

Hot Water Extraction of Anaerobic Digested Dairy Fiber for Wood Plastic Composite Manufacturing

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Dairy farmers worldwide are facing the difficulty of managing or disposing of dairy manure. Anaerobic digestion (AD) is an option for treating dairy manure and producing biogas. A byproduct of AD is fiber, which is only partially being used despite its potential for different products, including wood plastic composites (WPCs). However, some properties of WPCs need to be improved to use them in high moisture content environments. This work evaluates the effect of hot water extraction (HWE) (at 160 °C for 60 min) of the AD dairy fiber on properties of WPCs. WPCs were produced using AD fiber *via* extrusion and tested for mechanical properties and water affinity. The WPCs produced with HWE fiber exhibited increased mechanical strength (36%) and stiffness (30%), and reduced strain at break (15%) compared to composites produced with untreated fiber. Water sorption and thickness swelling were reduced by 39% and 36%, respectively, after immersion in water for 98 days. The diffusion constant of WPCs produced with HWE fiber was also reduced by 64%. These results show that HWE is an effective method for enhancing mechanical properties and reducing hydrophilicity of WPCs produced from AD fiber.

Keywords: Anaerobic digestion; Dairy fiber; Hot water extraction; Wood plastic composites

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INTRODUCTION

Anaerobic digestion (AD) has been recognized worldwide as a profitable and sustainable solution for the treatment of dairy manure for greenhouse gas mitigation, indicator pathogen control, and odor and solids strength reduction, while providing renewable fertilizer nutrients and producing energy (Informa Economics 2013). Dairy manure is rich in recalcitrant fibrous matter surviving the animal digestive process, representing around 52.6% of total dry matter within as-produced manure (Chen *et al.* 2003). Subsequent, traditional AD does little to reduce this fibrous mass, resulting in a large by-product of fibrous solids.

Traditionally, AD fiber is used directly as animal bedding or treated to produce compost for soil amendment. Composted AD fiber can be used for topsoil bedding, nursery greenhouse bulk soil, turf top-dressing, or peat replacement (Winandy and Cai 2008; MacConnell *et al.* 2010). There is also interest in using AD fiber for producing other types of products, such as engineered bio-composite products (Winandy and Cai 2008), biochar (Streubel *et al.* 2012), activated carbon (Qian *et al.* 2008), or even as a raw material for bioethanol production *via* enzymatic hydrolysis (Yue *et al.* 2011). Unfortunately, many of

these product streams remain unrealized, with AD fiber supplying relatively low value within still undeveloped markets (MacConnell *et al.* 2010).

Some characteristics of AD fiber (*e.g.*, its particle size and geometry) make it suitable to substitute fiber for engineered wood products (Winandy and Cai 2008) such as wood plastic composites (WPC). WPCs are engineered wood products widely used for decking and, more restrictedly, for other purposes like automobile components. The global market for WPC has been growing rapidly (Eder and Carus 2013) due to its better outdoor durability compared with wood if fungicides and insecticides are added to the formulations for producing the composite (Morrell *et al.* 2010) and as it avoids deforestation (Markets and Markets 2014). In 2010, WPC global production was 1.5 million extruded tones (Eder and Carus 2013). WPCs global market is projected to grow from \$2579 million in 2014 to \$4601 million by 2019 (Markets and Markets 2014). North America and Asia accounted for more than 75% of the WPCs consumed in 2014, and emerging countries, such as China, India, and Brazil, have been significantly increasing their WPC consumption (Markets and Markets 2014).

One problem that limits the use of WPCs in environments with high moisture content is water affinity. Tests carried out under laboratory (Cameron 2009) and outdoor conditions (Kiguchi *et al.* 2007) show that weathering deteriorates WPC surfaces, and water penetration reduces its strength and stiffness (Pilarski and Matuana 2005; Panthapulakkal *et al.* 2006). Moisture sorption causes WPC swelling, which stresses the interfacial bond between fibers and plastic and compromises composite strength (Stark 2001). Because the properties of WPCs are affected by the chemical composition of the fiber used in the composite, modifying the raw materials' composition is a strategy for improving critical properties of WPCs such as water resistance (Pelaez-Samaniego *et al.* 2013a, b; Chen *et al.* 2014).

Yue *et al.* (2011) and MacLellan *et al.* (2013) reported that AD degrades attached proteins and fats adhering to fibrous particles within the manure and partially degrades the lignocellulosic matrix, removing as much as 38% of the hemicelluloses. Thus, AD is somewhat efficient for cleansing the fibrous particles, partially reducing hemicelluloses content, and potentially preparing the fibrous particles for further hemicelluloses removal.

Hemicelluloses in the raw material are highly responsible for the water affinity of WPCs. Consequently, the reduction of hemicelluloses content can positively impact WPC properties. One way to remove hemicelluloses from lignocellulosic materials is thermochemical pretreatment such as hot water extraction (HWE) (Pelaez-Samaniego *et al.* 2013a,b). HWE processing allows the recovery of hemicelluloses-derived fractions, which could be used for the production of biofuels.

