

## Article

# C-O Bond Hydrogenolysis of Aqueous Mixtures of Sugar Polyols and Sugars over $\text{ReO}_x\text{-Rh/ZrO}_2$ Catalyst: Application to an Hemicelluloses Extracted Liquor

Modibo Mounguengui-Diallo <sup>1</sup>, Achraf Sadier <sup>1</sup>, Eddi Noly <sup>1</sup>, Denilson Da Silva Perez <sup>2</sup>, Catherine Pinel <sup>1</sup>, Noémie Perret <sup>1,\*</sup> and Michèle Besson <sup>1,\*</sup> 

<sup>1</sup> Univ Lyon, Université Claude Bernard, CNRS, IRCÉLYON, UMR5256, 2 Avenue Albert Einstein, F-69626 Villeurbanne, France

<sup>2</sup> Institut FCBA, InTechFibres, Domaine Universitaire, CS 90251, F-38044 Grenoble, France

\* Correspondence: noemie.perret@ircelyon.univ-lyon1.fr (N.P.); michele.besson@ircelyon.univ-lyon1.fr (M.B.); Tel.: +33-472-445-446 (N.P.); +33-472-445-356 (M.B.)

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**Abstract:** The recovery and upgrade of hemicelluloses, a family of heteropolysaccharides in wood, is a key step to making lignocellulosic biomass conversion a cost-effective sustainable process in biorefinery. The comparative selective catalytic C-O bond hydrogenolysis of C5-C6 polyols, sugars, and their mixtures for the production of valuable C6 and C5 deoxygenated products was studied at 200 °C under 80 bar  $\text{H}_2$  over  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts. The sugars were rapidly converted to the polyols or converted into their hydrogenolysis products. Regardless of the reactants, C-O bond cleavage occurred significantly via multiple consecutive deoxygenation steps and led to the formation of linear deoxygenated C6 or C5 polyols. The distribution of products depended on the nature of the substrate and C-C bond scission was more important from monosaccharides. In addition, we demonstrated effective hydrogenolysis of a hemicellulose-extracted liquor from delignified maritime pine containing monosaccharides and low MW oligomers. Compared with the sugar-derived polyols, the mono- and oligosaccharides in the liquor were more rapidly converted to hexanediols or pentanediols. C-O bond scission was significant, giving a yield of desired deoxygenated products as high as 65%, higher than in the reaction of the synthetic mixture of glucose/xylose of the same C6/C5 sugar ratio (yield of 30%).

**Keywords:** hydrogenolysis; polyols; monosaccharides; hemicelluloses extracted liquor;  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts

## 1. Introduction

Until recently, chemicals have mostly been derived from fossil resources. The utilization of non-edible, abundant and renewable lignocellulosic biomass from agriculture and forestry has emerged as an interesting alternative for the chemical industry and polymer production in particular [1–6]. Lignocellulose consists of carbohydrate polymers (cellulose and hemicelluloses) embedded in a lignin matrix [4,7]. Cellulose (30–50%) is a water insoluble linear homopolysaccharide of  $\beta$  (1  $\rightarrow$  4) linked glucose units with strong intra- and intermolecular hydrogen bonds and with a degree of polymerisation as high as 15,000 units. Different to cellulose, hemicelluloses (20–35%) are branched polymers made of structures of hexoses (D-galactose, D-mannose, D-glucose) and pentoses (D-xylose and L-arabinose) and some sugar acid subunits, with a low degree of polymerization of 80–200 units. The composition of hemicelluloses varies depending on the source of biomass: in general, softwood hemicelluloses are mainly composed of

O-acetyl-galacto-glucomannans and some arabino-4-O-methyl-glucuronoxylan [8–10], whereas in hardwoods, O-acetyl-4-O-methylglucuronoxylans are the most abundant [11,12]. In addition, lignin is an aromatic polymer with a complex composition of phenylpropane units linked by ether bonds. In order to utilize the woody biomass efficiently, all three main components should be used in a biorefinery to maximize economic returns [13].

Although cellulose has been much studied for the conversion to fuels and chemicals, there has been less effort in the conversion of hemicelluloses, which are the second most abundant polysaccharides. During the conventional Kraft process in the pulp and paper industry, the cellulose fraction is the core product to be used in papermaking, while most hemicelluloses are currently degraded and accumulated in the black liquor along with lignin, and are burnt to produce energy. However, if the hemicelluloses are pre-extracted or hydrolyzed to their structural C5 and C6 sugars—which are building blocks for numerous biomaterials or chemicals—with a minimum effect on subsequent pulping step, this makes a better valorization of this under-utilized fraction in paper mills feasible [14,15]. The potential of valorization is up to the millions of tons of wood treated by the Kraft process.

The relatively low degree of polymerization and the branched side groups allow a large fraction of hemicelluloses to dissolve in aqueous solution. Various effective methods have been proposed for hemicelluloses extraction from wood chips prior to cooking, including the use of acids, water, and alkaline solutions [16–27]. Many applications for the extracted hemicelluloses have been developed [28]. Moderate treatment provides polymeric hemicelluloses with sufficient molecular mass to be recovered by precipitation and valorized after chemical modification [29–31] as hydrocolloids [32,33], surfactants [34–36], coating materials [37], emulsion stabilizers [38] or as packaging materials [39], among others. In some more severe extraction processes where autohydrolysis takes place, the backbone of hemicelluloses is hydrolysed into oligomers with a low degree of polymerization, hexoses, pentoses, and uronic acids, which may be subsequently upgraded in further steps for various applications.

Though the pH may influence the composition of liquor after extraction (sugars, distribution of oligomers), extraction using only hot water (120–240 °C) has been shown to be an attractive environmentally friendly method [21,40]. Some auto-hydrolysis occurs due to release of acetic acid from the deacetylation of hemicelluloses and uronic acids. The glycosidic bonds between the sugar units of hemicelluloses are cleaved by a hydrolysis reaction to the partially hydrolyzed dimers, trimers and other oligomers or the sugar monomers, depending on the operating conditions and on hemicelluloses source [41]. Once separated, they can be further processed into chemicals. They may be a source for furans and their derivatives for ethanol [14,28,42–44], but also for the production of suitable monomers by catalytic hydrogenation [45–47] or oxidation [48] of the extracted sugars.

Like most of the biomass derivatives, the compounds in the extracted hemicellulosic stream are characterized by a much higher oxygen content compared with fossil-derived feedstocks. Usually, the target products, such as monomers for polymer synthesis, have a comparatively lower oxygen content. Triols and diols are useful as chemical intermediates for the production of polymers, agrochemicals and surfactants. For example,  $\alpha,\omega$ -diols, especially C5 and C6  $\alpha,\omega$ -diols, can be used as plasticizers and as co-monomers in polyesters and polyurethanes manufacture [49–51]. Therefore, methodologies for upgrading of the hemicelluloses stream to monomers necessitate a controlled removal of oxygen—containing functional groups from sugars. One route is catalytic-selective hydrolysis/hydrogenolysis of soluble hemicelluloses/polysaccharides/monomers in the presence of supported metallic catalysts. Hydrogenolysis of C-O bonds has been applied to alcohols and polyols to produce more or less deoxygenated polyols. The transfer of hydrogenolysis has been applied to polyols over heterogeneous catalysts using H-donors (alcohols, formic acid) [52,53]. Under hydrogen pressure, although monometallic catalysts such as Cu, Ni, and Ru have been reported for dehydroxylation [54–57], a better control is obtained using catalysts that contain a noble metal (Pt, Pd, Rh, Ir) modified by an oxophilic metal (Re, Mo, W) [58]. These bimetallic catalysts have been found to be highly active and selective for —C-O- cleavage reactions of various biomass-derived substrates, including glycerol,

2-(hydroxymethyl)tetrahydropyran or tetrahydrofurfuryl alcohol (the full saturation product of furfural), and others [59,60]. Partial hydrodeoxygenation of glycerol to 1,2- or 1,3-propanediol was investigated intensively and reviewed [61–65]. It is much more difficult to selectively remove OH groups from substrates with four or more OH groups such as erythritol, xylitol, or sorbitol [66–72]. During this process, several products are very often obtained by unwanted reactions (hydrogenation, isomerization, dehydration, C-C bond cleavage by retro-aldol condensation, decarbonylation and decarboxylation).

The objective of this work was to evaluate the feasibility of catalytic hydrogenolysis of an hemicellulose extract from delignified maritime pine wood chips that contained simple sugars such as glucose or xylose or partially hydrolyzed dimers, trimers and other oligomers, to prepare more or less deoxygenated linear C6 and C5 polyols. We used  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts, which were particularly efficient in our previous work on the hydrogenolysis of erythritol, xylitol and sorbitol [68,69]. Before performing the catalytic hydrogenolysis of the hemicelluloses liquor, we studied the reaction of aqueous solutions of sugar polyols and sugars of different compositions.

## 2. Results and Discussions

### 2.1. Characterization of Catalysts

Three batches of  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts were prepared with Re/Rh molar ratios of 1.5 (8.8%Re–3.3%Rh), 1.6 (9.4%Re–3.2%Rh), and 1.8 (10.2%Re–3.0%Rh). The BET surface areas were  $109 \text{ m}^2 \text{ g}^{-1}$ , slightly lower than that of the support of  $129 \text{ m}^2 \text{ g}^{-1}$ . The X-ray diffraction patterns of the support and 9.4%Re–3.2%Rh/ $\text{ZrO}_2$  are presented in Figure S1 as a representative example. Except the peaks characteristic of  $\text{ZrO}_2$ , there were no other peaks that could be assigned to Rh or Re species, suggesting a very good dispersion of Rh and Re. As observed previously, TEM and CO chemisorption confirmed a low mean particle size of ca. 3 nm [70].

