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Aqueous phase reforming of the residual waters derived from lignin-rich hydrothermal liquefaction: investigation of representative organic compounds and actual biorefinery streams / Pipitone, G., Zoppi, G., Bocchini, S., Rizzo, A.M., Chiaramonti, D., Pirone, R., Bensaid, S.. - In: CATALYSIS TODAY. - ISSN 0920-5861. - ELETTRONICO. - 345:(2020), pp. 237-250. [10.1016/j.cattod.2019.09.040]

Availability:
This version is available at: 11583/2761773 since: 2019-10-20T19:22:09Z

Publisher:
Elsevier B.V.

Published
DOI:10.1016/j.cattod.2019.09.040

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26 November 2026

Catalysis Today 345 (2020) 237–250

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Aqueous phase reforming of the residual waters derived from lignin-rich hydrothermal liquefaction: investigation of representative organic compounds and actual biorefinery streams

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ARTICLE INFO

Keywords:
Aqueous phase reforming
Hydrothermal liquefaction
HTL by-product streams
Biorefinery
Hydrogen production
Lignin

ABSTRACT

Secondary streams in biorefineries need to be valorized to improve the economic and environmental sustainability of the plants. Representative model compounds of the water fraction from the hydrothermal liquefaction (HTL) of biomass were subjected to aqueous phase reforming (APR) to produce hydrogen. Carboxylic and bicarboxylic acids, hydroxyacids, alcohols, cycloketones and aromatics were identified as model compounds and tested for APR. The tests were performed with a Pt/C catalyst and the influence of the carbon concentration (0.3–1.8 wt. C%) was investigated. Typically, the increase of the concentration negatively affected the conversion of the feed toward gaseous products, without influencing the selectivity toward hydrogen production. A synthetic ternary mixture (glycolic acid, acetic acid, lactic acid) was subjected to APR to evaluate any differences in performance compared to the tests with single compounds. Indeed, glycolic acid reacted faster in the mixture than in the corresponding single compound test, while acetic acid remained almost unconverted. The influence of the reaction time, temperature and carbon concentration was also evaluated. Finally, residual water resulting from the HTL of a lignin-rich stream originating from an industrial-scale lignocellulosic ethanol process was tested for the first time, after a thorough characterization. In this framework, the stability of the catalyst was studied and found to be correlated to the presence of aromatics in the aqueous feedstock. For this reason, the influence of an extraction procedure for the selective removal of these compounds was explored, leading to an improvement in the APR performance.

1. Introduction

During the last few decades the interest in biomass processing has increased, due to the growing demand of energy and the rapid development of the bioeconomy sector worldwide. Thermochemical processes aim at producing sustainable alternatives to conventional fossil fuels. Among the possible biomass conversion pathways, hydrothermal liquefaction (HTL) has been studied to produce an intermediate energy carrier, namely biocrude, with an oxygen content depending on the feedstock used and the reaction conditions [1]. The main advantage of HTL with respect to similar processes (e.g. pyrolysis) is the possibility to treat feeds with a high moisture content (up to 90 wt.%, such as in the case of aquatic biomass), eliminating or drastically reducing the need for a drying pre-treatment [2].

As well as the desired biofuel, HTL also produces a gas phase (rich in carbon dioxide), a solid phase (containing most of the inorganics present in the feed) and an aqueous phase, which contains short chain oxygenated hydrocarbons that are not soluble in the organic phase. While the relevant research works available in the scientific and technical literature focus on the optimization of the reaction conditions to improve the yield and quality of the biocrude, few authors have addressed the characterization of the aqueous phase [3]. As a matter of fact, one of the key bottlenecks for the development of this technology is represented by the need to recycle the residual water back into the process inlet, in order to minimize the water make-up from external sources [4].

Panisko et al. characterized the aqueous phase obtained from the HTL of pine forestry residuals showing that it is mainly constituted by

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https://doi.org/10.1016/j.cattod.2019.09.040
Received 20 July 2019; Received in revised form 15 September 2019; Accepted 25 September 2019
Available online 26 September 2019
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organic acids, such as glycolic acid and acetic acid, as well as alcohols (methanol and ethanol) and ketones (acetone and cyclopenta-ones) [5]. Overall, the waste water contains about 2 wt.% of organic carbon; however, it is even more important to highlight that the carbon yields in the aqueous phase (i.e. the fraction of carbon that ended up in the aqueous phase with respect to the original carbon content in the biomass feed) are in a range of 28–45 wt.%. This result not only points out the need to valorize also the organic compounds in the HTL-derived water, if the entire carbon heritage of the feedstock is to be exploited, but it also underlines the necessity to treat this water phase in order to allow its recycling within the process, thereby reducing the make-up of fresh water in the HTL feed. Similar considerations derive from the characterization of the aqueous fraction originating from the HTL of algae and municipal/food industry wastes [6,7].

Confirming the strategic importance of the valorization of secondary streams, two reviews have recently been published addressing the urgent need for of new processes to tackle this challenge [8,9].

Presently, catalytic hydrothermal gasification and anaerobic digestion are the two main technologies proposed to face the post-HTL water treatment issue [4]. However, the former has an important drawback related to the energy demand for heating water up to 350–400 °C, necessary to obtain a gas phase rich in methane [10]; while the latter has a long reaction time and requires large land surfaces [11].

In the present work, we approach the conversion of the water-soluble organic compounds derived from HTL through the aqueous phase reforming (APR), with the purpose of producing renewable hydrogen to be integrated into biorefinery processes.

APR was developed by the research group of Dumesic, identifying many organic substrates viable for the production of a hydrogen-rich gas mixture. The reaction stoichiometry in the case of carbohydrates is reported in Eq. (1) [12]. The possibility to perform the reforming reaction of oxygenated compounds at a lower temperature (220–270 °C) than the one used in conventional steam reforming of alkanes leads to two main advantages: i) a more energy-efficient process (avoiding vaporization of water); ii) the possibility to carry out the water gas shift reaction in the same reactor, thus increasing the hydrogen production while at the same time reducing the capital costs [13].

$$C_nH_{2y}O_n + nH_2O \leftrightarrow nCO_2 + (y + n)H_2 \quad (1)$$

In our previous work we performed a screening of several representative model compounds based on the cited literature works, and evaluated their reactivity for the APR process at different temperatures (230–270 °C) [14].

The aim of the present work is to investigate if APR can be a viable option to valorize the water stream derived from a hydrothermal liquefaction process. Indeed, as an alternative to the above cited gasification and/or anaerobic digestion, the APR can also contribute to the production of the hydrogen necessary for upgrading the HTL biocrude through hydrotreatments. In this context, the aqueous phase reforming would be perfectly integrated in a biorefinery concept, reducing the dependency from external sources of hydrogen, helping to generate a biofuel with an oxygen level compatible with the final specification downstream processing (Fig. 1). We initially investigated the APR of model compounds, looking at the influence of the nature of the substrate, its concentration and the reaction time. The majority of the literature research has been devoted to the study of alcohols and polyalcohols such as methanol and glycerol (for example [12,15–20]), but the majority of the remaining compounds has not been studied yet in detail for aqueous phase reforming (i.e. glycolic acid, propionic acid, cyclopentanone, guaiacol), despite their importance for the sustainability of the process. A ternary mixture was also tested to simulate a possible multi-component aqueous phase composition.

Finally, in order to be as close as possible to the actual application, we performed the APR of a water produced by the hydrothermal liquefaction of a biorefinery-derived lignin-rich stream. To the best of our knowledge, this is the first work that reports such investigation. A thorough study was performed in order to evaluate how the solvent, used during the extraction of the aqueous phase, affects the following APR step, referring in particular to the influence on the activity and stability of the catalyst.

2. Materials and methods

2.1. Materials

Glycolic acid, acetic acid, glutaric acid, methanol, guaiacol, ethanol and cyclopentanone were purchased from Sigma Aldrich. Lactic acid and propionic acid were purchased from Fluka. Deionized water was obtained in laboratory. A developmental 5% Pt/C catalyst was provided by Johnson Matthey.

2.2. Preparation of the aqueous phase for the APR

The aqueous phase used in the APR (hereafter referred to as HTL-AP) tests was produced at RE−CORD (affiliation [3]) during the batch hydrothermal conversion of the lignin-rich co-product from second generation lignocellulosic ethanol plant. The HTL conditions were: process temperature of 350 °C, autogenous pressure, residence time of 10 min, dry lignin-rich coproduct to water ratio of 10% by weight. Details of the batch experimental apparatus and HTL test procedures can be found elsewhere [21]. The reactor consists of an AISI 316 ¾" (outer diameter) tube with a length of 300 mm (~43 ml of internal volume). In order to prepare batch experiments, dried feedstock was dispersed in ultrapure water (0.055 μS cm^{-1}) to attain the desired biomass-to-water mass ratio. The mass of slurry loaded into the reactor was 33 g for each test. Prior to each experiment, a leakage test was performed with argon pressurized at 8 MPa. Then, three purging cycles with nitrogen (0.5 MPa) were carried out in order to remove air and ensure an inert atmosphere in the reactor. An initial pressure of 3 MPa was set using argon, then the reactor was immersed into a fluidized sand bath. Counting of residence time started when the inner reactor temperature reached 2 °C below the set reaction temperature: as the design residence time was completed, the reactor was rapidly cooled by immersion in a water bath. After nearly 20 min, the pressure was gradually released, the reactor opened and disconnected from the test bench.

2.3. Aqueous phase reforming test

The APR reactions were performed in a 300 ml Parr reactor (4560 series mini bench top reactor) equipped with a reactor controller (4848 model). The reactor was filled for ¼ of its total volume with 75 ml of the aqueous solution and 375 mg of catalyst. The catalyst was used as received without any pre-treatment. Pure nitrogen was used to purge the reactor atmosphere and to pressurize it at 0.3 MPa; the stirring rate was kept fixed at 400 rpm. The time of reaction started once the set temperature was reached, typically for 2 h; shorter and longer time were used to study the influence of reaction time. Once reached the desired time, the heating was stopped, the reactor cooled down at 22 °C and the reached pressure was recorded. The produced gas phase was collected in a syringe and sent to micro-GC to evaluate its composition; a quantification was also possible thanks to the initial nitrogen used as internal standard, the results being consistent (error ± 5%) with the quantification derived by the pressure transducer. The liquid phase was recovered, filtered to remove the catalyst and then analyzed by TOC and HPLC. The spent catalyst on filter paper was dried overnight in the oven (105 °C), recovered and weighted. For catalyst reuse tests, the recovered catalyst was used without any further treatment.

