Identification of the Fractions Responsible for Morphology Conservation in Lignocellulosic Pyrolysis: Visualization Studies of Sugarcane Bagasse and its Pseudo-Components

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Abstract: Pyrolysis of lignocellulosic materials typically form carbonaceous residues (chars) with structures similar to the starting material. However, previous studies reported in the literature have shown that fast pyrolysis of cellulose and lignin form a molten intermediate liquid resulting in chars with smooth surfaces and evidences of intense bubbling. The fraction responsible for morphology conservation during pyrolysis is not known. In this article, pyrolysis visualization studies were carried out with a fast camera on cellulose, xylan, Organosolv lignin (OL), milled wood lignin (MWL), and lignocellulosic sugarcane bagasse to identify the component responsible for morphological conservation. The materials were heated using a modified Pyroprobe with measured sample heating rates close to 100 °C/s. Our studies confirm that cellulose, lignin, and deashed xylan are completely transformed into an intermediate liquid; the intensity of bubbling for lignin was far superior that of cellulose. Xylan as received, however, only forms a small amount of intermediate liquid; it does not fully melt and maintains its general shape during pyrolysis. These results suggest that the presence of mineral matter is critical for lignocellulosic materials to retain their original morphology. We repeated the studies on raw bagasse and acid washed bagasse. The raw bagasse retains its morphology; the acid washed bagasse shrank dramatically, but was not completely converted into a liquid. Our results suggest

that in addition to hemicellulose with the presence of ash, other biomass fractions or the different temperatures at which the different fractions melt and solidify could also be contributing to maintain the structure of the lignocellulosic material during pyrolysis.

Keywords: Fast pyrolysis, intermediate liquid phase, hemicellulose, Pyroprobe, visualization

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1. Introduction

Many physical and chemical phenomena occur simultaneously during thermochemical processes like pyrolysis, gasification, and combustion, making it difficult to accurately predict the product distribution [1]. It has been recently shown that during the pyrolysis of lignocellulosic components, a liquid intermediate phase is formed as cellulose and lignin depolymerize. As such, this liquid phase is mostly composed of heavy oligomeric compounds with boiling points higher than the temperatures of the depolymerization reactions [2–6]. The formation of excessive liquid intermediate is problematic for the operation of fluidized bed reactors as it can lead to bed defluidization due to agglomeration of particles [7]. In pyrolysis, the heavy components in the liquid intermediate can be thermally ejected in the form of aerosols through micro-explosions [5,8,9]. This phenomenon explains the presence of oligomeric products in bio-oil, which are typically not well-characterized. Within the liquid phase many physiochemical phenomena occur simultaneously: solid / liquid reactions, mass and heat transfer in the liquid-solid-gas, bubbling (nucleation, coalescence, death, and growth), and others which have not yet been identified. These reactions and phenomena are controlled by the type of material studied, the final temperature to which the particle is heated, the particle size, and pressure [10]. Although there are many parametric studies on the effects of these variables on the distribution of products [11–15], very little literature exists regarding the effect of biomass composition on the formation and behavior of resulting liquid intermediate.

It is difficult to understand these phenomena mainly due to short reaction times in fast pyrolysis (<1 s) and limitations with real-time sampling systems [16]. Some authors have used SEM, TEM [17–20] and other optical techniques [18,21] to visualize the changes in the internal structure of particles undergoing pyrolysis. This information has been correlated with surface area analysis [22,23] to provide quantitative information on changes of the porous structure before and after pyrolysis.

Two interesting studies on the morphological changes of biomass (*Miscanthus*) and its pseudo-components during pyrolysis have been published by Dufour, et al. [24,25]. In the first, the authors used ^1H -MNR, to monitor changes to each pseudo component during devolatilization

with slow heating rates. The authors concluded that the lignin is completely fluid between 200 and 225 °C, before the start of the mass loss. Hemicellulose has medium fluidity of 61% between 200 and 275 °C, and cellulose only achieved 40% fluidity between 300-350 °C. In the second study, the research extended to visco-elastic behavior pseudo components in a parallel plate reactor (viscometer). The authors show that lignin has an elastic behavior between 150-350 °C; after this, re-solidification of the material (char production) begins. Likewise for cellulose between 250-340 °C a high viscosity liquid forms with the most fluidity at 340 °C. For xylan, the fluid phase forms between 200-250 °C, then re-solidifies at 270 °C. These studies were conducted at low heating rates. Wang et al. [26,27] tested SEM images at low heating rates on cellulose. Under low heating rate amorphous cellulose forms a liquid intermediate while crystalline cellulose forms a solid. Under high heating rates both amorphous and crystalline cellulose forms a liquid intermediate [28–30].

