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Towards the sustainable hydrogen production by catalytic conversion of C-laden biorefinery aqueous streams

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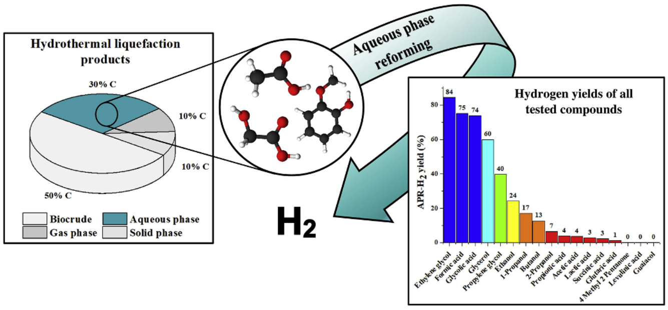
HIGHLIGHTS

- Compounds representatives of biorefinery streams were tested by APR.
- Several molecules were investigated for the first time.
- Binary and ternary mixtures were explored to evaluate collateral effects.
- Acetic acid was found as a key intermediate/by-product of APR.

GRAPHICAL ABSTRACT



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ABSTRACT

An extensive screening of representative molecules of a post-hydrothermal process side stream has been performed with the aim of producing a gas mixture rich in hydrogen by catalytic aqueous phase reforming. The survey enlightens possible routes of valorisation of these by-products, scarcely investigated with other processes so far. The influence of reaction temperature was studied in the 230–270 °C range, looking at both the composition of the gas phase and the characterization of the liquid products. Indeed, the information coming from the condensed phase may provide relevant insights on the components that are not easily reformed, and that should be studied to improve the performance of the process. Binary and ternary mixtures of four selected compounds were tested to investigate synergistic and inhibiting effects, going towards the direction of a real biorefinery stream. The spent alumina-supported catalyst was characterized, outlining possible deactivation mechanisms of the catalytic system, and reused in two successive tests.

1. Introduction

The hydrothermal processing of biomass has gained interest in the last decades mainly with the aim of producing alternative fuels [1]. Water at near-critical or super-critical conditions becomes a peculiar reaction medium thanks to the drastic change of its physical–chemical characteristics. For example, at subcritical conditions, the pH-value strongly decreases, thus enabling to carry out acid-catalysed reactions without the use of a dedicated catalyst. Moreover, water polarity changes thanks to the diminishing dielectric constant, being able to dissolve non-polar substances [2]. Apart from the actual properties of water, the exploitation of a hydrothermal process allows the use of

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biomass with high moisture content, without the need for a drying step that would limit the overall process economy [3].

Depending on the temperature of the process, three main hydrothermal processes can be classified: hydrothermal carbonization (below 520 K), hydrothermal liquefaction (between 520 and 647 K, the latter being the critical temperature of water) and hydrothermal gasification (above 647 K) [4].

Focusing on the liquefaction, it has been investigated mainly with the goal of producing an organic product, often referred as biocrude, with a relatively high heating value [5,6]. However, its high oxygen content compared to the commercial fuels leads to the necessity of a further upgrading step.

Nevertheless, in order to make the whole process economically sustainable, the other products of liquefaction should be exploited and valorised as well. To confirm this point, it was estimated that the cost of the aqueous phase waste treatment is second only to the one of the feedstock [7].

Despite the strategic importance of this issue, there are just few examples in literature focusing on the aqueous phase obtained after a hydrothermal process [8]. The major efforts have been carried out at the PNNL (Pacific Northwest National Laboratory) in the USA, where the aqueous samples obtained from many different feedstocks (lignocellulosic, algae, municipal wastes) where characterized [9–11].

Panisko et al. analyzed the hydrothermal liquefaction of pine forestry residuals or corn stover and from the hydrotreatment of fast pyrolysis bio-oils [9]. The experiments showed that the aqueous phase coming from the latter process contained negligible amounts of organic carbon; on the other hand, the samples coming from the former contained about 2 wt% of organic carbon. It was mainly constituted by organic acids, such as glycolic acid (i.e. a hydroxyacid) and acetic acid. Moreover, alcohols (methanol and ethanol) were present, together with numerous ketones (acetone and cyclopentanones). The same research group performed a quantitative characterization of the aqueous fraction from the HTL of four fresh water and four seawater algae, identifying also nitrogenous compounds, in addition to the ones found from the lignocellulosic feedstocks [10].

A recent work started from municipal and food industry wastes: the influence of the selected feedstock on the classes of compounds in the aqueous phase that can be originated from the hydrothermal treatment, was highlighted [11].

Many organic species present in the aqueous by-products are valuable, so their selective recovery might be evaluated. However, they are present in low concentrations; therefore, the stream should be subjected to a drying step that would be not economically feasible at an industrial scale. For this reason, it seems reasonable to consider a process that valorises the entire set of substances present in the HTL-derived aqueous stream.

Anaerobic digestion and catalytic hydrothermal gasification (CHG) have been suggested as possible processes for the valorisation of the aqueous stream [12]. Hence, Elliott et al. carried out the CHG of the HTL aqueous by-product, producing a methane-rich gas [13].

In this work, we want to investigate the possibility to exploit the aqueous phase reforming (APR) conditions for producing a high-value gas in terms of hydrogen concentration. APR is a catalytic process that allows to obtain a gas mixture rich in hydrogen, while working at milder temperatures (about 500 K) compared to the more severe conditions (typically higher than 800 K) of the conventional steam reforming of hydrocarbons [14] (Eq. (1)).

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

In a previous work, we enlarged the portfolio of investigated molecules exploring the APR of alginate, a polysaccharide present in the outer wall cell of brown macroalgae [15].

In the present work, several model compounds belonging to the different classes found in the aqueous phase of lignocellulosic feed were screened. Main attention was put on the composition of the gas phase, looking at the tendency of each compound to be reformed at different reaction temperatures; however, a big effort was put also to investigate the composition of the liquid phase after the reaction, searching for key intermediates or final by-products in the reaction mechanism that could be defined as “bottleneck-species” for the production of hydrogen. To the best of our knowledge, this is the first work in which the current set of compounds, belonging to various classes and being representative of the aqueous phase post-HTL, was investigated in one experimental system, including gas and the liquid phase characterization. Attention was put also on the characterization of the catalyst recovered after the reaction. Furthermore, mixtures of two and three compounds were tested to analyze possible synergistic or inhibiting effects, making a step forward in the direction of the investigation of a real biorefinery stream.

2. Materials and methods

2.1. Materials

Lactic acid and propionic acid was purchased from Fluka. Deionized water was obtained in laboratory. All other reagents were purchased from Sigma Aldrich. The tested catalyst is a commercial 5% Pt/Al_2O_3 from Sigma Aldrich. Gas cylinders were supplied by SIAD S.p.A., Bergamo (Italy). All the chemicals were used as received without further purification.

2.2. Experimental procedures

The APR tests were conducted in a 300 mL 4560 series mini bench top reactor (Parr) equipped with a 4848 model reactor controller (Parr). In the typical run, the reactor was loaded with 75 mL of aqueous solution with a constant molarity (0.133 M); 0.375 g of 5% Pt/Al_2O_3 catalyst was added without any pretreatment. Preliminary tests in which the catalyst was subjected to a reducing environment did not affect its catalytic properties. The atmosphere was purged from the atmospheric oxygen by nitrogen five times; then it was pressurized with 0.3 MPa of N_2. The temperature was programmed to reach the desired set value and kept constant for two hours. The stirrer was set at 400 rpm. The reaction time was considered starting when the set temperature was reached. At the end of the reaction, the reactor was cooled thanks to the internal water-cooling coil. The pressure value obtained by the transducer was recorded, in order to quantify the produced gas by the ideal gas law. The gas phase was collected in a sampling bag and analyzed by micro-GC, to evaluate its composition. The initial pressurization with nitrogen helped also in the quantification of the produced gas by gas chromatography (GC), because it can be seen as an internal standard. The results from the transducer and the micro-GC were coherent, within a deviation of ± 5%. The liquid product was recovered from the reactor and filtered by gravity to remove the catalyst; then it was subjected to total organic carbon (TOC) and high pressure liquid chromatography (HPLC) analysis. The filtered solid phase (i.e. the spent catalyst) was put in an oven at 90 °C overnight, recovered and weighted. Some samples were then subjected to further characterization analysis.

2.3. Analytical methods

The analysis of the gas phase was performed with a SRA Micro-GC, equipped with a Molsieve 5A column (for the analysis of permanent gases such as hydrogen, nitrogen, methane and carbon monoxide) and argon as carrier (column temperature: 100 °C); a PoraPLOT U column was used for the separation of carbon dioxide, ethane and propane, with helium flow as carrier (column temperature: 85 °C). The detection of the species was due to a TCD detector. The injection temperature was fixed at 100 °C and the pressure at 30 psi.

HPLC analysis (Shimadzu) was performed with a Rezex ROA-

Organic acid H^+ (8%) column (300 mm * 7.8 mm). The mobile phase was 5 mM H_2SO_4 in water. The flow rate was fixed at 0.7 mL/min and the temperature of the column at 50 °C. The products were determined by means of a refractive index detector (RID) and a photodiode array detector (PDA), that worked in the range 190–380 nm. Purchased standards were used for quantitative characterization, performed by external calibration curves.

Total carbon (TC) and inorganic carbon (IC) analysis was performed using a Shimadzu TOC-V_{CSH} analyzer equipped with a nondispersive infrared detector.

A Micromeritics Tristar 3020 instrument was used to measure the N_2 adsorption/desorption isotherms of the fresh and spent catalysts at 77 K. Prior to the characterization, the samples (about 0.05 g) were degassed at 200 °C under nitrogen flow for 2 h by means of a Micromeritics Flow Prep 060 degassing system. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) equation, whereas the pore size distribution and the pore volume in accordance to the Barrett-Joyner-Halenda (BJH) method.

Morphological properties of the catalysts were investigated through field emission-scanning electron microscope (FESEM Zeiss Merlin, Gemini-II column).

X-ray diffraction (XRD) was performed by means of a Panalytical X'Pert Pro diffractometer (Cu Ka radiation) on a fresh and spent catalyst sample to assess if any structural change was present after the reaction. Cristobalite was used as internal standard for quantification.

The presence of platinum loading in the solution after the test was measured via a Thermo Scientific iCAP Q ICP-MS (Thermo Fisher).

Thermal gravimetric analyses (TGA) was carried out on about 10 mg samples using a TG 209 F1 Libra® (NETZSCH GmbH), at 10 °C min^{-1} heating rate, from 25 °C to 800 °C under nitrogen or air flow (60 cm^3/min). Experimental error was estimated to be by typically less than 0.05 mg (approximately ± 0.5%). Fourier Transformed Infrared Spectroscopy (FT-IR) transmittance spectra were collected on a Nicolet 5700 FTIR Spectrometer (ThermoFisher). The samples were prepared by the KBr disc technique using a finely ground mixture of 1 mg of sample and 200 mg of KBr pressed at 74 MPa for 2 min. 16 scans were signal-averaged at a resolution of 2 cm^{-1} from 4000 to 400 cm^{-1}.

