Combination of Autohydrolysis and Catalytic Hydrolysis of Biomass for the Production of Hemicellulose Oligosaccharides and Sugars

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Abstract: Three different types of biomass sourced from forestry waste (eucalyptus residues), agricultural waste (wheat straw), and energy crop (miscanthus) were used as starting materials to produce hemicellulosic sugars, furans (furfural and hydroxymethylfurfural), and oligosaccharides. A two-step hybrid process was implemented; biomass was first autohydrolysed without any additive to extract hemicelluloses and dissolve it in water. Then, the hydrolysate was treated with a solid acid catalyst, TiO_2-WO_x, in order to achieve hydrolysis and produce monomeric sugars and furans. This article investigates the role of the biomass type, autohydrolysis experimental conditions, polymerisation degree and composition of hemicelluloses on the performance of the process coupling autohydrolysis and catalytic hydrolysis. The highest global yields of both oligosaccharides and monomeric sugars were obtained from Eucalyptus (37% and 18%, respectively).

Keywords: wheat straw; eucalyptus residues; miscanthus; hemicellulose; autohydrolysis; solid acid catalyst; furfural; HMF; sugars

1. Introduction

Considering fossil resource depletion and global climate change, the need for alternative sources of carbon is on the raise. Lignocellulose, the main component of non-edible terrestrial biomass, is a major source of renewable carbon [1]. It contains 25–40 wt.% hemicelluloses, which are water-soluble polysaccharides [2]. Therefore, the promotion of hemicelluloses is a key-element in the economic balance of biorefineries; however, hemicelluloses are often neglected in biorefinery design [3].

Hemicelluloses are a heterogeneous group of polysaccharides that may be composed of pentoses (xylose, arabinose), hexoses (galactose, mannose, glucose), and acetyl and glucuronyl groups. A hemicellulose molecule usually contains a backbone of sugar with branching sugars and acetyl groups. For example, in arabinoxylan, xylose is the backbone unit and arabinose the branched unit. The degree of polymerization (DP) of hemicelluloses ranges from 50 to 300 [4,5]. Their valorization can lead to numerous value-added compounds [6]; oligosaccharides (OS) can be used as texture additives or probiotics in the agrifood industry [7], rare sugars can be used as sweeteners in flavor industry [2], and xylose can be hydrogenated to xylitol [8], a widely used compound in food industry and one of the Top 12 molecules in a famous DoE report [9], or dehydrated to furfural, a building block for many processes [10].

Before further valorization, hemicelluloses must be extracted from the lignocellulosic composite matrix, then the extracted hemicelluloses (often degraded as oligosaccharides with lower DP) must be depolymerized to obtain monomers. Hemicellulose extraction usually occurs during biomass pretreatment. This pretreatment can be done under several reaction conditions [11–13]: with alkaline solutions [14,15], dilute acids [16,17], organosolv [18,19], or inorganic salts [20,21], all of which require the use of non-recyclable mineral or organic additives; in ionic liquid [22], which is recyclable but expensive to produce; or in steam explosion [23] and autohydrolysis [24–27], where water is the only reagent. In autohydrolysis, biomass is heated in liquid water and hemicelluloses are extracted by the action of hot water and protons generated by autoprotolysis of H_2O. This process does not need any additive [12,13]. Autohydrolysis has been recognized as an effective process to extract and partly hydrolyze hemicelluloses into water-soluble oligosaccharides [28], and has been applied successfully to several different biomasses including eucalyptus wood [29,30], rice straw [31], wheat straw [32,33], miscanthus [34,35].

Oligosaccharide depolymerization to monomer sugars requires an acid catalyst for the hydrolysis reaction. Sulphuric acid is often used in the literature [36–39]. Alternatives include using organic acids [40] or enzymatic processes [41]. More recently, solid acid catalysts have been used successfully to hydrolyze hemicelluloses [2,42]. Organic resins [43], functionalized carbons [44], clays [45] and zeolites [46–48] have all been described as hydrolysis catalysts, and more recently, in our group, doped titania [49].

Coupling of autohydrolysis and catalytic hydrolysis in a hybrid process has been attempted by adding a solid catalyst in the autohydrolysis process, e.g., TiO_2 and ZrO_2 based catalysts [50] to produce furfural and HMF (10% and 9% yield at 300 °C), bentonite to produce levulinic acid [51] (15% yield at 200 °C), and $RuCl_3/MCM$-48 [52] and SO_4^{2-}/Fe_2O_3 [53] to produce oligosaccharides (78% yield of AOS at 180 °C and 63% yield of OS at 140 °C). For sugar production, autohydrolysis and enzymatic hydrolysis have also been coupled [54].

From the perspective of biorefineries, the design of sustainable processes for hemicellulose valorization must fulfill the principles of green chemistry [55]. The starting materials cannot be edible and must come from waste materials as much as possible in order to enhance the circular bioeconomy; the use of mineral acids and bases must be avoided, as they generate large amounts of waste after neutralization, are a source of corrosion for reactors, and are dangerous to handle; organic solvents must be limited and/or replaced by water whenever possible; and catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

In the present work, starting materials from various sources were studied: wheat straw from agricultural waste, eucalyptus residues from forestry waste, and miscanthus, which is an herbaceous energy crop. The process chosen for hemicellulose extraction was autohydrolysis. To depolymerize the produced oligosaccharides, acid catalytic hydrolysis was performed with a solid acid catalyst. The hybrid combination of autohydrolysis and heterogeneous catalytic hydrolysis to produce sugars, furfural and HMF were investigated, without any intermediate purification between both steps (Scheme 1). The products of each step were carefully characterized in order to understand the behavior of hemicelluloses in both processes. The impact of biomass composition and the reaction parameters on the production of sugars and furans was assessed in order to propose future axes for designing efficient biorefinery processes.
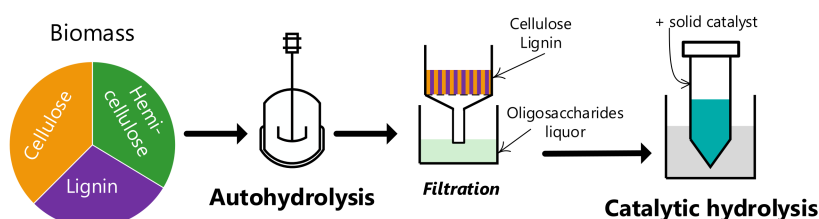
Scheme 1. Overview of hybrid autohydrolysis/catalytic hydrolysis for hemicellulose valorization.

