

Coupling hydrothermal liquefaction and aqueous phase reforming for integrated production of biocrude and renewable H-2

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## RESEARCH ARTICLE

Reaction Engineering, Kinetics and Catalysis

Coupling hydrothermal liquefaction and aqueous phase reforming for integrated production of biocrude and renewable H<sub>2</sub>

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## Abstract

Lignin-rich stream from lignocellulosic ethanol production was converted into biocrude by continuous hydrothermal liquefaction (HTL) while hydrogen was produced by aqueous phase reforming (APR) of the HTL aqueous by-product. The effects of Na<sub>2</sub>CO<sub>3</sub> and NaOH were investigated both in terms of processability of the feedstock as well as yield and composition of the obtained products. A maximum biocrude yield of 27 wt% was reached in the NaOH-catalyzed runs. A relevant amount of dissolved phenolics were detected in the co-produced aqueous phase (AP), and removed by liquid-liquid extraction using butyl acetate or diethyl ether, preserving the APR catalyst stability and reaching an hydrogen yield up to 146 mmol H<sub>2</sub> L<sup>-1</sup> AP. Preliminary mass balances integrating HTL and APR showed that the hydrogen provided by APR may account for up to 46% of the hydrogen amount theoretically required for upgrading the HTL biocrude, thus significantly improving the process performance and sustainability.

## KEYWORDS

advanced biofuels, aqueous phase reforming, biorefinery, hydrothermal liquefaction, lignin, renewable hydrogen

## 1 | INTRODUCTION

The recent EU Renewable Energy Directive II (REDII), promotes the use of residual and waste feedstocks for the production of sustainable fuels.<sup>1</sup> The Annex IX Part A of REDII sets a list of feedstocks, the conversions of which generate so-called advanced biofuels. These bio-based fuels can be double-counted by EU Member States toward RES-T (Renewable Energy Sources in Transports) and GHG emission reduction targets. EU REDII sets a goal in 2030 of 3.5% double-

counted advanced biofuels, corresponding to 1.75% in terms of actual volumes.

The European Union also prioritizes those sectors where electrification is more difficult, as aviation, heavy duty vehicles and maritime sectors. While drop-in biofuels for diesel engines and heavy-duty vehicles are a mixture of renewable hydrocarbons fully equivalent to diesel oil, marine fuels are for many aspects similar to biocrudes (BCs), in particular as regards their high viscosity. The production of these fuels can be reasonably addressed by using lignocellulosic feedstocks

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and thermochemical conversion routes: upgrading these BCs will also require significant amounts of  $H_2$ . Given the policy framework, the interest in the conversion of lignocellulosic materials into transport fuels has largely increased in the last decades.<sup>2,3</sup> For example, the lignocellulosic ethanol route has achieved full industrial scale, providing increasing amounts of very wet (60–70 wt%) lignin-rich streams (LRSs) as co-product, which is a suitable material for hydrothermal liquefaction (HTL).<sup>4</sup>

Among other thermochemical conversion options, HTL is a process well-suited to wet biomasses, converting organic material in hot compressed water.<sup>5</sup> Generally, reaction conditions consist in moderate temperatures combined with high pressures (250–400°C; 4–30 MPa) and residence times below 1 h. Feedstock thus decomposes into a BC, a solid residue, noncondensable gases (mostly  $CO_2$ ) and organics dissolved in an aqueous phase (AP), in which a relevant amount of the feedstock carbon is retained. BC is the main product, which must be upgraded to a conventional hydrocarbon fuel after heteroatoms removal and molecular weight reduction via hydrotreating and hydrocracking.<sup>6</sup> Batch HTL experiments of LRS were described in previous articles,<sup>7,8</sup> focusing on the effects of reaction conditions and alkaline catalyst on reaction mechanism and products composition. Temperature was found to be the most influencing parameter, increasing LRS depolymerization efficiency. Moreover, a  $T$  increase from 300 to 370°C led to a greater phenolic monomer content in BC and AP, together with a reduction of the content of acids in the AP.

The use of an alkaline catalyst (KOH) improved LRS conversion, increasing the formation of lower molecular weight compounds and the content of water-soluble organics in AP. Moreover, a higher yield of methanol was observed in AP, thus confirming the positive effect on lignin structure depolymerization of the alkaline catalyst. Conversely, the alkaline medium did not enhance the formation of phenolic monomers. Several studies focused on the conversion of woody biomass, but the hydrothermal degradation of lignin was less investigated. The effects of NaOH catalyst on degradation of hydrolysis lignin obtained from hardwood fractionation process was studied by Mahmood et al.,<sup>9</sup> who reported an efficient depolymerization at high loading of NaOH (10 wt% of feedstock) while almost no depolymerization was observed at lower loading rates. Jensen et al. investigated the HTL of lignin-rich enzymatic hydrolysis residues obtained from wheat straw and *Miscanthus*.<sup>10</sup> The HTL experiments were performed in aqueous solution of KOH (5.6 wt%) and the results showed an increase of light molecular weight compounds at increasing of HTL reaction temperature. Moreover, they observed that the differences in yield of aromatic monomers was also related to the type of lignin and plant species.

For an effective carbon utilization and minimization of process waste streams, the management of the carbon-laden AP must be properly addressed. Zhu et al. reported that reducing the loss of carbon in the water phase after HTL leads to the largest reduction in the biofuel production cost.<sup>11</sup> Some proposed routes regard the reuse of the AP for biomass (microalgae) cultivation.<sup>12</sup> However, this option required heavy dilutions (200–400×) to avoid the effect of growth inhibitors. Another possibility is the recycle of the AP at the inlet of

the HTL step, affecting the BC yield.<sup>13</sup> The most common options reported in literature for the valorization of HTL-AP are the anaerobic digestion (AD) and the catalytic hydrothermal gasification (CHG). These processes aim mainly at the production of a methane-rich gaseous phase and showed promising results so far.

Posmanik et al. investigated the integration between HTL of food waste and AD, highlighting that the methane potential was lower when the HTL temperature increased and that the biodegradability of the HTL-AP was influenced by its chemical composition.<sup>14</sup> Fernandez et al. looked at the wastewater from HTL of algae *Tetraselmis* and *Chlorella*, pointing out a reduction in methane production if the AP was not diluted below 40 vol%.<sup>15</sup> Most of the bioconversion techniques have a limited organic loading working range: for example, 10 g COD (chemical oxygen demand) per liter is typically required in anaerobic fermentation, so they should be diluted. Moreover, it is known that AD microorganisms may be inhibited by some organic and inorganic compounds found in the HTL-AP (e.g., phenol and ammonia).<sup>16</sup>

CHG was proposed by Zhang et al. for the HTL-AP valorization of sludge.<sup>17</sup> Working at 750°C, 24 MPa and with a weight hourly space velocity (WHSV) of  $6\text{ h}^{-1}$ , the authors attained an  $H_2$  yield equal to 53.9 mol/kg using a Ru-modified Ni catalyst. Li and coworkers studied an integrated process where CHG of algae HTL-AP removed 97% of the carbon and produced a gas phase with a high calorific value (90 MJ/kg) that was proposed for on-site electricity and heat production.<sup>18</sup> Nevertheless, it has been pointed out that CHG is an energy-intensive and expensive process, due to the harsh reaction conditions in terms of temperature and pressure.

Seen the urgency of the issue, several recently published reviews evaluated the technologies cited above, as well as others, identifying the challenges and the opportunities for their development toward the commercial scale.<sup>19,20</sup>

In this scenario, despite its peculiarities, the aqueous phase reforming (APR) has not received great attention to assess its potential for exploitation of the carbon-laden HTL-AP. APR is a catalytic reaction able to convert oxygenated hydrocarbons into  $H_2$ -rich gaseous products.<sup>21</sup> The process can be carried out at mild temperatures (220–270°C) in compressed liquid water, so to avoid water and oxygenates vaporization while ensuring an efficient use of energy. Thanks to the favorable working temperatures, water gas shift is also thermodynamically promoted, so that low CO concentration and high  $H_2$  productivity can be reached in one single reactor. Due to these characteristics, it is worthy to investigate the integration of APR with HTL, since this synergy may reach a double objective: on one side, APR can reduce the organic content to facilitate the costly wastewater treatment step; on the other side, it can produce in situ the  $H_2$  necessary for the upgrade of the BC itself.<sup>22</sup> Most of the available literature takes into consideration only model compounds, such as methanol, glycerol, or sorbitol.<sup>23</sup> However, the AP derived from biomass processing is characterized by multi-component mixtures, with different functionalities as well (carboxylic acids, alcohols, ketones, and aromatics).<sup>24–26</sup> For this reason, APR investigation should look

also at the complexity induced by this heterogeneity to evaluate the feasibility of this technology.