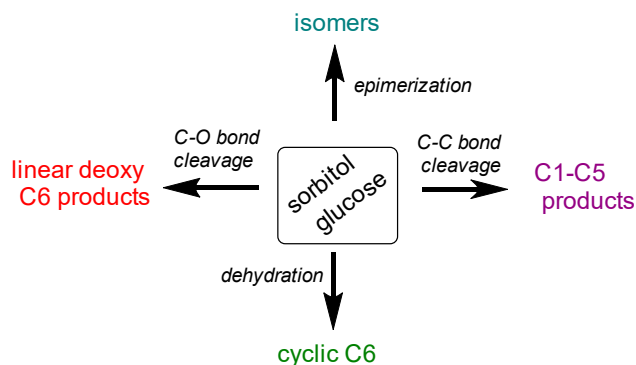
### 2.2. Hydrogenolysis of Polyols or Sugars Separately

The reaction conditions (200 °C under 80 bar of  $\text{H}_2$ ) were selected from our previous study on hydrogenolysis of sugar polyols (erythritol, xylitol, sorbitol) which allowed us to obtain the highest selectivity to deoxy C4 to C6 polyols over the  $\text{ReO}_x$ -modified Rh catalysts [70,71]. Since the extraction of hemicelluloses liberates sugars and their oligomers, we first compared the results for the hydrogenolysis of the C5 or C6 sugars with those of the corresponding C5 or C6 polyols.

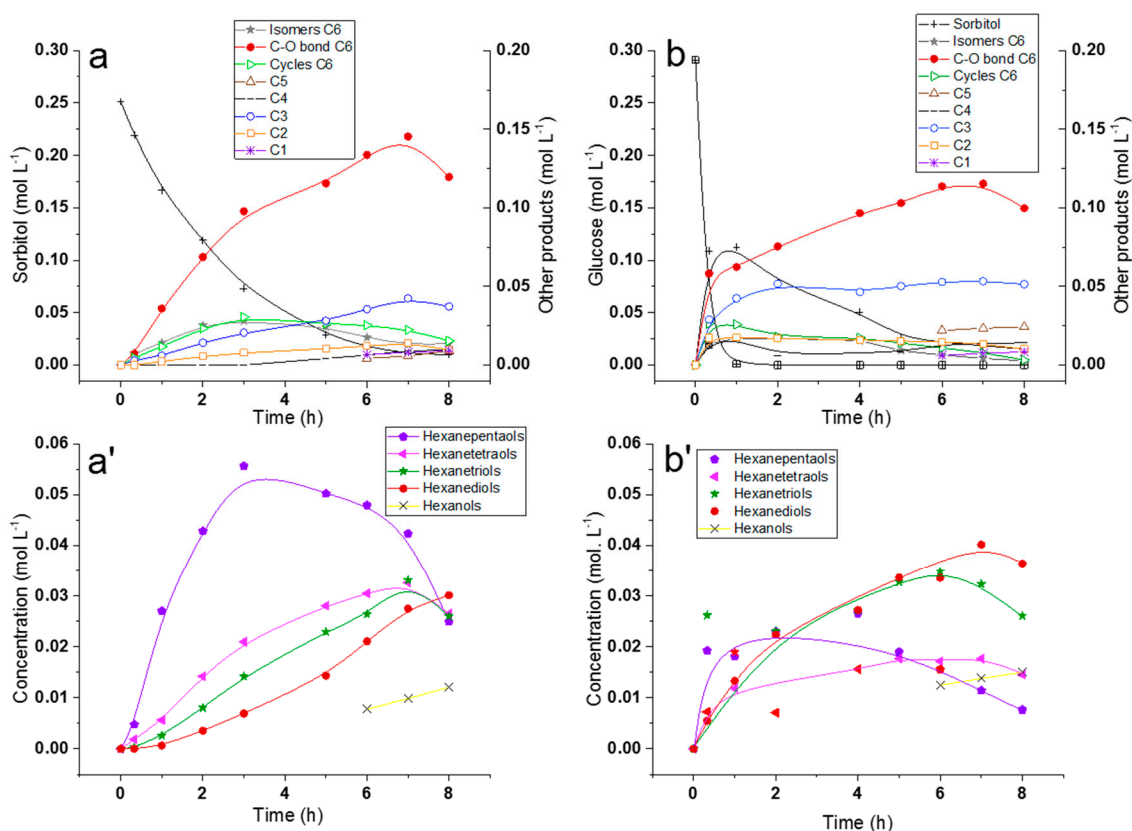
#### 2.2.1. Comparison of Sorbitol and Glucose Hydrogenolysis

As shown previously [70], many reactions take place during hydrogenolysis (Scheme 1, Scheme S1), which produces different families of products: (1) isomers of sorbitol by epimerization reaction (mannitol, iditol, and dulcitol), (2) more or less deoxygenated linear C6 compounds by multiple C-O bond cleavage reactions; (3) cyclic C6 compounds by dehydration reaction, mainly sorbitans and isosorbide and (4) products of C-C bond cleavage (C1–C5), including C5 products (such as 1,2-pentanediol, 1,5-pentanediol, 1-pentanol and tetrahydrofurfuryl alcohol among others), C4 products (such as 1,2-butanediol and 1-butanol), C3 products (such as glycerol, 1,2-propanediol and 1-propanol), as well as ethylene glycol and ethanol, and finally methanol. Specifically, C6 deoxygenated products consist of different sub-families: hexanepentaols (one C-O bond cleavage), hexanetetraols (two C-O bond cleavages), hexanetriols (3 C-O cleavages), hexanediols (4 C-O cleavages) and hexanols (5 C-O cleavages).

Hydrogenolysis reactions of sorbitol and glucose (6 g of substrate in 120 mL water, i.e., 0.25 M and 0.29 M, respectively) were compared over Rh-Re/ $\text{ZrO}_2$  (Re/Rh molar ratio = 1.5 or 1.6) at 200 °C under 80 bar  $\text{H}_2$  (Figure 1). Figure 1a,b shows the evolution of the concentrations of substrate (sorbitol or glucose) and families of products as a function of the time of reaction (Scheme S1). Figure 1a',b' shows the evolution of the sub-families of linear deoxyhexitols.



**Scheme 1.** The reactions taking place during the hydrogenolysis of sorbitol or glucose.



**Figure 1.** The evolution of the concentration of (a,b) the different families of products and (a',b') the sub-families of linear deoxygenated C6 compounds during hydrogenolysis of (a,a') sorbitol (0.25 M), and (b,b') glucose (0.29 M), over  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts ( $\text{Re/Rh}$  molar ratio = 1.5 for sorbitol, 1.6 for glucose) at 200 °C under 80 bar  $\text{H}_2$ ,  $n_{\text{sorbitol}}/n_{\text{Rh}} = 188$ ,  $n_{\text{glucose}}/n_{\text{Rh}} = 218$ .

Figure 1a, focused on sorbitol hydrogenolysis, indicates that the substrate was almost fully converted after an 8-h reaction. The main products formed were a mixture of linear deoxygenated C6 compounds, showing that selective C-O bond cleavage is achievable with appreciable selectivity. The concentration was increasing substantially over time to attain ca. 0.15 M (60% yield) at 7 h, in line with previous observations [57,71]. The other reaction products were formed in lower amounts. Isomerisation of sorbitol and transformation to cyclic compounds was significant from the beginning of the reaction, however, the concentrations of the isomers and cycles decreased after 3 h of reaction (maximum concentration of each ca. 0.025 M). Like sorbitol, the isomers were easily hydrogenolysed, whereas the cyclic compounds were more inert to further hydrogenolysis. C-C bond cleavage reactions also occurred and competed with C-O hydrogenolysis; the concentration of the C5, C4, C3, and C2

products increased slowly during the 8 h-reaction and accounted for very low concentrations. Finally, the C3 polyols were the main C-C bond cleavage products, with a maximum concentration of 0.04 M after 7 h (ca. 16% yield) (Figure 1a). These C3 polyols are mainly formed by retro-aldol reaction of C6 polyols [55,72].

In comparison to sorbitol (0.25 M,  $n_{\text{sorbitol}}/n_{\text{Rh}} = 188$ ), glucose (0.29 M,  $n_{\text{sorbitol}}/n_{\text{Rh}} = 218$ ) was very rapidly fully converted within only 1 h (Figure 1b). Sorbitol was the main product formed by the hydrogenation of glucose, along with all the compounds observed above in the hydrogenolysis of sorbitol. The presence of all the other products of the reaction besides sorbitol (deoxygenated C6 products, C6 cyclic compounds, and C1C5 products) from the beginning of the hydrogenolysis reaction is indicative of the direct hydrogenolysis of glucose as well as the fast hydrogenation of glucose to sorbitol. Sorbitol concentration was maximum at total conversion of glucose at 1 h (0.07 M, ca. 24% yield), then it decreased up to almost full conversion at 8 h. The reaction rates of formation of the different products were significantly higher during the hydrogenolysis of glucose than during the reaction of sorbitol. This was especially observable for C3 products that were formed much more rapidly with a plateau of 0.055 M (ca. 19% yield) after 2 h. The formation of these C3 compounds was probably due to the retro-aldol reaction of glucose, which led to the significant formation of glycerol [73,74]. At the end of the reaction, the distribution of the families of products was not too different when starting either with glucose or sorbitol. Deoxygenated C6 compounds (Figure 1b) represented the majority of the compounds after 2 h of reaction, with a final concentration (0.12 M, i.e., 41% yield) lower than that formed from sorbitol (0.15 M, i.e., 60% yield). Kinetic models based on the complex pathway proposed in Scheme S1 should be developed in order to confirm the mechanism.

