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Review

Aqueous phase reforming process for the valorization of wastewater streams: Application to different industrial scenarios

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ABSTRACT

Wastewater is of general concern for environmental sustainability. At the industrial level, carbon-laden aqueous streams must be treated and should be valorized to reduce environmental and economic concerns. Lignocellulosic biomass processing (such as hydrolysis, pyrolysis, and hydrothermal liquefaction) results in secondary aqueous streams in which a high fraction of the initial carbon content of the biomass is virtually lost; food industry (like breweries and cheese factories) produces streams with a variety of organic load and salinity, which may complicate conventional valorization treatments; biodiesel production leads to glycerol excess in the market, which needs to be valorized. Among other alternatives, aqueous phase reforming (APR) has been proposed as a process driven at relatively mild conditions, able to convert oxygenated molecules into hydrogen. Despite its potential, APR has commonly been investigated with model compounds, and a systematic study on the possible fields of application of this technology is lacking. In the present review, the study of the available literature was focused on the valorization of complex feedstocks, such as real waste streams or synthetic mixtures, showing the outcome derived from laboratory-scale experiments. The results were critically discussed, pointing out the present limitations for the full development of this process and its application to the industrial scale. Despite the challenges of APR, its potential is noteworthy for the development of a circular low-waste economy.

1. Introduction

The worldwide increase of industrialization brought an escalation in the production of wastewater streams, which are by-products of human activity (industrial, agricultural, domestic and commercial) [1]. This has risen the necessity to control and detect contaminants, reducing as much as possible the negative damage to the environment. In the 2030 Agenda, the sustainable development goal (SDG) number 6 is indeed dedicated to water, with the aim of improving its quality, minimizing the presence of hazardous chemicals and halving the percentage of untreated wastewater (which is nowadays more than 80 %) [2]. Furthermore, exploiting the remaining organic content and reusing it, for example to produce chemicals or fuels, meets another SDG, the number 12, which is related to the sustainable production and consumption.

The food and agricultural sectors are responsible of considerable amount of wastes. Focusing on the former, it has an important water footprint since it simultaneously consumes fresh water and produces contaminated aqueous streams. The characteristics of the waste streams (amount generated per kg of desired product, chemical and biological oxygen demand −COD and BOD – etc.) vary according with the type of industry. For example, soy bean processing leads to 7−10 tons of wastewater per ton of soy bean, COD in the range of 10−20 g/L and contains a wide range of compounds; dairy industries also have a high production of aqueous phase (0.2–10 liter of water per liter of milk) [3]; during cheese making processes, about 9 kg of cheese whey are created for each kg of cheese [4]. The brewery industries, one of the main consumers of fresh water, leads to 3−10 liters of wastewater per liter of beer [5]. Beer is the fifth most consumed beverage in the world: in 2014, the world production amounted to 191 million kiloliters [6]. Each of these numbers is sufficient to understand the potentiality of the problem.

Apart from food processing industries, other industrial sectors suffer from a strong impact in terms of water effluents. For example, hydrothermal processes of lignocellulosic biomass, which are investigated for the production of alternative bio-fuels [7]. Apart from the desired organic phase, an aqueous phase is produced in large amounts, whose treatment and utilization are considered pivotal for the industrialization of this technology. The organic content may vary in a large range

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(2.38–104.2 g/L), as well as the chemical oxygen demand (11.35–185 g/L) [8]. Moreover, the classes of compounds dissolved in water span from simple alcohols and carboxylic acids up to amides and heterocyclic compounds [9].

Overall, these streams are generally characterized by a high organic loading, sometimes in addition to heavy metals, inorganics, or chemicals and biological pollutants, and are produced in high amount [10]. They are commonly treated using a combination of different technologies, such as physical, chemical and biological processes, to adapt their characteristic to the environmental regulation [11]. Advanced treatments involve ozonation, chlorination, filtration through the use of activated carbon or membrane [12]. It is worthy to highlight here that one of the limitations in the development of effective treatment processes concerns the lack of knowledge of its complex composition. The characterization of fast pyrolysis and catalytic fast pyrolysis aqueous phase, for example, shows the presence of different classes (organic acids, aldehydes, ketones, aromatics, sugars, alcohols) with different proportions depending on the feedstock and reaction condition [13].

Hydrogen is mainly produced from non-renewable and unsustainable sources, such as steam reforming of natural gas and partial oxidation of heavy oil fractions. Alternative processes under investigation using biomass are the steam reforming of the aqueous fraction of bio-oil [14,15] or supercritical water reforming [16,17]. Bio-processes like photo-fermentation or dark fermentation have been suggested as well for the conversion of carbon-rich industrial wastewater into hydrogen or value-added compounds [18,19].

Aqueous phase reforming (APR) has been proposed to convert oxygenated hydrocarbons dissolved in water into hydrogen at milder conditions compared to steam reforming (230−270 °C and autogenous pressure) [20]. The reaction is catalytically activated often by a noble metal supported catalyst (commonly Pt). This process may be exploited by coupling it with industries which need a way to reduce the organic content of their liquid by-products (for environmental obligations) and at the same time obtain a higher value product (overcoming economical constraints). Despite the potential of this process, APR has been mostly investigated with simple model compounds, such as glycerol, methanol, sorbitol (e.g [21–23].). On the other hand, more challenging solutions, such as multi-component synthetic mixtures or even actual wastewaters, were less investigated.

For this reason, the aim of this work is a systematic review of the available literature which, over the past 15 years, focused on the valorization of diluted wastewater streams through APR to produce a gas phase rich in hydrogen. Only tests with synthetic complex mixtures or actual streams will be reported, showing the differences with model compounds and the issues that must be solved. Information regarding the influence of reaction conditions and catalytic systems, mostly carried out with mono-component solutions, are reported in proper works, and should be considered out of the scope of the present review [24,25].

Once that the fundamentals of APR are reported, the following paragraphs are devoted to different fields of application. Firstly, a focus will be dedicated on lignocellulosic biomass, looking not only to the wastewater derived from its processing (e.g. hydrolysis, pyrolysis, hydrothermal liquefaction, Fischer-Tropsch), but also to its exploitation as energy crop, and investigated as such (i.e. as solid biomass); afterward, wastewater valorization from food processing (e.g. breweries) and biodiesel plants will be reported. In conclusion, a comparison among the cited different industrial scenarios will be examined, considering their strong and weak points. Moreover, the perspectives of APR, looking at the future challenges and important aspects for its application, such as the cost of the feedstock, the mass and energy integration with other facilities and the development of effective catalysts, will be reported.

2. APR reaction

Aqueous phase reforming is a catalytic reaction performed at mild temperature (200−270 °C) and pressure (15−55 bar). In these conditions, water is in the liquid state, therefore hydrogen can be produced avoiding the energy requirement for the vaporization. Eq. 1 and Eq. 2 are the reactions involved in the APR of oxygenated hydrocarbons as reported by Dumesic and coworkers [24]. The former is referred to the typical stoichiometry of carbohydrates reforming, which are characterized by a C:O ratio of 1:1; the latter is the water-gas shift reaction (WGS), that, at the typical reaction conditions of APR, is favored as well. It derives in Eq. 3, being the summation of the formers, the reaction which describes the production of hydrogen and carbon dioxide from oxygenated hydrocarbons.

$$C_nH_{2y}O_n \leftrightarrow nCO + yH_2 \quad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2)$$

$$C_nH_{2y}O_n + nH_2O \leftrightarrow nCO_2 + (y+n)H_2 \quad (3)$$

Multiple practical consequences derive from the favorable thermodynamics of these reactions. For example, performing the WGS in the same reaction conditions of the reforming allows the minimization of carbon monoxide in the outlet gas stream, so that the product can be used in a PEM fuel cell; at the same time, the hydrogen yield is further prompted, since hydrogen can be obtained not only from the biomass but also extracting it from the solvent. Moreover, being produced at moderately high pressure (15−55 bar), the gas mixture can be separated via PSA, recovering the hydrogen and carbon dioxide in different streams. Finally, short alkanes may be present as well, due to side-reactions.

Under the kinetic point of view, several selectivity challenges are faced by the catalyst designer to maintain a high hydrogen yield. The most important ones are reported in Fig. 1, taking ethylene glycol as model compound. The first step (I) is the dehydrogenation: this stage creates an intermediate adsorbed on the surface catalyst; the adsorbed species can be formed either through the formation of metal-carbon bond (option A) and/or by the formation of metal-oxygen bonds (option B). For example, the formation of Pt-C bonds is more stable than Pt-O ones; nevertheless, it might be formed. The first pathway involved the C—C cleavage leading to the formation of hydrogen and carbon monoxide; the CO can react with water by the water gas shift reaction (step III) to produce H_2 and CO_2. Consecutive reactions of CO_2 and or CO (IVa; IVb) consume hydrogen to produce water and methane.