2.4. Analytical methods

The gas phase was characterized through a SRA micro-GC. The

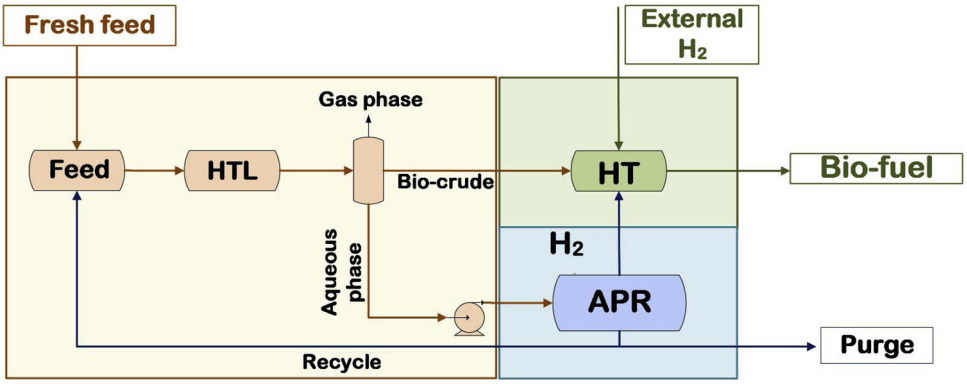


Fig. 1. Block flow diagram of a HTL-APR integrated plant. HTL: hydrothermal liquefaction; HT: hydrotreatment (upgrade block).

instrument is equipped with two columns: a Molsieve 5A column, which works with argon as carrier and a temperature of 100 °C to separate hydrogen, nitrogen, methane and carbon monoxide; a PoraPLOT U used to separate methane, carbon dioxide, ethane, ethylene, propane working with helium as carrier and a temperature of 85 °C. The detector is a TCD detector. The injection temperature was fixed at 100 °C and the pressure at $2*10^5$ Pa.

Regarding the liquid phase from APR, the characterization was performed thanks to Shimadzu HPLC equipped with a Rezex ROA-Organic acid H^+ (8%) column (300 mm * 7.8 mm); the flow rate of the mobile phase (5 mM H_2SO_4 aqueous solution) was fixed at 0.7 ml/min and the working temperature at 50 °C. The detection of the species was made by means of a refractive index detector (RID) and a photodiode array detector (PDA), in the range 190–380 nm. External calibration curves were made thanks to purchased standards.

The water phase from HTL was also characterized by dilution with 2-propanol in a GC 2010 with a GCMS-QP2010 mass spectrometer (Shimadzu) equipped with a ZB-5 MS column (30 m length, internal diameter 0.25 mm, film diameter 0.25 µm, Phenomenex). The temperature was held at 40 °C for 10 min and then increased to 200 °C (heating rate 8 °C min^{-1}, holding time 10 min) and 280 °C (heating rate 10 °C min^{-1}, holding time 30 min).

The concentration of the water soluble organics in the aqueous phase from HTL was evaluated by HPLC (LC-20 AT Prominence Shimadzu) equipped with a refractive index detector, a Hi-Plex H column 300 × 7.7 mm (Agilent) and a guard column PL Hi-Plex H 50 × 7.7 mm (Agilent), operating at 40 °C with a flow of 0.6 ml min^{-1} with 0.005 M sulfuric acid as mobile phase. Twenty-five microliters of each aqueous sample were injected after a 0.2 µm syringe filtration.

The total carbon analysis was made using a Shimadzu TOC-V_{CSH} analyzer equipped with a nondispersive infrared detector.

The analysis of the inorganics was performed using a Thermo Scientific iCAP Q ICP-MS (Thermo Fischer).

TGA-FT-IR analyses were performed using a TG 209 F1 by NETZSCH Thermal Analysis. Approximately 10 mg of sample in alumina pans were heated from 30 to 1000 °C (20 °C/min) under pure nitrogen (20 ml/min). The system was coupled by a Netzsch-TGA-IR coupling line to a Bruker Tensor II spectrophotometer equipped with DTGS detector and a Bruker heated gas chamber analysis accessory. The CO_2, CO, CH_4, H_2O and carbonyl groups were followed by analyzing the 2359, 2173, 3016, 1506 and 1792 cm^{-1} peaks respectively. Aliphatic stretching was followed using C–H stretching at 2965 cm^{-1}. Depending on the nature of C–O stretching, the C–O stretching was followed using the peak at 1064 cm^{-1} in the presence of primary alcohols and 1174 cm^{-1} in the presence of anhydrides.

XPS measurements were carried out with a PHI Model 5000 electron spectrometer equipped with an aluminum anode (1486 eV) monochromatic source, 25.0 W power, and high-resolution scan with 11.75 eV pass energy. The binding energies obtained by XPS analysis were corrected for specimen charging by referencing the C1s = 284.6 eV.

Five parameters were used to estimate the performance of the process (based on the ones frequently found in literature). The carbon to gas conversion, defined as the ratio between the moles of carbon in the gas product $mol_{fin}C_{gas}$ and the moles of carbon in the feed $mol_{in}C_{feed}$ (Eq. (2)); the APR hydrogen yield $APR\text{-}Y_{H2}$, defined as the ratio between the moles of produced hydrogen in the gas phase mol_{fin} H_2 and the moles of feed (it is highlighted here that (y + n) is added according to the reaction stoichiometry to reach a maximum 100% yield) (Eq. (3)); the hydrogen gas distribution GD_{H2}, defined as the ratio between the moles of hydrogen present in the gas phase as molecular hydrogen (mol_{fin} H_2) after the reaction and the moles of total hydrogen present in the final gas phase (that is, also as alkanes) (Eq. (4)); the APR H_2 selectivity $APR\text{-}S_{H2}$ defined as the ratio between the moles of hydrogen and carbon dioxide in the final gas phase (H_2/CO_2), divided by the theoretical ratio $(H_2/CO_2)_{teo}$ according to the reaction stoichiometry reported in the Eq. (1) (Eq. (5)); please note that this value may exceed 100% if other reactions (e.g. dehydrogenation) occur. Finally, the hydrogen productivity is defined as the moles of hydrogen produced divided by the moles of carbon in the feed (Eq. (6)). The last parameter was useful especially for the HTL-AP, where the complex composition does not allow to use parameters involving the classical reaction stoichiometry.

$$\text{Carbon to gas (\%)} = 100^* \frac{\text{mol}_{\text{fin}}\,\text{C}_{\text{gas}}}{\text{mol}_{\text{in}}\,\text{C}_{\text{feedstock}}} \quad (2)$$

$$\text{APR}-\text{H}_2\text{ yield (\%)} = 100^* \frac{\text{mol}_{\text{fin}}\,\text{H}_2}{(\text{y}+\text{n})^*\text{mol}_{\text{in}}\,\text{feedstock}} \quad (3)$$

$$\text{H}_2\text{ gas distribution (\%)} = \frac{\text{mol}_{\text{fin}}\,\text{H}_2}{\text{mol}_{\text{fin}}(\text{H}_2 + 2^*\text{CH}_4 + 3^*\text{C}_2\text{H}_6 + 4^*\text{C}_3\text{H}_8)} \quad (4)$$

$$\text{APR H}_2\text{ selectivity(\%)} = 100^* \frac{\text{mol}_{\text{fin}}(\text{H}_2/\text{CO}_2)}{(\text{H}_2/\text{CO}_2)_{\text{teo}}} \quad (5)$$

$$\text{H}_2\text{ productivity} = \frac{\text{mol}_{\text{fin}}\,\text{H}_2}{\text{mol}_{\text{in}}\,\text{C}_{\text{feedstock}}} \quad (6)$$

3. Results and discussion

3.1. Model compounds

3.1.1. Influence of carbon concentration

Based on the analysis of the literature and authors' previous work, ten compounds were selected for the evaluation of the influence of the concentration on the APR process [5,14].

The main results are reported in Table 1 for each compound in the range 0.3–1.8 wt% of carbon. This range was chosen in order to

Table 1
Influence of carbon concentration on APR of model compounds. Reaction conditions: Liquid phase amount: 75 g, 0.375 g Pt/C, reaction temperature 270 °C, reaction time 2 h.

Concentration (wt. %C)	APR H_2 yield (%)	Carbon to gas (%)	APR selectivity (%)	H_2 gas distribution (%)
Glycolic acid				
0.3	65.1	65.9	99.8	98.8
0.9	55.3	53.2	104.4	99.4
1.8	31.1	33.9	92.4	99.1
Acetic acid				
0.3	1.2	79.2	3.3	2.9
0.9	0.6	33.5	4.1	3.4
1.8	0.5	16.0	7.0	6.0
Lactic acid				
0.3	2.3	66.8	8.1	7.0
0.9	1.0	32.7	5.6	7.4
1.8	0.8	19.9	5.8	11.5
Propionic acid				
0.3	2.2	75.1	8.8	6.3
0.9	0.8	28.2	7.7	5.9
1.8	0.2	4.4	8.5	8.0
Glutaric acid				
0.3	2.5	76.6	3.4	7.1
0.9	0.8	37.1	1.7	6.3
1.8	0.4	22.6	1.3	6.7
Glycerol				
0.3	58.9	74.4	102	80.6
0.9	37.8	53.4	96.4	76.0
1.8	19.9	31.9	85.7	73.6
Methanol				
0.3	58.8	54.7	109.9	98.4
0.9	32.1	29.2	113.5	98.2
1.8	19.9	19.4	105.4	98.0
Guaiacol				
0.3	0.3	18.6	2.8	4.2
0.9	0.2	12.5	3	2.9
1.8	0.2	2.2	20	14.5
Ethanol				
0.3	23.8	70.0	75.4	48.4
0.9	24.4	70.5	75.0	49.3
1.8	17.0	51.0	70.9	48.8
Cyclopentanone				
0.3	0.9	4.4	25.7	65.0
0.9	0.8	3.9	35.2	42.4
1.8	0.5	0.4	131	96.9

investigate the diluted conditions commonly observed in literature.

Acetic acid and propionic acid were chosen to represent the carboxylic acids class. Both compounds showed a drastic decrease of the carbon conversion to gas with the increase of the concentration in the solution, moving from 80% to 15% for acetic acid and from 75% to 5% for propionic acid. Even if the reaction conditions did not allow to extrapolate kinetics, we may assume that there was a strong inhibiting effect of the feed, as the levels of conversion are inversely proportional to the concentration [16]. On the other hand, the selectivity towards alkane formation (i.e. the hydrogen gas distribution) and the H_2/CO_2 ratio remained constant on the whole range. It should indicate that new reaction pathways are not favored.