2. Materials and Methods

2.1. Materials

TiO_2, tungstic acid and corncob xylans were purchased from Alfa Aesar, Sigma Aldrich, and Carbosynth, respectively. *Eucalyptus globulus* forestry residues mainly contained leaves, bark, and small branches, and were kindly supplied by The Navigator Company (Setúbal, Portugal). Upon arriving in the laboratory, they were dried at room temperature. Wheat straw was provided by the Portuguese National Agricultural experimental station (Elvas, Portugal) in bale form. *Mischanthus* sp. biomass was purchased from Comgoed (NL) by TU Delft, and distributed as pellets by TNO within the Brisk 2 project consortium. All biomass samples were stored in closed plastic containers at room temperature prior to use. Eucalyptus residues and wheat straw were milled to pass a 6 mm screen using a laboratory knife mill. Mischanthus pellets were used as provided.

2.2. Chemical Characterization of the Feedstock

The chemical characterization of structural carbohydrates and lignin in the feedstock was carried out by means of quantitative hydrolysis with sulfuric acid, as described in the NREL/TP-510-42618 protocol. The quantification of the produced monosaccharides and acetic acid was carried out by HPLC, as described in Sections 2.6 and 2.7. The acid-insoluble residue was considered as Klason lignin, after correction for the acid insoluble ash.

2.3. Autohydrolysis

Autohydrolysis was performed in a 2 L stainless steel Parr autoclave equipped with an internal cooling system, a double turbine, an external thermocouple in a dwell and a pressure probe. Biomass and water at a 1:7 mass ratio was loaded in the reactor (187 g of dry biomass and 1.3 kg of pure water). The stirring rate was set at 150 rpm. The autoclave was heated. The temperature ramp was monitored, and took 60 min to reach 190 °C and 72 min to reach 210 °C. Meanwhile, pressure increase was monitored and reached 13 bar at 190 °C and 19 bar at 210 °C. When the temperature reached the desired value (190 °C or 210 °C), the autoclave was cooled immediately. When the temperature decreased below 70 °C, the reactor was opened. To recover the liquid trapped in the solid and maximize the liquid recovery, the solid was pressed thoroughly using a manual hydraulic press up to 220 bar (Sotel, Portugal). Then, the liquid phase was filtrated under vacuum over paper filter (size 20–25 μm) and concentrated at 50 °C, 60–70 mbar in a rotary evaporator. Concentration by a factor of 6 to 9 took around 3 h.

2.4. Catalyst Preparation

The catalyst preparation was performed as described elsewhere [49]. Briefly, TiO_2 was mixed in distilled water to form a suspension. H_2WO_4 was dissolved in 30% H_2O_2 (W concentration 0.25 M). The tungsten solution was added drop by drop over TiO_2 suspension under stirring using a syringe pump. The suspension was stirred overnight and then centrifuged for 30 min. The recovered solid was dried at 110 °C overnight and crushed afterward, then calcined at 600 °C for 3 h under air flow.

2.5. Catalytic Hydrolysis Reaction

Liquor concentration was adjusted with deionised water to reach 25 $g_C.L^{-1}$ in oligosaccharides + sugars. Liquor (10 mL) was placed in an Ace pressure tube with 250 mg of catalyst TiO_2-WO_x and placed in an oil bath at the desired temperature (140 to 160 °C). The suspension was stirred at 650 rpm for 3 h and then cooled immediately. Aliquots were taken for HPLC analysis and post-hydrolysis treatment.

2.6. HPLC Analysis

HPLC samples were filtrated using a syringe filter (0.45 μm). They were analysed in a Shimadzu HPLC chain equipped with a RID detector and a UV detector. The columns were a Biorad Aminex HPX87-H and a Phenomenex Rezex ROA, able to separate sugars,

aliphatic acids, HMF and furfural. However, some sugars were co-eluted. A Phenomenex Rezex RPM column was used to solve co-elution issues. Concentrations were calculated using commercial standards and external calibration.

2.7. Post-Hydrolysis

Oligosaccharide content was quantified following a method based on NREL protocol [56]; 10 mL of sample was placed in a pressure tube with 0.349 mL of H_2SO_4 72% and heated at 121 °C for 1h. HPLC samples were prepared by filtration of the hydrolysate. Oligosaccharide concentration was calculated by comparing the difference in the concentration of sugars before and after post-hydrolysis treatment, including a degradation factor corresponding to the degradation of sugars during post-hydrolysis. Details and calculations are given in NREL protocol TP-510-42623. Oligosaccharides are composed of five different sugars, xylose, glucose, arabinose, mannose, and galactose, arranged in complex polymeric structures. As a simplification, the composition of oligosaccharides was expressed as a theoretical composition of xylo-oligosaccharides (XOS) from xylose analysis, gluco-oligosaccharides (GOS) from glucose analysis, arabino-oligosaccharides (AOS) from arabinose analysis, manno-oligosaccharides (MOS) from mannose analysis and galacto-oligosaccharides (GalOS) from galactose analysis. XOS, GOS, AOS, MOS and GalOS are theoretical polymers and do not represent the real structure of hemicelluloses, only the sugar composition of the polymer.

2.8. Size Exclusion Chromatography (SEC) Analysis

SEC analysis was performed on chromatographic 1260 Infinity Agilent Technologies equipment connected to two Ultrahydrogel linear columns (Waters) in series, coupled online to a Wyatt Optilab T-Rex differential refractometer. Sample solutions at 5 mg/mL were prepared from autohydrolysis liquors and eluted in $NaNO_3$ 0.1 M (pH 6). Solutions were previously filtered through 0.45 µm pore size membranes (Millipore) before injection. The eluent flow rate was 0.5 mL/min. The conventional calibration with pullulan standard was used.

2.9. Carbon Analysis

Carbon total content in reaction products was quantified using a homemade carbon analyser developed in ISA: ten microliters of the biomass sample were injected in a quartz tube, which was then inserted in an oven hold at 770 °C under oxygen flow. The gases produced by biomass combustion were fully oxidized on a catalyst (Pt + Cu_2O) at 784 °C, producing a mixture of CO_2 and H_2O. After the oven, the gases passed by a cold trap to condense water and then by a non-dispersive infrared cell Rosemount NGA 2000 to quantify CO_2. The apparatus was calibrated with various standard glucose solutions. Samples of the concentrated autohydrolysis liquors were diluted twice with pure water before analysis.

2.10. Calculations of Yields and Conversions

Autohydrolysis yield was calculated using the mass of products calculated from mass concentration and volume of filtrate and the initial mass of biomass:

$$Y_i(wt.\%) = C_i \times \frac{V_{filtrate}}{m_{biomass}} \tag{1}$$

where C_i is the mass concentration of i (g.L^{-1}), $V_{filtrate}$ is the volume of filtrate after autohydrolysis (L), and $m_{biomass}$ the dry mass of biomass introduced in autohydrolysis reactor (g).

