Effect of Pre-Extraction on Composition of Residual Liquor Obtained from Catalytic Organosolv Pulping of Sugar Maple Bark

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Abstract: Background: We have determined previously that the water extract of sugar maple bark contained an important quantity of a complex sugar. In this study, we investigated the organosolv pulping of pre-extracted bark to follow the acid conversion of sugars into major products, furfural and 5-hydroxymethyl-2-furfural (HMF), while comparing the structures of organosolv lignins. Methods: The bark particles were pre-extracted with an ethanol–water mixture or water only. The extractives-free barks were then converted into cellulosic pulp and lignin by a patented organosolv process. The composition of residual liquor was determined by using HPLC-UV. Results: The pre-extraction with water was more efficient for complex sugars recovery than with the ethanol–water system. HMF was determined to be more abundant in residual liquor than furfural after ethanol–water pre-extraction while their quantities were comparable in the residual liquor after water pre-extraction. The higher yield of HMF from ethanol–water pre-extracted bark (1.18%) than from water pre-extracted (0.69%) could be related to the efficiency of complex sugar removal during the pre-extraction step. Conclusions: The pre-extraction before pulping affected, at least in part, the composition of residual liquor in terms of HMF production. These results demonstrate how the bark can be converted into valuable products and intermediates for organic synthesis.

Keywords: sugar maple bark; pre-extraction; organosolv bark lignin; residual liquor; furan compounds

1. Introduction

Lignocellulosic biomass is a sustainable and renewable resource, mainly composed of cellulose, hemicellulose and lignin that are organized in a complex structure [1]. An integrated use of biomass components constitutes a great opportunity for biorefinery industries to increase their revenue and profit [2,3]. In this context, lignocellulosic biorefineries are supposed to produce biofuel and value-added chemicals, which can be used as alternatives of fossil-derived products [3–6]. One of the foremost target transformations of lignocellulosic biomass has been the conversion of residual sugars from carbohydrate biopolymers into their immediate dehydrated derivatives, notably furan compounds, such as 5-hydroxymethyl-2-furfural (HMF) and furfural [5,7,8]. These compounds can serve as platform chemicals that can be used for the production of a variety of important chemicals on an industrial scale. Examples of such products where derivatives of HMF and furfural could find applications are paints and varnishes, fuels, plastics and composites [9].

Obviously, the production of furan compounds is related to the treatment process of lignocellulosic biomass. Through a biorefinery approach, the valorization of each component in separate fractions requires a multi-step biomass processing [8,10]. Nowadays, the organosolv pulping process represents an alternative to traditional pulping methods, such as alkaline kraft and acidic sulfite chemical pulping.
Advantages of organosolv in comparison with other methods include mainly the separation of high purity cellulose and the production of high-quality lignin. In addition, the organosolv process uses an organic solvent (such as ethanol, acetic acid, esters, soda amine and ethanol alkali) as a delignifying agent to separate biomass components [13].

We have developed a new catalytic organosolv pulping process using an ethanol–water (1/1, v/v) solvent system with a Lewis acid as catalyst (ferric chloride), which originally implicated a pre-extraction step using the same solvent system before pulping [14]. The strategy of the patented organosolv process was to sequentially remove the extractives (notably phenolic compounds) from bark before pulping, which could reduce the efficacy of the ferric chloride by interacting with phenolic extractives. Since the extractives are removed, the catalyst can better promote the cleavage of the covalent bonds between lignin and polysaccharides, allowing for an efficient delignification [14–16]. In an effort to valorize byproducts of wood transformation (barks and wood), produced in huge quantities by the Canadian forest industry, our research group has studied the extractives and organosolv lignins from sugar maple wood and bark. Sugar maple (Acer saccharum) is one of the most important Canadian forest species, not only for the high quality of its greatly appreciated wood for numerous applications, but also for the production of sap, which is used for the production of maple syrup [17]. Extraction of sugar maple bark using hot water had demonstrated the ability to extract the important phenolic compounds along with a complex sugar in our previous study [18]. The study on the complex polysaccharide present in hot water extract demonstrated that it is composed of hexose sugars and its biological activities are an object of an ongoing research in order to valorize that stream of sugar maple bark processing as well. Other studies from our laboratory have demonstrated that the organosolv process has been revealed to adequately isolate lignin with high purity (around 80% lignin recovery) [15,16,19]. Subsequently, the studies have focused on the catalytic hydrolysis of hemicellulose leading to the production of furfural and HMF found in residual liquor [15,16,19]. Apart from the role of the catalyst used in the organosolv process, the pre-extraction step appeared to have an impact on the composition of the residual liquor.