HWE can potentially be used to pretreat AD fiber, as no previous steps (*e.g.*, drying) are required. Previous studies with softwood have shown that HWE at 160 °C for 90 min removes approximately 20% of the original mass, in the form of an aqueous solution that is rich in sugars, acetic acid, and other compounds, mostly derived from hemicelluloses (Chaffee 2011; Pelaez-Samaniego *et al.* 2015). Based on these previous studies, HWE can be a valid strategy for improving the properties of WPCs manufactured from AD fiber. The objective of this work was to evaluate the impact of HWE on AD dairy fiber and how changes in AD fiber affect WPC properties.

EXPERIMENTAL

Materials

AD dairy fiber was obtained from George DeRuyter and Sons Dairy Farm in Outlook, WA, which is a 3000 wet cow equivalent dairy and uses a typical high-energy feed diet. The manure was collected using a flush manure handling system, where the dilute manure wastewater is sent to a clarifier before entering a mesophilic, 20-day mixed plug-flow anaerobic digester. After digestion, the effluent is sent to a slope screen attached to dewatering roller presses for mechanical recovery of digested fibrous solids with an approximate moisture content (MC) of 72%.

A representative portion of the digested fiber (approximately 30 kg) was transferred to Washington State University, where it was partially dried at room conditions for one week. The AD fiber was subsequently dried at 103 °C for 24 h and stored prior to characterization and production of WPCs. Untreated AD fiber (*i.e.*, not thermochemically treated and not ground) is herein referred to as fiber ‘as received’ (or UUF).

Other materials used for WPC production were a) eastern white pine (*Pinus strobus*) wood flour (American Wood Fibers, passed through a 60-mesh sieve), b) ground (passed through a 60-mesh sieve) not thermochemically treated AD fiber and c) ground (passed through a 60-mesh sieve) thermochemically treated AD fiber, here referred to as a) pine, b) GUF, and c) GTF, respectively.

Other additives used for WPC production were virgin HDPE (Lyondell/Equistar LB010000) (Equistar Chemicals, LP, Mansfield, TX, USA), zinc stearate (former Crompton Corp, Middlebury, CT, USA) as lubricant, zinc borate (US Borax/RioTinto, <http://www.borax.com>) as a biocide, and talc (Nicron 403 from RioTinto, <http://www.imerystalc.com>). These formulations were intended to obtain products comparable to previously reported composites (Pelaez-Samaniego *et al.* 2013a).

Hot Water Extraction

AD fiber ‘as received’ was subjected to HWE using a 1-L Parr 4521 bench top reactor (Moline, IL, USA) controlled by a 4842 Parr controller and coupled with a water circulating cooling system (Pelaez-Samaniego *et al.* 2015). Five different temperatures of 120, 140, 160, 180, and 200 °C were tested for 60 min. The proportion in mass of E-pure-water to fiber was 5:1. This relatively high water to fiber ratio resulted from the necessity of keeping the fiber moist because small particles absorbed water very quickly.

In HWE, some sugars are degraded during the heating up phase, especially when this step is long (Borrega *et al.* 2011). Thus, it is recommended to convert the heating up time into an equivalent isothermal reaction time by adding a temperature time correction factor (Borrega *et al.* 2011; Pelaez-Samaniego *et al.* 2015). The activation energy of the fiber required for the correction was determined using thermogravimetric analysis (TGA) (TGA/SDTA 851e Mettler Toledo, Columbus, OH, USA) of the ‘as received’ fiber at different heating rates (1, 2, 5, and 10 °C/min), following ASTM E1641-07 (2007).

After each treatment, a sample of the liquid phase was collected by wrapping the HWE material with cotton tissue to filter the liquid and retain the solid particles and squeezing it. The collected liquid sample was then stored at 4 °C for further sugars analyses. The pH of each liquid fraction was measured.

Characterization of the Liquid Products

Approximately 5 mL of the liquid fraction of each HWE process was filtered using a Millex® - HV 0.45 µm sterile filter with Durapore® PVDF membrane. The filtrate was then diluted with E-pure water and used for sugars analyses using a Dionex ICS-3000 ion chromatograph (IC) (Waltham, MA USA) as described (Pelaez-Samaniego *et al.* 2015).

Characterization of the Solid Products

Immediately after HWE, the solid phase of each treatment was washed with tap water several times, using a 200-mesh sieve to avoid loss of the product. The material was then dried at 103 °C until the mass change was negligible and stored in glass containers. The mass loss during HWE was calculated from the difference between the initial dry mass (*i.e.*, before HWE) and the final dry mass (after HWE). These materials were used for chemical composition, proximate, and elemental analyses. The material treated at 160 °C was chosen for WPC production, and it was analyzed for particle size distribution and bulk density before and after grinding to 60 mesh. Pine and fiber ‘as received’ were also analyzed for particle size distribution and bulk density. Both untreated and treated fiber were additionally analyzed using a FEI Quanta 200F scanning electron microscope–SEM (Hillsboro, OR, USA) to visualize the structure of the fibers. Prior to microscopy, the fibers were gold coated using Hummer V sputtering equipment.

Proximate analysis

The ash content of the fibers was determined following ASTM D1102-84 (2007), by burning the material at 550 °C for 2 h. Volatiles were indirectly determined using TGA following ASTM E1868-04 (2004), where the fiber was heated in a nitrogen environment from 25 °C to 600 °C at a heating rate of 10°C/min. Fixed carbon was calculated by difference.

Elemental analysis

Carbon, hydrogen, and nitrogen content were determined using a LECO® TruSpec CHN instrument (St. Joseph, MI, USA) coupled with a LECO® 628S S module, in duplicates, as described (Pelaez-Samaniego *et al.* 2015).

