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Oxidation of Aldoses Contained in Softwood Hemicellulose Acid Hydrolysates into Aldaric Acids under Alkaline or Noncontrolled pH Conditions

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ABSTRACT: The hemicellulose-derived aqueous solution of C6 and C5 sugars (D-mannose, D-galactose, D-glucose, D-xylose, L-arabinose), obtained from the extraction and hydrolysis of the hemicellulosic polymers in softwoods prior to the production of pulp, was catalytically converted to the corresponding aldaric acids under alkaline (Pt/C) or native (Au–Pt/ZrO₂) aqueous conditions with air. The inhibiting effect of some residual impurities and degraded compounds in the hydrolysate was confirmed, such as colored unsaturated compounds and 5-hydroxymethylfurfural. A combined purification process consisting of filtration, demineralization by ion-exchange resins, evaporation, and active carbon treatment of the raw aqueous-stream gave a purified hydrolysate of aldoses that was oxidized to hexaric and pentaric acids. The yields were close to those of a synthetic solution of the pure sugars with the same distribution. The yields of aldaric acids accounted for ca. 50% of hexaric acids and up to 70% of pentaric acids.

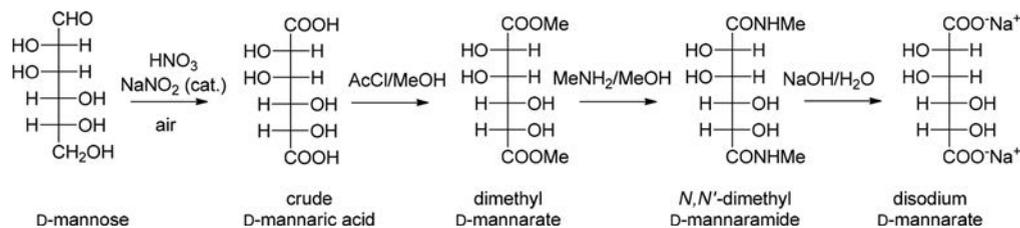
1. INTRODUCTION

Lignocellulosic biomass composed of carbohydrate polymers (cellulose, hemicelluloses) and a complex aromatic polymer (lignin) represents an abundant and cheap source of sugars for the production of many chemicals. The cellulosic fraction currently has a high value and is mainly used to produce paper and cellulosic polymers, or bioethanol. The hemicellulosic part, which is the second most abundant biopolymer representing typically 25–35% of softwood (dry weight basis), is not currently utilized to its maximum potential. For instance, in the Kraft pulping technology of wood, hemicelluloses are degraded during the cooking process used to extract the cellulose fibers; the residual processing black liquor containing the lignin and the hemicelluloses fragments is ultimately burned for energy production. Therefore, increased attention is being placed on a better utilization of hemicelluloses: as feedstock for bioethanol,

as raw material for various biopolymers, or by converting them into sugar monomers, which can in turn be further upgraded into higher value products.^{1–6} In recent years, selective extraction of the hemicelluloses from wood by pretreatment of wood chips prior to pulping has gained increased importance in the biorefinery concept.^{6–8} The biorefinery aims at utilizing the whole biomass for different products and maximizing economic return.

Compared to the other components, and due to their lower degree of polymerization and the presence of branched side groups, hemicelluloses are quite easily hydrolyzed to the

Scheme 1. Synthesis of the Noncommercial Disodium Aldarates As Illustrated for D-Mannarate



monosugars, the hexoses (D-mannose, D-galactose, D-glucose) as well as the pentoses (D-xylose and L-arabinose).⁹ Among the various pretreatment methods, hot water autohydrolysis and dilute sulfuric acid posthydrolysis under moderate temperature (120–160 °C) has proven to be adequate for selective dissolution of the sugars in hemicelluloses, without significant degradation of the cellulose fibers and with little sugar decomposition.¹⁰ The extracted wood chips can still be used for pulp production without any impact on pulp quantity and quality, whereas the extracted sugar monomers in the separated hydrolysate can be further converted into high value-added compounds.

The present work addresses the catalytic oxidation with air of the aldoses in the sugar rich aqueous liquor, separated after prehydrolysis of softwood hemicelluloses with diluted sulfuric acid.¹⁰ The oxidation to the corresponding aldaric acids involves a selective double oxidation of both the aldehyde group as well as the terminal hydroxyl group of the aldoses. The sugar diacids are currently produced on a small scale, but are considered to have great potential. Glucaric acid, derived from glucose, has been ranked as a “top value-added chemical” from biomass.¹¹ It is a promising raw material for polymers, as well as detergent builder, chelating agent, deicing agent, and corrosion inhibitor.^{12–14} Its derivatives have also been studied for therapeutic purposes.^{15,16} Aside from glucaric acid, the other carbohydrate diacids (mannaric, galactaric or mucic, xylaric, and arabinaric acids) could also be used to make a range of bioproducts,¹⁷ and a class of polymers referred as polyhydroxypolyamides,^{18–22} or silicon polyamides.²³ Oxidation of the aldoses to the corresponding aldaric acids can be conducted using nitric acid,^{14,24–30} TEMPO or 4-acetylamino-TEMPO mediated oxidation in aqueous solutions at high pH of 11–12.³¹ Aldaric acids have also been obtained by catalytic oxidation with oxygen or air. Metallic or bimetallic noble metal catalysts under basic conditions,^{32–39} or without need of base addition^{40–43} have been employed for producing selectively glucarate or glucaric acid.

In our earlier studies, the oxidation of glucose was performed in alkaline aqueous solutions to glucarate over Pt/C³⁷ or in native aqueous solutions over AuPt/ZrO₂.⁴³ These procedures involved the formation of numerous side-products, but resulted in yields over 50% in batch reactors. We also examined the influence of potential contaminants of the hydrolysates, including residual sulfuric acid, furans, phenolics, weak acids, and oligosaccharides. Indeed, during hydrolysis in acidic medium, degradation of pentoses to furfural and hexoses to 5-hydroxymethyl furfural (HMF), release of acetic acid from O-acetyl groups in the polysaccharides, formation of soluble lignin-derived phenolics, and incomplete hydrolysis may occur. Among them, furanic and phenolic derivatives were shown to be inhibitors of the catalytic oxidation reaction under both operating conditions, suggesting that the hydrolysates will

certainly not be used directly and they will have to be purified prior to the oxidation reaction.

The principal goal of this research was to perform the catalytic oxidation of the sugars in the hemicelluloses hydrolysate, separated after autohydrolysis with hot water and posthydrolysis with diluted H₂SO₄ of softwood chips, to a mixture of the corresponding aldaric acids. The reactions of synthetic solutions of the different aldoses were performed, separately or in mixture, in the presence of Pt/C with pH control at 9, or in the presence of AuPt/ZrO₂ without pH control, before the evaluation of the performance of the catalysts for the oxidation of the hydrolysate purified to various degrees.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Wherever possible, sugars, aldaric acids, and other chemicals were purchased from Alfa Aesar or Sigma-Aldrich at the highest purity obtainable (>98%). The synthesis of some noncommercial aldarates was necessary for identification and quantification by chromatography (vide infra and the Supporting Information).