Some efforts were lately devoted to the application of the APR to more complex feedstocks, such as lignocellulosic ones, or derived from other thermochemical processing, or from food industry wastewater, as recently reviewed in Reference 27. Irmak and coworkers performed the APR of the hydrolysate of lignocellulosic biomass.<sup>28–30</sup> Nowadays, these energy crops have gained significant attention thanks to their low cost and widespread availability to produce alternative liquid (e.g., bioethanol) and gaseous fuels. In their works, the APR of kenaf, wheat straw, and switchgrass hydrolysate allowed to obtain a gas phase with high H<sub>2</sub> concentration (typically more than 50 mol%). Oliveira et al. used the APR to valorize the AP derived from brewery and fruit juice processing.<sup>31,32</sup> In addition, Seretis et al. studied the APR of crude glycerol derived from biodiesel industry, as reported in Reference 33. This route would be particularly interesting due to the high production of glycerol in the biodiesel sector (0.1 kg glycerol/kg biodiesel) and which is saturating the market.

Previous works from our research groups aimed at the valorization of the water fraction from lignin-rich HTL via APR.<sup>34,35</sup> It has been reported that the AP leads to severe catalyst deactivation by fouling, attributed to phenolic compounds which may oligomerize and cover the active sites. Interestingly, the combination of liquid-liquid extraction (LLE) with an organic solvent and/or adsorption with activated carbon allowed to reduce this phenomenon, increasing the catalyst life, and the H<sub>2</sub> production.

However, to the best of our knowledge, there are not previous works which combine HTL and APR looking at the interferences between the two processes, toward a holistic approach. Therefore, the aim of the present work is to investigate the coupling of HTL and APR for the production of an upgraded biofuel thanks to the valorization of the organics retained in the HTL-AP. As regards HTL, the focus here was dedicated to analyzing the issues encountered in processing LRS in a small continuous unit. Moreover, the effect of alkaline additives was investigated in terms of yield and composition of obtained products. Consequently, the use of those additives was evaluated on the results of APR (i.e., H<sub>2</sub> production, carbon conversion to gas, and catalyst stability). Secondly, the effect of butyl acetate (ButAc) and diethyl ether (DEE) as solvents for the LLE was assessed for the APR performance, together with the influence of the adopted solvent-to-aqueous phase (S/AP) ratio. HTL and APR integration was finally investigated in terms of mass balances in order to find the most suitable configuration with respect to C yield to BC and H<sub>2</sub> production from APR, taking into account the two major carbon outputs of the HTL, that is, the BC and AP.

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

All solvents and reagents (ACS reagent grade) were purchased from Carlo Erba and Sigma Aldrich, and used as received. Water for high

performance liquid chromatography (HPLC) and tetrahydrofuran for gel permeation chromatography (GPC) were HPLC grade. Analytical standards for gas chromatography (GC) and HPLC were ≥98% purity. Chemical standards for HHV and CHNS calibrations were purchased from Leco. All gases were purchased from Rivoira. Argon, air, nitrogen, and oxygen were supplied with a 99.999% purity, while helium was at 99.9995%.

The catalyst used for the APR reaction was a 5% Pt/C, provided by a commercial supplier in powder form, of which 80% had a size <106 μm. The catalyst was used as received.

The LRS was obtained from an industrial cellulosic ethanol plant fed with poplar. The feedstock was dried in an oven for 48 h at 75°C for proper storage, knife-milled, and sieved to 0.25 mm. The lignin content of this material was 53.0 wt% (d.a.f.), while its dry base elemental composition was 54.2 wt% C, 5.9 wt% H, 1.0 wt% N, 0.2 wt% S, 36.1 wt% O, and 2.6 wt% ash. Its main inorganic elements were Na (6287 ppm), K (3341 ppm), Ca (1117 ppm), and P (452 ppm). Additional information regarding the feedstock characterization was reported in Reference 8.

### 2.2 | Methods

The complete description on the HTL and APR test conditions, as well as the procedure followed for the LLE, are reported in the Supporting information. Furthermore, the products extraction and analysis were thoroughly explained. A simplified scheme of the continuous HTL unit is also depicted in Figure S1. Two solvents were investigated for LLE of HTL AP: DEE and ButAc. The LLE of the AP from the NaOH run was carried out by investigating the effect of DEE and ButAc at different S/AP ratios: 1 and 5 for the former; 0.2, 1, and 5 for the latter. For the sake of clarity, the APs were named as x-Solvent, where x is the S/AP ratio used, and Solvent is DEE or ButAc.

The yields of BC and solids were determined according to the following equation:

$$\text{Yield (\%)} = \frac{\text{product mass}}{\text{feedstock dry mass}} \cdot 100 \quad (1)$$

The performance of the APR reaction was evaluated using the following indicators: Equation (2) indicates the conversion of the C into gaseous products, obtained through micro-GC analysis; Equation (3) estimates the yield of H<sub>2</sub> according to the APR stoichiometry of the single organic compound (here glycolic acid is taken as an example).

$$\text{Carbon to gas conversion (\%)} = 100 \cdot \frac{\text{mol}_{\text{fin}} C_{\text{gas}}}{\text{mol}_{\text{in}} C_{\text{feed}}} \quad (2)$$

$$\text{H}_2 \text{ yield (\%)} = 100 \cdot \frac{\text{mol}_{\text{fin}} \text{H}_2}{3 \cdot \text{mol}_{\text{in}} \text{Glycolic ac.}} \quad (3)$$

where  $\text{mol}_{\text{fin}} C_{\text{gas}}$  are the moles of carbon in the gas phase at the end;  $\text{mol}_{\text{in}} C_{\text{feed}}$  are the moles of carbon in the feed;  $\text{mol}_{\text{fin}} H_2$  are the moles of  $H_2$  at the end;  $\text{mol}_{\text{in}} \text{Glycolic ac.}$  are the moles of glycolic acid in the feed solution.

