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Aqueous phase reforming of sugar-based biorefinery streams: from the simplicity of model compounds to the complexity of real feeds

Giuseppe Pipitone[a], Giulia Zoppi[a], Alessandra Frattini[b], Sergio Bocchini[c], Raffaele Pirone[a], Samir Bensaid[a,*]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129, Turin, Italy
[b] Biochemtex SpA, Grp Mossi & Ghisolfi, Str Savonesa 9, I-15050 Rivalta Scrivia, AL, Italy
[c] Istituto Italiano di Tecnologia (IIT), Corso Trento, 21, 10129 Torino, Italy

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ABSTRACT

Glucose, xylose and corresponding sugar alcohols (sorbitol and xylitol) have been subjected to aqueous phase reforming for the production of hydrogen as representative compounds of hemicellulose. The aim of the investigation was to explore new valorization pathways for pentoses sugars, nowadays still not effectively exploited. A developmental platinum-based catalyst supported on carbon was used to perform the reaction in a batch system. The influence of temperature and carbon concentration were investigated in the 230–270 °C and 0.3–1.8 wt.% range, respectively. Moving towards the exploitation of a biorefinery side-stream, wheat straw hydrolysate was subjected to the same reaction conditions. A hydrogenation step was used as pre-treatment to selectively convert the sugars to their corresponding sugar alcohols, and a net hydrogen production was obtained. Deactivation phenomena were investigated during the APR of sugars reusing the catalyst after the reaction. The characterization of the spent catalysts through TGA-IR allowed to confirm the presence of superficial organic deposits responsible for the lack of the catalyst stability.

1. Introduction

Biomass is a strategic raw material for the sustainable production of energy and chemicals being the only renewable source of organic carbon on the planet. Lignocellulosic biomass is the most abundant biomass and, for this reason, it plays a key role to replace fossil oil [1]. It is constituted by approximately 50% cellulose, 30% hemicellulose, with the remaining being mostly lignin. Cellulose is a highly ordered homopolymer of β-linked glucose; hemicellulose is an amorphous polymer containing typically five different C5-C6 sugars; lignin is a complex three-dimensional phenolic polymer.

The interest in lignocellulosic biomass is increasing thanks to the possibility to consider it as a feed to produce bioethanol. Indeed, it offers several advantages compared to the first generation-based bioethanol (mainly from edible sugarcane or corn): lignocellulosic biomass is often a waste, it can be found at low price, and it does not raise ethical dilemmas, being not in overlap with the food chain [2]. Bioethanol production consists of several steps: briefly, it begins with the pre-treatments necessary to destroy the complex linkage between cellulose, hemicellulose and lignin. Afterwards, the carbohydrates are subjected to hydrolysis (enzyme- or acid-catalyzed) leading to a mixture of simple sugars (hydrolysate). Finally, the hydrolysate is later fermented by dedicated yeasts or bacteria producing ethanol, which is ultimately distilled and purified [3].

In order to ensure the economic sustainability of a process based on biomass, the utilization of each component of the feed should be maximized. The lignin is mainly used to generate electricity, even if many efforts are put in valorizing the lignin coproduct by conversion to biofuels and/or commodity chemicals [4].

Despite their utilization in the fermentation step, the hemicellulose-derived sugars are not effectively exploited, as *S. cerevisiae* yeasts are unable to utilize pentoses [5]. For this reason, a lot of effort has been put in the modification of the conventional strains to allow them also the fermentation of the pentoses [6]; anyway, the efficient exploitation of these sugars is still ongoing. Studying the most effective way to separate the hemicellulose from the other fractions in a bioethanol plant is also an important research theme, necessary to taking advantage of the entire organic content [7].

Butanol is an option as product from the hemicellulose fraction, used, for example, as drop-in biofuel. Lessard et al. valorized the C5 sugars producing high octane oxygenates blended in the gasoline pool [8]. Another alternative is pentoses fermentation to lactic acid by using

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* Corresponding author.
E-mail address: samir.bensaid@polito.it (S. Bensaid).

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Lactobacillus plantarum [9]. Furthermore, furfural synthesis is one of the most interesting path as it would lead to a sustainable way to produce an important intermediate for solvent, plastics, fuel additives etc. [10].

Moreover, it has been proposed to utilize the xyloses to produce biohydrogen, namely through dark fermentation [11]. A potentially relevant route for hydrogen production starting from a carbohydrate source, alternative to biologically based conversion pathways, is the aqueous phase reforming (APR). It is a catalytic reaction carried out at lower temperatures than the conventional steam reforming (473–553 K), enabling higher energy efficiency, leading to a hydrogen-rich gas mixture as main product, according to the reaction reported in Eq. (1) [12].

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

Dumesic and co-workers proposed this process and, since their pioneering works, the research has focused on this topic because of its potentiality to manage diluted aqueous wastes to obtain a valuable product [13]. Among the several possible molecules of interest, sorbitol (i.e. glucose's corresponding sugar alcohol) has been thoroughly studied as model compound for APR [14–22], while xylitol (the xylose's corresponding sugar alcohol) has been studied with less extent [17,23–26]. Moreover, apart from the first works, glucose has been poorly investigated, possibly due to the low thermal stability and hydrogen production compared to the corresponding alcohol [12,27,28]. Meryemoglu et al. performed the wheat straw hydrolysis, followed by APR of the derived solution with precious (Pt, Pd, Ru) and non-precious catalysts (Ni Raney), with platinum showing the best results among the former ones, and Ni reporting the highest hydrogen production [29]. Surprisingly, to the best of our knowledge, xylose has never been subjected to APR.

For this reason, in this work we evaluated for the first time the production of hydrogen from xylose, the most abundant C5 sugar in hemicellulose, therefore seen as representative compound of a biorefinery stream (i.e. pentoses sugars) not yet well valorized, following the scheme reported in Fig. 1. In the scheme it is assumed to follow the pretreatments necessary to maximize the recovery of the hemicellulose fraction, as reported in [5]. Afterwards, the C6 sugars can be effectively converted to bioethanol through fermentation using conventional yeasts, while the C5 sugars can be addressed to aqueous phase reforming. A systematic approach was used globally to evaluate the influence of temperature and concentration on the reforming of glucose, xylose and corresponding sugar alcohols. Moreover, we subjected to APR a stream from a bioethanol plant after the hydrolysis step (from here on referred as hydrolysate). A model mixture glucose-xylose, imitating the composition of the hydrolysate, has been tested as well. As it is known from literature, and reported here, the sugar alcohols are more prone to hydrogen production [30]. For this reason, we compared the performance obtained with the sugar mixture with a sorbitol-xylitol solution. A two-step process hydrogenation-APR was studied in order to evaluate if a total positive production of hydrogen was obtained; this scheme has been investigated for the hydrolysate as well. Finally, a study on the reuse of the catalyst and its characterization has been carried out, looking for deeper information on the solid phase obtained during the reaction.

2. Materials and methods

2.1. Materials

Glucose, xylose, sorbitol and xylitol were purchased from Sigma Aldrich and used as received. Deionized water was obtained in laboratory. A developmental 5 wt.% Pt/C catalyst was provided by Johnson Matthey for APR experiments and a 5% Ru/C commercial catalyst was purchased from Sigma Aldrich for hydrogenation tests. Two tests performed using pre-reduced catalysts showed analogous outcomes to the ones performed with the untreated catalysts. For this reason, the results reported in this manuscript were obtained with the catalysts used as received, without any pretreatments.

Biomass hydrolysate coming from wheat straw pretreated with PROESA technology was kindly provided by Beta Renewable S.p.A.

2.2. Aqueous phase reforming test

The APR tests were conducted in a 300 mL 4560 series mini bench top reactor (Parr) equipped with a 4848-model reactor controller (Parr). A 75 mL aqueous solution with the required carbon concentration was prepared and 0.375 g of 5% Pt/C were added. The reactor was purged with nitrogen and then pressurized at 0.3 MPa. The stirring rate was fixed at 400 rpm. The reaction time was fixed at 2 h, starting when the set temperature was reached. The internal cooling loop and an external water bath quenched the reaction at the desired reaction time; the gas phase was collected in a syringe and analyzed by μGC. The liquid product was recovered from the reactor and filtered by gravity to remove the catalyst; then it was subjected to TOC and HPLC analysis. The spent catalyst was dried in an oven at 105 °C overnight, recovered and weighted. When reuse tests were performed, the catalyst was used as such (named spent catalyst), without any further treatment after the drying step.

2.3. Hydrogenation test

The hydrogenation tests were conducted in a 300 mL Berghof reactor equipped with a gas-induced stirrer. A 75 mL aqueous solution was prepared with the desired carbon concentration; at a later time, 0.188 g of 5% Ru/C were added. The reactor was purged with nitrogen and then pressurized with hydrogen at the desired pressure (either 15 or 25 bar), plus 1 bar of nitrogen as internal standard for the following gas analysis. The stirring rate was fixed at 600 rpm and the reaction time at 1 h, starting when the set temperature (140 °C) was reached. The temperature was decided according to the literature available for sugar hydrogenation [31–33] and from exploratory screening in our laboratory not reported in this work. An external ice water bath quenched the reaction at the desired time. The analysis of the products was performed in analogy with the procedure followed in the aqueous phase reforming test.