The distribution of the sub-families of linear deoxy C6 products during sorbitol and glucose hydrogenolysis is compared in Figure 1a',b'. During sorbitol reaction, hexanepentaols, -tetraols, -triols, -diols and hexanols were observed. Hexanepentaols were formed initially at a significant rate to reach a maximum of ~0.055 M at 3 h (22% yield). The successive formation of hexanetetraols, -triols, -diols and hexanols confirms the previously observed multiple sequential deoxygenation pathway [61,70]. Finally, there was a mixture of products of C-O bond cleavages (ca. 0.03 M, i.e., 12% yield of each after 8 h), while the yield of hexanols after 6 h remained below 4%.

During the reaction of glucose under similar conditions (Figure 1b'), hexanepentaols, -tetraols and -triols were more rapidly converted into hexanediols, which finally were the major products from the reaction time of 6 h; their concentration was 0.04 M (14% yield) at the maximum. Hexanols were present in slightly higher concentrations than during sorbitol conversion (ca. 0.012 M, <4% yield).

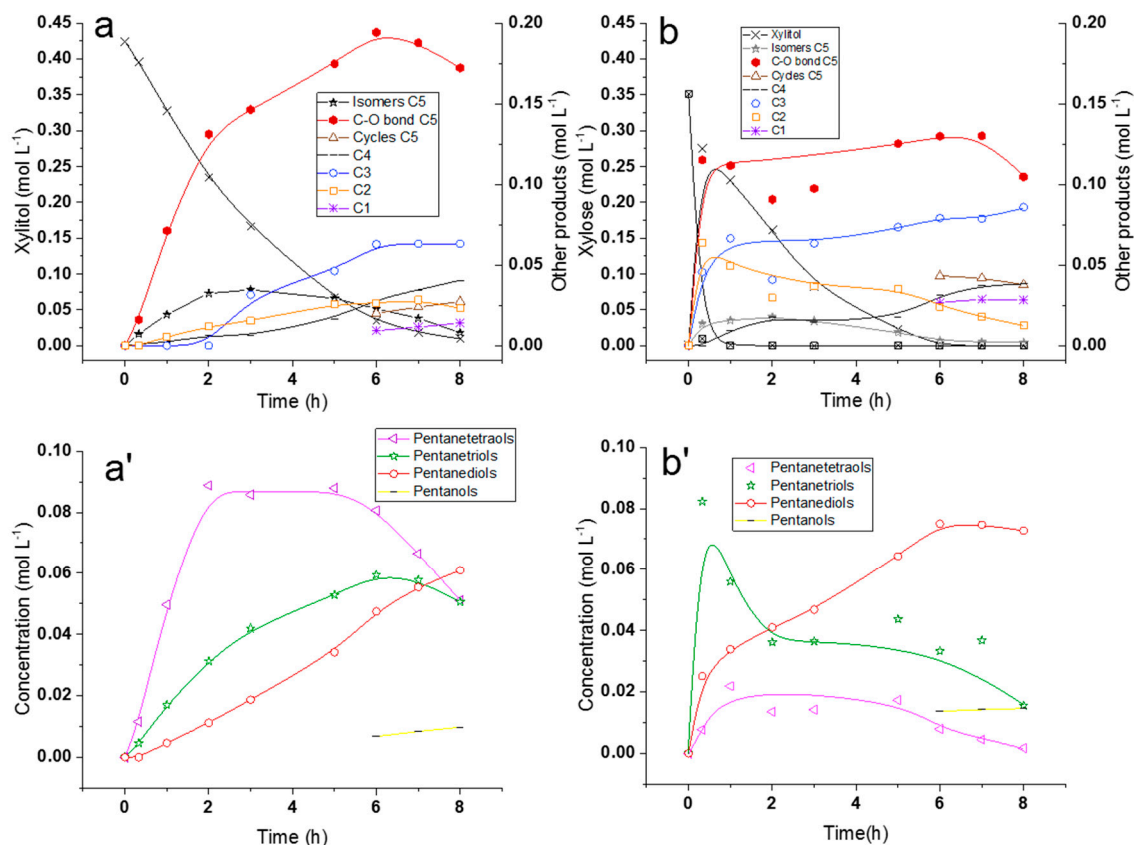
### 2.2.2. Comparison of Hydrogenolysis of Xylitol and Xylose

Like sorbitol and glucose, the hydrogenolysis of xylitol and xylose was compared under the same operating conditions (200 °C, 80 bar H<sub>2</sub>, 6 g substrate over 500 mg of ReO<sub>x</sub>-Rh/ZrO<sub>2</sub>). The families of products from the main reactions (epimerization to arabitol and adonitol), linear C5 deoxygenated polyols, C-C bond cleavage to C1-C4 polyols, and dehydration (yielding anhydroxylitol and tetrahydrofurfuryl alcohol) are shown in Scheme S2.

Figure 2 compares the evolution of the concentration of C5 reactant (xylitol or xylose) and all the products as a function of reaction time. The same trends as in the comparison of sorbitol and glucose hydrogenolysis were observed.

Xylitol (0.42 M) was gradually converted up to full conversion at 8 h (Figure 2a). Under these conditions, and as described previously [71], xylitol hydrogenolysis afforded mainly the desired deoxy C5 compounds, with a maximum concentration of ~0.20 M (48% yield) at 6 h. After exhibiting a maximum yield of 7%, the concentration of the C5 isomers decreased. Relatively stable 5-membered cyclic compounds were formed. As for sorbitol, C3 compounds still represent the main products of C-C bond breakage (0.06 M i.e., 14% yield at the end of the reaction).





**Figure 2.** Evolution of (a,b) products families and (a',b') C-O bond C6 sub-families concentrations during hydrogenolysis of (a,a') xylitol (0.42 M), and (b,b') xylose (0.35 M), over ReO<sub>x</sub>-Rh/ZrO<sub>2</sub> catalysts (Re/Rh molar ratio = 1.5 for xylitol, 1.8 for xylose) at 200 °C under 80 bar H<sub>2</sub>,  $n_{\text{xylitol}}/n_{\text{Rh}} = 316$ ,  $n_{\text{xylose}}/n_{\text{Rh}} = 264$ .

The transformation of xylose (0.35 M) was significantly faster than for xylitol and the monosaccharide was nearly totally converted within only 20 min (Figure 2b). Xylitol was formed and was in turn fully consumed within 6 h. All the products detected in xylitol hydrogenolysis were also analysed during sugar hydrogenolysis, i.e., the C5 isomers that were further converted, cyclic C5 compounds, and different C1–C4 polyols. The deoxy C5 products were formed with a maximum yield of 37%. One may note that compared to xylitol hydrogenolysis (Figure 2a), the concentrations of C2 and C3 products (initially, and during all the reaction) were clearly higher (Figure 2b). The products with shorter chains of carbon were formed to the detriment of the C5 deoxygenated products. As mentioned above, appropriate kinetic models based on the suggested reaction network in Scheme S2, which agree well with the experimental concentration–time profiles starting from xylitol or xylose, should be developed.

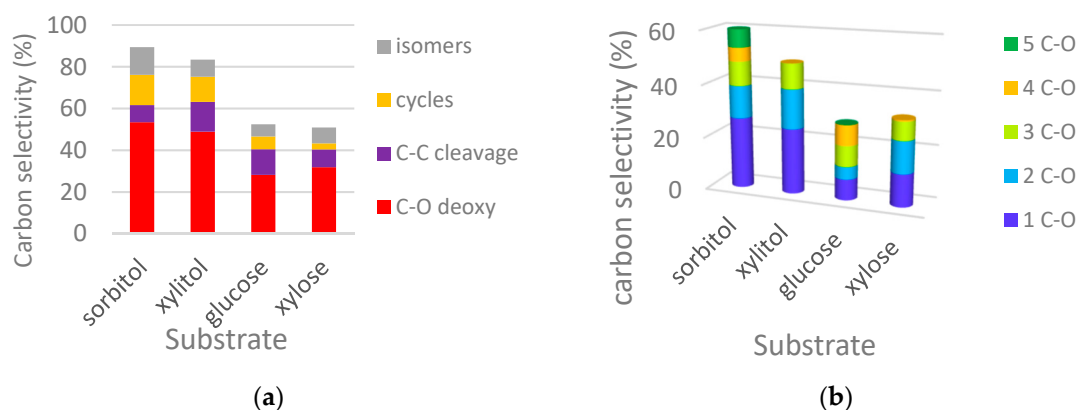
The distribution of the C5 deoxypentanols during hydrogenolysis of xylitol followed the successive mechanism of deoxygenation reported previously [71]: pentanetetraols > pentanetriols > pentanediols > pentanols (Figure 2a'). A higher amount of diols was obtained from xylitol compared with the reaction of sorbitol, simply due to the lower number of hydroxyl groups to be broken in the 5-carbon polyol; the yield of pentanediols was 17% after 8 h in xylitol hydrogenolysis.

A higher yield of 22% pentanediols was observed from xylose at 8 h (Figure 2b'), since pentanetetraols and pentanetriols were deoxygenated deeper.

### 2.2.3. Discussion on Hydrogenolysis of Polyols vs. Hydrogenolysis of Sugars

For an easier comparison of the results of hydrogenolysis of the sugars vs polyols, the carbon selectivities to the different families of products for the different substrates (sorbitol, xylitol, glucose,

and xylose), (Figure 3), were compared at about 80% conversion of the polyols (sorbitol, xylitol) or at about 20% sorbitol or xylitol remaining to be converted (glucose, xylose).



**Figure 3.** Hydrogenolysis of polyols and sugars over  $\text{ReO}_x\text{-Rh/ZrO}_2$  at ca. 20% sorbitol or xylitol remaining to be converted: (a) carbon selectivity to families of products and (b) selectivity to C-O bond sub-families, 200 °C under 80 bar  $\text{H}_2$ .

First, it was noted that the total carbon selectivity in the liquid phase was higher for the polyols than for the sugars. This was confirmed by the comparison of the carbon balance calculated from chromatographic analysis and the measurement of total organic carbon (TOC) in the liquid phase, which are in relatively good agreement within the experimental errors (not shown). This also confirms the relatively adequate analysis of all the products in the liquid phase. This indicates an important loss of carbon material transferred to the gas phase, which was the result of all C-C bond scissions occurring during the reaction of the sugars, probably by decarbonylation and retro-aldol reactions [57].