Oligosaccharide (OS) conversions in catalytic hydrolysis were calculated by dividing the converted OS concentration in $g_C.L^{-1}$ by the initial concentration. For oligosaccharides of type N (N = gluco-, manno-, galacto-, xylo or arabino-),

$$X_{NOS}(C\%) = \frac{[NOS]_{t=0} - [NOS]_{t=3h}}{[NOS]_{t=0}} \qquad (2)$$

Monomer yields in catalytic hydrolysis were calculated by dividing the concentration of produced sugars by the initial concentration of corresponding oligosaccharides. For sugars of type N (N = glucose, mannose, galactose, xylose or arabinose),

$$Y_N(C\%) = \frac{[N]_{t=3h} - [N]_{t=0}}{[NOS]_{t=0}} \qquad (3)$$

where [N] is the concentration of compound N ($g_C.L^{-1}$) at time zero or after 3 h of reaction. The same calculation was applied for furfural and HMF, assuming that furfural was produced from pento-oligosaccharides and pentoses (i.e., xylose and arabinose) and HMF from hexo-oligosaccharides and hexoses (i.e., glucose, mannose and galactose).

3. Results

### 3.1. Lignocellulosic Starting Materials

The composition of lignocellulosic starting materials was determined using the post-hydrolysis method (Table 1). The main component in all of the samples is glucan, i.e., cellulose, which varies from 34 wt.% in wheat straw to 41 wt.% in miscanthus. Hemicelluloses represent the second most abundant compounds, from 24 wt.% in eucalyptus residues to 32 wt.% in wheat straw. Lignin accounts for 17 wt.% in wheat straw and 27 wt.% in eucalyptus residues. These values are in agreement with the composition of biomass reported in the literature: average hemicellulose content was reported to be 23–60% for woody biomass, 33% for wheat straw, and 26–40% for herbaceous biomass [57]. The rather high content of hemicelluloses in eucalyptus is due to leaves and barks being used in this study rather than stems [57]. Straws and herbaceous materials (miscanthus) are both known for being rich in hemicelluloses.

Table 1. Composition of starting materials.

(wt.%, Dry Basis)	Eucalyptus	Wheat Straw	Miscanthus
Glucan	36.1	33.7	41.3
Hemicelluloses	23.8	32.3	27.4
Xylan/Mannan/Galactan	*16.9*	*24.2*	*n.d.*
Arabinan	*2.0*	*4.6*	*n.d.*
Acetyl groups	*4.9*	*3.5*	*n.d.*
Klason lignin	26.7	16.8	23.1
Ash	2.4	5.0	6.4
Protein	2.8	5.4	n.d.
Fat	1.9	1.4	n.d.
Soluble saccharides	1.7	5.3	n.d.
Total	**95.4**	**99.9**	**98.2**

3.2. Autohydrolysis

Figure 1 depicts the results of autohydrolysis reaction on three different biomasses at 190 °C and of autohydrolysis at 210 °C for eucalyptus residues. The yields of sugars, furans (HMF and furfural) and acetic acid vary with the autohydrolysis conditions and the nature of the biomass. For eucalyptus residues at 210 °C, the yield in free sugars reaches 6 wt.%, together with 1.7 wt.% furans and 0.4 wt.% acetic acid; however, the yield of oligosaccharides is only 3.4 wt.%. At 190 °C, yields of free sugars and acetic acid from eucalyptus residues drops by a factor of three (2.4 wt.% and 0.1 wt.%, respectively), and furans are absent. However, the yield of oligosaccharides reaches 11 wt.%.
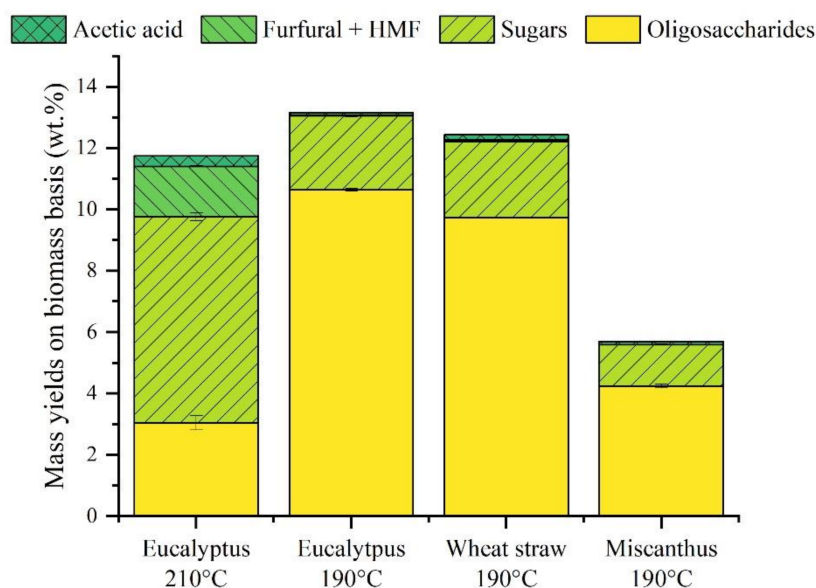
Figure 1. Oligosaccharides and monomers yields of autohydrolysis reaction on the basis of total biomass.

Obviously, increasing the temperature of autohydrolysis from 190 °C to 210 °C leads to the depolymerization of oligosaccharides in monomer sugars and to the degradation of sugars in furans and humins without enhancing hemicellulose extraction (e.g., oligosaccharides from lignocellulose).

For the rest of the study, autohydrolysis was performed at 190 °C. The highest yields of oligosaccharides were obtained from eucalyptus residues (11 wt.%), followed by wheat straw (10 wt.%) and miscanthus (4 wt.%). At 190 °C, the yield of monomer sugars remained low, at 2.4 wt.% for eucalyptus residues, 2.5 wt.% for wheat straw and 1.3 wt.% for miscanthus. HMF and furfural are absent in the autohydrolysis liquor of eucalyptus and miscanthus. Acetic acid is present at low concentrations (0.1 wt.% for eucalyptus residues and miscanthus, 0.3 wt.% for wheat straw). High hemicellulose content in wheat straw results in high yield of OS in the autohydrolysis liquor. However, this correlation was not verified for miscanthus, which is rich in hemicelluloses but had a low yield of OS. Other parameters can influence OS yield during autohydrolysis, for example mass transfer resistance.

