

Review

A Short Overview on the Hydrogen Production Via Aqueous Phase Reforming (APR) of Cellulose, C6-C5 Sugars and Polyols

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Abstract: The use of lignocellulosic biomasses for the production of renewable hydrogen is surely among the hot-topic research tasks. In this review, we report on the recent advances in the catalytic conversion of cellulose and its derived C6-C5 sugars (glucose, fructose, and xylose) and polyols (sorbitol and xylitol) into hydrogen via aqueous phase reforming (APR) reactions. The APR processes are considered to be new sustainable catalytic routes for converting the carbohydrate fraction of biomasses into hydrogen at milder reaction conditions if compared with the traditional reforming reactions. Particular emphasis is given to the development of new and active catalysts and to the optimization of reaction conditions that aimed to maximize hydrogen production with a low concentration of CO avoiding, at the same time, the formation of alkanes.

Keywords: aqueous phase reforming (APR); hydrogen; renewable energy; lignocellulosic biomasses; cellulose; sugars; glucose; xylose; fructose; polyols; sorbitol; xylitol

1. Introduction

Nowadays, with the depletion of fossil fuels, increasing interest has been attributed to the development of more sustainable routes that are based on the use of renewables to obtain energy, chemicals and fuels [1–5] in line with the 7th principle of Green Chemistry, proposed by Anastas and Warner in the 1990s [6]. In this context, the use of lignocellulosic biomasses has increased over the years and it already represents a sector of enormous value for the chemical industry. An interesting example of the appeal of this topic and the potential economic interest involved is the development of the process regarding the synthesis of polyethylene furanoate (PEF) from sugars-based plants [7]. This bio-based polymer is expected to progressively replace polyethylene terephthalate (PET) for soft drink bottles production and many important companies have already invested or planned to realize this strategy (e.g., Coca-Cola, Ford Moto, Heinz, Nike, and P&G) [8].

Hydrogen is one of the major energy vectors that, at present, is mainly produced from fossil-derived feedstocks; however, it could be obtained from renewables with applications in several technologies. During the last decades, the growing production of biodiesel has driven attention on the possibility to use glycerol (the mayor co-product of the biodiesel manufacturing), as starting material for H₂

production through reforming processes (both aqueous phase reforming (APR) and steam reforming (SR)) [9].

With an annual availability of several thousands of million dry tons worldwide (1,3 only in the US) [10], lignocellulosic biomasses are considered to be the only practical alternative feedstock to fossil fuels for the sustainable production of chemicals and hydrogen [11,12]. Biomasses are composed by three main biopolymers, such as cellulose (from 40 to 50 wt.%), hemicellulose (25–35 wt.%), and lignin (15–20 wt.%), as sketched in Figure 1 [13]. The intrinsic complexity of this raw material and the variability of the feedstock compositions obstacle its valorization at full potential. Indeed, several processes have been proposed to produce renewable fuels and hydrogen from biomasses, namely:

- (i) pyrolysis under inert atmosphere, working in a temperature range between 400 and 800 °C and the consequent valorization of the bio-oil fraction produced by reforming processes [14];
- (ii) biomass gasification in order to produce syngas, working at temperature higher than 800 °C, in the presence of a suitable catalyst and gasification agents [15]
- (iii) catalytic partial oxidation [16];
- (iv) photocatalytic reforming [17];
- (v) aqueous phase reforming (APR) [16];
- (vi) catalytic transfer hydrogenation/hydrogenolysis [18,19].

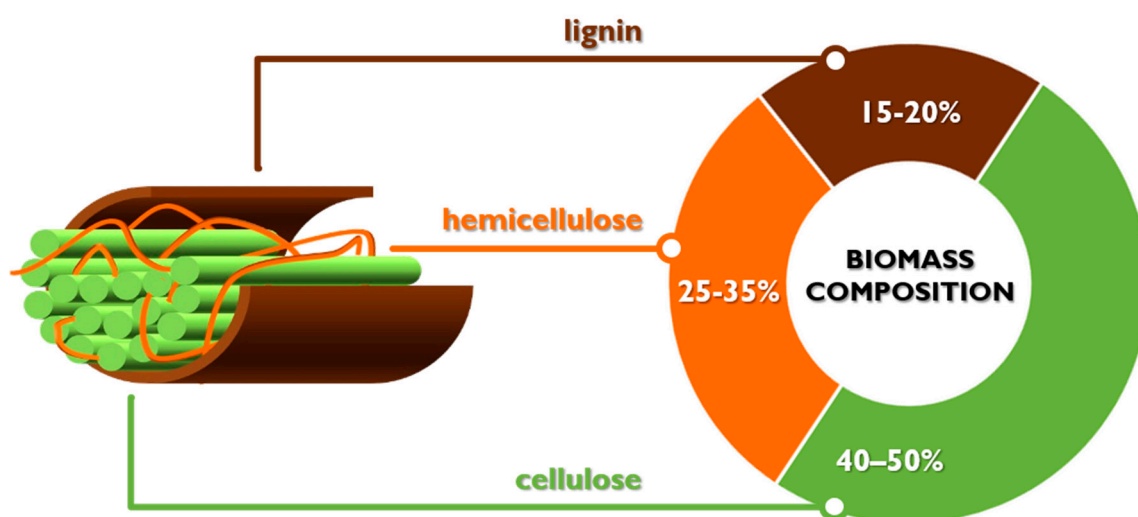
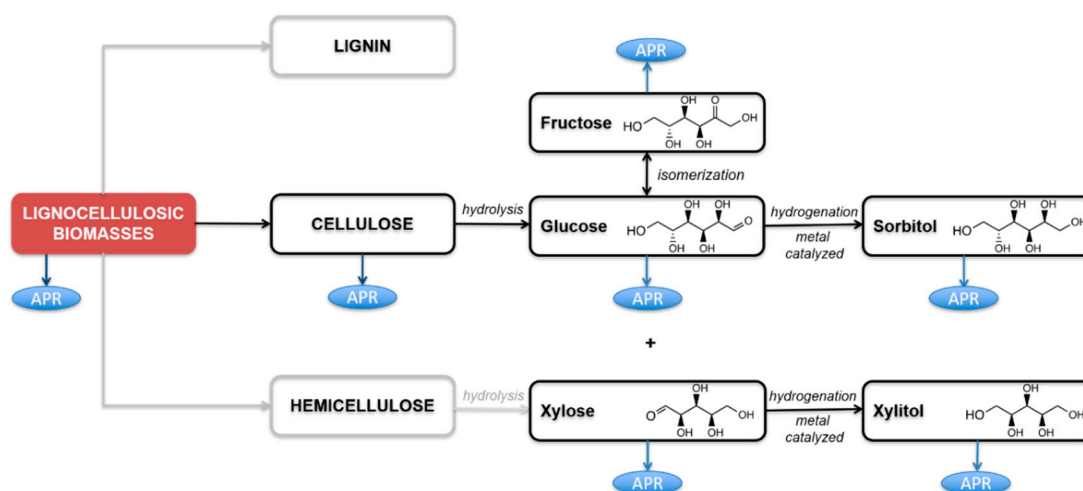