The polyols and sugars can undergo both C-C and C-O bond cleavage processes. Figure 3a clearly shows that the products formed by successive C-O bond cleavages were the main products, regardless of the substrate. The selectivity to deoxygenated polyols was ca. 28% and ca. 32% from glucose and xylose, respectively, it was higher from sorbitol and xylitol (ca. 55% and ca. 49%, respectively). The selectivity to C-C bond cleavage products was in the range 8–15%. It appeared to be higher in the hydrogenolysis of C5 substrates than in the reaction of C6 substrates. Cyclic compounds are more easily formed from C6 substrates.

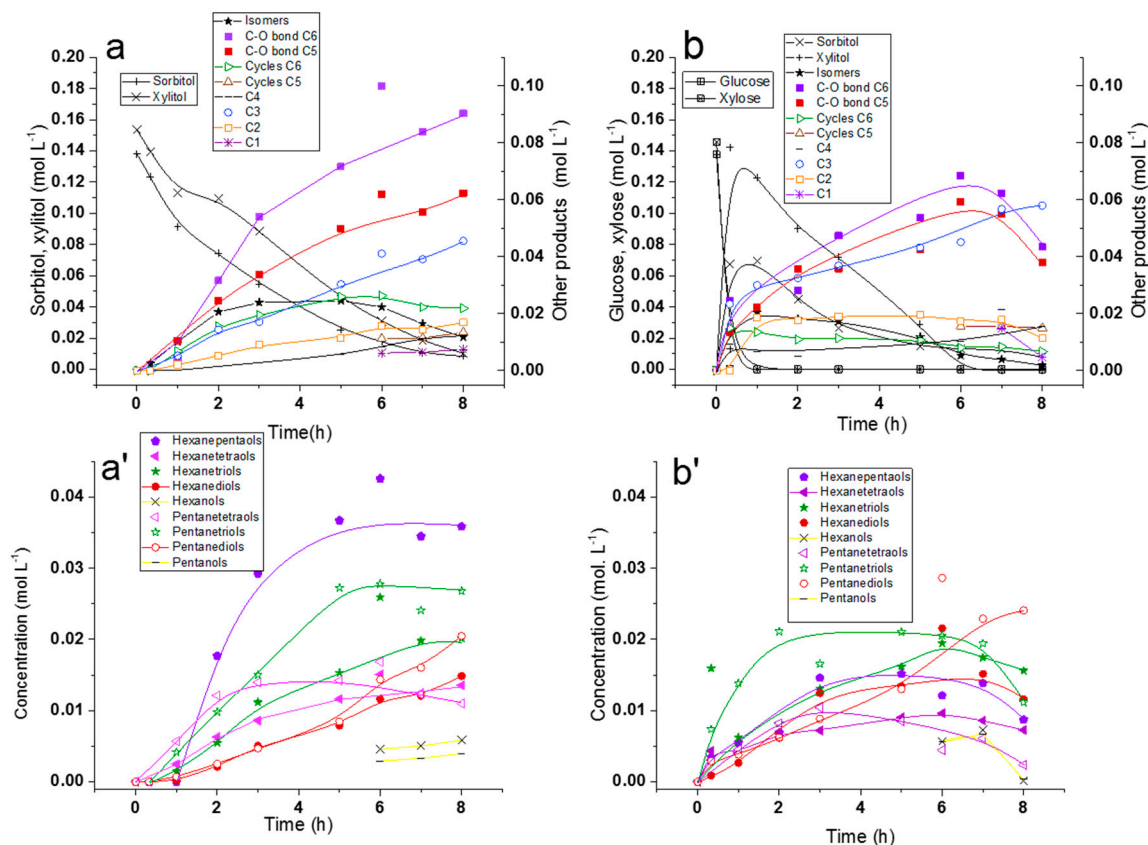
Figure 3b, representing the carbon selectivity to the different sub-families of C-O bond cleavage products, shows a higher degree of dehydroxylation of the sugars compared to the sugar polyols.

### 2.3. Hydrogenolysis of Mixtures of Polyols and Sugars

The composition of hemicelluloses composition may vary depending on their origin. After extraction, the hemicellulose streams contain C5 and C6 sugar monomers and oligomers of various compositions. In order to analyze the reaction medium of hydrogenolysis of hemicellulose extracts, this study was continued by investigating the hydrogenolysis of mixtures of polyols (sorbitol and xylitol) and then of sugars (glucose and xylose) of various composition at 200 °C under 80 bar  $\text{H}_2$ .

#### 2.3.1. Hydrogenolysis of Sorbitol/Xylitol Mixtures

Different compositions of polyols between pure xylitol and pure sorbitol were examined. As an example, the results for the hydrogenolysis of an equimolar mixture of sorbitol/xylitol (1/1, 0.29 M) is shown in Figure 4a,a'.



**Figure 4.** Evolution of concentrations of: (a,b) families of products and (a',b') C-O bond cleavage C6 and C5 sub-families during hydrogenolysis of (a,a') mixture of sorbitol (0.14 M) and xylitol (0.15 M) and (b,b') of mixture of glucose (0.14 M) and xylose (0.15 M) over  $\text{ReO}_x\text{-Rh/ZrO}_2$  ( $\text{Re/Rh} = 1.6$ ) at 200 °C under 80 bar  $\text{H}_2$ ,  $n_{\text{substrate}}/n_{\text{Rh}} = 218$ .

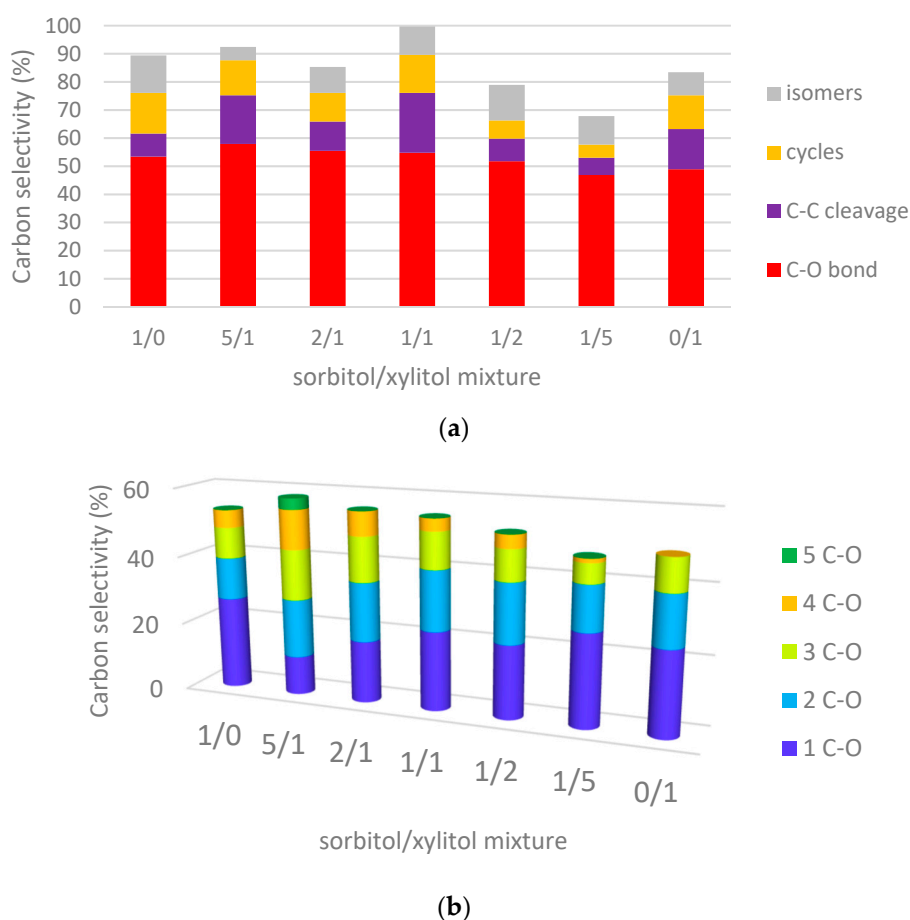
The concentration profiles as a function of time show that both sugar polyols were converted simultaneously and totally within 8 h (Figure 4a). All the reaction products corresponding to those obtained during hydrogenolysis of sorbitol and xylitol alone could be clearly detected after 1 h of reaction. No new products were detected, which eliminates the possibility of inter-reaction between both substrates or their products. The concentrations of the families of products for both substrates in the mixture evolved similarly to those during the hydrogenolysis of sorbitol and xylitol alone. In fact, the sum of the concentrations of C5 and C6 isomers reached a maximum of ca. 0.02 M at 3 h (7% yield, Figure 4a), the cyclic compounds followed the same trends as in separate experiments, C3 polyols were still the main C-C bond cleavage products (0.045 M, ca. 15%) and the concentration of the C-O bond cleavage products attained 0.16 M (55% yield, Figure 4a) vs. 60% and 48% from sorbitol and xylitol, respectively. The C6 deoxy products were produced in slightly higher concentration than the C5 deoxy products.

More or less all deoxygenated polyols were formed by successive C-O bond cleavage (Figure 4a'). Among these deoxy compounds, hexanepentaols (one C-O cleavage) and pentanetriols (2 C-O bond cleavage) were the major products of the sorbitol/xylitol mixture. Pentanetetraols that were formed initially were rapidly further deoxygenated. The final concentrations of the hexanediols and pentanediols were 0.015 M and 0.02 M (11% and 13% yield, respectively) after 8 h. Only the low concentration of hexanols and pentanols (0.005 M) were measured (yield < 2% each).