### 3 | RESULTS AND DISCUSSION

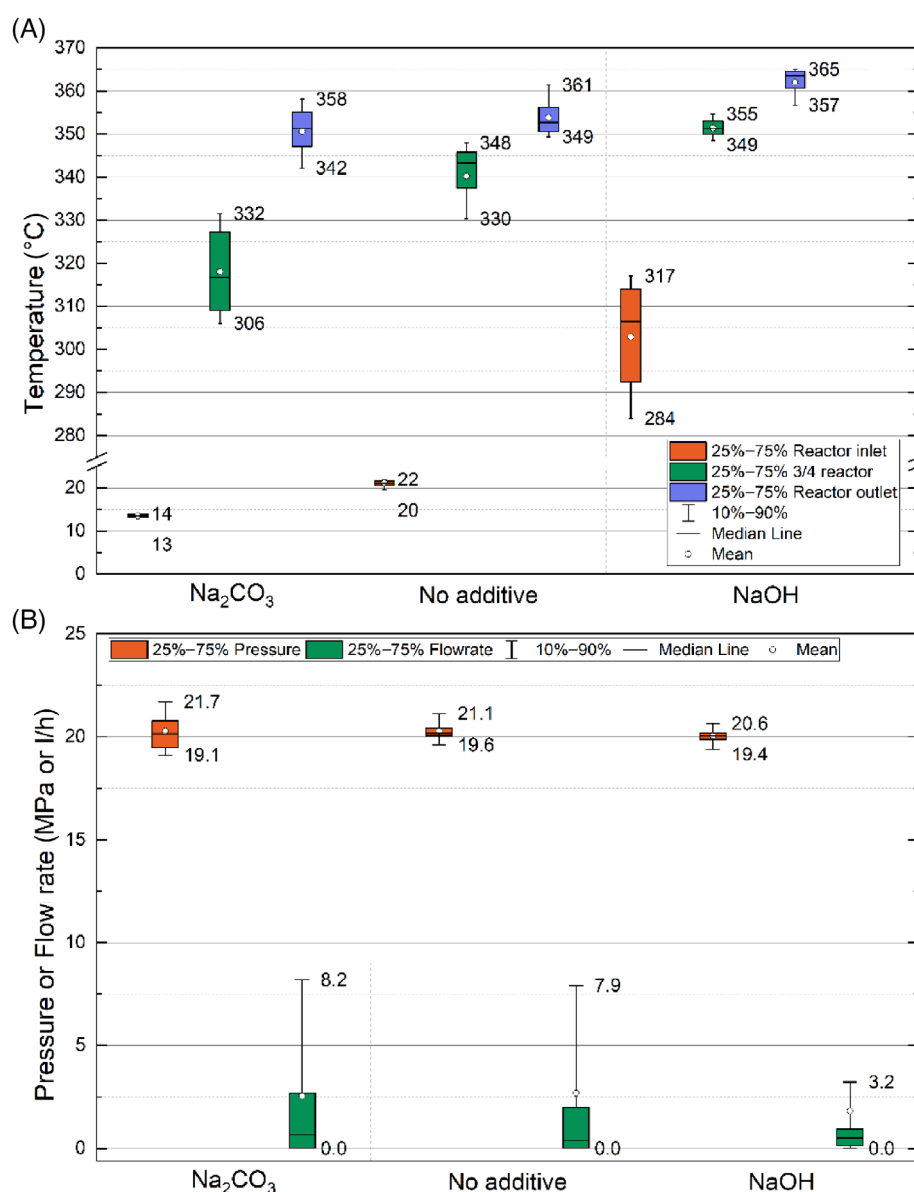
#### 3.1 | HTL tests

Pipe blockage occurred in the continuous runs with sodium carbonate and the cumulative processing time at steady state reached 3.8 h with an average flow rate of 2.5 L/h. Figure 1 reports the boxplot of process parameters during selected runs: pressure and flow rate values were very dispersed during the  $\text{Na}_2\text{CO}_3$  run and the range of pressure values between 10th and 90th percentiles was almost 0.26 MPa.

After these runs, some optimizations and modifications were carried out in order to avoid plugging.

During the experiments without alkaline additive the cumulative processing time at steady state reached 4.5 h, but pipe blockage still occurred and further modifications were implemented, such as the installation of a preheater before the reactor and heaters in the depressurization system, keeping the after-cooler temperature between 70 and 80°C. Pressure and flow rate values were generally less dispersed confirming the better performance of the new control logic (Figure 1B): the average flow rate value was 2.7 L/h and the range of pressure values between 10% and 90% was reduced of almost 41%.

Two runs were performed at the same previous operating conditions but by mixing the feedstock with a 0.05 mol/L NaOH solution. Contrarily to  $\text{Na}_2\text{CO}_3$ , NaOH has the advantage of not producing carbonates when mixed with water and has a stronger alkaline effect.



**FIGURE 1** Boxplot of process parameter for selected hydrothermal liquefaction runs: (A) temperatures, (B) pressure and flow rate

With the new plant configuration, no blockage occurred, and the runs reached 7 h of processing time at steady state before being intentionally halted. The average process temperatures were higher if compared with the previous experimental runs (Figure 1A) and temperature values at  $\frac{3}{4}$  reactor and at reactor outlet were also less dispersed compared to the previous runs. With the newly installed preheater, temperature at the reactor inlet was highly influenced by the flow rate: a decrease of the latter led to an increase in the former. The temperature values were dispersed but the average value was 303°C. The better performance of the control logic was also confirmed by the less dispersed values of the flow rate with an average value of 1.8 L/h. Table 1 shows the summary of the results of the continuous runs for each reaction conditions. The BC yield refers to the highest value obtained in the two runs, while the cumulative processing time is intended as the sum of both feeding time. The best results were obtained in NaOH-catalyzed runs with a total processing time of 12.8 h and a BC yield of 27 wt% d.b. in the second run. This latter higher value was obtained thanks to the flushing of acetone after the run: this led to the recovery of an additional fraction of BC, that is, the one deposited in the inner walls of the pipes. Thanks to this washing the BC yield significantly increased from 15 to 27 wt% d.b.

### 3.1.1 | Biocrude characterization

Table 2 reports the results from the elemental and proximate analysis of the BC collected from selected runs. Similar values of carbon and H<sub>2</sub> content were observed in the BCs, ranging from 68.1 to 70.3 wt% (d.b.), and from 6.5 to 6.8 wt% (d.b.), respectively. However, higher nitrogen content was detected in BC from NaOH-catalyzed experiments (1.0 wt% d.b.). The HHV was slightly affected by alkaline additives and the highest value of 30.3 MJ/kg was observed in the BC from the second run with NaOH. Similar results were obtained in batch experiments using different collection procedure.<sup>7</sup> At the same

reaction temperature (350°C) but at different B/W ratio (10% and 20%) without alkaline additive, the carbon content of total BCs were slightly lower ranging from 64.9 to 67.9 wt%, while H<sub>2</sub> content moved from 6.1 to 7 wt%. Moreover, the calculated HHV ranged from 27.0 to 29.1 MJ/kg.

The average molecular weight (Mw) and the polydispersity index (PDI) of the BCs are reported in Figure 2. The highest average Mw was obtained in the uncatalyzed experiments (916 g/mol). The alkaline catalyst increased the rate of depolymerization and consequently led to a decrease of BC Mw: the increment of low molecular weight compounds can be correlated to the formation of a higher amount of methanol (which is dissolved in the AP, as reported in the next paragraph) due to the demethylation of the methoxy groups during the cleavage of the lignin methoxyaromatic building blocks. Indeed, in previous batch experiments<sup>8</sup> performed on the same lignin-rich substrate, the addition of KOH as alkaline homogenous catalyst had positive effect increasing the lighter fraction of BC and decreasing the yield of heavy molecular weight compounds.

A BC with a lower average molecular weight is desired as viscosity is strongly correlated with it. In addition, a lower molecular weight indicates a higher percentage of low boiling point fraction. The BC NaOH output and Na<sub>2</sub>CO<sub>3</sub> (Figure 2) were both recovered from liquid products after gravimetrically separation of most of the BC and solids. The higher average molecular weight in NaOH run was probably due to lower catalyst concentration in the slurry that led to lower LRS depolymerization. Moreover, in NaOH run, the plant was optimized in terms of processability (flow rate, pressure, and temperature control) and a greater amount of BC was recovered. It is suggested that in Na<sub>2</sub>CO<sub>3</sub> run a higher fraction of BC was deposited in the pipes and it was not recovered by flushing the plant with acetone. Indeed, the Mw of the BC fraction extracted from the deposits in the pipes (NaOH cleaning) is considerably higher. This is also indicated by the higher PDI, confirming a wider compounds distribution.

Table S1 compares the results obtained in this work with the performances obtained in other continuous HTL pilot plants. Most of the

**TABLE 1** Summary of the results from the hydrothermal liquefaction continuous runs

	Cumulative processing time (h)	Higher biocrude yield (wt% d.b.)	Average $T_{3/4}$ reactor (°C)	Average $T_{\text{reactor out}}$ (°C)	Issues	Solution
Na <sub>2</sub> CO <sub>3</sub>	3.8	13	318	351	Flow rate oscillations, Blockage of reactor outlet	PID for flow rate control Installation of a straight tube at reactor outlet
No additive	4.5	3	340	354	Blockage between reactor and pressure let-down system	Improved insulation installed after the reactor Band heaters installed on the pistons of pressure let-down system, PID-controlled proportional valve installed in the cooling line, Installation of preheater
NaOH	12.8	27 <sup>a</sup>	351	362	None	—

<sup>a</sup>Yield evaluated after flushing the unit with acetone.