As we reported in [14], in which a Pt/Al_2O_3 catalyst was used, acetic acid and propionic acid mainly lead to the formation of a gas mixture composed by 50% carbon dioxide and 50% methane (or ethane in the case of propionic acid). This result was confirmed with the active carbon support used in this work, highlighting that the gas product distribution is neither influenced by the concentration nor by the support used for the catalyst, the nature of the active sites being the main responsible of the catalytic decomposition to CO_2 and alkanes. Given the low H_2 selectivity, the APR-H_2 yield was low at each tested concentration.

Glycolic acid and lactic acid were chosen as the most representative hydroxyacids in the aqueous effluent of hydrothermal liquefaction. Indeed, glycolic acid was reported as the main compound in the aqueous phase coming from the HTL of corn stover [5]. Despite a decrease of the carbon conversion to gas, the influence of the concentration is less evident as compared to the case of the carboxylic acids. On the other hand, a strong difference between the two compounds can be observed looking at their hydrogen yield. Glycolic acid showed a decrease in the hydrogen production due to the lower conversion, but maintained at least 30% yield at 1.8 wt.% C. Instead, the lactic acid yield was always below 5%, despite similar levels of conversion. As reported in the following section 3.1.2, lactic acid produces carbon dioxide and ethane due to the formation of propionic acid as reaction intermediate, recalcitrant to hydrogen production. On the other hand, the glycolic acid led only to a slight production of acetic acid, while selectively produced carbon dioxide and hydrogen in a ratio close to the stoichiometric one. Please note that the APR H2 selectivity higher than 100% are ascribed to further hydrogen-producing reactions, such as dehydrogenation (the same comment is valid for methanol).

Methanol and ethanol were investigated as they are likely present in the post-HTL aqueous phase [5]. The carbon conversion to gas of methanol decreased with the increase of the carbon concentration from 58% to 20%, while the APR-H_2 selectivity and H_2 gas distribution remained almost constant and close to 100%. Methanol was largely investigated as model compound for APR since it is the simplest alcohol to perform this kind of investigation [12,15,16,22–24]. These results can be explained by the structure of the alcohol that is readily dehydrogenated producing only hydrogen and carbon monoxide, reducing parallel and consecutive reactions (e.g. methanation or Fischer-Tropsch) involving different fragments of the molecule (such as alkyl groups); afterwards, the carbon monoxide is converted to carbon dioxide and hydrogen by reaction with activated water. Ethanol showed higher carbon to gas conversion than methanol thanks to the production of methane, together with carbon dioxide. Due to the production of the alkane, the hydrogen gas distribution was nearly 50%, constant in the whole range of concentration. It is interesting to observe that no difference in performance were reported between 0.3% and 0.9%. This fact should be due to the lower strength of adsorption of ethanol compared to methanol, that caused an apparently linear rate of consumption up to 0.9% of carbon.

Cyclopentanone was reported as one of the most present ketones in the post-HTL aqueous phase [5]. It is a valuable compound used, for example, in the preparation of specialty chemicals for the pharmaceutical or cosmetic sector [25]. Nevertheless, as it is present in very diluted concentrations, it is uneconomically envisaging a selective recovery. It was almost unreactive in the investigated reaction conditions (with about 20% of conversion of the feed in the whole range of concentration), showing the lowest carbon conversion to gas among the ten screened compounds. It is interesting to observe that the hydrogen gas distribution and the APR-H_2 selectivity were strongly influenced by the carbon concentration. The latter increased strongly with the increase of the concentration, thanks to the fact that the hydrogen production linearly increased in the studied range, while the carbon dioxide production had a maximum at 0.9% wt.% carbon. Moreover, it was observed that the weight of the catalyst recovered was higher than the initial 375 mg (the accuracy of the recovery procedure should be in ± 5% range, assessed in organics-free blank tests). For this reason, it can be assumed that high-molecular weight compounds may be produced by aldol-condensation [26].

Glutaric acid was chosen as a typical example of bi-carboxylic acid. A strong decrease in the carbon conversion to gas was observed with the increase of the concentration, from 75% down to 25%. Interestingly, the analysis of the liquid phase showed an increase of the selectivity toward the formation of liquid products, mainly butanoic

acid. In fact, while the conversion to gas phase decreased, the conversion of the feed remained approximately constant, favoring the formation of liquid by-products (propionic and acetic acid together with the butanoic acid). In analogy with the mono-carboxylic acid, the first reaction seems to be therefore the decarboxylation. Afterwards, as they are recalcitrant towards hydrogen production, the APR-H_2 yield remained low in all the investigated concentration range.

Guaiacol was studied as representative aromatic compound. As reported in the paragraph 3.3, aromatics can be present in the aqueous phase in the case of the hydrothermal liquefaction of lignin. As shown in the Table 1, the carbon conversion to gas decreased from 20% to 3%, while the hydrogen gas distribution and APR-H_2 selectivity increased. This is due to an increase of the hydrogen production, together with a decrease of the formation of methane and carbon dioxide. The analysis of the liquid phase can give a hint on the reason behind these results. The methane can be obtained by breaking the ether bond of the guaiacol, leading to catechol [27]. The HPLC chromatograms showed a decrease of the catechol production with the increase of the concentration, resulting in a greater hydrogen gas distribution. Phenol, the second most present by-product, can be obtained by consecutive deoxygenation from catechol itself.

Glycerol was also investigated in order to include in our study molecules not strictly related to the aqueous phase post lignin HTL, but still generally interesting for the valorization of organics dissolved in water. Glycerol can be found as soluble organic in the water phase, in particular from the hydrothermal liquefaction of aquatic biomass [28,29]. This is due to the hydrolysis of triglycerides, that lead to fatty acids (ending up in the biocrude) and glycerol (ending up in the aqueous phase). The carbon to gas conversion constantly decreased from 73% to 30%; contrarily to the other compounds screened in the present work, a clear influence of the carbon concentration was observed also in the case of the hydrogen gas distribution and APR-H_2 selectivity, due to the change of selectivity in the intermediate liquid products (i.e. hydroxyacetone).

3.1.2. Influence of reaction time

Based on results available in literature [5], three compounds were selected as the most representative ones of a post-HTL aqueous stream: glycolic acid, acetic acid and lactic acid. The APR of these compounds was performed at different reaction times to evaluate the presence of reaction intermediates and suggest a plausible reaction pathway. Since the sampling of the gas phase during the reaction is experimentally difficult, a series of tests was carried out at different time durations with the same initial conditions. For the sake of clarity, 0 h is intended as the point in which the set temperature is reached (heating time approximately 60 min) (Fig. 2).

Acetic acid converted up to 35% before reaching the set temperature, producing with a high selectivity a gas mixture with a 1:1 carbon dioxide/methane ratio (Fig. 2-A). It is clear that the consumption of acetic acid moles is almost entirely ascribed to the formation of methane and carbon dioxide. The relative production of the gas remained almost constant during the investigated reaction times. Hydrogen was present in small amount. This is due to the favorable cracking of the C—C bond, as confirmed in literature at different reaction conditions, and in our previous work with an alumina-supported Pt catalyst [14].

Glycolic acid reached a 28% conversion during the heating time and almost complete conversion after 2 h. Hydrogen was the main product in the gas phase at each reaction time, reaching a plateau at about 2 h, while carbon dioxide slightly increased up to 8 h. According to the reaction mechanism suggested in our previous work, glycolic acid should produce 1.5 mol of hydrogen per mole of carbon dioxide [14]. This ratio is higher during the heating time, likely because the dehydrogenation (first step of APR) is predominant on the reaction mechanism compared to the reforming. In the following, it decreases also because of the formation of acetic acid, the only quantifiable liquid product. It may be obtained by the hydrogenation of the hydroxyl group of the glycolic acid, arising an issue of series-selectivity. As reported by Neira D'Angelo, the reactor configuration might be designed to allow the hydrogen to escape from the solution once formed, without being consumed in parasite reactions using a microchannel reactor, together with an inert gas stripping [30]. Acetic acid did not appreciably react because methane was barely detected in the gas phase.

Finally, lactic acid converted completely during the heating time. For this reason, it was decided to stop the heating period after 20 min (where reached temperature was about 165 °C) and 40 min (about 245 °C). While there was no conversion during the first step, at 245 °C a small conversion of the lactic acid was already observed. Two parallel but interacting pathways have been proposed for lactic acid (Fig. 3). In analogy with acetic acid behavior, lactic acid can be decarboxylated producing ethanol and carbon dioxide (light blue frame); subsequently, ethanol can readily react producing methane, carbon dioxide and hydrogen (red frame); for this reason, ethanol may not be observed by HPLC analysis. The second pathway involves the hydrogenation of lactic acid (using the hydrogen produced from ethanol APR) leading to propionic acid (green frame), that will subsequently lead to ethane and carbon dioxide, as reported in [14].

We tried to verify this hypothesis looking at the results of lactic acid conversion vs time evolution. At 0 h, 4.0 mmoles of methane have been produced; it follows that, according to the proposed reaction scheme, 8.0 mmoles of hydrogen and of carbon dioxide should be obtained as well (experimentally, 8.8 mmoles of CO_2 were quantified). The presumed amount of hydrogen was not detected as it almost completely reacted to produce propionic acid (9.4 mmoles detected at 0 h). From this point on, only propionic acid slowly reacted: from 0 to 8 h, 3.9 mmoles of propionic acid converted into carbon dioxide (3.7 mmoles measured increase from 0 h to 8 h) and ethane (3.4 mmoles measured increase over the same time), as the stoichiometry in the proposed scheme suggests.

The simplified scheme in Fig. 3, although not fully comprehensive of the possible reaction pathways involved in lactic acid conversion, is in fair agreement with the experimental observations, notwithstanding the possible uncertainties in gas and liquid phase quantifications.

3.2. HTL aqueous phase synthetic mixture

Glycolic, acetic and lactic acid were tested in a ternary mixture with global 0.9 wt% C concentration, equally divided in each component (Fig. 4). It was previously observed that the molecules own different reactivity if they are tested alone or in mixture, likely because of competitive adsorption issues [14]. In the present study, we further investigated this aspect, looking at the influence of the reaction time.