In the literature, the maximum yield of OS from Eucalyptus residues is c.a. 15 wt.%, and the maximum yield of sugars is c.a. 5 wt.% in harsh conditions, while the maximum yield of OS from wheat straw is around 18% [33] and the maximum yield of XOS from Miscanthus is below 10 wt.% [35]. Our results are in accordance with the reported values, except for miscanthus where a higher OS yield could be expected. However, the comparison with published results should be considered with caution, given that experimental conditions were different. In particular, the miscanthus biomass was pelletized by the supplier before autohydrolysis in our study, which could impede the hydrolysis reaction because of high mass transfer resistance.

The liquid phase obtained after autohydrolysis was filtrated and concentrated under vacuum. The only noticeable effect was the removal of furfural and HMF from the hydrolysate obtained at 210 °C from Eucalyptus residues due to their low boiling points (162 °C and 350 °C for furfural and HMF, respectively, at atmospheric pressure). All other products were found in similar proportions before and after concentration.

The composition of oligosaccharides and monomer sugars in autohydrolysis liquors is presented on Figure 2. In eucalyptus residues, the hemicelluloses are mainly methyl-glucurono-xylans [58,59], glucomannans [59], and arabinogalactans [60]. In these hemicelluloses, the backbone units are xylose, glucose, mannose, and galactose, respectively; arabinose is only a substituted (branched) unit in arabinogalactan. After autohydrolysis of

eucalyptus at 190 °C, the OS are composed primarily of XOS, then GOS, MOS and GalOS, which is consistent with the presence of xylan, glucomannan and arabinogalactan. Arabinose is present only as a free sugar, which indicates that the branching position favours a fast hydrolysis reaction. A XOS/MOS/GalOS ratio of 100/5.7/15.7 is observed for OS and a xylose/mannose/galactose ratio of 100/24/71 is observed in free sugars. This indicates faster hydrolysis of GalOS and MOS in galactose and mannose than for XOS in xylose. Moreover, a GOS/MOS ratio of 1/0.8 is observed in OS, and the glucose/mannose ratio is 1/2.1 in free sugars. For native glucomannans, the expected glucose/mannose ratio would be 1/3 [59]; the overproduction of GOS and glucose can be attributed to the partial hydrolysis of cellulose. After autohydrolysis of eucalyptus residues at 210 °C, the ratio of XOS/MOS/GalOS is 100/1.7/7, and the ratio of xylose/mannose/galactose is 100/5.2/28, which confirms the slower hydrolysis of XOS in xylose. The ratio of GOS/MOS is 1/1.5 and the ratio of glucose/mannose is 1/0.5, which is consistent with partial hydrolysis of cellulose, most probably the amorphous cellulose fraction.
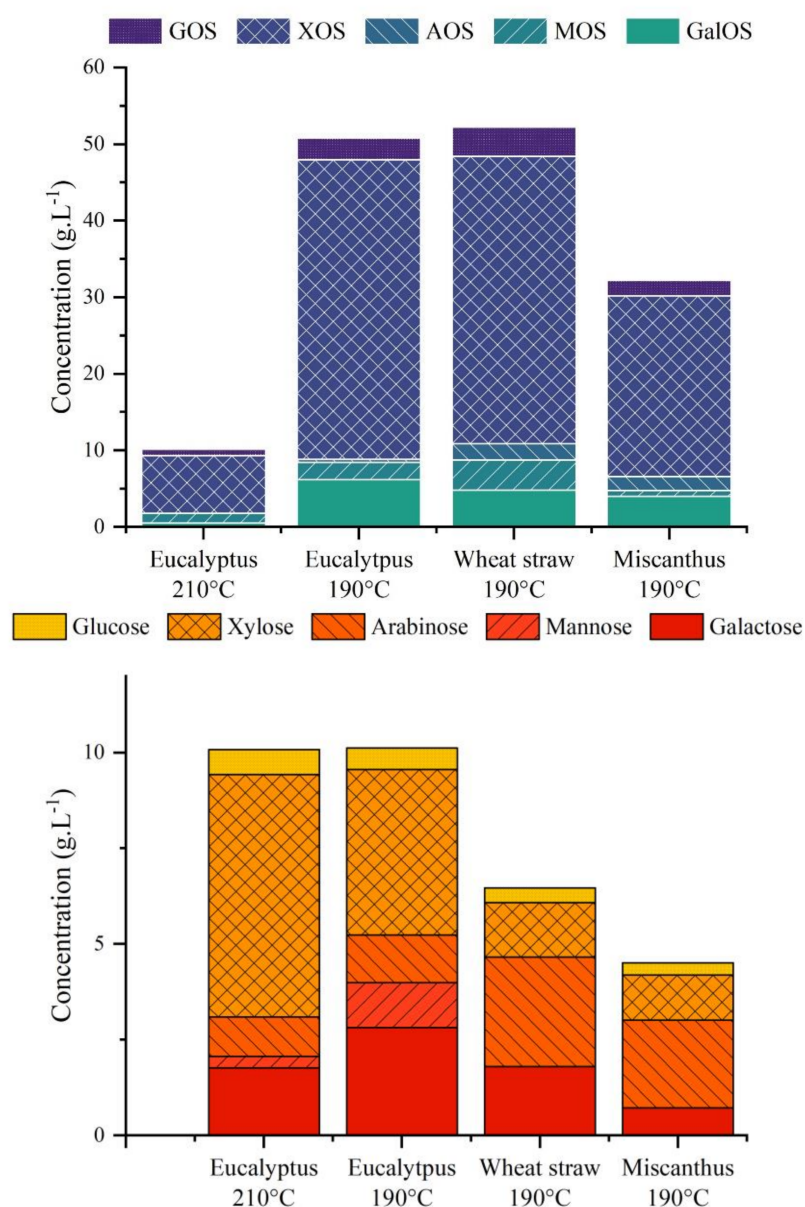
Figure 2. Oligosaccharide (**top**) and free sugar (**bottom**) compositions in concentrated autohydrolysis liquors.

For wheat straw, the main hemicelluloses are arabinoxylans [61]. After autohydrolysis at 190 °C, OS are composed primarily of XOS, then GOS and MOS; GalOS and AOS are present in minor amounts, which is consistent with the presence of arabinoxylans and a minor amount of galactoglucomannans. Free sugars are composed of arabinose in majority, then xylose, galactose and glucose in minor amounts; mannose is absent. The ratio of XOS/AOS is 100/6 in OS and the ratio of xylose/arabinose is 100/203. This indicates a fast hydrolysis of arabinose in arabinoxylan. The ratio of GOS/MOS/GalOS is 10/10/13 in OS and the ratio of glucose/mannose/galactose is 10/0/47. This indicates a fast hydrolysis of galactose in galactoglucomannan, where galactose is a branched sugar, and a slow release of mannose, which constitutes the backbone of galactoglucomannan. Again, the amounts of GOS and glucose exceed what can be expected from galactoglucomannan; a minor fraction of cellulose or other glucans was probably hydrolysed as well.