**TABLE 2** Biocrude elemental composition, proximate analysis, and higher heating value

Parameter	<sup>a</sup> Na <sub>2</sub> CO <sub>3</sub>	<sup>b</sup> No additive	<sup>a</sup> NaOH <sup>c</sup>	U.M.
Moisture	7.3	3.5	0.7	wt% d.b.
Ash	3.3	0.2	0.1 (0.03)	wt% d.b.
Volatiles	n.d.	78.5	78.7	wt% d.b.
Fixed carbon	n.d.	21.3	20.9	wt% d.b.
HHV	29.4	29.3	30.3	wt% d.b.
C	68.8 (0.70)	68.1 (0.15)	70.3 (0.26)	wt% d.b.
H	6.5 (0.12)	6.8 (0.17)	6.8 (0.06)	wt% d.b.
N	0.5 (0.01)	0.7 (0.02)	1.0 (0.13)	wt% d.b.
S	n.d.	0.2 (0.01)	0.2 (0.02)	wt% d.b.
O	21.0	24.1	21.6 (0.41)	wt% d.b.

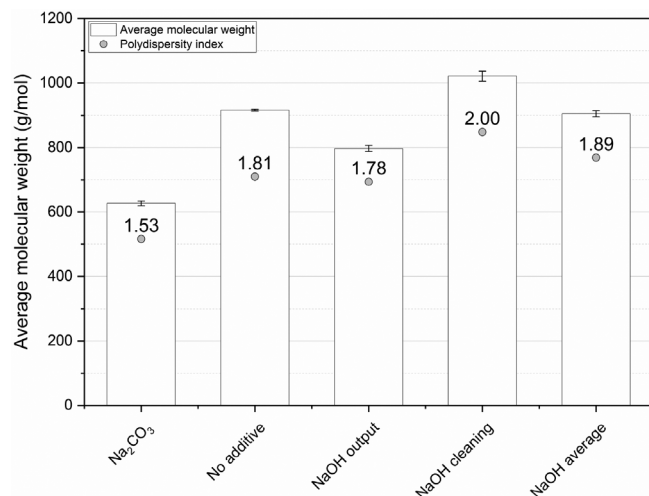
Note: Absolute standard deviation is reported in brackets where available.

Abbreviation: n.d., not determined.

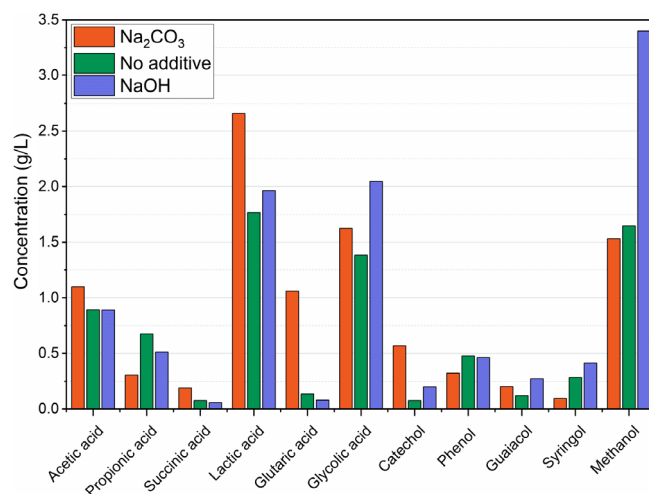
<sup>a</sup>Collected during run 2.

<sup>b</sup>Collected during run 1.

<sup>c</sup>Biocrude collected from the unit before acetone flushing.

**FIGURE 2** Biocrude molecular weight and polydispersity index of continuous hydrothermal liquefaction tests

research activities focused on the conversion of algae or sewage sludge that form homogeneous slurries and therefore are easier to process in continuous plant. The use of alkaline catalysts was mostly reported in the conversion of lignocellulosic materials because it increased the BC yield and improved the pumpability of the inlet slurry. The BC yield is highly correlated on the type of feedstock, pilot plant, and extraction procedure; in addition, great variances were reported in literature despite processing the same feedstock. However, the BC yield obtained in this work was comparable with other results and the lower yield was mostly related to the difficulties of the collection procedure. In batch results with the same LRS feedstock and reaction conditions, a BC yield of almost 52 wt% was achieved.<sup>7</sup> Looking at the HHV, higher values were achieved with lignocellulosic material while the values for sewage sludge and microalgae BC were more dispersed.

**FIGURE 3** Concentration of detected water-soluble organics in selected aqueous phase samples

### 3.1.2 | Aqueous phase characterization

The concentration of water-soluble organics in the AP samples from the selected HTL runs were evaluated by HPLC (Figure 3).

In-depth characterization of this stream is scarcely reported in literature but is particularly relevant as great volumes of organic-laden water phase are produced from the process. Carboxylic acids (acetic, glutaric, propionic, and succinic), hydroxyacids (glycolic and lactic), and methanol were the most abundant detected compounds. Dissolved oxygenated aromatics, such as catechol, phenol, guaiacol, and syringol were due to the depolymerization of the aromatic structure of lignin and their partial solubilization in the water fraction. As previously demonstrated,<sup>8</sup> lactic acid was not produced during the reaction, as it was already present in the feedstock, deriving from bacterial contamination in the upstream fermentation, but it was converted to gases.



The degradation of glucose in neutral or alkaline medium leads to the generation of acetic acid,<sup>8</sup> but the concentration was almost constant in all the runs suggesting that it was dissolved in water during upstream ethanol fermentation.

Methanol concentration was an indication of lignin depolymerization. As said before, the higher extent of demethylation reactions in the NaOH run led to an almost double concentration of methanol compared to the other tests and it confirmed the success of the experiment.

Table S2 reports the concentration of inorganics, the pH, and the total organic carbon of the AP collected from the runs without additive and with NaOH. Sodium, potassium, and calcium were the most abundant inorganic elements in the feedstock and therefore were also detected in the aqueous samples. The higher amount of Na was due to the NaOH addition. As previously reported, sulfur constitutes 0.2 wt% of the feedstock, and the AP was inevitably contaminated by this element. The higher concentration of dissolved organics in the NaOH run was confirmed by the total organic carbon, that reached a value of 7.0 g/L.

### 3.1.3 | Hydrochar characterization

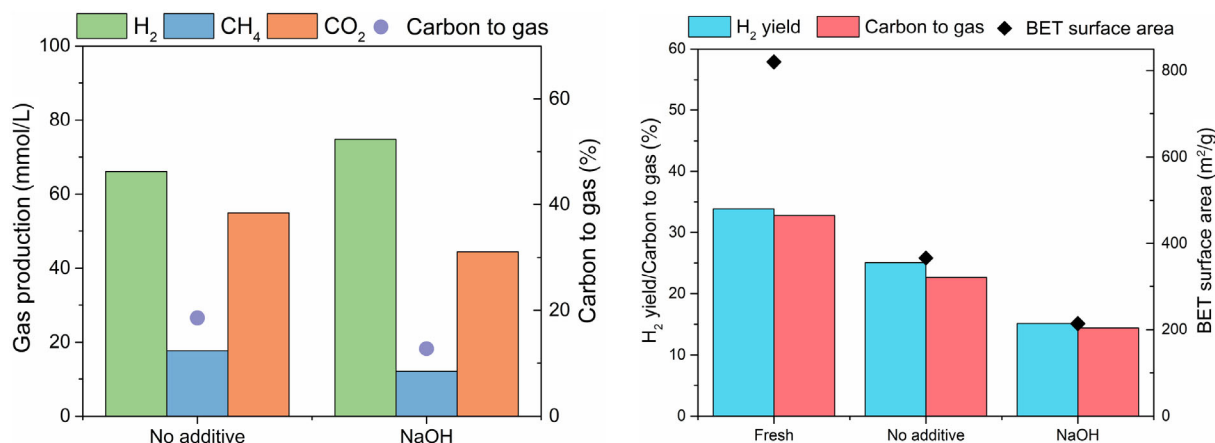
The elemental analysis was performed on hydrochar samples taken from selected runs. Higher H<sub>2</sub> content was detected in alkaline catalyzed experiments (5.0–5.1 wt% d.b.) compared to uncatalyzed run (4.4 wt% d.b.). The lowest carbon and nitrogen content were obtained in Na<sub>2</sub>CO<sub>3</sub> run (60.8 and 0.9 wt% d.b., respectively). In the uncatalyzed and NaOH-catalyzed runs, carbon content ranged between 64.4 and 64.8 wt% d.b., while similar nitrogen contents were detected (around 1.5 wt% d.b.). The initial LRS carbon recovered in hydrochar was a limited amount, but HHV was still relatively high (23.8–26.0 MJ/kg) and, in a perspective of a future scale up of the process, it could be used to provide a fraction of the required heat.