Figure 5a compares the distribution of the different families of products as the sorbitol/xylitol molar ratio was varied from pure sorbitol to pure xylitol at around 80% conversion of sorbitol or xylitol (initial substrate or formed during reaction). The selectivity to C-O cleavage products, C-C bond cleavage cyclic products, or isomers represent all products issued both from the C6 and C5 polyols.



The 1/1 sorbitol/xylitol mixture corresponds to Figure 4, 1/0 corresponds to sorbitol separately (Figure 2), and 0/1 to xylitol (Figure 3).



**Figure 5.** Evolution of carbon selectivity (a) to families of products and (b) to C-O bond sub-families versus sorbitol/xylitol mixtures during hydrogenolysis of polyols over  $\text{ReO}_x\text{-Rh/ZrO}_2$  at ca. 80% conversion, 200 °C under 80 bar  $\text{H}_2$ , substrate/nRh ~ 200–300.

With increasing amounts of xylitol in the mixture, the carbon balance in the aqueous phase decreased, in line with the data discussed above, comparing pure sorbitol and xylitol. The products issued from different degrees of C-O bond cleavage always represented the main products. The selectivity to these desired compounds was in the range 47–58%. It was not possible to identify any directional trend from sorbitol to xylitol with increasing amounts of xylitol, due to a possible margin of error of  $\pm 10\%$  in the determination. Selectivity to C-C bond breakage was in the range 6–17% at 80% conversion, while the selectivity to C5 and C6 cycles varied between 6% and 15%. Less cycles were formed from xylitol-rich solutions than from sorbitol-rich ones. Isomers were formed with selectivity in the range of 7% to 13%.

Figure 5b details the carbon selectivity to linear deoxygenated products after 1 to 5 C-O bond cleavages of C5 or C6 polyols, at ca. 80% conversion. Globally, a sequential deoxygenation was confirmed for all compositions, and the selectivity to the different deoxygenation degrees was in the order:

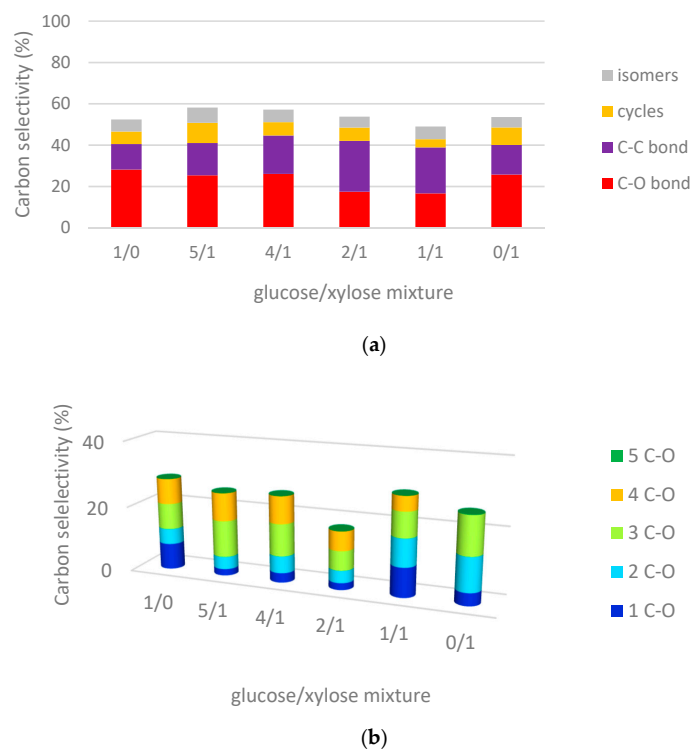
1 C-O bond (12–27%) > 2 C-O bonds (12–17%) > 3 C-Os bond (6–15%) > 4 C-O bonds (0–12%) > 5 C-O bonds (0–3%).

### 2.3.2. Hydrogenolysis of Mixtures of Glucose/Xylose

In fact, extracts from hemicelluloses contain mixtures of sugars whose hydrogenolysis behavior were essential for this study. The hydrogenolysis treatment of an equimolar mixture of glucose and xylose under the same operating conditions as for polyols is shown in Figure 4b. The conversion of both sugars was total within only 1 h, in line with their high reactivity when reacted separately (Figures 2b and 3b). Xylose and glucose were essentially transformed to xylitol or sorbitol, and the usually observed hydrogenolysis products. The maximum concentration of the corresponding polyols was very rapidly attained after 20 min at 0.08 M (57% yield) and 0.04 M (27% yield), respectively. The polyols were then progressively converted; xylitol disappeared at a higher rate than sorbitol and transformation was total after 6 h vs. >8 h. The evolution of the concentrations of the different families of products in the mixture of sugars was very similar to that of sugars alone (Figure 3b). The maximum total concentration of the deoxy C5 and C6 compounds was 0.13 M (yield ca. 45%) after 6 h.

As expected from the comparison of polyols and sugars, (Figure 4b), deoxygenation after 7 h of hydrogenolysis of the glucose/xylose 1/1 mixture was more complete than from the mixture of sorbitol/xylitol 1/1 because of the very high reactivity of the sugars. At the end of the reaction, pentanediols were dominant (0.025 M), followed by pentanetriols (0.02 M), hexanetriols (0.018 M), hexanediols (0.016 M), hexanepentaols (0.014 M), hexanetetraols (0.009 M) and finally by pentanetetraols, hexanols and pentanols (~0.006 M each), which almost follows the distribution of the sub families of C-O bond cleavage products during hydrogenolysis of glucose and xylose alone (see in Section 3.1, Figure 4b').

As for the polyol mixtures, the C6/C5 composition of the sugars was varied between pure glucose (1/0) and pure xylose (0/1). The results summarized in Figure 6a confirm the higher loss of material in the liquid phase for the mixture of monosaccharides than for polyols. Selectivity to C5 plus C6 deoxygenated products was in the range of 17% to 32%.



**Figure 6.** Evolution of carbon selectivity: (a) to the different families of products and (b) to the sub-families of C-O bond breakage products during hydrogenolysis of sugar mixtures over  $\text{ReO}_x\text{-Rh/ZrO}_2$ , 200 °C under 80 bar  $\text{H}_2$ ,  $n_{\text{substrate}}/n_{\text{Rh}} \sim 200\text{--}300$ , 20% of the sugars remaining as polyols.

All deoxygenated compounds (1 to 4 –C-O- bond scissions) were formed (Figure 4b).

#### 2.4. Hydrogenolysis of Sugar Isomers

Table 1 compares the hydrogenolysis of glucose, mannose, galactose (ca. 0.25 M) on one hand, and xylose and arabinose (ca. 0.35 M) on the other hand (Scheme S3) over a  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalyst (with same Re/Rh ratio of 1.8). The results associated with glucose and xylose correspond to Figure 6 (1/0 and 0/1, respectively).

**Table 1.** Hydrogenolysis of C6 and C5 monosaccharides. Data at 20% of the corresponding polyol remaining.

Carbon Selectivity to Products (%)	Glucose	Mannose	Galactose	Xylose	Arabinose
C-O bond scission	26.3	34.3	47.4	31.9	32.9
C-C products	9.1	23.5	10.1	15.2	18.9
Cycles	6.8	11.3	5.3	2.9	1.4
Isomers	7.8	1.2	6.3	7.6	3.5
1 C-O breaking	10	13.4	17.1	12.3	12.3
2 C-O breakings	5.0	3.7	11.7	12.1	12.6
3 C-O breakings	5.5	8.5	10.1	7.0	7.5
4 C-O breakings	5.8	8.7	8.5	0.5	0.5
5 C-O breakings	-	-	-	-	-

The results were compared at total conversion of the sugar (that occurs in less than 1 h) and ca. 20% of the corresponding polyol remaining (sorbitol, mannitol, or dulcitol; xylitol or arabitol). The conversion of the different C6 and C5 sugar isomers was little affected and they were converted in less than 1 h. The composition of products at around 20% remaining polyol is given in Table 1.

The global selectivity to the deoxy C6 products depending on the nature of the isomer was as follows: glucose (23.3%) < mannose (different from glucose by the orientation of OH-group at carbon in position 2; 34.3%) < galactose (different in orientation of OH-group at carbon in position 4; 47.4%). Hydrogenolysis of mannose was characterized by a higher level of C-C bond breaking, leading to a selectivity of 23.5% to C-C products; these were mainly C3 and C2 compounds (not shown). On the other hand, xylose and arabinose behaved very similarly and the composition to the different families were comparable. Among the C-O bond scission products, polyols with one or two dehydroxylation processes were formed as major products at the end of the reaction.

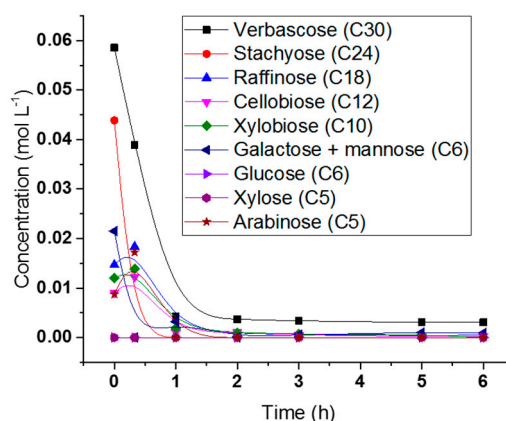
These results may be analysed in parallel with the mechanistic study by Kühne et al. on C-O hydrogenolysis of polyols over Raney<sup>®</sup> Cu [57]. The steric orientation of OH-groups in sorbitol and mannitol did not affect the activity and global selectivity to C-O deoxy C6 products. However, the arrangement of these OH-groups strongly modified the hydrogenolysis pathway, as shown in the study of the reactivity of various polyol compounds.

The results obtained during hydrogenolysis of mixtures of polyols and sugars and of different component sugars of hemicelluloses should help us to better analyze and understand the behavior during hydrogenolysis of the extracted hemicellulose liquor presented in the next section.