The path B) involved the formation of metal-oxygen bonds; the adsorbed species can follow the pathway II and form alcohols by C—O break and further hydrogenation; the alcohol can undergo further reactions on the metal surface, starting from the beginning. In addition, the adsorbed species can be subjected to desorption and rearrangement to form an acid that can start to react again to form, as the alcohol, methane, carbon monoxide, carbon dioxide, ethane, hydrogen and water.

By tuning the catalyst formulation, the reaction conditions and the reactor configuration it is possible to shift the production from hydrogen to alkanes [26]. As a matter of fact, this version of APR is the only version commercialized so far (see Perspectives). However, the society is pushing towards the production of hydrogen from renewable sources (mainly electrolysis) and APR can enter as an option in this sense.

As previously reported, methanol, ethylene glycol, glycerol, xylitol and sorbitol are model compounds commonly studied for APR, since they can be considered representatives of oxygenated hydrocarbons derived from biomass processing and dissolved in the aqueous phase. Table 1 reports the APR stoichiometry and the theoretical hydrogen yield for the single compounds. Organic acids and sugars were added to include other molecules commonly present in wastewater. In this work, we focused our attention to the reforming of complex mixtures, that can be considered closer to a large-scale application. APR of these mixtures typically produces a gas and a liquid stream. The liquid composition is complex, usually not well characterized, and varies according to the used feedstock. The gaseous product can be composed by H_2, CO (trace),

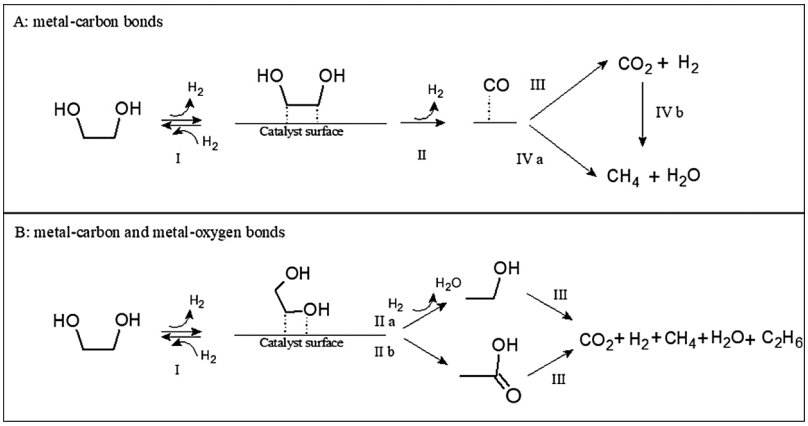


Fig. 1. Reaction pathways of ethylene glycol, as proposed in [24].

Table 1
APR reaction stoichiometry and theoretical hydrogen yield for common oxygenated present in wastewater fraction. 1 g of carbon was assumed as basis for the calculation.

Compound	APR Reaction	H_2 yield (mg H_2/g C)
Glycerol	$C_3H_8O_3 + 3H_2O \longrightarrow 3CO_2 + 7H_2$	390
Methanol	$CH_4O + H_2O \longrightarrow CO_2 + 3H_2$	500
Glycolic acid	$C_2H_4O_3 + H_2O \longrightarrow 2CO_2 + 3H_2$	250
Acetic acid	$C_2H_4O_2 + 2H_2O \longrightarrow 2CO_2 + 4H_2$	330
Ethanol	$C_2H_6O + 3H_2O \longrightarrow 2CO_2 + 6H_2$	500
Lactose	$C_{12}H_{22}O_{11} + 13H_2O \longrightarrow 12CO_2 + 24H_2$	330
Glucose	$C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 12H_2$	330

CO_2, CH_4 and other light alkanes (C_2-C_6) [27].

In the next paragraphs the experimental results of real streams, also containing the molecules above presented, will be summarized. In most cases, the theoretical hydrogen yield is not reached for several reasons which will be presented and discussed.

3. Lignocellulosic biomass: biorefineries approach

Lignocellulosic biomass is constituted by cellulose, hemicellulose and lignin. Each of these fractions is potentially able to produce hydrogen via APR. In the following, experimental results on several real (kenaf, pine sawdust, wheat straw, sorghum, switchgrass, miscanthus, corn kernel) and synthetic lignocellulosic-derived compounds will be reported. Moreover, some studies focused to the valorization of the whole biomass (i.e. in a solid form) will be reported as well. In fact, if the proposed technologies can convert each portion of the biomass, lignocellulosic feedstock may have a chance to substitute fossil fuels.

3.1. Hydrolysis

Lignocellulosic biomass can be subjected to hydrolysis to remove the lignin fraction, increase the porosity of the material and reduce cellulose crystallinity [28]. In this way, sugar monomers are released from the structure of the biomass and can be valorized following different pathways [29].

Kenaf is reported as an interesting substrate because of its fast growth rate and large production. Irmak and Ozturk performed the APR of the liquid phase obtained from kenaf hydrolysis (150 and 250 °C – 27.58 MPa carbon dioxide) and of the solid biomass itself on a 5% Pt/C catalyst [30]. They showed that the hydrolysate constituted by low-molecular weight compounds (i.e. the one obtained at 250 °C) produced more gas than the one with higher molecular weight (104.2 vs 16 mL), also due to the higher carbon concentration in the feed (4431 mg C/L vs 1504 mg C/L). The conversion of the single components of the mixture was not reported, likely because of its complexity: in fact, only xylose was recognized as simple monosaccharide in the starting solution. A comparison with glucose at the same concentration was performed as well. In this case, the TOC removal (i.e. the fraction of carbon that was converted into a gas/solid species after the reaction) increased by 60 %, while the hydrogen yield was almost three times higher. In order to better understand the efficiency of the process, we compared this value with the theoretical one reported in Table 1, which is equal to 330 mg H_2/g C). The authors reported that the TOC removal was 80 %, so the yield should have been approximately 260 mg H_2/g C; the presence of other gaseous species, such as methane and ethane, and the lower H_2/CO_2 ratio compared to the stoichiometric one, infers reaction pathways other than the simple reforming.

APR of solid kenaf biomass increased the gas production, but the hydrogen content globally decreased. Kenaf was also used for the production of activated carbon as support for Pt-based catalysts for APR [31].

The APR of wheat straw hydrolysate was investigated in [32]. 5% Pt/carbon, 5% Pt/alumina and Raney Ni 2400 were used as catalysts, with the latter producing far more gaseous species than the formers (Fig. 2). It is worthy to highlight that the use of an inexpensive Ni-based catalyst can be advantageous under the economical point of view. The gas phase also presented a higher hydrogen concentration than the Pt-based cases (68.9 mol.%) and no carbon monoxide. It is interesting to observe that the gas production was also higher than the case of kenaf hydrolysate previously reported, also considering the similar organic

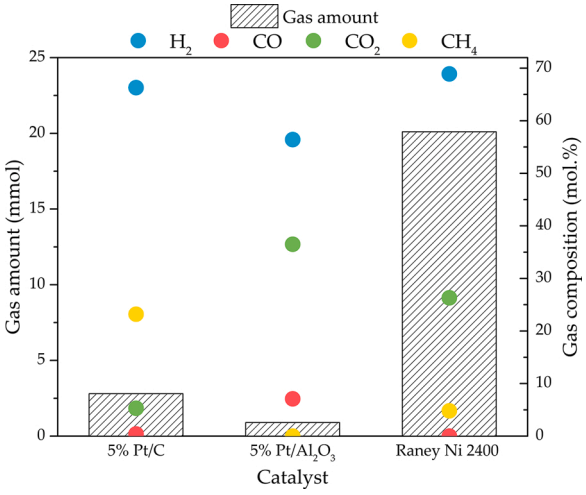


Fig. 2. APR of wheat straw hydrolysate with different catalysts. Reaction conditions: 250 °C, 2 h, 50 mL hydrolysate (data from [32]).

carbon (4965 mg C/L vs 4431 mg C/L) [30]. This difference may be ascribed to the different hydrolysate composition.

The authors did not mention the formation of a solid residue. Pipitone et al. tested wheat straw hydrolysate with different concentration (0.3−1.8 C wt.%) using a 5% Pt/C [33]. The authors reported the presence of a solid residue due to humins formation from glucose and xylose. Humins are water insoluble compounds that derive from the polymerization and condensation of furfurals in the hydrothermal environment [34]. In fact, glucose and xylose may be dehydrated via an acid-catalyzed mechanism into hydroxymethylfurfural (HMF) and furfural, respectively; afterwards, it can be rehydrated to 2,5-dioxo-6--hydroxyhexanal, which polymerize via aldol condensation to form humins. Two important consequences were correlated to humins formation. On one side, hydrogen yield was reduced because of alternative pathways taken by the intermediate products; on the other side, the catalyst surface was covered by this material, blocking the active sites. The authors observed that humin formation increased with the increase of feedstock concentration and with the decrease of reaction temperature. The first outcome was because this is a homogeneous first order reaction, so it is more favored by the concentration increase than the reforming reaction, which is fractional order. The second result was related to the more favorable C-C breaking reaction by increasing the temperature, so decreasing the humin formation.