Some characteristic outcomes can be highlighted. First of all, it was observed that glycolic acid was the compound with the highest initial rate of consumption, reaching 92% of conversion during the heating period. Hydrogen and carbon dioxide were produced from glycolic acid with the same selectivity reported in the single test, i.e. about 1:1.5 ratio hydrogen: carbon dioxide, and 1 mol of CO_2 per mole of glycolic acid converted. On the other hand, lactic acid, that almost disappeared in the test reported in the previous section, showed an initial low conversion. This result suggests a clear competition in the adsorption of the molecules on the active sites. In the case of the mixture, the adsorption of a reactant implicates also the displacement of the other adsorbed specie, leading to a more complex scenario compared to the test with a single compound [31]. It can be hypothesized that glycolic acid and lactic acid, co-adsorbing on the surface sites, limited the adsorption of acetic acid and, as a consequence, decreased strongly its reactivity [32]. The conversion of acetic acid from 2 h to 8 h led to the selective increase of carbon dioxide and methane in 1:1 ratio, with the same selectivity noted in the single test.

In the following Fig. 5A the influence of the total carbon concentration on the APR parameters is reported. A decrease in the carbon conversion to gas from 35 to 20% was observed, while the hydrogen gas

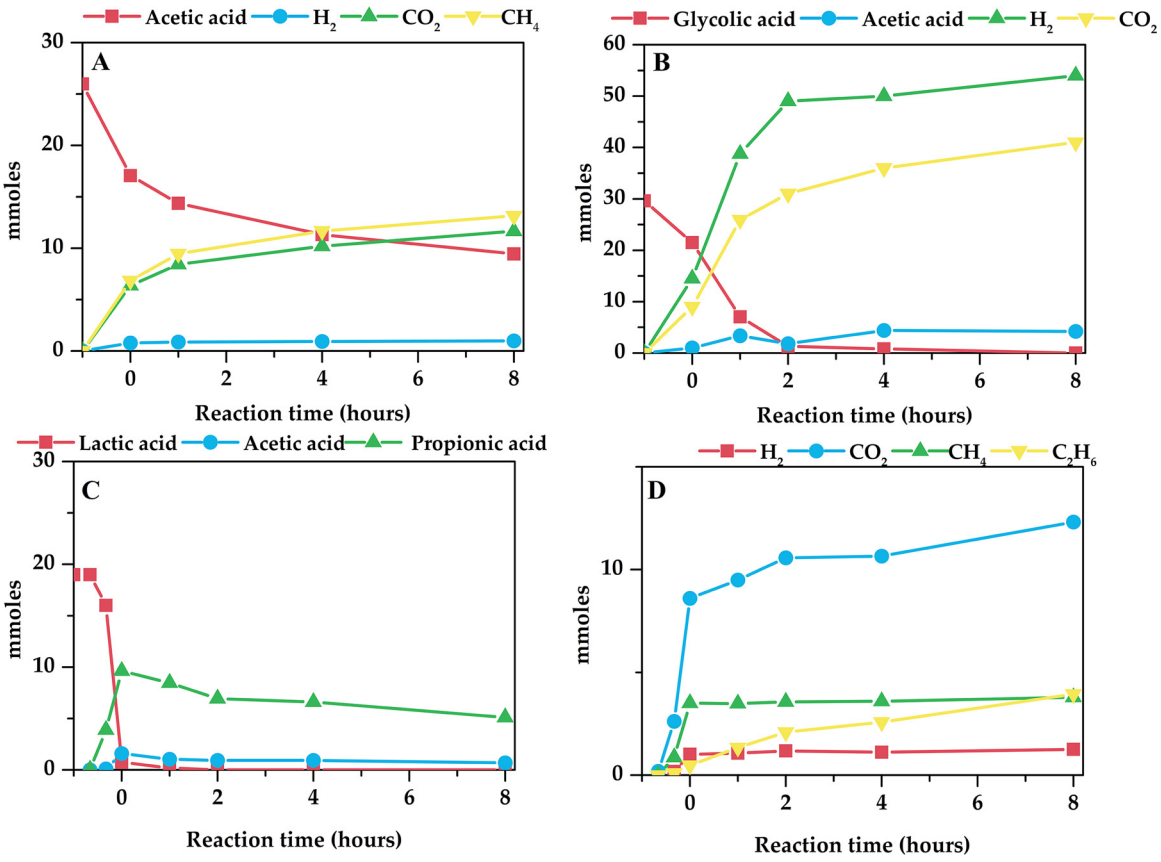


Fig. 2. Amount-time profile for APR of acetic acid (A), glycolic acid (B), Lactic acid (C–D). Reaction conditions: liquid phase amount 75 g, 0.375 g Pt/C, 0.9 wt. % C feed, reaction temperature 270 °C.

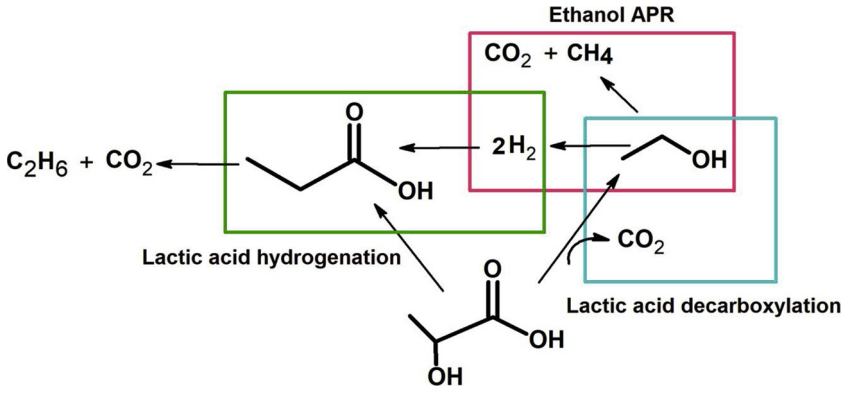


Fig. 3. Proposed reaction scheme for lactic acid APR.

distribution and the APR H_2 selectivity increased from 59% to 82% and from 47% to 68% respectively. The different trends between the conversion and the selectivity led to an almost constant hydrogen yield in the investigated range of carbon concentration. In order to understand this behavior of the mixture, it is interesting to observe the conversion of each molecule (Fig. 5B). Moving from 0.3 to 0.9 wt% of carbon, glycolic acid still fully converted and lactic acid up to 90%, while acetic acid remained almost unconverted. Due to this different reactivity, likely linked to the previously described influence of reaction time, the carbon conversion to gas decreased, but the selectivity increased (mainly thanks to the intrinsic high selectivity of glycolic acid). In an analogous way the increase of the selectivity from 0.9 to 1.8 wt% can be explained. Indeed, as the conversion of the lactic acid decreased to 20%, the produced gas phase was mainly ascribed to the conversion of glycolic acid.

Finally, the influence of the reaction temperature is reported in Fig. 6. A constant increase of the carbon to gas conversion was observed, in accordance to literature, due to the more readily breakable C—C bond [13]. The APR-H_2 selectivity decreased slightly from 250 and 270 °C because of the higher carbon dioxide production due to the higher conversion of acetic acid. At the same time, the higher reactivity of acetic acid at higher temperature led to higher production of methane and, therefore, to a smaller hydrogen gas distribution.

3.3. Case study: APR of the water fraction from HTL of lignin

3.3.1. Characterization of the aqueous phase

In order to assess the possible valorization of the aqueous phase from biomass hydrothermal liquefaction via APR, an organics-laden aqueous stream originated from the HTL of lignin was investigated.

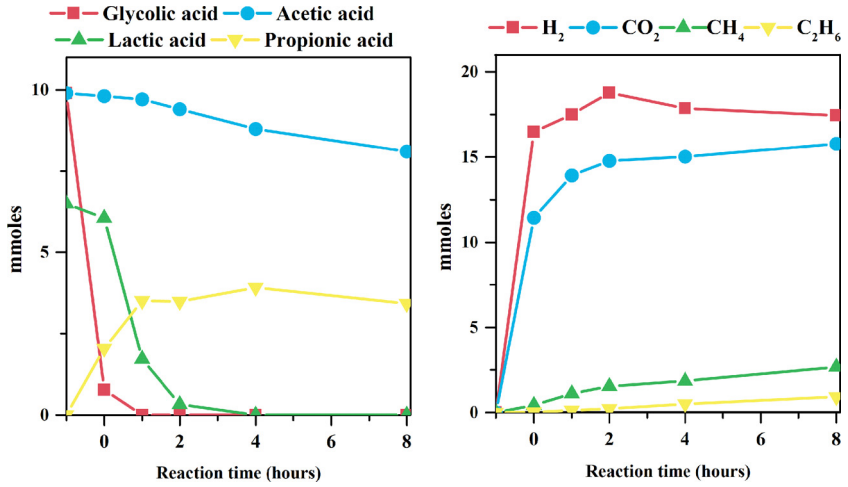


Fig. 4. Amount-time profile for APR of a synthetic ternary mixture. Reaction conditions: liquid phase amount 75 g, 0.375 g Pt/C, total 0.9 wt.% C glycolic, acetic and lactic acid (0.3 wt.% C per component), reaction temperature 270 °C.

Indeed, the available literature lacks on knowledge about the APR real water streams, underestimating the complexity deriving from mixtures of compounds, inorganics etc.

Few works reported an extensive characterization of the products of lignin HTL [33]. In the following Table 2, the classification and quantification of the main compounds present in the water are reported. While the sample named simply "HTL-AP" was obtained with a separation by gravity filtration, the samples named "Treated HTL-AP x" were obtained washing with an excess diethyl ether in a 5:1 ratio to reduce the phenolic compounds concentration, whose motivation will be clearer n the following. From the HPLC and GC analysis, it was possible to identify most of the compounds in the water fraction (approximately 70% of the total organic content). Fig. 7 shows the HPLC chromatograms of the HTL-AP sample. Several classes of compounds were identified, such as carboxylic acids (e.g. acetic acid, glycolic acid, lactic acid), alcohols (methanol, ethanol, 2-propanol), ketones (acetone), polyalcohols (glycerol), aromatics (phenol, catechol, guaiacol) and aldehydes. As it can be noticed, the screening of model compounds performed in the paragraph 3.1 reflects the species found in the actual aqueous phase.

