Cellulose-Lignin interactions during slow and fast pyrolysis

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A B S T R A C T
The interactions between lignin and cellulose during the slow pyrolysis of their blends were studied by means of Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). Fast pyrolysis was studied using Pyrolysis–Gas Chromatography/Mass Spectroscopy (Py–GC/MS). Crystalline cellulose (Avicel), amorphous cellulose, organosolv lignin, and their blends containing 20, 50, and 80 wt.% of lignin were used for the experiments. Differential thermogravimetry (DTG) revealed that the interaction between crystalline cellulose and lignin resulted in a shift toward higher decomposition temperatures, but for lignin/amorphous cellulose mixtures this effect was small. No effect of adding lignin to cellulose was observed on the yields of bio-char. Cellulose-lignin interactions during fast pyrolysis in Py–GC/MS did occur. Products from cellulose fragmentation reactions (hydroxyl-acetaldehyde and acetol) were not influenced by the presence of lignin. In general, production of lignin derived phenolics remains quite similar at 500 °C, but the yield of many methoxylated monophenols increases at 350 °C in the presence of both types of cellulose. Importantly, it was found that the presence of lignin enhanced the yield of levoglucosan, but decreased the yield of some of their dehydration products (e.g., levoglucosenone, 5-Hydroxymethylfurural, Furfural). This result could be explained by the reduction of residence time of cellulose products in liquid intermediates, a phase where most of the dehydration reactions occur. Lignin seems to enhance micro-explosions, decreasing in this way the residence time of cellulose derived products in the liquid intermediates.

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1. Introduction

Fast pyrolysis of lignocellulosic biomass is a process in which biomass is converted, in the absence of oxygen, to bio-oil, char and gas [1–3]. The main bio-polymers constituting lignocellulosic biomass are cellulose, hemicelluloses and lignin. The bio-oil obtained from these building blocks contains many different compounds like anhydrosugars (e.g., levoglucosan), mono-phenolics (e.g., guaiacols, catechols and phenols), furans (e.g., furfural, hydroxymethylfurfural) and lights (e.g., hydroxyl-acetaldehyde, acetic acid and acetol) [4–5]. The yields of these products depend on the content of cellulose, hemicellulose and lignin in the biomass. In addition, ash in biomass is known for influencing the product yields [6–8]. For example, a small amount of ash significantly reduces the yield of levoglucosan, an important platform chemical [9].

Far less information is available on possible interactions between the different biomass building blocks; cellulose, hemicellulose and lignin. This information might be important in order to optimize the pyrolysis process toward interesting chemicals such as levoglucosan. Another important factor determining the pyrolysis product distribution are the process conditions like the final pyrolysis temperature and heating rate [10]. In general, studies on interactions of the biomass building blocks might be divided into two regimes depending on their heating rate, namely slow pyrolysis and fast pyrolysis.

In many publications thermogravimetric analysis (TGA) is typically used to study reaction mechanisms with heating rates <100 °C/min (slow pyrolysis). Thermal analysis of wood shows three different degradation peaks for the three building blocks of biomass which might lead to the thought that they will react independently. Indeed, most of the literature demonstrated no or negligible interactions among the components [11–13]. Moreover, the wood behaved as a sum of its components when weight loss curves and char yields are considered. Differences in formation of single compounds due to interaction during pyrolysis were, how...
ever, observed when a FTIR analyzer was coupled with the TGA [14]. Fast pyrolysis of biomass and its major components is often studied using Py–GC/MS and entrained flow/fluidized bed reactors. Typical heating rates used in these studies are >100 °C/sec. Alén et al. reported minor interactions amongst the three components in comparison with the whole biomass. Their finding was only based on the observation that the same type of compound classes, produced by individual building blocks, were also present in the products of whole biomass [15]. More in-depth analysis of the interactions among components was recently performed by Wang et al. [16] Considerable interaction was observed among the components during fast pyrolysis. For example, the oil yields were considerable lower for pyrolysis of four different mixed components (hemicellulose, cellulose and lignin in certain weight ratios) compared to the calculated sum of oil of the individual components while taking into account their weight ratios in the samples.
The observed interactions may be associated with the exchange of hydrogen or free radicals from cellulose and lignin. Previous research [13,14] found that holocellulose acted as an H donor during lignin pyrolysis [17]. Hosoya et al. [18,19] found that the presence of lignin enhances levoglucosan production at gasification temperatures (800°C), which could be explained by the protection of levoglucosan in the presence of aromatic compounds.