The performance of the process was estimated according to parameters frequently applied in the evaluation of aqueous phase reforming. In this work we used four parameters. The carbon conversion to gas *CtoG*, defined as the ratio between the carbon atoms in the gas products C_{gas} and the carbon atoms in the original feedstock C_{feed} (Eq. (2)); the APR hydrogen yield *APR-*Y_{H2}, defined as the ratio between the moles of produced hydrogen in the gas phase $(H_2)_{gas}$ and the maximum moles that could be obtained according to the reaction stoichiometry reported in Eq. (1) (Eq. (3)); the hydrogen gas distribution, defined as the ratio between the molecular hydrogen present in the gas phase and the total hydrogen (possibly present also in the gaseous alkanes) (Eq. (4)); finally, the APR H_2 selectivity *APR-*S_{H2}, an indicator of how much the reaction path is close to the APR reaction, defined as the ratio between the hydrogen and the carbon dioxide moles in the gas phase $(H_2/CO_2)_{gas}$, divided by the stoichiometric reforming ratio (*RR*): it is commonly defined as the ratio between hydrogen and carbon dioxide moles in the reaction stoichiometry (Eq. (5)).

$$\mathrm{CtoG}\,(\%) = 100 * \frac{C_{gas}}{C_{feed}} \tag{2}$$

$$\mathrm{APR\text{-}Y_{H_2}}\ (\%) = 100 * \frac{(H_2)_{gas}}{(y+\ n) * n_{feed}} \tag{3}$$

$$\mathrm{GD_{H_2}}\ (\%) = \frac{H_2}{H_2 + 2 * CH_4 + 3 * C_2H_6 + 4 * C_3H_8} \tag{4}$$

$$\mathrm{APR\text{-}S_{H_2}}\ (\%) = 100 * \frac{(H_2/CO_2)_{gas}}{RR} \tag{5}$$

The results obtained with the mixtures were compared to the linear combination of the results obtained in the single compound solution. As an example, the linear combination referring to the carbon to gas conversion has been calculated according to the following equations; in particular, Eqs. (6) and (7) refer to binary mixtures, while 8 and 9 to ternary mixtures.

$$CtoG_{\ 133\ mM} = 1/2 * (CtoG_{glycolic\ 133\ mM} + CtoG_{acetic\ 133\ mM}) \tag{6}$$

$$CtoG_{67\ mM} = 1/2 * (CtoG_{glycolic\ 67\ mM} + CtoG_{acetic\ 67\ mM}) \tag{7}$$

$$CtoG_{\ 133\ mM} = 1/3 * (CtoG_{glycolic\ 133\ mM} + CtoG_{acetic\ 133\ mM} + CtoG_{lactic\ 133\ mM}) \tag{8}$$

$$CtoG_{44\ mM} = 1/3 * (CtoG_{glycolic\ 44\ mM} + CtoG_{acetic\ 44\ mM} + CtoG_{lactic\ 44\ mM}) \tag{9}$$

where $CtoG_{133\,mM}$ is to the value obtained with the binary or ternary mixture. $CtoG_{glycolic\ 133\,mM}$ is the value of carbon to gas conversion obtained in the test with glycolic acid at 133 mM initial concentration. The same nomenclature applies to the tests performed at 67 or 44 mM.

3. Results and discussion

3.1. Influence of the reaction temperature

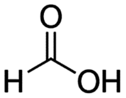
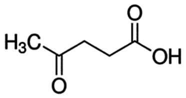
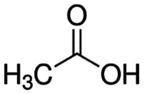
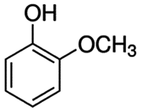
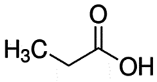
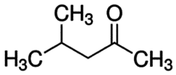
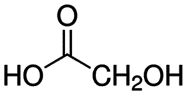
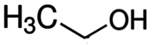
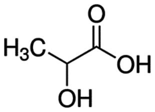
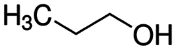
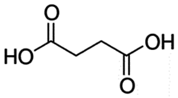
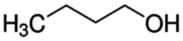
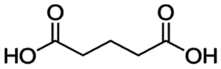
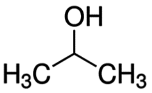
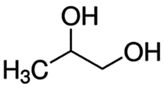
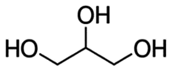
The APR of seventeen characteristic compounds was performed at three different temperatures: 230, 250 and 270 °C. These species were chosen accordingly to the work of Panisko et al., selecting the most representative ones in terms of abundance in the aqueous solution post-HTL, to our end [9]. The list of the molecules is reported in the Table 1. As it can be observed, at least one compound from each of the main classes possibly found in the aqueous stream was investigated. It is noteworthy that some of them (e.g. glycolic acid, 4-methyl-2-pentanone, guaiacol) were subjected to APR for the first time in this work.

As reported in the experimental section, the solutions were prepared without modifying the pH, leading to an autogenous initial pH dependent on each compound's pKa. In literature, the influence of pH is reported [16], and basic values of pH are beneficial towards hydrogen production. As a consequence, the starting pH of the solution may affect the comparison of the screening compounds. Nevertheless, the aim of the present work is to perform an evaluation of the reactivity and tendency to produce hydrogen by compounds present in aqueous side-streams; in order to be as close as possible to the real application, it was decided not to modify the pH in the reactive solution.

3.1.1. Carboxylic acids

The carboxylic acids were the first compounds to be investigated. As reported from Panisko, they are the second most abundant class in the aqueous phase post-HTL [9]. Moreover, they can be considered representative also of other contexts, like in bio-oil pyrolysis, thus widening the interest related to this class of compounds. The results regarding the gas phase are reported in the following Fig. 1-A. First of all, it was observed that formic acid differs from the other acids. There was almost no influence of the temperature on all the parameters, and they were globally higher than the other carboxylic acids. Also, the gas composition remained unchanged at every temperature investigated. An uncatalyzed test showed almost the same result, with 70% of carbon to gas, 69% hydrogen yield and 99.8% as hydrogen gas distribution. These observations supported the idea that a thermal decomposition is responsible for these results and not an actual reforming process. This outcome is coherent with the work of Yasaka et al. [17]. CO is present in relatively high amount (12000 ppm at 270 °C) compared to the other tested molecules (maximum 1000 ppm at 270 °C), which may be due to the high production of carbon monoxide by decarbonylation; in this case, the catalyst is not able to convert CO completely by water gas shift. In the liquid phase, the total conversion of the molecule was

Table 1
List of investigated model compounds.

Carboxylic acids		**Ketoacids, aromatics, ketones**	
Formic acid		Levulinic acid	
Acetic acid		Guaiacol	
Propionic acid		4 methyl 2 pentanone	
Hydroxyacids and dicarboxylic acids		**Alcohols**	
Glycolic acid		Ethanol	
Lactic acid		1-propanol	
Succinic acid		Butanol	
Glutaric acid		2-propanol	
		Polyalcohols	
Ethylene glycol		Propylene glycol	
	Glycerol		

observed. Interestingly, propionic acid was responsible for 40% of the carbon present in the liquid phase, indication of some condensation pathways that involve formic acid.

Acetic acid and propionic acid showed different behaviours compared to formic acid. They exhibited an increase of the carbon conversion to gas, together with the hydrogen yield, with a drastic rise at 270 °C. Anyway, despite the moderate carbon conversion to gas, the hydrogen yield was particularly low. Carboxylic acids have been rarely investigated in the aqueous phase reforming process, but as it was observed, they are important by-products in post-HTL aqueous stream. Some research focused more on the steam reforming of acetic acid, where the reaction mechanism has been studied on platinum-based catalysts [18]. The difficulty for reforming may be due to the presence of a methyl group that is not activated by a hydroxyl one, as suggested from the original work of Dumesic that hypothesized the first reaction mechanism for APR [14]. Looking at the gas composition, an almost 1:1 ratio between carbon dioxide and methane is observed for acetic acid; at the same way, for the propionic acid, the ethane is the most abundant gaseous alkane (Fig. S1). This means that the C—C bond with the carboxylic group was preferably broken. In this case it is not possible to think that a thermal phenomenon is ongoing: in fact, a not catalytic test with acetic acid a 270 °C showed 1% of carbon conversion to gas and 97% of hydrogen gas distribution.

In the liquid phase, the conversion of acetic acid was 22% at 230 °C and it increased up to 56% at 270 °C, being almost the only compound (Fig. 1-B). This observation might suggest a possible reaction mechanism based on the activity of Matas Güell et al. on the steam reforming of acetic acid at 320 °C on Pt/C [18]. At first, acetic acid adsorbed on the Pt sites, with CO_2 that is primarily set free; then the recombination of CH_{3ads} and H_{ads} may be the main pathway, with the formation of CO_2 and CH_4 in equimolar amounts. Looking at the run at 270 °C, it was observed that, compared to this ideal mechanism, 88% of methane and 84% of carbon dioxide is obtained, supporting the idea that this path may be the main reaction route for acetic acid in these reaction conditions. The small presence of hydrogen may be due to the minor path of recombination of the H_{ads} (Fig. 2-A), but this would be not sufficient to explain still great part of the hydrogen present. This means that other mechanisms, such as dehydrogenation of the feed, may be present, even if less important than the main route leading to methane and carbon dioxide. The same behaviour may be reported for propionic acid, where the ethyl group may be recombined with the atomic adsorbed hydrogen, giving ethane (Fig. 2-B). In this case, other paths may be expected because the ratio is not exactly as hypothesized looking at the previous mechanism. In a future work, tests at different reaction times and concentrations will be reported to elucidate the reaction mechanism during APR conditions. For example, working with a differential reactor should help identifying key reaction intermediates that may give a hint on the true reaction mechanism. On the other hand, in this work, it was decided to operate in integral mode as the main goal was to have a wide view on the reactivity of several