#### 2.5. Hydrogenolysis of Hemicelluloses Liquor

Prior to hemicelluloses extraction, a mild and selective delignification treatment using sodium chlorite in buffer aqueous medium was carried out. Hemicelluloses extraction took place on fully delignified samples by applying water extraction at 160 °C during 30 min. Breakdown of hemicelluloses, dissolution of the corresponding oligomers, and degradation of oligomers to monomeric saccharides occur during hot water extraction. The extracted liquid was filtrated and the hemicelluloses high weight fraction precipitated by addition of ethanol. The final recovered liquid phase containing low MW oligosaccharides and sugars (see experimental part) was treated over active carbon and subjected to catalytic hydrogenolysis after the elimination of ethanol, under the same reaction conditions (over  $\text{ReO}_x\text{-Rh/ZrO}_2$  at 200 °C under 80 bar  $\text{H}_2$ ).

Figure 7 shows the concentrations of the sugar oligomers and monomers detected by HPLC during hydrogenolysis of this hemicelluloses liquor. Galactose and mannose could not be separated properly on the  $\text{Ca}^{2+}$  column used for the sugars analysis, therefore, they were analysed together. The analysis revealed the presence of oligosaccharides such as verbascose (C30, stachyose with an additional unit of  $\alpha$ -D-galactopyranose), stachyose (C24, two  $\alpha$ -D-galactose units, one  $\alpha$ -D-glucose unit, and one  $\beta$ -D-fructose unit sequentially linked), raffinose (C18, trisaccharide composed of galactose, glucose, and fructose), cellobiose (C12) and xylobiose (C10). It is important to mention that the peaks of raffinose, stachyose and verbascose taken as standards for HPLC analysis may also be attributed to maltopentaose (C30), maltotetraose (C24) and maltotriose (C18), respectively. With the same DP, they could not be separated and analysed in a satisfactory manner, as also previously observed [75].



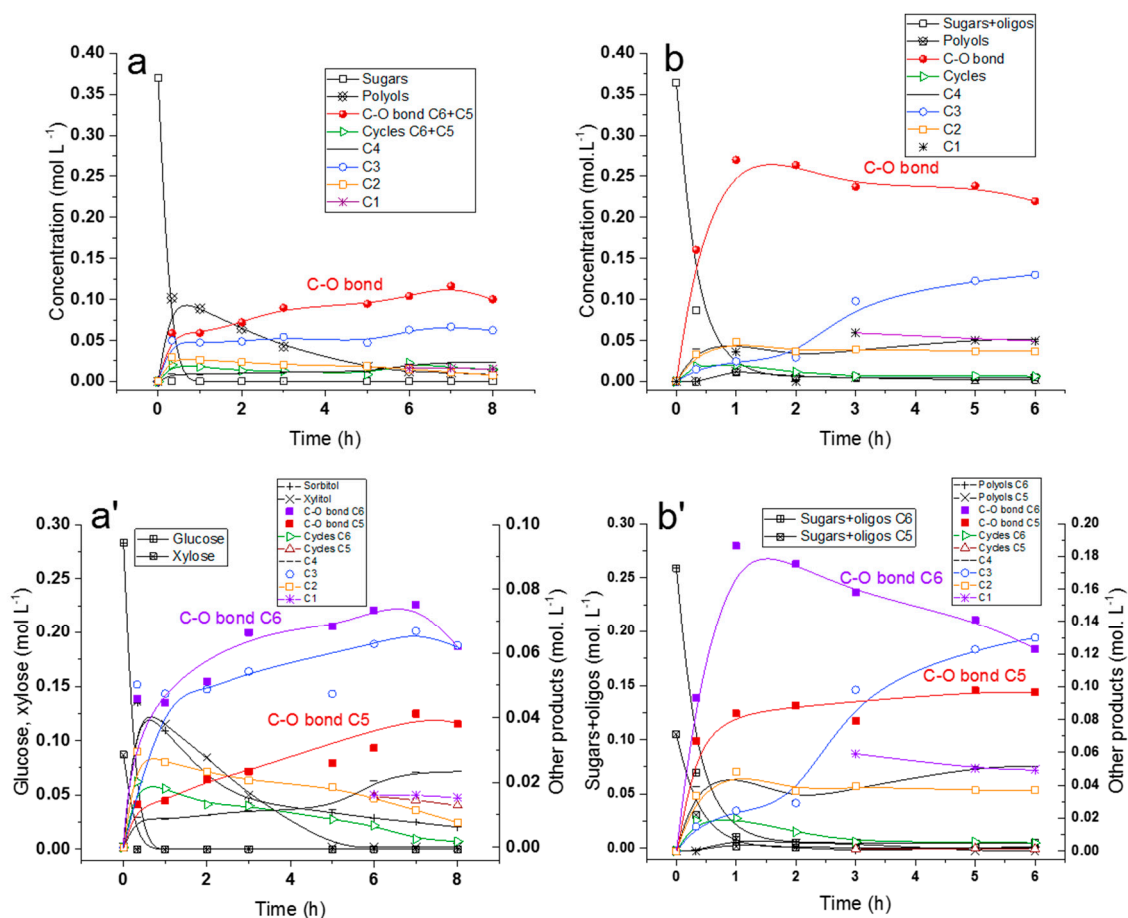
**Figure 7.** The evolution of oligomers and sugars during the hydrogenolysis of hemicellulose over  $\text{ReO}_x\text{-Rh/ZrO}_2$  at 200 °C under 80 bar  $\text{H}_2$ .

Verbascope and stachyose were the main products detected before the reaction, which is not surprising since the low weight molecular fraction of hemicellulose after extraction with hot water contains small oligomers. Raffinose, lactose and xylobiose were also observed with a maximum concentration at 0.33 h of reaction, due to partial conversion of verbascose and stachyose to these secondary products. The concentration profile of xylobiose indicates that there were probably C5 oligomers with DP > 10, that may have been transformed into xylobiose. They were presumably not detected by the HPLC system used or they were not soluble. In fact, C5 hemicelluloses, such as xylan, may be insoluble in water and they very often require alkaline medium to be extracted and stabilized at room temperature [16]; moreover, a low pH facilitates the formation of humins [69]. Galactose, mannose and arabinose were also detected faintly as free-sugars in the hemicelluloses extract. All the products were almost fully transformed within 1 h, except verbascose, whose concentration remained at a low stable value of  $0.003 \text{ mol L}^{-1}$ .

Secondly, in order to determine the composition of constituent sugars, hydrolysis of hemicelluloses was performed in HCl at 90 °C for 24 h (see experimental part). These hemicelluloses are composed of mannose and galactose ( $0.17 \text{ mol L}^{-1}$ ), xylose ( $0.053 \text{ mol L}^{-1}$ ), arabinose ( $0.051 \text{ mol L}^{-1}$ ) and glucose ( $0.036 \text{ mol L}^{-1}$ ). This composition compared well with those reported by Gonzalez-Munoz et al. [9,10], and Rivas et al. [76] for maritime pine. A few oligomers with low DP were still present as stachyose ( $0.025 \text{ mol L}^{-1}$ ), raffinose ( $0.015 \text{ mol L}^{-1}$ ), and cellobiose ( $0.011 \text{ mol L}^{-1}$ ), indicating incomplete hydrolysis. As expected, oligomers are the primary products of hemicellulose hydrolysis, which are further degraded to sugars.

Finally, the hydrogenolysis reaction was performed on the hemicelluloses extract. The results are shown in Figure 8. The total initial concentration (ca. 0.35 M) of free sugars and small oligomers were based on the concentrations measured after hydrolysis of the hemicelluloses extract with HCl at 90 °C. The C6/C5 molar ratio of sugars was ca. 2/1. Therefore, the reaction was compared to the reaction of an equivalent 2/1 synthetic mixture of glucose and xylose. Interestingly, the hemicelluloses extract

liquor gave almost the same products and demonstrated a comparable evolution of the family products as the synthetic mixture of sugars. Levulinic acid, hydroxymethylfurfural (HMF), and furfural were also observed, but in very low amounts (not shown).

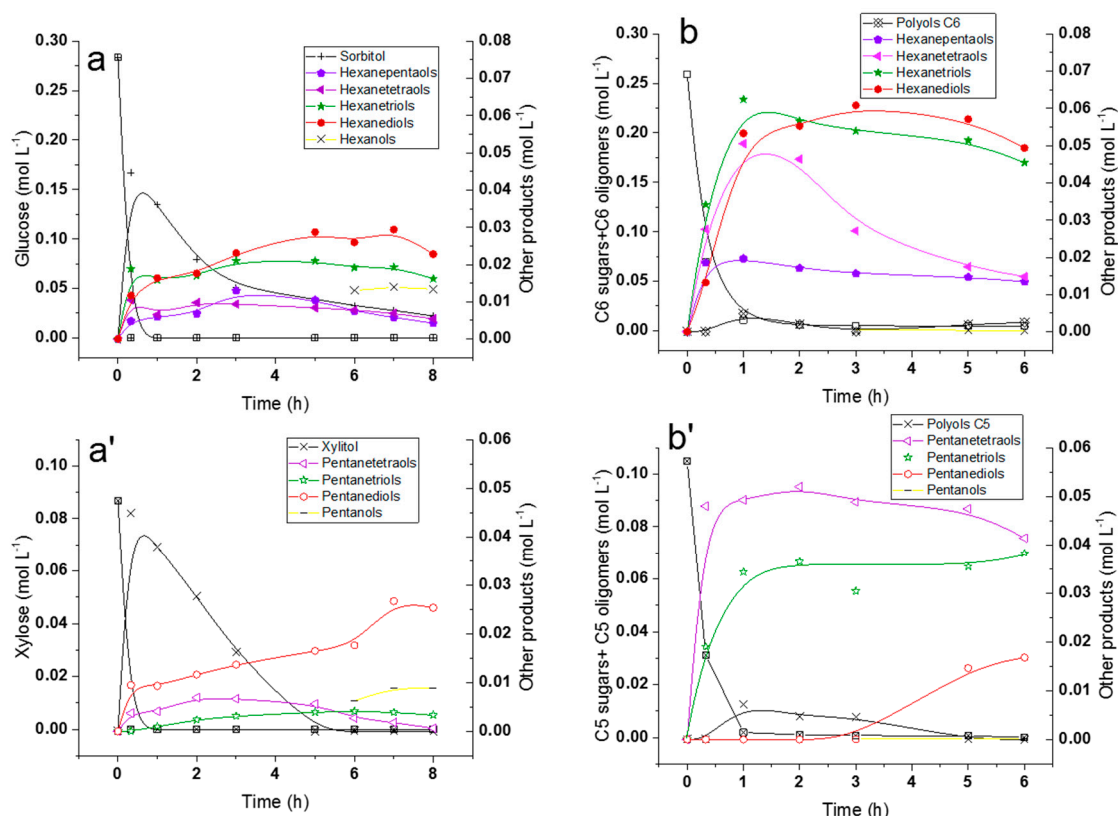


**Figure 8.** Evolution of families of products concentrations during hydrogenolysis of (a,a') glucose/xylose mixture (2/1) and of (b,b') hemicelluloses liquor over  $\text{ReO}_x\text{-Rh/ZrO}_2$  at 200 °C under 80 bar  $\text{H}_2$ .