Figure 1. General composition of lignocellulosic biomasses.

The APR of lignocellulosic biomass (or derived bio-platform molecules) represents a suitable and efficient alternative for the hydrogen production, since this process takes place in relatively mild conditions (200–250 °C) and it is compatible with water-soluble or wet feedstocks. Most important, very little energy supply is necessary to carry out APR reactions and pressures, generally adopted in APR processes, lead to a very low amount of CO [16]. However, in APR reactions, the methanation of CO₂ as well as the production of alkanes and alcohols, are competitive processes that lower the overall H₂ yield [16,20]. Indeed, the reaction can take place in a single step, working with aqueous solutions in the presence of a catalyst.

APR processes are also strongly influenced by the choice of the starting raw material and they may differ from both the catalytic system and the reaction conditions applied. For this reason, several different strategies will be discussed in detail in the following sections. The direct production of H₂ from lignocellulosic biomasses feedstocks is surely among the most important challenge of future biorefinery; however, at present, this approach is yet poorly investigated due to the intrinsic complexity of cellulose and hemicellulose fractions. For this reason, in most studies presented in the last years, their derived sugars (mainly glucose and fructose) and polyols (e.g., sorbitol and xylitol) were used

as the starting substrates for APR processes. Scheme 1 reports a simplified scheme of the main transformations of lignocellulosic biomass derivatives and the most investigated starting materials to produce hydrogen through the APR process.



Scheme 1. Lignocellulosic biomass average composition and valorization processes, namely hydrolysis, hydrogenation, and Aqueous Phase Reforming (APR).

In this review, the catalytic conversion of lignocellulosic biomass-derived compounds to obtain H_2 will be considered with a bottom up approach starting from C6 and C5 polyols, namely sorbitol and xylitol, to finally address the cellulose, with the aim of unraveling the reactivity and selectivity, and understanding the overall reactions that are involved through APR processes. The state of the art of the recently investigated reaction pathways involved in hydrogen production will be discussed in detail with a special focus on the improvements made in the last years in the design of both the reaction conditions and the catalytic systems, which have ensured both high conversion of the substrates and enhanced selectivity to H_2 .

2. From Polyols to Cellulose: Unravelling all Sustainable Catalytic Routes in the H_2 Production Via Aqueous Phase Reforming (APR) Reactions

2.1. Aqueous Phase Reforming of C5 and C6 Polyols

Cellulose can be easily deconstructed through acid/reductive hydrolysis into C6-C5 sugars that can be further hydrogenated into the related C6 and C5 polyols, namely sorbitol and xylitol. In the last ten years, huge efforts have been made in the investigation and development of suitable catalysts for the valorization of sorbitol and xylitol into hydrogen and fuels.

At the same reaction conditions and applied catalytic system, the products distribution is strictly related to the chemical structure of the feed molecules. For instance, the increasing of polyol size generally leads to a consecutive decrease of hydrogen production, which fosters the light alkanes selectivity [21,22]. Additionally, for this reason, an impressive amount of work has been performed in the investigation of the APR of the simplest polyol, ethylene glycol (EG), and its higher, bio-based analogue, glycerol [9,21,23]. Figure 2, (adapted from Scopus[®]), shows the number of the peer review manuscripts containing the keywords “X aqueous phase reforming” (with X = methanol, ethanol, ethylene glycol, glycerol, sorbitol etc. . . .) in the abstract, keywords, and titles published over a twenty years range. The data reported in Figure 2 clearly show the huge amount of work that has been done in the investigation of the reforming of C1-C3 compounds. In particular, EG and glycerol have both been widely investigated in the literature as starting material for the production of H_2 [21,22,24–27].