The final morphology of the biomasses during fast pyrolysis can be affected by the intensity of two competitive processes after the depolymerization reaction: *oligomer evaporation* and *crosslinking reactions* in the liquid phase. Typically, it has been reported that at high heating rates ($>10^3$ °C/s), a small biomass particle rapidly reaches high temperatures where the evaporation of oligomers (sugars, anhydrosugars with $DP < 7$, and pyrolytic lignin) are promoted, leaving the solid matrix and avoiding carbonization reactions. However at low heating rates, the intermediate liquid compounds, have more time inside the particle to react by crosslinking reaction in liquid phase. This liquid could act as an electrolyte, catalyzing solid-liquid reactions that produce char [31,32]. This kind of behavior has been specially proposed for pure cellulose [8,33–35], however it could be extrapolated to other biomass constituents. Dufour et al. [24,25] have shown that during thermal degradation each biomass component passes through a thermoplastic state, where visco-elastic properties depend strongly on the structure. The thermoplastic behavior of biomasses cannot be correlated like a linear combination of the behaviors of its components. Under slow heating rates, melting on the char surface loses the competition to secondary cross-linking. At high heating rates, biomass behaves similarly to intumescent (heat swelling) coals with significant chemical bond breaking before the cross-linking starts to be important; it's behavior is more like a fluid phase [32,36].

The interactions of different components with each other and with mineral matter, specially alkali and alkali earth metals, produce rigid structures due to cross-linking and dehydration reactions [37,38]. Shafizadeh, et al. [39], suggest that hemicellulose has a strong effect on maintaining of solid morphology, specially by association of minerals through ion exchanges with acid functional groups belongs to pyran rings. In general the morphological changes in biomass during fast pyrolysis are due to multiple effects such as heating rate, mineral matter composition, particle size, and lignocellulosic composition.

Real-time visualization studies [5,21,25,40,41], show tissue level changes including the expansion of cell walls and the appearance of a yellow resinous substance that fills the porous cavities as the reaction proceeds. It has been shown [9,42–44] that this substance is mainly constituted by oligomers. Dauenhauer, et al, [5,41,45,46] using a torch reactor reported the appearance of an ephemeral liquid intermediate (order of ms) during pyrolysis of cellulose, where the appearance of microbubbles is evident. Bubbles are formed as products of decomposition reactions in the liquid. These bubbles burst at the gas-liquid interface, promoting the ejection of aerosols (reactive boiling ejection). Their visualization studies confirm that under high heating rates cellulose is fully converted into an intermediate fluid between 300-350 °C [5]. Studies with lignin are scarce, but literature confirms that this pseudo-component also forms a intermediate liquid and the micro explosion intensity is much more violent than for cellulose [47].

Nevertheless, studies of ^1H -NMR, rheological, and visualization have not fully explained why lignocellulosic materials result in the formation of chars with a similar structure to the starting material [21,24,25]. For cellulose, ^{13}C NMR experiments coupled with computational chemistry tell us that until 300 °C, dehydration reactions create ether bonds between cellulose chains. Between 300 and 400 °C, rings start to form, and above 400 °C aromatic ring formation dominates

[48]. It is critical to note that the depolymerization reactions occur in the same temperature range (400-500 °C), so there is a definitive competition between depolymerization and cross-linking reactions in cellulose pyrolysis; future work may prove the same competition in hemicellulose and lignin as well.

In this article, we examine through high speed visualization techniques the formation of the intermediate liquid phase in cane bagasse and model pseudo-components during fast pyrolysis (heating rates > 100 ° C/s). Our goal is to identify the fraction responsible for the conservation of the morphology when biomass is pyrolyzed. Our results also provide insight into the bubbling phenomena and structural morphology of lignocellulose undergoing fast pyrolysis.

2. Materials and Methods

2.1. Materials and preparation

Sugarcane bagasse was obtained from the sugarcane mill Risaralda (Km 2 via La Virginia-Balboa, Risaralda-Colombia, 4°54'22.42"N, 75°53'45.46"O). The material was analyzed as received (proximate and elemental analysis, ash composition and content of pseudo-components) and was then acid washed to reduce the content of alkalines and a fraction of hemicellulose. For acid washing, sugarcane bagasse was soaked in 1.76 wt.% sulfuric acid solution (15 mL solution/g solid) at 152.6 °C for 21 minutes [49]. After acid wash, the solids were rinsed and centrifuged with nano-pure water four times to remove residual H₂SO₄.

