3	FPhOH	25	Phenol	25	19.1 (25)
	FAromatic	25	Hydroquinone	15	9.6 (12)
	FLargeAcid	25	Catechol	15	9.6 (12)
	FShortAcid	25	Oxalic acid	50	13.4 (18)
			Malonic acid	6	1.9 (3)

Maleic acid	19	7.7 (10)
Fumaric acid	5	1.9 (3)
Formic acid	15	3.8 (5)
Acetic acid	24	9.6 (12)

*: in brackets percentage of total organic carbon

2.4. APR experiments and analytical procedures

APR experiments were performed in stainless steel batch reactors (BR100, Berghoff) at 220 °C and 24 - 28 bar during 4 h, using 0.6 g of catalysts in 30 mL of reaction volume under Ar inert atmosphere. The reactors were purged with Ar several times before each run. The gas produced was collected in multilayer foil sample bags (Supelco). The aqueous phase resulting from APR was filtered and characterized by Total Organic Carbon (TOC), measured in a TOC-VCSH apparatus (Shimadzu), and by Chemical Oxygen Demand (COD), determined according to standard method (ASTM D1252). Organic acids were analysed by ionic chromatography (883 Basic IC Plus, Metrohm), whereas phenol, hydroquinone and catechol were analysed by HPLC (Varian Pro Star-UV/DAD) using a C₁₈ column and 4 mM sulphuric acid as eluent. The gas phase was collected using inert foil sampling bags (Supelco) and analysed by a GC/FID/TCD (7820A, Agilent), using Ar as carrier gas, and two packed columns and a molecular sieve allowing to detect H₂, CO, CO₂, CH₄, C₂H₆ and C₃H₈.

TOC and COD removal were calculated as Eq. (1), where X corresponds to the TOC or COD value.

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

Carbon conversion to gases (*CC gas*) was calculated according to Eq. (2) and H₂ and CH₄ yields (*Y_j*, where *j* corresponds to H₂ or CH₄) were calculated according to Eq. (3).

1

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

$$Y_j (mmol/g_{TOC_i}) = \frac{mmol_j}{TOC_{initial(g)}} \quad (3)$$

4

5 *2.5. Adsorption tests*

6 Adsorption tests were carried out to learn on the adsorption contribution to TOC
7 removal. These tests were carried out during 24 h at room temperature and ambient
8 pressure using the same feedstock to support mass ratio as in APR experiments.

9

10 *2.6. Coupling of APR and CWAO*

11 After assessing the effect of oxidation in processability using synthetic mixtures, the
12 proof of concept was finally made by subjecting a FPhOH feedstock to a first stage mild
13 CWAO (partial oxidation) and then to a second stage APR. CWAO of FPhOH
14 feedstock was carried out in stainless steel batch reactors (BR100, Berghoff) at 150 °C
15 during 4 h, using 50 mg of a commercial catalyst (0.5 wt. % Pt/Al₂O₃) and 30 mL of
16 feedstock. Before heating, batch reactors were purged and pressurized to 20 bar with an
17 air-Ar gas mixture (30 % air and 70 % Ar) in static mode. The conditions for oxidation
18 were set after preliminary experiments based in former works (Joglekar et al., 1991; Lee
19 et al., 2010). After the CWAO step, the gas in the reactor was purged, the Pt/Al₂O₃
20 catalyst was removed by filtration and the filtered aqueous phase was introduced in a
21 new batch reactor where APR step was conducted using the Pt/C catalyst as indicated
22 above.

23

24 **3. Results and Discussion**

25 *3.1 Adsorption on carbon support*

TOC removal from adsorption tests can be seen in Figure 1. Higher removal of TOC was observed in the case of FPhOH and FAromatic (57 and 67 % respectively). These feedstocks contain phenol, hydroquinone and catechol, which can interact more strongly with the surface of the carbon support, due to the aromatic ring of their structures. In adsorption experiments with FLargeAcid and FShortAcid, containing organic acids mixtures, lower TOC removal values of 31 and 14 %, respectively, were observed. These results provide useful information about adsorption behaviour of feedstocks onto the support, even though adsorption conditions tested differ from APR conditions.