Methanol is the most present compound, followed by lactic acid, phenolic compounds, glycolic acid, acetic acid and glycerol. Moreover, the quantification of inorganic species (sodium, calcium, potassium, sulfur and phosphorous) is given in the same table. Since the presence

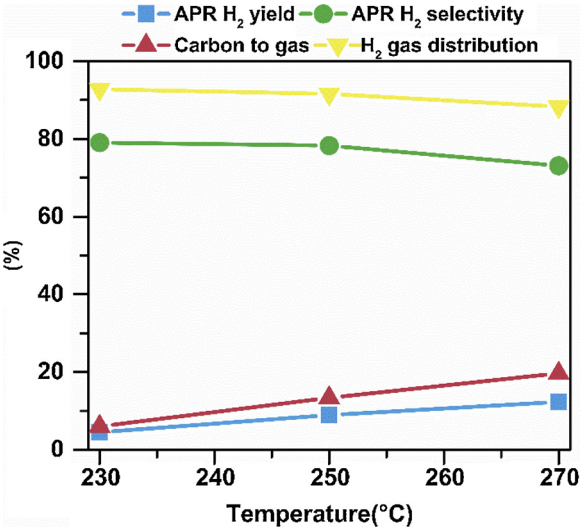


Fig. 6. Influence of reaction temperature on the reaction parameters of APR of the synthetic mixture. Reaction conditions: liquid phase amount 75 g, 1.8 wt. % C, reaction time 2 h.

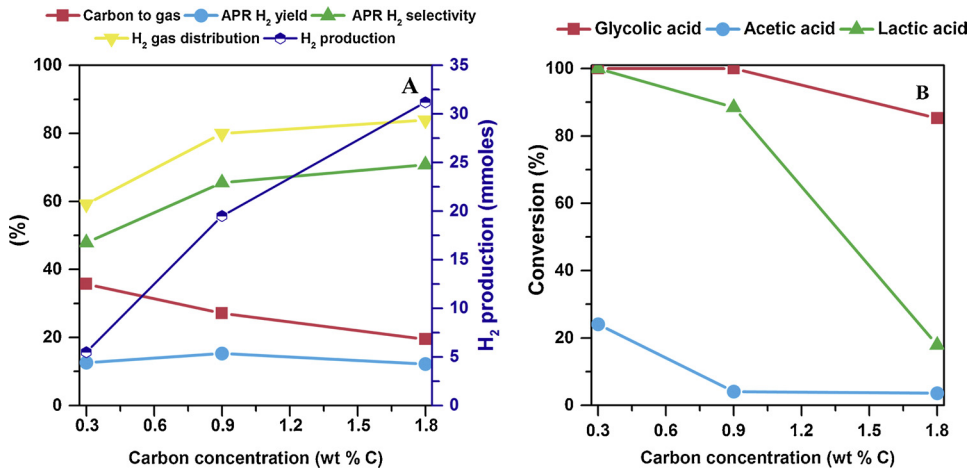


Fig. 5. Influence of carbon concentration on the reaction parameters (A) and conversion (B) of APR of the synthetic mixture. Reaction conditions: liquid phase amount 75 g, reaction temperature 270 °C, reaction time 2 h.

Table 2
HTL-AP quantification of main compounds and ICP analysis.

	Carbon weight concentration (wt. % C)						Inorganic species (ppm)					
Sample	Glycolic	Lactic	Acetic	Methanol	Glycerol	Phenolic compounds	Na	K	Ca	S	P	Total organic carbon (mgC/L)
HTL-AP	0.047	0.112	0.083	0.138	0.029	0.116	518	281	13	116	11	11558
Treated HTL-AP 1	0.049	0.102	0.078	0.124	0.022	0.056	190	140	15	19	1	10810[a]
Treated HTL-AP 2	0.051	0.109	0.051	0.099	0.020	0.017	n.a.	n.a.	n.a.	n.a.	n.a.	10540[a]
Treated HTL-AP 3	0.050	0.099	0.044	0.096	0.020	≈ 0	350	233	0	53	43	10358[a]

[a] excluding DEE.

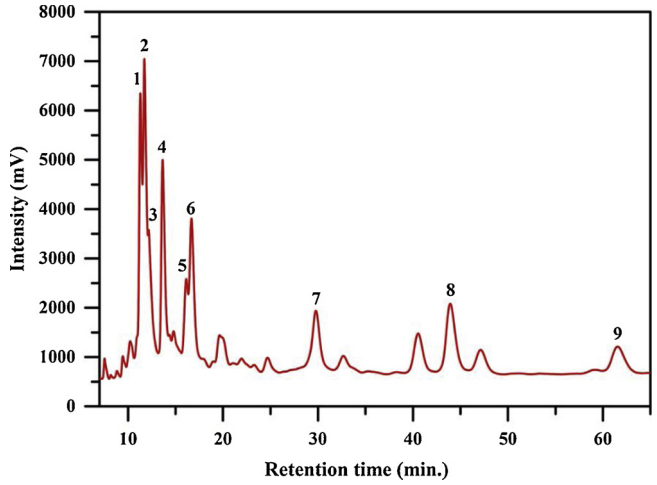


Fig. 7. HPLC chromatograms of the HTL-AP (1: glycolic acid, 2: lactic acid, 3: glycerol, 4: acetic acid, 5: acetaldehyde, 6: methanol, 7: catechol, 8: phenol, 9: guaiacol).

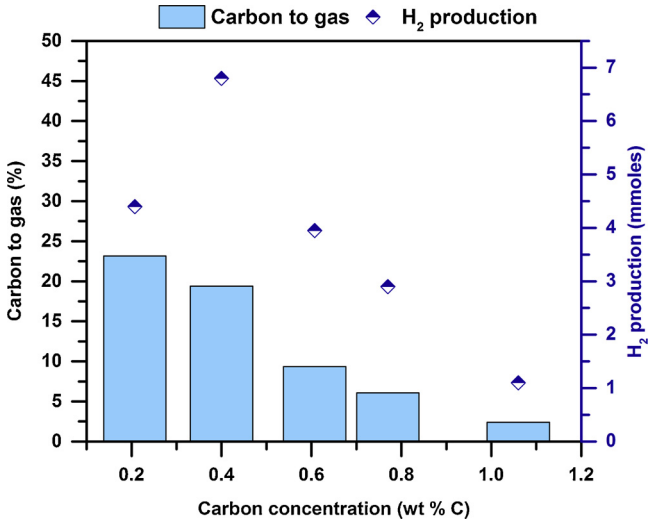


Fig. 8. Influence of carbon concentration on reaction parameters of APR of the HTL-AP. Reaction conditions: liquid phase amount 75 g, reaction temperature 270 °C, reaction time 2 h.

of inorganics can affect the catalyst lifetime, an investigation was performed in paragraph 3.3.3. As far as the total organic content is concerned, the tested samples have a carbon content of around 1 wt.% C. This value is lower than the typical ones reported in literature from the hydrothermal liquefaction of lignocellulosic biomass [5].

The storage of the sample was carried out at -5 °C: despite the low temperature, the formation of solid particles was observed during storage, likely due to oligomerization reactions involving the phenolic compounds [34]. In order to evaluate the influence of this solid phase, two tests were performed with and without a filtration of the aqueous phase (results reported in the supporting information, Figure S1). Both carbon conversion and hydrogen production were negatively affected by the presence of the particles. For this reason, as they can contribute to affect the activity and the stability of the catalyst, a pre-filtration of the as-received liquid phase was performed in the following experimental campaign with a 0.2 µm nylon filter.

3.3.2. HTL-AP catalytic tests

The influence of the carbon concentration on the carbon to gas conversion and hydrogen production of the APR of the HTL-AP is shown in the Fig. 8. It is important to highlight that the amount of hydrogen (reported in mmoles) obtained in the gas phase decreased strongly at increasing carbon concentration. This was a surprising result, as the increase of the concentration may surely negatively affect the hydrogen yield, but the amount of product should at least remain constant (unless of the rare case of kinetics with negative reaction orders).

In Fig. 9 (right) the chromatogram of the feed and liquid product of the APR performed on 1 wt% C HTL-AP is reported (named in the figure Product 1st test). It is possible to notice a similar peak intensity of most of the present molecules in the APR product (glycolic acid, lactic acid, glycerol, methanol) with respect to their original content in the feed, leading to a low carbon conversion to gas and a negligible hydrogen production. This outcome was not coherent with the previous results reported for the synthetic mixture (paragraph 3.2), where glycolic and lactic acid were highly reactive and converted completely before the end of the reaction.

In order to exclude an experimental error, the obtained solution after the filtration was subjected again to an APR test, using a fresh catalyst. The HPLC chromatogram of the liquid APR product obtained at the end of the 2nd test is reported in Fig. 9 (left) and is compared to the one at the beginning of the test, which in fact is the liquid phase obtained after the 1st test.

As it can be noticed, thanks to the 2nd test, most of the initially present compounds were converted, being the peaks of glycolic acid, lactic acid, glycerol and methanol almost disappeared. Please note that the higher conversion cannot be due to the global longer reaction time (as the HTL-AP was subjected in this way to two runs, each one at 2 h) because a test performed on a HTL-AP for 4 h reaction time led to the same result obtained with the 2 h test.

The higher conversion in the 2nd test led to a higher hydrogen production, as showed in Fig. 10A, where the hydrogen productivity (i.e. the hydrogen production normalized by the moles of carbon in the feed) is reported for the 1st and 2nd tests. It can be observed that the 2nd test reported a higher and almost constant hydrogen productivity, contrarily to the trend obtained by the 1st runs, that was decreasing in the entire range of carbon concentrations investigated. It is highlighted here how the 2nd test had a lower starting carbon concentration compared to the corresponding 1st test. This is due to the impossibility to recover the entire liquid phase after the first reaction and, secondarily, to the low but not negligible conversion obtained during the 1st test.