2.4. Analytical methods

The methods for the characterization of the products were focused both on the gas and liquid phase. The gas phase was analyzed by an SRA Micro-GC, equipped with Molsieve 5A and PoraPLOT U columns,

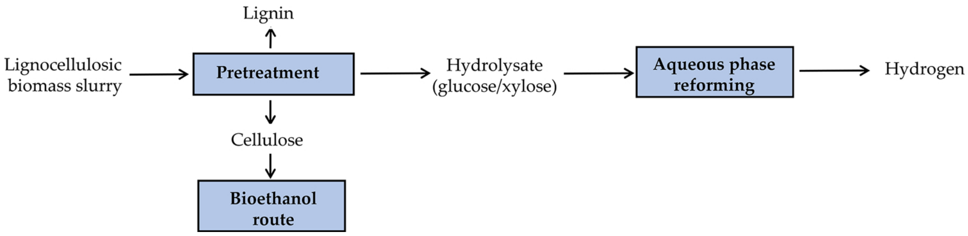

Fig. 1. Block-flow diagram of a bioethanol plant with valorization of the C5 sugars via APR.

Table 1
Characterization of the wheat straw hydrolysate.

TOC (mgC/L)	Monosaccharides (wt.%)		Inorganics (ppm)		
	Glucose	Xylose	Na	K	Ca
42400	5.3	2.2	3585	504	351

with a TCD detector.

HPLC analysis (Shimadzu) was performed with a Rezex ROA-Organic acid H^+ (8%) column (300 mm * 7.8 mm). The mobile phase was 5 mM H_2SO_4 in water. The flow rate was fixed at 0.7 mL/min and the temperature of the column at 50 °C. The products were determined by means of a refractive index detector (RID).

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

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

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

TGA-FT-IR analyses were performed using a TG 209 F1 by NETZSCH Thermal Analysis. Approximately 10 mg of sample in alumina pans were heated from 30 to 1000 °C (20 °C/min) under pure nitrogen (20 ml/min). The system was coupled by a Netzsch-TGA-IR coupling line to a Bruker Tensor II spectrophotometer equipped with DTGS detector and a Bruker heated gas chamber analysis accessory. The CO_2, CO, CH_4, H_2O and carbonyl groups were followed by analyzing respectively the 2359, 2173, 3011, 1503 and 1726 cm^{-1} respectively.

ATR FT-IR spectroscopic measurements were performed without any further process using a Bruker Tensor II spectrophotometer equipped with DTGS detector and single-reflection Bruker Platinum ATR accessory with the diamond crystal. All the spectra were recorded at a resolution of 2 cm^{-1}, 32 scans in the spectral range 3800–600 cm^{-1}.

To estimate the performance of the process five parameters were used (based on the frequently used ones in literature). The carbon conversion to gas *CtoG*, defined as the ratio between the moles of carbon in the gas product $mol_{fin}C_{gas}$ and the moles of carbon in the feed $mol_{in}C_{feed}$ (Eq. (2)); the APR hydrogen yield $APR\text{-}Y_{H2}$, defined as the ratio between the moles of produced hydrogen in the gas phase mol_{fin} H_2 and the moles of feed (it is highlighted here that (y + n) is added accordingly with the reactions stoichiometry to reach a maximum 100% hydrogen yield) (Eq. (3)); the hydrogen gas distribution GD_{H2}, defined as the ratio between the moles of hydrogen present in the gas phase as molecular hydrogen (mol_{fin} H_2) after the reaction and the moles of total hydrogen present in the final gas phase (that is, also as alkanes) (Eq. (4)); the APR H_2 selectivity $APR\text{-}S_{H2}$ defined as the ratio between the moles of hydrogen and carbon dioxide in the final gas phase $(H_2/CO_2)_{fin}$, divided by the theoretical ratio $(H_2/CO_2)_{theor}$ according to the reaction stoichiometry reported in the Eq. (1) (Eq. (5)).

$$\mathrm{CtoG}\ (\%) = 100^{*}\frac{\mathrm{mol_{fin}\ C_{gas}}}{\mathrm{mol_{in}\ C_{feedstock}}} \tag{2}$$

$$\mathrm{APR} - \mathrm{Y_{H_2}}\ (\%) = 100^{*}\frac{\mathrm{mol_{fin}\ H_2}}{(\ \mathrm{y}+\ \mathrm{n})^{*}\mathrm{mol_{in}\ feedstock}} \tag{3}$$

$$\mathrm{GD_{H_2}}\ (\%) = 100^{*}\frac{\mathrm{mol_{fin}\ H_2}}{\mathrm{mol_{fin}(H_2 + 2^{*}CH_4 + 3^{*}C_2H_6 + 4^{*}C_3H_8)}} \tag{4}$$

$$\mathrm{APR} - \mathrm{S_{H_2}}\ (\%) = 100^{*}\frac{\mathrm{mol(H_2/CO_2)_{fin}}}{\mathrm{mol(H_2/CO_2)_{theor}}} \tag{5}$$

Regarding the hydrogenation reactions, we defined the conversion of the feed (glucose and xylose) as the ratio between the reacted and the starting moles (Eq. (6)); the yield was defined as the ratio between the moles of product and the starting moles of the feed (Eq. (7)). As an example

$$\mathrm{Conversion_{glucose}}(\%) = 100^{*}\frac{\mathrm{mol_{in}glucose} - \mathrm{mol_{fin}glucose}}{\mathrm{mol_{in}glucose}} \tag{6}$$

$$\mathrm{Yield_{sorbitol}}(\%) = 100^{*}\frac{\mathrm{mol_{fin}sorbitol}}{\mathrm{mol_{in}glucose} + \mathrm{mol_{in}xylose}} \tag{7}$$

3. Results and discussion

3.1. Characterization of the hydrolysate

Wheat straw hydrolysate was kindly furnished by Beta Renewable S.p.A. In the following Table 1, its characterization is reported. The pretreated biomass with PROESA technology generally provides an aqueous solution with the following composition (ranges according to pretreatment operating conditions): glucose 50–75 g/kg, xylose 20–30 g/kg, arabinose 0.7–1.5 g/kg, glycerol < 0.3 g/kg, formic acid 0.5–1.2 g/kg, lactic acid < 0.5 g/kg, acetic acid 1.8–2.5 g/kg, 5-HMF < 0.2 g/kg, furfural < 0.3 g/kg. Oligomers of the above-mentioned might be present. The pH of the solution was around 5.1.

In the present research work, the main characterized monosaccharides were glucose and xylose, as reported in Table 1, whose concentration fall in the lower boundary of the formerly presented ranges (5.3 wt.% for glucose and 2.2 wt.% for xylose), being the aqueous solution quite diluted. These values were used to mimic the real hydrolysate in the preparation of synthetic mixtures of the two sugars (as later described), adopting the same relative concentrations of glucose and xylose (70% and 30% respectively).

The TOC of the hydrolysate was 4.24 wt.% (Table 1), of which 70% carbon comes from the contribution glucose + xylose. The remaining 30% carbon may be constituted by the oligomers and it was not identified by HPLC analysis. Other compounds identified by chromatography were present in traces (e.g. acetic acid). Finally, the hydrolysate contained some inorganics, originally present in the biomass (also reported in Table 1).

3.2. Influence of the reaction temperature and carbon concentration

3.2.1. Influence of the reaction temperature on the model compounds APR

In this section, the influence of the reaction temperature in the range 230–270 °C is discussed, working at 0.9 wt.% carbon in the feed.

In Fig. 2, the trend of the indicators is reported for each model compound. Looking at the glucose (2-A), the carbon conversion to gas slightly increased with the temperature, due to an enhancement of the C-C cleavage step that leads to gaseous products. The H_2 gas distribution and APR H_2 selectivity had a steep increase between 250 and 270 °C. This is due to two phenomena: on one side, less alkanes were obtained in the gas phase, leading to an increase of the H_2 gas distribution; on the other side, the H_2/CO_2 ratio increased, leading to a higher APR H_2 selectivity. To the best of our knowledge, only Dumesic and coworkers looked at the influence of temperature on the APR of glucose at 225 and 265 °C [12]. Coherently with Dumesic, there is a positive effect of increasing temperature on the carbon conversion, but different trends in the selectivity were obtained. Nevertheless, it is difficult to perform a direct comparison between the two results because of the differences in the reaction condition. In a previous work where alginate (a model oligosaccharide from the cellular wall of macroalgae) was studied, the increase of the temperature showed