Chemical composition

Cellulose, hemicelluloses, and lignin in AD fiber were determined following the NREL method (Sluiter *et al.* 2010). Insoluble lignin was considered as the mass lost after burning the hydrolysis solid fraction in a furnace at 550 °C. Soluble lignin was determined by analyzing the hydrolysis liquid fraction with a Shimadzu UV-2550PC UV/Vis spectrophotometer (Kyoto, Japan). The total lignin is the sum of both soluble and insoluble lignin. A Dionex ICS-3000 ion chromatograph (Sunnyvale, CA, USA) was used to determine sugars in the hydrolysis liquid.

Particle size distribution and bulk density

The particle size distribution of the pine wood floor and the fibers was analyzed according to ANSI/ASAE S319.4 (2013). The sieves used for pine (herein referred to as ‘pine’), ground untreated AD fiber (*i.e.*, GUF), and ground treated AD fiber (*i.e.*, GTF) ranged from 70 to 140 mesh, and those used for fiber ‘as received’ (*i.e.*, UUF) from 14 to 45 mesh. Bulk density of the fibers was tested following ASTM E873-82 (2006).

Wood Plastic Composites Production and Testing

WPC production

Prior to WPCs manufacture, torque rheology was conducted for formulations of HDPE with pine, UUF, GUF, and GTF. A mixture of 60% of each fiber and 40% HDPE (50 g total, to fill more than 80% of the rheometer chamber) was used in a Haake Rheomix 600 torque rheometer (Waltham, MA, USA) equipped with roller-blade rotors for 10 min at 20 rpm and 160 °C. Composites were produced *via* extrusion, in which 2.5 kg of a mixture containing 58% dry filler, 32% HDPE, 3% lubricant (zinc stearate), 2% zinc borate, and 5% talc were blended for 10 min in a Ross ribbon blender. This formulation was chosen following that used by Pelaez-Samaniego *et al.* (2013a), for comparison of results. Prior to extrusion, the blends were left in the oven at 103 °C for 24 h. The extrusion process was carried out in a 35 mm intermeshing twin-screw extruder (Cincinnati Milacron Inc., Cincinnati, OH, USA) equipped with a 37 × 10 mm cross-section die. First, the pine-HDPE formulation was extruded, followed by UUF, to compare both resulting materials, and then GUF followed by GTF, also to compare results. The extruder operating conditions were set with a 160 °C barrel, screen and die temperature of 155 °C, and a screw rotation of 5 rpm.

WPC evaluation

Evaluation of the properties of WPCs consisted of flexural (modulus of rupture, MOR; modulus of elasticity, MOE) and water sorption tests. For flexural, six specimens of each formulation, randomly selected from the corresponding board, were sawn to the required length outlined by ASTM D790-10 (2010). Each specimen of pine and UUF WPC had final dimensions of 38.1 × 10.2 × 203.2 mm. For the GTF-HDPE and the GUF-HDPE formulations, the specimens were cut to remove part of the edges (due to surface imperfections) leading to final dimensions of 25.4 × 7.6 × 177.8 mm. The specimens were then conditioned at 25 °C and relative humidity (RH) of 55% for 48 h, and the composite densities were determined prior to flexural tests. For the tests, a universal test frame equipped with a 907 kg load cell, with a support span of 157.5 mm and a crosshead speed of 4.2 mm/min (ASTM D790-10, 2010) was used. The test consisted of applying load to the specimens until the breaking point to determine MOR, MOE, and strain at break.

For water sorption tests, the thermoplastic-rich skin of the composites was removed using a knife planer, following a previous procedure (Pelaez-Samaniego *et al.* 2013a). Three randomly chosen specimens of UUF and pine formulations, with dimensions 25.4 × 6.3 × 127.0 mm, and GUF and GTF composites of 25.4 × 7.6 × 127.0 mm were conditioned at 25 °C and 50% RH for 48 h. The test consisted of immersing the specimens in distilled water at room temperature. The specimen thickness and weight were measured before the test started and periodically, according to ASTM D570-98 (2010). The diffusion constant is a parameter that can evaluate the rate of moisture sorption for a specific material. The diffusion constant was calculated using Fick's law of diffusion in the hygroscopic range (from zero percent moisture to the fiber saturation point) taking into account diffusion through the material edges (Rangaraj and Smith 2000; Stokke *et al.* 2014).

Analysis of variance was carried out for mechanical properties and water sorption results using SAS[®] statistical software (Cary, NC, USA). The same software was used for analysis of covariance to evaluate the influence of density on other mechanical properties.

After flexural tests, cross sections of the GTF and UTF boards were analyzed by SEM to visualize the composites and determine the possible effects of HWE on fiber.

RESULTS AND DISCUSSION

Results of the HWE Process

The computed activation energy of the AD fiber was 190 kJ/mol, which was used to calculate the time-temperature correction, which resulted in a total treatment time of 62 min, instead of 60 min.

The pH and the sugars content of the aqueous phase of each treatment are presented in Table 1. The average percent of mass lost during the treatments was 11.8, 16.3, 21.0, 31.6, and 36.0% for HWE at 120, 140, 160, 180, and 200 °C, respectively. As expected, mass loss was higher at higher treatment temperatures. Table 1 also shows the sugars content in the liquid phase. During HWE, acetic acid is formed from the acetyl groups bound to hemicelluloses (Borrega *et al.* 2011). Thus, it was expected that the pH of the aqueous phase would become lower when increasing the treatment temperature.