The sum of the hydrogen mmoles produced during 1st test (black) and 2nd test (red) are showed in Fig. 10-B. It can be observed that the

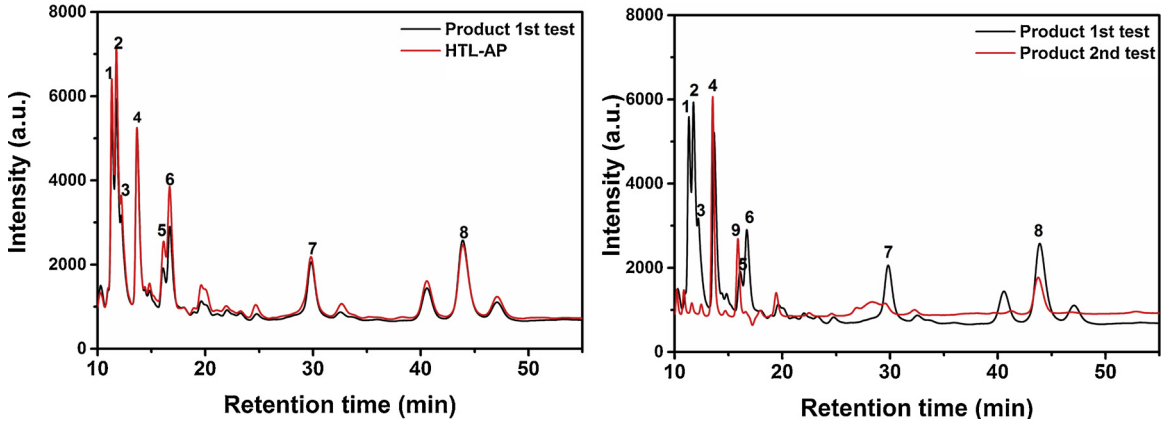


Fig. 9. HPLC chromatograms of the feed and product for the first test (left) and second test (right) of the HTL-AP sample. Reaction conditions: liquid phase amount 75 g, 1% wt.% C, reaction temperature 270 °C, reaction time 2 h (1: glycolic acid 2: lactic acid 3: glycerol 4: acetic acid 5: acetaldehyde 6: methanol 7: catechol 8: phenol 9: propionic acid).

decreasing trend observed in the 1st runs, was substituted by an almost constant hydrogen production (about 10 mmoles) if the 2nd tests are added to the 1st ones.

The dramatic difference in the performance between 1st and 2nd test denoted the probable deactivation of the catalyst because of species (organic or inorganic) present during the first test. For this reason, the next paragraph is devoted to the investigation of this important issue, hardly reported in literature because of the lack of study on HTL-derived actual streams.

3.3.3. Deactivation of the catalyst

In order to assess the hypothesis of catalyst deactivation, further experiments were performed, and the spent catalysts characterized.

As it was assumed an endogenous deactivation, the stability of the catalyst could not be evaluated with the common procedure of re-using the catalyst with a fresh solution. In fact, we would have observed still a negligible conversion, and no other conclusion could have been drawn. For this reason, it was decided to test the stability of the catalyst versus a reactive reference compound. The catalyst used during the 1st APR run on HTL-AP was recovered, dried overnight (105 °C) and used for the APR of glycolic acid (formerly proven to provide high H_2 yields).

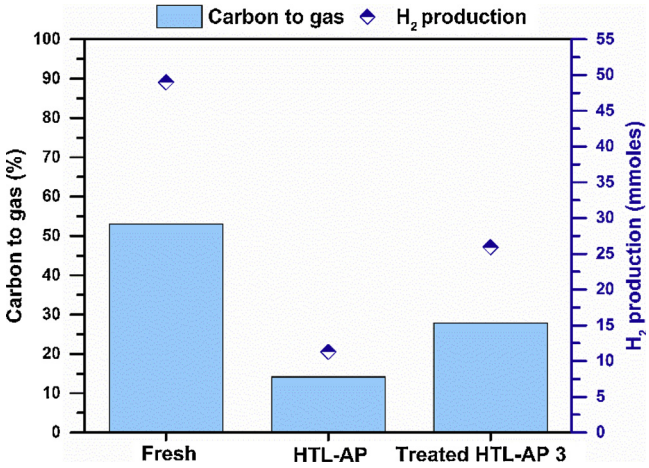


Fig. 11. APR of glycolic acid with different catalysts. Reaction conditions: Liquid phase amount 75 g, 0.9 wt.% C glycolic acid, reaction temperature 270 °C, reaction time 2 h.

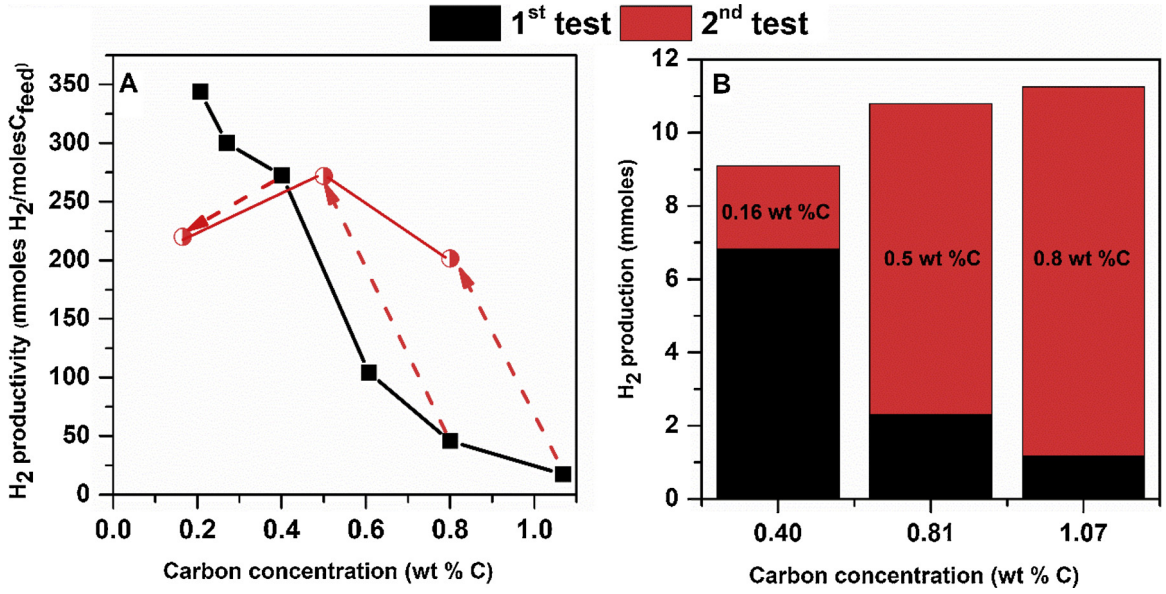


Fig. 10. H_2 productivity (A) and H_2 production (B) for the APR of HTL-AP. Reaction conditions: liquid phase amount 75 g, reaction temperature 270 °C, reaction time 2 h.

The carbon to gas conversion and hydrogen production of the reference test (obtained with a fresh catalyst) and of the runs with two used catalysts are compared in the following Fig. 11. We previously assessed that the stability of the catalyst was maintained after an APR run with glycolic acid, therefore the differences cannot be ascribed to the hydroxyacid itself.

The catalyst used with the HTL-AP showed a serious deactivation: the conversion of the glycolic acid in the liquid phase decreased from 91% to 20%. On the other hand, the test named "Treated HTL-AP 3″ is the APR of glycolic performed with the catalyst that had previously undergone an APR test with the treated HTL-AP 3 aqueous phase reforming. It is important to observe that the deactivation was still present, but at a lower extent than the previous one referred to the APR of an untreated feed (HTL-AP). Indeed, the conversion of glycolic acid raised to 42%, with the carbon to gas and the hydrogen production more than doubled.

Two main reasons were investigated to explain the deactivation of the catalyst, i.e. the presence of phenolic oligomers and sulfur-containing molecules.

HTL-AP solution washed with diethyl-ether had the effect of selectively removing the phenolic compounds from the water, while keeping the other organic compounds nearly unchanged in terms of concentration in the water (Table 2). Afterwards, they were tested to assess if the phenolics can be associated to the catalyst deactivation. Few works studied the deactivation of noble metal catalyst in the presence of phenolics, and no works were found in the currently investigated APR conditions with Pt/C as a catalyst. APR of glycerol with the purpose of hydrogenating phenol in-situ was studied with Raney Ni® [35]: the investigation showed an improvement of glycerol conversion due to the shift of the equilibrium. On the other hand, other researchers reported catalyst deactivation due to deposits formation on the catalyst surface, in different reaction conditions. Hydrodeoxygenation (HDO) of guaiacol with noble metal catalysts (Pt, Pd, Rh, Ru) supported on activated carbon led to catalyst deactivation due to polyaromatic deposits in different extents for each catalyst [36]. The catalytic wet air oxidation of phenol was studied on Pt/Al_2O_3 and Pt/CeO_2 during the reaction deposit of carbonaceous material were deposited on the catalyst leading to a catalyst deactivation [37]. De Souza et al. studied the HDO of phenol over Pd catalyst with different supports; they assessed a deactivation of the catalyst supported on Al_2O_3, SiO_2, TiO_2 and ZrO_2 [38].

From a preliminary glance, it is not possible to infer in our case that the deactivation is due to the presence of phenolic monomers (phenol, guaiacol, catechol). As reported in Fig. 8 (left), there is no apparent difference between the feed and the 1st test product in terms of the phenolics amount. However, there was an improvement of the performance in 2nd test: it is more likely that phenolic oligomers, not visible in the HPLC analysis, underwent polymerization during the 1st reaction, blocking the pores of the catalyst (as suggested by the textural analysis in the following), which therefore acted as a sacrificial adsorbent that removed them from the product of the 1st test. Consequently, these compounds were likely absent in the 1st test product and consequently did not affected the catalyst in the 2nd test.

For this reason, the phenolic compounds were removed via an HTL-AP treatment with DEE, whose effect was is showed in Fig. 12. As observed in the chromatogram, the main consequence of washing the aqueous phase with the organic solvent is the elimination of phenolics (monomers and presumably also oligomers), without affecting the concentration of the remaining compounds. This is an important result, because it allows an easier interpretation of the results as only the different concentration of aromatics can be considered. Each treatment was able to extract different amount of phenolics, depending on *a-posteriori* evaluated effectiveness of the procedure. In the side-table, the phenolic content (guaiacol peak number 10, phenol peak number 9 and catechol peak number 8) of these batches is reported.

The hydrogen production as a function of carbon concentration (excluding diethyl-ether) is reported in the following Fig. 13; when the phenolics content increased, the hydrogen production decreased to reach almost zero at the highest phenolics content. Moreover, it is clearly highlighted the difference in the hydrogen production between 1st and 2nd test on the HTL-AP, but in comparison to the treated HTL-AP 1. Finally, it can be observed that the treated HTL-AP 3 (with no detected phenolics) led to a trend analogous to the synthetic mixture, with a hydrogen productivity almost constant on the investigated carbon concentration range, equal to 300 mmol H_2/mol C.

In order to assess the contribution of DEE to the hydrogen production, we performed the APR of DEE alone and together with the synthetic mixture glycolic/acetic/lactic acid (as in paragraph 3.2). As reported in the Table 3, the amount of the main produced gas during the aqueous phase reforming of the synthetic mixture with and without DEE is almost identical. This means that the addition of the solvent for the removal of the phenolics did not change the product distribution and the hydrogen yield. It is highlighted that, despite the APR of DEE (0.9 wt.% C) produced considerable amount of hydrogen, the different selectivity in terms of methane/hydrogen ratio in the synthetic mixture + DEE test and in the DEE-alone test suggests that its conversion is negligible in the mix test, therefore negligible in terms of hydrogen production. The reason may be ascribed to the competitive adsorption of DEE against, for example, glycolic and lactic acid, which are readily converted.