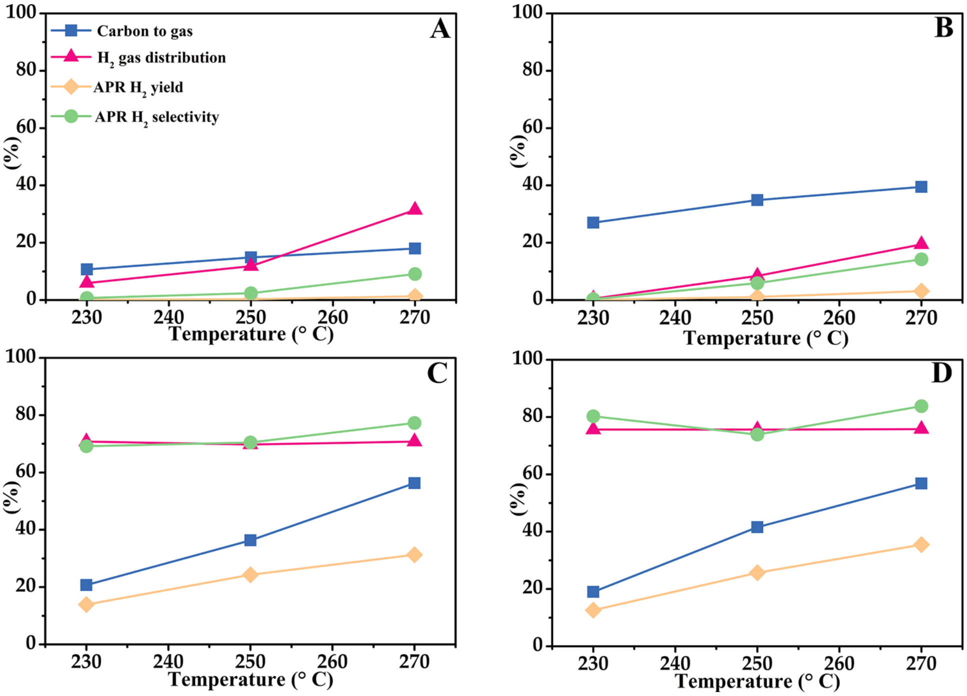

Fig. 2. Influence of temperature on the APR performance of glucose (A), xylose (B), sorbitol (C) and xylitol (D). Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 0.9 wt.% carbon concentration.

similar results, with a slight increase of the carbon conversion to gas and the increase of the selectivity to hydrogen production [34]. The gas phase was mainly constituted by CO_2, at each investigated temperature (from 90% at 230 °C to 75% at 270 °C), despite a strong increase is observed in the hydrogen concentration (Fig. S1). It may indicate that higher temperatures favor the reforming path more than decarboxylation-like reactions. Koklin et al. showed also that, in similar conditions, carbon dioxide is the main component of the gas phase produced by the transformation of glucose in aqueous solution in an inert environment [35].

In the liquid phase, glucose reached complete conversion already at the lowest investigated temperature. Among the by-products, glycolic, acetic and lactic acid decreased their concentration with the increase of temperature. As a result, they contributed to the increase of the conversion to gaseous products, as they are prone to be reformed to produce hydrogen and alkanes [36].mg_C/L

As it is known from literature, sugar decomposes at high temperature in hydrothermal conditions, leading to the formation of a solid residue. The same occurred during the current experimental campaign, which is expected to be the main cause for the lack of carbon required to reach carbon balance closure, if only the contribution of gaseous and liquid organic products is considered. A decreasing tendency to produce a solid residue was observed, going from 255 mg at 230 °C to 170 mg at 250 °C and 150 mg at 270 °C. It is worth being highlighted that these amounts were calculated as the difference between the solid phase recovered after drying and the initial amount of catalyst at the same conditions. This is an important information, as it would complete what is known in literature regarding the production of the solid phase only according to different concentrations. This result is in agreement with the trend of the increasing selectivity at higher temperature, that should favor reforming instead of decarboxylation/decomposition. Further information on the solid phase are reported in the paragraph 3.5, where its effect on the stability of the catalyst is discussed.

Aqueous phase reforming of xylose was investigated in this work for the first time. It had a small increase in the carbon conversion to gas, from 25 to 37%, with a trend similar to the one of glucose, but with relatively higher values. This result may be due to the smaller length of the molecule, that may favor the production of gas more than liquid products. In fact, reducing the molecular weight of the starting compound helps to increase the probability to obtain carbon containing gaseous compounds, enabled by the C—C bond breaking reactions. Looking at the composition of the gas phase, we observed a strong influence of the temperature on the alkane formation, that is reflected in the H_2 gas distribution (Fig. S1–B). In fact, at 230 °C propane was present in high concentration (about 20%), decreasing down to 17% at 250 °C and to 13% at 270 °C. It may be obtained from consecutive decarboxylation reactions that lead to the production of gaseous products other than the expected H_2 and CO_2. Interestingly, the higher the temperature the lower is the production. At first, it may be hypothesized that higher temperature may lead to cracking reactions. On the other hand, methane and ethane did not increase appreciably. Therefore, we may conclude that the increase of the temperature changed the reaction pathways, not favoring the production of alkanes but rather the production of hydrogen (as seen also for glucose previously).

In the liquid phase, one observed that xylose exhibited a considerable conversion already at 230 °C; the HPLC chromatogram showed a pattern similar to the one of glucose. About 60% of the liquid compounds was identified, with hydroxyacetone being to main compound (about 6% of the starting carbon), followed by glycolic and lactic acid (3%) at 230 °C; anyway, their concentration decreased with temperature: at 270 °C the carboxylic acids were the main compounds, i.e. propionic acid (3.5%), acetic acid (2.3%) and butanoic acid (1.9%). The acids may come from the rearrangement of C—O bonds, as happens in the isomerization of poly-alcohols leading to the corresponding carboxylic acid [37].

Sorbitol has been studied in much higher detail in the past, as compared to glucose. It was anyway studied in this work to make a rigorous comparison with its corresponding sugar and similar compounds thanks to the fact that the experimental campaign has been performed in the same set-up, without the influence of many possible variables other than the different reaction conditions whose influence was under investigation.

The carbon conversion to gas moved from 20 to 50%, and the gas composition seemed uninfluenced by the reaction temperature. In fact, contrary to the corresponding sugar, the composition of the gas phase remained constant at each temperature, with H_2 (55%) and CO_2 (35%) as main component. The selectivity of the aqueous phase reforming was not affected as well, therefore the increase of the yield of hydrogen is ascribed substantially to the higher conversion obtained (Fig. S1-C). So, dealing with the sugar alcohol, the increase of the temperature had the effect of increasing the activity, without substantially affecting the selectivity.

Sorbitol converted 50% at 230 °C, 80% at 250 °C and completely at 270 °C. At 270 °C there were many more molecules coming from the feed fragmentation; in this case, in contrast with the glucose, alcohols and poly-alcohols were the main compounds, i.e. propylene glycol, ethylene glycol, ethanol, coming likely from the successive dehydrogenation and C—C bond cleavage of the molecule. It is likely that higher reaction time would have led to higher hydrogen production, as these by products are known to be prone to give hydrogen in the current reaction conditions. This is probably the reason why a decrease in the selectivity was not observed. Indeed, the reaction path lead to the production of beneficial by-products, not recalcitrant to further APR and thus following the reforming pathway, contrary to the case of glucose, where carboxylic acids were obtained. The number of compounds was lower as compared to other works in literature, presumably due to the longer reaction time and higher temperature used in this work. For example, Kirilin et al. reported the identification of hundreds of compounds in the liquid phase, but much fewer by-products were obtained in our reaction conditions [16].

As in the case of sorbitol, xylitol reached about 55% of carbon to gas conversion at 270 °C. The APR hydrogen yield exceeded 30%, higher than the C6 sugar alcohol. The temperature did not affect the gas composition, with hydrogen and carbon dioxide remaining the main gaseous products (Fig. S1-D).

In the liquid phase, xylitol reached 40% of conversion at 230 °C, 80% at 250 °C and complete conversion at 270 °C. Even then, C2, C3 and C4 poly-alcohols were the main liquid by-products.

3.2.2. Influence of the reaction temperature on the hydrolysate APR

The influence of the reaction temperature was evaluated for the hydrolysate looking only to the carbon to gas and the H_2 gas distribution, as the other indicators would need a complete knowledge of its composition to define a reaction stoichiometry (Fig. 3).

It was observed that the temperature had no effect on the carbon to gas conversion: this was unexpected as glucose and xylose alone showed, despite slightly, a clear increase with temperature. One explanation may be given referring to the carbon present in the feed as oligomers, constituting about 30% of the total carbon. Probably this fraction of carbon was not activated in these reaction conditions and does not contribute to the pool of carbon that may go in the gas phase. A confirmation of this hypothesis may come from the results that will be showed in the paragraph 3.3, where a model mixture constituted only by glucose and xylose had results that are totally coherent with the single compounds (i.e. with a slight but evident increase of the carbon conversion to gas with higher temperature). Therefore, as the fraction of carbon that can undergo reforming decreased from the model compounds to the real stream, the small increase of the production of gaseous products could not be observed. Moreover, the influence of pH should be taken into account. Indeed, the lower pH of the hydrolysate feed may have hindered the production of short-chain molecules, reducing the carbon to gas conversion [13]. The hydrogen gas distribution showed an evident increase. In fact, looking at the gas composition, the trend observed agrees with the one reported for the model compounds. This result, that can be ascribed to the glucose/xylose fraction, seems to confirm that higher temperatures are beneficial towards reforming reactions, as compared to side reactions.

3.2.3. Influence of the carbon concentration on the model compounds APR

Being 270 °C the temperature leading to the highest hydrogen production, the influence of the concentration was investigated only at this temperature in the 0.3–1.8 wt.% carbon (i.e. 0.75–4.5 wt.% of the feed).

Glucose reported a dramatic decrease of the performance working at higher concentrations, in terms of carbon conversion to gas, hydrogen selectivity and therefore, globally, on the hydrogen yield (Fig. 4A). This phenomenon can be ascribed to the more favorable homogenous side reactions in contrast to the reforming reactions: as a matter of fact, the former ones have first-order dependence on the feed concentration, while the latter have fractional-order dependence. The gas composition was strongly influenced by the concentration (Fig. S2). Indeed, while hydrogen was present at 40% in the diluted conditions, it reached less than 10% at 1.8% of carbon, with the main compound being CO_2.