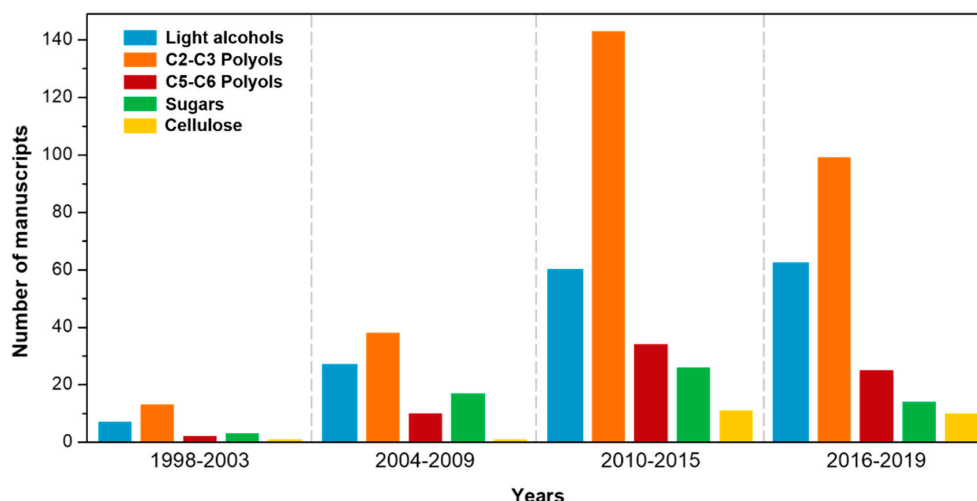
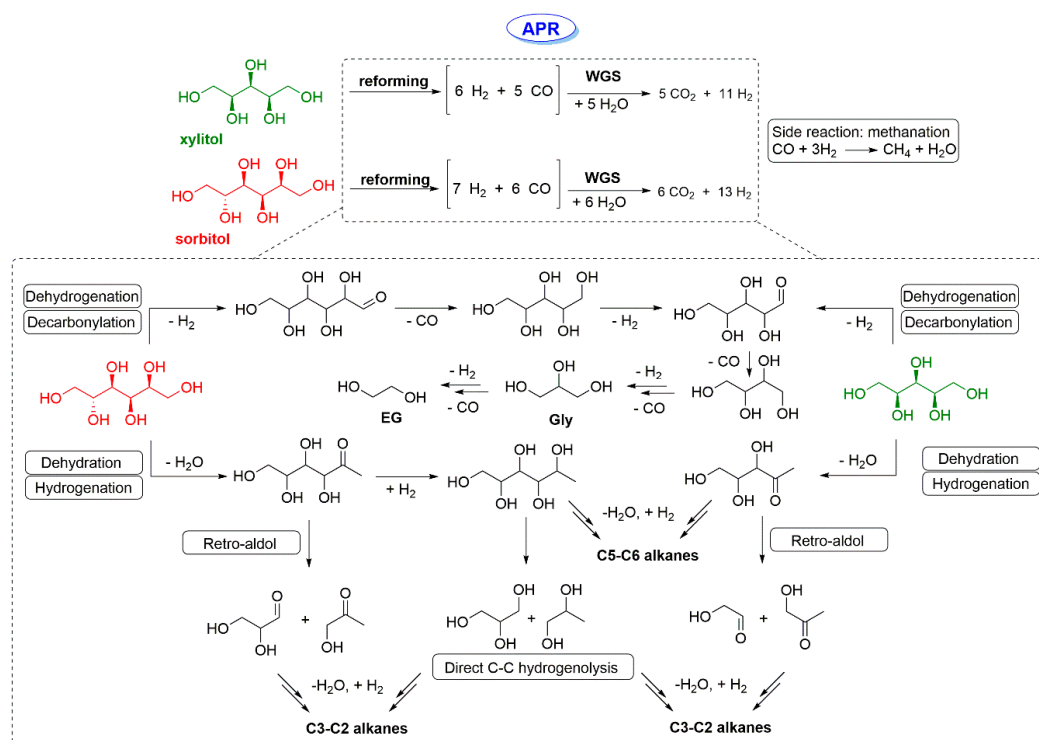


Figure 2. Trend of the peer review manuscripts containing “X aqueous phase reforming” in abstract, keywords, and title from 1998 to 2019. X = methanol and ethanol (combined as “light alcohols”), EG and glycerol (combined in “C2-C3 polyols”), xylitol and sorbitol (combined in “C5-C6 polyols”), glucose, fructose and xylose (combined in “Sugars”) and cellulose. Adapted from Scopus® [accessed on Oct 4, 2019].

Nevertheless, the reforming of sugars-derived polyols, namely sorbitol and xylitol (C6 and C5 respectively), which are directly derived from lignocellulosic biomass (both from cellulose and hemicellulose hydrolysis and hydrogenation), are of great relevance and they have been investigated in literature in the last decade being included in the list of the 12 most promising renewable bio-derived platform molecules. Despite the complex reactions pathways that can operate on these substrates, a careful tuning of the catalyst properties can effectively boost the production of hydrogen, disfavoring the formation of both liquid products (namely, shorter alcohols or polyols, ketones, and acids) and light alkanes (C5-C1). Scheme 2 show a scheme of this pathway.



Scheme 2. Possible reaction pathways occurring in aqueous phase reforming (APR) of polyols, namely sorbitol (C6) and xylitol (C5) [28,29].

From an accurate analysis of scientific papers, a few important considerations can be underlined. The reactions are generally carried out under continuous flow conditions with hydrogen being produced in relatively good yields (20–40%) while using mono metallic (mainly Pt) based catalysts, in which the most investigated supports are well designed mesoporous carbon materials (e.g., Sibunit type, three dimensional bimodal carbons, activated carbons etc.) [28,30,31]. Alumina represents definitely the other most investigated support for both monometallic [29,32,33] and bimetallic or other way modified Pt-based catalyst [34–36].

Table 1 summarizes the main results that were obtained in the reforming of sugar-derived polyols.

Both kinetics and mechanism investigations have been performed to compare the sorbitol and the xylitol reactivity. Higher hydrogen yield and selectivity (83%) can be obtained in the case of xylitol, but with an incomplete conversion (ca. 66%). The reaction mechanism goes through the dehydrogenation/dehydration of the polyols leading to formation of the corresponding aldehydes, which undergo decarbonylation to obtain shorter but more reactive polyols intermediates that are ready to be reformed in a similar way [37,38]. When the reaction is performed in the presence of hydrogen (from 20 to 40 bar), both Pt or Ni catalysts supported on more acidic supports (e.g., H-ZSM-5 or mesoporous nanosilicas MCM-22), are able to promote a very selective synthesis of alkanes. In particular, 2 wt.% Ni/MCM-22 leads to the formation of pentane starting from xylitol with a yield higher than 90% at 240 °C; while Pt-based catalysts lead to the formation of mixtures of pentane and shorter chain alkanes [39,40]. It is noteworthy that production of alkanes can be boosted by the addition of Re. Indeed, bimetallic Pt-Re catalysts, supported over alumina or titania, have been proved to promote the formation of light alkanes (mainly propane, ethane, and methane), starting from xylitol or sorbitol [30,35]. This is probably due to the ReO_x particles, dispersed over Pt, which favour the adsorption of the polyols and the selective hydrogenolysis of C–O bonds.