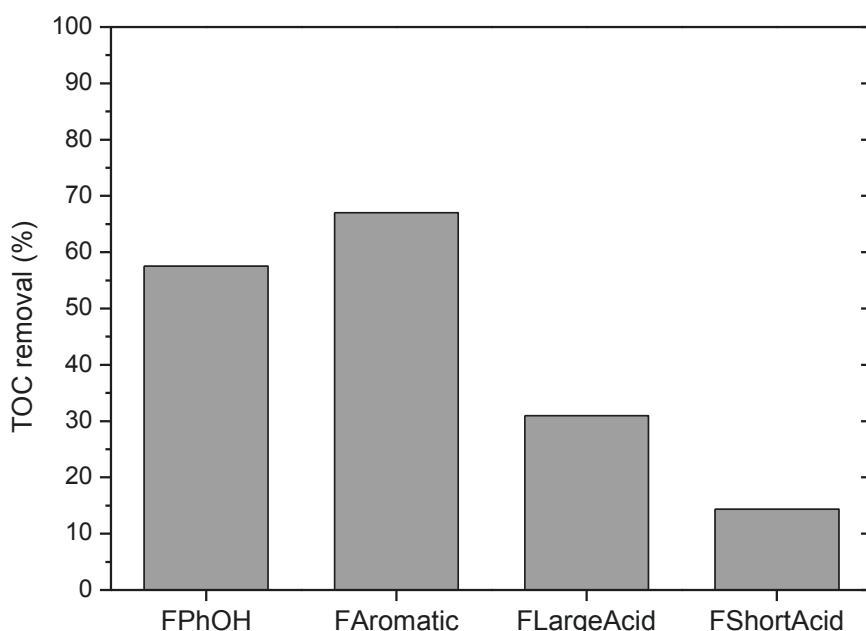


Figure 1. TOC removal in adsorption tests

3.2 APR of feedstocks

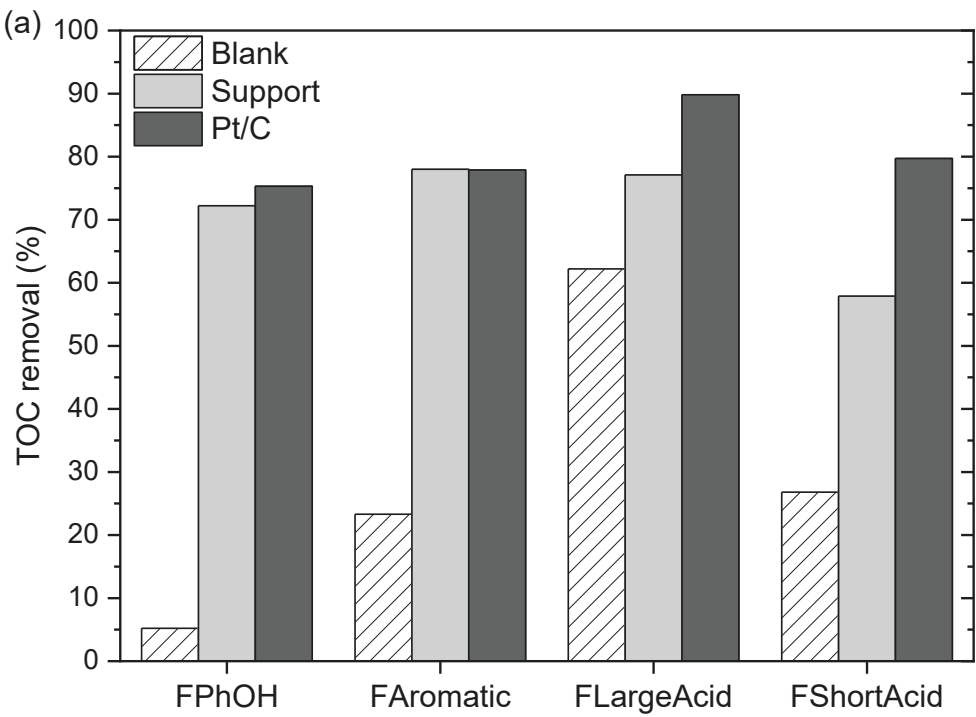
Figure 2 shows the TOC and COD removal in the APR experiments. The runs performed without catalysts or metal-free support (blank) showed a wide range of TOC and COD removal, varying between 5 and 62 %. Hydrothermal carbonization (HTC)