The two-step hydrolysis of the pinewood chips from a French pulp mill by hot water followed by 5 g L⁻¹ sulfuric acid was carried out by Pagora at 160 °C, using a liquor to wood ratio of 4.¹⁰ The softwood hemicelluloses primarily consisting of galactoglucmannans and some arabinoglucuroxylans were thus hydrolyzed to their primary components. The resulting raw hydrolysate was filtered on 1.2 μm filter using a Büchner funnel to remove suspended solids, and was concentrated by vacuum evaporation. The HPLC analysis and purification of hydrolysate samples were carried out at Novasep. The purification included an ion-exchange demineralization operated in columns (Novasep resins XA3112 and XA7111MB) and a granulated active carbon (GAC) treatment performed in stirred batch. The concentration of monosaccharides in the resulting evaporated acidic solution (pH 0.7) was around 46 g L⁻¹. It contained mainly mannose, glucose, galactose, xylose, and arabinose. Hexoses were responsible of 72 wt % of its sugar composition, while pentoses represented 28 wt %. The liquor contained also diverse degradation products including acetic acid, furans (mainly 5-hydroxymethylfurfural), oligosaccharides, lignin degraded phenolics. Residual inorganic salts (conductivity 12 mS cm⁻¹, measured with a WTW LF conductimeter) were also present in the hydrolysate after filtration-evaporation.

2.2. Synthesis of Disodium Aldarates. Dipotassium D-glucarate and D-galactaric acid (mucic acid) were commercially available. Disodium D-mannarate, D-xylarate, and D-arabinarate, as well as D-altrarate were synthesized by a multistep reaction from the aldoses via dimethylamide intermediate, based on protocols described in the literature (Scheme 1).^{29,44,45} The synthesis and characterization by ¹H and ¹³C NMR, and high-resolution mass spectrometry (HRMS) are described in the Supporting Information.

2.3. Preparation of Pt/C and AuPt/ZrO₂ Catalysts. A 4.7% Pt/C catalyst was prepared via wet impregnation and liquid phase reduction by formaldehyde and KOH using the previously reported procedure.³⁷ The 3.5%Au-3.5% Pt/ZrO₂ catalyst was prepared by wet impregnation with an aqueous solution of HAuCl₄ and H₂PtCl₆ and using NaBH₄ as the reducing agent, as previously reported.⁴³

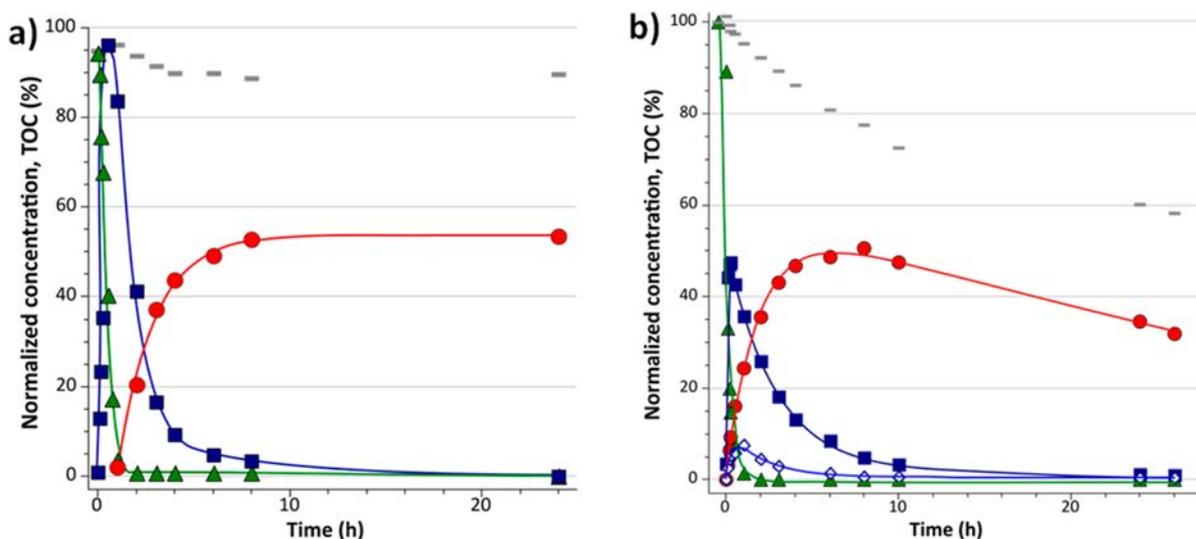


Figure 1. Concentration profiles during oxidation of glucose to (a) glucarate over 3%Pt/C or (b) glucaric acid over 3.5%Au-3.5%Pt/ZrO₂. Reaction conditions: (a) [glucose]₀ = 0.25 M, glucose/Pt molar ratio 157, $T = 60\text{ }^{\circ}\text{C}$, 0.5 L min^{-1} air, pH 9; (b) [glucose]₀ = 0.25 M, glucose/metal = 80, $T = 100\text{ }^{\circ}\text{C}$, 40 bar of air. (▲) glucose, (■) gluconate or gluconic acid, (◇) guluronic acid, (●) glucarate or glucaric acid, (—) TOC.

Characterization of these catalysts were described in these previous publications.

2.4. Oxidation Reaction Tests. Synthetic solutions of the different aldoses, separately or in mixture, and the hydrolysates were oxidized with alkaline pH control over Pt/C ([aldose]₀ = 0.25M, aldose/Pt (n/n) = 157, pH 9 (NaOH 10 wt %, $T = 60\text{ }^{\circ}\text{C}$, air flow 0.5 L min^{-1}) or in non-neutralized conditions over AuPt bimetallic catalyst ([aldose]₀ = 0.25M, aldose/metal = 80, $T = 100\text{ }^{\circ}\text{C}$, air pressure = 40 bar).

The oxidation tests over Pt/C were carried out at atmospheric pressure and controlled pH of 9 in a mechanically driven stirred 500 mL round-bottom jacketed glass reactor.³⁷ In a typical run, 300 mL of an aqueous solution of sugars and the catalyst were introduced into the reactor under N₂ flow. The temperature was increased to $60\text{ }^{\circ}\text{C}$, the pH of the reaction mixture was adjusted to 9 with 10 wt % NaOH, and the flow rate was switched to air (0.5 L min^{-1}).

The oxidation experiments over AuPt/ZrO₂ were conducted batchwise in a 300 mL C22 Hastelloy autoclave, equipped with a magnetically driven stirrer.⁴³ Typically, the catalyst and 100 mL of an aqueous solution of carbohydrates were introduced into the reactor. After purging with Ar three times, the reaction medium was heated under Ar to $100\text{ }^{\circ}\text{C}$, and the pressure was set at 40 bar of air.

2.5. Product Analysis. To follow the progress of the reaction, we periodically took and analyzed samples of the reaction medium. Ion chromatography (Methrom Professional IC850 equipped with the 872 extension module and 889 autosampler) was used to separate and quantify the liquid products after separation from the solid catalyst by filtration. Prior to the analysis the samples were diluted by a factor 50 to 500.