The main aim of this study is to evaluate the impact of pre-extraction treatments, using water and ethanol–water (EtOH–water) as the solvent systems, before pulping on the composition of the residual liquor of sugar maple bark, while estimating the impact on lignin recovery and structure. The pulping of the pre-extracted bark with EtOH–water or water only, were performed by organosolv process. Besides EtOH–water, water was also selected as solvent for pre-extraction since it was reported to extract significant quantities of complex sugars from sugar maple bark [18]. It is assumed that the presence or absence of complex sugars (depending on the efficiency of pre-extraction treatment processes) along with sugar released by hydrolysis of hemicelluloses may affect the yield of furanic compounds in residual liquor. The yields of extractives, cellulosic pulp, organosolv lignins, and composition of residual liquor are investigated to portray a comprehensive valorization of sugar maple bark.

2. Materials and Methods

2.1. Pre-Extraction Procedure

Sugar maple bark was ground to 250–500 µm particle size, as previously described [18]. Prior to delignification, the bark particles were pre-extracted with either EtOH–water mixture (1:1 v/v) or water. A total of 100 g of bark particles were extracted in 1L of solvent at 80 °C for 6 h in a Soxhlet extractor to remove phenolic and other extractive compounds, along with volatile materials, which could interfere with delignification. After filtration, extractive-free bark particles were dried at 80 °C for 24 h prior to pulping. The crude extracts obtained after elimination of solvent, were dried under vacuum at 45 °C for 24 h prior to analysis.
2.2. Total Sugar Content

Total sugar content of the extracts was determined by the phenol–sulfuric acid method. Briefly, 1 mL of extract (100 µg/mL) was mixed with 500 µL of phenol reagent (4% m/v water) and 2.5 mL of concentrated sulfuric acid (36N) and reacted for 10 min in a water bath at 25 °C–30 °C. The blank was set initially with all reagents without extract. Absorbance of the thus obtained solution was read at 490 nm and the sugar content was expressed with an Arabinose-Rhamnose-Galactose-Fructose calibration curve (mg ARGF/g dry extract).

2.3. Catalytic Organosolv Pulping

The extractives-free barks were treated under the same pulping conditions, as described previously [15] (see the schema in Figure 1). Briefly, the extractives-free bark, ethanol–water mixture (1:1, v/v; 0.5 L of final volume for 50 g of bark) and ferric chloride (9 mmol of FeCl₃·6H₂O for 100 g bark) as a catalyst were introduced into a Parr reactor series 4842 (2 L). After 90 min of cooking at 180 °C, the reaction mixture was left to cool down to room temperature. The obtained organosolv pulp was separated by filtration and washed three times with water–ethanol system (300 mL) to recover all dissolved lignin. The organosolv lignin was precipitated from the dark-brown residual liquor (to which ethanol–water from washing was added) by acidification with 2 M HCl to pH 1.5. The residual liquor was stocked for further analysis and the precipitated organosolv lignin was filtered and dried under vacuum at 40 °C overnight. Organosolv lignin was obtained in the form of solid brown powder.

![Figure 1. Schematic representation of different processes studied in this work.](image)

2.4. HPLC and LC–HRMS Analysis of Residual Liquor

In order to identify the major compounds of the two residual liquors, molecular weights and the UV spectra were determined using LC–HRMS and HPLC-DAD, respectively. Analytical HPLC consisted of an Agilent 1100 liquid chromatography system (Agilent Technologies, Palo Alto, CA, USA) equipped with a binary pump, autosampler, a thermostatically controlled column compartment (30 °C), DAD and Agilent ChemStation software (Agilent Technologies). The LC separation was performed on an Agilent Zorbax SB-C18 column (4.6 mm ID × 250 mm, 5 µm particle size). The major residual liquor constituents were monitored at 280 nm. The mobile phases consisted of A (water) and B (acetonitrile); the optimized solvent gradient was: 12% B at 0–10 min, 12–25% B at 10–15 min, 25% B at 15–30 min,
with a 0.7 mL/min flow rate, based on the gradient used for hot water red maple bud extract. Using an electrospray interface and an Agilent 6520 Acurate-Mass Q-TOF (Agilent Technologies) equipped with MassHunter Workstation software (Agilent Technologies), ESI-QTOF-MS analysis was performed in positive mode using full scan mode with a mass range of 100–1000 Da. The HRMS parameters were as follows: drying gas (N₂) flow rate, 5.0 L/min; drying gas temperature, 325 °C; nebulizer, 30 psi; capillary voltage, 4000 V; fragmentor 175 V; skimmer voltage, 65 V; and octopole radio frequency, 250 V.