1 must be the main mechanism of TOC and COD removal in the blank experiments. After
2 blank experiments, a black solid was separated by filtration, and the aqueous phase
3 contained short chain acids such as oxalic, acetic or formic, which are common by-
4 products of HTC (X. Li et al., 2015). In the blank experiments, FPhOH feedstock
5 yielded the lowest removal values (5 %), while the highest was obtained for
6 FLargeAcid (62 %).

7
8 In the case of runs performed using metal-free carbon support, TOC and COD removal
9 increased up to 48 – 81 %, which can be ascribed to HTC and adsorption onto the
10 support. Some contribution of the support to HTC may also occur, since Krishnan et
11 al.(Krishnan et al., 2014) showed that graphene oxide accelerated carbonization in HTC
12 of glucose. TOC and COD removal was higher for FPhOH, FAromatic and FLargeAcid
13 feedstock, than for FShortAcid. This can be ascribed to the greater adsorption of species
14 in FPhOH and FAromatic feedstocks onto carbon support compared to organic acids
15 feedstocks, taking into account the TOC and COD removal obtained in blank runs.
16 Removal of TOC and COD from FLargeAcid feedstock was relatively small in both
17 blank and metal-free support runs, suggesting that the contribution of HTC is higher
18 compared to adsorption.

19
20 APR experiments performed with catalyst yielded the highest values of TOC and COD
21 removal, in the range of 73 – 90 %. The small differences between runs with catalyst
22 and with metal-free supports for FPhOH and FAromatic feedstock indicates a small
23 contribution of the APR to the removal. Conversely, organic acid feedstocks showed
24 significant differences in TOC and COD removal between catalysed and metal-free
25 runs. Nevertheless, it is also worthy to note that the contribution of the HTC could also

1 be much higher in the case of FLargeAcid compared to FShort Acid feedstocks as can
2 be seen from the comparison to the results of blank experiments.
3



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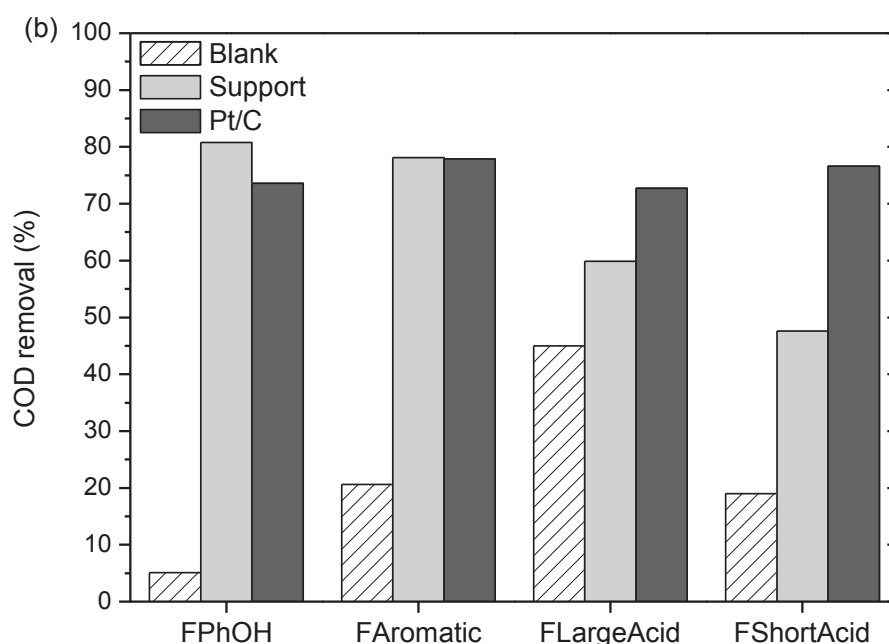


Figure 2. TOC (a) and COD (b) removal in APR experiments with different feedstocks