Separation and analysis of monosaccharides were performed with a CarboPac PA1 (250*4 mm) column after a guard column. The column was coupled to a Pulsed Amperometer Detection (PAD). The eluent gradient was set at 2.5 mM NaOH isocratic for 45 min with a step to 100 mM NaOH over 5 min to regenerate the column, and re-equilibration at 2.5 mM for 10 min at a flow rate of 1 mL min^{-1} and a temperature of $17\text{ }^{\circ}\text{C}$ maintained by a Pelletier effect oven.

Separation of aldarates was also performed using the CarboPac PA1 column with an eluent composed of 5 mM NaOH and 200 mM NaOAc, as adapted from the literature for the determination of sialic acids.⁴⁶ Precise quantification of the outcome of the oxidation reactions was made possible by analysis with the amperometric PAD detector and by comparison with authentic aldaric samples. The response of the aldaric acids on the gold electrode was much lower than the response of the sugars; moreover, the intensity of the signal was dependent on the chain length of the aldarates, the signal of C5

aldarates being much less intense than that of C6 aldarates. Figure S1 shows the separation of the different components: arabinose, galactose, glucose, xylose, mannose, and fructose on the one hand, and galactarate, glucarate, xylarate, arabinarate, and mannarate on the other hand.

The other carboxylates formed during the reaction of glucose oxidation could also be analyzed using an IonPac AS11-HC (250*4 mm) column maintained at $35\text{ }^{\circ}\text{C}$ and a suppressed conductivity detector; the NaOH eluent concentration increased from 2 mM to 35 mM over 25 min, followed by 100 mM over 5 min to ensure flushing off of all potential contaminants. However, the conductometry does not allow the detection of noncharged species such as alcohols and aldehydes. In addition, the separation of hexarates is not possible using the AS11-HC column. Caution should be taken, because arabinarate, if formed, is coeluted with glucarate.

The total organic carbon (TOC) in solution was measured with a TOC analyzer (Shimadzu TOC-VCHS) equipped with an ASI-automatic sampler.

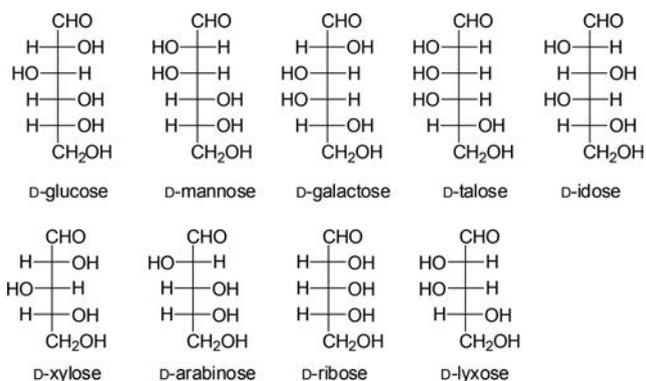
3. RESULTS AND DISCUSSION

3.1. Oxidation of Sugars Alone or As a Mixture. In our previous studies, we performed the catalytic oxidation of glucose to glucarate over Pt/C and to glucaric acid over Au-Pt/ZrO₂.^{37,43} Figure 1 reminds the temporal evolution of the concentrations of glucose, gluconic acid, and glucaric acid, as well as the TOC measure in liquid phase.

The oxidation of glucose to glucarate (glucaric acid) was clearly shown to be a process of consecutive and parallel reactions as the result of the relatively low reactivity of the primary alcohol compared with the aldehyde group. Glucose was first oxidized to gluconate (or gluconic acid), glucarate (glucaric acid) was then formed via guluronate (guluronic acid) by consecutive oxidation of the alcohol function. Many byproducts were analyzed as C2–C4 (di) acid salts or (di) acids, respectively, as the result of overoxidation and fragmentation of the C6 oxidized products. The consequence was also a decrease of the TOC concentration during reaction. About 10% of initial TOC was lost during reaction at pH 9; a drastic loss of 40% was observed in the oxidation of glucose to glucaric acid, due to the larger formation of CO₂, as revealed by analysis of the gas phase.^{37,43}

In this work, we first examined the oxidation of the different C6 and C5 sugars that were present in the hydrolysate of pinewood. In the hydrolysate containing a total sugar concentration of 45 g L⁻¹, mannose was the most important monomer (44%), followed by xylose (21%), galactose (15%), glucose (13%), and arabinose (7%). The structures of the aldoses studied and mentioned in the discussion are shown in Scheme 2.

Scheme 2. Structure of the Aldoses Cited in the Manuscript



The sugars were first oxidized separately at a concentration of 0.25 M. Figure 2 depicts the results for the series of aldoses over both catalytic systems. For reasons of clarity, only the yield of the corresponding aldarate or aldaric acid is shown. The byproducts are overoxidation C2–C4 diacids or their salts, such as tartaric, tartronic, glyceric, glycolic, and oxalic acids.^{37,43}

In the presence of Pt/C at pH 9 (Figure 2a), the initial reaction rates of formation of the aldarates were close, though it was found a little higher for arabinose oxidation. The maximum yield of aldarate was obtained after 8 h of reaction. It was in the range between 40% from galactose and 70% from mannose, whereas it was about 46% from glucose. It slightly decreased then upon pursuing the reaction to 24 h.

One may note that for glucose oxidation under alkaline conditions the maximum yield of glucarate (46%) was lower when analyzed by amperometry than when analyzed by conductimetry, as given previously (54%).³⁷ Indeed, arabinarate which is formed during the reaction of glucose by decarboxylation (vide infra) was coeluted with glucarate on the AS11-HC column connected to the conductometer. In this study, all aldaric acids were analyzed using amperometry, which allowed us to detect decarboxylation products issued from the hexaric acids, and to give more accurate results.

In the presence of Au–Pt/ZrO₂ under noncontrolled pH conditions (Figure 2b), the rates of formation of the pentaric acids were lower than the ones of the hexaric acids. The maximum yield of aldaric acid after 8 h was in the range from 25% (arabinose) to 60% (galactose). The overoxidation reactions leading to the decrease of the yield of aldaric acid when the reaction was prolonged were more significant than in the alkaline medium; for instance, the yield of mannaric acid decreased from 51% after 8 h to 29% after 24 h.