Table 1. Results of aqueous phase reforming of different polyols.

Polyols	Cat.	T (°C)	P (bar)	Conv.	H ₂ Yield (%)	Ref.	Notes
Sorbitol *	7 wt.% Pt/3D-BMC-12	250	45	-	28	[31]	Continuous flow, WHSV = 2 h ⁻¹ .
Sorbitol *	7 wt.% Pt/2D-CMK-3	250	45	-	9	[31]	Continuous flow, WHSV = 2 h ⁻¹ .
Sorbitol *	6 wt.% Pt-Fe (1:3)/CMK-9	250	45	-	23	[34]	Continuous flow, WHSV = 2 h ⁻¹ .
Sorbitol **	2.8%Pt/Al ₂ O ₃	225	29	61	21	[29]	Continuous flow, WHSV = 1.2 h ⁻¹ .
Xylitol *	6 wt.%Pt-Fe (1:3)/CMK-9	250	45	-	30	[34]	Continuous flow, WHSV = 2 h ⁻¹ .
Xylitol *	2.5%Pt/C	225	29	80		[28]	Continuous flow, WHSV = 2 h ⁻¹ .
Xylitol *	2.5%Pt-Re/C	225	29	100		[30]	Continuous flow, WHSV = 2 h ⁻¹ .
Xylitol *	8%Pt-Re/TiO ₂	225	29	91		[35]	Continuous flow, WHSV = 3.6 h ⁻¹ .
Xylitol **	2.8%Pt/Al ₂ O ₃	225	29	79	26	[29]	Continuous flow, WHSV = 1.2 h ⁻¹ .
Xylitol*	5%Pt/Al ₂ O ₃	225	29	66	33	[37]	Continuous flow, WHSV = 1.8 h ⁻¹ .

Conv.: Conversion; Sel.: Selectivity; * Concentration of the feed: 100 g/L; ** Concentration of the feed: 1 g/L.

Techno-economic analyses have been performed to check the feasibility of the APR of sorbitol on an industrial scale. Interestingly, sorbitol current market price (650 \$/t in 2018) is the major contributor for the out-stream hydrogen cost (ca. 13 \$/kg). For this reason, the most feasible way to make the APR economical sustainable is the production of polyols from lignocellulosic biomass, instead of the first generation sugars, finally lowering the price of the raw materials [41].

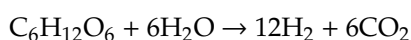
It is noteworthy that few authors reported so far the possibility to perform a two-step process in which a sugars solution (particularly glucose) is firstly hydrogenated over Ru/C or Pt/Al₂O₃ in order to obtain a mixture of sorbitol and mannitol, which is successively reformed in a second reactor that is filled

with Pt/C or Pt/Al₂O₃ catalyst. H₂, in the gaseous mixture (reformate), can be purified and separated from CO₂ by pressure-swing adsorption or using specific membranes [42–45]. The production of CO is strongly limited by the water gas shift (WGS) reaction, which is favored by both the APR conditions (aqueous phase, temperature applied) and catalyst used. In this way, highly pure hydrogen, suitable for fuel cells, is produced. This approach has been used in both a semi-continuous and continuous flow conditions, by recycling part of the produced hydrogen to sustain the first hydrogenation step [46,47].

2.2. Aqueous Phase Reforming of Sugars

Glucose is the most abundant monosaccharide that is present in nature [48,49] and it represents an ideal raw material for hydrogen production through APR, especially because it is already produced in aqueous stream, which can be directly treated, reducing the need of separation steps. On the other hand, fructose is far less common in nature and, therefore, it is more expensive and less employed [50].

Aqueous phase reforming of glucose can be generally expressed with the following equation:



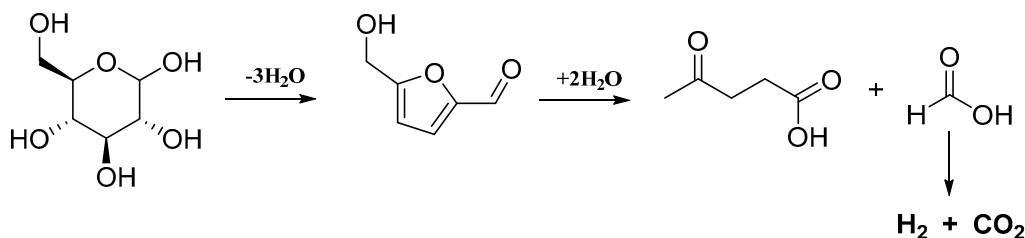
This is not a direct reaction and a wide plethora of intermediates are formed during the pathway from reagents to products. Moreover, other reaction pathways, which lead to different side products, can occur. The hydrogenation of carbon dioxide or carbon monoxide and the hydrogenolysis of polyols can lead to the formation of light alkanes, while dehydration reactions would lead to ketones and aldehydes, which generally afford a detrimental effect in both hydrogen selectivity and carbon balance (Schemes 2 and 3). Thus, catalyst's features and properties have to be carefully tuned to drive the selectivity of the overall process. In particular, a good catalyst should be able to break C-C, C-H, and O-H bonds, while preserving the C-O bonds, which favors the production of CO [51]. Moreover, it must be active in the water gas shift reaction (WGS), using the excess of water to enrich the hydrogen content and convert carbon monoxide to carbon dioxide. For these reasons, Ni is often used as active phase due to both its C-C cleavage properties and its relative low price. Noble metals are also used, especially Pt, which generally provides higher activity and selectivity when compared to Ni. In addition, the identification of the proper conditions for glucose APR is challenging due to spontaneous glucose homogeneous side reactions that occur at high temperature (e.g., retro aldol and aldol condensations) [52]. A computational investigation shows that the C-C bonds of glucose are adsorbed on Pt to a maximum extent at 200 °C [53]. On the opposite, the unwanted C-O cleavage would be favoured over the preferred C-C at lower temperatures [47]. Different authors have focused their attention on the development of appropriate catalysts, as selectivity is an open issue in glucose APR.