The purpose of this paper was to increase our understanding on the cellulose-lignin interactions during slow and fast pyrolysis and elucidate the potential effect of the degree of cellulose crystallinity on these interactions. Blends of cellulose with lignin (0, 20, 50, 80 and 100%) were prepared. At low heating rates the research is focused on the important physical processes in the solid phase (melting, bubbling, swelling, etc.), and their relation to thermal decomposition rates and char yields were explored. Fast pyrolysis
was performed in PY–GC/MS at 350 and 500 °C. Interactions were observed between lignin and crystalline/amorphous cellulose.

2. Materials and methods

2.1. Materials

Cellulose and organosolv lignin samples were used for this study. Cellulose samples have previously been described elsewhere [20–22]. Crystalline cellulose powder was obtained from Sigma–Aldrich (11365 Fluka, Avicel® PH-101, ~50 μm particle size [CAS 9004-34-6]), with a degree of crystallinity of approximately 60%. Ball-milled cellulose (henceforth referred to as amorphous cellulose) was prepared by ball-milling the Avicel sample for 24 h (using a PQ-N2 Across International planetary ball mill). This process reduced the degree of crystallinity to approximately 6%, as describe elsewhere [20]. The organosolv lignin was obtained from Sigma–Aldrich (371.017 Aldrich, [CAS 8068-03-9]). The content of alkalines in the samples studied (crystalline cellulose CC, amorphous cellulose AC, and organosolv lignin OL) was not measured but it is known [8,21,23,24] that the small quantities of alkalines present in these samples can modify the yield and composition of the products.

2.2. Sample preparation

Cellulose-lignin samples were prepared by blending crystalline cellulose or amorphous cellulose with organosolv lignin. Cellulose (either crystalline or ball milled cellulose) was blended with 20, 50, and 80% of lignin using 15 mL centrifuge tubes (Fisher Scientific) and shaking for four hours with a mechanical shaker. The blends were then stored overnight in a freezer intending to make physical blending easier.
Table 1
Compounds identified in Py–GC/MS with their major ion and retention time (RT).

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Formula</th>
<th>Compound</th>
<th>RT (min.)</th>
<th>Ion (m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C\textsubscript{4}H\textsubscript{10}O</td>
<td>Carbon dioxide</td>
<td>1.551</td>
<td>44</td>
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<tr>
<td>2</td>
<td>C\textsubscript{6}H\textsubscript{12}O</td>
<td>2-methyl-Furan</td>
<td>2.197</td>
<td>82</td>
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<tr>
<td>3</td>
<td>C\textsubscript{6}H\textsubscript{12}O</td>
<td>2,5-dimethylfuran</td>
<td>3.086</td>
<td>96</td>
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<td>4</td>
<td>C\textsubscript{6}H\textsubscript{12}O</td>
<td>Vinylfuran</td>
<td>3.308</td>
<td>94</td>
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<td>C\textsubscript{6}H\textsubscript{10}O</td>
<td>Phenol</td>
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<tr>
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<td>Furanone</td>
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<td>55</td>
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<tr>
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<td>Furfural</td>
<td>5.235</td>
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<tr>
<td>25</td>
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<td>2-propyl furan</td>
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<tr>
<td>26</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>dihydro-4-hydroxy-furanone</td>
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<td>44</td>
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<tr>
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<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>2-hydroxy-2-Cyclopenten-1-one</td>
<td>7.381</td>
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<td>114</td>
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<td>30</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>2-hydroxy-3-methyl-2-cyclopenten-1-one</td>
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<td>112</td>
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<td>31</td>
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<td>1,4:3,6-Dianhydro-α-D-glucopyranose</td>
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<td>97</td>
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<tr>
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<td>Levoglucosone</td>
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<td>Unknown compound 2 (sugar-like)</td>
<td>13.927</td>
<td>41</td>
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<td>36</td>
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<td>Acetone</td>
<td>14.573</td>
<td>69</td>
</tr>
<tr>
<td>37</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>1,6-Anhydro-β-D-glucopyranose (levoglucosan)</td>
<td>21.23</td>
<td>57</td>
</tr>
<tr>
<td>38</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>1,6-Anhydro-α-D-glucuronic acid</td>
<td>24.439</td>
<td>73</td>
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<tr>
<td>39</td>
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<td>58</td>
</tr>
<tr>
<td>40</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>2-oxo-propanoic acid</td>
<td>2.072</td>
<td>68</td>
</tr>
<tr>
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<td>hydroxy-acetaldehyde</td>
<td>2.691</td>
<td>32</td>
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<td>42</td>
<td>C\textsubscript{7}H\textsubscript{10}O</td>
<td>Acetol</td>
<td>3.096</td>
<td>96</td>
</tr>
</tbody>
</table>