Table 3 shows the concentration of individual components identified in the feedstock and after the APR experiments with catalyst. In the runs performed with FPhOH feedstock significant amounts of hydroquinone and catechol were found. These compounds were not observed in blanks and in the experiments with the metal-free support, due to different mechanisms for APR and HTC. This can also be observed in the case of the runs performed with FAromatic, where lower amounts of intermediate species were detected in the degradation pathway of catalysed APR. Interestingly, some phenol was detected in the catalysed runs, which can be due to dehydration of hydroquinone or catechol (Bai et al., 2012; H. Li et al., 2015). Likewise, 84 % of the starting phenol from FPhOH disappeared, and removal of hydroquinone and catechol from FAromatic was as high as 99 % and 94 %, respectively. In general, acetic and formic acids were found as end products of the degradation pathway, even though the

mechanism for catalysed APR and HTC in the presence of support are different for FPhOH and FAromatic feedstocks.

Runs carried out with feedstocks constituted by organic acids showed high conversion in catalysed experiments. In the case of FLargeAcid, conversion of oxalic, maleic, malonic and fumaric acids was close to 99 %. In the case of FShortAcid feedstock, the values of conversion of oxalic, acetic and formic acids were close to 100, 96 and 88 %, respectively.

A carbon balance gap in the liquid phase can be inferred by comparison of TOC and individual compounds concentration data in Figure 2 and Table 3, which is due to differences in HTC and APR mechanism, leading to a large number of minor species (Funke and Ziegler, 2010; Godina et al., 2015; Kirilin et al., 2010) that were not analysed in the present study. The set of compounds selected and shown in Table 3 describe between 50 and 100 % of C in the liquid phase.

Table 3. Composition of the aqueous phase in blank and catalysed APR experiments with different feedstocks

Feedstock	Run	Compounds								
		Phenol (mg / L)	Hydroquinone (mg / L)	Catechol (mg / L)	Oxalic (mg / L)	Maleic (mg / L)	Malonic (mg / L)	Fumaric (mg / L)	Acetic (mg / L)	Formic (mg / L)
FPhOH	Initial	102.0	-	-	-	-	-	-	-	-
	Blank	81.5	-	-	0.4	-	-	-	4.8	0.7
	Support	26.0	-	-	0.1	-	4.5	-	1.4	-
	Pt/C	16.0	3.3	0.8	0.3	-	-	-	2.5	0.5
FAromatic	Initial	-	57.5	58.0	-	-	-	-	-	-
	Blank	-	19.8	26.3	0.4	1.3	-	-	6.9	5.3
	Support	-	2.2	5.6	0.5	0.4	4.4	-	12.8	3.7
	Pt/C	10.9	0.3	3.3	0.1	-	-	-	0.9	0.6
FLargeAcid	Initial	-	-	-	112.5	68.5	20.4	13.4	-	-
	Blank	-	-	-	0.3	0.7	9.5	1.0	23.4	6.5
	Support	-	-	-	0.4	-	9.6	-	13.5	2.3
	Pt/C	-	-	-	0.2	-	-	-	2.1	0.8
FShortAcid	Initial	-	-	-	75.7	-	-	-	97.2	54.3
	Blank	-	-	-	0.3	-	-	-	97.0	11.3
	Support	-	-	-	1.5	-	-	-	75.3	0.6
	Pt/C	-	-	-	0.2	-	-	-	4.4	6.3

Figure 3 shows the values obtained for *CC gas* in APR runs with the different feedstocks tested. The blank runs and those with the metal-free support did not show important differences, giving rise to *CC gas* in the 6 – 40 % range, the highest values corresponding to the FLargeAcid feedstock. The runs performed with catalyst yielded higher *CC gas* values within a wide range (21 - 74 %), with significantly higher values for the FShortAcid feedstock. FPhOH, as well as FAromatic feedstocks, gave always lower *CC gas* values than FLargeAcid and FShortAcid. The differences observed among feedstocks are higher than those observed for the removal of TOC and individual compounds.