2.5. NMR Analyses of Lignins

The 31P NMR spectra of organosolv bark lignins were recorded on a Varian NMR spectrometer at 500 MHz at 256 scans. A total of 45 mg of oven-dry (OD) lignin was dissolved in 0.5 mL of anhydrous pyridine/CDC13 mixture (1.6/1, v/v) [14,15]. A total of 4.5 mg of an endo-N-hydroxy-5-norbornene-2,3-dicarboximide as the internal standard and 2.7 mg of chromium (III) acetylacetonate used as relaxation reagent were successively added in lignin solution. The mixture was transferred into a 5 mm NMR tube and 150 µL of 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane was added as phosphitylating reagent for NMR analysis. Data processing was performed using MestReNova 8.1.1 software. Quantitative 31P NMR utilizing published procedures were used.

2.6. Statistical Analyses

The obtained results are presented as means ± SD of three different experiments with triplicate determinations for each sample. Statistical analysis was performed using student’s ‘t’-test using GraphPad Prism version 6 (GraphPad Software Inc., La Jolla, CA, USA). The values of $p < 0.05$ were considered as statistically significant.

3. Results

3.1. Chemical Composition of Sugar Maple Bark

The main chemical components of the sugar maple bark are presented in Table 1. Bark was largely composed of sugars (65.45%) followed by lignin (25.28%), extractives (5.88 to 7.90%) and ash content (3.54%). Glucose, xylose and arabinose have been identified as the most abundant monosaccharide after analyzing the acid-hydrolyzed bark by HPLC-RI.

| Entry | Main Constituents | Bark (%) |
|-------|------------------|----------|
| 1     | Total sugar *    | 65.45 ± 1.55 |
|       | Glucose          | 28.85 ± 0.04 |
|       | Xylose           | 15.4 ± 0.21 |
|       | Arabinose        | 2.2 ± 0.07 |
| 2     | Total lignin     | 25.28 ± 0.95 |
|       | Acid soluble lignin | 0.53 ± 0.73 |
|       | Klason lignin    | 24.74 ± 0.22 |
| 3     | Extractives yield|           |
|       | Water solvent    | 7.90 ± 0.50a |
|       | Ethanol–water solvent | 5.88 ± 0.60b |
| 4     | Ash              | 3.54 |

Yield expressed as % of oven dry mass of bark. Different letters indicate significantly different results according to student’s ‘t’-test at 95% confidence level. * Total sugar was determined using phenol–sulfuric acid method.

Prior to organosolv pulping, sugar maple barks were pre-extracted with ethanol–water or with hot water as solvents using Soxhlet extractor at 80 °C for 6 hours. The pretreatment of bark with water and EtOH–water solvent showed significantly different ($p < 0.05$) extraction yields of $7.90 ± 0.50%$ and $5.88 ± 0.60%$, respectively (Table 1).
3.2. Monosaccharide Composition and Total Sugar Content of Bark Extracts

Table 2 summarizes the individual monosaccharide and total sugar content of sugar maple bark extracts obtained from different pre-extraction treatments. HPLC-RI analysis was performed on acid hydrolyzed extracts to identify the monosaccharides. The glucose contents are the highest, representing more than 60% of total sugar content, in both extracts. The contents of other monosaccharide in descending order are galactose, arabinose, rhamnose and fructose. The monosaccharide composition of extractives obtained from water solvent was not significantly different to that obtained from EtOH–water. Fructose was present in the lowest content in water-extract, whereas it was not detected by HPLC-RI in EtOH–water extract.

The total sugar content of two extracts was determined by the phenol–sulfuric acid method. As seen from Table 2, water-extract presented significantly higher (p < 0.05) total sugar content (55.40 ± 2.11% of dry extract), about 2-fold, compared to water–ethanol extract (26.74 ± 0.92% of dry extract).