Since HMF and furfural are intermediates from sugars, a pre-hydrogenation step to sugar alcohols was evaluated to avoid homogeneous reactions. In Fig. 3-A the hydrogenation of a glucose-xylose solution at different carbon concentration is reported (5% Ru/C catalyst was used in this case). The solution was almost completely hydrogenated, and in a selective way (without side-products). The APR of this solution was further subjected to APR and the results are reported in Fig. 3-B. The net hydrogen production, i.e. mole $H_{2\ produced}$ − mole $H_{2\ consumed}$, in the two-steps case was much higher than the one-pot case (without pre-hydrogenation). This difference is due to the more selective reforming of sugar alcohols compared to sugars.

A similar approach was reported for kenaf hydrolysate [35], sucrose [36] and maltose [37], which were pre-reduced to increase the hydrogen selectivity. The attempt for an in situ hydrogenation of xylose to xylitol thanks to the conversion of formic acid into hydrogen in the reactant mixture did not succeed, overall decreasing the hydrogen selectivity for xylose APR [38].

Different carbon supports for Pt catalysts have been studied thanks to their tunable properties for the APR of wheat straw hydrolysate [39]. The results reported that activated carbon was the support with the highest hydrogen production (2.17 mmoles), followed by single wall carbon nanotube (1.72 mmoles), graphene oxide (1.10 mmoles), super-darco carbon (0.66 mmoles) and multi wall carbon nanotube (0.59 mmoles). Graphene oxide produced the gas phase with the highest hydrogen concentration (56 mol.%). Due to the large dimension of the molecules present in the hydrolysate, the support should have proper textural characteristics to permit the accessibility of the active site. Interestingly, in this work the liquid phase after APR was characterized as well. Activated carbon also allowed a higher formation of sugar alcohols in the liquid phase (e.g. glycerol, xylitol, sorbitol etc.) and breaking down of soluble organic compounds derived from lignin fraction (4-methoxyphenol, vanillin, syringaldehyde etc.).

Sorghum hydrolysate may be an alternative feedstock due to its drought tolerance, fast growth rate, high starch content together with low ash, fat and protein [40]. Response surface methodology was used to investigate the effects of temperature (200−270 °C), feed flow rate (0.3−1 mL/min) and biomass feed concentration (1000−4000 mg C/L) on the APR process using a Raney nickel catalyst. The former variable was the main factor on the H_2 yield, which was higher at higher temperature. In fact, working at this condition suppressed methanation, and hydrogen production increased by three times moving from 200 to 270 °C.

The use of microwaves for the pretreatment of switchgrass and miscanthus has been investigated for the deconstruction of the recalcitrant crystalline cellulose fraction [41]. Similarly with previous works, the composition of the hydrolysate was not reported. Once treated with microwaves, they were hydrolyzed in subcritical water and subjected to APR with a Pt/C catalyst to evaluate its hydrogen productivity. Miscanthus produced 20 % more hydrogen than switchgrass, likely due to the higher organic content (for the untreated, it was 1350 mg C/L vs 1132 mg C/L). The lower TOC in the case of the microwave-treated feedstock decreased the hydrogen production; moreover, it increased the formation of solid carbon residue after APR. As reported earlier, this is a problem for the implementation because it severely affects the catalyst lifetime.

Corn kernel may be a suitable feed for APR application, since it is present in excess in the US for its valorization into bioethanol [42]. Irmak and Tiryaki, with a preliminary economic analysis based only on the price of the feeds, showed that the cost of the corn kernel is about 1.7 times higher than methane to produce the same amount of hydrogen. The hydrolysis of corn kernel at 200 °C produced an aqueous solution with approximately 2500 mg/L TOC concentration and yielded 2.3 times more hydrogen then corn stover biomass (5.8 mmol H_2/g C vs 2.6 mmol H_2/g C, respectively) [43]. Various corn kernels were evaluated for gas production (field corn, non-genetically modified field corn, yellow field corn, white field corn and popcorn) [44]. The hydrolysate TOC ranged between 5230 and 5850 mg C/L, with the field corn showing the highest concentration of glucose. No significant differences were found among the varieties in terms of gas production and hydrogen yield, with

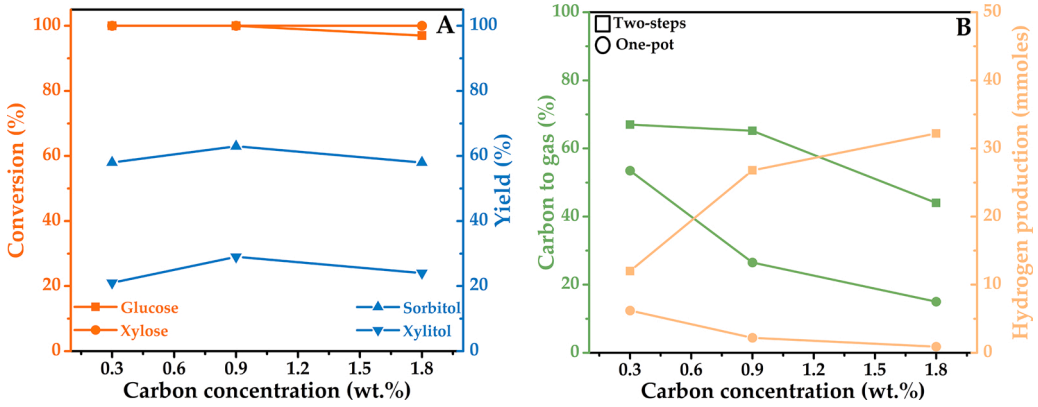


Fig. 3. Influence of carbon concentration on the hydrogenation of a glucose-xylose mixture (A) and on the APR of the hydrogenated feed (B). Hydrogenation reaction conditions: 0.188 g Ru/C catalyst, 1 h reaction time, 180 °C, 15 bar H2 pressure. APR reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C. Reproduced with permission from [33].

the latter being 130 mL/g corn on average.

Finally, using a systematic approach, Irmak et al. investigated the APR of the cellulose, hemicellulose and lignin fraction of kenaf and wheat straw [45]. The hydrolysis of each biomass fraction was conducted a 250 °C in a CO_2 atmosphere of 17.24 MPa. The results showed that the hydrolysis of the cellulose fraction led to the highest TOC content, whereas lignin to the lowest one. The obtained hydrolysates (only the polysaccharide weight distribution was reported) were subjected to APR at 250 °C for 2 h using a Pt/C catalyst. The highest hydrogen yield was obtained in both cases from the cellulose fraction, while hemicellulose was the most selective. Furthermore, lignin did not report any hydrogen production, despite it presented the highest TOC removal. This outcome may be linked to adsorption phenomena between the carbon support and the lignin-derived species [46]. Apart from the higher gas production, kenaf left less solid residue. Further investigation on APR of lignin can be found in [47].

In Table 2 a summary of the main results obtained with different biomass discussed in the paragraph is reported. The hydrolysis and APR conditions were reported, specifying also the used catalyst. It can be observed that Pt is the most used metal among the reviewed investigation. This choice leads primarily to an economic drawback, but the challenges of actual streams require high activity, selectivity and stability to justify its use. So, its use can be meaningful since it is commonly the one with the best performances (among the monometallic catalysts).

Apart from the cited exceptions, the characterization of the starting and product solutions is not evaluated, likely because of the complexity of the liquid phase. The ash content is commonly reported, but the possible influence is not investigated. Most commonly, the molecular weight distribution of the polysaccharides and the TOC were showed. From the latter, it can be observed that these solutions have most of the TOC close or below 5000 mg C/L, hindering their catalytic treatment and increasing the costs since larger equipments are necessary. The TOC

Table 2
APR of different lignocellulosic biomass. n.a.: not available.