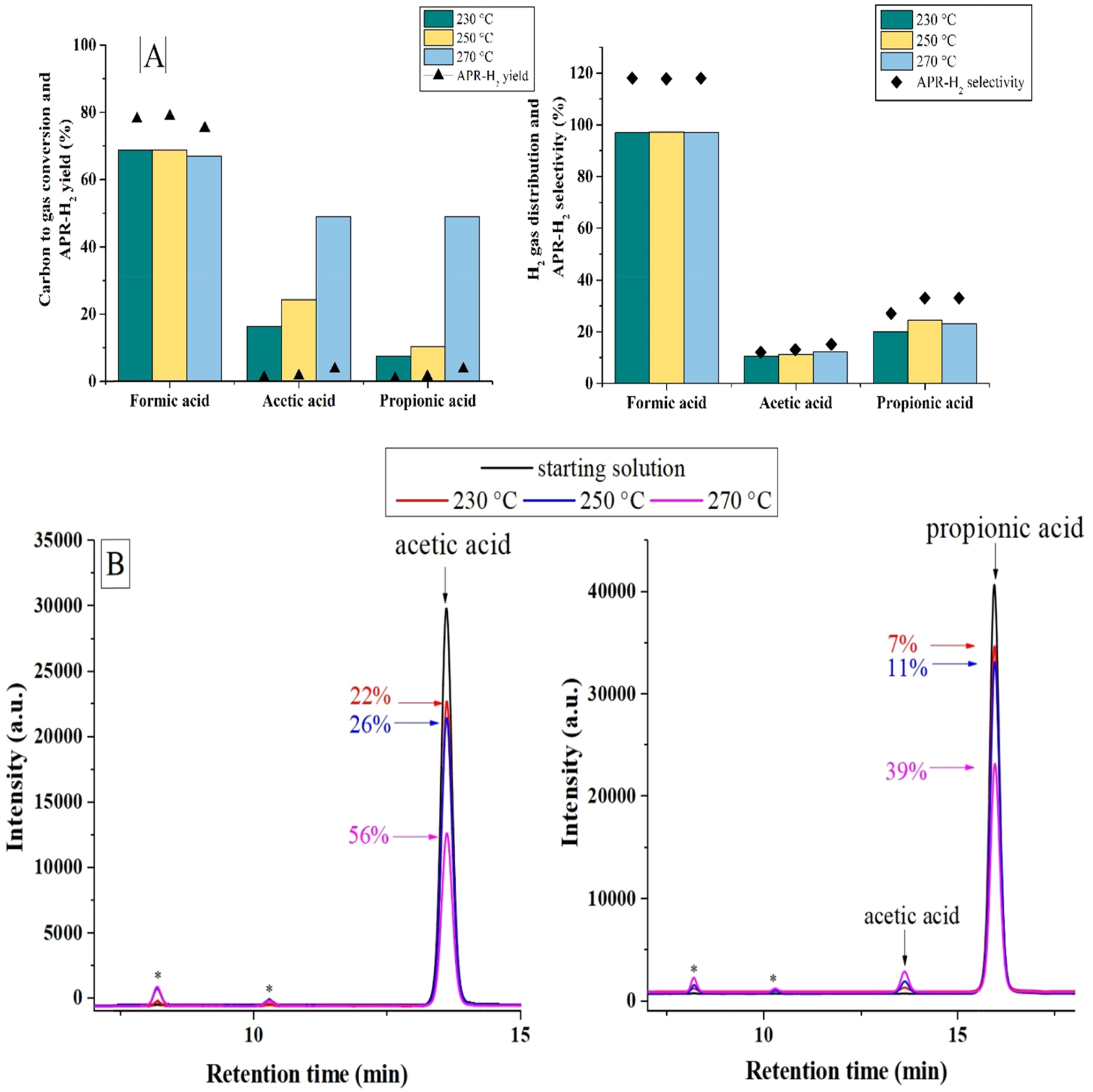


Fig. 1. Influence of the reaction temperature on the APR of carboxylic acids (A) and on the composition of the liquid phase after the APR of acetic acid (B-left) and propionic acid (B-right); the % assigned to the reactant peak refers to its conversion at the end of the APR test; *: unknown compounds.

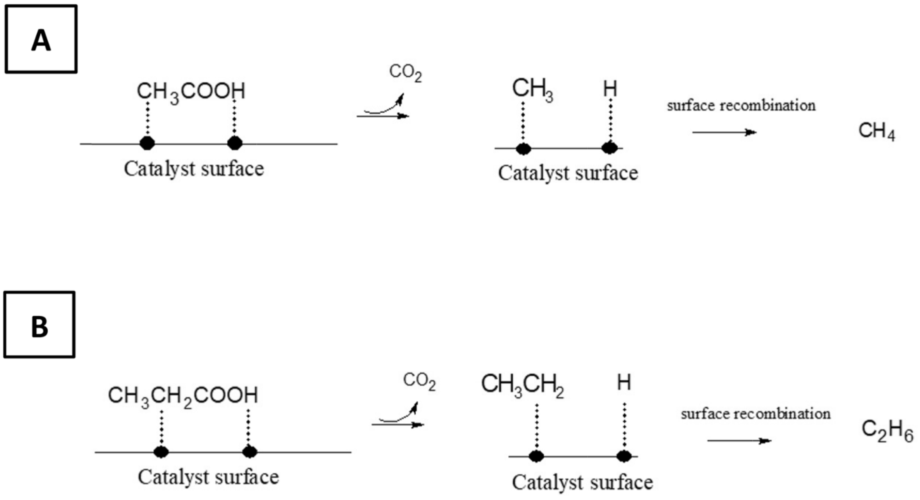


Fig. 2. Proposed mechanism for the reforming of acetic acid (A) as suggested from [15] and propionic acid as proposed in this work (B).

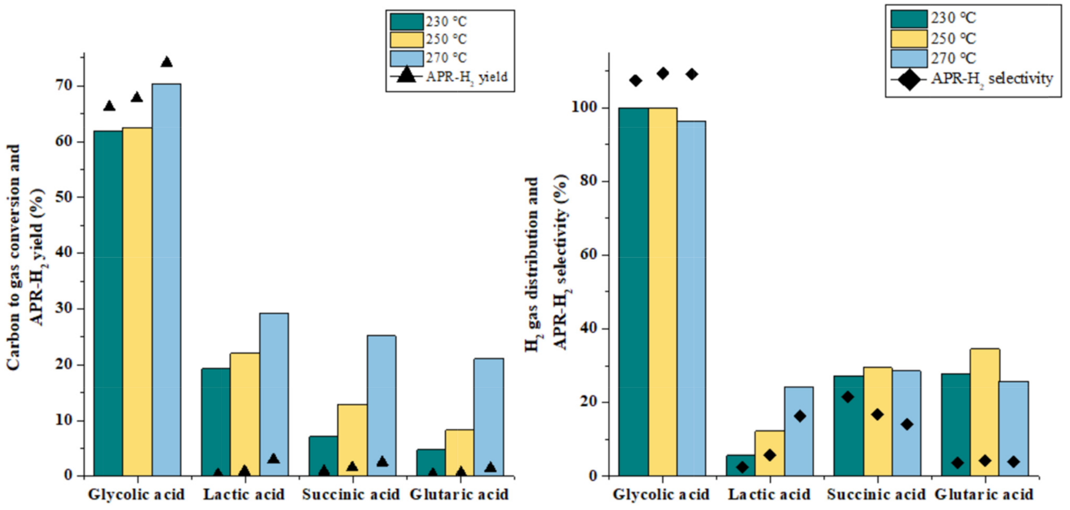


Fig. 3. Influence of the reaction temperature on the APR of hydroxyacids and bicarboxylic acids.

compounds in a subject not deeply investigated yet.

Propionic acid conversion goes from 7% at 230 °C to 39% at 270 °C. In line with the previous case, the feed was the main liquid compound, representing 93% of the carbon remained in the liquid phase; acetic acid was the second most important liquid compound, and its importance increased with the reaction temperature, from 1% to 7% of the carbon in the liquid phase. Its concentration may be the result of two competitive phenomena: its production because of the higher conversion of propionic acid, and its consumption, because of the higher reactivity of acetic acid itself at higher temperature, as previously reported. In fact, despite a constant concentration of methane, its amount increased consistently, more than six times from 230 to 270 °C, perhaps reflecting the increase of acetic acid in the liquid phase.

3.1.2. Hydroxyacids and bicarboxylic acids

In Fig. 3 the results for two hydroxyacids (glycolic and lactic acid) and two bicarboxylic acids (succinic and glutaric acid) were reported. These compounds are particularly interesting because, as reported by Panisko et al., the post-HTL aqueous phase, at least in the conditions cited in their work, contained glycolic acid as main product [9]. Therefore, it was worthy investigating this compound and, to the best of our knowledge, this work is the first to perform this study.

Glycolic acid reported about 70% of carbon conversion to gas at 270 °C, with about 74% of hydrogen yield. Looking at Fig. 4-A it can be observed that no alkanes were produced, and the gas is composed just by hydrogen (60%) and carbon dioxide (40%). Please note that APR H_2 selectivity exceeds 100%, which is an indication that not only APR occurs, leading to this apparently atypical result. Working with an integral reactor, it is not possible to study the reaction mechanism, but some analogies starting from the behaviour of acetic acid can be highlighted. Indeed, glycolic acid contains a carboxylic group, as acetic acid, so it may be inferred that the first step involves a decarboxylation. After that, the two radicals present on the surface may recombine (as reported in the 3.1.1 paragraph) leading to the production of methanol. It is important to observe that this intermediate was not found in the liquid phase. However, this would not be surprising, as it is known that methanol can be easily reformed following the path suggested by Dumesic's research (Fig. 5-A) [16]. The proposed mechanism would explain also the 3:2 ratio hydrogen:carbon dioxide present in the gas phase.

In the liquid phase glycolic acid was completely converted at each investigated temperature, but not all the carbon is in the gas phase (Fig. 4-B). Indeed, 90% of the carbon in the liquid phase was present as acetic acid. This may be due to the hydrogenation of the hydroxyl group, with a problem of selectivity due to in series reactions, where part of the produced hydrogen is consumed in subsequent hydrogenation reactions. It is fundamental to control and minimize this phenomenon, since it may have consequences on the performance of the process. As a matter of fact, 30% of the starting carbon remained in the liquid phase as acetic acid, that we reported before to be a recalcitrant molecule to APR. Despite these observations, the obtained results with glycolic acid are encouraging for the exploitation of APR to valorise these streams.

The carbon to gas conversion of lactic acid was much lower than the one of glycolic acid. Despite such small values, a strong dependence of the hydrogen yield on the reaction temperature was observed, ranging from 0.3% at 230 °C to 2.9% at 270 °C. Together with this increase, there is a decrease of the percentage of carbon dioxide and methane, with a global increase of the hydrogen selectivity.

Possible reaction schemes for lactic acid can be inferred in analogy with the glycolic acid and carboxylic acids mechanisms (Fig. 5-B). If decarboxylation was the first step, then ethanol may be produced that, in turn, would lead to the production of hydrogen, carbon dioxide and methane (as reported in the following paragraph). Propionic acid was the most abundant product in the liquid phase (70% of the carbon at 270 °C): therefore, it is reasonable to assume that a fraction of the lactic acid may be converted to propionic acid through two possible reaction paths. One would involve the C—O hydrogenolysis on the Pt site; the other one would involve also the nature of the support, that may cause dehydration followed by hydrogenation on the Pt site [19]. In addition, thermodynamic considerations report that hydrogenation of lactic acid to propionic acid is nine orders of magnitude more favourable compared to the production of propylene glycol near the present reaction conditions: in fact, the latter compound was not observed in the liquid phase [20]. Either of the two would anyway require a molecule of hydrogen, and for this reason the path has been lumped in the step 2. In turn, propionic acid can lead to ethane and carbon dioxide as reported in the previous paragraph, explaining also the presence of the C2 alkane in the gas phase.

Acetic acid accounts for 10% of the carbon in the liquid phase, and a small but still 5% is butanoic acid, indication that condensation reactions are involved.

Succinic and glutaric acid, bicarboxylic acids with four and five carbon atoms respectively, showed a low performance towards APR, with a maximum H_2 yield of 2.5 and 1.4% respectively. The reason may be the stability that the acids show even at these temperatures.