Table 2. Total sugar content and monosaccharide composition of sugar maple bark extracts obtained with water and EtOH–water solvent.

| Compositions     | Water Extract (%) | EtOH–Water Extract (%) |
|------------------|-------------------|------------------------|
| Glucose          | 61.59 ± 1.82      | 60.61 ± 0.53           |
| Galactose        | 25.96 ± 1.02      | 27.45 ± 0.91           |
| Fructose         | 1.34 ± 0.10       | N/d                    |
| Rhamnose         | 4.34 ± 0.13       | 5.94 ± 0.10            |
| Arabinose        | 6.76 ± 0.16       | 5.99 ± 0.13            |
| Total sugar *    | 55.40 ± 2.11a     | 26.74 ± 1.18b          |

Yield expressed as % of oven dry mass of extract. Different letters indicate significantly different results according to student’s 't'-test at 95% confidence level. * Total sugar was determined using phenol–sulfuric acid method.

3.3. Organosolv Pulping of Pre-Extracted Bark

After cooking, the solid organosolv pulp was separated by filtration and then washed with water–ethanol to recover the remaining lignin. The results on organosolv pulps composition and lignin recovery are presented in Table 3. The pre-extraction with water seems to be favorable to recover the organosolv lignin with 87.1% compared to that of EtOH–water pre-extraction (66.96%). This result might suggest that the organosolv lignin recovery from sugar maple bark is affected by the extraction method used prior to pulping.

Table 3. Compositions of Organosolv pulps obtained from pre-extracted bark and lignin recovery.

| Compositions     | Ethanol–Water (wt%) | Water (wt%) |
|------------------|---------------------|-------------|
| Cellulosic pulp  | 48.42 ± 3.26        | 49.83 ± 6.11|
| (Lignin in cellulosic pulp *) | 8.09 ± 1.52        | 3.21 ± 0.52 |
| (Ashes)          | 0.25 ± 0.11         | 0.18 ± 0.09 |
| Organosolv lignin yield | 16.27 ± 0.26       | 21.59 ± 0.71 |
| Lignin recovery, % of total lignin in bark | 66.96 ± 2.35b | 87.1 ± 3.12a |

Yield expressed as % of oven dry mass of pre-extracted bark; * content in cellulosic pulp are expressed on pre-extracted OD bark. Different letters indicate significantly different results according to student’s 't'-test at 95% confidence level.

In addition, the data obtained by quantitative $^{31}$P NMR spectral analyses of studied lignins are shown in the Supplementary Materials (Figures S1 and S2). Table 4 presents similar patterns of different hydroxyl groups distribution in studied organosolv lignins, with comparable contents of phenolic, aliphatic and carboxylic functionalities. The results also confirm that the organosolv lignins of sugar maple bark are Guaiacyl-Syringyl-Hydroxylphenylpropane (G-S-H) type lignin, with a predominance of G units. However, it can be observed that the lignin recovered from water pre-extracted bark had a somewhat lower hydroxyl concentration of S units than that of ethanol–water pre-extracted bark. This could be attributed to the complex and irregular structure of lignin in the samples of the same
origin (sugar maple bark) but could potentially indicate, to a certain extent, a loss of some syringly moieties during water prehydrolysis.

Table 4. Structural properties of recovered organosolv lignins.

| Type of -OH   | EtOH–Water (mmol/g Lignin) | Water (mmol/g Lignin) |
|--------------|-----------------------------|-----------------------|
| Aliphatic    | 1.71                        | 1.73                  |
| Syringyl (S) | 1.61                        | 1.04                  |
| Guaiacyl (G) | 1.87                        | 1.54                  |
| p-Hydroxy    | 0.11                        | 0.07                  |
| Carboxylic   | 0.57                        | 0.48                  |

The structural properties of the organosolv lignins issued from pulping of sugar maple bark pre-extracted with two different solvent systems seem to be quite comparable. Additional trials would be required to explain the differences observed for lignin recovery.

3.4. Composition of Residual Liquors after Organosolv Lignin Removal

After the separation of biopolymer, cellulosic pulp and organosolv lignin, the fraction of residual liquor was obtained, and the yield was calculated according to Equation (1):

\[
(1 - \frac{\text{cellulosic pulp} + \text{lignin organosolv}}{\text{O.D bark}}) \times 100\%
\]  

(1)

The yield of residual liquor and their chemical composition are reported in Table 5. It can be observed that the xylose content is higher than that of glucose in residual liquor obtained after both types of pre-extraction, thus indicating a good preservation of cellulose originally present in the bark. The residual liquor was analyzed by the HPLC-DAD in order to follow the conversion of the polysaccharides into major products, namely furfural and 5-hydroxy-methyl furfural (5-HMF). Another compound C-3 was also detected as one of the major constituents of the studied residual liquor. The LC-HRESI–MS/MS spectrum of the unidentified compound C-3 showed the characteristic ions at 53, 81, 109, 177 and 223 m/z (Figures 2 and 3) which is quite similar to those from 5-HMF derivatives. Therefore, this product seems to be an artifact formed during the sugar conversion process.