At the diluted conditions, the small carboxylic acids were the main compounds (acetic acid, propionic acid). As reported in the previous section, glucose reforming led to the production of a solid phase. It was evident as the weight of the solid phase recovered on the filter after the drying step was higher than the one that may be attributed only to the catalyst. Indeed, it has been recovered up to 770 mg at 1.8 wt.%, 460 mg at 0.9 wt.% and 150 mg at 0.3 wt.% of carbon concentration composed by solid residue and 375 mg of original catalyst.

In analogy with glucose, carbon conversion to gas of xylose decreased from 60% at 0.3 wt.% of carbon to less than 30% at 1.8 wt.%. The gas composition was influenced by the starting concentration as well, as a constant decrease of hydrogen was observed; on the other hand, carbon dioxide increased up to 70%, with 16% also of propane.

In the liquid phase, xylose completely reacted at each concentration. Acetic acid was the main identified liquid product, constituting about 20% of the total carbon identified in the condensed phase.

The solid phase of xylose moved from 80 mg at 0.9% C to 360 mg at 1.8% C (it was not appreciable at 0.3% C): therefore, it is evident that more concentrated solutions favor condensation reactions, producing

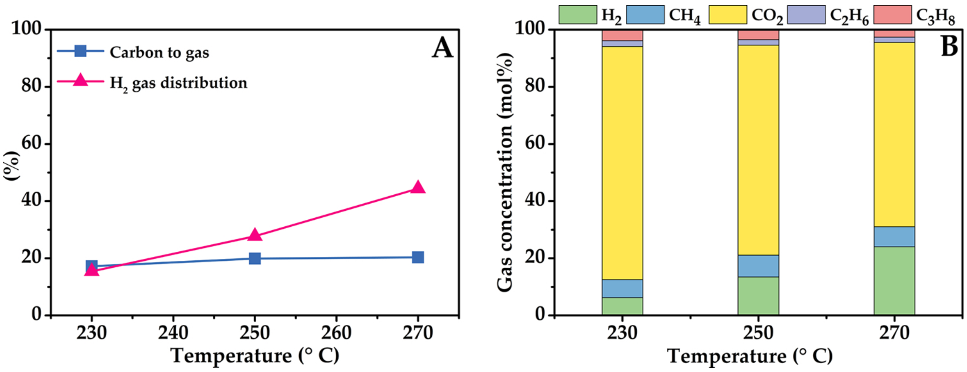

Fig. 3. Influence of reaction temperature on APR performance of wheat straw hydrolysate (A) and composition of the produced gas phase (B). Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 0.9 wt.% carbon concentration.

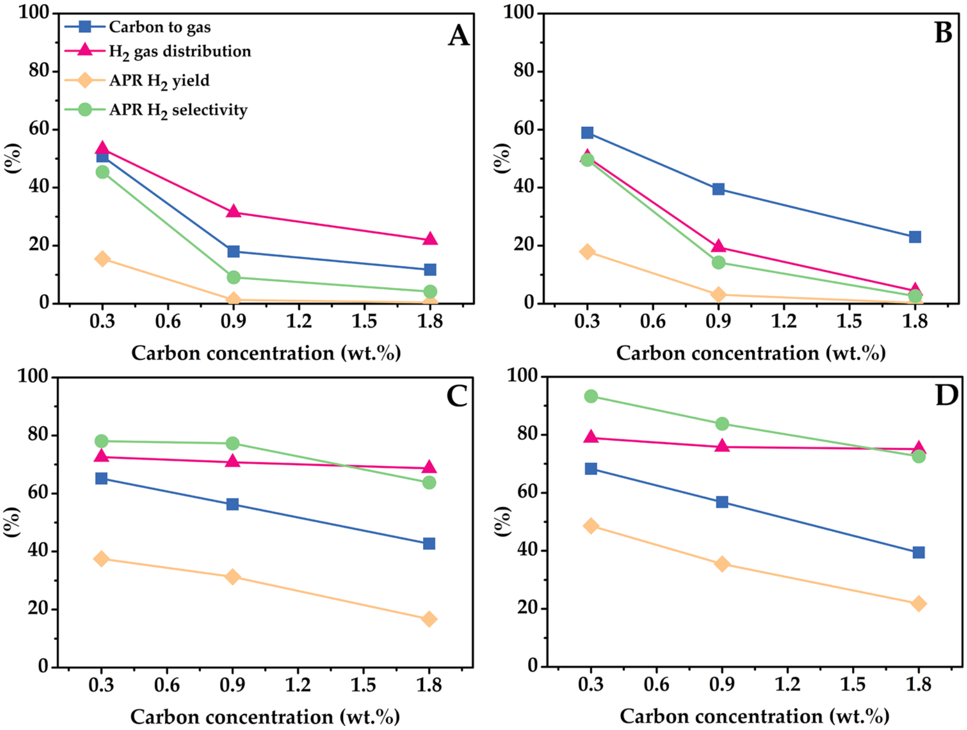

Fig. 4. Influence of the carbon concentration on the APR performance of glucose (A), xylose (B), sorbitol (C) and xylitol (D). Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C reaction temperature.

likely high molecular weight compounds, maybe with a more pronounced hydrophobic nature. Indeed, as reported later, during a washing step performed on the catalyst, ethanol was able to better extract organic compounds as compared to water: this may be an indication of a different chemical characteristic of the deposit on the surface of the catalyst, being ethanol less polar than water.

The hydrogen gas distribution of sorbitol was not influenced by the carbon concentration, that is, the production of alkanes was not favored at high concentrations, differently to glucose. On the other hand, the APR-H_2 selectivity decreased for the higher production of carbon dioxide, globally leading to the half of the hydrogen yield at the highest concentration investigated. The reason may be due to a higher presence of intermediates at high concentration, that can be subjected to hydrogenation, leading to a consumption of the produced H_2, that has the consequence to decrease the selectivity. Sorbitol converted at 80% at 1.8 wt.%, while it converted completely at lower concentrations; hydroxyacetone was the second most present compound in these conditions. When sorbitol was tested, a solid phase was not observed apart from the used catalyst. This implies that the involved reactions are completely different from the APR of glucose. Thus, working with the reduced form of the sugar is of paramount importance. For this reason, Davda et al. proposed to use a hydrogenative pretreatment to overcome the side reactions that involve the sugars and not the sugar alcohols [38]. The results obtained studying this reaction configuration will be reported in the paragraph 3.4.

Xylitol behaved analogously to sorbitol: even in this case, the hydrogen gas distribution was constant, while the APR H_2 selectivity, involving the relative production of hydrogen and carbon dioxide, decreased with the concentration.

In the liquid phase xylitol converted at 78% at 1.8%, but quantitatively at lower levels of concentration. Xylitol, at the same way of sorbitol, did not produce a solid phase that may be ascribed to the formation of high molecular weight compounds.

3.2.4. *Influence of the carbon concentration on the hydrolysate APR*

In accordance with the study of the model compounds, increasing the concentration hindered the conversion to carbon-containing gaseous species (Fig. 5). Hydrolysate is constituted mainly by glucose and

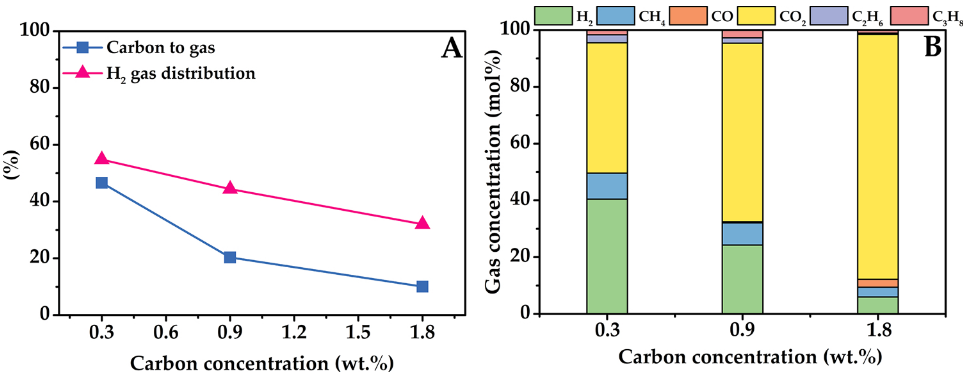

Fig. 5. Influence of the carbon concentration on APR performance of wheat straw hydrolysate (left) and composition of the produced gas phase (right). Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C reaction temperature.

xylose; therefore, this result can be ascribed to the homogeneous phenomena in which they are involved. Also, the hydrogen distribution decreased, as the production of gaseous alkanes became more favorable working at higher concentrations. This outcome can be highlighted looking at the distribution of the gaseous products.

In the liquid phase, both glucose and xylose were converted considerably. The main identified liquid products are carboxylic acids (acetic acid, propionic acid, butanoic acid). The test performed at 1.8 wt.% showed also isomers of glucose and xylose, as the isomerization is known to be one of the first reactions in hot aqueous systems [39]. Comparing the chromatograms obtained with the hydrolysate and the model compounds, we observed that there are approximately the same peaks. This may be an indication that only glucose and xylose effectively contributed to the reaction, while the remaining 30% of carbon present in the oligomers did not influence the product distribution.