## 3.2 | APR of HTL-derived water fraction

### 3.2.1 | Influence of alkaline additive on APR

As reported in the previous paragraphs, the use of additives during HTL affected mainly the BC yield, together with its average molecular weight, and the organic content of the by-product AP. Since the performance of APR depends on the composition of the water fraction, it was interesting to investigate how the reported variations influenced the results in this context.

Figure 4 (Left) shows the production of the main gaseous compounds, that is, H<sub>2</sub>, CO<sub>2</sub>, and methane, in decreasing order. When no additive was present in the HTL, H<sub>2</sub> constituted about 47 mol% of the gas phase, slightly increasing (up to 53 mol%) with NaOH addition. It is known that under APR conditions, metallic platinum can interact with the oxygenated compounds following different pathways.<sup>36</sup> It has been reported in literature that, in the case of alcohols with a C:OH ratio equal to one, the first step is the dehydrogenation, followed by C–C cleavage. At this point, being formed the CO adsorbed intermediate, it can undergo water gas shift with the production of H<sub>2</sub> and CO<sub>2</sub>. This pathway (excluding the C–C cleavage) can be assumed valid in our reaction conditions for the dissolved methanol. When other classes of compounds are present, such as glycolic acid, or even more complex species, such as aromatic ones, the interpretation of the reaction pathway becomes more difficult. For example, we suggested that the presence of the carboxylic group in the hydroxy acid molecule (glycolic acid and lactic acid) firstly led to decarboxylation, that is, C–C cleavage as CO<sub>2</sub>; afterward, the remaining moiety would be similar to methanol and ethanol, and this would lead to more conventional pathways.<sup>34</sup> Looking at the fate of carbon, it can be observed that the carbon to gas conversion decreased from 19% to 13% by adding NaOH. The carbon to gas can be considered as a measure of the effectiveness of the C–C bond cleavage, since this reaction would gradually decrease the average molecular weight of the molecules, eventually leading the production of CO<sub>2</sub> and/or alkanes. However,

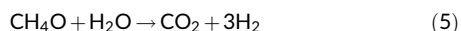
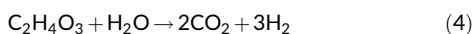


**FIGURE 4** Left: influence of additives on aqueous phase reforming (APR) of the HTL-AP. Reaction conditions: 75 ml AP, 270°C, 2 h, 0.375 g 5% Pt/C; Right: APR of glycolic acid with spent catalyst. Reaction conditions: 75 ml AP 2.85 wt% glycolic acid, 270°C, 2 h, 0.2 g 5% Pt/C)



the carbon balance closed only to 61% and 69%, without and with additive, respectively. It implies that there were important adsorption phenomena on the catalyst surface, which could not be directly quantified through micro-GC and TOC analysis. These solid-liquid interactions mainly involve the phenolic compounds, which show great affinity with the activated carbon support. As a matter of fact, the use of activated carbons is considered as one of the most effective methods to remove these kinds of pollutants from wastewaters.<sup>37</sup>

Despite the complexity of the liquid phase, we can inspect the HPLC chromatograms to derive some insights. As reported in the previous paragraph, NaOH addition led to a higher carbon content in the AP, with glycolic acid and lactic acid which increased their concentration by 40% and 15%, respectively, while methanol doubled. The same was reported for the aromatic fraction of the dissolved oxygenated. Glycolic acid and methanol lead to H<sub>2</sub> production following Equations (4) and (5), respectively.



In the case of the test without additive, glycolic acid conversion was approximately 95%; when NaOH was added, the conversion drastically decreased to 28%; on the other hand, the conversion of methanol increased from 32% to 75%. This shift may be one of the reasons for the observed increase of H<sub>2</sub> concentration in the gas phase. However, it did not explain the presence of methane in the gas phase: the latter was mainly ascribed to the high conversion of lactic acid (95% without NaOH, 59% with NaOH), whose complex reaction pathway involved also the production of short alkanes.<sup>38</sup>

Apart from the desired APR reaction, platinum can also activate parasite reactions, mainly hydrogenation. In fact, before escaping from the active site, H<sub>2</sub> could be consumed in the hydrogenation of glycolic and lactic acid into acetic and propionic acid, respectively. In this respect, also the structure of the support can play a role. Ordinate mesoporous structures could decrease the H<sub>2</sub>-consuming reactions because they facilitate the transport from the active site to the bulk of the solution.<sup>39</sup> On the other hand, the high microporosity of the support used in this work (0.242 cm<sup>3</sup>/g out of 0.745 cm<sup>3</sup>/g of total pore volume) may not go into this direction. For example, acetic acid concentration actually increased by 35% after the reaction and this could be related to glycolic acid hydrogenation. However, we cannot exclude that its formation was due also to other side-reactions, such as from the intermediate ethanol formation.<sup>38</sup>

We suggest that NaOH addition in the HTL step has an indirect effect on the APR, that is, it plays a role mainly due to the different organic distribution in the AP. In fact, the pH, which can affect the APR performance, changed only slightly between the samples with and without NaOH, remaining in the acidic range. However, the presence of Na ions (about 1000 mg/kg from IC analysis) could influence the activity of the catalyst. Lehnert and Claus suggested that the presence of NaCl in the reforming of crude glycerol poisoned the catalyst by blocking its active site.<sup>40</sup> Similarly, Boga et al. showed a strong

decrease of the glycerol conversion when NaCl was added to the synthetic solution.<sup>41</sup> Saenz de Miera et al. evaluated how the fruit juice wastewater APR changed between 320 and 640 mg/L of NaCl (in addition to other salts).<sup>32</sup> They reported that the carbon conversion to gas decreased from 40.6% to 29.4%, which would agree, at a first sight, with the outcome reported in the present work. However, the presence of salts should promote dehydrations, condensation and polymerization reactions, which should decrease the carbon balance closure in the case with NaOH, compared to the case without additive. Being not the case herein, we can conclude that possible deactivation derived from Na species should be negligible. Despite Na is only dispersed in the reaction medium, and was not added to the catalyst during its preparation step, Na may also have a promoting effect on Pt, favoring the CO oxidation and boosting the WGS activity.<sup>42</sup>

The run named “fresh case” was actually the second use of the catalyst after a first run with glycolic acid, to guarantee a fair comparison since the catalyst was exposed to the same hydrothermal conditions of the HTL-derived AP. The run named “No additive” refers to the case when the spent catalyst was re-used for the APR of glycolic acid, once recovered after the APR of the HTL-AP without additive; analogously for the “NaOH” run.

In Figure 4 (Right), it can be observed that the fresh case reported the highest H<sub>2</sub> yield. This catalyst was also the one which maintained the highest surface area, which was close to the initial one (831 vs. 923 m<sup>2</sup>/g). On the other hand, the catalysts used with the real AP showed a drastic decrease in the surface area, accompanied by the decrease in the H<sub>2</sub> yield. It is important to observe that the run without additive showed better performance than the one with NaOH. This seems in accordance with the APR tests of the real AP, where higher conversions of the substrates were obtained when NaOH was not used during HTL, likely due to the reduced deactivation. The worsening of the performance could be attributed both to the presence of phenolics and inorganics. The next paragraph considers the first issue, looking at the influence of a LLE prior to APR test.