Table 5. Chemical compositions of residual liquor.

| Pre-Extraction | Fraction of Residual Liquor (%) | Glucose (%) ** | Xylose (%) ** | HMF (%) ** | FF (%) ** | C-3 (%) ** |
|----------------|---------------------------------|---------------|--------------|------------|-----------|-----------|
| EtOH–water     | 35.31 ± 2.47                    | 1.59 ± 0.06b  | 2.91 ± 0.13a | 1.18 ± 0.41a | 0.38 ± 0.01b | 0.15 ± 0.01 |
| Water          | 28.58 ± 6.92                    | 1.82 ± 0.12b  | 2.67 ± 0.05a | 0.69 ± 0.05b | 0.61 ± 0.03a | 0.10 ± 0.01 |

Different letters indicate significantly different results according to student’s ‘t’-test at 95% confidence level.

*Estimated as difference of 100%—sum of the rest of the constituent (cellulosic pulp and lignin organosolv) in Table 3.

**Contents in % expressed on oven dry fraction of residual liquor.
4. Discussion

As mentioned above, the main objective of the current study was to evaluate the effect of pre-extraction on chemical composition of residual liquor after organosolv pulping.

It is observed that the yield of water extraction of sugar maple bark was higher than that of EtOH–water. Multiple studies have demonstrated that hot water generally extracts various compounds of different molecular weights, including large ones such as tannins, proteins and polysaccharides. In contrast, EtOH–water is a more selective solvent because of its higher ability to selectively solubilize several polar compounds, mainly polyphenols and tri-terpenes [20,21]. Our results are in accordance with these findings and confirm that water extract is more concentrated in

The data presented in Table 5 shows that 5-HMF was identified to be more abundant in residual liquor than furfural after EtOH–water pre-extraction (1.18 ± 0.41% and 0.38 ± 0.01%, respectively) while their quantities were comparable in the residual liquor after water pre-extraction (0.69 ± 0.35% and 0.61 ± 0.03%). Beside furfural and HMF, the C-3 compound was also detected, but in a too low a quantity to allow for its isolation and identification with certainty.

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of different molecular weights, including large ones such as tannins, proteins and polysaccharides. In contrast, EtOH–water is a more selective solvent because of its higher ability to selectively solubilize several polar compounds, mainly polyphenols and tri-terpenes [20,21]. Our results are in accordance with these findings and confirm that water extract is more concentrated in carbohydrates than ethanol extract. This is also supported by our previous study, which reported that hot water extract of sugar maple bark had total sugar content higher than those evaluated in red maple bark extract. Additionally, an important complex sugar (oligo- and/or poly-saccharides) was detected in that study [18] and could be consisted of polysaccharides such as glucan and derivatives, oligosaccharides, pectin and/or water-soluble fibers which are ubiquitous in woody plants. Interestingly, the present study demonstrated that acid hydrolysis of the two crude extracts indicated the presence of glucose (around 60%), as major monosaccharide (Table 2). The complex sugars previously detected may therefore consist of a glucan or its derivatives that are more efficiently removed by water than by EtOH–water, as confirmed by higher HMF yield in residual liquor obtained from pulping of sugar maple bark pre-extracted with ethanol–water versus that pre-extracted with water only. Some of the remaining glucan polysaccharide after EtOH–water pre-extraction could thus be contributing to the acid conversion into HMF.

On the other hand, the organosolv pulp obtained from pre-extracted sugar maple bark contained high residual lignin and ash contents. The high residual lignin content in pulp could be attributed to condensed structure of bark lignin with 5-5 and other C-C linked substructures which could have survived pulping reactions [16]. Besides, Klason lignin in cellulosic pulp was higher when EtOH–water pre-extraction (8.09 ± 1.52%) than when water pre-extraction was applied, which also significantly affected the lignin yield from bark. These results could suggest that the catalyst (FeCl₃) is playing a more important role in the water pre-extracted bark delignification than in ethanol–water counterpart. This could be interpreted as the water pre-extraction being quite effective in removing extractives which could affect the action of the catalyst.