The model components used were Avicel cellulose (Fluka 11365, Avicel PH-101, 50 µm, CAS 9004-34-6, with a degree of crystallinity of 60%), Organosolv lignin (371,017 Aldrich, CAS 8068-03-9) and beech wood xylan (Sigma Aldrich CAS 9014-63-5)). All samples were reduced to particle sizes less than 100 µm. The physicochemical characterization of these materials is presented in Table 1. Xylan was subjected to acid washing using 1 M HCl, sonicated for 1 hr at 25 °C, then washed and centrifuged with water four times until the acid was removed, as verified using a silver nitrate indicator.

The milled wood lignin herein studied was obtained from hybrid poplar heart wood using a method described elsewhere [50–52]. Briefly, the wood was extracted with 9:1 acetone: water followed by 2:1 ethanol/benzene for 8 h each in a Soxhlet extractor. The solids were oven dried at 45 °C, then ball milled (Planetary ball mill, Across International) for 50 h, 15 min on 15 min

rest, at 600 rpm with ceramic balls and cup. Lignin dissolution was performed in dioxane: water (DW) (96:4, 10 mL DW/g wood) for 24 h AT 50 °C. This was allowed to settle, then centrifuged and liquid was transferred to a round bottom flask to evaporate dioxane. The residue in the evaporation flask was dissolved in acetic acid/water (9:1) (20 mL/g) and added gradually into a 10 times larger volume of 4 °C distilled water directly into 6 250 mL centrifuge tubes. Let sit in refrigerator. The acetic acid/water is removed by centrifugation (10 min 10,000 rpm, 4 °C). Decant and discard liquids. Remaining acetic acid was removed by adding ethanol and rotovaping 3 times. This is crude MWL (~10% carbohydrates). Dissolve crude lignin in dichloroethane: ethanol (2:1, v/v, minimal amount required for dissolution ~20mL/g lignin). Drop into anhydrous diethyl ether (10 times volume of dichloroethane/ethanol) to precipitate lignin. Centrifuge (10 min 10,000 rpm, 4 °C), decant ether. Wash 3 times with ether. Remove residual ether under vacuum. This is MWL typically contain ~4% carbohydrate. The elemental and proximate analysis of all the materials studied in this paper are shown in Table 2.

2.2. Characterization of materials

The lignocellulosic composition for bagasse was determined following the protocol NREL TP-510-42618, with results shown in Table 1. The elemental analysis was done following the procedure described elsewhere [53]. Proximate analysis followed ASTM D7582 – 15 [54], coupled with modifications for smaller sample size in our Mettler Toledo TGA/SDTA851^e. [55]. The results obtained are shown in Tables 2 and 3.

Metal analysis was conducted for the Douglas fir in an ICP-MS (Agilent 7500cx) following the same procedure described by Pecha et al [56]. As we see in this table the content of catalytic metals is quite low; potassium, for example, only has reported significant catalytic activity above 1% w / w [57,58]. An important fraction of the ash is silica.

Table 1

Table 2.

Table 3.

2.2 Modified Pyroprobe pyrolysis visualization reactor

The formation of the intermediate liquid phase for both bagasse and the pseudo components studied, was visualized with fast speed photography. The materials were placed on sapphire discs which rested on the platinum wire resistor in a modified *Pyroprobe 5000 (CDS Analytical)* described [59]. Briefly, the reactor chamber is a glass tube (Pyrex 9825) open at both ends, screwed into a solid block of aluminum with a valve to regulate the continuous flow of nitrogen. The display of the samples was performed by a fast speed camera (*Troubleshooter LE Imaging Fastec*) at 125 fps, using two 25 mm extension tubes each connected in series with a macro lens (Tokina, 100 mm f 2.8). The camera was positioned maintaining an approximate 45 ° angle to the main axis of the reactor and perpendicular thereto (see Figure 1).

Figure 1.

For visualization, a Fastec-Sportscam 1000 ME (Fastec Imaging Corporation, San Diego, CA) was used. An external source of white light (Solarc LB50, Ushio) was used for supplemental lighting. ImajeJ and the video editing toolbox in MatLab R2014 were used to process the videos. The amount of sample used in each experiment is approximately 0.5 mg with particle sizes <100 µm, positioned in the center of the quartz disc. Nitrogen continuously flows at 5 ml / min to prevent fumes from blocking the field of view. In all experiments pixel size calibration was made considering the platinum filament diameter was 0.3556 mm.

2.3. Temperature Calibration

The temperature was measured for both touching the sample-free sapphire disc surface as well as inside the 0.5 mg sample piles, but not actually touching the disc surface. Each measurement was performed in triplicate. The Pyroprobe nominal heating rate set point was 800 °C / s with final temperature set point of 337 °C to reach a measured disc temperature of 500 °C. The calibration

was done with an Omega thermocouple (40 AWG), which has a response time of 2.36 ms. A National Instruments USB-TC01 data acquisition device sends a record of the temperature every 0.25 s in the MatLab for processing.