### 3.2.2 | Influence of solvent extraction

Despite the direct catalytic valorization of the AP derived from HTL is interesting, it has been reported here and previously that the phenolic oligomers in the AP might significantly affect the catalyst performance leading to its deactivation via fouling-like mechanisms.<sup>35</sup> To avoid this inconvenience, one possible route is to carry out a LLE that selectively removes the aromatics while preserving the content of the other oxygenates prone to produce H<sub>2</sub>. DEE has been shown to be an effective solvent for this separation.<sup>34</sup> However, its properties are not fully compatible with its application on a commercial scale plant due to severe issues related with safety, health, and environmental criteria.<sup>43</sup> Looking only to the latter, on a scale from 1 (being water) to 10, DEE was ranked 7 as regards to the environmental score due to its low boiling point, and so on. ButAc is considered a recommended alternative (ranking score 3), being a more environmentally friendly solvent. For this reason, these solvents were compared for LLE of the water

fraction collected after the NaOH-assisted HTL; moreover, the effect of the S/AP ratio was evaluated. Primarily, the effectiveness of this pretreatment was assessed in terms of selectivity for the extraction. In Figure 7, the extraction of organics acids and aromatics in the case of different solvents and S/AP ratios is reported. Regarding the organic acids, the recovery was defined as the ratio between the sum of glycolic, lactic, and acetic acid concentration (the three most present organic acids) in the AP postextraction and in the one without extraction (Equation 6). The highest the organic acid recovery, the most effective the treatment: ideally, no organic acids should be removed during this stage.

$$\text{Organic acids recovery (\%)} = 100 \cdot \frac{(\text{glycolic} + \text{lactic} + \text{acetic})_{\text{Treated HTL-AP}}}{(\text{glycolic} + \text{lactic} + \text{acetic})_{\text{Untreated HTL-AP}}} \quad (6)$$

$$\text{Aromatics recovery (\%)} = 100 \cdot \frac{(\text{Aromatics PDA 212 nm Area})_{\text{Treated HTL-AP}}}{(\text{Aromatics PDA 212 nm Area})_{\text{Untreated HTL-AP}}} \quad (7)$$

It can be observed that these compounds, thanks to their hydrophilicity, were not removed whatever solvent and S/AP ratios were used. This outcome, which was limited for the sake of clarity to the three most abundant compounds, is reported Figure 5A, where the HPLC chromatograms are depicted as well. These chromatograms refer to the use of a refractive index detector, which is suitable for organic acids and alcohols detection. This is an important result because the un-selective recovery of the oxygenates would hinder the H<sub>2</sub> production. In fact, apart from being a cause of deactivation, phenolics were recalcitrant compounds under the reported reaction conditions, therefore their valorization would be difficult.<sup>38</sup>

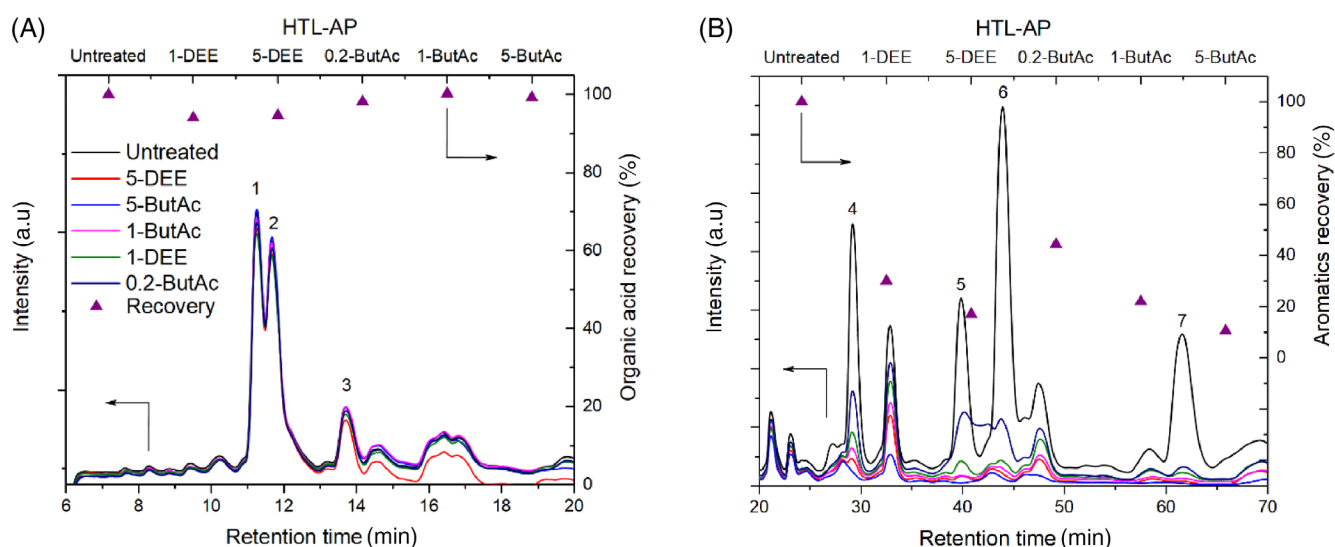
The same evaluation was performed looking at the aromatic fraction of the water-soluble compounds (Equation 7). In this case, the

chromatograms reported in Figure 5B are referred to the photo diode array detector, which is more sensitive than the RID to these compounds. Catechol, 3-methoxycatechol, phenol, and guaiacol were the most present aromatics and they constituted 50% of the aromatic fraction. Both solvents significantly removed the aromatics.

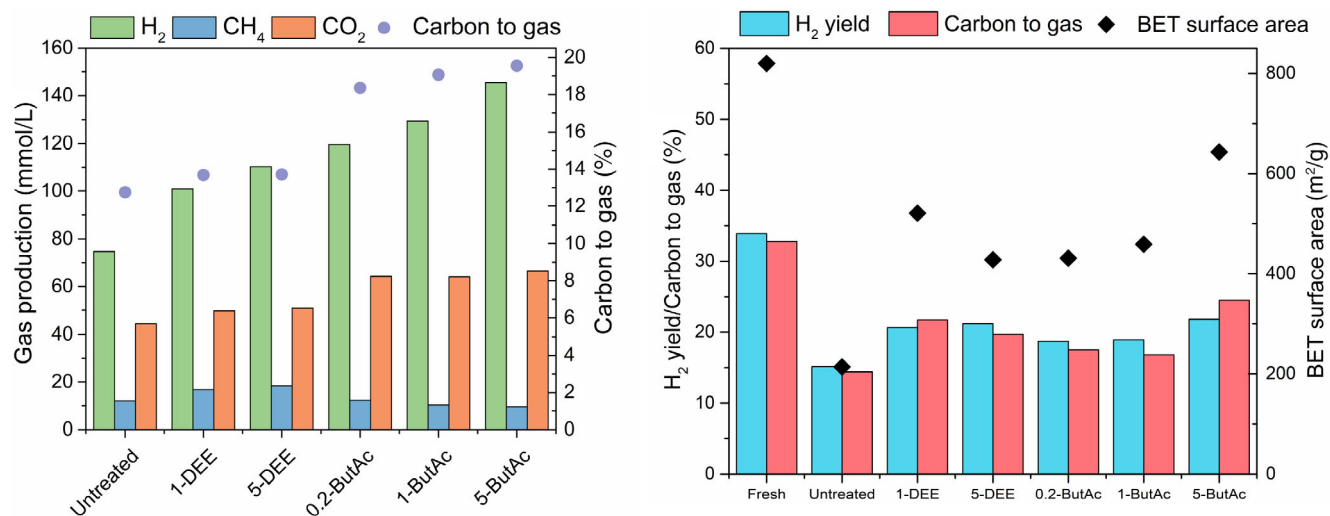
Interestingly, ButAc was more effective, since it allowed a higher recovery at equal S/AP ratio. This is an important element to consider, because it proved that this step can be performed with high selectivity, using a greener solvent. Furthermore, under an industrial point of view, the lower solubility in water (7 g/L) compared to DEE (69 g/L) reduces its loss and, consequently, the need for make-up, overall decreasing the operating costs.

The APR results obtained after the LLE are reported in Figure 6 (Left). For comparison, the untreated AP was added to the graph, showing its lowest gas production for each of the main components. When DEE was used, an improvement in the H<sub>2</sub> production was observed both at 1:1 and 5:1 solvent: AP ratios, with an increase equal to 35% and 48%, respectively. A similar increase rate was observed for methane (40% and 50%), while CO<sub>2</sub> production was almost constant. This outcome was likely due to the higher conversion of methanol. In fact, it reacts following the stoichiometry reported in Equation (5), so leading to three moles of H<sub>2</sub> per mole of CO<sub>2</sub>. Consequently, this may be the reason for the higher H<sub>2</sub>/CO<sub>2</sub> ratio. The carbon to gas conversion increased only slightly, being 13.7% at both the S/AP ratios. It should be noted that for the determination of this indicator the carbon content of the solvents was excluded since it was considered as inert.