The different aldoses, and subsequent aldinate or aldonic acid intermediates, did not display the same reactivity. These observations may be explained by the different configurations of the carbohydrates involved (Scheme 2). Such a rate effect has been reported in the literature for the catalytic oxidation of various pentoses and hexoses to the corresponding aldonates at controlled alkaline pH under atmospheric pressure over Au, Pd, and Pt catalysts.^{47–49} The sugars are present mainly in cyclic conformation (pyranose or furanose) that induces different steric hindrance of both faces depending on the configuration. Over the three catalysts, arabinose and ribose displayed higher activity than lyxose and xylose. More precisely, catalytic activity over Pt was higher for ribose compared to lyxose (the configuration of the OH-4 group is different); also the configuration of the OH-2 group influenced the activity, the rate for arabinose oxidation was higher than for ribose. The reaction rate was also influenced by the structure of the hexoses, but not in the same manner depending on the catalyst; galactose was oxidized faster than glucose over Pt, whereas the inverse was observed over Au. On the other hand, the

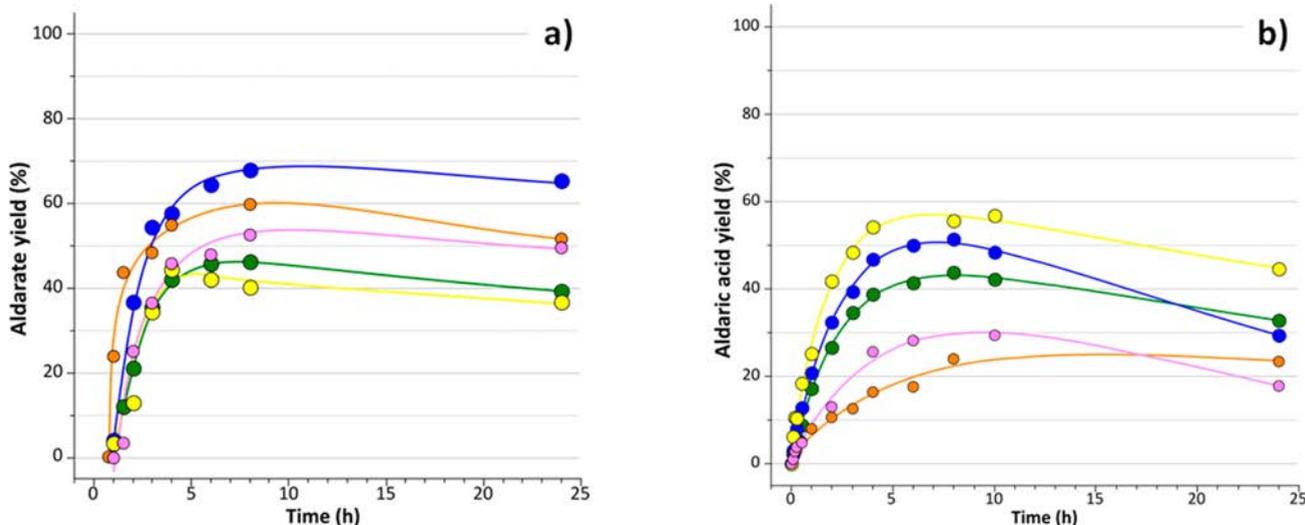


Figure 2. Yield of aldarate (aldaric acid) during oxidation of each aldose separately in the presence of (a) Pt/C and (b) Au–Pt/ZrO₂. Reaction conditions: (a) 4.7%Pt/C, [aldose]₀ = 0.25 M, aldose/Pt molar ratio = 157, pH 9, 60 °C, 0.5 mL min⁻¹ of air; (b) 3.5%Au-3.5%Pt/ZrO₂, [aldose]₀ = 0.25M, aldose/Au+Pt = 80, 100 °C, 40 bar of air. Orange, arabinaric acid; pink, xylaric acid; green, glucaric acid; yellow, galactaric acid; blue, mannaric acid.

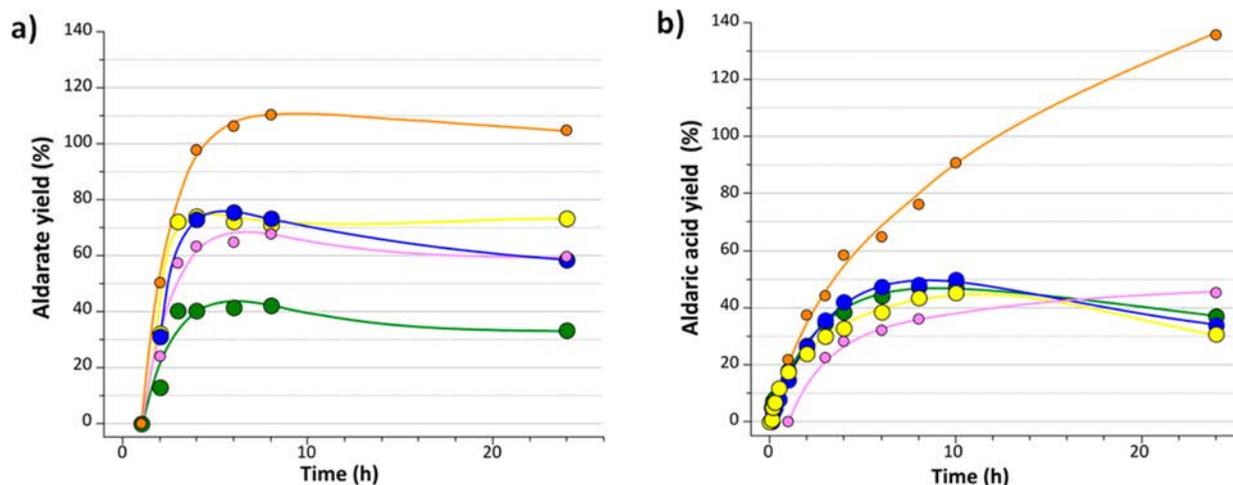


Figure 3. Evolution of yields of (a) aldarates over Pt/C and (b) aldaric acids over Au-Pt/ZrO₂. Reaction conditions: (a) 4.7%Pt/C, [mannose]₀ = [glucose]₀ = [galactose]₀ = [xylose]₀ [arabinose]₀ = 0.05 M, aldose/Pt molar ratio = 157, pH 9, 60 °C, 0.5 mL min⁻¹ of air; (b) 3.5%Au-3.5%Pt/ZrO₂, [mannose]₀ = [glucose]₀ = [galactose]₀ = [xylose]₀ [arabinose]₀ = 0.05 M, aldose/Au+Pt = 80, 100 °C, 40 bar of air. Orange, arabinaric acid; pink, xylaric acid; green, glucaric acid; yellow, galactaric acid; blue, mannaric acid.

comparative transformation of the sugars in the absence of added base has been little explored. In the oxidation of various pentoses over three different 4 wt % Pt catalysts in 1 mL vials, under the same reaction conditions (90 °C, about 5 bar of O₂) the yield of pentaric acid after 8 h was higher when the reaction was conducted starting from arabinose and ribose (34–52%) than from xylose (14–29%).⁴²

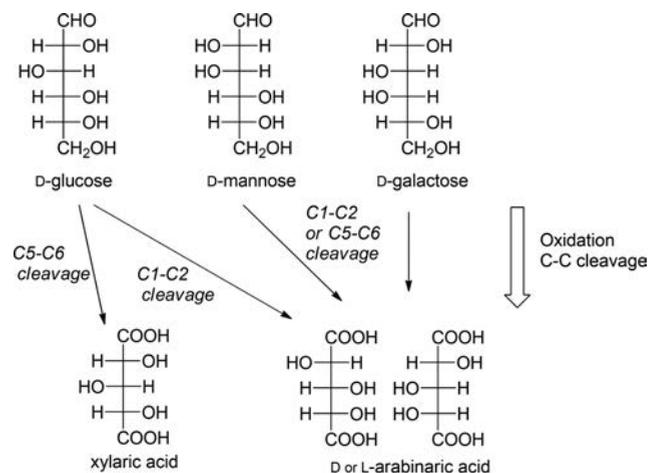
The reaction of an equimolar mixture of the sugars (0.05 M each) was then studied. The results are shown in Figure 3 under alkaline or noncontrolled pH conditions.