Figure 2 shows the measurements of the temperatures of the blank disc and the samples. The maximum heating rate for the blank disc was 181 °C / s, and average biomass and pseudo components were the order of 120 °C / s. In Figure 8, it can be seen that the final temperatures of most materials are similar (~ 380 ° C for lignin and cellulose, ~ 340 ° C for biomass and Xylan). For other materials, differences in the final temperature correspond different physicochemical properties of carbonaceous residues generated. At the end of each test the correlation between the temperature of the sample and the image corresponding to each time point is to make the phenomenological description of each event pyrolysis.

Figure 2.

The behavior of milled wood lignin is notably different from the others. Unlike the Organosolv lignin, the primary structure of the MWL is not degraded and is quite similar to how it is in the native biomass [60,61]. MWL has been shown to have more β -O-4 linkages than Organosolv lignin [60]. These bonds are weak and are more likely to be broken at lower temperatures. Alternatively, the Organosolv lignin possibly formed a char with a lower thermal conductivity, which results in lower temperatures at the top surface of the char. Both explanations are simply hypotheses, but neither discredit the experimental results that show that the MWL had a lower temperature.

The differences in final temperatures between Organosolv lignin and MWL are likely due to Organosolv lignin forming a final product with lower thermal conductivity; thus the heat transfer to surroundings is lower than for MWL char. Visualization experiments (Figures 3 and 4) and SEM micrographs (Figure 10) bolster this hypothesis: the Organosolv lignin produces bigger bubbles more intensely than MWL, and the final char has a porous structure with more voids that will reduce the final thermal conductivity and heat transfer with surroundings.

2.5. SEM analyzes of solid residues

SEM imaging was performed to analyze the char residue from all of the samples after pyrolysis on the quartz disc surface as described above. Discs with solid residues were first sputter coated with 3 nm thick platinum/palladium (Cressington Sputter Coater) followed by SEM imaging using an FEI Quanta 200F SEM at the Franceschi Microscopy and Imaging Center at Washington State University.

3. Results and discussion

3.1. Behavior of organosolv lignin during pyrolysis

The first lignocellulose pseudo-component to be discussed is lignin. Figure 3 shows the sequence of video snapshots taken when Organosolv lignin was heated in the pyrolysis visualization reactor. The appearance of molten material can be seen 1.88 s after the experiment begins. The temperature at which melting of the sample initiates is 176.9 °C (see Frame A). This observation is close to results reported in the literature (150-154 °C) [25,62]. At 2.34 s the lignin is partially melted. The portion of the sample that is in direct contact with the disc is completely melted, leaving the top unchanged. The height of the lignin pile, estimated by image processing, is 0.31 mm, indicating that the process is controlled by the heat transfer (“thermally thick”) [63].

The sample is 100% melted at 2.74 s, when the average temperature of lignin is 241.75 °C. A slight swelling of the pile can be seen, as well as the appearance of small gas bubbles in the liquid (bubble diameter ~33 μm). The appearance of these micro bubbles is indicative of vapor formation within the liquid phase via fragmentation reactions of β-O bonds to form phenols, alkoxy-ketones, and light gases [64].

This behavior has been reported in previous studies by Zhou et al. [65]. According to Dufour et al. [24,25], at this temperature the mass loss is less than 12%; this is consistent with the video between 1.88 and 2.74 s, where no significant outgassing is observed. When the sample exceeds

253 °C (2.86 s), the now continuous liquid slowly swells and bubbles grow at the surface of the quartz disk, though the release of vapors is not clearly observable in the videos. This indicates that decomposition reactions primarily are occurring in the liquid phase, but the bubbles do not achieve sufficient energy to explode yet.

At 3.74 s (295 °C), growth of gas bubbles is continuous and becomes more intense, especially in areas close to the disk surface. Here the gas formation rate has increased and they also overcome the barrier of the surface tension and release the vapors via explosion (popping). The pile appears to swell because of coalescence of all the molten material. In the video a white trail of gas can be seen, which corresponds to the release of vapors by the bubbles. Dufour et al. [25] show that in this temperature range, both the viscous modulus and elasticity of lignin increase. This indicates that the liquid phase begins to gain stiffness. Chemically, this likely reflects dehydration and crosslinking reactions which produce char.