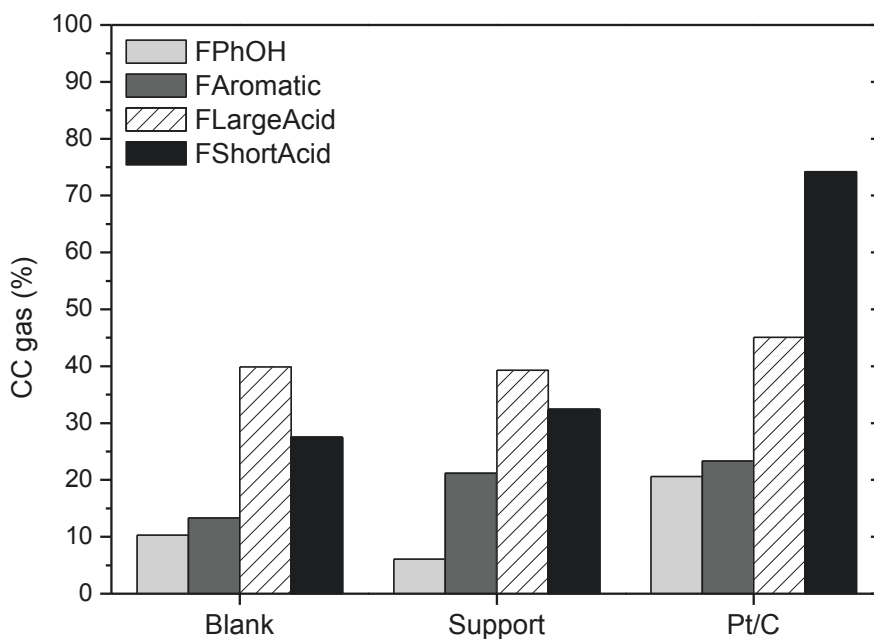


Figure 3. *CC gas* obtained in APR runs with different feedstocks

Table 4 shows gas production, gas composition and Y_{CH_4} from the APR experiments with the feedstocks tested. The use of catalyst increased the gas volume produced, in agreement with previous *CC gas* results. The percentage of H_2 in the gas fraction was low in all the experiments (0 to 1.7 %), and much lower than in former works dealing with APR of other substances such as glycerol or brewery wastewater (Ciftci et al., 2014; Menezes et al., 2011; Oliveira et al., 2019). CO_2 was the major component of the gas even in the catalytic APR experiments. The percentage of CO_2 in the gas decreased significantly in favour of alkanes in the catalytic runs with acids feedstocks, being CH_4 the main component and resulting in high Y_{CH_4} . The high production of CH_4 in these runs could be ascribed to the acidic medium, which favours methanation reactions in turn consuming the H_2 and CO produced in by APR. For some species, such as acetic acid, the direct formation of CH_4 can be achieved by the C-C bond scission, in which methyl group can easily evolve to CH_4 . On the opposite, phenol, catechol and hydroquinone yielded essentially CO_2 , indicating that for aromatic species HTC is by far the prevailing degradation route, being very low the contribution of reforming. Condensation reactions on the surface of the carbon support can be an additional competing pathway in the degradation of aromatic species (Zazo et al., 2006).

Table 4. Gas production and composition from APR runs of different feedstocks

Runs	Feedstock	Gas Volume (mL)	Gas composition (% mol)			Y_{CH_4} (mmol CH_4 / g TOC_i)
			H_2	CO_2	Alkanes	
Blank	FPhOH	0.4	0.1	91.3	8.6	0.6
Blank	FAromatic	0.6	1.1	98.4	0.6	0.1
Blank	FLargeAcid	1.8	0.2	98.9	0.9	0.2
Blank	FShortAcid	1.2	0.6	99.1	0.2	<0.1
Support	FPhOH	0.3	0.4	96.4	3.2	0.1
Support	FAromatic	0.9	0.3	98.9	0.8	0.1
Support	FLargeAcid	1.8	0.9	96.0	3.1	1.0
Support	FShortAcid	1.5	0.2	99.4	0.4	0.1
Pt/C	FPhOH	0.9	1.7	96.4	2.0	0.3

Pt/C	FAromatic	1.0	0.5	96.7	2.7	0.5
Pt/C	FLargeAcid	2.0	0.4	72.9	26.7	8.4
Pt/C	FShortAcid	3.4	<0.1	71.0	28.9	17.8

3.3 APR of mixtures of feedstocks

Figure 4 shows the experimental results of TOC and COD removal upon APR of mixtures of feedstocks (see Table 2). For the sake of comparison, Figure 4 also shows removal values calculated by linear combination of the previous results obtained with individual feedstocks.