Hydrolysate produced a solid phase; the amount recovered increased up to 375 mg at 1.8%, coherently with the decreasing carbon conversion to gas. Therefore, working at higher concentration shifted the fate of carbon from the gas phase, where it is mainly under the form of carbon dioxide, to the liquid and solid phase.

It is important to highlight that the effect of the inorganics on the APR performance cannot be excluded at this stage. This issue has not been fully addressed by the available literature and opposing outcomes have been reported. Lehnert et al. reported for the first time the APR of crude glycerol [40]. They ascribed the deactivation and the lower hydrogen production to the inorganics (e.g. NaCl). Conversely, Boga et al. reported, using a synthetic mixture to imitate the composition of a crude glycerol, that the salts of the fatty acids are likely the main responsible for the worsening of the performance [41]. This aspect has not been deeply analyzed in the present work; however, we may suppose, following Boga's outcomes, that the only presence of inorganics may have not influenced drastically the obtained results. Further investigation should be addressed to confirm this hypothesis.

3.3. Mixtures of model compounds

In the view of an industrial application, a mixture of sugars rather than a single compound will be the feedstock for the process. For this reason, a synthetic binary mixture of glucose and xylose was subjected to APR. This is an important step because collateral inhibitory phenomena (e.g. competitive adsorption) may happen. Moreover, we tested a synthetic mixture of the corresponding sugar alcohols, i.e. sorbitol and xylitol.

The mixture is constituted by 70% of glucose and 30% of xylose (and with the same ratio in the case of the sorbitol-xylitol mixture), in order to have results as close as possible to the hydrolysate and facilitate the comparison of the results. It is worthy to underline that the acids have not been included for modeling the hydrolysate. This choice has been justified by the about twenty times higher concentration of the sugars compared to the acids (acetic acid, lactic acid), and by the low hydrogen yield obtained by the latter, both alone and in mixtures, as reported in [36].

In Fig. 6, the results of the influence of the temperature on the APR of glucose-xylose mixtures at 0.9 wt.% carbon are reported.

All the indicators increased with temperature, at the same way of the single compounds, as reported in the relevant section. We compared the results with the linear combination of the single test and plotted the outcomes. The linear combination related to the carbon to gas conversion was calculated according to the following Eq. (8) (in an analogous way the calculations for the hydrogen yield and for the sorbitol-xylitol mixture were performed).

$$\mathrm{CtoG}_{\mathrm{linear\ combination}}\ (\%) = 100^*(0.7^*\mathrm{CtoG}_{\mathrm{glucose}} + 0.3^*\ \mathrm{CtoG}_{\mathrm{xylose}}) \tag{8}$$

It is highlighted that the points coming from the linear combination are close to the experimental results (the points of the H_2 selectivity were not reported for the sake of clarity of the figure). This is an interesting result because it should imply that there are no inhibitory phenomena between the compounds, as on the other hand we observed with small organic acids [36]. This means, for example, that there is not a competitive adsorption on the surface of the catalyst. Therefore, the mixture can be thought as a pseudo-compound, whose results are the combination of the results from the components of the mixture itself.

In order to complete this piece of knowledge, we investigated also the sorbitol-xylitol mixture at different temperatures. Even in this case, the linear combination points are close to the experimental results. Moreover, xylitol may be thought as the result of the first dehydrogenation/decabonylation of sorbitol [18] and the liquid by-products of sorbitol are the same of xylitol. For this reason, the sorbitol-xylitol mixture can be considered, even more than the glucose-xylose one, a pseudo-component. This information may give an indication for the modeling and design of a plant that may valorize this feed.

At the same way of the model compounds, we investigated also the influence of the carbon concentration on the performance of the synthetic mixtures.

In the Fig. 7A the experimental results for the glucose-xylose mixture are reported, together with the linear combination of the single compounds results linked with a dotted line. First of all, also in the case of different concentrations, it has been observed a similar trend of all the indicators with the single compounds. The carbon conversion to gas and the APR-H_2 selectivity almost halved between 0.3 and 0.9%, leading to a negligible APR-H_2 yield already at 0.9%. Moreover, not only the yield, but also the amount of hydrogen decreased substantially despite the increase in the amount of the feed (Fig. 8, left). The linear combination reflected the experimental outcomes also in this case, evidencing the absence of collateral phenomena of interreference between the compounds not only at different temperatures, but also at different concentrations.

The sorbitol-xylitol reported analogous results (Fig. 7B). The indicators had the same trend reported for the single compounds, with the decreasing carbon conversion to gas main responsible for the decreasing APR-H_2 yield. Anyway, despite of this decrease, the amount of H_2 produced increased, contrarily to the glucose-xylose mixture (Fig. 8, right). Also, with the sugar-alcohol mixture, the linear combination points are in perfect agreement with the experimental results, pointing out the similar reactivity of the components related to the possible reaction pathways at the experimental conditions investigated.

3.4. Hydrogenation-APR tests

From the previous results, it has been clear that the mixture of sugar alcohols led to much higher hydrogen production compared to the corresponding sugars. This is due to the possibility to work at higher concentration with the alcohols, without losing in productivity because of the homogeneous reactions. On the other hand, the alcohols are not the primary feedstock, as only the sugars would be available if we think to the bioethanol plant. The approach suggested by Dumesic and coworkers was followed to evaluate the feasibility of a two-step process, in which the APR is preceded by a selective hydrogenation to convert the sugars in sugar alcohols, trying to prevent the homogenous reactions that hinder the hydrogen production [38]. Irmak et al. tested a similar configuration with kenaf biomass hydrolysate reformed with an alumina supported catalysts, showing better performance of the hydrogenated feed [42]. Aim of this section is evaluating if the total hydrogen production is higher in the two steps process than in the one-pot (i.e. without pre-hydrogenation). As reported in the experimental section, the hydrogenation tests were performed with a commercial 5% Ru/C catalyst.

3.4.1. Hydrolysate-like mixture

The synthetic glucose-xylose mixture (referred also as hydrolysate-like mixture) was tested with the same composition reported in the

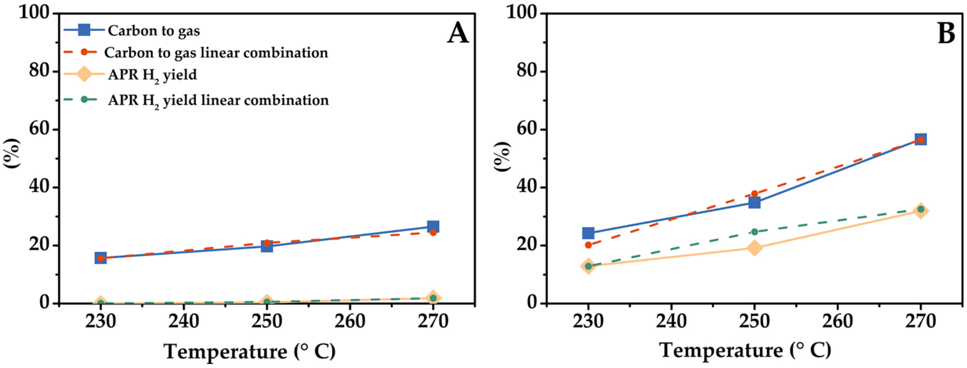

Fig. 6. Influence of reaction temperature on the performance of APR of a glucose-xylose (A) and sorbitol-xylitol (B) mixture (black points). The red points are referred to the linear combination of the singular components. Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 0.9 wt.% total carbon concentration.

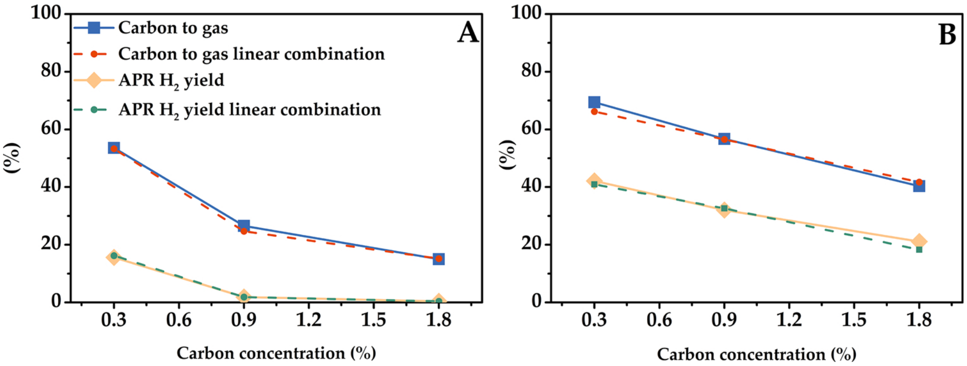

Fig. 7. Influence of carbon concentration on the performance of APR of a glucose-xylose (A) and sorbitol-xylitol (B) mixture (black points). The red points are referred to the linear combination of the singular components. Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C reaction temperature.

previous section (i.e. 70% glucose, 30% xylose). In the Fig. 9 (left) the results of the hydrogenations are reported at different concentrations. Both sugars were converted at a high extent, also for the highest concentration. The selectivity to the sugar alcohols was almost complete, with sorbitol and xylitol being the main products, but with the presence also of arabitol and traces of threitol (C4 sugar alcohol). The effective hydrogenation of sugars is a known process and its good performance is of paramount importance for the success of the process scheme, as the consumption of hydrogen in side reactions must be minimized in this step.