For temperatures near 300 °C, bubbling in the liquid phase is intense; there is continuous nucleation, bubble coalescence, and breakup. Fluid expansion fills the entire surface of the quartz disc with film as result of viscous bubble explosion and retraction. This dynamic continues until the sample reaches 342 °C (5.12s). This is a transition region where the bubbling pattern has changed due to increases in viscosity, surface tension, and other properties in the liquid phase.

Figure 3.

3.2. Behavior of milled wood lignin during pyrolysis

Although Organosolv lignin is commonly used by researchers because it is easy to purchase on the market, it is generally accepted that milled wood lignin (MWL) is less degraded during the extraction process. The image sequence for videos of pyrolysis of milled wood lignin (MWL) can be seen in Figure 4. Evidence of a liquid intermediate can be seen as soon as 129 °C (6A) and the sample appears fully melted by 166 °C (6B). Structurally, MWL contains more β -O-4 linkages than Organosolv lignin; these bonds are known to break at a lower temperature [60,66]. Other researchers have reported similar results in slow-heating thermogravimetric analysis. Yang

et al. [61] and Jakab et al. [67] found that MWL decomposes in two regimes. The first, between 111 and 200 °C, corresponds to water and low molecular weight gas release. The second regime, between 200 and 350 °C, corresponds to decarboxylation reactions which release monomers. Mamdouh et al. [68] found that below 200 °C, endothermic phenomena are decomposition of weak ether bonds, solid softening, melting, and evaporation of water. In Figures 4A and 6B, small bubbles (~24 µm) can be seen, which indicate decomposition and evaporation inside the liquid phase. Between 166 and 230 °C (6C), a darkening of the liquid intermediate phase can be seen. Other researchers have reported exothermic reactions at these temperatures [69]. Here, the liquid intermediate swells due to expansion of gases and liquids. The bubbles are very small and bubble bursting cannot be visualized in these recordings. The MWL has a broad molecular weight distribution (400-5000 MW) [61,70,71] which means that the liquid phase should be quite viscous, limiting bubble coalescence and transport [72,73].

Figure 4.

Because the liquid phase is very dark, it impedes observation of bubbles in the interior. In frames 837-838 and 872-878, the collapse of a large bubble that covers the entire volume of the liquid phase can be seen. A bubble of this size indicates a high rate of bubble coalescence which forms one large bubble that grows until the internal energy is sufficient to overcome the viscous and surface energy barrier to explode [74,75]. After 260 °C (4E), the liquid phase swelling slows down, indicating a decrease in gas generation and an increase in viscosity by polymerization reactions [24,25]. Finally, after 298 °C (4F), volatile and gas release ceases and swelling and shrinking cannot be observed because the carbon residue has formed. These observations match those obtained in previous works [62].

3.3 Behavior of xylan (as received) during pyrolysis

Xylan, one of the many hemicelluloses in biomass, can be easily purchased from chemical vendors. Figure 5 shows the behavior of xylan during pyrolysis. In the first 3.6 seconds of the reaction, when the sample has reached 231 °C, no morphological change is apparent and there is no evidence of vapor release (see Figure 5 B). The same behavior continues until 4.23 s when the

surface of the xylan begins to darken. Darkening without formation of intermediate fluid is a clear indication of solid phase reactions. At this time, the sample temperature reaches 280 °C. It has been reported that the hemicellulose begins to decompose at 273 °C [76–78]. The xylan surface has completely darkened when the sample reaches 323 °C. At this temperature cracking and material mass loss is observed as the sample shrinks a bit, although there was no visualization of vapor release. Critically, the sample does not completely melt as with lignin and cellulose. However, there is a liquid film just in contact with the quartz disk; due to optical properties and the low rate of formation, it is difficult to distinguish through the images. With very careful analysis between frames 600-1000, the liquid at the heated surface is more evident.

Until 323 °C, not much change is seen from the original shape of the sample, except for some cracks in the central area. The bubbles formed within the liquid phase are very small (see Figure 5, Frames D-F), and are not possible to track with our camera's low resolution.

When the xylan has reached 366 °C, some swelling of the liquid phase can be seen throughout almost all the volume of the sample. However, bubbling is minimal, and it is not possible to see any coalescence or rupturing of them. Vapor formation is difficult to see in the videos. One explanation for this behavior is that dehydration and crosslinking reactions between the different branches of xylan favor the production of char with very low outgassing.

Figure 5.

It is known that in the pyrolysis of cellulose, breakage of glycosidic bonds produces levoglucosan, by stabilizing the cation at carbon 1, with the hydroxyl group on carbon 6. However for xylan, the lack of a sixth carbon precludes this chemical route; the carbon cation is rather stabilized by a dehydration reaction, generated water, char, and furans. After 366 °C, swelling or shrinking of the liquid phase is not observed. Instead, the material resolidifies and no changes can be seen after 1 minute. In the end the char retains most of the initial structure of xylan, though there was a 36.3% shrinking of the surface area of the material.