The same trend was observed when ButAc was used as solvent. Again, an increase in the S/AP ratio led to an increase in the H<sub>2</sub> production and a constant CO<sub>2</sub> production; the methane production reported a slight decrease. Comparing the APs treated with equal amount of solvent, the ButAc-treated ones gave better results than



**FIGURE 5** (A): organic acids recovery after LLE and HPLC-RID chromatograms (1: glycolic acid, 2: lactic acid, 3: acetic acid); (B): aromatics recovery after LLE and HPLC-PDA (212 nm) chromatograms (4: catechol, 5: 3-methoxycatechol, 6: phenol, 7: guaiacol)



**FIGURE 6** Left: Influence of the solvent and S/AP on the aqueous phase reforming (APR). Reaction conditions: 75 ml AP, 270°C, 2 h, 0.375 g 5% Pt/C; Right: APR of glycolic acid with a spent catalyst. Reaction conditions: 75 ml AP 2.85 wt% glycolic acid, 270°C, 2 h, 0.2 g 5% Pt/C

the DEE-treated ones, with the 5-ButAc leading to almost double H<sub>2</sub> production compared to the untreated sample. The carbon to gas showed a greater improvement, reaching up to 19.6% when the highest amount of ButAc was used. It is worth to note that the decrease of phenolic content penalized the occurrence of adsorption, yielding a higher carbon balance closure (85% average).

The reason why ButAc led to better performance than DEE is not trivial. The removal of the aromatics, despite significant, does not seem to be the only reason, since the 0.2-ButAc sample had a higher content of these compounds than 1-DEE and 5-DEE, but a higher H<sub>2</sub> production. It has been reported in literature that the pH can affect the APR performance. However, in this case, the difference cannot be attributed to different pHs, since the two solvents have an almost neutral behavior. Furthermore, blank experiments where only the solvents were subjected to APR, showed a negligible H<sub>2</sub> production, demonstrating that the solvents did not contribute to the observed performance. We suggest that the lower solubility of ButAc could decrease the onset of competitive adsorption phenomena which, particularly in the liquid phase, can be of great importance.<sup>44</sup>

Figure 6 (Right) depicts the APR results of the re-use tests, together with the data on the surface area of the spent catalysts. The textural characterization of the catalysts used with treated AP reported an increase of the surface area compared to the untreated one. However, a clear trend was not observed, since it apparently decreased with the increase of DEE, while increased at higher ButAc/AP ratios. The H<sub>2</sub> yield and carbon to gas conversion were quite similar for DEE, while they had a slightly increasing trend in the case of ButAc. Therefore, despite ButAc led to higher H<sub>2</sub> yield in the reaction stage, it seems that it did not improve the stability of the catalyst to a higher extent than DEE. Further investigations on the influence of the inorganics are ongoing to verify their impact on the catalyst lifetime.

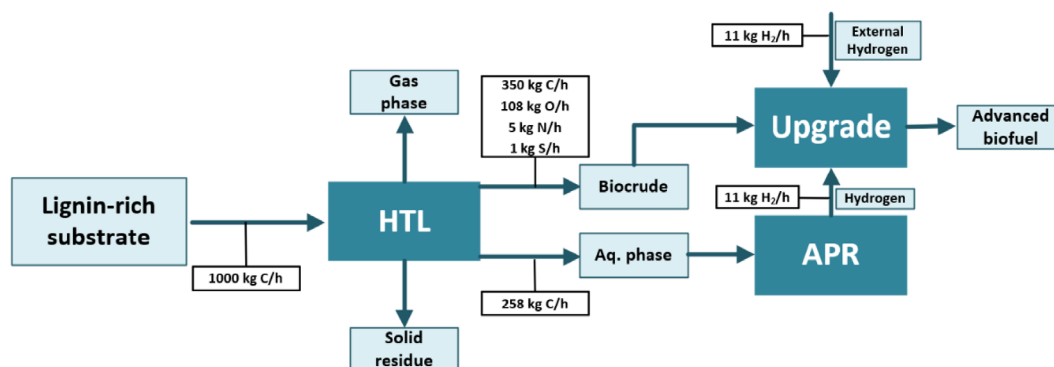
Table S3 compares the results obtained in this work with some other performances reported in literature for the APR of complex

streams. In order to make a fair comparison, the results of simple mono-component solutions were excluded. The H<sub>2</sub> yield, expressed as mg H<sub>2</sub>/g C in the water fraction in the case of the hydrolysis of lignocellulosic biomass (kenaf, wheat straw, switchgrass) is comparable or even lower to the one obtained in this work from the HTL-AP of lignin residue. On the other hand, brewery, fruit juice, and crude glycerol wastewaters reported much higher H<sub>2</sub> yield compared to the lignin-rich HTL-AP case. This could be attributed to the composition of these water fractions, which are rich in carbohydrates (from brewery and fruit juice) or polyalcohols (crude glycerol). These molecules are prone to produce H<sub>2</sub> thanks to their chemical structure with C:OH close to 1, and therefore, as reported above, suitable to carry out the reforming and water gas shift reaction with high activity and selectivity.<sup>45</sup>

### 3.3 | TOWARD HTL AND APR INTEGRATION

One aim of the present work is to evaluate the possibility that HTL and APR may work, in a synergistic way, to decrease—ideally eliminating—the need of H<sub>2</sub> for the upgraded biofuel and obtain a nearly zero-waste biorefinery, thanks to the valorization of secondary streams. For this reason, it is important to perform some preliminary calculations in order to assess how much lab scale results are close to this target.

The BC obtained from HTL still contains too much oxygen to be valorized in the fuel market, and therefore needs an upgrading step. While the H<sub>2</sub> used nowadays for this process mainly derives from fossil fuels via steam reforming,<sup>11</sup> our investigation addressed the possibility to use the C-laden wastewater as source of H<sub>2</sub>. A scheme of the integration among the two units, together with the upgrade step, is reported in Figure 7. We assumed 1000 kg C/h as feed to the HTL block, roughly corresponding to 1845 kg/h of dry lignin-rich substrate.



**FIGURE 7** Mass balance integration between hydrothermal liquefaction and aqueous phase reforming of a plant processing 1845 kg/h of lignin-rich substrate (dry base)

According to the obtained results, 350 kg C/h are converted into BC (i.e., 35% of the initial carbon). Taking into consideration the elemental composition of the BC, this means that 108 kg/h of O should be removed. After the HTL, 258 kg C/h are virtually lost in the AP (i.e., 25.8% of the initial carbon).

In order to determine the H<sub>2</sub> production from this stream, we considered the gas production reported in Figure 6, in the case of ButAc as solvent with a 5:1 solvent/AP ratio (i.e., 5-ButAc). Being the H<sub>2</sub> production 146 mmol/L of wastewater, and being the carbon concentration in the AP equal to 0.7 wt%, we derived that approximately 11 kg/h of H<sub>2</sub> would be produced in the APR step and available for the upgrading (i.e., hydrodeoxygenation).<sup>46</sup>

To the best of our knowledge, there are no studies regarding the upgrade of lignin-derived BC, therefore it is difficult to estimate the H<sub>2</sub> consumption during this step. However, it can be worthy of consideration trying to estimate as best as possible a theoretical H<sub>2</sub> requirement, in order to understand the effectiveness of HTL and APR integration. If we take into account the elementary stoichiometry in which 1 mole of H<sub>2</sub> is necessary to remove 1 mole of O and S, while 1.5 moles are necessary for the removal of 1 mole of N, then 14.6 kg/h of H<sub>2</sub> would be necessary, against the 11 kg/h experimentally obtained. It means that in ideal stoichiometric conditions, APR would be able to provide 74% of the H<sub>2</sub> required by the upgrade. In addition to this amount, the effectiveness of the hydrodeoxygenation should be considered, since a fraction of H<sub>2</sub> will be lost in the production of by-products, such as light alkanes. In order to evaluate this factor, we used the experimental data provided by a technical report from Pacific Northwest National Laboratory (PNNL).<sup>47</sup> There, the authors reported that the actual H<sub>2</sub> requirement was 0.046 g H<sub>2</sub>/g of BC against a stoichiometric H<sub>2</sub> demand of 0.034 g H<sub>2</sub>/g BC, calculated from BC elemental composition. Therefore, assuming that the ratio between stoichiometric and experimental requirements is the same also for our case, the H<sub>2</sub> demand accounting for side reactions would be increased by 1.36 times compared to the stoichiometric one. It follows then, that the APR-produced H<sub>2</sub> would now provide 54% of the required H<sub>2</sub>. Finally, H<sub>2</sub> should be recovered from the gas mixture produced during APR. In this analysis, we hypothesized that pressure swing adsorption (PSA) could be used, and that 85% H<sub>2</sub> recovery could be achieved.<sup>48</sup>