In general, the experimental removal was higher than that expected from the results with individual feedstocks, particularly in the case of M-1 and M-3 mixtures, suggesting some promoting effect of hydroquinone and catechol. This could be ascribed to the formation of semiquinone free radicals produced by the thermal decomposition of the hydroquinone and/or catechol (Dellinger et al., 2007).

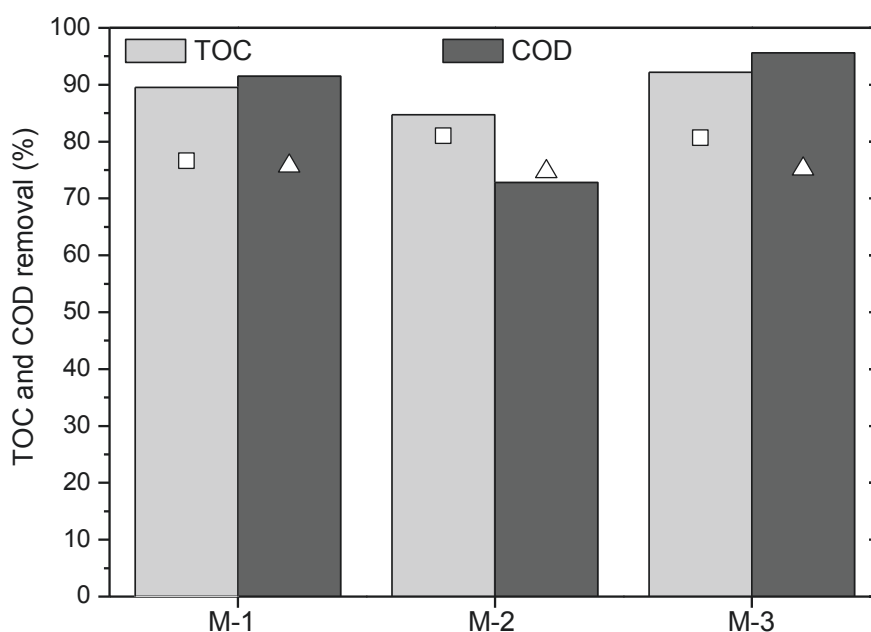


Figure 4. TOC and COD removal upon APR runs of mixtures of feedstocks with Pt/C catalyst. Symbols correspond to the calculated values from the behaviour of individual feedstocks (Figure 2)

Table 5 shows the initial and final concentration of individual compounds in the liquid phase for the APR experiments with mixtures of feedstocks. In general, high conversion values (between 87 and 100 %) were achieved for all the compounds. In the runs performed with mixtures containing malonic acid (M-2 and M-3), a low conversion of this compound was observed (7 – 22 %). This result differs from the observation when FLargeAcid feedstock was treated individually by APR, where the final concentration of the all species was negligible, despite their higher initial concentration. The identified compounds represent 48 and 35 % of C remaining in the liquid phase for mixtures M-1 and M-2, respectively, while for mixture M-3, they represent 85 %.

Table 5. Initial and final composition of the aqueous phase in APR of feedstock mixtures with Pt/C catalyst

Mixture	Run	Compounds								
		Phenol (mg / L)	Hydroquinone (mg / L)	Catechol (mg / L)	Oxalic (mg / L)	Maleic (mg / L)	Malonic (mg / L)	Fumaric (mg / L)	Acetic (mg / L)	Formic (mg / L)
M-1	Initial	53.4	32.5	32.1	-	-	-	-	-	-
	Pt/C	1.9	0.2	0.5	0.2	3.9	-	-	2.5	0.2
M-2	Initial	33.4	-	-	62.8	21.3	6.8	4.3	35.0	18.2
	Pt/C	0.6	0.2	0.4	0.8	-	6.3	-	1.5	0.3
M-3	Initial	25.4	19.0	16.0	48.3	15.8	4.9	3.3	25.4	13.3
	Pt/C	3.3	1.0	0.3	0.2	-	3.8	0.2	-	-

Table 6 shows the comparison between gas production, gas fraction composition, CC_{gas} and Y_{CH_4} obtained upon APR of mixtures of feedstocks. The results were also compared with the values calculated from the lineal combination of the results with the individual feedstocks.