3.4. Behavior of de-ashed xylan during pyrolysis

It is generally accepted that the mineral content has a strong influence on the behavior of biomass during pyrolysis [57,70,79]. In particular, sodium can catalyze dehydration and crosslinking reactions in sugars that help form char more rapidly [38,80,81]. Normally, xylan is extracted from biomass using NaOH, so a significant quantity of Na remains in the xylan purchased commercially. The xylan was thus subjected to an acid wash (1 M HCl) as described in the materials and methods section to remove minerals and compare the behavior of xylan as received with ash-free xylan. HCl was used to minimize hydrolysis of the hemicellulose. Table 1 shows that the ash content was reduced from 5.85% to 0.0112% by this acid washing procedure. Figure 8 presents the sequence of images obtained during pyrolysis of de-ashed xylan.

Figure 6.

The behavior of de-ashed xylan is very different from the behavior of xylan as-received. In Figure 6A, the formation of the liquid phase can be seen as the sample reaches 276 °C (4.6 s). In the corresponding video, physical ejection of partially reacted xylan from the pile can be seen. It is known that CO₂, acetic acid and formic acid are rapidly produced from hemicellulose [70]. The violent release of these gases can expel aerosol particles. In Figure 6C, the entire lower layer of xylan at the quartz surface is melted, and the top melts slowly because that bottom layer swells and restricts heat transfer. The xylan accumulates internal energy until most of the sample is melted, forming a liquid similar what is seen in melting of simple sugars. In this liquid phase, it is difficult to monitor the dynamics of bubble nucleation, growth, coalescence, and other properties. The behavior is very chaotic. After 9.5 s, the liquid phase formation has ceased and a carbonaceous residue remains.

The impact of removing the ash from xylan is striking. When the ash is present, the char formation appears to compete much more heavily. Further, the ash physically takes up space in

the material and will contribute to the solid structure of the char. Without ash, the xylan looks much more like the amorphous, bubbling lignin.

3.4 Behavior of Cellulose

Cellulose is the most abundant component in most lignocellulosic biomass. The still video frames for cellulose can be seen in Figure 7. During the first two seconds of heating, the sample reaches 229 °C, but no color changes, shrinkage, swelling, or release of gases can be seen (see Figure 7 A-B). Only when the sample has exceeded 255 °C does it begin to develop small drops of liquid material on the surface of the hot disc. The top of the cellulose pile is unchanged, due to poor heat transfer. The disk surface at this time (2.5 s) is 297 °C, at which point melting is evident.

Although the images do not fully tell the story, the video shows that as soon as the liquid droplets are formed, a release of white smoke can be seen. This could be attributed to ejection of aerosols [5,41].

An interesting phenomenon is observed at 3.36 s, when the top of the sample is on average 290 °C (T disc 338 °C). Much of the sample has already been consumed by evaporation of the liquid phase, but a solid material remains on the surface. This is likely due to the fact that the material is in poor contact with the disk surface due to Leidenfrost effects [82], in which the vapors rise solid sample, drastically reducing the rate of energy transfer by conduction (see Frames C-D).

Figure 7.

The cellulose sample continues to evaporate and when the disc surface has reached 430 °C, the cellulose is completely melted (sample temperature 344 °C). No obvious Leidenfrost phenomenon can be seen. Because of the optical properties of the liquid phase, it is also difficult to track the dynamics of bubbles.

3.4. Behavior of sugarcane bagasse

Figure 8 shows the video frames of pyrolysis of sugarcane bagasse. During the first 1.64 s, ($T = 140.12\text{ }^{\circ}\text{C}$) no change is observed in the biomass. When the average pile temperature has reached $282\text{ }^{\circ}\text{C}$, darkening of the edges can be seen where the temperature is higher than the average pile temperature (Figure 8B). At this temperature, the hemicellulose has begun decomposing and lignin has changed phase. There is no dramatic change in the volume of the sample, as with lignin.

Figure 8.

More interesting behavior is seen when the sample has reached $332\text{ }^{\circ}\text{C}$. At this temperature there is a complete change in the color of biomass, and the surface becomes smooth and molten. At this temperature, cellulose has now melted. No volume changes (swelling or shrinking) or Leidenfrost effects are observed. The behavior here is quite similar to the xylan containing metals, with the difference that here the formation of fractures in the structure due to formation of small bubbles trapped inside the micro molten phase. Although the behaviors of xylan containing metals and biomass are not equal, they are more similar than they are to lignin or cellulose.