(further considerations are reported in the Supporting Information, Table S1, looking at the comparison with the real biomass).

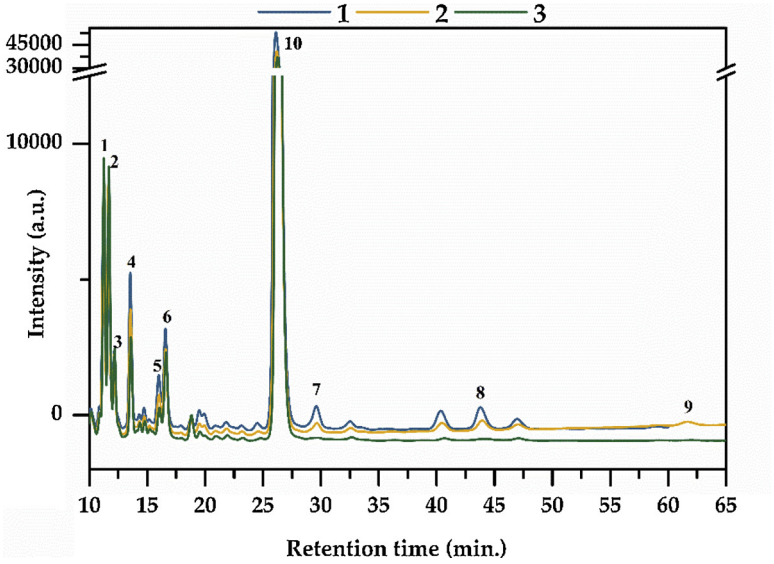
The textural analysis of some selected catalysts, together with the characterization of the fresh one, is reported in the Table 4. The catalyst used for the APR of the HTL-AP (i.e. with the highest content of phenolics) showed the highest decrease of the surface area and pore volume, indicating that high molecular weight compounds blocked the pore of the catalysts, reducing the availability of active sites for the reaction. Coherently with the reported results, both the pore volume and surface area of the catalyst used for the 2nd test of the HTL-AP sample were higher than the former. Analogously, the catalyst used for the APR of the treated HTL-AP 3 (i.e. with negligible content of phenolics) showed a minor loss of textural properties compared to the untreated feed. It can be noticed anyway a strong difference compared to the fresh catalyst, that is in line with the results reported with the glycolic acid (Fig. 10), where a worsening of the performance was noticed anyway.

The spent catalysts were also characterized thanks to thermogravimetric analysis coupled with infrared spectroscopy.

The fresh catalyst showed a total weight loss equal to 15 wt.% when exposed to a heating treatment up to 1000 °C under inert flow, divided into three different steps: the first one, with a maximum at 80 °C, due to the loss of adsorbed water; the second step, between 200 °C and 600 °C, was due to the decomposition of the carbon support, which is composed from a certain percentage of oxygen, with formation of carbon dioxide; the third step is a further decomposition of the carbon substrate with formation of carbon monoxide [39]. In fact, the infrared analysis of the curves of developed gasses showed a maximum for water at around 100 °C, a maximum at 600 °C for CO_2 and an increase in CO concentration over the 600 °C (Figure S2).

The TGA analyses of the spent catalysts showed that the weight loss is quite similar for all the catalysts, ranging from 15 to 20 wt.%. Please note that this information cannot be directly linked to the amount of deposits on the catalyst as the tests were not performed in an oxidative environment to allow the IR analysis of the evolved species. However, the degradation products were quite different whether the catalyst was used for a 1st or 2nd test (Figs. 14 and 15, respectively).

On one hand, the spent catalysts used for the 1st tests showed the presence of degradation products such as CO_2, CO, H_2O, aliphatic fragments and the presence of primary alcohols; for the sake of representativeness, the TGA-IR of the sample HTL-AP is reported in the Fig. 15 (analogous results were obtained for the samples treated HTL-AP 1 and treated HTL-AP 2 and are reported in Figure S3-S4).



BATCH	C wt.%
Treated HTL-AP 3	~ 0
Treated HTL-AP 2	0.017
Treated HTL-AP 1	0.05
HTL-AP	0.16

Fig. 12. HPLC chromatograms of HTL-AP and treated HTL-AP feeds (1: glycolic acid 2: lactic acid 3: glycerol 4: acetic acid 5: acetaldehyde 6: methanol 7: catechol 8: phenol 9: guaiacol 10: DEE).

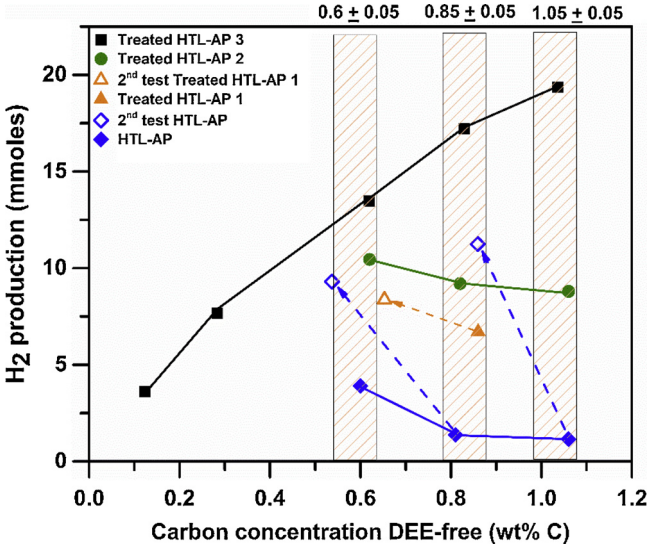


Fig. 13. Influence of carbon concentration and DEE pre-treatment on the H_2 production for APR of different batches. Reaction conditions: liquid phase amount 75 g, reaction temperature 270 °C, reaction time 2 h.

Table 3
Aqueous phase reforming of synthetic mixtures with and without DEE. Reaction conditions: Liquid phase amount: 75 g, 0.9 wt.% C acids + 0.9 wt.% C DEE, 270 °C reaction temperature, 2 h reaction time.

Test	Hydrogen (mmoles)	Carbon dioxide (mmoles)	Methane (mmoles)
Synthetic mixture	19.5	16.1	2.0
Synthetic mixture + DEE	20.6	16.5	2.2
DEE	4.9	3.6	4.0

The degradation of the catalyst occurred in a single step with a maximum of degradation speed at about 383 °C (from the slope of the weight loss curve in Fig. 14A). The main volatile products of this degradation were visible in the infrared spectra at 408 °C (Fig. 14C). The infrared spectra showed the presence of water, carbon dioxide, carbon monoxide, and methane derived from the degradation of the organic substrate adsorbed on the catalyst. The spectra showed also more

Table 4
Textural characteristic of the fresh and spent catalysts. Reaction conditions: 270 °C, 2 h reaction time.

Sample	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore size (nm)
Fresh	923	0.632	5.1
HTL-AP 0.8% C	195	0.344	5.7
HTL-AP 1.1% C	216	0.361	5.6
HTL-AP 1.1% 2nd test	430	0.480	5.2
Treated HTL-AP 3 0.8% C	410	0.471	5.3

complex degradation products: between 2800 and 3000 cm^{-1} the stretching of CH_2 and CH_3 from aliphatic fragments were easily recognized, while the band at 1064 cm^{-1} is typical of primary alcohols. From the figure it was possible to consider that the first part degradation is mainly due to the evaporation of aliphatic compounds containing alcohols, while at higher temperatures the organic compounds (presumably of higher molecular weight and non-volatile at these temperatures) decomposed to form carbon monoxide, carbon dioxide, methane and water. The presence of alcoholic species can be considered as an indication of the low reactivity of these catalysts. Indeed, it was showed throughout the present work as the alcohols are characterized by high reactivity: for this reason, their presence on the surface of the catalyst states the sites are not available for activating the breaking of the molecules. The characteristic band of phenolics in the gaseous phase are located at about 3650 cm^{-1}, 3100-3000 cm^{-1} and 1600-1500 cm^{-1}. However, these bands are covered from water and methane, therefore it was not possible to recognize the presence of phenol, guaiacol, catechol or other molecules containing phenolic groups.

On the other hand, different phenomena were observed for the catalysts used for the 2nd tests investigation and similarly for the treated HTL-AP 3 (that is the batch without phenolic content and with the best performance). In these cases, the main degradation step of the catalyst used for the second test of the feed HTL-AP, had a maximum at 322 °C (Fig. 15A). The degradation products in the first part of this step, namely below 200 °C, were mainly CO_2 and volatile organic molecules with anhydride functionalities as underlined from the CO asymmetric and symmetric stretching at 1792 and 1773 cm^{-1} and from the COC stretching at 1174 cm^{-1} in Fig. 15B and from the IR adsorption peak during TGA (Fig. 15D). Above 300 °C, more complex organic fragments