The yields of hexarates (or hexaric acids) evolved in a similar manner as when the reaction was conducted with the sugars separately; the yields observed were in the range 40–70% (Figure 3a). In contrast, the yields of pentarates (or pentaric acids) were much higher than expected from the experiments described above. Under alkaline conditions, the yield of xylaric acid was around 70%, the yield of arabinaric acid was even 110% after 10 h of reaction. This observation can be explained by some terminal C–C cleavage of the C6 aldarates occurring during the reaction. Under noncontrolled pH conditions, the effect was still more evident (Figure 3b). Arabinaric acid was continuously formed all along the reaction and the yield after 24 h was 135% based on the initial concentration of arabinose. The yield of xylaric acid also increased, however, at a lower rate and it attained 47% at the end of the reaction. This evolution again can be explained by decarboxylation of the terminal carbon of the diacids.

We further analyzed the distribution of the pentaric acids (Scheme 3). If one considers that no isomerization took place during reaction, and according to the different stereoisomers of the initial sugars, decarboxylation of mannose and galactose will lead to arabinaric acid, whereas glucose will lead to xylaric or arabinaric acid depending on the location of the terminal decarboxylation. Therefore, arabinaric acid will be formed in higher concentrations by decarboxylation.

Finally, during oxidation of glucose or of the synthetic mixture of the aldoses over the Au–Pt catalyst, an unidentified peak with a very small intensity was detected at 26.5 min, suggesting another C5 or C6 diacid. Though no fructose or mannose was detected during reaction of glucose, the formation of diacids after epimerization of the aldoses was

Scheme 3. Pentaric Acids Formed by Decarboxylation of Hexaric Acids during Catalytic Oxidation



checked. The injection on the CarboPac PA1 column connected to PAD of a standard of ribaric acid, the third possible pentaric acid stereoisomer, showed a retention time close to that of arabinaric acid, which excluded this C5 diacid. The synthesis of disodium D-altraric acid from D-talose (Supporting Information) also excluded altraric acid, which could be formed after epimerization of mannose or galactose. The formation of D-idaric acid via epimerization of glucose at position C5 is another possibility that we did not check because of the nonavailability.

3.b. Oxidation of Hemicellulose Hydrolysate after Various Purification Treatments. The hydrolysis of wood generated a raw hydrolysate that was purified according to several protocols. The composition of the more or less purified hydrolysates is shown in Table 1.

After filtration to eliminate the residual solid materials, and concentration by evaporation under vacuum (100 mbar, 40 °C) to eliminate volatile compounds (furfural and a portion of acetic acid), the acidic stream hydrolysate 1, called H1 (pH 0.7) was yellow-colored and contained around 46 g L⁻¹ monosaccharides. These are composed of a high proportion

Table 1. Composition of the Purified Hydrolysates before the Oxidation Reaction

	hydrolysate 1	hydrolysate 2	hydrolysate 3
	filtration evaporation	filtration demineralization evaporation	filtration demineralization evaporation GAC treatment
[glucose] ₀ (g L ⁻¹)	5	4	4
[mannose] ₀ (g L ⁻¹)	22	15	13
[galactose] ₀ (g L ⁻¹)	8	6	5
total [hexoses]₀ (g L⁻¹)	35	25	22
[xylose] ₀ (g L ⁻¹)	5	4	4
[arabinose] ₀ (g L ⁻¹)	6	2	1
total [pentoses]₀ (g L⁻¹)	11	6	5
pH	0.7	10.7	6.5
[furfural] (g L ⁻¹)	0	0	0
[HMF] (g L ⁻¹)	1.1	0.5	2.8 × 10 ⁻³
conductivity (mS cm ⁻¹)	12.0	<1 × 10 ⁻³	<1 × 10 ⁻³
color	yellow	colorless	colorless

of mannose (22 g L⁻¹), along with glucose (5 g L⁻¹), galactose (8 g L⁻¹), xylose (5 g L⁻¹), and arabinose (6 g L⁻¹). 5-Hydroxymethylfurfural (HMF, 1.1 g L⁻¹) resulting from hexoses dehydration was detected. Size Exclusion Chromatography (SEC) on the sample revealed the presence of water-soluble polymers with molecular weight above 300 g mol⁻¹; the precise characterization of these polymers was not possible, however oligomeric sugars have been evidenced (the signature of disaccharides was observed) as well as soluble humins which were unstable and precipitated during storage (characterized by

¹³C CPMAS and ¹H NMR in DMSO-d₆). Lignin degraded phenolics such as guaiacol and vanillin were also identified by mass spectrometry after liquid-liquid extraction using dichloromethane. Inorganic salts accounted for the relatively high conductivity of the solution (12 mS cm⁻¹). A demineralization step by ion-exchange resins removed almost all the salts in solution (conductivity <1 × 10⁻³ mS cm⁻¹). Resin treatment was also effective in discoloration, while HMF still remained (0.5 g L⁻¹). A colorless hydrolysate named H2 was thus generated. After an additional active carbon treatment the residual unsaturated compounds were completely removed, in particular HMF, to give hydrolysate H3. Solutions H2 and H3 were slightly diluted for the experimental tests.

The hydrolysates were examined in the oxidation reactions and the results were compared to those obtained with a synthetic solution of the same composition of sugars.

Oxidation of Hydrolysate H1. Solution H1 was the raw hydrolysate that was just concentrated by evaporation, which also removed furfural. The pH was very acidic, due to the presence of acetic acid produced from the cleavage of acetyl groups in hemicelluloses. Further, it still contained HMF (1.1 g L⁻¹) and the amount of inorganic salts was high as shown by the conductivity measurement. The results of oxidation of solution H1 under alkaline or noncontrolled pH conditions are shown in Figure 4. When the reaction was performed under alkaline conditions over Pt/C (Figure 4a), the pH of the solution was adjusted to 9 before heating under nitrogen; then, during the reaction some base was consumed to neutralize the acids and diacids formed, and maintain the pH constant. Figure 4a shows the total concentration of the aldoses and the added molar equivalents of NaOH as a function of time for the reference experiment (synthetic solution of same composition of sugars) and for hydrolysate H1. Similarly, Figure 4b shows the evolution as a function of time of total concentration of aldoses, the pH value, and TOC evolution for the reference solution and for H1.