For miscanthus, an herbaceous crop, the main native hemicelluloses are arabinoxylans, with mannans and glucomannans in minor amounts [62]. After autohydrolysis at 190 °C, OS are composed primarily of XOS, then GOS, MOS; GalOS and AOS are present in minor amounts, which is consistent with the presence of arabinoxylans, mannans and glucomannans in the liquor. Free sugars are composed primarily of arabinose, then xylose, galactose and glucose in minor amounts; mannose is absent. The ratio of XOS/AOS is 100/8.2 in OS and the ratio of xylose/arabinose is 100/195, which is very close to the values observed for wheat straw. Again, this indicates fast hydrolysis of arabinose in arabinoxylan. The ratio of GOS/MOS/GalOS is 10/4/19 in OS and the ratio of glucose/mannose/galactose is 10/0/23. GalOS and galactose are present in large proportions, which indicates the presence of galactan hemicelluloses (e.g., arabinogalactans) rather than only galactoglucomannans. The trends for glucose and mannose are similar to those observed for wheat straw.

Finally, branched sugars such as arabinose in arabinoxylan and arabinogalactan and galactose in galactoglucomannans seem to be released faster than backbone sugars such as xylose or mannose. This phenomenon was already observed by Chen et al. for hardwood [63].

SEC analysis with pullulan calibration was performed on the concentrated autohydrolysis liquors (Figure 3). All chromatograms showed a multimodal distribution of molecular weights corresponding to the complex composition of biomass liquors. A first peak corresponding to monomer compounds (sugars, acids, small compounds) was present for all samples, with a more intense one obtained for eucalyptus residues at 210 °C. The peaks corresponding to saccharides were present from 0.2 kDa to 3 kDa for eucalyptus residues autohydrolysed at 210 °C, from 0.2 to 11 kDa for eucalyptus residues autohydrolysed at 190 °C, and from 0.2 to 120 kDa for wheat straw and miscanthus. Three different peaks can be drawn for the liquors obtained at 190 °C: one in the region of oligomers (DP < 10), also present for eucalyptus residues −210 °C); one in the region of small polymers (DP < 100); and a small one in the region of large polymers (DP > 100). The latter is visible as a minor peak for miscanthus and wheat straw. Its presence may not be due to hemicellulose oligosaccharides, as the DP of hemicellulose is usually found between 50 and 300 [4]. Fragments of cellulose or other impurities (e.g., lignin, proteins) may be found here; thus it was not taken into account in the analysis of SEC data (Table 2).

Table 2. Data of SEC analysis.

Biomass Type	Peak 1 (Monomers)			Peak 2 (Oligomers)			Peak 3 (Polymers)		
	Mw (Da)	PD	Mass%	Mw (Da)	PD	Mass%	Mw (Da)	PD	Mass%
Eucalyptus liquor—210 °C	52.1	1.42	69%	594.6	1.34	31%	-	-	-
Eucalyptus liquor—190 °C	54.8	1.36	22%	339	1.19	22%	2 552	1.57	56%
Wheat straw liquor—190 °C	55.7	1.31	13%	342	1.14	23%	5 116	3.10	64%
Miscanthus liquor—190 °C	52.7	1.29	15%	326	1.15	18%	4 495	2.33	67%
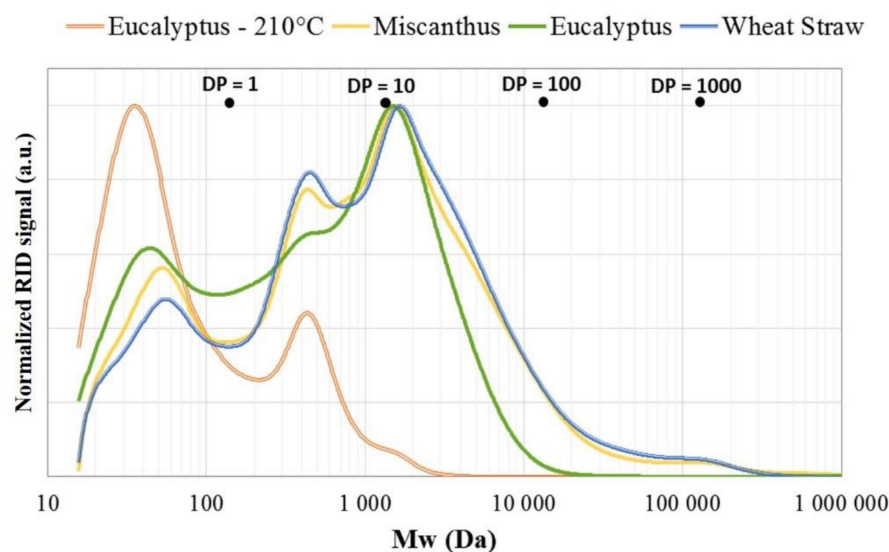
Figure 3. SEC analysis of concentrated autohydrolysis liquors. Autohydrolysis liquors were obtained at 190 °C unless otherwise mentioned.

A detailed analysis of the SEC data shows that the eucalyptus residues products obtained at 210 °C are composed primarily of monomers and small molecules (69%) and small oligomers, with an average Mw of 594 Da, i.e., a degree of polymerisation around 4. Eucalyptus residue liquor obtained at 190 °C is composed less by monomers and small molecules (21%) and oligomers (22%), with polymers in the majority (56%) and an average degree of polymerisation around 19. Wheat straw and miscanthus liquors have a similar distribution of polymers, with a majority of polymers (64–67%) with a large DP (34–38), a fraction of 18–23% oligomers with a small DP (2–3), and a small fraction of oligomers and small molecules (13–15%). The fraction of monomers is similar to the one analysed by HPLC. One can see that autohydrolysis is efficient to solubilise hemicelluloses and to partially hydrolyse their structure: DP of OS after autohydrolysis is inferior to the degree of polymerization of native hemicellulose reported in the literature. It has already been reported that autohydrolysis is efficient to solubilize only oligosaccharides with DP inferior to 25 [63].