Biomass	Hydrolysis conditions	APR conditions	Catalyst	Feed TOC (mg C/L)	TOC removal (%)	Gas composition			H_2 yield (mg H_2/g C)	Ref
						% H_2	% Alkane	% CO_2		
Kenaf	7.5 g solid in 350 mL water, pretreated 20 kHz, 27.58 MPa CO_2, 150 °C	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	1504	n.a.	49.6	4.3	38.8	9.4	[30]
	7.5 g solid in 350 mL water, pretreated 20 kHz, 27.58 MPa CO_2, 250 °C			4431	50	60.0	7.6	32.4	25.2	
Glucose	–	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	4400	80	57.4	8.6	34.0	72.7	[30]
Wheat straw	10 g solid in 350 mL water, pretreated 20 kHz, 27.58 MPa CO_2, 250 °C	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	4964	27	66.3	24	7.3	15.0	[32]
			0.12 g 5% Pt/Al_2O_3	4964	37	56.4	n.d.	36.5	4.2	
			0.6 g Raney Ni 2400	4964	52	68.9	4.8	26.3	111.8	
Wheat straw	Enzymatic hydrolysis (from a commercial plant – PROESA™ technology)	75 mL, 270 °C, 2 h, batch reactor	0.375 g 5% Pt/C	3000	47	40.5	13.6	45.9	25.6	[33]
				9000	20	24.0	11.4	64.5	5.3	
				18,000	10	6.0	4.5	86.2	0.5	
Wheat straw	10 g solid in 350 mL water, pretreated 20 kHz, 27.58 MPa CO_2, 250 °C	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	n.a.	n.a.	49.0	11.0	39.0	n.a.	[39]
Switchgrass	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, no pretreat microwave	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	1132	20	72.1	6.2	21.1	85.9	[41]
	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, 120 °C microwave			1541	15	65.4	6.1	27.2	51.2	
	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, 150 °C microwave			1679	11	67.5	5.9	25.4	39.8	
Miscanthus	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, no pretreat microwave	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	1350	22	71.4	5.6	24.7	88.8	[41]
	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, 60 °C microwave			1550	13	67.9	5.8	24.9	47.7	
	5 g solid in 350 mL water, 25.52 MPa CO_2, 220 °C, 80 °C microwave			1742	13	71.0	6.2	22.2	56.0	
Corn kernel	6 g solid in 350 mL water, 13.79 MPa CO_2, 200 °C	350 mL, 250 °C, 1.5 h, batch reactor	0.2 g 5% Pt/C	5670	n.a.	71.7	n.a.	24.4	17.6	[43]
Wheat straw - cellulose	4 g solid in 200 mL water, 17. 24 MPa CO_2, 250 °C	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	5256	19	20.7	9.9	67.6	8.5	[45]
Wheat straw - hemicellulose				4180	11	27.0	13.5	58.8	7.3	
Wheat straw - lignin				595	32	0.0	7.2	92.8	0.0	
Kenaf - cellulose	4 g solid in 200 mL water, 17.24 MPa CO_2, 250 °C	50 mL, 250 °C, 2 h, batch reactor	0.12 g 5% Pt/C	5216	22	21.1	10.3	66.9	10.1	[45]
Kenaf - hemicellulose				4985	17	24.0	8.0	68.0	9.5	
Kenaf - lignin				606	31	0.0	8.3	91.7	0.0	

removal is often showed, without info on conversion or selectivity. The gas composition was reported in terms of volume percentage of hydrogen, alkane (sum of methane, ethane and propane) and carbon dioxide. Carbon monoxide concentration was not reported since it is commonly negligible. Among the results, it is interesting to observe that Raney Ni 2400 reached the highest hydrogen yield; furthermore, low selectivity towards methanation was observed, in contrast with common results reported in literature [48]. On the other hand, high concentration of the hydrolysate and the lignin-fraction of the biomass led to negligible hydrogen yields.

This comparison may be further studied in deep with the aim to find suitable substrates for hydrogen production via APR. However, the differences in the hydrolysis and APR conditions can affect a rigorous analysis at this stage.

Valenzuela et al. reported APR of solid actual biomass, pine sawdust, for the first time [49]. The presence of platinum catalyst doubled the hydrogen production compared to the one acid-catalyzed (5% H_2SO_4). Sulfur poisoning was considered the main cause for deactivation (S/Pt elemental ratio equals to 24.3).

Cellulose is a more readily available feedstock than glucose. Degreased cotton, filter paper and microcrystalline cellulose were investigated looking at the effect of different degree of polymerization [50]. Filter paper gave 20.3 mmol H_2/g of cellulose, much higher than Valenzuela et al. [49] (0.96 mmol/g). The authors observed that the hydrogen selectivity increased with the increase of the degree of crystallinity. In fact, it is related to the hydrolysis rate of cellulose. Since hydrogen selectivity is negatively affected by glucose concentration, slower hydrolysis caused lower local concentration, favoring hydrogen production. No measurable leaching and sintering were observed for Pt, while carbon deposition was mainly considered (just 80.3 % carbon balance). Despite not comparable with gasification performance (43.2 mmol), it was more energy effective.

3.2. Thermochemical conversion technology

In the recent years, due to the growth of energy demand, thermochemical conversion technologies (TCC) have been revisited. As a matter of fact, they are not a recent route to convert biomass, but they were abandoned due to low petroleum price. The main TCC process are gasification, hydrothermal liquefaction (HTL), pyrolysis, direct combustion, and supercritical fluid extraction [51].

Fig. 4 summarizes the thermochemical conversion routes of biomass [52]. Heat is the main output from combustion; a CO/H_2 mixture (syngas) is the main product of gasification, which can be used as building block for the petrochemical sector or trough Fischer-Tropsch (FT) synthesis can be converted into transport fuels; pyrolysis and hydrothermal liquefaction are processes able to convert biomass into a crude biofuel, which, upon upgrade to reduce its oxygen content, can be used in conventional engines. They also produce an aqueous phase (AP) with organic compounds dissolved in, which should be valorized to minimize carbon waste.

The aqueous phase produced by HTL process contains an organic content varying between 15–50 % of initial carbon [53] and must be valorized to make the hydrothermal processes economically feasible. The complexity of the mixture and the high dilution of the organic compound makes difficult their recovery. Davidson et al. studied other possible routes of valorization such as catalytic upgrading of carboxylic acids and the improvement of steam reforming thanks to a dual bed in combination with a cleanup process of the aqueous phase [53].

Leng at al. [8] reviewed the main options for HTL water phase treatment proposed by the state of the art so far. The water treatment after hydrothermal processing is a key point for its industrial development. However, these streams are very complex and they contain inhibitory substances. The reported technologies are anaerobic digestion, super critical water gasification (SCWG), microbial fuel cell, microbial electrolysis cell, microalgae cultivation and recirculation of the aqueous phase to HTL. All these routes present advantages and disavantages and are strongly related to the starting feedstock. SCWG is the one which can be applied to most phases but it is higly energy expensive and the catalyst deactives quickly. The anaerobic digestion, the bioelectrochemical treatment and the microalgae options suffer from the presence of inhibitory compounds; finally the AP recirculation can limit the application to the dry biomass and can cause the building up of undesired compounds.

A deep characterization of the water fraction is generally adviced to determine which is the best treatment applicable to these streams. Panisko et al. [54] found in the AP from corn stover HTL several classes of compounds, from alcohols to carboxylic acids, from hydroxyacids to ketones and aromatics. Starting from this knowledge and following simulations [55], the work carried out by Pipitone et al. [56] had the goal to understand the reactivity of the molecules dissolved in the aqueous phase, with particular attention to the tendency to hydrogen production; furthermore, synthetic binary and ternary mixtures were tested. The tests were devoted to the study of compounds not usually subjected to APR, such as hydroxyacids, carboxylic and bicarboxylic acids, ketones and aromatics. The increase of the temperature between 230 and 270 °C showed mainly a benefic effect on the activity, without affecting the selectivity.

In Table 3 the experimental hydrogen yield produced by some of the molecules is compared with the theoretical one, i.e. considering complete conversion of the substrate and selectivity. Furthermore, alkane yield was reported.

Interestingly, the glycolic acid, which was never tested before, showed great hydrogen production, thanks to its OH group. Its lower hydrogen production than the theoretical one was ascribed to the parasite formation of acetic acid in the liquid phase, which derived from

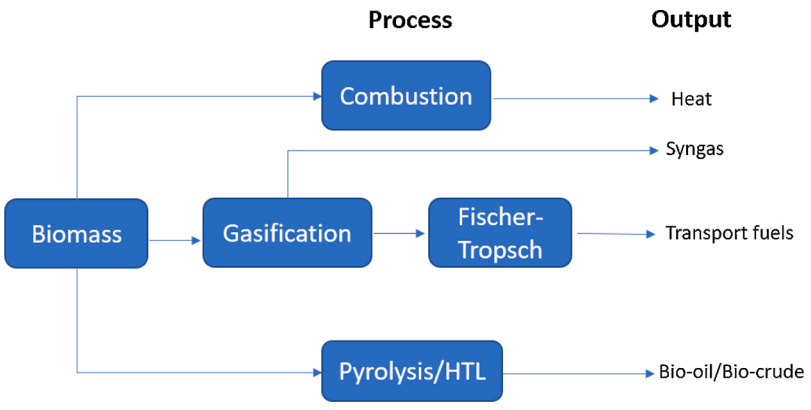


Fig. 4. Thermochemical conversion routes and main outputs of biomass.