Therefore, we ended up that the H<sub>2</sub> provided by APR could be able to satisfy 46% of the upgrade necessity. Please note that this value should be seen just as an indication of the potential integration between the two technologies, due to the strong dependence on the reaction conditions of the two processes. For example, the APR of HTL-AP derived from other substrates (e.g., corn stover), may provide a higher fraction of H<sub>2</sub> for the upgrade, since the AP composition is richer in H<sub>2</sub>-producing molecules, like glycolic acid (and in a minor extent methanol and ethanol).<sup>24</sup> On the other hand, this fraction may decrease if a more concentrated HTL is performed; in fact, even if we assume the same carbon and oxygen distribution among the products, it is known for APR that a higher carbon concentration in the feed results in a higher selectivity toward liquid products.<sup>23</sup>

It is worthy to consider that, in this scenario, approximately 80% of the carbon present in the feed of APR would still remain in the liquid phase, since the carbon conversion to gas was about 20% (Figure 6). This outcome was related to multiple reasons. Firstly, the chosen reaction time did not allow for a higher conversion of active compounds, such as glycolic acid, which would lead to CO<sub>2</sub> as main C-containing product; secondly, recalcitrant liquid by-products may be obtained from the feed molecules (e.g., acetic acid from glycolic acid) which would not end up in the gas phase; thirdly, the catalyst deactivation which occur during the reaction may block the APR of small molecules, such as methanol, globally reducing the carbon conversion to gas. Thanks to optimized and stable conditions, the carbon conversion to gas of the model compounds present in the lignin-rich HTL-AP could range from 4.4% to 79.2%.<sup>34</sup> The results showed in this work highlights the potential of APR for carbon removal from the wastewater, but it requires further investigation to increase it and reach the “zero-waste” goal. In this sense, the recycle of the partially cleaned AP to HTL may be evaluated as a substitute of fresh water.

Despite the preliminary calculations brought to a lack of H<sub>2</sub> compared to the necessary, a significant reduction of the external need can be considered a large improvement of the process for several reasons. First of all, the wastewater treatment cost would be reduced if the organic load is converted into a valuable product, with the remaining one being recycled; secondly, it compensates the environmental cost of the fossil H<sub>2</sub>; moreover, if a green H<sub>2</sub> source is

proposed (i.e., electrolysis powered by renewable energy), it would currently have higher costs. Furthermore, partial deoxygenation of the BC would be beneficial for the storage properties and avoid the increase of the viscosity.<sup>49,50</sup> In fact, several research groups showed that partially upgraded BCs could be processed together with fossil-derived fuels in conventional refineries.<sup>51</sup>

Other technologies investigated for the production of H<sub>2</sub> via the processing of HTL-AP are, among the others, supercritical water gasification (SCWG), also called hydrothermal gasification (HTG) and electrochemical oxidation (EO). Regarding SCWG, Watson et al.<sup>52</sup> reported a H<sub>2</sub> production of 7.43 g H<sub>2</sub>/kg dry feedstock (in HTL slurry) using AP from HTL of human feces, while Zhang et al.<sup>17</sup> reported a production of 46.2–142.2 g H<sub>2</sub>/kg carbon (TOC) using AP from HTL of sewage sludge. Assuming the H<sub>2</sub> production showed in Figure 6 (5-BuAc), a lower amount of H<sub>2</sub> is produced through APR (5.6 g H<sub>2</sub>/kg LRS or 40 g H<sub>2</sub>/g organic carbon). However, it should be considered that APR is performed at a considerably lower reaction temperature (280°C) than SCWG (400–700°C), so it is less challenging from a technological point of view, as well as more sustainable under the energy perspective. Cherad et al. gasified under supercritical conditions (600°C, 35 MPa) the AP from microalgae HTL.<sup>13</sup> The authors observed that processing the undiluted AP led to 2.1–4.8 mg H<sub>2</sub>/g BC, without and with the addition of NaOH. These values are similar to those obtained in the present work.

Electrochemical oxidation is a promising technology for the removal of pollutants that are recalcitrant to conventional biological and chemical routes in wastewater treatments.<sup>53</sup> Matayeva et al.<sup>54</sup> applied EO to AP from HTL of wheat straw and sewage sludge for simultaneous removal of recalcitrant organics and H<sub>2</sub> production. They reported that only 21 and 22% (v/v) of the H<sub>2</sub> required for the on-site upgrading of the BC (from wheat straw and sewage sludge) could be produced, while the APR process may satisfy approximately 80% of the upgrade need.

Table S4 shows a summary of the comparison between the previously described technologies. Thanks to its milder reaction conditions, it appears that APR may compete with other technologies for H<sub>2</sub> production from HTL-AP. However, important bottlenecks mainly linked to the catalyst deactivation remain. For this reason, it is important that APR is being investigated now with actual mixtures, going toward industrially relevant environment to determine challenges which are not considered with synthetic mixtures. For this reason, the influence of the inorganics dissolved in the AP is currently under evaluation.

## 4 | CONCLUSION

In this work, the HTL of a lignin-rich feedstock and the APR of the HTL water effluent were investigated. The HTL was performed in a continuous pilot plant looking at the influence of Na<sub>2</sub>CO<sub>3</sub> and NaOH on several performance parameters (pumpability, BC yield, etc.). The main issues encountered during the operation of the continuous HTL plant were the pumpability of the inlet slurry and pipes blockage due

to products deposition. The temperature control was improved in the after-cooler section maintain ~80°C, decreasing the products viscosity and increase the flowability. The addition of NaOH (0.05 mol/L), improved the pumpability of the slurry allowing to achieve a processing time of 6 h in a single run and increased the BC yield (27 wt%). Moreover, alkaline additives led to lighter BCs compared to uncatalyzed one, suggesting an increase of LRS depolymerization in alkaline environment. Dissolved oxygenated aromatics were detected in AP samples and the highest presence of methanol in NaOH run confirmed the increase in lignin depolymerization through demethylation. The carbon-laden AP derived from HTL was subjected to APR with the aim of producing H<sub>2</sub> for the upgrading of the BC. It was observed that the AP with NaOH additive led to the highest gas production. Since the dissolved phenolics hindered the catalytic activity, they were removed by LLE using DEE or ButAc, with different S/AP ratios. ButAc was found more effective, and higher H<sub>2</sub> yields were obtained. The reuse of the catalysts showed a moderate decrease of the textural characteristics. The results reported in this work, dealing with the combination of two innovative processes, pave the way to a treatment route addressing both the organic load reduction of process water and H<sub>2</sub> generation. Their synergy defined a new pathway, which allows to obtain an advanced biofuel by reducing the need for fossil H<sub>2</sub>. In fact, preliminary calculations reported that, for the feedstock under consideration, about half of the amount of H<sub>2</sub> required for the BC upgrade can be provided by APR. Further investigation on the process design and techno-economic assessments of the integrated HTL-APR plant will be the subject of a future work.

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## AUTHOR CONTRIBUTIONS

**Arturo Di Fraia:** Data curation (equal); formal analysis (equal); writing – review and editing (equal). **Edoardo Miliotti:** Formal analysis (equal); investigation (equal); methodology (equal); writing – review and editing (equal). **Andrea Maria Rizzo:** Investigation (equal); methodology (equal); project administration (equal); supervision (equal); writing – review and editing (equal). **Giulia Zoppi:** Conceptualization (equal); formal analysis (equal); investigation (equal); methodology (equal); validation (equal); writing – review and editing (equal). **Giuseppe Pipitone:** Conceptualization (equal); investigation (equal); methodology (equal); validation (equal); writing – review and editing (equal). **Raffaele Pirone:** Conceptualization (equal); supervision (equal). **Luca Rosi:** Conceptualization (equal); validation (equal); visualization (equal). **David Chiamonti:** Conceptualization (equal); project administration (equal); resources (equal); writing – review and editing (equal). **Samir Bensaid:** Conceptualization (equal); project administration (equal); supervision (equal); writing – review and editing (equal).

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.



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## SUPPORTING INFORMATION

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