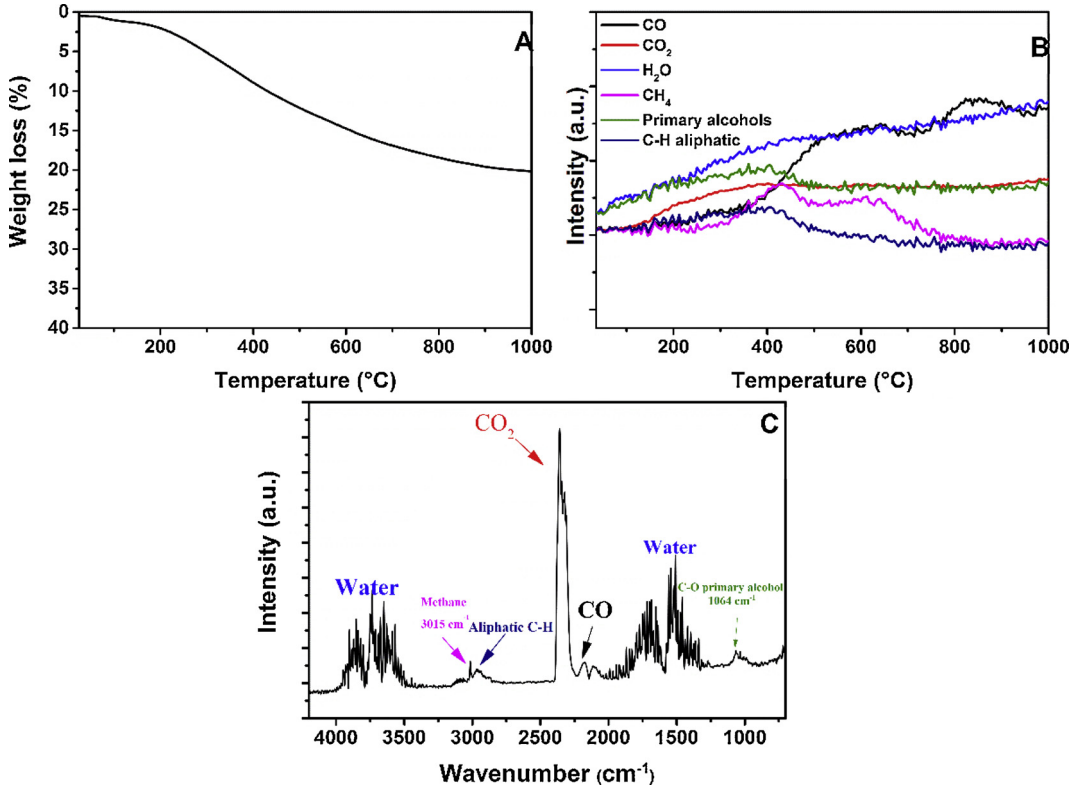


Fig. 14. TGA-IR of spent catalyst after APR 1st test of HTL-AP. Reaction conditions: 0.8 wt.% C, reaction temperature 270 °C, reaction time 2 h. Analysis conditions: heat from 30 °C to 1000 °C @ 20 °C/min in nitrogen atmosphere with a purge rate of 20 ml/min under nitrogen. A: TG results; B: IR-Absorption peak during TGA of water, CO_2, CH_4, aliphatic fragments and primary alcohols; C: Infrared spectra at 408 °C.

are produced with an increase of the stretching of CH_2 and CH_3 from aliphatic fragments between 2800 and 3000 cm^{-1} and the appearance of a small quantity of water (Fig. 15 C–D). At temperatures higher than 500 °C the degradation products are mainly water, CO_2 and CO (Fig. 15B). This behavior was similar for all the spent catalysts with high conversion in APR experiments (i.e. used in the 2nd tests or in the absence of detectable phenolic content) and is reported in the Supporting Information (Figure S5-S6). In these cases, the alcohols were not identified, giving an indication of the higher reactivity of these catalysts; at the same time, anhydride peaks were present. It can be supposed that the anhydrides derived from the reaction of the carboxylic acids formed during dehydrogenation reaction that underwent dehydration during the TGA. The presence of carboxylic acids can be a further proof of the better performance of the catalysts as they are by-products of alcohols reforming [14].

The second possible cause of deactivation is related to the presence of organosulfur compounds, derived from lignin. As it is known, sulfur can chemisorb irreversibly on the Pt sites, leading to their deactivation.

ICP-MS analysis was performed on the spent catalyst to assess the presence of sulfur. The catalysts used for APR of HTL-AP and treated HTL-AP 3 showed the existence of sulfur on the catalyst, in the 0.08-0.2 wt.% range. This amount may be enough to explain the worsening of the performance; on the other hand, only the ICP-MS does not allow to understand the degree of interaction of the sulfur with the catalyst.

For this reason, potential chemical bonds between platinum and sulfur have been investigated by XPS. In Fig. 16, the XPS spectra of Pt_{4f} of fresh and spent catalysts after APR of HTL-AP and treated HTL-AP 3 are reported. First of all, it is observed that the binding energies of the doublet in the fresh catalyst agree with the literature data regarding Pt metal, with the typical 3.33 eV splitting. Moreover, none of the spent catalysts showed an increase in the binding energies, being an indication of the lack of strong (chemical) interactions between the platinum and sulfur [40]. Therefore, based on this result, the sulfur poisoning can be reasonably excluded as cause for the catalyst deactivation and its presence may be ascribed to the physical adsorption of S-containing species compounds on the high surface-area carbon support and to a negligible extent to the chemisorption on the active sites.

4. Conclusion

The water fraction from the hydrothermal liquefaction of lignin was subjected to aqueous phase reforming for the production of hydrogen. A screening performed with representative model compounds allowed to identify the molecules prone to reforming, while the study of a synthetic mixture highlighted competitivity issues on the active sites. This outcome is particularly crucial for the valorization of secondary streams as they are complex mixtures constituted by several different classes of compounds. The study of the real water fraction showed a dramatic dependence of the performance on the phenolics content, highlighting the necessity of pretreatment of the water phase to increase the stability of the catalyst. Indeed, the lower was the concentration of phenolics (i.e. phenol, guaiacol, catechol) in the feed, the higher was the hydrogen production. The textural characterization showed that the worsening of the performance may be associated to a decrease of the surface area and pore volume, likely due to the fouling mechanism caused by phenolic oligomers. At the same time, sulfur-related poisoning mechanisms were excluded. Despite the coupling of hydrothermal liquefaction and aqueous phase reforming needs further investigation, it gives promising results in the direction of decreasing the need of hydrogen for a biorefinery, helping to reduce both the economic and environmental impact.

Acknowledgements

The project leading to this research has received funding from the European Union's Horizon 2020 research and innovation program

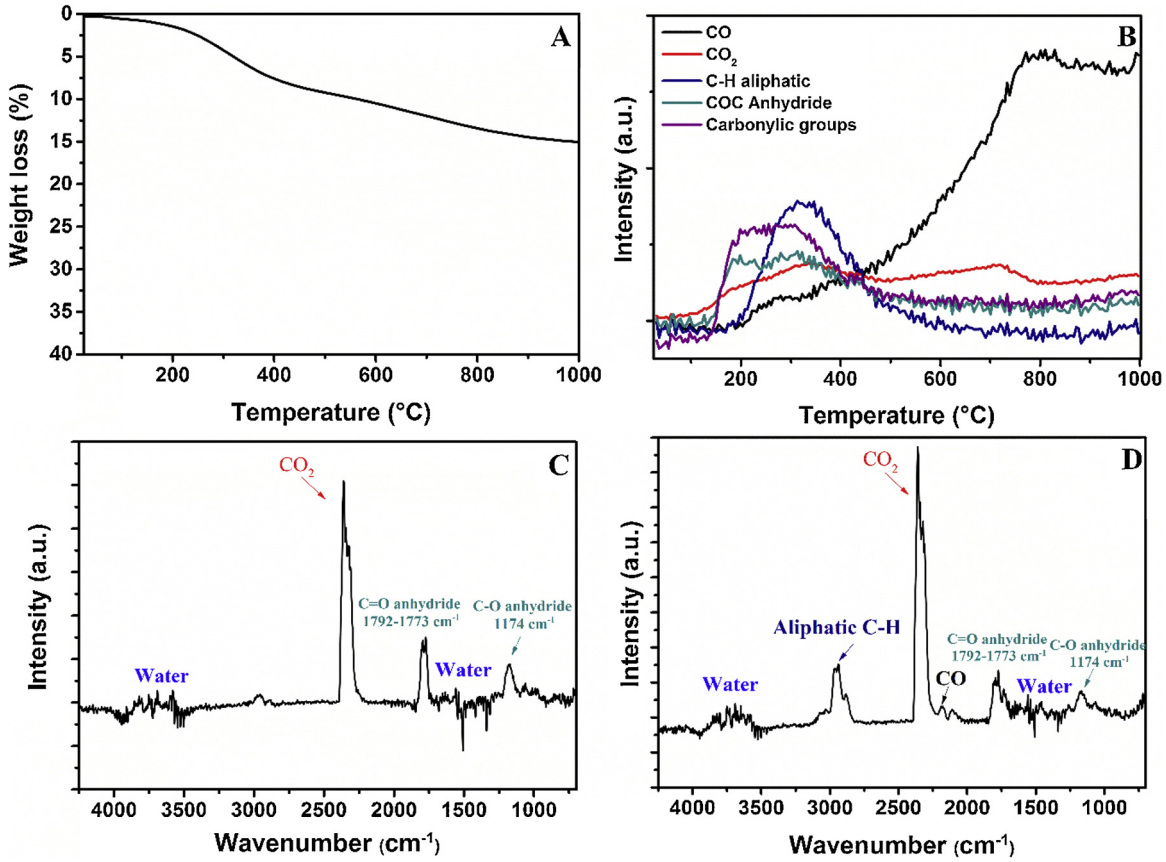


Fig. 15. TGA-IR of spent catalyst after APR 2nd test of HTL-AP. Reaction conditions: 0.8 wt.% C, reaction temperature 270 °C, reaction time 2 h. Analysis conditions: heat from 30 °C to 1000 °C @ 20 °C/min in nitrogen atmosphere with a purge rate of 20 ml/min under nitrogen. A: TG results; B: IR-Absorption peak during TGA; C: Infrared spectra at 198 °C; D: Infrared spectra at 298 °C.

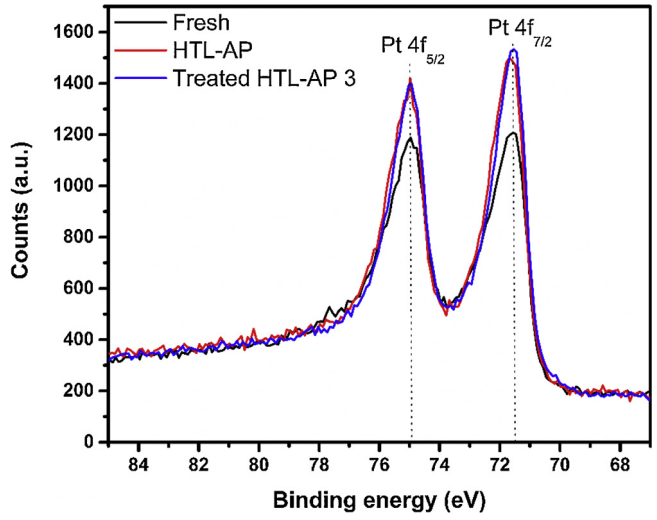


Fig. 16. XPS spectra of fresh and spent catalysts after aqueous phase reforming. Reaction conditions: 0.8 wt.% C feed (HTL-AP or treated HTL-AP 3), 270 °C reaction temperature, 2 h reaction time.

under grant agreement No 764675. The authors sincerely thank ing. Salvatore Guastella for the XPS analyses and ing. Camilla Galletti for ICP-MS analysis.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.09.040.

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