CC gas values were in a range from 32 to 66 %, being the highest values those obtained with M-2 and M-3 mixtures. Small differences were found between gas composition and the corresponding results calculated by lineal combination of the behaviour of the individual feedstocks. The highest Y_{CH_4} was achieved for M-2 mixture (11.0 mmol CH₄ / g TOC_i), which contained the highest concentration of organic acids, while Y_{H_2} was very low in all cases (<0.2 mmol H₂ / g TOC_i).

Table 6. Gas production and composition from APR of mixed feedstocks with Pt/C catalyst

Runs	Mixture	Gas Volume (mL)	Gas composition (% mol)			CC gas (%)	Y_{H_2}	Y_{CH_4}
			H ₂	CO ₂	Alkanes		(mmol H ₂ / g TOC _i)	(mmol CH ₄ / g TOC _i)
Pt/C	M-1 Exp.	1.4	0.4	96.2	3.4	32.2	0.1	0.9
Pt/C	M-1 Calc.	1.0	1.1	96.5	2.4	21.9	0.2	0.4
Pt/C	M-2 Exp.	2.9	0.3	76.4	23.3	65.7	0.2	11.0
Pt/C	M-2 Calc.	2.1	0.7	80.1	19.2	46.6	0.1	8.9
Pt/C	M-3 Exp.	2.2	0.2	85.6	14.2	51.1	0.1	5.0
Pt/C	M-3 Calc.	1.8	0.7	84.2	15.1	40.8	0.1	6.8

3.4 Coupling of APR and CWAO

Looking at the poor results obtained in the of APR of aromatic compounds, where CO₂ was the major component of the gas produced, and the better results in the APR of acids feedstocks and mixtures, a new approach was explored. This consists in subjecting the phenolic feedstock to CWAO before the catalytic APR stage. The CWAO stage in mild conditions allows partial oxidation of phenol and aromatic intermediates into carboxylic acids, while maintain high TOC for subsequent reforming to valuable gases in the APR stage.

Figure 5 shows TOC and COD removal upon coupled APR-CWAO of FPhOH feedstock with Pt/C catalyst. It can be observed that some mineralization of the feedstock occurred during CWAO stage, as 26 % of the initial feedstock TOC was removed in this stage, and that additionally 53 % of the initial feedstock TOC was removed in the APR stage, totalizing 79 % removal. The total removal of COD (65 %) was lower than total TOC removal. Figure 5 also shows that the removal of TOC in direct APR of FPhOH feedstock was 75 %, therefore the coupled APR-CWAO process achieved as slightly higher removal of TOC.