Guodong et al. studied the aqueous phase reforming of glucose at 260 °C, while using a Ni based catalyst that was impregnated on Al₂O₃ through two different impregnation procedures and with different Ni content [54]. A two-step impregnation procedure provides better results than the classical impregnation method. The hydrogen selectivity and yield increase together with the Ni content of the catalyst, reaching the values of 46% and 15%, respectively, at the highest Ni content (48 wt.%). Glucose conversion reaches the 95% value, although the carbon conversion to gas products is only 32.6%, which indicates that different products are solved in the liquid phase or absorbed over the catalytic surface. In fact, liquid phase contains several products, such as propanal, acetone, 2-butanone, ethanol, 1-propanol, cyclopentanone, 1-pentanol, 3-pentanol, 2,5-hexanedione, 2,3-dimethylcyclopentenone, 5-ethylidihydro-2-furanone, and phenol, while 34% of the initial carbon is deposited over the catalyst. Hydrogen production is hindered in the first stages of the reaction when higher concentrations of glucose are present, while the reforming reaction dominates at longer reaction times. Finally, Ni oxidation is also observed and it contributes to catalyst deactivation, together with the formation of solid products cited above.

Taccardi et al. employed an ionic liquid able to easily dissolve the carbohydrates, but it is characterized by a low hydrogen solubility, in order to increase the selectivity and to reduce hydrogen

consuming reactions [55]. This allows for the formation of gaseous stream enriched in both CO₂ and hydrogen.

Moreover, an isotopic labelling study was carried out indicating that glucose first dehydrates to HMF, followed by the formation of levulinic and formic acid (Scheme 3). Only the latter is then selectively decomposed to hydrogen and carbon dioxide.



Scheme 3. Mechanism of hydrogen production from glucose through a dehydration-hydrolysis pathway. Adapted with permission from [55]. Copyright Royal Society of Chemistry, 1999.

Noble metals can be used to favour the selectivity towards the desired reaction pathway. Pt is able to provide higher C-C cleavage rather than that of the C-O one, as reported by Tanksale et al., who studied the glucose APR on Pt/Al₂O₃ at temperatures that ranged between 180 °C and 220 °C [56]. In fact, Pt is also reported to provide higher hydrogen production rates from glucose (and sorbitol) than Pd and Ni active phases [56–58]. In addition, Pt has also been employed by Meryemoglu et al. while using carbon supports with different size distribution [59]. In particular, authors show that it is advisable to employ catalysts with a narrow particle size distribution. This in fact increases both hydrogen selectivity and productivity. However, the Pt/C catalyst shows that, at low reaction temperature (140 °C), the conversion of glucose to gas products is negligible and higher temperatures (200 °C) are needed to increase this value to 9% [60]. Nevertheless, Pt is a promising active phase for the aqueous phase reforming of glucose, even though its cost might reduce the employment on large scale. However, Pt and Pd, doping the Ni active phase, show that the C-C cleavage selectivity and hydrogen production are increased, even when low amounts of noble metals are used [61].

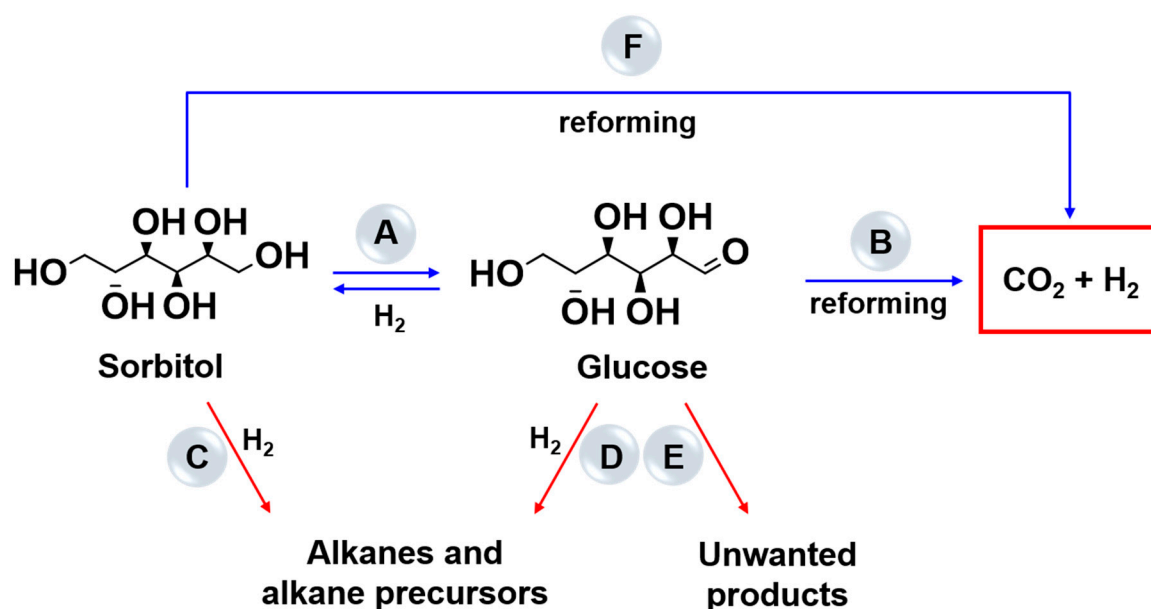
The support choice plays an important role in the APR reaction due to the large amounts of pathways that are involved, which can be favoured or hindered by non-innocent supports. Alumina and modified zirconia, possessing an acidic character, were tested. The latter was able to provide higher hydrogen yields at the beginning of the reaction, but boosted the unwanted dehydration pathway as reaction proceeded [61].