Succinic acid converted from 26% at 230 °C up to 78% at 270 °C. The increase in the temperature affected in this case also the APR selectivity, that decreased because of the increase in the carbon dioxide production compared to hydrogen. CO_2 is the main gaseous product,

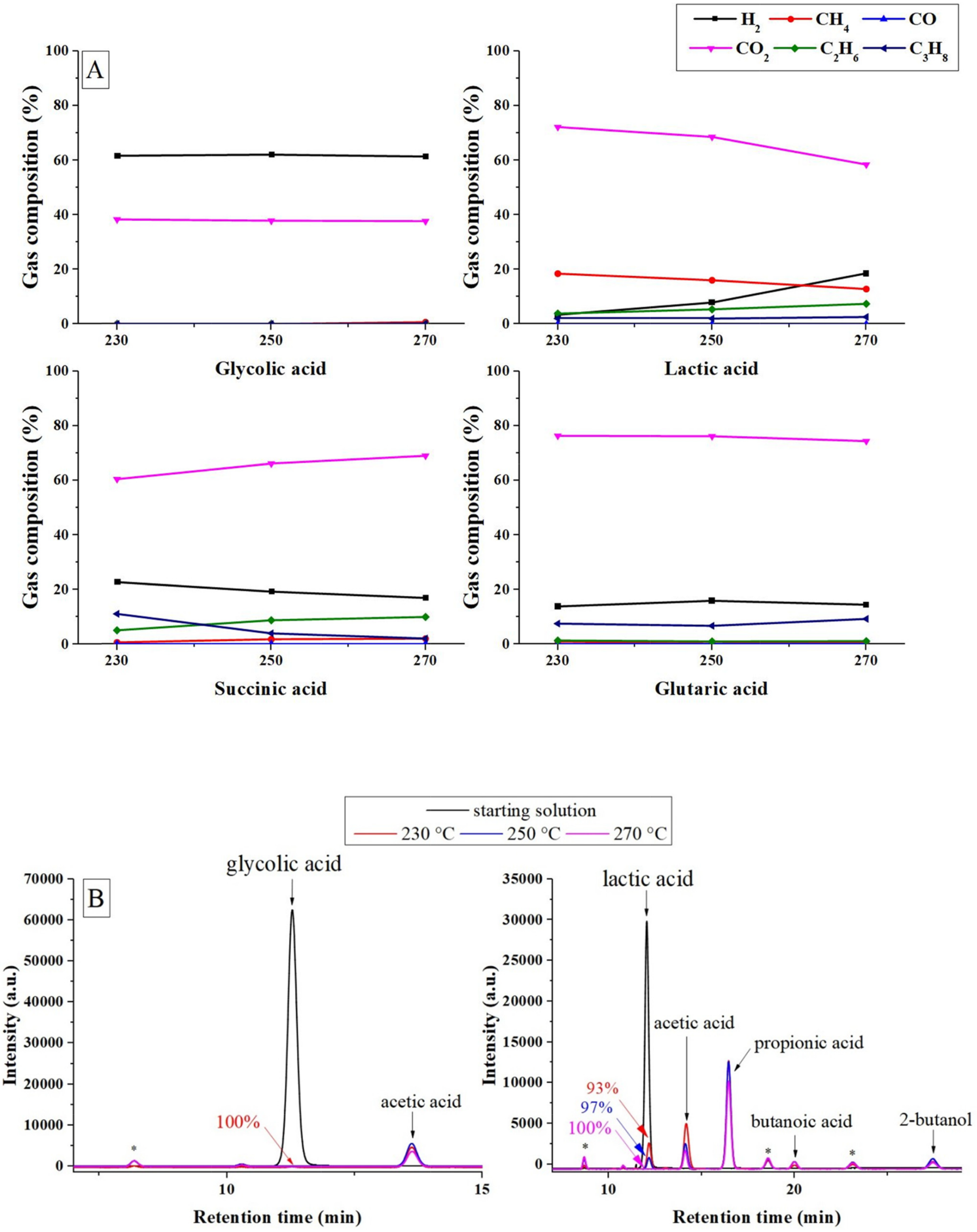


Fig. 4. Influence of the reaction temperature on the composition of the gas phase obtained from the APR of hydroxyacids and bicarboxylic acids (A) and on the composition of the liquid phase from the APR of glycolic acid (B-left) and lactic acid (B-right); the % assigned to the reactant peak refers to its conversion at the end of the APR test; *: unknown compounds.

and the reason may be the path of decarboxylation in which the succinic acid is involved. Indeed, in the liquid phase propionic acid is the main product, accounting for 65% of the carbon. A confirmation of this hypothesis is that ethane is the most present alkane at 270 °C: so, it seems that the mechanism involved first the formation of propionic acid by decarboxylation, followed by the production of ethane from the latter, as reported also in the section dedicated to the carboxylic acids. Butanoic acid, that would be the product of direct hydrogenation of the carboxylic acid, was present in negligible amounts (30 times less than propionic acid).

Glutaric acid reported, as in the case of succinic acid, a strong dependence of the conversion on the temperature, ranging from 35% at 230 °C to a maximum conversion of about 88% at 270 °C. In the liquid phase, 80% of the remaining carbon is constituted by butanoic acid. In line with the previous hypothesis, it may be produced if one thinks to decarboxylation mechanisms: these would explain the carbon dioxide as main gaseous component. The propane is another gas component with higher percentage than usual, and it may be produced by successive reactions of the butanoic acid. It is interesting to observe that, despite glutaric acid and glycolic acid solutions have similar pH (2.6 vs 2.3), the latter had an APR H_2 yield 30 times higher. This may be a confirmation that the intrinsic reactivity of the molecule might have a higher impact on the APR performance as compared to the pH values.

In definitive, despite the low tendency of the bicarboxylic acids to produce hydrogen, they are quite reactive, but the main issue is that their intermediates (the corresponding mono-carboxylic acids) have

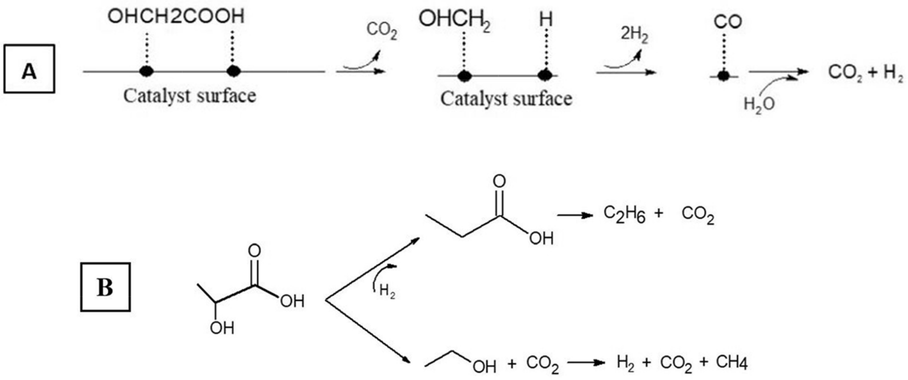


Fig. 5. Proposed reaction mechanism for the APR of glycolic acid (A) and lactic acid (B).

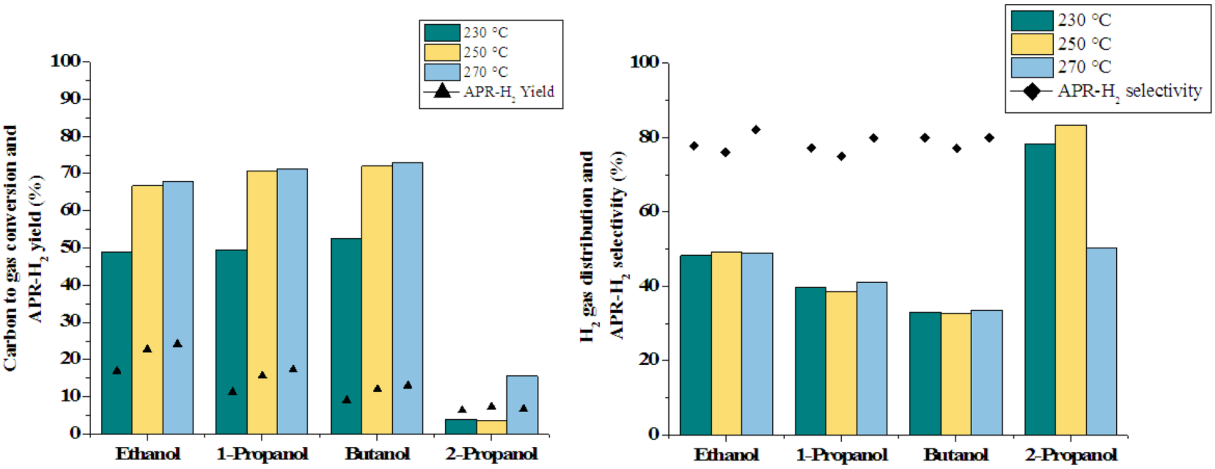


Fig. 6. Influence of the reaction temperature on the APR of monoalcohols.

also a low reactivity. The efforts of the research therefore should be in maximizing the yield of the carboxylic acids, because they seem to be the key compounds in the pathway to produce renewable hydrogen.

3.1.3. Mono-alcohols

In Fig. 6 the results of four mono-alcohols are reported. Ethanol, 1-propanol and butanol were chosen as representative in aqueous phase and also because their similar behaviour may give a hint on the mechanisms of reaction. (2)-propanol, as will be shown later, behaved in a drastically different way, underlining the importance of the position of the hydroxyl group in the structure of the molecule. Ethanol reached about 68% of carbon conversion to gas, while its global conversion increased from 78% at 230 °C to almost complete conversion (99%) at 270 °C. As it is reported in Fig. 7-A, hydrogen constituted 50% of the gas phase, with methane and carbon dioxide being almost 25% each. About 30% of the carbon from ethanol remained in the liquid phase (Fig. 7-B): 60% of that carbon is acetic acid, that is the corresponding carboxylic acid of the starting alcohol. However, it accounts for just 6% of the initial moles of ethanol, so it may be considered as a minor by-product, involved in side reactions of hydro-dehydrogenation. This result is in agreement with some works in literature: Tokarev et al. [21] reported a double production of hydrogen compared to the one of methane and carbon dioxide from the APR of 10 wt% of ethanol.

1-Propanol gave the same results of ethanol regarding the carbon conversion to gas and the selectivity; also, the absolute amount of hydrogen produced was the same, but it resulted in a lower yield considering the higher presence of hydrogen in the starting molecule. Ethane and carbon dioxide have the same molar ratio, and hydrogen accounts for half of the gas phase, as was the case with ethanol. In the liquid phase it reached 96% of conversion at 270 °C and in this case 20% of the carbon remained as propionic acid, its corresponding carboxylic acid. These analogies were confirmed also with butanol. In fact, in this case we put our attention on the C_3H_8:CO_2 ratio, that is again a bit more than unity; again, hydrogen is 50% of the gaseous product species.

Butanol reached 98% of conversion at 270 °C. As observed in the Fig. 6-A, 73% of the carbon goes to the gas phase. 58% of the remaining carbon in the liquid phase was constituted, in agreement with the previous alcohols, by butanoic acid.

The analogy between ethanol, 1-propanol and butanol allowed us to propose a similar reaction pathway (Fig. 8). As suggested by Dumesic, the first step of the reforming is the dehydrogenation of the molecule to give adsorbate intermediates [16]. A key difference in our case is that we are dealing with the presence of alkyl groups. Gursahani et al. performed a DFT study for ethanol on Pt in which they proposed the initial dehydrogenation of the alcohol leading to adsorbed acetaldehyde [22]. Subsequently, the C—H scission may lead to an CH_3CO intermediate that, after C—C bond cleavage, produces methane and carbon monoxide; finally, the latter would produce hydrogen and carbon dioxide via WGS in our reaction conditions. As outlined in the cited work, the CH_3CO intermediate is present also in the catalytic conversion of acetic acid, creating a link between the two pathways. As it was observed in the analysis of the liquid phase, acetic acid was indeed the main liquid product in the APR of ethanol. An analogous reaction pathway can be suggested for 1-propanol and butanol, where the corresponding carboxylic acids were found analogously. It is important to observe that in our conditions the aldehydes corresponding to the studied alcohols were not found, contrarily to a recent published work