Table 3
APR of model compounds and differences with theoretical values. Reaction conditions: 5% Pt/Al_2O_3 catalyst, temperature 270 °C, reaction time 2 h, feed concentration 133 mM, 75 mL batch reactor (data from [56]).

Molecule	Theoretical	Experimental		
	H_2 yield (mg H_2/g C)	H_2 yield (mg H_2/g C)	Alkane yield (mg alkane/g C)	Substrate conversion (%)
Glycolic acid	250	184.6	19.9	100
Acetic acid	330	12.0	327.9	56
Ethanol	500	121.4	515.8	99
Ethylene glycol	420	351.0	59.5	100
Glycerol	390	233.2	168.7	100

glycolic acid hydrogenation.

Acetic acid APR led to a gas phase constituted by roughly 50 % carbon dioxide and 50 % methane, so that only 4 % of the theoretical hydrogen was produced. It derived a general consideration for carboxylic acids, which followed the path reported in Eq. 4.

Ethanol produced a gas mixture rich in hydrogen (50 %), but with the 25 % of it being methane, which increased the gap between theoretical and experimental hydrogen produced. For ethanol, and in general for molecules with C:OH ratio different than one, a modified APR stoichiometry can be written, which takes into consideration also the real mechanism of reaction [57,58]. In fact, when only one hydroxylic group is present in the molecule, only one CO group can be extracted and converted to H_2 and CO_2 (Eq. 5). Consequently, the corrected theoretical hydrogen is three times lower (167 mg H_2/g C) and closer to the experimental one.

Ethylene glycol thanks to its C:OH ratio equal to 1 had a good accordance between theoretical and real hydrogen production, even if the alkane yield was three times higher than the one obtained by APR of glycolic acid.

Finally, glycerol reached a complete conversion. However, the discrepancy between the two values could be explained in this case not by the different C:OH ratio (which is equal to 1 and has a molecular structure similar to ethylene glycol). The higher molecular weight and complexity of the molecule caused the presence of alternative reaction pathways which lead to gaseous (methane) and liquid by-products (hydroxyacetone, propylene glycol, acetic acid) decreasing the hydrogen production.

$$CH_3COOH_n \leftrightarrow CH_4 + CO_2 \quad (4)$$

$$CH_3CH_2OH + H_2O \leftrightarrow 2H_2 + CO_2 + CH_4 \quad (5)$$

The study of binary and ternary mixtures allowed to understand that acetic acid (one of most present compound) in mixture suffered from competitive adsorption on the active site of the catalyst. Consequently, the theoretical gas production ideally obtained from the linear combination of the present compound was different from the real one.

This outcome was confirmed in a successive work, where the influence of reaction time on single compounds and mixtures showed the difference in the reactivity [59]. Furthermore, the APR of the water fraction derived from lignin-rich hydrothermal liquefaction was tested for the first time. The use of this stream deactivated the catalyst. In fact, the high surface area of the activated carbon used as support presented a strong affinity with the aromatic oligomers present in the aqueous phase. A liquid-liquid extraction with diethyl ether, or the use of activated carbon as adsorbing solid prior to the reaction, allowed the retention of the textural characteristics of the catalyst and reduced the deactivation issue [46]. The production of hydrogen from HTL-derived wastewater can be a sustainable approach for the upgrading step necessary for the bio-crude. In fact, the high oxygen content of the bio-crude does not permit its direct use in conventional engines. Its upgrade is carried out by a hydrodeoxygenation, which requires high hydrogen pressure, typically provided by a steam reformer. The coupling of hydrothermal liquefaction and aqueous phase reforming may establish a benefic synergy, ideally eliminating the need for external fossil hydrogen to guarantee the production of valuable bio-fuels.

The low-boiling fraction of the bio-oil derived from fast pyrolysis of rice husk was subjected to APR using a Pt/Al_2O_3 catalyst [60]. The increase of reaction temperature allowed the increase of the gas production, moving from 20.3 mmol at 503 K to 52.9 mmol at 563 K; at the same time, the hydrogen selectivity remained constant, and its concentration of the gas phase was about 65 vol.%. In the liquid phase, acetic acid was the main compound, with its area in the GC–MS chromatogram being 86 % of the total area.

As reported in Fig. 4, gasification of biomass is a process which converts the solid feedstock into hydrogen, carbon monoxide and carbon dioxide (syngas). It can be further coupled to a Fischer-Tropsch (FT) reactor to produce liquid fuels. In this process a contaminated water is also obtained, containing light oxygenates at low carbon concentration. A possible route for the valorization of this side stream was reported in [61].

The APR of the water fraction produced by low temperature Fischer-Tropsch (LTFT) was performed in [58]. The water was characterized, and it contained 0.5 C wt.%, divided in short chain alcohols and carboxylic acids. Thanks to APR, the COD of the streams was reduced up to 90 % at 270 °C (5% Pt/C catalyst) with an almost complete conversion of all the present alcohols. The catalyst showed high stability, likely due to the presence of only small alcohols and acids, and not of inhibitory compounds (such as aromatics or inorganics). Moreover, it was pointed out how also that the position of the OH group in the molecule plays a key role in determining the product distribution. In fact, testing primary and secondary alcohols gave important differences in terms of hydrogen production and gas/liquid composition.

Finally, Coronado et al. performed the kinetic modelling of FT water APR on a Ni-Cu catalyst supported on ceria-zirconia [62]. The results showed that C2-C4 alcohols adsorbed similarly to the catalyst surface and reacted with analogous rate and mechanism. Moreover, using a synthetic mixture, it was reported that copper addition increased the stability of the catalyst, at the expense of the hydrogen yield [63].

4. Food industry

Containing a high concentration of water, hydrothermal valorization of food processing side-streams has been proposed thanks to the energetic advantage of avoiding the drying step [64].

Tuna cooking waste water was subjected to APR since the high salinity and different organic loads can make difficult the use of a biological treatment [65]. Pt supported on different carbon materials were used as catalysts. The characterization of the wastewater is reported in Table 4. In the absence of catalyst, hydrothermal carbonization occurred and was responsible for 20 % TOC removal. The catalyst caused a lower TOC removal than the bare support since the high surface area was assumed responsible for the adsorption (e.g., 70 % vs 50 % for CAPSUPER – commercial - and Pt/CAPSUPER, respectively). However, a higher production of hydrogen and alkanes was obtained adding Pt (5.4 vs 1.4 μmol). A comparison between batch and semi-continuous set-up showed similar amount of valuable gases. However, alkane percentage was reduced, suggesting that hydrogen-consuming reactions (e.g., methanation, hydrogenation etc.) were prevented thanks to the decrease in the hydrogen partial pressure inside the reactor [66]. The observed catalyst deactivation was attributed to the presence of acetic and phosphoric acids or chloride; for example, P species can prevent CO adsorption on Pt, hindering the WGS. The authors admitted that it was not possible to ascribe the catalyst deactivation to single compounds due to the complexity of the wastewater. The increase of platinum particle size was responsible for the decrease of methanation and increase of

Table 4
Main characterization and results of APR of wastewaters derived from different food-processing. Inorganics: sum of phosphate, sulfate, sodium chloride; LSC: low salt content – HSC: high salt content. All reported experiments are carried out in batch reactor.