3. Methods

3.1. Thermogravimetric analysis (TGA)

The thermal degradation behavior of crystalline cellulose, ball-milled cellulose, organosolv lignin, and their blends was studied using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA851\textsuperscript{e}, In/Al calibrated, ceramic crucibles without lid, nitrogen purge gas). The samples were heated from 25 to 600 \degree C at two different heating rates: 10 \degree C/min and 50 \degree C/min. Approximately 9 mg of each sample was used for each test. For analysis of results, the mass percentage was set to 100\% at 150 \degree C to disregard the presence of moisture in the samples. The derivative was determined as the ratio of the difference between two weight loss data points to their corresponding difference in time. The temperature of a derivative data point was set to the average temperature of the two points. The predictions of the thermal degradation behavior of the blends were calculated on mass basis by averaging the values of pure compound analysis.

3.2. Scanning electron microscopy (SEM)

Solid residues obtained from the thermo-gravimetric analyses were used for SEM analysis. Prior to SEM analysis, the samples were gold sputtered. SEM images of the char were prepared using an FEI 200F SEM system with large field detector and vacuum conditions (130 Pa). High voltage was set at 30 kV and different magnifications (50–500) were used.

3.3. Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS)

Py–GC/MS was used to determine the products of the fast pyrolysis of cellulose/lignin blends. The volatile pyrolysis products were analyzed using an Agilent technologies 6890 N Network GC system and an Inert XL MSD 5975B with EI ionization, following a process described elsewhere \cite{21}, with some modifications. The system was equipped with a pyroprobe (CDS 5000 series with a platinum coil probe and a valve interface) for manual sample injection. The GC/MS consisted of an HP-5MS capillary column (30 m × 0.25 mm, 0.25 \mu m). Approximately 0.6 mg of sample was loaded in a cleaned quartz tube (2 mm × 25 mm) for the tests. The amount was weighed with the thermogravimetric analyzer (Mettler Toledo). The pyroprobe interface and GC liner were kept at 270 \degree C. After placing the pyroprobe with the quartz tube in the valved interface, the tube was held at 270 \degree C for 1 min and then at 350 or 500 \degree C for 1 min. This temperature was reached with a heating rate of 100 \degree C/s. Prior to pyrolysis, the temperature in the probe was calibrated using an
Fig. 9. Effect of lignin blends on yield of levoglucosan and 1,6-anhydro-D-glucopyranose from crystalline cellulose and amorphous cellulose and dehydration products of levoglucosan and 1,6-anhydro-D-glucopyranose during pyrolysis at 350 and 500 °C.
Fig. 10. Effect of cellulose/lignin blends on the yield of 5-HMF, furfural, MEF, 2-furanone, and 2-propylfuran at 350 and 500 °C.
Omega type K thermocouple. The pyrolysis products were transferred to the GC/MS for separation at 40 °C with 6 °C/min to 280 °C and kept at that temperature for 5 min. Each test was conducted in triplicate. Peaks in the resulting pyrolysis chromatogram were analyzed based on the most abundant ion at a specific retention time. The peak area (abundance) was divided by the sample loading mass and the results of the three samples were used to calculate an average value with an error based on the 95% confidence interval. Finally, the specific peak area (i.e., abundance/sample loading) was plotted against the organosolv lignin percentage for every pyrolysis compound. Yields of the pyrolysis products of crystalline and amorphous cellulose were plotted in the same graph for comparison of the results. However, separated graphs were prepared for the two different temperatures. In the graphs, a dashed line joining the yields of cellulose with the yields of lignin pyrolysis products, was plotted to represent the predicted values of abundance of the corresponding pyrolysis product.