Analysis of carbon in concentrated autohydrolysis liquors was used to quantify unknown compounds in solution (Table 3). Unknown compounds can correspond to phenolics extracted from lignin, proteins, etc. Low levels of unknown compounds were detected, which indicates that autohydrolysis is a selective process for extraction of oligosaccharides. The highest content of unknown compounds was found in eucalyptus liquor obtained at 190 °C, with a 5.3 C% yield of unknown compounds; this yield was halved for eucalyptus liquor obtained at 210 °C. It is likely that unknown compounds precipitated at higher temperature, as for example phenolic compounds extracted from lignin can condensate into insoluble materials in harsh conditions [64]. The yield of unknown compounds also depended on the type of biomass, with the following range: eucalyptus > wheat straw > miscanthus. This range is correlated with the lignin content in each biomass (see Table 1).

3.3. Catalytic Hydrolysis

The catalyst for catalytic hydrolysis was chosen from a previous work [49] in which the activity of TiO_2-WO_x for the hydrolysis of cellobiose and commercial xylan was evidenced along with its stability in hydrothermal conditions. The support was a mesoporous anatase TiO_2 with a large surface area. It was doped by tungsten oxides in order to enhance acidity (Table 4).

The concentration of OS and sugars in the liquors was adjusted to 25 g_C·L^{-1} with pure water addition. After adding the catalyst, the suspension was heated and stirred at

temperatures between 140 and 180 °C for 3 h. For the sake of comparison, two commercial xylans were also tested, one with a small DP (4–5) and one with a large DP (200).

Table 3. Unknown compound quantification in concentrated autohydrolysis liquors.

	Eucalyptus 210 °C	Eucalyptus 190 °C	Wheat Straw 190 °C	Miscanthus 190 °C
OS (quantified by HPLC—$g_C.L^{-1}$)	10.2	50.8	60.1	32.3
Sugars (quantified by HPLC—$g_C.L^{-1}$)	10.1	10.1	5.9	4.5
Others (quantified by HPLC—$g_C.L^{-1}$)	4.7	3.4	4.1	2.9
Total carbon (TOC analysis—$g_C.L^{-1}$)	**31.6**	**88.2**	**96.4**	**40.2**
Unknown compounds (calculation—$g_C.L^{-1}$)	6.7	23.9	9.4	0.5
Unknown compounds yield (C%—biomass basis)	**2.5**	**5.3**	**1.9**	**<0.5**

Table 4. Catalyst properties (from [49]).

BET specific surface area ($m^2 \cdot g^{-1}$)	97
Average pore diameter (nm)	13
Crystalline phase	Anatase
W loading (wt.%)	5.6
Acid sites number ($\mu mol_{eq.NH3} \cdot g^{-1}$)	245

Figure 4 shows the global conversion of oligosaccharides during catalytic hydrolysis. Two distinct behaviors can be observed: for oligosaccharides with low DP, i.e., eucalyptus residue liquor obtained at 210 °C and commercial xylan with low DP, a significant conversion can be obtained at 140 °C and increases with temperature, finally reaching 96% for commercial xylan and 55% for eucalyptus residue liquor obtained at 210 °C. For oligosaccharides with higher DP, i.e., the three liquors obtained at 190 °C from eucalyptus, wheat straw and miscanthus as well as commercial xylan with high DP, conversion is very low at 140 °C and increases slowly with temperature to reach 29% for eucalyptus residues liquor, 12% for wheat straw liquor, 5% for miscanthus liquor and 16% for the commercial xylan with high DP. Therefore, the molecular weight of oligosaccharides has a strong effect on the degree of conversion of oligosaccharides, and to a minor extent, the type of biomass also influences the conversion rate.

Figure 5 shows the global monomer yields (sugars, furfural and HMF). Again, two distinct behaviours can be observed depending on the DP: for oligosaccharides with low DP, monomer yield reaches a maximum at 160 °C and decreases at 180 °C, evidencing the degradation of monomers at high temperature. Degradation products are described in the literature as humins, i.e., products of condensation of furanic derivatives and sugars [65]. For oligosaccharides with high DP, monomer yield remains very low and increases with temperature only for Eucalyptus residue liquor. Hence, in the latter case, the rate of monomer degradation is higher than their rate of production through hydrolysis reaction.

A closer look at the different oligosaccharides (Figure 6) reveals different conversions as a function of oligosaccharide type. For liquor of eucalyptus residue obtained at 210 °C, the highest catalytic conversions at 180 °C are obtained with MOS and GalOS, i.e., with galacto(gluco)mannans and arabinogalactans, and the lowest with GOS and XOS, i.e., with arabinoxylans and glucans. For eucalyptus residue liquor obtained at 190 °C, the highest catalytic conversion is AOS, showing the complete release of arabinose from arabinogalactans and arabinoxylan. GalOS is converted up to 42%; GOS and XOS are partly converted; and MOS are only converted up to 11%. This indicates partial depolymerization of arabinoxylan, arabinogalactan and galactoglucomannans. Wheat straw and miscanthus liquors lead to similar results, with MOS giving the highest conversion, AOS medium

conversion, and GOS, XOS, and GalOS conversions negligible; i.e., mannans are massively depolymerized in the presence of solid acid catalysts for these biomasses. Xylans, glucans and galactans seem resilient to catalytic hydrolysis.
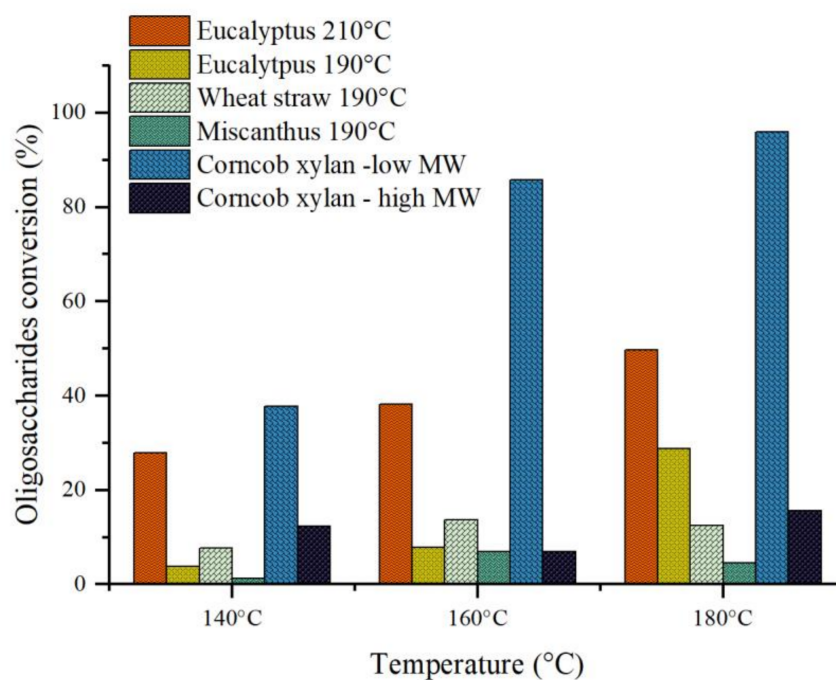