Table 1. pH and Relative Amount of Sugars in the Aqueous Phase of each HWE

| HWE Temperature (°C) | pH | Mass lost in the process (%) | Sugars (%)* |
|----------------------|------|------------------------------|-------------|
| 120 | 6.44 | 11.8 | 0.00 |
| 140 | 5.97 | 16.3 | 1.21 |
| 160 | 5.44 | 21.0 | 2.04 |
| 180 | 4.62 | 31.6 | 3.18 |
| 200 | 4.62 | 36.0 | 0.06 |

* Percentages refer to the ash free corresponding material

Properties of the Solid Products

Proximate analysis

Figure 1 presents the percentage of ash, volatiles, and fixed carbon for the untreated fiber (HWE at 25 °C) and the AD fiber treated at different temperatures. The percentage of ash decreased as the HWE temperature increased, reaching a minimum at 180 °C. The amount of fixed carbon increased and, as expected, the presence of volatiles decreased. A slight decrease in ash content was observed as the temperature of HWE increased, as noted previously (Chaffee 2011; Pelaez-Samaniego *et al.* 2015).

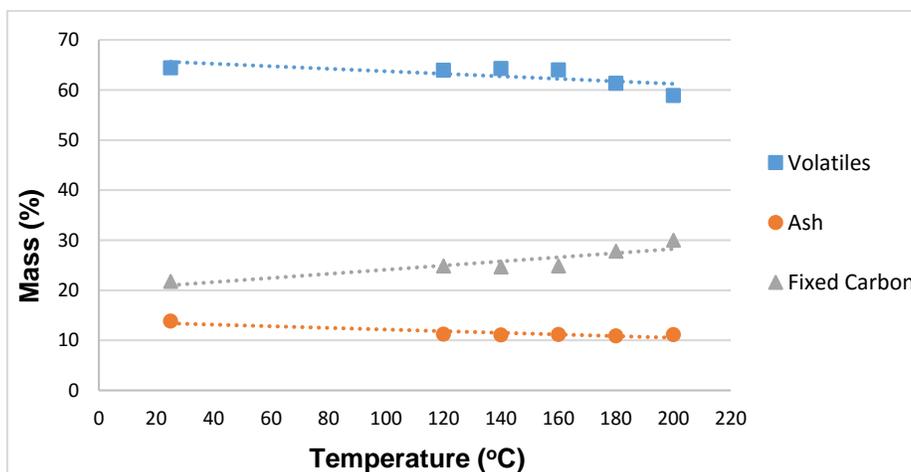


Fig. 1. Percentage of volatiles, ash, and fixed carbon for each treated and untreated (HWE) fiber

Figure 2 shows the mass loss in material treated at different HWE conditions (*i.e.*, from 25 to 600 °C). The corresponding DTG curve is presented in Fig. 3. The TGA curves show that untreated fiber and fibers treated at 120, 140, and 160 °C started to degrade at lower temperatures than fibers treated at 180 and 200 °C. The DTG curve of untreated material (Fig. 3) presents a perceptible shoulder, which is less visible with the increase of HWE temperature. After 160 °C, the shoulder in the DTG curve is not visible anymore, which is in agreement with the reduction of hemicelluloses content in the solid fraction (see Fig. 5), as this shoulder is associated with the hemicelluloses content (Pelaez-Samaniego *et al.* 2013a). Figure 3 also shows a slight shift of the peak corresponding to cellulose degradation to a higher temperature as the HWE temperature increased. This result suggests that inorganic salts in the AD fiber cause cellulose decomposition at a lower temperature. As HWE removed these inorganic salts, cellulose thermal stability increased (Várhegyi *et al.* 1997; Benitez-Guerrero *et al.* 2014).