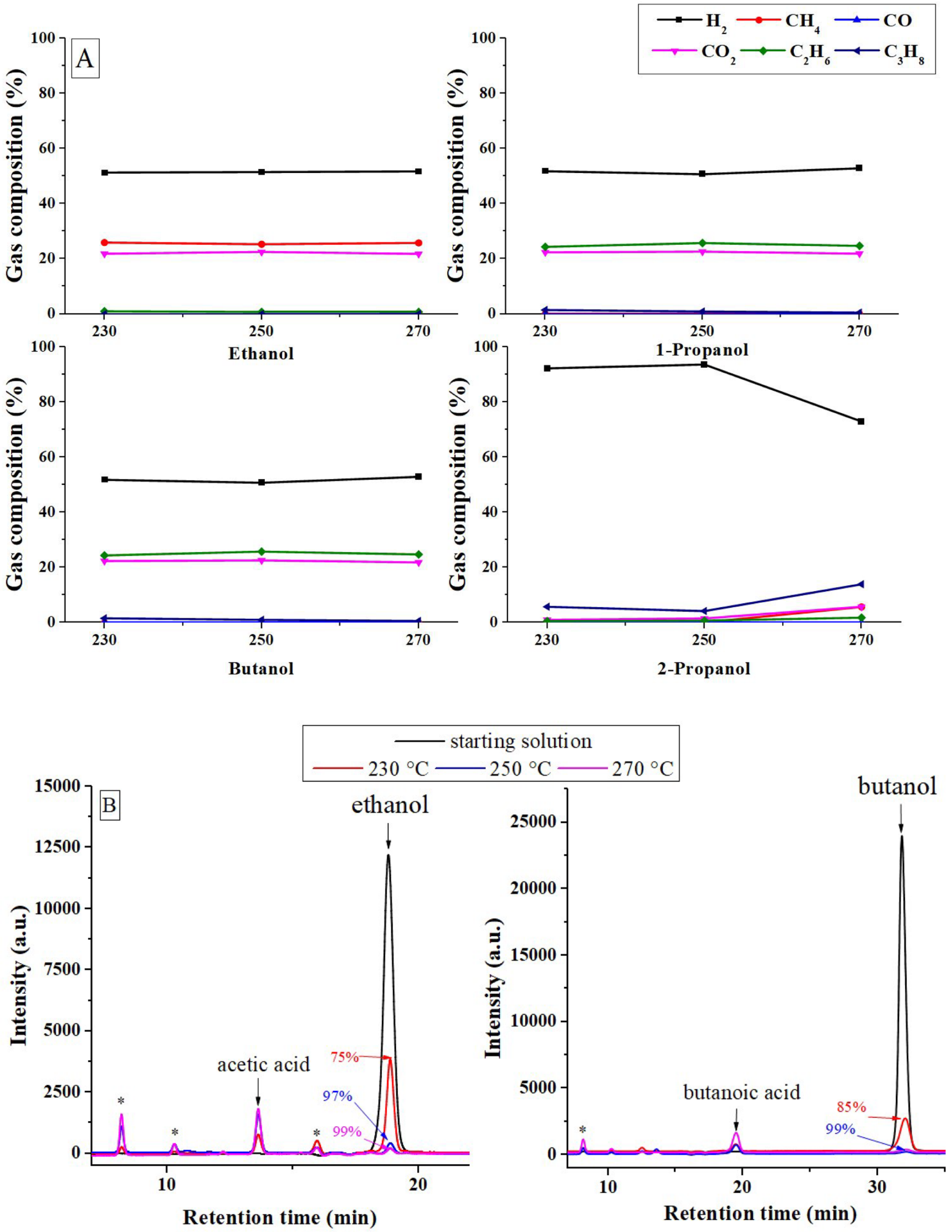


Fig. 7. Influence of the reaction temperature on the composition of the gas phase obtained from the APR of monoalcohols (A) and on the composition of the liquid phase from the APR of ethanol (7-B left) and butanol (7-B right); the % assigned to the reactant peak refers to its conversion at the end of the APR test; *: unknown compounds.

that investigated the APR of ethanol and propanol with different nickel-based catalysts [23]. The discrepancy may be due to either a longer reaction time in our work, that would allow a complete conversion of these reactive intermediates; or to the use of a different catalyst, since in the cited work it is highlighted that the catalytic systems affected the obtained product distribution.

1-propanol and butanol may follow an analogous mechanism, leading respectively to ethane and propane as main alkanes in the gas phase.

2-propanol showed a completely different behaviour, compared to the previous series and, for some aspects, also to all the other investigated molecules. It had strongly less carbon conversion to gas (maximum 16%) but almost complete conversion was reached in the liquid phase (98%). It has high hydrogen gas distribution, due to the fact that almost no alkanes were present, except for propane at about 20%. This result may be due to hydrodeoxygenation pathways, that removed the oxygen leading to propane. The APR-H_2 selectivity was up to two orders of magnitude higher than the usual values, and for this reason it was not reported in the relative graph. This result, that is at first sight illogical, may hide an indication on the mechanism of the production of hydrogen. We may infer that in this case it is not associated to a reforming path, that would lead to the simultaneous production of hydrogen and carbon dioxide in similar amount, but to a dehydrogenation mechanism. Confirming this hypothesis, acetone was

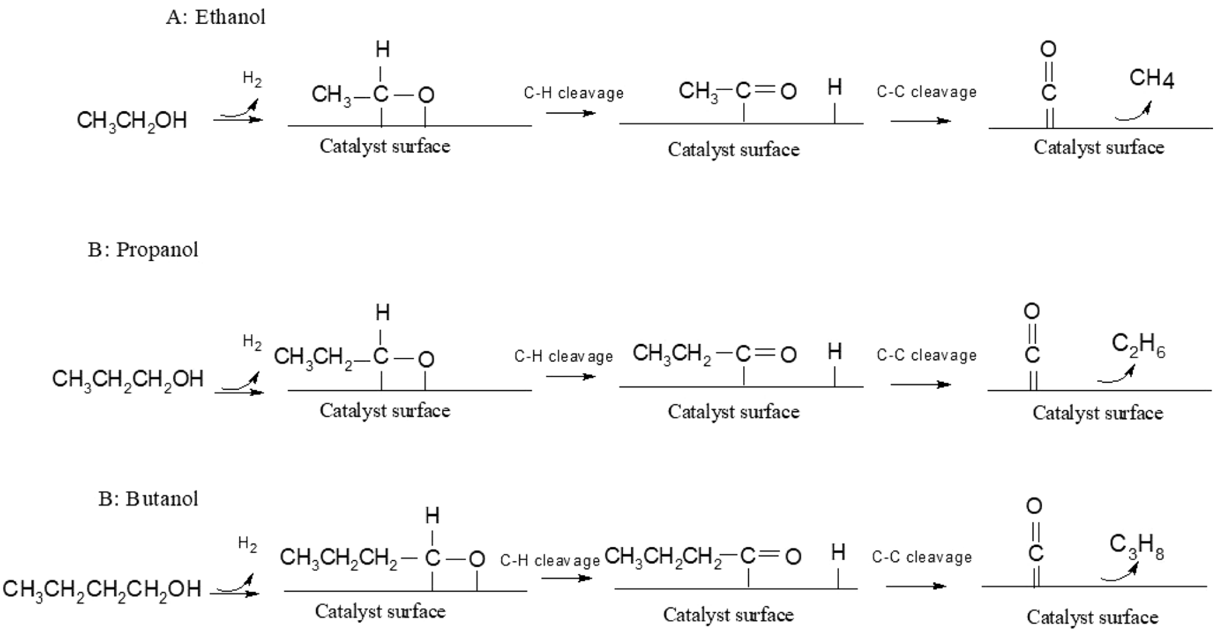


Fig. 8. Proposed reaction mechanisms for monoalcohols.

the main compound present in the liquid phase, accounting for 90% of carbon. It can be the result of the catalytic dehydrogenation of 2-propanol on the catalyst [24]. This path would explain the high value of the APR-H_2 selectivity.

3.1.4. Poly-alcohols

In the following Fig. 9 the performance obtained by the reforming of three poly-alcohols were reported. Ethylene glycol is one of the most studied compounds for aqueous phase reforming [25–27]. In this work we showed that it maintained the same selectivity for the production of hydrogen, and temperature had an effect mainly on the conversion. Therefore, in these conditions, selectivity seemed not to be a significant challenge and phenomena of side reactions were not important, contrarily to what is reported in literature. The reason may be due to the dilute conditions in which the experiments are carried out. In the liquid phase, ethylene glycol reached 100% of conversion at 270 °C, but also in this case the effect of temperature is visible because the conversion was 42% at 230 °C and 73% at 250 °C.

Propylene glycol had also a strong increase of the carbon conversion to gas with the temperature, and, thanks to the constant selectivity, of the hydrogen yield. In the liquid phase it converted almost completely (99.8% at 270 °C). The APR-H_2 selectivity was lower than compared to ethylene glycol, maybe because of the methyl group that is not activated by a hydroxyl group. This causes the presence in the gas phase of methane (more than 10%) at the expense of hydrogen production (Fig. S2). In the liquid phase, ethanol is the main product at 230 °C, but its importance decreases with temperature, so that acetic acid becomes the main component at 270 °C (70% of the remaining carbon).

Similar considerations drawn for ethylene–glycol may be extended to glycerol. The selectivity was not affected by the temperature and the increase in the conversion led to a strong increase in the hydrogen yield. In the liquid phase glycerol converted up to 49% at 230 °C, but this value increased to 93% at 250 °C, reaching 100% at 270 °C. In the case of glycerol, the liquid composition changed drastically within the investigated temperatures. At 230 °C, the main liquid product is propylene-glycol, after glycerol, followed by ethanol and ethylene–glycol. At 250 °C, propylene-glycol remains the most present compound, but acetic acid started to be present. This is consistent with the results reported in the previous paragraph, where starting from the diol, acetic acid was produced as the main intermediate; also, ethanol and lactic

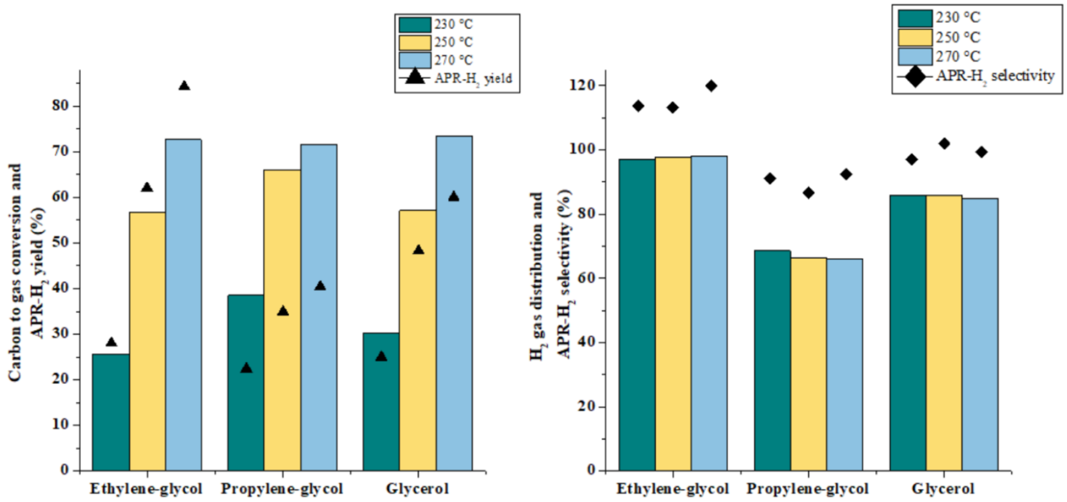


Fig. 9. Influence of the reaction temperature on APR of polyalcohols.