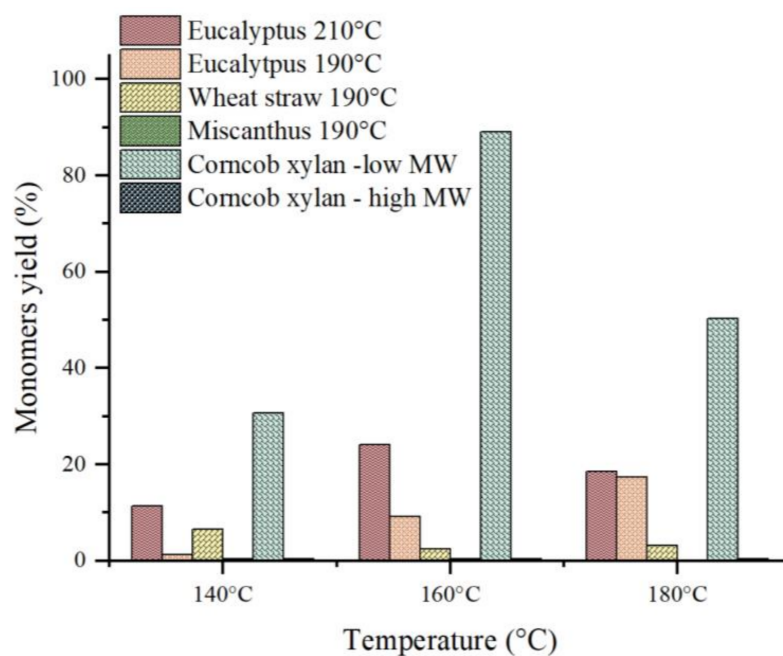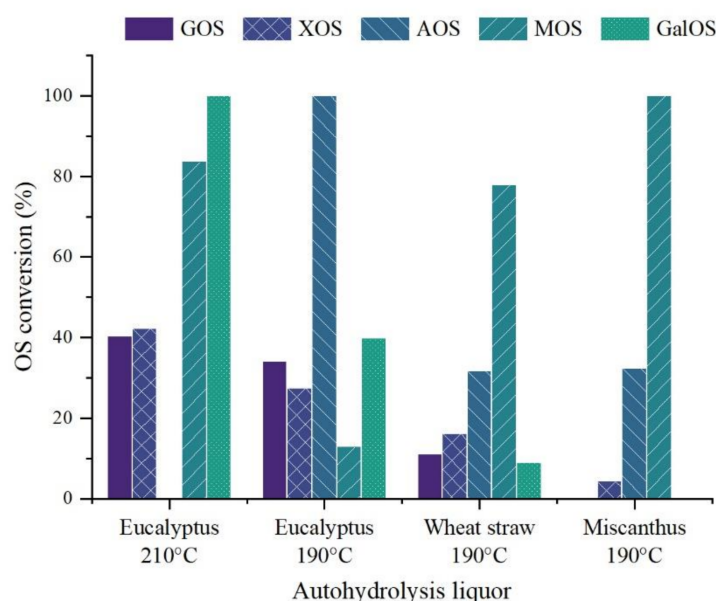**Figure 4.** OS conversion during catalytic hydrolysis.

Figure 5. Monomer yields during catalytic hydrolysis.

Figure 6. Conversion of oligosaccharides during catalytic hydrolysis of liquors.

The final monomer composition is depicted on Figure 7. Furfural and HMF are observed in the final mixture. The furfural amount is much more important than HMF, which evidences the faster degradation of HMF to form humins, as already described in a previous work [49]. A comparison with the sugars' composition before catalytic hydrolysis (Figure 2) shows a diversification in the type of sugars. Arabinose is less concentrated, and probably more prone to dehydrate and degrade to other compounds such as furfural and humins, particularly in eucalyptus residue liquor. Mannose is present in wheat straw liquor only, which corresponds to a high concentration in MOS before catalytic hydrolysis. The only liquor showing an increase in Xylose, Arabinose and Glucose amount is eucalyptus residue liquor obtained at 190 °C (notably, with a 17% yield in xylose). Eucalyptus residue liquor obtained at 210 °C shows an interesting yield of Furfural, a 24% yield based on pento-oligosaccharide and pentose concentrations.
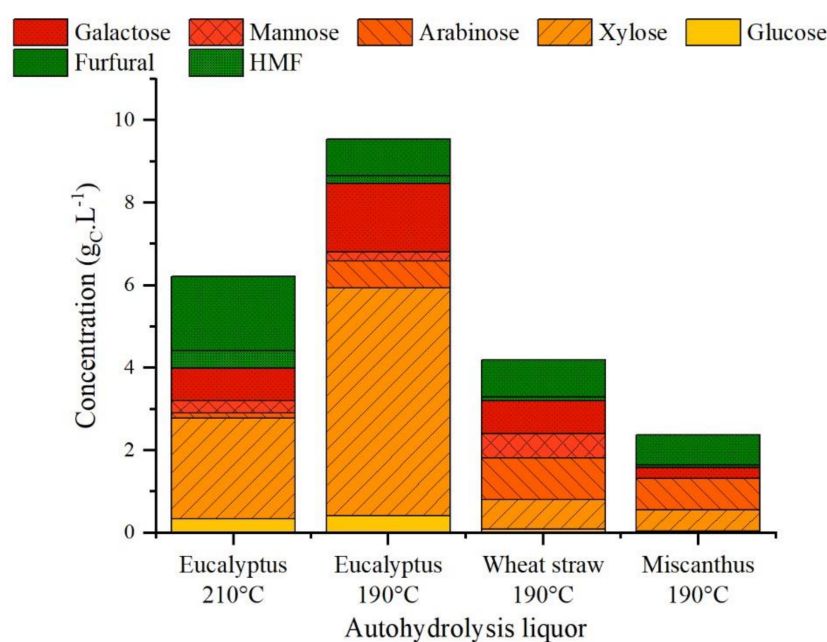
Figure 7. Monomer composition after catalytic hydrolysis at 180 °C.

Finally, after catalytic hydrolysis at 180 °C, Eucalyptus residue liquor −210 °C is enriched in furfural, Eucalyptus residue liquor −190 °C and Miscanthus liquor are enriched in free sugars and in majority in xylose, and wheat straw liquor is enriched in free rare sugars (mannose, galactose, arabinose). The type of biomass, type of autohydrolysis and temperature of catalytic hydrolysis are determining factors for final sugar production. The global yields of OS, sugars and furans are presented in Table 5. The best yields of OS and sugars are obtained with Eucalyptus at 190 °C; the best yield of furanic compounds is obtained with Eucalyptus residues at 210 °C.