However, the reaction rate and the products distribution were quite different (Figure 8a,b). First, one may notice a very low formation of gaseous products from hemicelluloses liquor. Moreover, a rapid and more important formation of products was issued from C-O bond scission reactions was attained ( $0.26 \text{ mol L}^{-1}$  after 1 h). Taking into account the initial concentration of free sugars and oligomers determined after acid hydrolysis of the extract, the selectivity to C-O bond cleavage products was around 65% vs. 30% for the synthetic solution. Overall, the distribution of the sub-families of C-O bond C6 products and C-O bond C5 products was coherent with the distribution of these products from the glucose/xylose (2/1) sugars mixture (Figure 8a',b'). Nevertheless, concentrations of deoxy C6, deoxy C5, C4, C3, C2 concentrations were doubled after 6 h for hemicellulose extract compared to those in the glucose/xylose 2/1 mixture. This may be attributed to the higher concentration of mannose and galactose in the hemicelluloses liquor.

Furthermore, the repartition of the differently deoxygenated C6 and C5 products is shown in Figure 9, both for the hemicelluloses liquor and for the synthetic mixture.



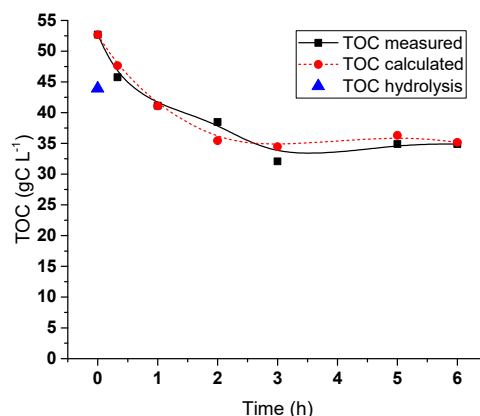


**Figure 9.** Temporal profiles of concentrations of sub-families during hydrogenolysis of (a,a') glucose/xylose mixture (2/1) and of (b,b') liquor of pine maritime over Rh-Re/ZrO<sub>2</sub> at 200 °C under 80 bar H<sub>2</sub>.

The rapid transformation of the C6 polyols in the hemicelluloses stream clearly yielded successively hexanepentaols and hexanetetraols at the beginning of the reaction, followed by hexanetriols and hexanediols during the reaction (Figure 9b). Hexanols were not observed. The C5 polyols were also very rapidly converted into pentanetetraols (Figure 9b'), which, in this case, was hardly transformed into pentanetriols and pentanediols in comparison with the model mixture (Figure 9a'). Nor were pentanols observed, confirming that gaseous products were very poorly formed during hydrogenolysis of the hemicelluloses liquor.

Finally, the relatively good accuracy of analysis of all categories of products was confirmed by TOC measurement (Figure 10). There was a good fit between TOC calculated from chromatography and TOC measured. Both indicate the loss of material in the aqueous phase during reaction (ca. 10 gC L<sup>-1</sup>). It is important to note that a small fraction of ethanol could not be completely removed after extraction and was still present in the reaction medium.

The reason for the large difference between the hydrogenolysis of the synthetic solution of mixture of sugars and the real hemicelluloses sample is not clear. Although the hemicelluloses were extracted from delignified wood and further purified by treatment with active carbon, which is a good adsorbent for removing unsaturated products, during the hydrothermal treatment, furfural and 5-hydroxymethylfurfural may be formed from the dehydration of pentoses and hexoses, respectively. In addition, uronic acids (glucuronic, galacturonic) may be released during hydrolysis. These by-products may be strongly adsorbed on the catalyst surface and play the role of selective poisoning of the C-C bond breaking. Further research is needed to explain such different behaviours and the possible effect of these residual by-products.



**Figure 10.** Hydrogenolysis of hemicelluloses liquor: comparison TOC measured, TOC calculated from chromatography, and TOC measured after hydrolysis with HCl.

### 3. Experimental

#### 3.1. Catalyst Preparation

The  $\text{ReO}_x\text{-Rh/ZrO}_2$  catalysts were prepared by successive impregnation as previously described [70].  $\text{ZrO}_2$  was supplied by MEL Chemicals (XZO 632/18,  $129 \text{ m}^2 \text{ g}^{-1}$ , mesoporous, average pore diameter 9 nm). In a typical preparation,  $\text{ZrO}_2$  was first wet-impregnated with an aqueous solution of  $\text{RhCl}_3$  at room temperature for 7 h. After the evaporation of water, the resulting solid was dried at  $100^\circ\text{C}$  overnight and calcinated under air at  $500^\circ\text{C}$  for 3 h. The second impregnation was conducted with an aqueous solution of ammonium perrhenate ( $\text{NH}_4\text{ReO}_4$ ), followed by a second calcination, a reduction step under  $\text{H}_2$  at  $450^\circ\text{C}$ , and passivation under 1%  $v/v$   $\text{O}_2/\text{N}_2$ .

#### 3.2. Maritime Pine Extraction and Hydrolysis

##### 3.2.1. Extraction of Hemicelluloses

The chemical composition of maritime pine wood used in this work (on a dry weight basis) was 41.4% glucan, 26.1% lignin, 13.1% mannan, 7.3% xylan, 4.6% extractibles, 2.5% galactan, and 1.3% arabinan (balance 96.3%).

Wood chips (1.2 kg) were ground and sieved to size particle below 1 mm. Wood powder was first delignified using sodium chlorite in an acetate buffer medium (liquor/wood weight ratio = 6) in a 5 L glass reactor, at  $60^\circ\text{C}$ , under mechanical stirring and nitrogen gas flow [77]. Chlorite sodium was progressively added to the medium until complete delignification (around one week of extraction for each batch). The delignification was followed by the measurement of Kappa number (carried out using the ISO 302-2015 standard method) of the treated wooden material. At the end of the delignification, the wood particles were totally converted into fibres, which were thoroughly washed with demineralized water until neutral pH.

The hot water extraction of hemicelluloses was performed after elimination of lignin by a sodium chlorite treatment. Typically, the delignified wood chips (300 g, dry basis, particles below 1 mm) and deionized water (1800 mL) at a water/wood ratio of 6 were filled into a 5 L batch stainless-steel oil-heated autoclaves. Temperature was raised from  $25^\circ\text{C}$  to  $120^\circ\text{C}$  in 30 min, followed by a plateau at  $160^\circ\text{C}$  for 30 min. Subsequently, the liquor was separated from the solid material by filtration over a 4-L Büchner porosity 2. The pH of the collected filtrate was acidic (due to the release of small amounts of acetic or uronic acids upon extraction) and its value was then raised to 6 with the addition of NaOH.

The extracted stream was then further fractionated. The supernatant solution was concentrated by evaporation, and subsequent addition of ethanol (1/3 water–2/3 ethanol) caused the precipitation of high molecular weight hemicelluloses polymers. The remaining aqueous extract, containing monosaccharides and low molecular weight oligosaccharides [78], was finally purified with active

carbon in order to remove all unsaturated by-products. This liquor phase was used for the hydrogenolysis reactions after the removal of EtOH using a rotary evaporator at 40 °C under vacuum (175 mbar).

### 3.2.2. Analysis of Carbohydrates in Hemicellulose Extract

The low MW hemicelluloses extracted liquor was analysed by high performance liquid chromatography (HPLC, see below) for monosaccharide contents (glucose, xylose, mannose, galactose and arabinose). The carbohydrate composition was determined after a second acid post-hydrolysis of the liquor to depolymerize all remaining oligomers to monosaccharides using 37% HCl aqueous solution (pH 1) for 24 h at 90 °C in an autoclave, according to the protocol described in [79,80].

Table 2 shows the chemical compositions of the unhydrolyzed and post-hydrolyzed hemicelluloses liquor.

**Table 2.** Amounts of monosaccharides in the extracted purified liquor before and after acid post-hydrolysis.

	Glucose (mg L <sup>-1</sup> )	Xylose (mg L <sup>-1</sup> )	Mannose (mg L <sup>-1</sup> )	Galactose (mg L <sup>-1</sup> )	Arabinose (mg L <sup>-1</sup> )
Non-hydrolyzed liquor	35.3	235.7	113.6	95.0	818.8
Post-hydrolysis liquor	1229.9	2195.2	5575.5	437.4	1088.8

The sugars in the non-hydrolyzed extraction liquor were essentially present as oligomers. Arabinose was extracted early as monosaccharide, consistent with results of Grénman et al. [81] in their study of aqueous extraction of hemicelluloses from spruce chips. These authors demonstrated that this sugar experienced further reaction and degradation during extraction.