After the hydrogenation, the solution was filtered to remove the catalyst and put in the APR reactor, with the catalyst used for the reforming (i.e. 5% Pt/C). The results obtained are reported in Fig. 9 (right). The carbon to gas conversion and the hydrogen gas distribution reflected in a good way the results obtained with the sorbitol-xylitol mixture, indication of the effective hydrogenation. The important results come from the comparison between the hydrogen production in the two steps and the one pot process. In fact, while the former has an increasing trend, leading to about 32 mmoles of hydrogen (namely, the difference between the hydrogen produced in the APR step and the one consumed during the hydrogenation step), the latter has the trend reported in the section regarding the APR of the glucose-xylose mixture, with a negligible hydrogen production (about 1 mmole) due to the homogeneous phenomena previously reported. Godina et al. recently compared the APR performance between a sorbitol solution and a sorbitol/mannitol solution obtained by hydrogenation of sucrose [43]. They did not observe difference between the model and technical feeds, however the hydrogen production in the APR step was not enough to perform the hydrogenation of sucrose. The discrepancy with the present work can be due to the lower reaction temperature and higher feed concentration used by Godina, that lead to a lower hydrogen yield.

From these results it is highlighted that a process that aims to

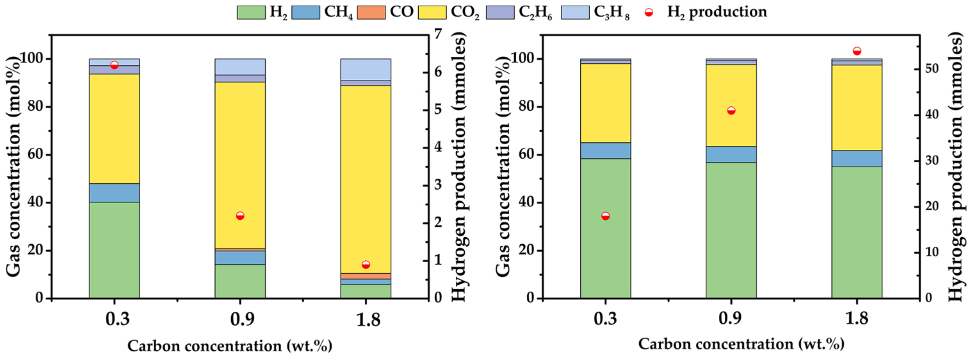

Fig. 8. Influence of carbon concentration on gas phase composition and hydrogen production of a glucose-xylose (left) and sorbitol-xylitol (right) mixture. Reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C reaction temperature.

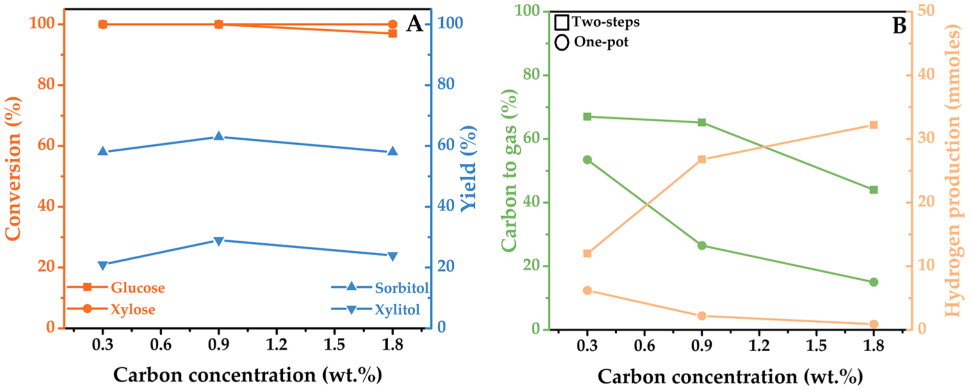

Fig. 9. Influence of carbon concentration on the hydrogenation of a glucose-xylose mixture (A) and on the APR of the hydrogenated feed (B). Hydrogenation reaction conditions: 0.188 g Ru/C catalyst, 1 h reaction time, 180 °C, 15 bar H_2 pressure. APR reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C.

valorize sugars through APR, with the necessity to work in concentrated solutions to reduce the reactor size, should foresee a pre-hydrogenation step to “stabilize” the feedstock, producing the corresponding sugar alcohols, leading to satisfactory hydrogen production and, possibly, increasing the life of the catalyst (see paragraph 3.5).

3.4.2. *Hydrolysate*

After the study of the synthetic mixture, the hydrogenation of the hydrolysate was performed, and the results are reported in Fig. 10.

It can be observed that the hydrogenation of the hydrolysate is much more difficult than the synthetic mixture. Maximum glucose conversion is 60% at 0.3%, and about 70% for the xylose, whereas it was complete with the hydrolysate-like. In addition, there is a strong dependence with the feed concentration, with a strong decrease of all the indicators working in more concentrated solutions. This important difference may be referred to the presence of oligomers in the solution. The valorization of polysaccharides passes through the formation of the monomer via hydrolysis, followed by the hydrogenation of the latter to the alcohol [44]. In our reaction conditions, using Ru/C as catalyst, there is a lack of acidic sites. Therefore, the carbon present in the oligosaccharides is not available for the production of the alcohols; at the same way, adsorbing on the catalyst, it may reduce the available sites for glucose and xylose and may participate to parasite hydrogenation reactions that consume hydrogen, but not leading to the final desired sugar alcohol.

3.5. *Reuse of the catalyst*

The stability of the catalytic system has a paramount importance in a process, therefore tests in which the catalyst was reused at different reaction temperatures were performed.

Blank experiments in which only the spent catalyst was present in the system were performed as references, leading to negligible but still more than zero carbon containing gaseous species. This is an interesting result because it highlights the presence of organic deposits on the surface of the catalyst, that can further react, although with low activity.

In the Fig. 11 the results for the hydrolysate-like mixture are reported. A decrease of the carbon conversion to gas was reported after the reuse of the catalyst at each temperature. It was observed that the lower the temperature, the higher the deactivation. This result is coherent with the observation that at lower temperature a higher amount of residue was produced, leading to a higher deactivation. At 270 °C, both the selectivity and the hydrogen yield are inferior to the results with the fresh catalyst; on the other hand, at lower temperatures, the hydrogen gas distribution and selectivity were higher than the fresh test (especially at 230 °C). During the reforming, a series-selectivity challenge involves the hydrogen, as it may be consumed by following reactions once it is formed. One possible reason for this result is that the presence of the organics, blocking the pores, reduced the activity (as fewer active sites were available), but on the other hand increased the selectivity, as most of the reaction did not involve the pores and hydrogen could escape more easily preventing consecutive hydrogenation.

Fig. 12 shows the results obtained when hydrolysate was used as feedstock. The carbon conversion to gas almost halved at each temperature investigated. It indicates that the temperature had not an influence on the degree of deactivation when the hydrolysate was used. On the other hand, the hydrogen gas distribution was only slightly affected by the reuse. Therefore, it seems that the lack in stability of the catalyst led mainly to lower conversion of the feed, maybe because of less available sites on the surface of the catalyst.

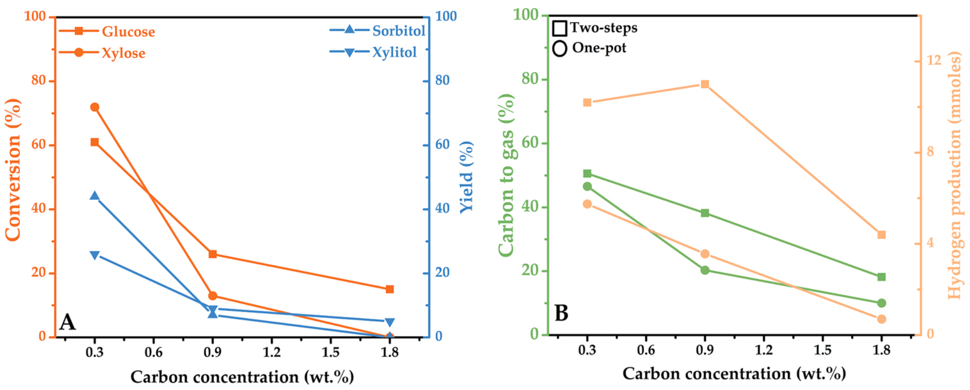

Fig. 10. Influence of carbon concentration on the hydrogenation of the hydrolysate (A) and on the APR of the hydrogenated feed (B). Hydrogenation reaction conditions: 0.188 g Ru/C catalyst, 1 h reaction time, 180 °C, 15 bar H_2 pressure. APR reaction conditions: 0.375 g Pt/C catalyst, 2 h reaction time, 270 °C.