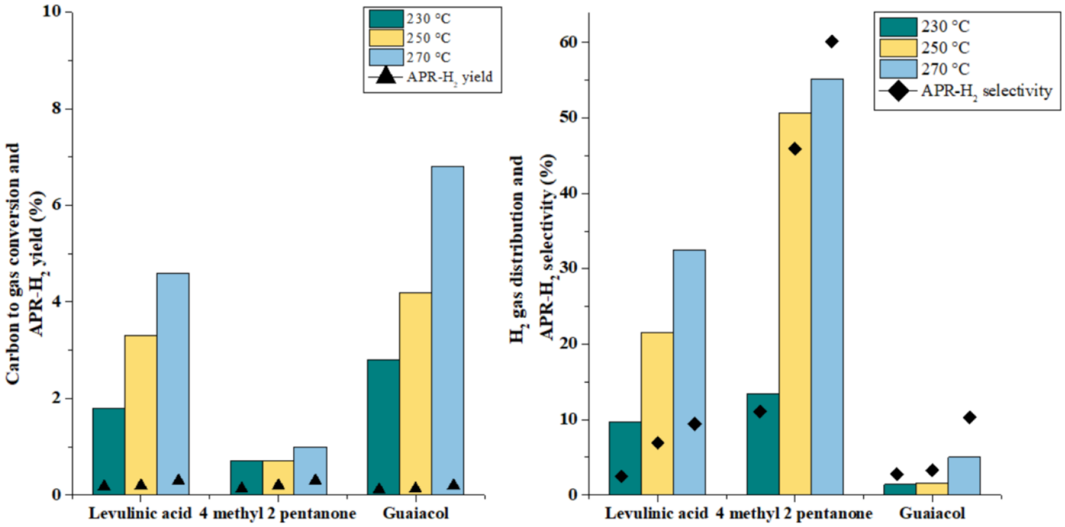


Fig. 10. Influence of the reaction temperature on APR of levulinic acid, 4 methyl 2 pentanone and guaiacol.

acid still increased their presence, maybe because of the higher glycerol conversion. Finally, at 270 °C, acetic acid was the liquid compound with the highest concentration.

3.1.5. Ketoacids, ketones and aromatics

Finally, the results regarding levulinic acid, 4 methyl 2 pentanone and guaiacol are reported in Fig. 10, namely a ketoacid, a ketone and an aromatic, respectively. In general, it is observed that the performance of these compounds were the worst among all the tested classes. The reason could be ascribed to the presence of recalcitrant groups (ketonic, carboxylic, aromaticity) that do not have any reactivity for hydrogen production, reducing drastically the APR-hydrogen yield. In Panisko's work, a plethora of ketones were present, despite with low concentration; the same can be reported for aromatics, where phenol was present as main aromatic compound [9]. For this reason, it is important investigate also these classes of compounds if APR should be used as a process that aims to exploit as much as possible the organic compounds present in the aqueous phase.

Levulinic acid's conversion was from 7% at 230 °C to 23% at 270 °C. The carbon conversion to gas was 4.6% at 270 °C, and the main product was carbon dioxide (Fig. S3). This result suggests that decarboxylation reactions may yield these products in the liquid phase, but this would give rise to the presence of small amount of MEK (2-butanone) in the liquid phase; actually, it was not present, but 2-butanol was observed indeed, moving from 3% to 9% of carbon in the liquid phase in the investigated range of temperature, with carbon dioxide that increased 2.8 times in the same range. This hypothesis seems reasonable because it is known that MEK is 100% selective to 2-butanol under reaction conditions milder than the ones present in this work [28]. Other minor products were propionic and butanoic acid, accounting for about 1% of carbon each at 270 °C.

4-Methyl-2-pentanone showed the lowest gas production among the molecules screened in this work at each investigated temperature. Within the low amount of gaseous products, interestingly the gas phase contained methane (from 40 to 20% going at higher temperatures), maybe because of the breakage of the methyl group present in the structure of the molecule. The analysis of the liquid phase was not as effective as in the other cases, and a small percentage of the carbon present was recognized. This may be seen as an indirect indication that the ketone does not produce the usual compounds that were recognized before (carboxylic acids, monoalcohols), so the reaction path is not trivial and requires further studies to allow the identification of the liquid by-products. In general, ketones behave as strong recalcitrant compounds for APR and would necessitate further efforts to improve its performance, using more severe reaction conditions, for example.

Compared to the previous compounds in this section, guaiacol reported the highest carbon conversion to gas, but it is not associated to a reforming path, i.e. to hydrogen and carbon dioxide production, but mainly to the presence of methane. This is likely due to the breakage of the ether group present in the molecule. Methane is present up to about 70% in the gas phase, giving the formation of cathecol, that was identified in the liquid phase.

Despite the poor performance of these representative compounds, it is worth to highlight the importance of better understanding the possible reaction pathways for these recalcitrant molecules because of their presence in the aqueous stream coming from lignocellulosic biomass. One of the main reasons may be the scarce presence of hydroxyl groups in the investigated molecules.

3.2. Binary and ternary mixtures

The screening of the seventeen model compounds helped to understand how the reactivity of the single molecule changes according to the reaction temperature, outlining the compounds easily reformed and the ones that have been reported as recalcitrant.

In this section, we performed tests of binary and ternary mixtures of four selected compounds. Four binary solutions and two ternary solutions were tested to examine if the reactivity changes and to go into the direction of the test of a representative biorefinery stream. The tests were carried out maintaining the same global molarity (133 mM). The results were evaluated according to the same indicators used in the screening. For comparison, we performed also tests in which the components of the mixtures were investigated at the concentrations used in the mixture (67 and 44 mM)

The performances of the mixture were also compared with two ideal values of linear combination, which were calculated with the Eqs. (6)–(9) reported in Section 2.3.

3.2.1. Influence of concentration

In Fig. 11, the influence of the concentration of the single substrate on the performance is reported.

First of all, we observed that glycolic acid maintained almost the same performance for all the reported parameters; in the liquid phase, its conversion remained very high. Regarding ethanol, comparable results can be observed. Fewer liquid products from ethanol at 67 mM are present compared with 133 mM, and the conversion of ethanol was similar (96.7%).

On the contrary, acetic acid increased steeply the carbon conversion

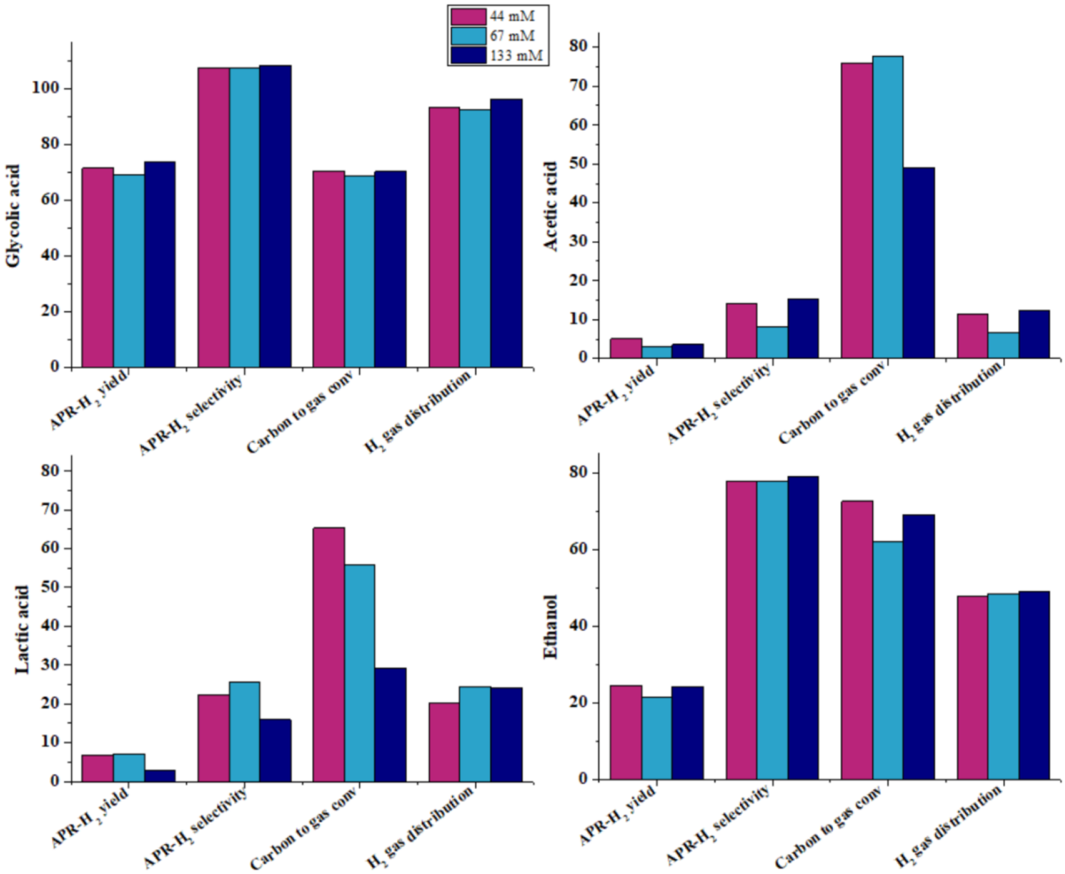


Fig. 11. Influence of the concentration of feed on the performance of APR.

to gas working at lower molarity and, as a consequence, the hydrogen selectivity decreased due to a higher concentration of both CO_2 and CH_4 in the gas phase. It is highlighted that also in the runs with different carbon concentrations, carbon dioxide and methane maintained almost the same molar ratio of 1:1.

The conversion of acetic acid increased from 56% to 99.8% at decreasing initial molarity. This means that the ratio catalyst/acetic acid plays a fundamental role in its reactivity within the investigated reaction conditions. Dealing with a catalytic reaction, the decrease of the conversion with the increase of the concentration may be an indication that a saturation of the catalyst sites was reached. Therefore, increasing the starting molarity would not affect the productivity because the catalyst is saturated and the superficial phenomena (adsorption of the reactants, chemical reaction, desorption of the products) may be the rate determining steps.

Finally, it is interesting to analyse the effect of the concentration on the lactic acid. It is observed that the concentration has an effect not only on the conversion but also on the selectivity of the hydrogen production. This means that the reaction pathways are sensitive to the concentration of the reactant, so it would be a positive effect working in dilute conditions for the sake of a higher selectivity. The higher selectivity to hydrogen involves a lower amount of propionic acid in the liquid phase, which is the product of hydrogenation of the hydroxyl group, and corresponds to 30% of the moles of lactic acid in the 133 mM test and it decreases at 10% in the 67 mM one.

3.2.2. Binary mixtures

The results obtained from the binary mixtures are reported in the Fig. 12. Each parameter is compared to the linear combination points, as explained before.

In the glycolic acid and acetic acid mixture test an interesting result was identified. Indeed, while the conversion of glycolic acid remained 100%, the one of the acetic acid decreased sharply to 3.5%. It is important to observe that acetic acid can be formed from the glycolic acid, so we should pay attention when we evaluate the conversion of acetic acid that may be actually produced during the reaction from glycolic acid. Even considering the highest production (133 mM test) the conversion would increase up to 16%, still too low compared to the test with acetic acid alone.

Moreover, looking at the amount of each gaseous compound, we observed that the moles of hydrogen in the mixture test are almost equal (just 2% more) of the test with glycolic alone at 67 mM and the same is for the carbon dioxide (6% more). This behaviour may indicate a selective adsorption of the glycolic acid at the expense of acetic acid. Because of this apparent lack of interaction between the catalyst and acetic acid, it is not surprising that the results obtained in the mixture were so far from the linear combination: actually, only glycolic acid is reacting.

It has important consequences not only when acetic acid is in the mixture, but also when it is an intermediate of reaction. In fact, if it had lower adsorption kinetics than the other molecules, it would not interact with the catalyst, increasing its concentration during the reaction time and not being converted. To better understand this phenomenon, it is interesting to observe the results obtained with other mixtures.