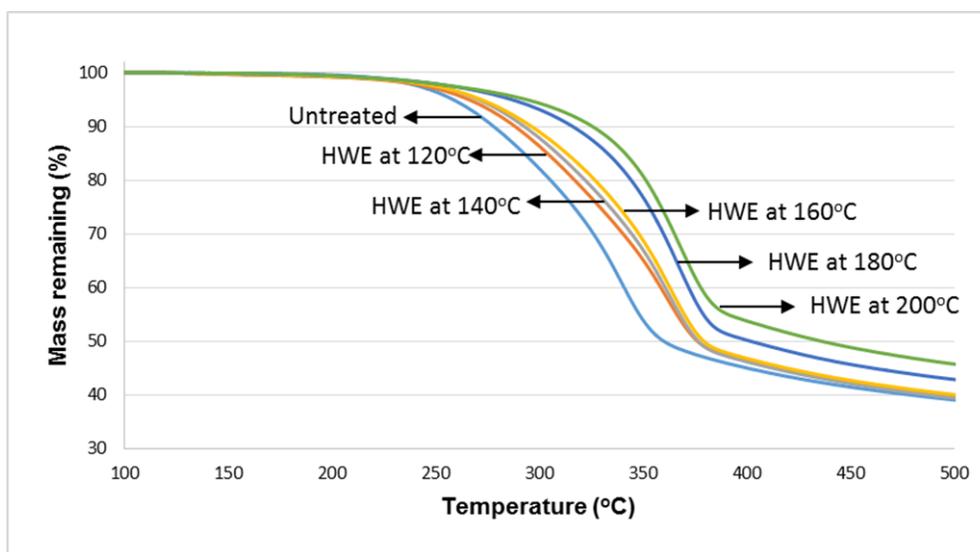


Fig. 2. TGA curves of untreated and treated materials at different conditions

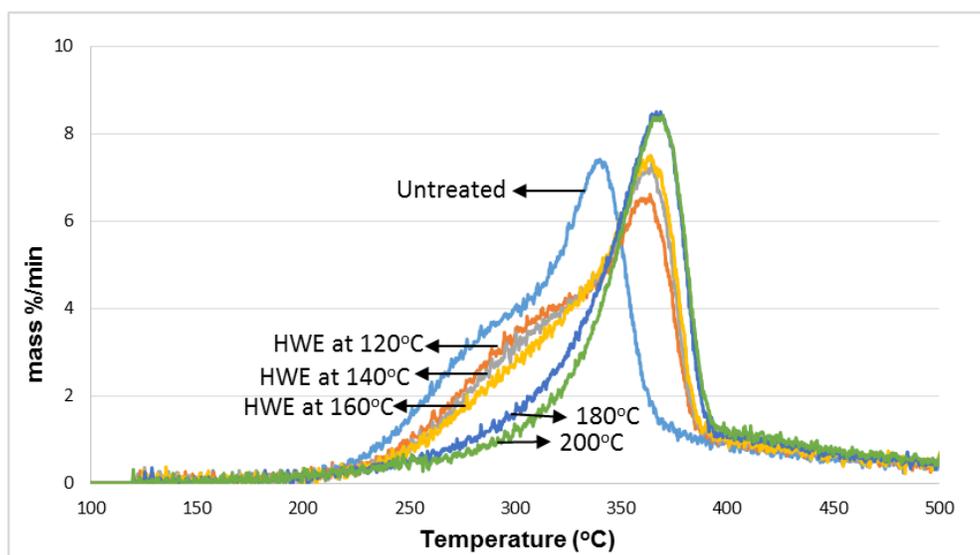


Fig. 3. Derivative of TG analysis for each HWE temperatures and the raw material

Elemental analysis

The relative amounts of C, H, N, and O for each treatment are presented in Fig. 4. The relative amount of carbon increased as the HWE temperature increased. The opposite happened with oxygen. Hydrogen and nitrogen content remained approximately constant. These results are in agreement with those found in the literature (Pelaez-Samaniego *et al.* 2015).

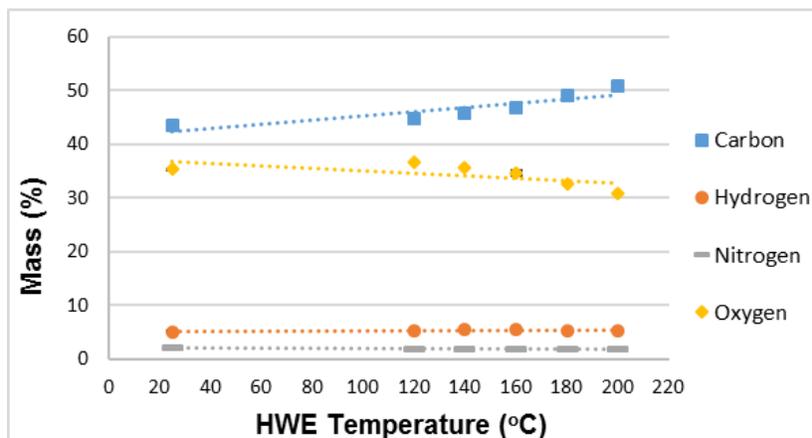


Fig. 4. Variation of elemental composition of HWE fiber as the temperature of the treatment changes

Chemical composition

The percentages of cellulose, hemicelluloses, and lignin were multiplied by the mass percent remaining after each treatment (Fig. 5). The amount of all compounds decreased when the temperature of the treatment increased. As expected, hemicelluloses content decreased faster than the other constituents, indicating that higher amounts of hemicelluloses were removed as the temperature of the HWE process was augmented. In Fig. 5, the mass balance of the untreated material (*i.e.*, at 20 °C) is approximately 100% if the ash content (as per Fig. 1) is added. The hemicelluloses content in the material pretreated at 160 °C was approximately 10%, and complete removal of hemicelluloses was possible only by increasing the pretreatment temperature above this temperature.

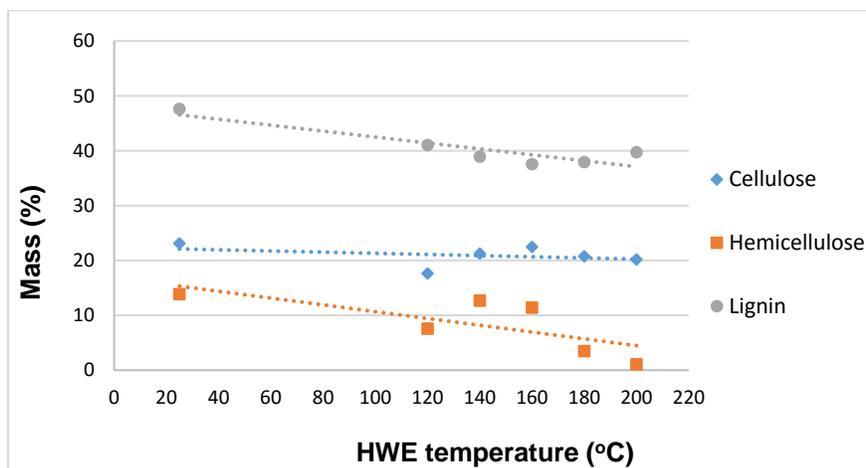


Fig. 5. Chemical composition of untreated (20 °C) and each treated fiber multiplied by the mass yield of the respective treatment