The yield of residual liquid fraction was estimated as a difference of the 100% sum of the rest of the constituents (organosolv pulp and lignins). The composition of residual liquor was analyzed by HPLC-RI and HPLC-DAD. The pulping of pre-extracted sugar maple bark has yielded a residual liquor with a higher xylose content than glucose, which could indicate a good preservation of cellulose originally present in bark. We identified in both extracts three major peaks corresponding to: 5-hydroxy-methylfurfural (HMF), furfural (FF) and compound C-3. The latter compound remains unidentifed due to the difficulties encountered during its isolation and its low quantity, which was insufficient for the NMR analysis. In addition, the LC-HRESI–MS/MS spectrum of C-3 compound presents molecular ion ([M+H]+ = 223 m/z) and mass fragments (53, 81, 109, 177 m/z) that could not be associated with any of the compounds described in the literature [22]. This raises the possibility that the C-3 compound may be an artifact formed during the cooking process at elevated temperatures. In fact, it is well established that HMF or FF under certain conditions react to form dimers, such as 5,5′-oxydimethylenebis(2-furfural) or furfural polymerization product formed through Diels—Alder reaction [19,23]. Therefore, considering the spectral characteristics (MS and UV), it is plausible that the C-3 compound may be a dimer formed by coupling of furfural and 5-HMF, a possible reaction under the acidic conditions of organosolv process [19,22]. However, no products of further decomposition of HMF, such as levulinic and formic acid, have been identified in residual liquor and quantified by the HPLC method [7,24].

Finally, it is well known that FF and 5-HMF are produced from hydrolysis of hemicelluloses and cellulose via xylose and glucose or other hexose monosaccharide cyclodehydrations, respectively [1,24,25]. During the organosolv process, lignin is dissolved in the liquor while cellulosic pulp is obtained in solid form, while the hemicelluloses are hydrolyzed to a great extent. This suggests that the amount of FF and HMF may be mainly related to hemicelluloses from the pre-extracted bark [16,25]. However, our studies demonstrated that HMF is identified to be more abundant in residual liquor than FF after EtOH–water pre-extraction. On the other hand, the quantities of HMF
and FF are comparable in the residual liquor after water pre-extraction. These results suggest that
the complex sugar (glucan), which is less efficiently extracted by ethanol–water, could contribute to a
certain extent to HMF production. In addition, several studies reported that organosolv pulping seems
to depend on the applied catalyst. In terms of chemical composition of residual liquor, sulfuric acid is
a better catalyst than ferric chloride for FF production from xylan, while the HMF production from
glucan is further enhanced through glucose isomerization into fructose in presence of ferric chloride as
catalyst, since fructose is a better substrate for HMF conversion. Therefore, the higher yield of HMF
in residual liquor from ethanol–water pre-extracted bark may also be explained by the presence of
remaining hexose sugars resulting from complex sugars, which are favorably transformed into HMF
by ferric chloride as catalyst.

5. Conclusions

In summary, the present study allows for a broader look into polysaccharides present in sugar
maple bark by applying two different pre-extractions.

Water pre-extraction removed more extractives (including sugars) than EtOH–water pre-extraction,
which according to this parallel study is beneficial due to the potential applications of these complex
sugar mixtures.

Water pre-extraction has the benefit, compared to the addition of ethanol, of there being no need
for ethanol evaporation or recycling.

The higher removal of extractives in the water-only pre-extraction has resulted in higher
delignification and recovery of organosolv lignin in this study. On the other hand, the higher
delignification after water-only pre-extraction, the amount of residual lignin in the pulp was much
lower, which increases its potential uses and/or facilitates the downstream delignification of this
cellulosic fraction.

The results obtained on the determination of chemical composition of residual liquor will help
to evaluate the potential of HMF conversion into diformyl furan (DMF) and other products of acid
conversions of sugars as important starting materials for organic synthesis. The results of this study
demonstrate the potential of converting the solid bark waste into valuable products and intermediates
while preserving the water pre-extraction stream for valorizations based on the bioactivity of the
complex polysaccharide.

Supplementary Materials: The following are available online at http://www.mdpi.com/2673-4079/1/1/2/s1.
Figures S1 and S2: 31P NMR spectra of organosolv lignins.

Author Contributions: P.B.K. performed all assays, analyzed the results, interpreted them, wrote the first draft of
the manuscript and improved its final version. S.B. helped guide the analysis and critically revised the manuscript.
T.S. was responsible for the conception of the studies, guided the analysis and carried out major revisions of
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