In alkaline medium (Figure 4a), the aldoses in the synthetic solution were completely converted after 3 h and the final

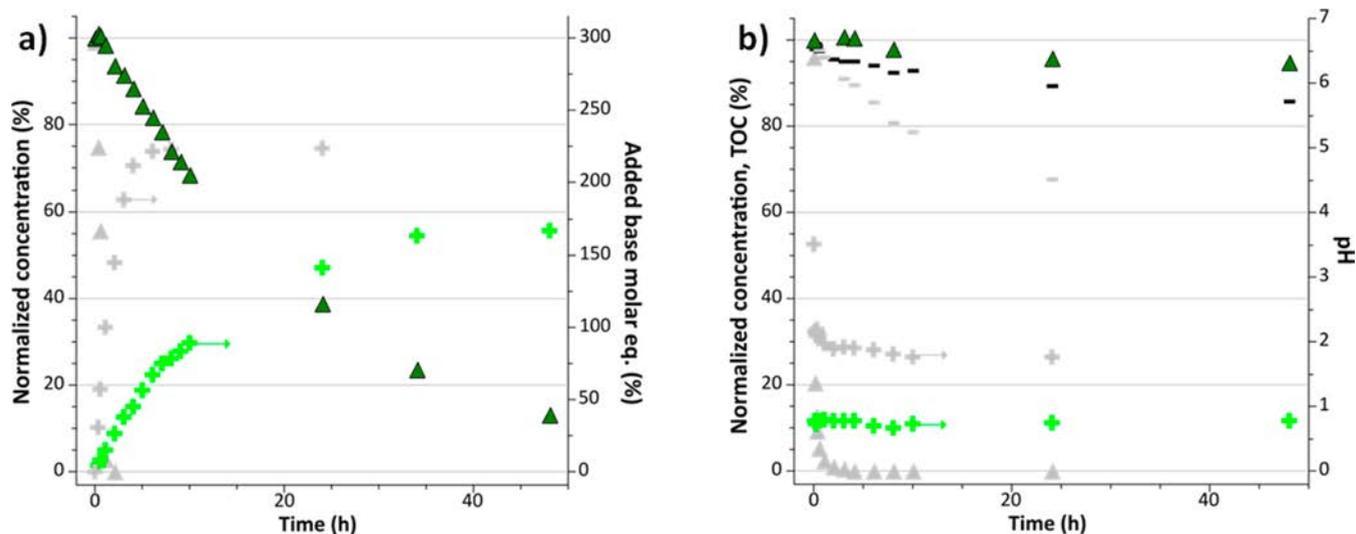


Figure 4. Evolution of the reaction during oxidation of the mixture of aldoses (gray symbols) and in hydrolysate H1 (46 g L⁻¹ aldoses) (green symbols). Reaction conditions: (a) 4.7%Pt/C, [aldose]₀ = 0.25 M, aldose/Pt molar ratio = 157, pH 9, 60 °C, 0.5 mL min⁻¹ of air, (b) 3.5%Au-3.5% Pt/ZrO₂, [aldose]₀ = 0.25M, aldose/Au+Pt = 80, 100 °C, 40 bar of air. (a) Gray and green triangles, aldoses, gray and green plus signs, NaOH consumption; (b) Gray and green triangles, aldoses; gray and green plus signs, pH, gray and green negative signs, TOC.

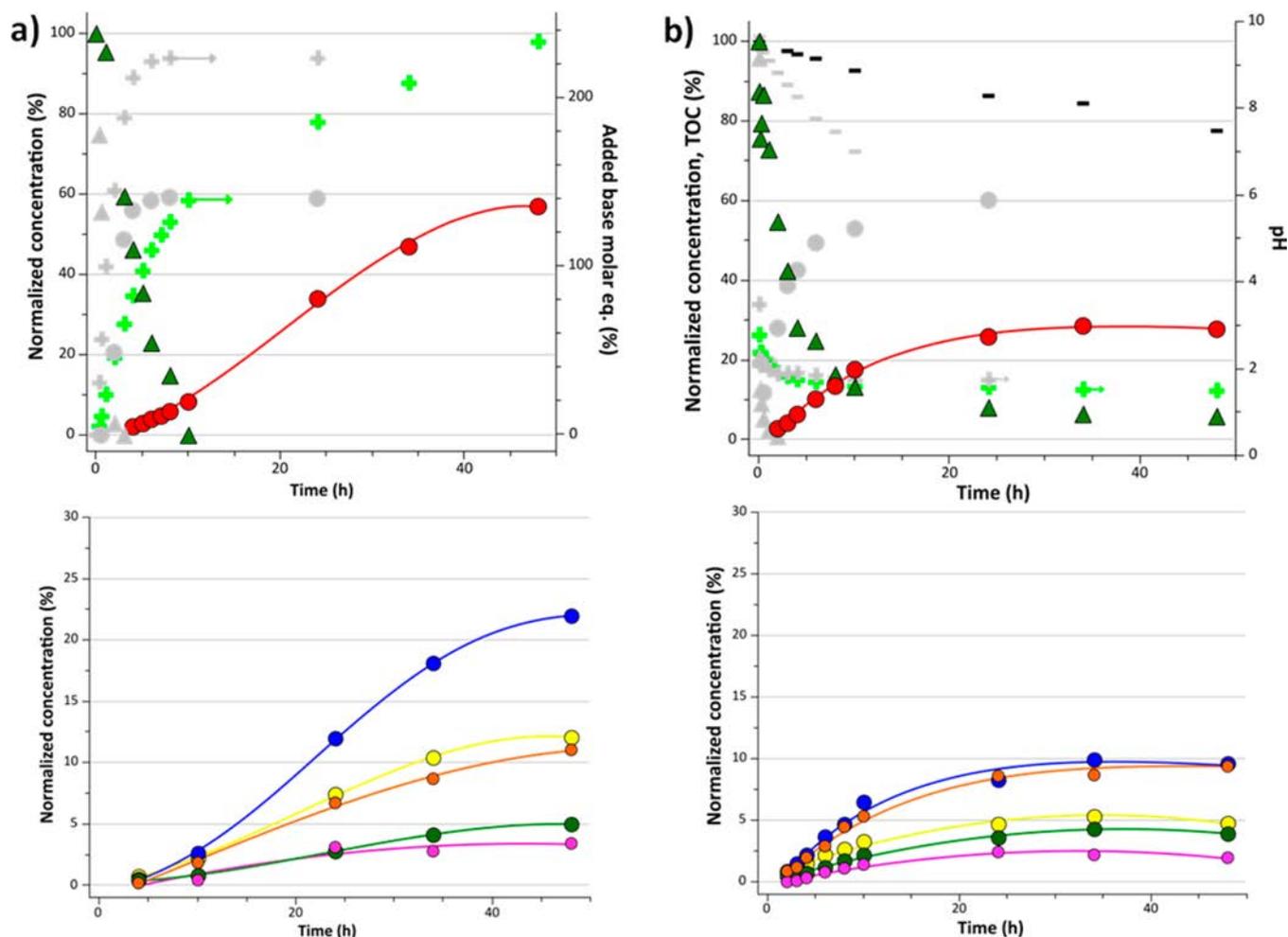


Figure 5. Oxidation of sugars in the mixture of aldoses (gray symbols) and in hydrolysate H2 (31 g L^{-1} aldoses) (symbols in color). Reaction conditions: (a) 4.7%Pt/C, $[\text{aldose}]_0 = 0.25 \text{ M}$, aldose/Pt molar ratio = 157, pH 9, $60 \text{ }^\circ\text{C}$, 0.5 mL min^{-1} of air, (b) 3.5%Au-3.5%Pt/ZrO₂, $[\text{aldose}]_0 = 0.25\text{M}$, aldose/Au+Pt = 80, $100 \text{ }^\circ\text{C}$, 40 bar of air. (a) Gray and green triangles, aldoses; gray and red circles, aldarates; gray and green plus signs, NaOH consumption; (b) gray and green triangles, aldoses; gray and green plus signs, pH; gray and green negative signs, TOC; (a and b) orange circles, arabinaric acid; pink circles, xylaric acid; green circles, glucaric acid; yellow circles, galactaric acid; blue circles, mannaric acid.