The results obtained from the equimolar mixture ethanol/acetic acid showed that, even in this case, acetic acid behaved differently from the mono-compound solution, reaching 8.9% of conversion. Here the problem of the intercorrelation between the two compounds is less evident, because acetic acid was obtained from ethanol with a less extent comparing to the case of glycolic acid. Similar to the previous result, the carbon conversion to gas is less than expected from the linear combination, while the selectivity is higher. This outcome suggests that also in the case of the binary mixture acetic acid – ethanol there is an issue of selective adsorption.

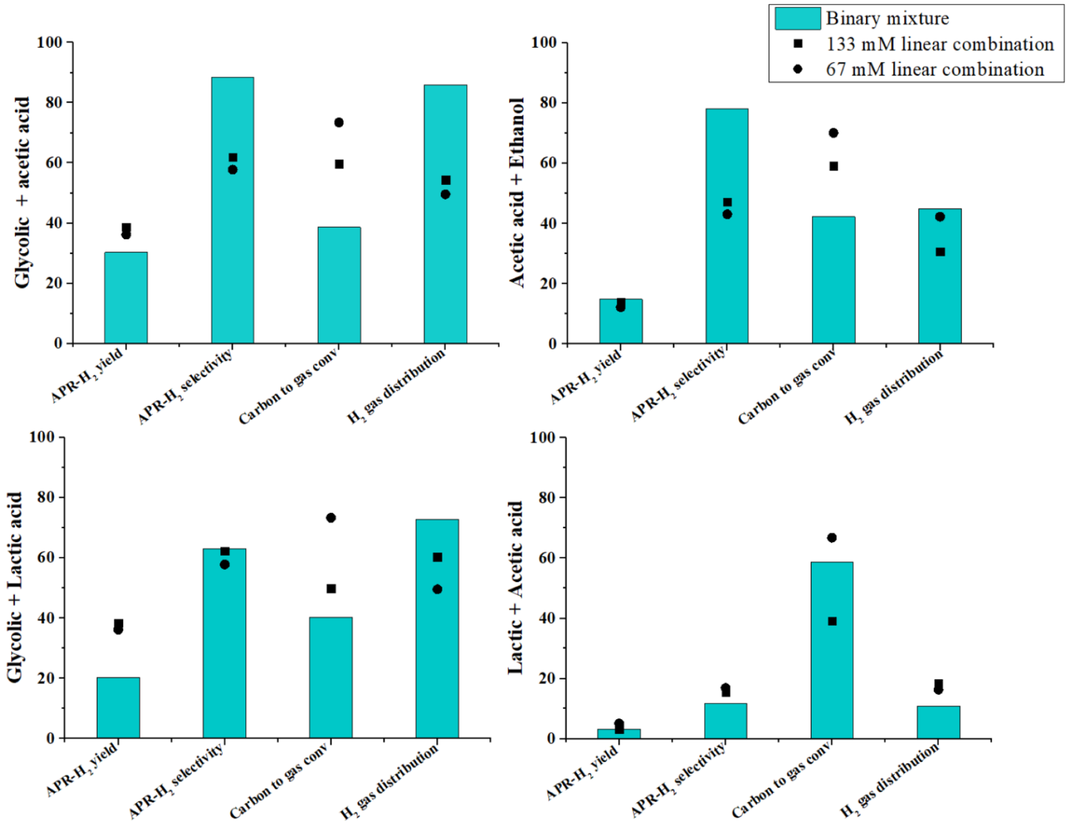


Fig. 12. Results of four equimolar binary mixtures – Glycolic and acetic acid (A), acetic acid and ethanol (B), glycolic and lactic acid (C), lactic and acetic acid (D).

The third investigated mixture was the glycolic and lactic acid binary system. Differently from the case of acetic acid, lactic acid converted completely in the liquid phase; looking at the composition of the liquid phase, propionic acid was the most present compound, reaching 93% of the carbon in the liquid phase. This was an unexpected result because, when the lactic acid was tested alone at 67 mM, gave propionic acid with less selectivity, as reported previously. So, it may come from the hydrogen that is produced from glycolic acid that, in this case, would hydrogenate selectively the lactic acid more than itself, giving acetic acid, that constituted just the remaining 7% of carbon. This would lead, as observed, to a decrease of the carbon to gas efficiency and hydrogen yield compared to the runs with one component.

Because of the peculiar results obtained when acetic and lactic acid were used, we were interested in investigating a binary mixture constituted by these two compounds. Indeed, the acetic and lactic acid mixture behaved differently from the others. It was observed that the performances obtained in the test were closer to the linear combination of the individual compounds. It is reasonable to assume that this is because there is not a competitive adsorption between the two species. It means that each molecule can interact with the catalyst as if it were the only compound in the reaction system. Indeed, it is observed that the conversion of the acetic acid is indeed higher than in the other cases, reaching 68%.

3.2.3. *Ternary mixtures*

In order to make a step forward in the valorisation of a post-HTL aqueous stream, we investigated two ternary mixtures. In the first one we tested glycolic and acetic acid and lactic acid; in the second one, we analysed the results of the ternary mixture constituted by glycolic acetic acid and ethanol. The obtained results are shown in Fig. 13.

Studying the first mixture, we observed that glycolic and lactic acid converted completely; on the other hand, acetic acid reached 27.6% of conversion. It was still higher compared to the binary mixture with the glycolic acid, but lower compared to the one with lactic acid. This is an interesting result because it gives an indication on the necessity to work on the nature of the catalyst to improve acetic acid adsorption. Indeed, being a representative compound of the water stream, and being a common intermediate component, it is necessary to develop strategies to improve its chemical affinity with the adopted catalyst.

In the glycolic-acetic-ethanol mixture a higher hydrogen selectivity was observed as compared to the linear combination, but a lower carbon to gas conversion: taking into accounts these considerations, the yield of hydrogen reached the theoretical one. In the liquid phase glycolic acid and ethanol converted quantitatively; on the other hand, confirming the previous outcomes, the acetic acid conversion dropped from almost 100% (acetic acid conversion in the test at 44 mM) to 6.4%.

Therefore, it can be concluded that especially acetic acid is a key component in the study of mixture because its adsorption may be a limiting step in the reactions conditions to perform its reforming. Further studies are suggested to improve the catalyst and its interactions with acetic acid.

3.3. *Characterization and stability of the catalyst*

The Pt/Al_2O_3 commercial catalyst, after its drying, was characterized by several techniques to address if some deactivation mechanisms occurred. First of all, we investigated if leaching phenomena may occur in our reaction conditions. To investigate this option, ICP analysis were carried out in the liquid solution that was recovered after the reaction. The results reported the absence of platinum dissolved in the solution, therefore we can exclude that leaching of the catalyst may happen during the experiment.

Coking is one of the possible deactivation mechanisms during aqueous phase reforming. The TGA, in inert and oxidizing environment, of the catalyst used for APR of acetic acid at 250 °C is reported in

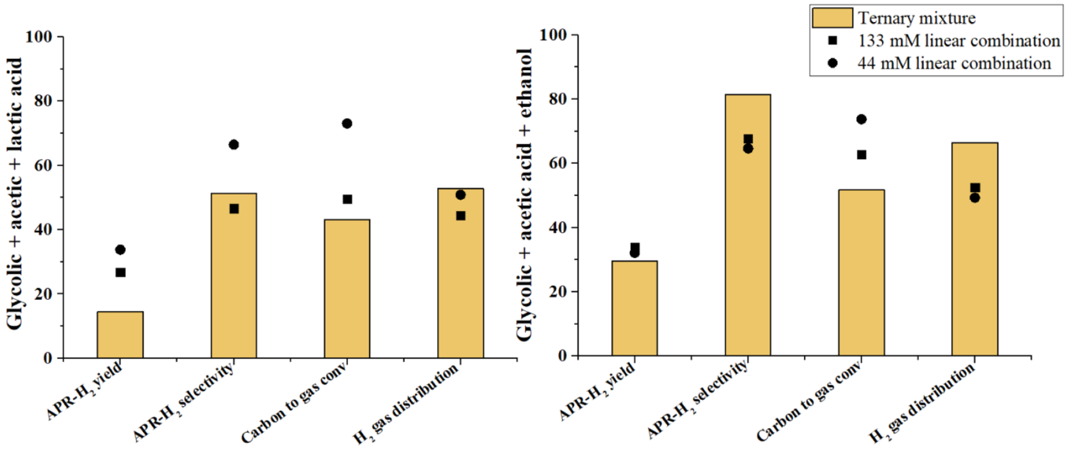


Fig. 13. Results from ternary mixtures constituted by glycolic acid, acetic acid and lactic acid (left) and glycolic acid, acetic acid and ethanol (right).

Fig. 14. The test was performed at first using nitrogen; then, after natural cooling, using air on the same sample. As it is reported, only the inert test presented a clear peak at 500 °C (apart from a small speak at about 50 °C ascribed to the presence of water physisorbed on the surface of the catalyst). When the subsequent oxidizing test was carried out, no peak indicating weight loss was observed. The inert test cannot decompose the coke possibly present on the surface; therefore, if high-molecular weight or carbonaceous compounds were present, they should have been decomposed/oxidized by the following treatment in air. As it was not the case, we assumed the absence of coking phenomena. From Fig. S4 it can be seen that other desorption peaks, between 150 °C and 400 °C are present in the TGA spectra (performed in nitrogen) on other spent catalysts: for instance, guaiacol seems responsible for the formation of compounds that adsorb on the catalyst and that desorb during the TGA test under nitrogen flow. Again, no remaining compounds were detected (in terms of weight loss) in the subsequent oxidative TGA treatment in air.

Therefore, we ascribed the peak at 500 °C to something that would be insensitive to the chemical nature of the flow, but just to its thermal effect. To go deeper in this issue, we evaluated if a structural change of the support was present by XRD.

The results reported in the Fig. 14 show the diffractograms of a fresh catalyst sample and a spent catalyst, after APR of acetic acid at 250 °C. Cristobalite was used as internal standard to quantitatively estimate the share of the catalyst possibly affected by structural modifications. The diffractogram of the fresh sample reported the peak of the defective spinel structure at 45.8° and 67° corresponding to the (4 0 0) and (4 4 0) crystal planes of gamma alumina. On the other hand, the hydrothermal conditions at which the catalyst was subjected during APR caused the appearance of new peaks. The characteristic angle of the new peaks (28.2°, 38.3°, 49°) allowed to ascribe these peaks to the formation of a crystalline phase, boehmite. The information coming from the quantification of the boehmite phase was compared to the weight loss obtained in the TGA analysis, assuming that, between 400 °C and 600 °C, it can be ascribed to the loss of structural water involved in this transition. The similarity in the quantities estimated thorough XRD and TGA (i.e. about 40% conversion of alumina to boehmite in both cases) confirmed that such a weight loss could be compatible – in quantitative terms- to this phenomenon.

In order to complete the characterization, morphological and textural features were analysed by FESEM and adsorption/desorption N_2 isotherms respectively. The latter gave no appreciable changes in the value of the surface area, pore volume and pore size distribution, maybe because of the small reaction time.