It is worth underlining that hydrogen production by glucose APR is lower than that can be obtained with other feedstocks [47,62]. This is caused mainly by spontaneous reactions such as isomerization, followed by decomposition or polymerization [52], and by hydrogenation reactions favoured by the catalyst itself, which consumes hydrogen, leading to alkane formation. In fact, hydrogenation reactions are favoured when using glucose with respect to other simpler feedstocks and, a decrease in hydrogen selectivity and a parallel increase in alkanes formation are observed in the case of glucose, with respect to methanol, ethylene glycol, and sorbitol [22]. Although this limits, hydrogen production from glucose, it can be used to obtain hydrocarbons. For instance, the Fischer-Tropsch reaction is observed in glucose APR, leading to hydrogen depletion and alkane formation and it is favoured by acid sites [47].

A problem that derives from glucose hydrogen and alkane production is the occurrence of homogeneous side reactions [52]. Different solutions have been employed to reduce the occurring of undesired side reactions and to increase the hydrogen productivity [22]. This results in improved hydrogen selectivity. However, the use of a diluted glucose fraction is not industrially viable due to the low productivity and the costs that are related to the reactor dimension.

The formation of a target intermediate can be pursued to facilitate the reforming reaction. Sorbitol can be easily obtained from glucose hydrogenation [63–67] and then directly reformed in the aqueous phase reforming process [47]. Thus, the use of a dual-reactor system has also been proposed [21].

This involves the presence of a low temperature hydrogenation reactor, followed by a reforming reactor, operating at a higher temperature. In fact, glucose hydrogenation has a lower activation barrier than glucose reforming and decomposition. For this reason, the formation of sorbitol is highly selective and it occurs at low temperature in the presence of relatively low hydrogen pressures [47]. Sorbitol aqueous phase reforming is more favoured than the glucose one. In fact, a study on 10%wt glucose/sorbitol feed has been carried out while co-feeding nitrogen or hydrogen at 265 °C [47]. It was found that the selectivity toward hydrogen was much higher for sorbitol (60%) than for glucose (13%). On the opposite, higher alkanes selectivity is observed for glucose. Thus, glucose is not selectively converted to sorbitol when hydrogen is fed in the APR conditions. However, if a pre-hydrogenation at 120 °C is used in the dual-reactor setup, high hydrogen selectivity (62%) is observed in the APR step at 265 °C. Finally, undesired reactions regarding organic oxygenated or carbonaceous compounds can occur [52]. These are first order on glucose and they are thermally activated without the need of a catalyst [47]. Furthermore, low concentration of glucose or the preliminary hydrogenation of glucose to sorbitol are needed to reduce the extent of parasite reactions [47]. In general, the rates of B, D and E reactions are favoured at high temperature with respect to that of A (Scheme 4) [47].



Scheme 4. Possible reactions involved in glucose and sorbitol reforming. Desired and undesired pathways are highlighted in blue and red respectively. Adapted with permission from [47]. Copyright Royal Society of Chemistry, 2003

The presence of undesired homogeneous reactions of glucose in the aqueous phase in the range of temperature normally applied for its APR (220–265 °C) limits the hydrogen selectivity and forces lowering the feed concentration (usually 1–3 wt.%). These aspects are crucial for the hydrogen productivity of the overall process and decisively limit its industrial potentials. Thus, more efforts have to be done in both catalyst and reactor design in order to make the APR of glucose feasible on an industrial scale [22,54]. Further research has to be carried out to make aqueous phase reforming of glucose competitive, with particular attention to hydrogen selectivity, catalyst stability, and to reduction of side products.

Fructose and sucrose have been also considered as starting materials for this process. Table 2 lists the performances of different catalysts in the APR of glucose, fructose, and sucrose.

Tanksale et al. studied the aqueous phase reforming of sucrose and that of a glucose-fructose mixture over different metal supported catalysts [56,57]. In particular, Pt, Pd, and Ni were impregnated over different non-innocent metal oxides, such as γ -Al₂O₃, ZrO₂, CeO₂, and Ce-Al mixed oxides. Interestingly, hydrogen is effectively produced at relatively low temperature (185–220 °C) and moderate

pressure (28 bar of inert gas). Increasing the temperature favors the initial hydrogen rate formation. The observed catalytic activity follows the order Pt > Pd > Ni, thanks to the enhanced C-C cleavage ability of the noble metals. Regarding the support choice, γ -Al₂O₃ provides the best results in terms of hydrogen production. Authors suggest that this behavior is related to the higher Bronsted acidity of γ -Al₂O₃ when compared to that of ZrO₂, CeO₂, and Ce-Al mixed oxides [68]. However, the catalyst deactivation is observed after only 3 h at 220 °C (due to formation of hydrogenated species, such as aromatic ethers and C₅-C₆ esters) and limits its use at the industrial scale. Thus, catalyst deactivation, due to deposition of heavy carbonaceous (coke-like) compounds, remains an open issue.

Table 2. Results of aqueous phase reforming of different sugars.