amount of base consumed after 48 h to neutralize the acids and diacids was approximately 2.25 mol. eqv. per aldose, close to the value for glucose oxidation under the same conditions.³⁷ After 48 h of reaction, final conversion of the aldoses in H1 was only 85%, and no aldarate was detected at all. Only peaks characteristic of the aldonates were observed but not quantified and the amount of base introduced was only 1.7 mol. equiv. per aldose.

In non-neutralized medium over Au–Pt/ZrO₂, the reaction was even worse. Conversion of the aldoses in the synthetic solution was total after 2 h, a time close to that previously observed for glucose oxidation,⁴³ pH decreased because of the formation of the carboxylic acid functions, and TOC decreased due to the overoxidation to shorter-chain diacids. In contrast, conversion of aldoses in solution H1 was only 7% in hydrolysate H1, pH and TOC remained roughly constant.

The results under both conditions point out the inhibiting effect of some of the compounds giving the color of the hydrolysate, and/or the inorganic salts in H1 and clearly evidence the necessity to pretreat the aqueous stream before upgrading, especially for aldaric acids production.

Oxidation of Hydrolysate H2. Demineralization of the filtrated raw hydrolysate was conducted before evaporation. By

adding this intermediate step to deliver solution H2, conductivity strongly decreased to less than $1 \mu\text{S cm}^{-1}$, half of the HMF was removed, and the aqueous stream became colorless, suggesting that most of the unsaturated compounds could be eliminated. The pH of H2 was over 10 because of the ion-exchange technology. Hydrolysate H2 was slightly diluted and contained 31 g L^{-1} aldoses. The results of catalytic experiments for the synthetic solution and hydrolysate H2 are shown in Figure 5 under both pH conditions.

After the addition of an intermediate demineralization pretreatment between filtration and evaporation, the kinetics of oxidation of the mixture of aldoses were accelerated, and C5 and C6 aldaric acids or their disodium salts were formed with relatively good yields. In alkaline medium (Figure 5a), conversion was complete after 10 h and the consumption of added sodium hydroxide after 48 h was over 2 mol. eqv. per aldose. As expected from the oxidation of sugars, mannarate concentration was the highest. At acidic pH (Figure 5b), the beneficial effect of demineralization was not as important. The residual HMF concentration of 0.5 g L^{-1} might be still too high in the stream and may have a decreasing effect on the reaction rate (10 h vs 3 h), as was clearly shown for a glucose synthetic solution.⁴³ In addition, the concentrations of aldaric acids in the