4. Result and discussion

4.1. Slow pyrolysis of cellulose–lignin mixtures

Fig. 1 shows the TG and DTG results of crystalline and amorphous cellulose and cellulose/lignin blends at a heating rate of 10 °C/min. The DTG curves of crystalline cellulose/lignin blends shifted to higher temperatures compared to the predicted curves (dotted lines). The shift in DTG curves for amorphous cellulose/lignin blends was less pronounced. Similar behavior was found with the heating rate of 50 °C/min (results not shown). As shown previously [20], the difference in thermal behavior might be explained by differences in physical and chemical processes due to the solid phase of crystalline cellulose and liquid phase of amorphous cellulose under heating rates typically used in TGA tests (2–50 °C/min).

The difference between the predictions and the observations on the thermal behavior of CC/lignin blends can be explained by the enhancement of micro-explosions when lignin is present as well as by the potential exchange of hydrogen and free radicals [17] between the cellulose and lignin.

4.2. Liquid–liquid and solid–liquid phases

SEM images of TGA residues from crystalline cellulose, amorphous cellulose, and organosolv lignin are provided in Fig. 2. It is shown that the residue from crystalline cellulose consists of small fibrous char, whereas the amorphous cellulose and organosolv lignin show some spaces that are apparently occupied by bubbles. This observation and the smooth surface areas of these char samples suggests the formation of a liquid intermediate during the experiment, whereas the fibrous char structures of crystalline cellulose did not form a liquid intermediate. More intensive bubbling can be observed for amorphous cellulose char samples compared to lignin, which has a more layered structure. It also appears that small solids are present in residues of amorphous cellulose probably because of the presence of a small amount of crystalline cellulose (approx. 6%) in the sample.

Fig. 3 presents pictures of TGA crucibles with the solid residues. The solid residue from lignin pyrolysis resembles a foam structure, again suggesting that bubbles were formed during heating of lignin. Images of crystalline cellulose show a different behavior since no bubbles can be observed. The pictures suggest that crystalline cellulose degrades via a solid phase, while amorphous cellulose and organosolv lignin via a liquid intermediate. The intensity of bubbling seems to be controlled by the heating rate.

Fig. 4 shows SEM pictures of the TGA residues of the two different cellulose samples blended with ~20 wt.% of organosolv lignin. Although the weight loss pattern during the TGA process was visibly influenced by lignin (Fig. 1), the crystalline cellulose blend still had a residue structure similar to that of crystalline cellulose, because crystallites can be observed. The fibril structure of cellulose likely provided a larger surface area for the lignin liquid intermediate to evaporate or to escape in the form of aerosols, while the lignin liquid intermediate could have acted as glue that bonds fibers. The structure of the residue shows less small bubbles, with a much thicker residue layer. The amorphous cellulose and lignin, apparently, tend to form a uniform liquid substance and “boil” together. Comparing to the pure amorphous cellulose, much less debris particles can be seen in this residue.

The cellulose samples blended with ~50 wt.% of organosolv lignin are presented in Fig. 5. The residue from the crystalline cellulose keeps a fibrous structure with evidences of a liquid on its surface acting as binder between the fibers. The amorphous cellulose blend exhibited a residue structure which is comparable to an organosolv lignin residue (see Fig. 2). On the pores of the bubbles thin films appeared, suggesting that higher surface tension strength was achieved from this blend.