The post-hydrolysis fraction consisted of a mixture of 7.24 g/L of hexoses and 3.28 g/L of pentoses, with a hexoses/pentoses ratio of 2.2. Mannose accounted for about 50% in the extracted purified liquor. This observation is in accordance with the fact that the main hemicelluloses of softwood are galactoglucomannans.

### 3.3. Catalyst Evaluation Experiments and Products Analysis

The model substrates D-Xylitol (99%), D-sorbitol (99%), D-xylose (99%), and D-mannose (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), D-glucose (99%), D-galactose (98%), and L-arabinose from Alfa Aesar. All reagents were used without further purification.

All the hydrogenolysis reactions of polyols, sugars, their mixtures, and the hemicelluloses liquor were performed in a batch Hastelloy Parr 4560 reactor (300 mL). For each run, the autoclave was loaded with 120 mL of aqueous solution and 0.5 g of catalyst. For the polyols (xylitol, sorbitol) and sugars (xylose, arabinose, glucose, mannose and galactose), 6 g of each product were previously dissolved in 120 mL of water. An amount of 120 mL of hemicelluloses liquor was loaded after elimination of ethanol. After sealing and flushing three times with 10 bar Ar to remove residual air, the reactor was pressurized with H<sub>2</sub> and heated to 200 °C under stirring (1000 rpm). The pressure increased during heating; hence, the pressure given of 80 bar reflects the pressure under the reaction conditions. Liquid samples were regularly collected during the reaction.

A detailed description of the analytical procedure of the reaction medium during hydrogenolysis of polyols can be found in our previous study [71]. Hexanepentaols, hexanetetraols, hexanetriols, hexanediols, pentanetetraols, pentanetriols, isosorbide, butanediols (mainly 1,2-butanediol), glycerol (GLY), 1,2 propanediol (1,2-PrDO), ethylene glycol (EG) were analyzed using a Shimadzu LC 20 A HPLC equipped with a Rezex ROA-Organic Acid H<sup>+</sup> column (crosslinked sulfonated styrene divinylbenzene copolymer) with a 0.005 N H<sub>2</sub>SO<sub>4</sub> mobile phase at a flow rate of 0.5 mL min<sup>-1</sup>) kept at 40 °C and connected to a RID detector.

The C1-C6 mono alcohols and tetrahydrofurfuryl alcohol (THFA), 1,2-pentanediol (1,2 PDO), 1,5-pentanediol (1,5 PDO), tetrahydrofuran (THF) present in the aqueous reaction medium were determined on a Shimadzu GC-2010 analyzer equipped with a Phenomenex FFAP 30 m × 0.25 µm

column (the temperature was increased from 40 °C to 100 °C at 5 °C min<sup>-1</sup>, and then to 250 °C at 8 °C min<sup>-1</sup>).

C6 and C5 sugars and sugar polyols (glucose, xylose, galactose, mannose, arabinose, sorbitol, xylitol, dulcitol, mannitol, arabitol, iditol) were analyzed on a Shimadzu LC 20 A HPLC using Rezex RCM-Monosaccharide Ca<sup>2+</sup> column heated at 65 °C with water as eluent and with refractive index detector (RID-10A) [67]. In fact, this column allows analysis of sugars, polyols, and can additionally provide analysis of oligosaccharides with low DP < 6. Therefore, in addition to the monosugars, available soluble oligosaccharides were used as analytical reference standards to attempt to identify the structures or homologs released during extraction, such as cellobiose, the raffinose family of oligosaccharides comprising raffinose (trisaccharide), stachyose (-galactosido-1,6-raffinose) and verbascose (α-galactosido-1,6-stachyose), but also sorbitan, 2-MeTHF, HMF, furfural, THFA, tetrahydropyran-2-methanol. Figure S2 presents the HPLC chromatogram of the hydrolysed extract, which shows that not only sugar monomers were formed, but also a high percentage of the hemicelluloses as dimers, trimers, and larger oligomers.

The calibration of products was carried out by injecting known concentrations of commercial standards. For a same family of product, the same response coefficient as the one of the commercially available product was considered.

The substrate conversion was calculated from Equation (1):

$$\text{Conversion (\%)} = \frac{[\text{Substrate}]_0 - [\text{Substrate}]_t}{[\text{Substrate}]_0} \times 100 \quad (1)$$

where  $[\text{Substrate}]_0$  is the initial concentration of s, and  $[\text{substrate}]_t$  the concentration at time t.

The yield of a given product was calculated according to Equation (2):

$$\text{Product yield (\%)} = \frac{[\text{Product}]_t}{[\text{Substrate}]_0} \times 100 \quad (2)$$

The carbon selectivity  $S_t^i$  to a desired product is based on Equation (3):

$$S_t^i(\%) = \frac{[\text{Product}]_t^i \times N_C^{\text{product } i}}{([\text{Substrate}]_0 - [\text{Substrate}]_t) \times n_C^{\text{substrate}}} \times 100 \quad (3)$$

where  $[\text{Product}]_t^i$  is the concentration of product i formed at time t,  $N_C^{\text{substrate}}$  and  $N_C^{\text{product } i}$  is the number of carbon atoms in the substrate and product I, respectively.

Total Organic Carbon (TOC) was measured using a TOC-V<sub>CSH</sub> Shimadzu analyzer. The values were compared with the TOC calculated from the analysis of the products in liquid phase by HPLC and GC by the following Equation (4):

$$\text{Calculated TOC}_t (\text{g L}^{-1}) = M_C \left[ \left( \sum_i^n N_{\text{carbon}}^i \times C_t^i \right)_{\text{HPLC}} + \left( \sum_i^n N_{\text{carbon}}^i \times C_t^i \right)_{\text{GC}} \right] \quad (4)$$

where  $M_C$  is the molar mass of carbon (12 g mol<sup>-1</sup>),  $N_{\text{carbon}}^i$  is the number of carbon atoms in compound i, and  $C_t^i$  is the concentration of compound i at time t (in mol L<sup>-1</sup>). The comparison between TOC calculated and TOC measured provides an indication as to the carbon balance in liquid phase.

#### 4. Summary

The pre-extraction of hemicelluloses from lignocellulosic materials before pulping processes generates sugars as feedstocks for hemicelluloses-based chemicals. In this work, the comparative hydrogenolysis of C5-C6 separate sugar polyols and sugars was studied over ReO<sub>x</sub>-Rh/ZrO<sub>2</sub> catalysts before evaluating mixtures and a liquid stream of hemicelluloses-based sugars.

A complete conversion of sugars was achieved very rapidly: the predominant reaction was hydrogenation to the corresponding sugar alcohol to yield the corresponding polyols by hydrogenation, but direct hydrogenolysis of the monosaccharides was observed from the beginning of the reaction, yielding all the products formed by hydrogenolysis of the sugar-derived polyols. Due to higher C-C cleavage and mainly related to the retro-aldol and decarbonylation reactions, the maximum global selectivity to deoxy linear polyols was lower from sugars (28% and 32%, from glucose and xylose) than from polyols (35% and 49% from sorbitol and xylitol). However, sugars underwent deeper C-O bond hydrogenolysis reaction, which favored the rapid formation of diols.

Hydrogenolysis of mixtures of polyols and sugars allowed the further analysis of the complete product spectra. The comparative hydrogenolysis of epimers of glucose and xylose also suggested that orientation of the OH-groups may affect the selectivity to the deoxy-products.

In the end, hot water extraction of hemicelluloses from a delignified maritime pine wood was performed. Conversion of the low molecular weight mono- and oligosaccharides in the recovered extract was studied by hydrogenolysis and the results were compared to a synthetic aqueous solution of glucose/xylose mixture of same C6/C5 composition of 2/1. The global selectivity to linear deoxygenated polyols was found to be higher than in the reaction of the synthetic solution. The yield of the deoxy polyols from the extracted hemicelluloses liquor was as high as 65% whereas it was only 30% from the 2/1 glucose/xylose mixture. This selectivity difference is mainly linked to the high concentration of mannose and galactose leading to improved selectivity compared to glucose. The presence of by-products from the extraction process, such as furfural or HMF formed from the dehydration of sugars, may play a role of selective poisoning adsorbate limiting the reduction of the undesired C-C bond breaking side reactions. These runs show the possibility of the production of value-added C6 and C5 tetraols, triols, and diols by catalytic hydrogenolysis of sugars and their oligomers present in the hemicellulose extracts. The next step should be to study the catalyst stability. Further research is also needed to develop kinetic models that describe adequately the experimental concentration of liquid products–time data and the complex networks of hydrogenolysis of either the polyols or the sugars. This kinetic analysis is essential for maximizing the yield of desired chemical products.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/9/9/740/s1>, Figure S1: XRD pattern of support  $\text{ZrO}_2$  and of catalyst 9.4%Re–3.2%Rh/ $\text{ZrO}_2$ , Figure S2: HPLC chromatogram of pine maritime hemicellulose after chlorite treatment, hot water extraction, and acid hydrolysis with HCl at 90 °C during 24 h using Rezex RCM-Monosaccharide  $\text{Ca}^{2+}$  HPLC column, Scheme S1: Reaction pathway during hydrogenolysis of sorbitol and glucose. Adapted from [71], Scheme S2: Reaction pathway during hydrogenolysis of xylitol and xylose, Scheme S3: C6 and C5 sugars in the hemicelluloses liquor Adapted from [71].

**Author Contributions:** Conceptualization: D.D.S.P., M.B., and C.P.; Design of experiments: M.B. and N.P.; Carrying the experiments and analyzing the data: A.S., M.M.-D., and E.N.; Writing original draft: M.M.-D.; Writing, review and editing: M.B., N.P.; Supervision: C.P., N.P. and M.B.

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