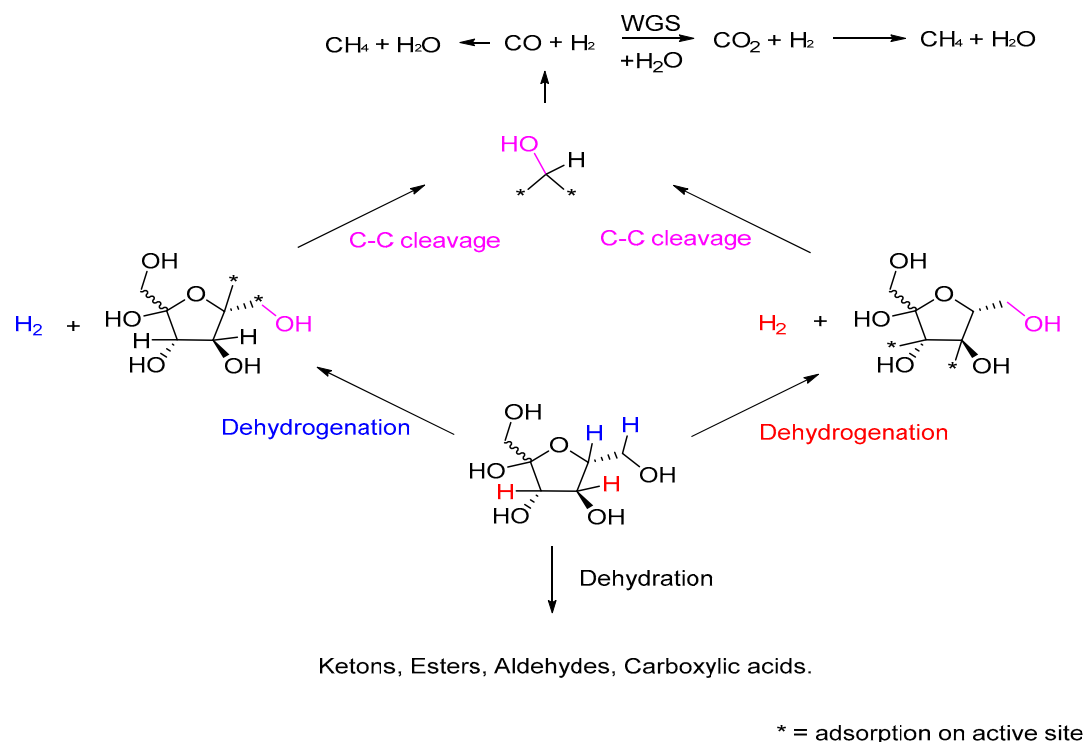
Sugar	Catalyst	T (°C)	Conv. (%)	Sel. H ₂ (%)	Ref.	Notes
Glucose	Ni48wt%/Al ₂ O ₃	260	95	46	[54]	Conv. to gas = 33% **
Fructose	Pt3%/Al ₂ O ₃	200		2.3 *	[56]	-
Glucose	Pt3%/Al ₂ O ₃	200		0.4 *	[56]	-
Sucrose	Pt3%/Al ₂ O ₃	200		0.6 *	[56]	-
Glucose-Fructose mix.	Pt3%/Al ₂ O ₃	200		1.3 *	[56]	-
Glucose	Pt3%/C	250	83		[60]	Conv. to gas = 9% **
Glucose	Ni/Al ₂ O ₃	200		0.2 *	[61]	after 3 h
Glucose	Ni/Zr ₂ O	200		0.3 *	[61]	after 3 h
Glucose	Ni/Al ₂ O ₃	200		0.2 *	[61]	after 9 h
Glucose	Ni/Zr ₂ O	200		0.1 *	[61]	after 9 h
Glucose	Pt/Al ₂ O ₃	310	93	63	[47]	Dual reactor
Glucose	Pt/Al ₂ O ₃	310	96	11	[47]	1 reactor with H ₂ atm
Glucose	Pt/Al ₂ O ₃	310	93	13	[47]	1 reactor with N ₂ atm

Sel.: Selectivity; * expressed as hydrogen production rate (mL/min); ** Conversion to gas expresses to percentage of glucose that has been transformed in gaseous products.

Fructose aqueous phase reforming was also investigated [56]. The results show that the initial rate of hydrogen formation, in a batch reactor, increases with the operative temperature. However, a decline in hydrogen production is observed at high temperature after 4–5 h, due to the formation of carbonaceous materials over the catalyst. A mechanism for the fructose reforming was proposed (Scheme 5). At first, the fructose dehydrogenation occurs on the metal surface, followed by the cleavage of C-C adsorbed bonds, to give adsorbed CH-OH groups. Their further dehydrogenation leads to CO and H₂ production. However, the methanation reaction, which giving water and methane, is also possible in the course of this step (thus consuming hydrogen). For this reason, an active phase that leads to a high selectivity toward the WGS reaction and a low one for methanation must be selected. Fructose can also undergo C-C cleavage to give adsorbed CH-OH and acetic acid, with consecutive hydrogen production. In the absence of a C-C cleavage catalyst, fructose can undergo an undesired C-O cleavage followed by hydrogenation on weak acid sites to give ketones and esters, which are difficult to further reform [69].

Sucrose APR was also investigated and its performances were compared to those that were obtained with mixtures of fructose and glucose [56]. It was shown that sucrose provides a lower hydrogen formation rate than the mixture of the two carbohydrates, which suggests that it is desirable to firstly break down sucrose into two molecules of fructose and glucose to enhance the hydrogen production.

Thus, hydrogen can be also produced from fructose and sucrose in the presence of a suitable catalyst. However, the employment of fructose, as precursor, for the valuable hydroxymethyl furfural (HMF), might hinder its application in the aqueous phase reforming.



Scheme 5. Mechanism of fructose APR as proposed by [56]. Desired and undesired pathways are highlighted in blue and red respectively.

2.3. Direct Production of H₂ from Cellulose and Lignocellulosic Biomasses Via APR

Valenzuela et al. reported the very first example of APR starting from the actual woody biomass in 2006 [70]. In this work, the depolymerization of both the lignin and the cellulose fraction of the southern pine sawdust was promoted by the acid catalyzed hydrolysis using H₂SO₄ followed by the reforming of the soluble smaller products over a Pt/Al₂O₃ catalyst in an one-pot two-step process. In this way, hydrogen is obtained (as a minor product in the gas phase) around 18 vol%, while the major light product is CO₂. Indeed, the CO content is dramatically reduced due to the facilitated water gas shift (WGS) reaction that was promoted by Pt in the conditions tested. Further investigations were performed by changing the raw material, in particular on studying the hydrolysis and the APR of the lignin fraction of lignocellulosic biomass (ranging from raft, soda, and alcell lignin along with sugarcane bagasse) with Pt/Al₂O₃ (and H₂SO₄ as co-catalyst), at low temperatures (225 °C) and pressures (29 bar of He) in a semi-batch reactor [71]. In the optimized conditions, aromatic platform molecules, such as guaiacol, syringol, and other similar products, are obtained as well as hydrogen and other light gases (mainly CO₂). The formation of the incondensable light compounds is ascribed to the hydrolysis of the methoxy functionality of the phenolics that were obtained from the lignin deconstruction, which leads to the in situ-production of methanol, which is readily reformed to produce hydrogen and carbon dioxide. A few years later, Erbaturo et al. reported the two-step valorization of wheat straw through the hydrolysis and the consequent APR of the hydrolysates solution. Although the first step is performed at very harsh conditions (250 °C and 276 bar), working with supercritical CO₂ and near supercritical water, authors prove the feasibility of the APR of the hydrolysates mixture. Indeed, the soluble polysaccharide fraction can be reformed with relatively good hydrogen selectivity (ranging from 55 to 70 mol% of the gaseous stream) at 250 °C. Again, Pt shows the best catalytic activity, followed by Ru and Pd, and activated carbon is the preferred support for increasing the dispersion of the metal nanoparticles (5%wt metal/C) [72]. These works represent the very few examples of the direct APR of actual lignocellulosic biomass. This is probably ascribable to factors that are related to the presence of strong mineral acids in the aqueous phase (necessary for the hydrolysis step), which lead to the leaching of the active noble metal in the solution, finally limiting the recyclability of the