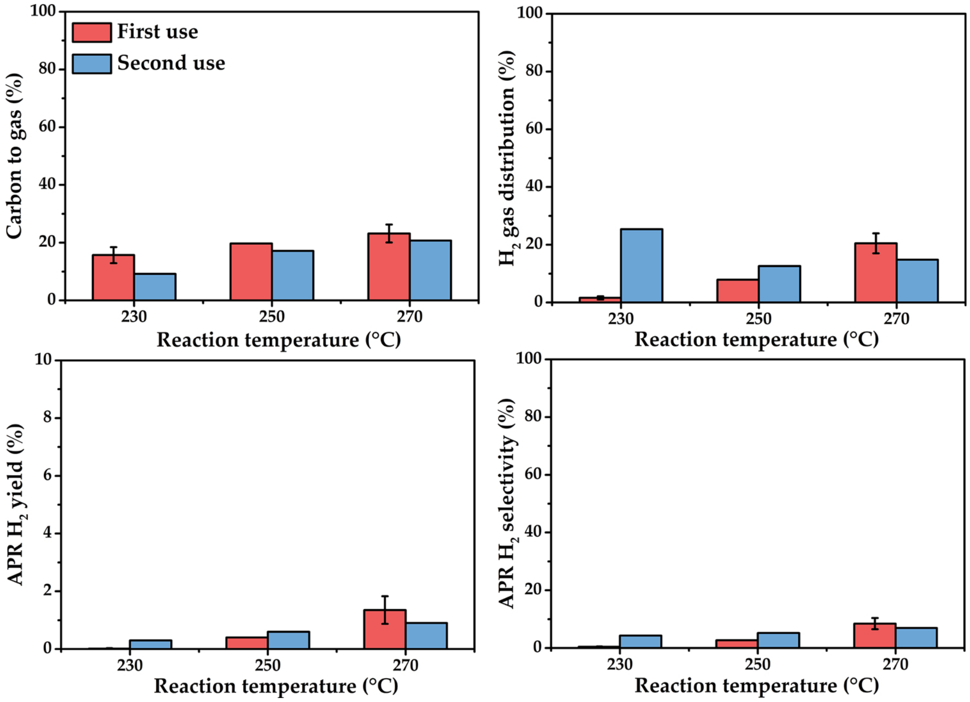

Fig. 11. Influence of the reaction temperature on the reusability of the catalyst with a glucose-xylose mixture. APR reaction conditions: 270 °C, 2 h reaction time, 0.9 wt.% C.

The catalyst recovered after the reaction performed at 270 °C underwent a washing treatment with ethanol and/or water (Fig. S3). It was observed that the organic solution (named as E) allowed the solubilization of adsorbed compounds, leading eventually a dark brown ethanolic solution. However, when water was used for the washing (named as W) of the already washed catalyst with ethanol, it did not experience a change in color: as a matter of fact, an HPLC analysis of the latter did not show the presence of any compound. Subsequent catalyst washings with ethanol further enhanced the organic compounds extraction in the liquid phase (E2-5 in Fig. S3).

This outcome suggested the presence of hydrophobic compounds on the surface of the catalyst, that may cause the observed deactivation. It is likely that these compounds are humic acids (humins), that are water insoluble and derive from the polymerization and condensation of furfurals, phenols and acids during the reaction [45,46].

Two tests performed with the treated catalysts after APR of glucose-xylose mixture and hydrolysate reported the same results of the untreated ones (Fig. S4). It is possible that the washing step removed only the organics on the external surface of the catalyst, not affecting the pores, therefore without changing the global performance.

3.6. Catalyst characterization

Although it is widely accepted that sugar solutions may be unstable in the APR reaction conditions, due to the formation of a solid residue, few works looked at the effects on the catalyst [47].

N_2 physisorption isotherms have been performed on the fresh and spent catalysts to evaluate the influence of the feedstock on the textural modifications (Table 2). It is observed that after the first use there is a dramatic decrease of the surface area and pore volume, likely due to the fouling caused by the humins. The re-use of the catalyst led finally to the complete loss of the original textural characteristics of the catalyst, having less than 1 m^2/g as surface area and negligible pore volume. On the other hand, when the sugar mixture was hydrogenated to sorbitol and xylitol, the decrease of the surface area is much less evident (about 15%), together with the pore characteristics (both volume and average size).

Analogous results were obtained with the hydrolysate. There was a decrease of 90% of the surface area with the untreated feedstock, while it was 70% in the case of the hydrogenated one, a result that must be improved in view of a practical application. It is evident that the

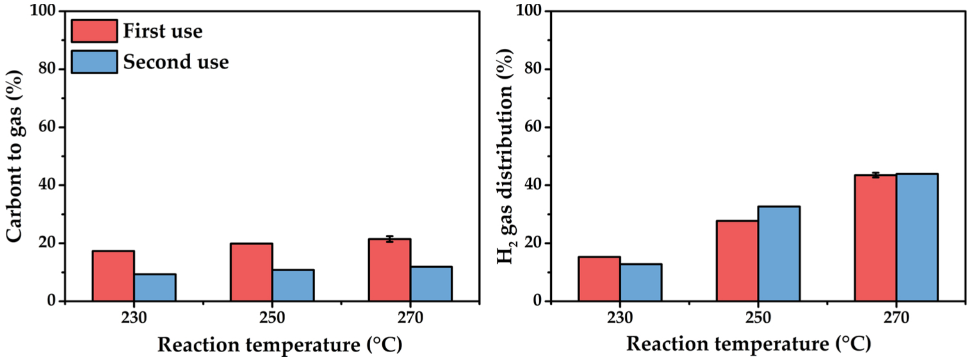

Fig. 12. Influence of the reaction temperature on the reusability of the catalyst with the hydrolysate. APR reaction conditions: 270 °C, 2 h reaction time, 0.9 wt.% C.

Table 2

Textural characteristic of the fresh and spent catalysts. All tested mixtures were at an overall 0.9 wt.% of carbon, except for the last line that was at 0.6 wt.%. Reaction conditions: 270 °C, 2 h reaction time.

Sample	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Average pore size (nm)
Fresh	923	0.632	5.1
Glucose-Xylose	35	0.121	10.1
Glucose-Xylose II use	0.9	0.002	10.4
Glucose-Xylose hydrogenated	772	0.606	5.1
Glucose-Xylose hydrogenated II use	750	0.583	5.1
Hydrolysate	76	0.208	7.8
Hydrolysate hydrogenated	247	0.411	5.5
Glucose-Xylose 0.6 wt.% C	567	0.538	5.2

conversion to the sugar alcohols allows to maintain at a greater extent the stability of the catalyst, as they do not lead to deposition phenomena. This is due to the avoidance of dehydration reactions, involving the formation furfural and hydroxy-methyl furfural starting from glucose and xylose, which are catalysed by an acid environment. For this reason, the pH of the solution or of the catalytic surface may play a key role in the selectivity towards solid by-products.

Finally, it can be observed that the concentration of the feed plays a key role in the stability of the catalyst. Indeed, reducing the carbon concentration to 0.6 wt% allowed to maintain a higher surface area and pore volume, one order of magnitude higher than in case of 0.9 wt.%.

Fesem images of the fresh and spent catalysts used for the hydrolysate APR are reported in Fig. S5. It was observed that the fresh catalyst (A) showed the typical morphology of an activated carbon, with microporosity on the surface. When the catalyst was used (B), the surface seemed much flatter and less porous, as if the solid deposits cover homogeneously the catalyst, blocking the pores and strongly reducing the performance of the reaction. The catalyst used with the hydrogenated feed (C) apparently showed an intermediate morphology. Despite there was not an equal distribution of micropores as evident in the fresh one, it maintained a partial porosity, as it was confirmed in the N_2 physisorption analysis.

Spectroscopic analysis (ATR) was used to derive information on the nature of the organic deposits, while the TGA was functional to the determination of the deposit fraction that decomposes under inert conditions. It is worth highlighting that the amount of decomposed deposit in the TGA is always lower than the one obtained from the weighting procedure of the spent catalyst.

The ATR analyses on the fresh catalyst showed a band at around 1550 cm^{-1} and 3450 cm^{-1} likely associated to the presence of absorbed water on the surface (Fig. S6). No other major bands are observed for the fresh catalyst.

The ATR analyses of the other catalyst samples are strictly depended from the substrate used in the APR reaction: hereafter, the results on spent catalysts from the aqueous phase reforming of a glucose-xylose hydrogenated solution, a glucose-xylose solution and the hydrolysate are presented.

The catalyst used with the glucose-xylose hydrogenated mixture showed a spectrum similar to the one of the fresh catalyst, indicating the absence (or small) amount of organic deposits. On the other hand, when sugar (glucose-xylose or the hydrolysate) solutions were used as substrate, an intense band with maximum at 1694 cm^{-1} appeared, together with the appearance of a shoulder at 1730 cm^{-1}. 1694 cm^{-1} can be attributed to species originated from the decomposition of glucose at high temperature in water, with the formation of unsoluble compounds such as humins [48]. This band is related to the carbonyl group stretches derived from adsorbed acids, ketones and aldehydes, that were not observed in the liquid phase obtained from glucose-xylose hydrogenated APR [45].

At the same time the presence of organic fragments is confirmed from the absorption between 3000 and 2800 cm^{-1} with the symmetric and asymmetric stretching of -CH_2- and CH_3 groups. Please note that the absorption at around 2300 cm^{-1} is referred to a noise due to a not perfect compensation of atmospheric CO_2.