Wastewater origin	COD (mg/L)	Acetate (mg/L)	Formate (mg/L)	Inorganics (mg/L)	Initial pH	APR conditions	Catalyst	Feed TOC (mg/L)	TOC removal (%)	H_2 (%)	Alkane (%)	CO_2 (%)	H_2 yield (mg H_2/ g C)	Ref
Tuna cooking	4996	1895	10	4354	6.1	20 mL wastewater, 200 °C, 4 h	0.4 g Pt/ CAPSUPER	1895	54	1.8	1.3	96.9	2.8	[65]
							0.4 g Pt/ SXPLUS		54	0.5	3.5	96.0	3.3	
							0.4 g Pt/ ENSACO		41	8.7	9.3	82.0	25.5	
Breweries - synthetic	6229	<1	<1	987	6.9	15 mL wastewater, 200 °C, 4 h	0.3 g Pt/ CAP	1968	82	5.7	36.1	58.3	30.5	[67]
						15 mL wastewater, 225 °C, 4 h			86	19.1	32.4	48.6	133.4	
						15 mL wastewater, 200 °C, 4 h	0.3 g Pt/ ENS250		79	35.4	26.8	37.8	318.9	
						15 mL wastewater, 225 °C, 4 h			88	48.9	22.7	28.4	829.2	
						15 mL wastewater, 200 °C, 4 h	0.3 g Pt/ ENS350		80	19.2	26.8	54.0	88.8	
						15 mL wastewater, 225 °C, 4 h			88	34.3	23.9	41.7	296.5	
						15 mL wastewater, 200 °C, 4 h	0.3 g Pt/ C_MESO		60	33.2	21.3	45.5	19.5	
						15 mL wastewater, 225 °C, 4 h			74	41.1	19.6	39.2	31.1	
Breweries - synthetic	5846	2	1	696	7	15 mL wastewater, 220 °C, 4 h	0.3 g Pt/ ENS	1871	60	46.7	21.3	32.0	595.4	[69]
					11	15 mL wastewater + NaOH, 220 °C, 4 h			66	51.4	23.0	25.6	387.3	
					11	15 mL wastewater + KOH, 220 °C, 4 h			70	52.7	22.2	25.1	594.8	
					7	15 mL wastewater, 220 °C, 4 h	0.3 g Pt/ KJB		83	23.5	19.6	56.9	91.2	
					11	15 mL wastewater + NaOH, 220 °C, 4 h			75	32.7	22.8	44.5	130.0	
					11	15 mL wastewater + KOH, 220 °C, 4 h			78	38.6	21.7	39.7	236.9	
Breweries - real	4764	172	37	56	11	15 mL wastewater, 220 °C, 4 h	0.3 g Pt/ ENS	1646	52	51.1	20.1	28.8	485.7	[69]
							0.3 g Pt/ KJB		69	53.6	19.9	26.5	798.1	
Fruit juice	5925	–	–	–	2	15 mL wastewater, 220 °C, 4 h	0.3 g Pt/ ENSACO	2317	92	27.8	11.9	60.1	288.3	[70]
					7				74	34.9	15.7	49.3	371.8	
					10				61	40.8	14.1	45.1	425.3	
					12				63	40.0	11.8	48.2	362.5	
Fruit juice - LSC	5925	–	–	483	10	15 mL wastewater, 220 °C, 4 h	0.3 g Pt/ ENSACO	2317	63	38.1	15.5	46.4	419.6	[70]
Fruit juice - HSC				967	10				65	35.1	16.3	48.6	269.4	

hydrogen concentration in the gas phase.

Breweries produce 3−10 liter of wastewater per liter of beer. The conventional treatment of this effluent consists of chemical, biological and physical step, but APR may be considered as an option [67]. A synthetic representative mixture was prepared using malt and yeast extract, peptone, maltose, ammonium sulfate, ethanol, monosodium and disodium phosphate. Without the catalyst, the hydrothermal carbonization (HTC) led to a reduction of COD and TOC of about 50 %. In this case, the APR with Pt/C increased the carbon removal significantly (about 80 %). It was reported that the presence of hydrogen in the produced gas phase increased with the increase of the concentration (range 474−414 mg C/L initial TOC), despite the TOC and COD removal decreased from 99 % to 51 %. The presence of carbonaceous compounds has been considered as the cause for the observed catalyst deactivation (in terms of hydrogen yield, not TOC removal). In Table 4 the hydrogen production is reported for different Pt-based catalysts at 200 °C and 225 °C. The better performance obtained by Pt/ENS250 was ascribed to its mesoporous texture and basic property. The mesoporosity can be beneficial to avoid mass-transfer limitations, since it facilitated the motion of reactants and products; the basicity could promote the water gas shift reaction, because it aided the water dissociation [68].

Since cleaning-in-place operations are performed in such plants with the use of alkaline solutions, the effect of NaOH and KOH was evaluated as well [69]. The characterization of the synthetic (using malt and yeast extract, peptone, maltose, ammonium sulfate and ethanol) and real brewery wastewater is reported in Table 4, together with the test results with specific attention to the carbon black samples, which did not present microporosity. Base addition was found useful to favor the hydrogen production thanks to the removal of CO_2 and hence supporting WGS, mainly when KOH was added, through the following Eq. 6

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O \quad (6)$$

This concept is similar to the one previously reported, which takes advantage of the surface basic properties of the support. Moreover, C—O bond cleavage can be favored with respect to C—C bond cleavage. The results between the two samples showed higher hydrogen production for the real one. One important reason can be ascribed to the different composition between real and synthetic sample. Acetate, formate, glycolate, phosphate, sulfate and maleate were identified and quantified in the initial samples. However, these species accounted only for 6% of the initial TOC, making difficult further discussion on the different performance. Finally, the influence of inorganics on the stability of the catalyst was not discussed.

Due to the sugar content of fruit juice wastewater, APR was explored as a possible alternative to conventional biological methods, since the variation of the organic load, pH, and salinity may hinder optimal performance [70]. The synthetic fruit juice wastewater was constituted by glucose, fructose, citric acid, ascorbic acid and galacturonic acid. Coherently with [69], the increase of pH increased the hydrogen yield together with a decrease of the carbon dioxide via carbonatation. The increase of the salinity did not affect the TOC and COD removal, while the hydrogen yield decreased: the authors attributed this outcome to catalyst deactivation, which in turn increased the contribution of the homogenous hydrothermal carbonization to the product distribution.

In Table 4 the results from APR of food processing are summarized. It can be observed that in the case of food processing wastewater the TOC of the feed is even lower than the one reported by hydrolysate, being always lower than 2500 mg C/L. The feed dilution hinders the application for very diluted streams since it means larger equipment in each section of the plant, feed pretreatment (heating/cooling and pumping), reaction and separation zone. The gas composition differs significantly moving from a type of substrate to the other one. For example, tuna cooking led mainly to carbon dioxide; this percentage decreased for other side streams, but a high concentration of alkane was anyway obtained. Nevertheless, typically higher hydrogen yields are observed compared to the one obtained from hydrolysate.

Cheese whey valorization via APR has been explored due to the environmental concern prompted by its co-production during cheese making processes, since about 9 kg/kg cheese are obtained [4]. Lactose is the primary compound in cheese whey, approximately 5 wt.%. Only one third is recovered, and the remaining is sent to waste treatment or even field spread. It is estimated that the full reforming of lactose produced by the U.S. cheese industry could generate up to 0.33 million tons of hydrogen (about 9% hydrogen production capacity of U.S. refineries in 2014) [71].

Traditionally, the treatment is addressed through filtration technologies or biological treatments (aerobic/anaerobic digestion, lactose fermentation). The effect of temperature (200−240 °C), pressure (38−50 bar), lactose concentration (1−10 wt.%) and catalyst (Ni-La/Al_2O_3) mass/lactose mass flow rate ratio (10−40 g cat min/g lactose) were investigated using a design of experiment approach for the APR of a model lactose solution. The lactose conversion was complete in each of the investigated conditions. It turned out that the gas production was favored by high temperature and pressure, together with high $W/m_{lactose}$ and lactose concentration [4]. Beside gas production, the carbon conversion to liquid ranged from 33 to 97 %, and the liquid products were constituted by aldehydes, carboxylic acids, alcohols, ketones and furans. Similarly, with the results reported for sugar solutions, a portion of the carbon was converted in a solid phase, within a range 0−59% according with the reaction conditions. This is an important aspect because the presence of insoluble compounds in a catalytic reaction can easily cause the deactivation of the catalyst by fouling. Despite this risk has been highlighted for concentrated sugar solutions, the authors reported that similar solid production can be obtained even at diluted conditions (1 wt.% lactose).

Overlayer bimetallic Pt on Ni or Co catalysts supported on alumina were tested for lactose APR [71]. Ni-Pt showed the highest hydrogen yield and selectivity. Interestingly, the work reported that the use of pseudomorphic overlayer bimetallic catalysts helped to decrease the H_2 and CO binding strength, favoring the H_2 production.

Finally, a comparison between cheese whey, filtered cheese whey (i.e. cheese whey with lower fat and protein fraction) and lactose solution was performed using a Ni-La/Alumina [72]. The cheese whey was mainly constituted by lactose (4.71 wt.%), sorbic acid (1.81 wt.%) and acetic acid (1.37 wt.%); moreover, ashes were present as well (0.52 wt. %). Cheese whey experiments showed less gas production than lactose experiments, attributed to the high formation of char in the former case; the filtration allowed to increase the gas production and reduced the char formation, suggesting that fats and proteins could play a role in its formation due to their high molecular weight. Moreover, it has been suggested that salts, promoting dehydration reactions, may be responsible for the great amount of char using the real feedstock compared to the model lactose solution. Tests performed in the continuous set-up clearly showed a decrease of the conversion to gas with the time on stream due to char formation, which eventually clogged the reactor.

Despite the potential interest of cheese whey as feedstock for APR, the low selectivity is a main obstacle. Alternative strategies, like the ones cited for sugar streams, or the optimization of the reaction conditions should be evaluated to assess its implementation beyond the laboratory scale.

5. Crude glycerol

During the production of biodiesel, a crude glycerol stream is obtained (0.1 kg crude glycerol/kg of biodiesel). Apart from being an environmental issue, this inconvenience may hinder the development of the biodiesel itself as alternative fuel. This is the reason why various valorization routes for glycerol have been explored [73–76].