catalysts and the industrial feasibility of the entire procedures (e.g., the problem related to reactor corrosion and low productivity).

The direct APR of cellulose (the major component of the lignocellulosic biomass) toward the production of hydrogen and/or alkanes is an attractive approach. Several cellulose feedstocks have been selected for the investigations and each of them differs from the others by the average degree of polymerization (DP). In particular, degreased cotton (DP ca. 1200), filter paper (DP ca. 500), and microcrystalline cellulose (DP ca. 200) are often taken into consideration as suitable raw materials.

A pioneering contribution in this field is ascribable to both G. Wen and Z. Tian et al. In their works, the direct APR of cellulose was investigated over different heterogeneous catalysts [73,74].

A wide range of noble metals, namely Pt, Pd, Ir (5 wt.%), and transition metals Ni and Co (20 wt.%) supported over carbon have been tested and found to be active for the target reaction at 260 °C, at autogenous pressure. These metals show different catalytic activity, in the cellulose reforming, in the order Pt > Pd > Ir \approx Co > Ni, as well as in the hydrogen selectivity: Pt > Ni > Pd \approx Co > Ir. Among them, Pt gives the best catalytic performances with the highest conversion of carbon to gas (ca. 70%) and hydrogen selectivity (ca 40%) at complete cellulose conversion, due to the Pt high selectivity toward the C-C bond cleavage [73].

Although the high catalyst loading (50 wt.% with respect to the dry cellulose), Pt/C has been proved to be recyclable without any leaching of the active phase in the solution, but with only a slight increase of the metal nanoparticles size. When considering these promising results, further investigations have been made by working with bimetallic metal catalysts supported over activated carbon (e.g., Pt-Ru/AC). However, no considerable improvements have been observed as compared to the previously reported results [75].

Some efforts are made for the development of cheaper and active catalysts that are based on transition metals, particularly Ni. In 1998, Minowa et al. investigated the APR of microcrystalline cellulose at different temperatures (from 200 to 350 °C) over different, highly loaded, Ni supported catalysts (50 wt.% nickel supported on silica, alumina, silica-alumina, and magnesia) [76]. However, low hydrogen production was reported due to Ni methanation activity, affording methane from CO₂ and H₂. Having observed that the gas production is not correlated to the catalyst's surface area, the authors suggest that only the Ni particles on the outer surface contribute to glucose conversion.

On the other hand, in 2011 Wen et al. reported an innovative cerium modified bulk Nickel Raney catalyst that allows for obtaining comparable results to those of Pt-based materials in the cellulose APR [74].

Recently, hydrotalcite has been considered as a precursor for the synthesis of layered double oxides, in which Ni particles are located on the surface in a narrow distribution and form abundant Ni-support interfacial interactions. The authors report a H₂ yield of 31% after four hours of reaction at 260 °C and claim a good catalyst stability due to the basic features of the support, able to inhibit the Ni leaching [77].

In all of the papers reported so far, glucose was proved to be the key intermediate for the APR of cellulose. Interestingly, no acid co-catalysts are added to the reaction mixture, which demonstrates that cellulose hydrolysis toward the formation of glucose is the rate-determining step, probably catalyzed by the H⁺ produced from the water self-ionization at temperature higher than 200 °C [78]. The slow cellulose hydrolysis allows for limiting glucose concentration in the solution finally reducing undesired side reactions. In this way, cellulose APR allows for obtaining comparable results with those that were obtained in the APR of sorbitol as well as a significant increase in hydrogen selectivity, when compared to that of glucose APR.

Noteworthy, both catalyst supports (e.g., Al₂O₃ or Fe₃O₄) and physical pretreatments (e.g., ball milling, steam explosion, sonification etc.), can be used to promote cellulose hydrolysis and reduce the crystallinity of the raw material, respectively, finally favoring the accessibility of the substrate and enhancing the kinetics [79,80].

3. Conclusions

Aqueous phase reforming reactions are surely one of the most promising core-processes in the catalytic conversion of lignocellulosic biomasses into H₂. The reactions are generally performed, under both batch and continuous flow conditions, at relative mild reaction conditions (temperature range: 200–300 °C, pressure range: 15–50 bar) that allow for obtaining high hydrogen purity.

In this survey, we show that APR processes are strongly affected by the nature of the feedstock used as well from the reaction conditions adopted. H₂ can be obtained in good yield by using xylitol and sorbitol as starting materials, while, at present, glucose and cellulose were found to be by far less efficient. Prolonged reaction/resident time as well as higher temperatures lower hydrogen selectivity increasing methane and alkanes production.

In the last years, huge progress has been attained in the development of heterogeneous catalysts that are able to promote APR of cellulose, sugars, and polyols. Generally, heterogeneous monometallic and bimetallic catalysts based on Pt and Ni metals supported on carbon or alumina supports have been efficiently used in APR reactions. However, catalyst deactivation, as well as mass transport limitations, represent important constraints for the use of aqueous-phase reforming reactions at industrial scale. Furthermore, techno-economic studies that are able to evaluate the potential scale-up of these processes represent an area of great interest in a future perspective.

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