Fig. 6 shows the cellulose samples blended with ~80 wt.% of organosolv lignin. Both crystalline and amorphous cellulose had similar residue structures and the strong bubble film found in amorphous cellulose 50 wt.% blends could again be observed in this TGA residue. Crystallites could hardly be observed in both samples. These observations support our hypothesis that cellulose could actually “dissolve” in the lignin liquid intermediate and form a viscous liquid mixture. Hosoya et al. found that levoglucosan could easily dissolve in an environment with (poly-) benzene and phenolic compounds, which are normally found in lignin pyrolysis, and prevented the thermal diffusion of levoglucosan [25]. A similar situation could be extended to cellulose [26].

It is very difficult to correlate the thermal behavior observed by TGA shown in Fig. 1 with the SEM pictures shown in Figs. 2, 4, 5 and 6 but in general we can state that the crystalline cellulose maintains
Fig. 12. Effect of cellulose/lignin blends on yield of 2-methoxyphenol, 2-methoxy-4-phenol, and 3-methoxy-1,2-dibenzodiol, 3,5-demethoxyacetone, 2-methoxy-4-vinylphenol, 2,6-dimethoxyphenol, disaspidinol, 1,2,4-trimethoxybenzene, 2,6-dimethoxy-4-(2-propenyl)-phenol, 1-(4-hydroxy)-3,5-dimethoxyphenyl-ethanone at 350°C.
its solid shape and that the amorphous cellulose and the lignin are the two fractions contributing most to the formation of the liquid intermediate.

The yield of char as a function of lignin content in the blend (Fig. 7) shows that, under slow heating rate (10 and 50 °C/min), the char yield followed a linear trend and had no significant effect with the amount of lignin blended. This finding is quite remarkable because of the very different physical processes involved. Moreover, the effect of liquid/liquid and solid/liquid phase processes did not influence the outcome of the char yield, nor the amount of vapors and gas produced during slow pyrolysis. It should be noticed that the composition of the gasses and vapors can be different, but is not measured in this TGA study.

4.3. Analytical fast pyrolysis of cellulose/lignin blends using Py–GC/MS

Typical Py–GC/MS chromatograms and their identified compounds of crystalline cellulose blended with organosolv lignin in a ratio of 50/50 (wt.) are shown in Fig. 8. Typical lignin pyrolysis derived compounds are marked by a number in red and compounds derived from cellulose pyrolysis are identified by blue numbers. The identification of all compounds is presented in Table 1. The origin and composition of products from pyrolysis of cellulose/lignin blends are discussed in the following sections.

Most hardwoods and softwoods have cellulose/lignin ratio close to 2. This corresponds to blends with approximately 67 wt.% of cellulose and 33 wt.% of lignin. Under these conditions the lignin could contribute to the micro-explosion and thermal ejection of cellulose pyrolysis products. Based on the results herein presented, it is very difficult to predict the behavior of lignocellulosic materials because the potential effect of the presence of hemicellulose, extractives and ash is difficult to predict.

4.3.1. Anhydrosugars and their dehydration products

Fig. 9 shows the effect of organosolv lignin on the yield of levoglucosan and 1,6-anhydro-α-D-glucopyranose obtained from pyrolysis of crystalline cellulose and amorphous cellulose. Both anhydrosugars yields show an overall increase compared to the predicted values (dotted lines). The increase of these sugars may result from the protection from lignin to further degradation of cellulose [18,19,25]. The yield of these compounds is lower at 350 °C compared with pyrolysis at 500 °C. The yields of the dehydration products from levoglucosan and 1,6-anhydro-α-D-glucopyranose (i.e., levoglucosenone and 1,4:3,6-dianhydro-β-D-glucopyranose) is significantly reduced (Fig. 9) in the presence of lignin. Since these are products from dehydration reactions, one of the many reasons for these lower yields might be a faster release of cellulose primary products (cellulose, cellobiosan) from the hot zone due to thermal ejection caused by the lignin liquid intermediate.