Particle size distribution and bulk density

Pine, UUF, GUF, and GTF were analyzed for particle size distribution (Fig. 6). Particle size of pine was distributed around 0.149 mm. Fiber ‘as received’ presented a random particle size distribution with no pattern. For GTF and UTF, more than 90% of the particles were 0.149 mm or less. According to previous studies (Bridgeman *et al.* 2010; Pelaez-Samaniego *et al.* 2013a), thermochemical treatments facilitate wood grinding. This can explain why treated fiber had smaller particle size than the untreated fiber. The bulk density of pine, UUF, GUF, and GTF were 0.215 ± 0.004 , 0.175 ± 0.005 , 0.390 ± 0.001 , and 0.324 ± 0.002 g/cm³, respectively.

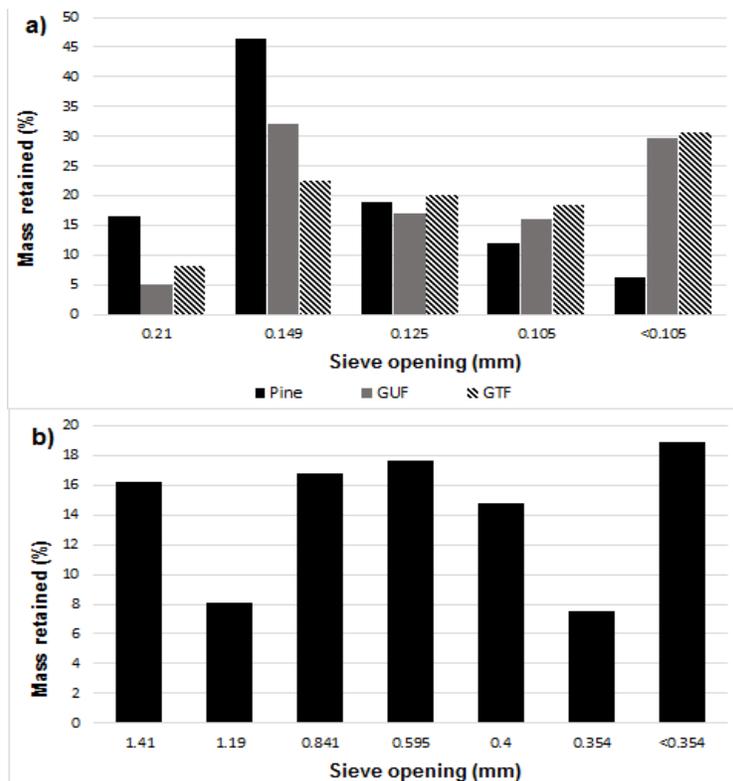


Fig. 6. Particle size distribution of a) pine fiber, ground untreated, and ground treated fibers, and b) fiber ‘as received’

Wood Plastic Composites Properties

Torque rheology results showed that the torque required for compounding treated fiber was higher than for the other fibers, which could result from the better adhesion between treated fiber and HDPE. HDPE has nonpolar characteristics, and treated fiber presents increased nonpolar characteristics (Mohanty *et al.* 2005). The values for the other materials were approximately the same. In the extrusion process, the extruder motor current intensity (amperage) was also different. It increased when switched from pine to fiber ‘as received’, and from untreated to treated fiber.

As observed in other works, the color of the WPC boards was darker than that of composites produced with untreated AD fiber. Oxidation of phenolic compounds, the presence of reduced sugars and amino-acids, and the emanation of formaldehydes are some factors that affect the color of the fiber during thermochemical treatments (Sandoval-Torres

et al. 2010; Pelaez-Samaniego *et al.* 2013a, b). Thus, it was not unexpected that the WPC produced with treated fiber would be darker than that containing untreated fiber.

The composite produced with ground treated fiber showed rough and irregular surface and edges, with a snake-skin appearance in some parts of the boards. Despite the irregularities, all boards were adequate to prepare samples for mechanical testing and water immersion conditions. Some published articles reported the same extrusion defects with maple-polypropylene composites (Slaughter 2004) and wheat straw-HDPE composites (Schirp *et al.* 2006). Further works could help to fix this problem by, perhaps, changing the extrusion parameters and/or changing the formulations.

Scanning Electron Microscopy Analysis

Figure 7 shows SEM pictures of untreated and treated fiber (*i.e.*, before and after HWE) at 20,000 \times magnification. The untreated material cell wall was more homogeneous and smoother than that of the HWE AD fiber. After treatment, fiber became rougher, with some coalesced droplets on the surface, which could be a lignin-rich material that migrated from the cell walls to the fiber surface (Selig *et al.* 2007; Sannigrahi *et al.* 2011; Pelaez-Samaniego *et al.* 2013a). Lignin softens and coalesces in the aqueous phase at temperatures within the range of temperatures studied (120 to 200 $^{\circ}$ C) (Selig *et al.* 2007; Singh and Harvey 2010), thus explaining the presence of droplet-like materials on the surface. This observation was confirmed by the SEM pictures of the fibers in the WPC (Fig. 8).