In the Fig. 15 there is a comparison between the fresh catalyst and the spent one, after APR of lactic acid at 230 °C. In the figure on the right it was observed the presence of nanocrystals, with sizes at around 200–400 nm. It is interesting to observe as this phenomenon appears on the surface of the catalyst, while it can be seen still the original structure on the bottom. As it was reported by Carrier et al., the transformation of γ-alumina into boehmite can occur via two mechanisms: one involves a surface hydration mechanism, the other one a dissolution of alumina, followed by its precipitation [29]. Because of the homogeneous covering of the surface we may propose that the first

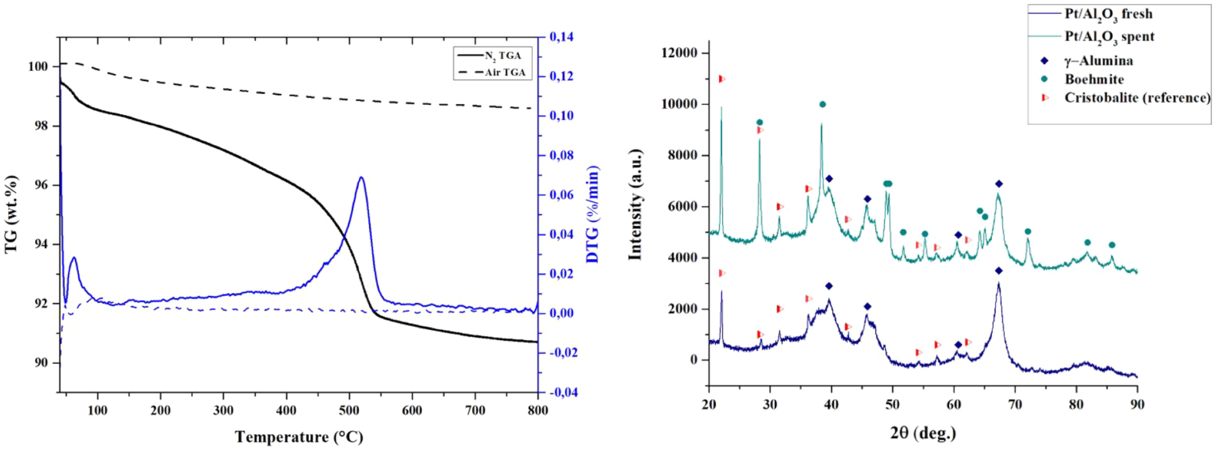


Fig. 14. Thermogravimetric analysis of the spent catalyst performed first in nitrogen and subsequently in air (left) and XRD analysis of the fresh and spent catalyst with cristobalite as internal standard (right).

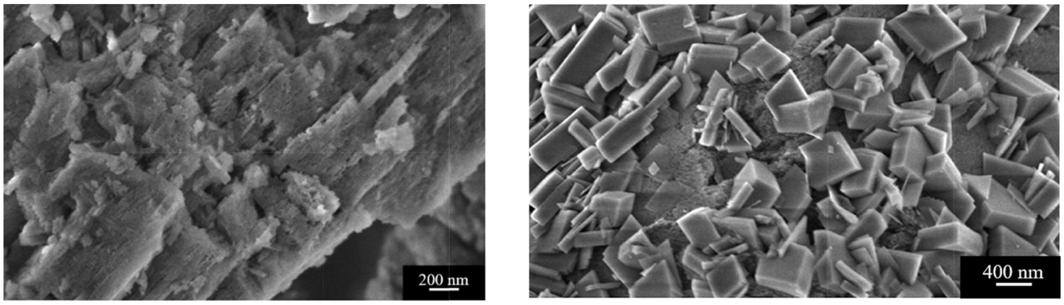


Fig. 15. FESEM images of the fresh (left) and spent catalyst (right) after APR of lactic acid at 230 °C.

mechanism was the most likely in our experimental conditions, but a definite answer cannot be reported just with this information.

The alumina-boehmite transition is a known phenomenon when dealing with hot liquid water. The stability of alumina support is therefore a known issue and it is one of the challenge for heterogenous catalysis applied to biomass valorisation. Interestingly, we observed that this phenomenon, despite dependent mainly on the solvent and the temperature, was not the same for each substrate investigated. Ravenelle et al. studied the stability of Pt/Al_2O_3 during APR of glycerol and sorbitol at 225 °C [30]. They observed minor tendency of the support to be converted into boehmite when the organics were present in the solution, and in particular when the catalyst was treated with sorbitol solution. They proposed that polyols form a protective layer on the alumina surface preventing the hydrolytic attack that initiated the boehmite formation. Taking advantage of the extensive screening of compounds, we evaluated how the molecules investigated may affect this phenomenon. In fact, as suggested by Ravenelle, the stability of catalysts under real APR conditions, which means considering also the substrate, is of critical importance.

We performed ATR-IR analysis on the catalysts recovered after the screening of the seventeen compounds at 270 °C. In the Fig. 16-left, some characteristic results are reported. Firstly, the absence of peaks characteristic of coke was observed. As reported by Karge et al., at 1610 cm^{-1} there is the so-called coke band, due to a complex mixture of carbonaceous, hydrogen-deficient deposits, as polyethenes and/or aromatics, while at 1540 cm^{-1} can be observed the presence of structures such as alkylnaphtalenes and polyphenylene [31]. Neither of these or other characteristic peaks was observed, again suggesting its absence.

The catalyst after APR of acetic acid, 2-propanol and glutaric acid presented a sharp peak at 1064 cm^{-1} and shoulder bands close to 3304 and 3124 cm^{-1} that are assigned to OH deformation and stretching vibrational modes of the boehmite phase, respectively [32]. Therefore, it seems that the transformation was insensitive to the fact that we dealt with a carboxylic acid, an alcohol or a bicarboxylic acid. Contrary to what suggested by Ravenelle, the increase in the carbon chain length moving from acetic to glutaric acid had no influence on the boehmite formation in this case. Anyway, some compounds did prevent this phenomenon to happen. It is reported that when APR of guaiacol was carried out, the recovered catalyst showed less evident boehmite peaks, and it is similar to the fresh catalyst sample, actually Pt/Al_2O_3. This is an interesting result because it showed clearly that not only the reaction conditions, but also the compound that is investigated must be taken into account to study the deactivation issues of the catalyst. The results obtained in the IR analysis are also coherent with the TGA performed on the same catalysts, that showed a constant decrease of the peak intensity present at 500 °C, indication of the decrease of the transformation of the support into boehmite (Fig. 16-right and, more in detail, S4). One can see that the transition to bohemite occurs only in the samples that underwent APR, as the fresh catalyst is not affected by the thermal treatment occurring in the TGA under nitrogen.

In order to determine which is the effect of the modification of the support on the performance of the reaction, two tests were performed reusing the catalyst after its recovery (Fig. 17). The tests were performed with the ternary mixture glycolic-acetic-lactic acid, at 1.8 wt% of carbon, in order to be close to the conditions observed by Panisko et al. in their work [9], at 270 °C for 2 h.

The results showed that the performances were maintained up to the third run (after that, an insufficient amount of catalyst was recovered to further investigate). This is an important observation as it points out that, despite the structural change, the catalyst remained active toward each indicator, and no deactivation was observed. Further experiments in a continuous system are planned to evaluate the stability at higher time on stream.

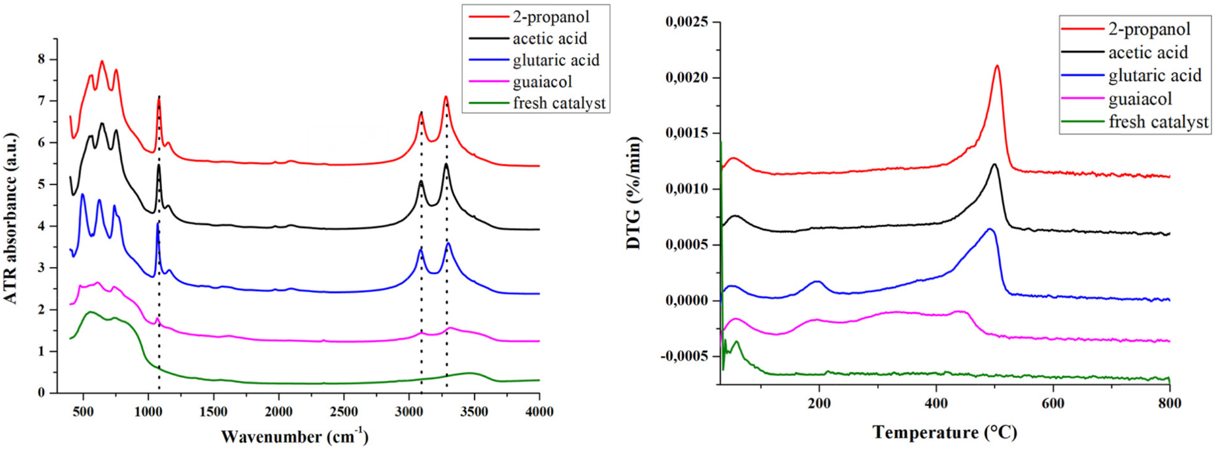


Fig. 16. ATR-IR spectra (left) and thermogravimetric analysis performed in nitrogen (right) of the spent catalyst after the APR of several compounds. The spectra of the fresh catalyst are added for comparison.

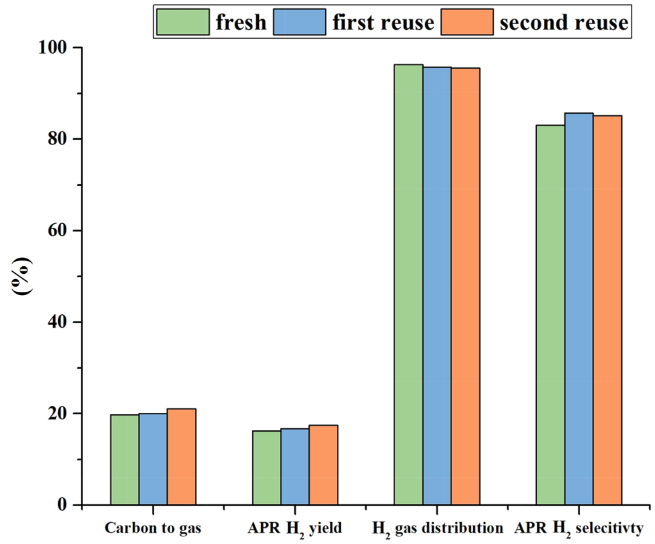


Fig. 17. Influence of catalyst reuse on the performance of APR of a glycolic-acetic-lactic mixture.

4. Conclusions

The aqueous phase after a hydrothermal process contains organics that need to be treated before disposal. In this work, the catalytic reforming of representative compounds present in these streams was investigated to attempt the valorisation of these by-products. Some of the molecules present in the work (e.g. glycolic acid, guaiacol, 4 methyl 2 pentanone) were subjected to APR for the first time. We observed an increase of the hydrogen yield with temperature, mostly thanks to the increase of the conversion and the constant selectivity to hydrogen production. Some compounds, such as acetic acid, were recalcitrant toward reforming, therefore they require major efforts to increase the possibility of their valorisation: this is because they are both present in the starting solution, but also common reaction intermediates. Decarboxylation mechanism appeared to be the main pathway in the case of carboxylic acids. Binary and ternary mixtures were tested to understand the behaviour of a possible synthetic biorefinery stream, and it was observed that adsorption kinetics on the catalyst may constitute an issue to overcome. Acetic acid decreased its conversion when present in a mixture compared to the test in which it was the only compound tested. The characterization of the catalyst showed that the degradation of the support depends also on the compound subjected to APR, but leaching and coking were excluded in the present reaction conditions; in spite of that, the catalyst showed stability at least for three consecutive runs. Thanks to this work, we tried to fill a gap in the field of the hydrothermal processes, where there is a lack of information in the study of the C-laden aqueous phases and their valorisation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2018.12.137.

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