Figure 9 shows the thermal behavior of the acid-washed bagasse, which starts to degrade when the sample has reached $260\text{ }^{\circ}\text{C}$. This is very close to the degradation temperature of the pure cellulose ($255\text{ }^{\circ}\text{C}$). The biomass shrinks quickly, and it is easy to see vapor release during the devolatilization. The devolatilization looks similar to a solid that is sublimating. Although some swelling can be seen, especially after the sample exceed $300\text{ }^{\circ}\text{C}$, it is not as vigorous as lignin. Instead, there is dramatic shrinking of the material, leaving only a small layer of char on the surface of the disc at the end.

In conclusion, the behavior of biomass without ash is completely different from its pseudo-components, but there are some similarities. It is possible the acid wash has affected the crystallinity of cellulose and the lignin structure beyond removing alkali and alkali earth metals, and ought to be studied in future work. It is important to note that while xylan began melting at $348\text{ }^{\circ}\text{C}$, lignin was completely melted at this temperature.

Figure 9.

It is accepted that in the microstructure of lignocellulosic biomasses, hemicellulose surrounds the cellulose chains. The lignin is present in the secondary cell walls as a binder between the stiff pore structures [83,84]. Research has shown that hemicellulose tightens cellulose chains together and changes the dimensions of the micro-fibrils, as seen in the crystal structure [84]. Of the various hemicelluloses, xylan in particular binds cellulose fibrils tighter in the paper-making process [85,86].

3.5 SEM imaging of solid residue from all materials studied

In order to compare the char structures after pyrolysis, SEM images were taken for all the materials, as shown in Figure 10. In the images, major and minor differences can be seen between the materials.

The Organosolv lignin and milled wood lignin both melt completely and form chars that look like liquids. The Organosolv lignin (Figure 10 A) is very smooth (except for cracks from thermal expansion/contraction) and does not appear to bubble as much as the milled wood lignin (Figure 10 B-C), which has small holes on the order of 5-40 μm in diameter. Organosolv lignin is produced at much higher temperatures than milled wood lignin, and its structure is likely more degraded so there will be less fragmentation reactions which produce gases and bubbles.

Figure 10.

The difference between xylan and de-ashed xylan is very dramatic. The xylan as-received (Figure 10 D) has a 3-dimensional structure that looks like coral, with extrusions and holes of all sizes. This structure is evidence of substantial gas production, catalyzed by metals. The de-ashed xylan, however, looks completely different (Figure 10 E-F). There is some evidence of bubbling, but it forms a very flat film that looks much more close to the Organosolv lignin than the xylan with ash.

The Avicel cellulose (Figure 10 G) forms strings of interwoven char which is evidence of a liquid intermediate that melts and moves around due to the Leidenfrost effect. Cross-linking reactions compete with depolymerization while the liquid intermediate boils. This char looks very different from the chars from lignin and xylan.

The sugarcane bagasse (Figure 10 H) appears to retain its original structure during pyrolysis, and the effect of the liquid intermediate formed is not very important. The acid washed bagasse, however, appears to have small layers of amorphous char on the surface, which is evidence of liquid intermediate formation. As a result, the char from acid washed bagasse appears to be less structured than the bagasse with ash. More work needs to be done to assess the impact of removing ash on the formation of liquid intermediates.

4. Conclusions

It is well known that char produced from lignocellulosic biomass retains its general structure during pyrolysis. In this work, the authors performed visualization studies on cellulose, Organosolv lignin, milled wood lignin, xylan, de-ashed xylan, sugarcane bagasse, and de-ashed sugarcane bagasse. The lignin melted, bubbled dramatically, but shrank again. The cellulose melted and shrank. Ash-free xylan melted completely and shrank into a pool, then carbonized. However, when ash content was high in the xylan, the xylan foamed dramatically and grew before carbonizing due to the catalytic effects of ash on gas formation. In sugarcane bagasse, removing the ash appears to have enhanced the formation of a liquid intermediate; SEM of the char indicates that more of the biomass melted (likely the hemicellulose and lignin). Future work needs to be done to better understand the effect of metal content on the formation of products responsible for char retaining the structure of the original biomass.

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Figure 1. Visualization setup for studying fast pyrolysis.

Figure 2. Calibration curves of the various components and the blank disc

Figure 3. Organosolv lignin melting and bubbling behavior during pyrolysis.

Figure 4. Milled wood lignin melting and bubbling behavior during pyrolysis

Figure 5. Xylan behavior during pyrolysis.

Figure 6. De-ashed xylan melting and bubbling behavior during pyrolysis: still frames from video recordings.