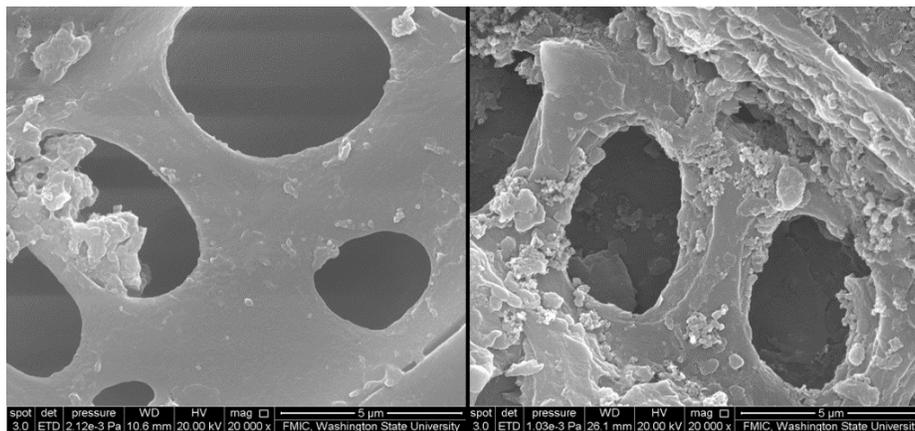


Fig. 7. SEM images of untreated AD fiber (left) and 160 $^{\circ}$ C HWE AD fiber (right) (20,000 \times)

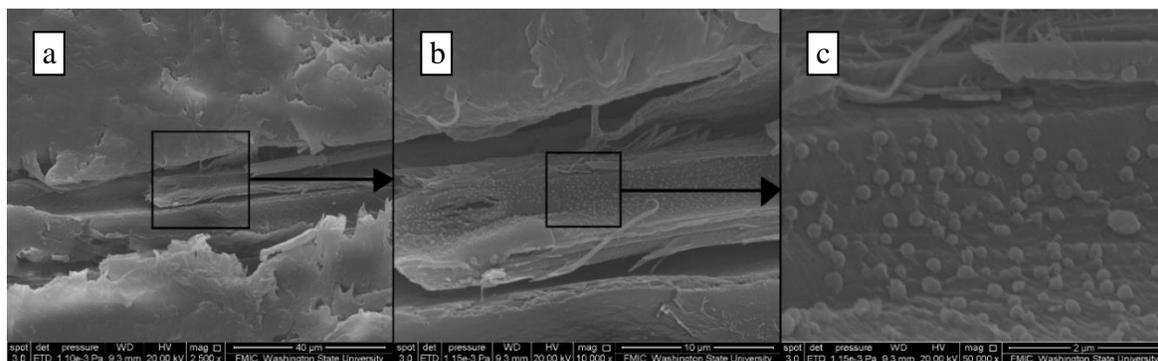


Fig. 8. SEM images of WPC produced with GTF at a) 2,500 \times , b) 10,000 \times , and c) 50,000 \times magnification

Mechanical and Physical Properties

Table 2 presents the calculated density of each material at 25 °C and 50% RH. The density of the composites produced with pine and UUF were not statistically different. The same result occurred with the composites produced with ground untreated and untreated fiber. In all cases, the densities were close to those reported by Pelaez-Samaniego *et al.* (2013a). Flexural test results (MOR, MOE, and strain at break) are also shown in Table 2. The MOR and MOE of WPCs produced with HWE AD fiber were better than the composite produced without HWE pretreatment. Analysis of covariance showed that density affected the MOR and MOE but not the strain at break. It is important to note that the MOR and the MOE of the composite produced with HWE fiber showed an increase of 36% and 30% compared with the composite that did not use the HWE material. Strain at break was also reduced by 15.4% when the treated fiber material was used. These results suggest that treating the fiber (*via* HWE) prior to extrusion produced a composite with increased mechanical properties.

Table 2. Mechanical Properties of Each Material Compared with Results Found in the Literature for WPC Using Untreated Ponderosa Pine and Ponderosa Pine Treated *via* HWE at 160 °C for 90 min

| Filler | Density (g/cm ³) | | MOR (MPa) | | MOE (GPa) | | Strain at Break |
|--------|------------------------------|-------|--------------|--------|-------------|-------|-----------------|
| Pine | 1.15 ± 0.03 A | | 19.08 ± 1.15 | | 2.94 ± 0.23 | | 0.008 ± 0.000 |
| UUF | 1.12 ± 0.03 A | | 17.24 ± 0.83 | | 2.09 ± 0.15 | | 0.012 ± 0.000 C |
| GUF | 1.20 ± 0.01 B | 1.18* | 15.85 ± 0.96 | 27.59* | 2.16 ± 0.07 | 3.77* | 0.013 ± 0.001 C |
| GTF | 1.23 ± 0.01 B | 1.18* | 21.59 ± 0.58 | 31.70* | 2.81 ± 0.11 | 3.75* | 0.011 ± 0.001 |

*Pelaez-Samaniego *et al.* (2013)

Note: The properties not significantly different are tagged with the same letter.