Glycerol is the most studied molecule for APR. However, it is mainly used in reagent grade, therefore the corresponding results will not be reported in the present work since out of the scope. Far more interesting in this context is understanding the effect of the impurities (methanol,

soap, salts) which are present in crude glycerol.

Lehnert and Claus compared for the first time the performance of pharma grade glycerol and crude glycerol on Pt catalyst and ascribed the decrease of the hydrogen production to the blocking of the active sites caused by inorganic salts [77]. The rate of hydrogen production at the steady state was 7.6 mmol/min·g_{cat} for pure glycerol whereas it was 1 mmol/min·g_{cat} for crude glycerol. In Fig. 5-A the difference in the hydrogen content between pharma grade and crude glycerol is reported.

Remon et al. studied the effect of acetic acid (up to 3 wt.%), potassium hydroxide (up to 2.8 wt.%) and methanol (up to 5 wt.%) at 220 °C using a Ni-La/Al_2O_3 catalyst [78]. The influence of one, two and three impurities on the glycerol conversion, carbon distribution, gas and liquid composition was systematically evaluated. Acetic acid decreased the carbon conversion to gas without affecting the glycerol conversion; potassium hydroxide increased the carbon conversion to gas, as well as the hydrogen concentration in the gas phase; methanol decreased the glycerol conversion. When the impurities were present in binary or ternary mixtures, neutralization and esterification could occur. Finally, acidic conditions promoted Ni and La leaching, whereas basic conditions favored Al leaching.

The influence of acidic and basic impurities have been further investigated in [79]. The acid impurities were acetic acid, sulfuric acid and phosphoric acid: these may be found due to the neutralization step; the basic impurities were potassium hydroxide and sodium hydroxide, since they may be used as catalyst during the transesterification for the biodiesel production. The authors reported that the impurities did not affect the catalytic performance (i.e. carbon conversion to gas or liquid or solid) during the first hour of experiment. However, they did deactivate the catalyst eventually, mainly via fouling/poisoning and leaching mechanisms. The latter was independent by the type of present impurities, confirming that leaching depended just on the pH of the solution (which was maintained constant in the experimental campaign at 7). Carbon deposition was negligible (less than 0.28 mg C/g catalyst). K deposition could help S and P deposition thanks to the higher electron deficiency of the catalyst, contributing to its deactivation. Furthermore, the type of acid and base influenced the alumina transition into boehmite. In the presence of KOH, the lowest transition was observed with H_3PO_4; in the presence of NaOH, it was the lowest with H_2SO_4. Unfortunately, no comparison with pure glycerol was reported in the work.

The effect of NaCl was studied in [80]. The authors reported that 1.25 wt.% NaCl did not affect the gas and liquid product distribution, but decreased the conversion to liquid products, using a silica-alumina supported nickel catalyst.

Finally, it is important to highlight that the support of the catalytic system plays a key role on the resistance to the impurities. Boga et al. observed a drastic decrease of the hydrogen selectivity moving from a pure 6.85 wt.% glycerol solution (64 % selectivity) to a crude glycerol solution constituted by glycerol, soaps, methanol and ester (1% selectivity) [81]. However, active carbon support maintained the performance similarly to the case of pure glycerol (Fig. 5-B). The separate investigation of the contaminants allowed to identify sodium oleate as the most dangerous one, due to its irreversible adsorption. In this sense, the use of activated carbon able to adsorb selectively the fatty acid improved the hydrogen selectivity from 1 to 18 %.

6. Perspectives: towards industrial APR application

To the best of our knowledge, only one commercial demonstration of the APR process is currently active, the BioForming Technology by Virent Energy Systems Co. in cooperation with several partners [82]. This plant has not the objective of producing hydrogen as main product; instead, it aims at the production of drop-in hydrocarbons from sugar-based aqueous solution.

The aim of this paragraph is to evaluate the possibility that an APR unit for hydrogen production can be integrated in an existing plant, comparing the results obtained with other technologies reported in literature, when available.

In Table 5 a summary of the wastewater mentioned in the review with their main difficulties and advantages regarding the APR application is presented. This table could be considered an initial screening for suitable APR substrates. That is, once an aqueous fraction is present in a plant, some characteristics could make it more appropriate than others for APR reaction.

First of all, higher organic content is favorable. This can be trivial in most of the cases; however, attention should be put in the case of sugar-laden water fractions, where homogeneous reactions can drastically reduce the hydrogen yield. Most of the investigated aqueous streams are really diluted, and only crude glycerol from biodiesel production and cheese whey from dairy industries present concentration higher than 5 wt.%. Looking at the composition, mono and polyalcohols, together with hydroxyacids should be favored, thanks to the presence of a C:OH moiety in the molecule, which can be activated producing hydrogen via dehydrogenation and water gas shift of the intermediate CO. Carboxylic

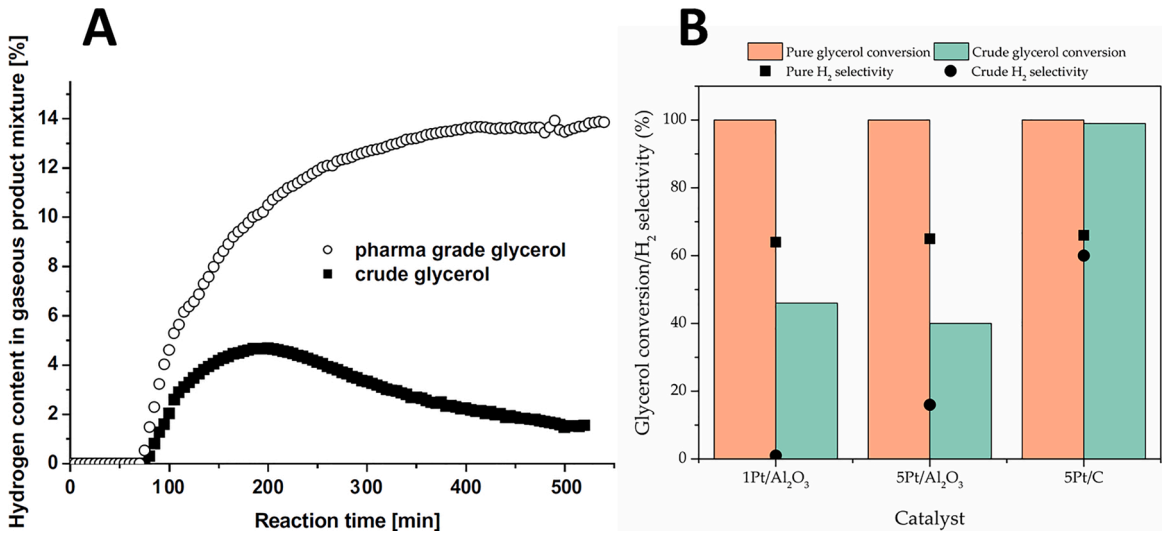


Fig. 5. A: Influence of glycerol grade on the hydrogen content in the gaseous stream, reaction conditions: 250 °C/20 bar, 10 wt.% glycerol, flow rate 0.5 mL/min, 0.3 g catalyst (Reproduced with permission from [77]). B: Influence of catalyst on APR of pure and crude glycerol, reaction conditions: 225 °C/29 bar, 3 h, 0.3 g catalyst (data from [81]).

Table 5
Summary of wastewater sources with corresponding characteristics, advantages and disadvantages in the field of APR.

Sources	Main characteristics	Main difficulties	Main advantages	Ref
Biodiesel production	0.1 kg crude glycerol/kg biodiesel 68.5-80 wt.% glycerol, 1-20 wt.% methanol, 0-5 wt.% sodium chloride, 1.5-14 wt.% water, 2-16.2 wt.% soaps 9 kg cheese whey/kg cheese COD: 50-102 kg/m^3	Inorganic salt Soaps Dilution is typically performed before APR Char formation/ Humin deposition due to salts presence	High concentration of the substrate High hydrogen yield thanks to the optimal C: OH ratio	[81, 83]
Dairy	4.5-6 wt.% lactose, 0.6-1.1 wt.% protein, 0.8-1 wt.% minerals, 93-94 wt.% water, fats and lactic acid below 1 wt.%		High concentration of lactose in the wastewater	[4, 72]
Brewery	3-10 L/L beer TOC 2000 mg C/L COD 6200 mg C/L 1000 mg/L malt extract, 500 mg/L yeast extract, 150 mg/L peptone, 860 mg/L maltose, 1000 mg/L ammonium sulfate, 2.8 mL/L ethanol	Carbonaceous deposits on the catalyst Diluted water fraction	High removal of TOC and COD, with production of hydrogen and alkanes	[67]
Hydrothermal liquefaction	10-50% of initial feedstock carbon ends up in the aqueous phase TOC 5000-20000 mg C/L 0.65-1.74 wt.% glycolic acid, 0.36-1.08 wt.% acetic acid, 0.073-0.46 wt.% methanol, others (ketones, aromatics etc.)	Phenolic oligomers deposition Competitive adsorption of carboxylic acids Diluted water fraction	Methanol, glycerol and glycolic acid presence improved the H_2 production Possible coupling HTL-APR for biocrude upgrading	[54, 56, 59]
Fischer-Tropsch	TOC 5000-10400 mg C/L C1-C5 alcohols and corresponding carboxylic acids	Scarce conversion of carboxylic acids Diluted water fraction	Alcohol are the main compounds so high hydrogen yield is obtained COD reduction up to 90%	[58, 62]
Carbohydrate processing	TOC: 5000-18000 mg C/L C5-C6 sugars	Humins deposition	With pre-hydrogenation step high H_2 production and TOC reduction is obtained	[33, 45]

acids are usually recalcitrant and with higher tendency to alkane formation. Ketones and aromatics are very stable compounds at the typical APR conditions, showing negligible conversion.