4.3.2. Furanic compounds and cyclopentenes

The pyrolysis yields of 5-hydroxymethyl-2-furfuraldehyde (5-HMF), furfural, 5-methyl-2-furfuraldehyde (also known as 5-methylfurfural MEF), 2-furanone, and 2-propylfuran as function of the lignin content in the feedstock and cellulose crystallinity at 500 °C and 350 °C are presented in Fig. 10. The results suggest that all three factors – lignin content of the feedstock temperature, and cellulose crystallinity – impacted the yield of these pyrolysis products. Lignin enhanced the yield of 5-HMF at the two pyrolysis temperatures and in both cellulose samples compared with the expected results, represented by the dotted line. The yield of furfural has been inhibited by the presence of lignin for both types of cellulose, except when the mixture was 50/50 (wt) for crystalline cellulose. It is known that the formation of furfural from cellulose follows two pathways during pyrolysis: (a) Pyranose ring rearrangement of the chain and then through 5-HMF intermediate [27,28], and (b) levoglucosan pyranose ring opening [29]. The lignin liquid environment apparently did not prohibit the rearrangement of pyranose ring to form a furanose ring and its dehydration to the yield of 5-HMF.

The effect of adding lignin to cellulose on the yields of 5-methyl-2-furancarboxaldehyde (MEF), 2-furanone and 2-propylfuran at both 350 and 500 °C is also shown in Fig. 10. The yields of these compounds have been reduced by the presence of lignin, independent of the pyrolysis temperature or the cellulose type tested. This result suggests that the dehydration reactions responsible for the formation of these compounds (which typically happen in the ionic environment of liquid intermediates) have been mitigated.

4.3.3. Phenolic compounds derived from organosolv lignin pyrolysis

The changes in the yield of products from the pyrolysis of organosolv lignin as a function of lignin content in the blend with amorphous and crystalline cellulose at pyrolysis temperatures of 350 and 500 °C are shown in Figs 11 and 12. There were no significant changes in yield of phenolic compounds observed at 500 °C (not shown) except for the two phenolic compounds shown in Fig. 11, when the lignin content was 20 or 50 wt%. For these two compounds we observe a decrease in the yield of the blend compared with the values expected for the cellulose and organosolv lignin separately.

However, at 350 °C we observed an increase in the yield of most of the methoxylated compounds analyzed (2-methoxyphenol, 2-methoxy-4-methylphenol, and 3-methoxy-1,2-dibenzediol, 3,5-dimethoxyacetophenone, 2-methoxy-4-vinylphenol, 2,6-dimethoxyphenol, disaspidinol, 1,2,4-trimethoxybenzene, 2,6-dimethoxy-4-(2-propenyl)-phenol, 1-(4-hydroxy)-3,5-dimethoxyphenyl-ethanone) (see Fig. 12).

4.3.4. Light compounds

Light compounds (1–3 carbons) identified in the pyrolysis (at 350 °C) products of blends of cellulose/lignin showed no effect of the addition of lignin (Results not shown). In fact, the yield of carbon dioxide, hydroxyacetalddehyde, acetal, and 2-oxo-propanoic acid remained approximately similar, independently of the amount of lignin added, that is the small differences observed were within the experimental error.

5. Conclusion

Crystalline cellulose, amorphous cellulose, and organosolv lignin, as well as blends of these materials were subjected to slow and fast pyrolysis to study its interactions. Slow pyrolysis studied in the thermogravimetric analyzer showed that lignin/crystalline cellulose interaction did occur, because the weight loss temperature shifted to a higher temperature region. The observed shift in temperature was less pronounced for lignin/amorphous cellulose blends. Remarkably, the char yield was not affected by cellulose-lignin interactions despite of differences in physical processes (e.g., boiling, swelling) of the various samples. Py–GC/MS was used to study fast pyrolysis of the blends. Lignin derived compounds (e.g., phenolics) were in general enhanced at 350 °C by cellulose and constant or only slightly decreased at 500 °C. The cellulose lignin interactions did not influence the cracking reactions toward light compounds (e.g., CO₂, acetal, acetic acid, etc.). The presence of lignin enhanced the production of anhydrosugars (levoglucosan) and suppresses the production of most of its dehydration products (e.g., levoglucosenone, 5-HMF, Furfural, MEF) likely due to the enhancement of thermal ejection when lignin was present.
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