Figure 7. Cellulose melting and bubbling behavior during pyrolysis.

Figure 8. Sugar cane bagasse melting and bubbling behavior during pyrolysis.

Figure 9. Acid washed bagasse melting and bubbling behavior during pyrolysis.

Figure 10. SEM micrographs of (A) Organosolv lignin, (B-C) milled wood lignin, (D) xylan, (E-F) de-ashed xylan, (G) cellulose, (H) sugarcane bagasse, and (I) acid washed sugarcane bagasse chars. Scale bars are indicated on the figures.

List of Tables:

Table 1. Composition of sugarcane bagasse as received and after acid wash on a dry ash-free basis. The sums slightly exceed 100% due to experimental error. The sugarcane bagasse before acid washing has a much higher extractives content than after acid washing, which contributes to relative changes in the glucan, xylan, arabinose, and lignin content.

Table 2. Physico-chemical characterization of the raw material. Moisture content is on as-received basis. Volatiles, fixed carbon, ash, glucan, arabinose, lignin, and extractives are reported on a dry basis (w/w). CHN-O data is reported on a dry, ash-free basis (DAF) [wt. %].

Table 3. Metal species analysis by ICP-MS for sugarcane bagasse and xylan before and after their respective acid washings. The acid washing reduces the metal content for all samples. Notably, the Na content in xylan is reduced from 14 mg/g to sub-detection limit concentrations and K to near detection limits. (mg/g)

Table 1. Composition of sugarcane bagasse as received and after acid wash on a dry ash-free basis. The sums slightly exceed 100% due to experimental error. The sugarcane bagasse before acid washing has a much higher extractives content than after acid washing, which contributes to relative changes in the glucan, xylan, arabinose, and lignin content.

	Sugar cane bagasse as received (wt.% DAF)	Acid washed sugarcane bagasse (wt.% DAF)
Glucan	31.0	51.3
Xylan	19.2	18.8
Arabinose	2.5	0.00
Lignin*	19.1	25.5
Extractives	29.3	5.8

* Lignin content was not nitrogen corrected.

Table 2. Physico-chemical characterization of the raw material. Moisture content is on as-received basis. Volatiles, fixed carbon, ash, glucan, arabinose, lignin, and extractives are reported on a dry basis (w/w). CHN-O data is reported on a dry, ash-free basis (DAF) [wt. %].

	Sugarcane bagasse	Acid-Washed sugarcane bagasse	Avicel Cellulose	Xylan	De-Ashed Xylan	Organosolv Lignin	Milled Wood Lignin
Moisture	5.25	2.71	3.65	7.95	6.48	1.19	2.70
Volatiles (dry)	82.6	86.8	87.7	71.9	82.6	70.6	75.8
Fixed Carbon (dry)	8.30	5.99	8.35	14.3	17.4	26.2	24.05
Ash (dry)	3.90	4.53	0.314	5.85	0.0112	2.02	0.205
C (DAF)	46.6	49.3	44.4	43.0	50.4	69.7	60.2
H (DAF)	5.92	5.90	6.49	6.45	8.29	5.86	5.90
N (DAF)	0.14	0.0497	0.064	0.0074	0.0	0.11	0.050
O (DAF)	43.5	31.4	45.5	37.5	35.4	21.3	31.4

Table 3. Metal species analysis by ICP-MS for sugarcane bagasse and xylan before and after their respective acid washings. The acid washing reduces the metal content for all samples. Notably, the Na content in xylan is reduced from 14 mg/g to sub-detection limit concentrations and K to near detection limits. (mg/g)

Species (unit)	Sugar cane bagasse as received	Acid washed sugarcane bagasse*	Xylan	Acid washed xylan
Na (mg/g)	-	0.32	14.2	-
Mg (mg/g)	0.30	-	-	-
K (mg/g)	2.32	0.03	20.3	0.02
Ca (mg/g)	2.18	0.54	2.17	0.37
Fe (mg/g)	0.40	0.00	0.15	0.06
Al (µg/g)	197.	216.	5.60	-
Zn (µg/g)	54.6	-	25.0	-
Cu (µg/g)	14.7	1.83	4.76	-
Ba (µg/g)	18.1	15.8	8.33	-
Pb (µg/g)	5.89	0.41	2.33	-
Mo (µg/g)	30.99	3.29	0.94	-
Mn (µg/g)	63.1	0.30	66.4	0.26
Ni (µg/g)	1.98	8.23	1.09	-
Sum of ICP analyzed metals (mg/g)	4.48	1.14	37.0	0.452
Silicates (calculated by difference from ash content) (mg/g)	34.5	44.2		

*This had a small sample size, which increases error (such as sodium content).