Thermogravimetric analyses of the catalysts led to conclusions coherent with the previous ones from ATR (Fig. 13). The fresh catalyst showed a total weight loss of about 15 wt.%, concentrated in three different steps: the first one with a maximum at 80 °C associated to a

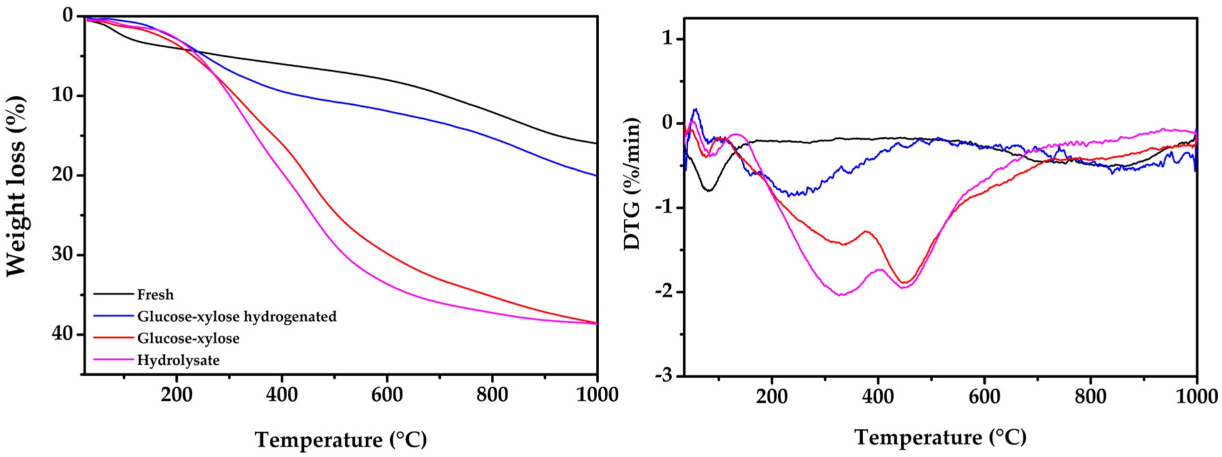

Fig. 13. Thermogravimetric analysis of fresh catalyst (black line) and spent catalyst after the aqueous phase reforming of a glucose-xylose hydrogenated solution (blue line), a glucose-xylose solution (red line) and a hydrolysate (purple line). APR reaction conditions: 270 °C, reaction time 2 h, 1.8 wt. % C. TGA temperature program: heat from 30 °C to 1000 °C @ 20 °C/min in nitrogen atmosphere with a purge rate of 20 mL/min.

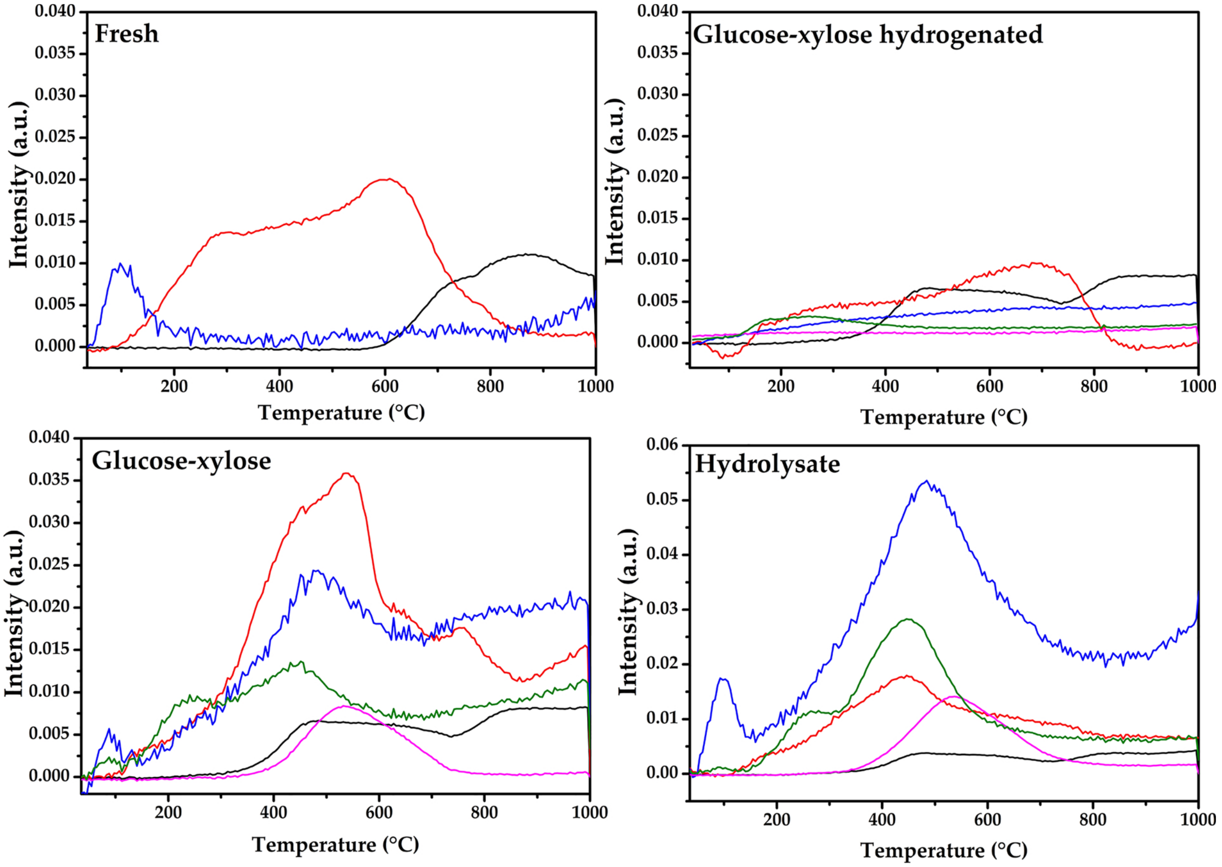

Fig. 14. IR analysis of evolving gas from fresh and spent catalysts reported in Fig. 13; water (blue line), carbon dioxide (red line), carbon monoxide (black line), methane (purple line), carbonylic groups (green line).

loss of adsorbed water; the second step, between 200 °C and 600 °C, can originate from the initial decomposition of the carbon support of the catalyst, which is composed from a certain percentage of oxygen, with the formation of carbon dioxide; the third step is a further decomposition of the carbon support, with the formation of carbon monoxide. This hypothesis is confirmed from the infrared analysis (Fig. 14) of the developed gasses: the curve shows a maximum for water absorption around 100 °C, a maximum at 600 °C for CO_2 adsorption and an increase in CO concentration over the 600 °C.

The catalyst used for APR of hydrogenated glucose-xylose showed comparable results with the fresh catalyst, with a total loss of about 19 wt.%, slightly higher than the pristine catalyst. The degradation was similar except for the initial water loss, probably for the process of drying of the used catalyst and the presence of a small quantity of carbonyl functionalities at low temperature (around 200–300 °C) derived from the low amount of organics still present. The carbon dioxide curve was instead almost equivalent to the one obtained for the fresh catalyst.

All the other spent catalysts had a higher weight loss, around 40 wt.% (Fig. 13). This means that, after normalization, the amount of deposits generated in the glucose-xylose APR was more than seven times higher than the one from the hydrogenated glucose-xylose APR, clearly explaining why the catalyst in the latter conditions was much more stable than in the former ones.

A similar weight loss and degradation in three main steps was noticed: the first one with a maximum below 100 °C and where only water was produced; the second step had usually a maximum around 300 °C and aliphatic substances with carbonyl groups were mainly produced. At higher temperature, the aliphatic compounds slowly decreased with an increase of CO_2, water and methane production, all of them being typical products of organic compounds pyrolysis. Therefore, the TGA with infrared analyses of the produced gases confirmed the presence of organic material that is formed only in the presence of sugars, and at a much lower extent with sugar alcohols.

4. Conclusions

A stream coming from the hydrolysis treatment of a bioethanol plant and its representative model compounds were subjected to APR to produce hydrogen. For the first time, in this work, we tested xylose as a strategic compound for the valorization of the hemicellulose fraction in lignocellulosic biomass. The influence of the reaction temperature and carbon concentration were systematically investigated to evaluate their impact on the APR performance, mainly in terms of carbon conversion to gas and hydrogen yield. The increase of the reaction temperature favoured the hydrogen production of each compound, leading also to less solid residue formation by the sugars. The same results were obtained with the investigated binary mixtures, showing a behaviour close to the linear combination of results obtained with the individual constituents of the mixture. On the other hand, the increase of the carbon concentration had a detrimental effect towards hydrogen production from both glucose and xylose, while it was not observed with sorbitol and xylitol. For this reason, a pre-hydrogenation step carried out on the sugar mixture showed an increase of hydrogen production with respect to the untreated one, even taking into consideration the amount of hydrogen consumed for the hydrogenation. The same pre-hydrogenation step was performed also on the hydrolysate, but it showed a worse performance than the synthetic mixture, maybe due to the presence of oligomers. The catalyst used for hydrolysate APR underwent deactivation phenomena, that caused mainly the decrease of the carbon conversion to gas, while maintaining almost the same selectivity. The catalyst characterization showed the presence of organic deposits (humins) that blocked the pores of the catalyst in the case of the sugar-rich feeds, while the hydrogenated mixture allowed a longer life of the catalyst. Further studies on the optimization of the reaction configuration hydrogenation-APR, or on the reaction conditions (i.e. pH modification) may allow to make a step forward in the exploitation of the pentoses, helping to satisfy the need of renewable hydrogen of a biorefinery.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.09.031.

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