Table 5. Yields of autohydrolysis reactions, catalytic hydrolysis reactions and global yields.

Biomass	T° (°C)	Autohydrolysis Yield on Hemicellulose Basis		Catalytic Hydrolysis 180 °C on OS Basis		Global Yield ** on Hemicellulose Basis		
		Yield OS (%)	Yield Sugars (%)	Yield Sugars (%)	Yield Furans (%)	Yield OS (%)	Yield Sugars (%)	Yield Furans (%)
Eucalyptus	210	12.8	28.2	−20.59 *	19.66	8.1	14.2	5.1
Eucalyptus	190	44.5	10.0	13.41	3.29	37.0	17.7	1.5
Wheat straw	190	30.1	7.7	−0.17 *	3.22	28.0	4.2	0.9
Miscanthus	190	15.2	5.0	−4.99 *	4.17	17.0	1.7	0.6

* Negative yields correspond to a conversion of sugars higher than conversion of OS. ** Global yield = amount of product (gC)/amount of hemicellulose in starting lignocellulosic materials (gC) × 100.

4. Discussion

The presented results illustrate the complexity of ex-hemicellulose processing directly from biomass.

4.1. During Autohydrolysis

The type of biomass as well as the temperature of autohydrolysis have a strong impact on the composition of resulting liquors.

Three biomasses were tested: hardwood (eucalyptus residues), straw (wheat straw) and energy crop (miscanthus). The type of biomass influences the yield of OS and free sugars after autohydrolysis (eucalyptus residues > wheat straw > miscanthus for OS and sugars) as well as the composition of OS and sugars. Even if XOS is the major oligosaccharides in all cases, more MOS was obtained from wheat straw and more AOS from miscanthus. More xylose was obtained from eucalyptus residues, and more arabinose from wheat straw and miscanthus. This corresponds to the high content of arabinoxylan in herbaceous materials. Branched sugars such as arabinose in arabinoxylan and galactose in galactoglucomannans are preferentially hydrolysed in free sugars during autohydrolysis for all biomasses. However, the average molecular weight of oligosaccharides is similar for all three biomasses. Two factors can explain these differences: the composition of hemicelluloses in the original biomass, and mass transfer during autohydrolysis [66]. Indeed, the shape and size of the biomass particles varies from one biomass source to another, as do the intrinsic biomass cell structures. The similarity of molecular weight distributions could also be due to solubility issues (i.e., the larger oligosaccharides were not soluble under the studied conditions). Indeed, it was reported that autohydrolysis solubilizes oligosaccharides with average DP lower than 25 [63].

Two temperatures were tested for eucalyptus residues, 190 °C and 210 °C. During autohydrolysis, temperature has a strong impact on the products obtained: oligosaccharides are in the majority at 190 °C, while free sugars predominate at 210 °C. Temperature also changes the oligosaccharide composition, with more MOS at 210 °C and more GalOS at 190 °C, as well as the composition of free sugars (mainly xylose at 210 °C, with more mannose, galactose and arabinose at 190 °C). It can be considered that the results at 190 °C represent an intermediate state of the results obtained at 210 °C, and the following

pathway can be drawn: oligosaccharides are already dissolved at 190 °C, and a small portion of them have already been hydrolysed to monomeric sugars; between 190 and 210 °C, the extraction of hemicelluloses from lignocellulose did not progress while the hydrolysis of oligosaccharides did, leading to a higher level of sugars, mainly xylose. Dehydration reactions to form furfural and HMF also occur to a minor extent. This pathway is corroborated by the evolution of molecular weight distributions, showing an important decrease in polymer size between 190 and 210 °C. The influence of temperature during autohydrolysis has been extensively studied in the literature [28,66]; in this study, only two temperatures were tested for eucalyptus in order to corroborate published results and to produce degraded oligosaccharides at 210 °C for the second part of the study, catalytic hydrolysis.

4.2. During Catalytic Hydrolysis

The liquor composition and the temperature of reaction also influences the performances of the process.

Between 140 and 180 °C, the temperature of catalytic hydrolysis has a strong effect on the progress of reaction as well as on the selectivity. Increasing temperature not only leads to an increase in the conversion of oligosaccharides but also to a decrease in selectivity, particularly after 160 °C, and finally to degradation of the produced sugars into humins.

In the liquor composition, three main factors can be considered: the size of polymer (i.e., the average molecular weight), the type of sugars and oligosaccharides, and the presence of other compounds in the liquors (not analysed in this work).

Increasing the size of polymers has a strong negative impact on catalytic hydrolysis activity. However, it must be noted that the analysis method used here does not allow for the observation of internal glycosidic bond cleavage in the polymer; hence, a part of the catalyst activity is underestimated, and this part increases with the size of the polymer. The rate of diffusion of large oligosaccharides in the mesoporous catalyst is also expected be very low.

The type of sugars in polymer is also important. Even if all the oligosaccharides are composed primarily of xylose units, rare sugars (mannose, galactose, arabinose) are also present. It appears that side-branched sugars such as arabinose in arabinoxylan and galactose in galactomannans are more prone to be hydrolysed. Mannose and xylose hydrolysis rates vary considerably with the type of biomass, suggesting that the fine structure of oligosaccharides is a key factor for catalytic hydrolysis.

Finally, other compounds present in the liquors may also play a role, which could explain the dissimilarities between wheat straw liquor and miscanthus liquor, which have very similar molecular weight distributions and very different catalytic hydrolysis results.

5. Conclusions

The combination of autohydrolysis and catalytic hydrolysis processes was studied for the production of oligosaccharides, sugars and furanic compounds from three different starting materials. Autohydrolysis produced a mixture of oligosaccharides, sugars and undetermined compounds. Catalytic hydrolysis produced more sugars from oligosaccharides in autohydrolysis liquors. Both processes were very sensitive to temperature and biomass type. The size and composition of oligosaccharides and sugars were investigated, and both had a strong impact on catalytic hydrolysis. Finally, liquors enriched in different sugars and/or in furfural could be produced depending on the starting material and the conditions of the reaction. The highest global yields of oligosaccharides and sugars were obtained from Eucalyptus after autohydrolysis at 190 °C and catalytic hydrolysis at 180 °C (37 and 18%).

In the near future, better control of the processes involved will be investigated through a different choice of reactors in order to achieve fast temperature ramps, short contact times and higher temperatures, and thus limit the degradation of oligosaccharides and sugars during autohydrolysis and catalytic hydrolysis.

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