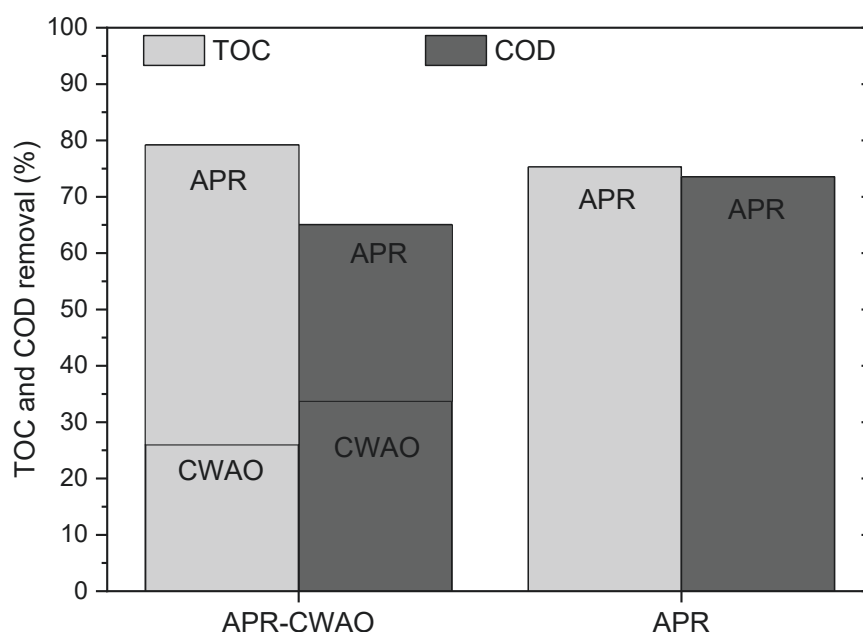


Figure 5. TOC and COD removal in APR-CWAO and direct APR of FPhOH with Pt/C catalyst

Table 7 shows the concentration of main components in the liquid phase resulting from CWAQ stage and the complete APR-CWAQ treatment of FPhOH. About 100 % of the carbon remaining in the liquid phase after the CWAQ stage was identified and the conversion of phenol was 39 %. Oxalic, maleic and formic acids were also identified, but in a very low concentration (<0.2 mg / L), while the concentration of malonic and acetic acids were high. After APR stage, the individual compounds identified were removed by more than 95 %, except in the case of malonic acid, whose concentration increased. Catechol, which was not identified in the initial feedstock, was detected after the APR stage. The main compounds analysed after the APR stage account for only 27 % of the organic carbon present in the liquid phase, showing that the effluent generated by APR-CWAQ of FPhOH is more complex than the resulting from direct APR of FPhOH, where 90 % of organic carbon was identified.

Table 7. Composition of the liquid phase after CWAO stage and complete APR-CWAO treatment of FPhOH feedstock with Pt/C catalyst

Run	Compounds								
	Phenol (mg / L)	Hydroquinone (mg / L)	Catechol (mg / L)	Oxalic (mg / L)	Maleic (mg / L)	Malonic (mg / L)	Fumaric (mg / L)	Acetic (mg / L)	Formic (mg / L)
CWAO	62.5	-	-	0.2	0.1	5.2	-	14.6	0.2
APR-CWAO		-	1.7	-	-	12.8	-	0.8	-

Table 8 shows the comparison between gas production, composition of the gas fraction, *CC gas* and yield to CH_4 obtained by APR-CWAO and direct APR of FPhOH. *CC gas* for APR-CWAO was 100 % higher than for direct APR. Y_{CH_4} was also significantly higher, but the percentage of H_2 in the gas fraction and Y_{H_2} were not improved. As shown in previous sections (e.g. Figure 2) poor results were achieved in direct phenol reforming, probably due to adsorption and deposition of condensation products onto the catalysts, and competition of HTC. In APR-CWAO the partial oxidation of phenol to compounds that can be reformed more easily increases *CC gas* and Y_{CH_4} , and also provides with slightly higher removal of TOC.

Table 8. Gas production and composition from direct APR and APR-CWAO of FPhOH with Pt/C catalysts

Runs	Gas Volume (mL)	Gas composition (% mol)			<i>CC gas</i> (%)	Y_{H_2} (mmol H_2 / g TOC_i)	Y_{CH_4} (mmol CH_4 / g TOC_i)
		H_2	CO_2	Alkanes			
APR	0.9	1.7	96.4	2.0	20.6	0.3	0.3
APR-CWAO	1.6	<0.1	77.6	22.4	48.3	<0.1	8.2

4. Conclusions

APR was coupled to CWAO as approach to removal and valorisation of phenolic compounds in wastewater to valuable gases. Coupled APR-CWAO of phenol feedstock

(FPhOH) led to TOC and COD removal slightly higher than direct APR. In addition, a much higher conversion to gases and yield to CH₄ (8.2 mmol CH₄ / g TOC_i) was achieved, although H₂ production remained low. The results show that coupled APR-CWAO process can be a promising approach to remove and valorise phenolic in wastewater, overcoming the low both conversion to gas and production of valuable gases observed in direct APR of aromatic compounds.

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