Preliminary process design studies were performed for APR [84,85]. They highlighted that no external heat can be provided if the gaseous alkanes by-products are used as fuel. Moreover, the facility may be located close to pulp mills for a stand-alone green diesel production plant where small-scale methane steam reformers would be not economically attractive [84]. This points out the possible synergy between two technologies. An important issue derived from the cost of the feedstock is also arose. Sladkovskiy et al. simulated a 500 kg/h hydrogen plant from sorbitol to satisfy the need of a 100,000 T/y green diesel plant [85]. With the current cost of sorbitol syrup, the hydrogen production costs would be seven times higher than the actual one with conventional technologies (roughly 13 $/kg vs 2 $/kg), and the feedstock would account from about 92 % of the total production cost [85]. For this reason, the use of waste or readily available feedstocks seems pivotal for its application at the industrial scale. In this sense, APR was applied to waste water fractions associated to the valorization of municipal waste [86–88], or in the treatment of sludge for reuse purpose thanks to the removal of micro-pollutants such as ibuprofen and caffeine [89].

The possibility to use the hydrogen directly in situ is the best condition for the applicability of APR combined with biorefineries or industries producing water.

Besides stand-alone options, the integration with other facilities should be foreseen, especially in the case where the aqueous stream is particularly diluted. These refer not only to the one cited regarding the upgrade of intermediate biofuels [90,91]. For example, the integration with dimethyl ether production, where its exothermicity may be coupled with the endothermicity of the reforming reaction, which in turn produces the syngas necessary for DME [92]. Another possibility is the use of the hydrogen *in situ* to produce other chemicals like methane [93] or deoxygenate fatty acids [94].

A comparison of APR performance with other technologies can be mentioned. Looking at the brewery wastewater, about 294 mL H_2/g COD was obtained with APR, while it was 150 mL H_2/g COD for the anaerobic digestion [95]. A techno-economic assessment compared hydrogen produced by glycerol reforming in aqueous and gaseous phase (80 kg/h size) [96]. The investigation estimated 3.65 $/kg cost production from glycerol steam reforming and 3.55 $/kg for glycerol APR. These values are comparable or even lower than other renewable hydrogen routes, such as biomass gasification (1.77–2.05 $/kg), dark fermentation (2.57 $/kg), solar thermal electrolysis (5.10–10.49 $/kg) [97].

The carbohydrate to hydrogen technologies have been recently reviewed in [29]. This research showed that the APR hydrogen yield (mol H_2/mol glucose) is comparable or higher than other technologies like anaerobic fermentation, photo-fermentation, electrohydrogenesis and ethanol partial oxidation reforming.

In view of the possible use of APR to industrial contexts, some important issues should be investigated and solved.

The characterization of the complex aqueous stream is often lacking. Nevertheless, it is necessary to identify the most suitable treatment and/or catalytic system. For example, microporous supports should be avoided in the case of large molecules in the feed, while they can be used when small organics (alcohols, carboxylic acids) are present, so that the dispersion of the active phase is maximized.

Lange depicted some catalytic performance criteria that should be targeted by biorefineries to reach the industrial scale, such as selectivity, activity, catalyst consumption and product concentration [98]: it is worth trying to understand where APR is in this pathway to industrialization. Industrial catalyst activity ranges from 0.1–1000 tons of product per ton of catalyst per hour. Despite it is not rigorous to adopt this criterion for batch reactors, we can roughly evaluate if APR is within this range. Looking at the results reported in [30], it can be estimated that the catalytic activity would be equal to 0.09 tons of hydrogen per ton of

catalyst per hour, and 0.27 in the case of glucose. Regarding the catalyst consumption, it is reported that it should be disposed after having produced product by an extent at least 1000–100,000 times higher than its mass. No such extended runs are available for APR and even short tests showed important deactivation phenomena such as poisoning and fouling. Most of the experiments were carried out in batch reactors, which prevented from studying the catalyst deactivation. This is the real hurdle to the use of noble metals; deactivation issues are often moderate for model compounds, but inevitably appear moving to actual streams.

As it commonly happens in the conventional industrial chemistry, pretreatments to clean the feed should be adopted when noble metals are used. Proper pre-treatment of the aqueous phase may be envisioned, involving the removal of large macromolecules which may poison the catalyst. Some examples were already reported, such as pre-hydrogenation of sugars to corresponding sugar alcohols, or liquid-liquid extraction/adsorption of the aromatics in HTL-derived water. In addition, apart from the cited works with crude glycerol, limited information on the effect of inorganic impurities such as sulfur and phosphorous were reported by the literature ([49,65]).

Most of the cited works used noble metal catalysts. In our survey, only Ni-based catalysts were reported as alternatives ([4,32,40,62]). Cheaper catalyst formulations would be necessary to increase the cost-effectiveness of the process. Furthermore, the addition of promoters able to facilitate the adsorption of carboxylic acids should be investigated, since the observed competitivity with other classes of compounds limited the organic abatement of the wastewater.

One final comment should be reserved to the effluent of the APR reactor. It has been reported that the conversion level does not affect the hydrogen selectivity in the case of methanol and ethylene glycol [24]. For real streams, Remon et al. showed that changing the space velocity can have different effects depending also on the reaction temperature and substrate concentration [4]. According to Murzin and coworkers, the pressure swing adsorption (PSA) may be the most efficient method to purify the gas products derived from APR, which is characterized by high hydrogen recovery (85–95 %) and low pressure-drop for the purified gas [85]. Apart from the gas phase, the liquid effluent should be carefully checked. In the ideal case, the TOC and COD removal should be sufficient to meet the environmental legislation. If it is not the case, further treatments or recycle loops should be proposed. In view of a possible industrial implementation of APR, also these rarely cited practical implications (downstream processing such as hydrogen separation from gas mixtures, regulatory COD and BOD levels) should be verified.

7. Conclusions

Biorefineries aim at zero-waste production processes, with small carbon and water footprints. Aqueous phase reforming can play a strong role in the technological integration necessary for the development of the so-called circular economy. Food processing industries, lignocellulosic biomass processing and biodiesel productions generate significant amount of carbon-laden water side-streams which can be valorized via APR into a hydrogen-rich gas phase. The experimental results presented in this review pointed out the research effort into the application of this technology to real or synthetic mixtures mimicking the complexity of actual wastewater.

The exploitation of lignocellulosic biomass through various processes (hydrolysis, hydrothermal liquefaction, pyrolysis) resulted in water fractions where different classes of oxygenated hydrocarbons are present: carboxylic acids, alcohols, ketones, aromatics, sugars. When subjected to APR, each of these classes had a different tendency for the hydrogen production. Moreover, the behavior of the mixtures is not linear compared with the single compounds, highlighting severe competitive adsorption issues on the catalyst. Food processing industries came out with considerable amount of wastewater, being in some cases one order of magnitude higher than the mass flowrate of the desired product. APR could be able of managing the variability in the organic and inorganic load, at the same time converting the organic content into a gas with a moderate heating value. In fact, due to the high presence of organic acids, APR was not able in this case to rich high hydrogen content in the gas phase. Finally, APR of crude glycerol was reported, highlighting that the presence of impurities such as inorganics and fatty acids could strongly affect the catalyst stability. In this sense, the development of suitable supports or alternative configurations (such as guard inert beds) might contribute to the maintenance of the performance.

Aqueous phase reforming is still at the infant stage in view of its application for wastewater treatment and valorization. However, further investigation on the exploitation of waste biomass, catalyst stability, synergy with other hydrogen demanding processes (e.g. upgrading of bio-oil or green diesel) will support the advancement of an effective and low-cost technology able to contribute to the sustainable development.

CRediT authorship contribution statement

Giulia Zoppi: Writing - Original Draft & Review. **Giuseppe Pipitone:** Writing - Original Draft and Review. **Raffaele Pirone:** Supervision. **Samir Bensaid:** Review, Supervision, Project administration. All: Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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