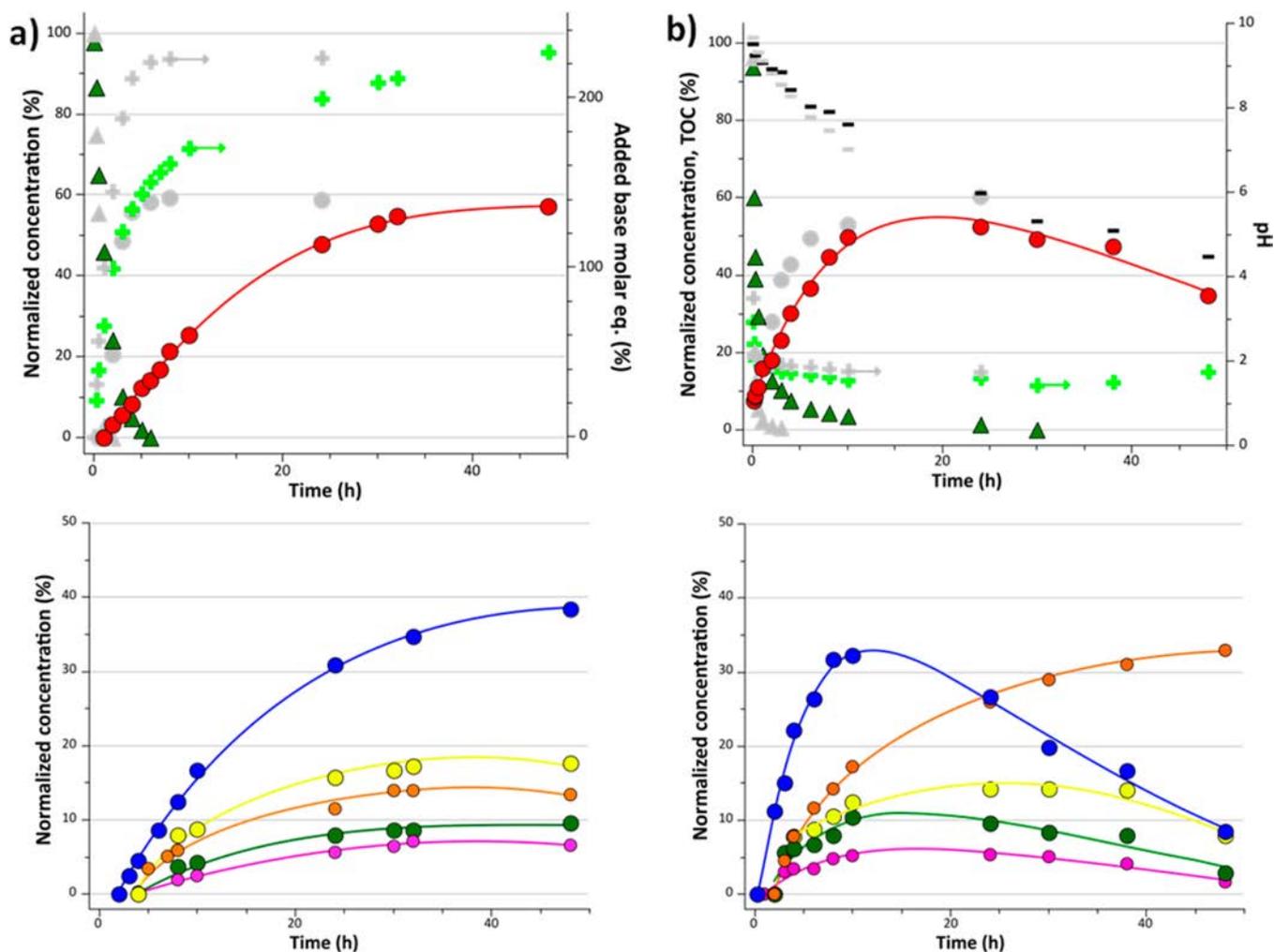


Figure 6. Oxidation of sugars in the mixture of aldoses (gray symbols) and in hydrolysate H3 (27 g L^{-1} aldoses) (symbols in color). Reaction conditions: (a) 4.7%Pt/C, $[\text{aldose}]_0 = 0.25 \text{ M}$, aldose/Pt molar ratio = 157, pH 9, 60°C , 0.5 mL min^{-1} of air; (b) 3.5%Au-3.5%Pt/ZrO₂, $[\text{aldose}]_0 = 0.25 \text{ M}$, aldose/Au+Pt = 80, 100°C , 40 bar of air. (a) Gray and green triangle, aldoses; gray and red circle, aldarates; gray and green plus signs, NaOH consumption; (b) gray and green triangles, aldoses; gray and green plus signs, pH; gray and green negative signs, TOC; (a and b) orange circles, arabinaric acid; pink circles, xylic acid; green circles, glucaric acid; yellow circles, galactaric acid; blue circles, mannaric acid.

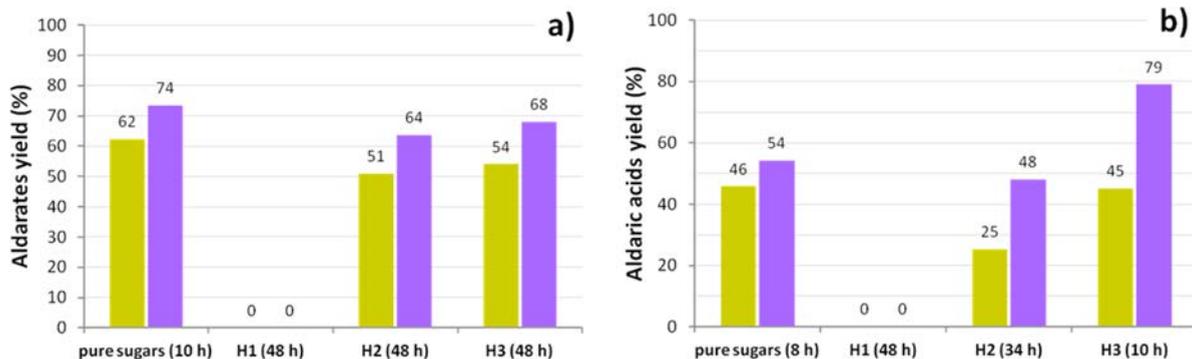


Figure 7. Maximum yields of aldarates (aldaric acids) and time to attain that yields during oxidation of synthetic solutions of sugars and hydrolysates H1–H3. Reaction conditions: (a) 4.7%Pt/C, $[\text{aldose}]_0 = 0.25 \text{ M}$, aldose/Pt molar ratio = 157, pH 9, 60°C , 0.5 mL min^{-1} of air, (b) 3.5%Au-3.5%Pt/ZrO₂, $[\text{aldose}]_0 = 0.25 \text{ M}$, aldose/Au+Pt = 80, 100°C , 40 bar of air. Yellow-green, C6 aldarates or aldaric acids; purple, C5 aldarates or aldaric acids.

final solution were in agreement with the previous observations (Figure 3) over Au–Pt/ZrO₂ with synthetic solution of aldoses, i.e., arabinaric acid concentration was high due to decarboxylation of hexaric acids.

Oxidation Profile of Hydrolysate H3. A final treatment by active carbon significantly improved the purity of the hydrolysate. It still retained some inhibiting unsaturated compounds, such as HMF whose concentration dropped to

0.02 mM, i.e. 10^{-4} mol. eqv. per total aldose. The results obtained during oxidation of H3 are shown in Figure 6.

After treatment with granular activated carbon GAC, the reaction rates of oxidation of the aldoses in the hydrolysate were greatly improved and the diacids were also formed much faster, especially over Au–Pt/ZrO₂. Indeed, under these noncontrolled pH conditions, the recorded data were very close to those observed during oxidation of the synthetic mixture. The concentration of arabinaric acid represented more than 32% of the aldaric acids after 48 h, although the initial concentration of arabinose was only 7%. This result shows again that decarboxylation of C6 diacids was very important using this catalytic system; arabinaric acid was formed, and therefore the TOC value decreased significantly.

Under both pH conditions, the main diacid detected was mannaric acid, consistent with the fact that mannose was the main aldose in the aqueous stream.

Finally, the global yields of hexarates (hexaric acids) and pentarates (pentaric acids) after oxidation of each purified hydrolysate were compared to those calculated from the oxidation of the synthetic solution with the same distribution of aldoses (Figure 7).

Elimination of furfural by evaporation was not sufficient to allow production of aldaric acids from H1. After demineralization, which partly eliminated unsaturated compounds and inorganic salts, moderate yields could be obtained at the condition of significant prolonging reaction time. Oxidation rates of sugars in the most purified H3 stream were much faster, showing that an active carbon treatment seems to be an indispensable step. These results are in good agreement with previous results on the effect of impurities on oxidation of glucose to the diacids.^{37,43} Lower reaction rates were observed in the presence of furfural, 5-hydroxymethylfurfural, lignin residues or guaiacol. In the present work, after 10 h, a mixture of hexaric and pentaric acids was obtained with yields close to those of the synthetic solution of pure sugars. The yields of hexarates and pentarates were 54% and 68%, respectively, over Pt/C; the yields of hexaric and pentaric acids were 45 and 79%, respectively, over Au–Pt/ZrO₂. Previous studies showed that Au–Pt/ZrO₂ catalysts could be recycled in batch reactor with no significant efficiency loss for glucose oxidation to glucaric acid, and they were stable over at least 1 week in a trickle-bed reactor.⁴³ Further study should also verify the long-term stability for the purified hydrolysates.

4. CONCLUSIONS

The high amount of hemicelluloses content of softwood offers significant potential for new biomass-based products. Prehydrolysis of softwood biomass prior to Kraft cooking provides a stream rich in the sugar components of hemicellulosic polymers and some undesired residues. The oxidation protocol studied for glucose oxidation to glucaric acid was successfully transferred to synthetic solutions of the series of pure aldoses present in the hydrolysate, and then to the hydrolysate. The oxidation of more or less purified hydrolysates confirmed the inhibitory ability of some of the residual compounds that were observed with glucose. After complete removal of inorganic salts and unsaturated compounds by a combined process consisting of filtration, demineralization, evaporation, and active carbon treatments to purify the hydrolysate, yields of aldarates under alkaline conditions over Pt/C or of aldaric acids over Au–Pt/ZrO₂ were close to those obtained in synthetic solutions of pure sugars.

To enable the utilization of sugar components in softwood hydrolysate, we have to eliminate most of the contaminants from hydrolysate.

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Notes

The authors declare no competing financial interest.

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