Figures 9 and 10 show the water sorption and thickness swelling results, respectively, for the four types of composites. Both the water sorption and the thickness swelling of the composite produced with pine were the highest among the tested formulations. Both composites produced with untreated fiber behaved very similarly.

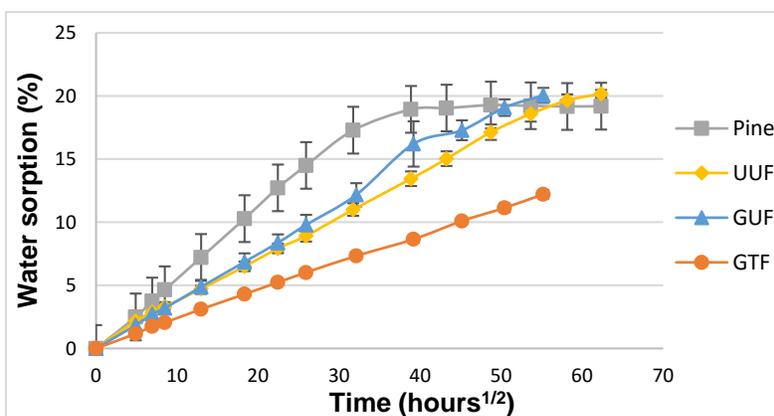


Fig. 9. Water sorption as a function of time comparing pine, fiber ‘as received’, ground untreated fiber, and ground treated fiber composites

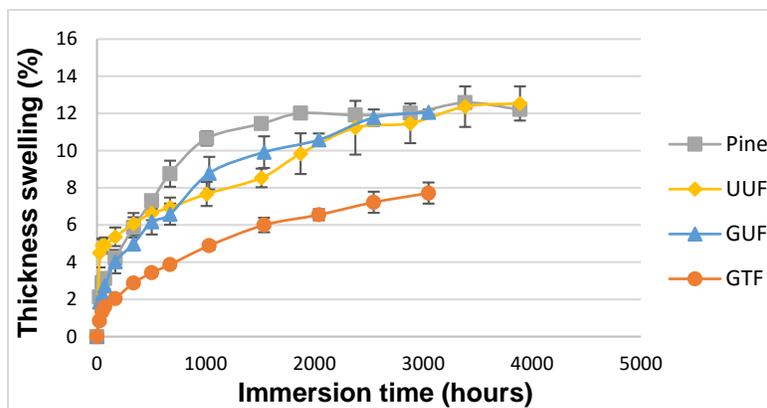


Fig. 10. Thickness swelling as a function of time comparing pine, fiber ‘as received’, ground untreated fiber, and ground treated fiber composites

Analysis of variance showed that water sorption in the GUF composite was significantly different from that of GTF. The thickness swelling of both untreated AD fiber materials was not significantly different. However, the composite produced with HWE AD fiber absorbed less water and swelled less than all other WPCs. For better comparison of results, after 127 days, pine, AD fiber ‘as received’, GUF and GTF absorbed $19.2 \pm 1.4\%$, $18.6 \pm 0.6\%$, $20.0 \pm 0.6\%$ and $12.2 \pm 0.3\%$ water and swelled $12.0 \pm 0.2\%$, $11.5 \pm 1.1\%$, $12.1 \pm 0.1\%$ and $7.7 \pm 0.6\%$, respectively. These results indicate that HWE reduced the moisture uptake by 39.1% and swelling by 36.0% after 127 days of water immersion.

The diffusion constants of WPCs made from pine, AD fiber ‘as received’, ground untreated AD fiber, and ground treated AD fiber were 1.13×10^{-6} , 3.92×10^{-7} , 6.15×10^{-7} , and 2.23×10^{-7} mm^2/s , respectively. These results, once again, showed that HWE treatment greatly decreased the composite water affinity by reducing the inherent hydrophilicity of the untreated material.

CONCLUSIONS

1. Hot water extraction shows potential as a pretreatment operation for using AD fiber for WPC manufacture.
2. Due to hemicelluloses removal, HWE was an effective method for reducing the hydrophilicity of AD dairy fiber and the resulting WPCs produced with HWE AD fiber. WPCs produced with treated fiber and HDPE absorbed less moisture than those produced with untreated fiber and HDPE.
3. The mechanical properties of WPCs produced with HWE AD fiber were better than those produced using AD fiber without the pretreatment step.

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REFERENCES CITED

- ANSI/ASAE S319.4 (2013) . “Method of determining and expressing fineness of feed materials by sieving,” American Society of Agricultural and Biological Engineers, St. Joseph, MI.
- ASTM D 1102-84 (1984; reapproved 2007). “Standard test method for ash in wood,” ASTM International, West Conshohocken, PA.
- ASTM D 570-98 (1998; reapproved 2010). “Standard test method for water absorption of plastics,” ASTM International, West Conshohocken, PA.
- ASTM D 790-10 (2010). “Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials,” ASTM International, West Conshohocken, PA.
- ASTM E 1641-07 (2007). “Standard test method for decomposition kinetics by thermogravimetry,” ASTM International, West Conshohocken, PA.
- ASTM E 1868-04 (2004). “Standard test method for loss-on-drying by thermogravimetry,” ASTM International, West Conshohocken, PA.
- ASTM E 873-82 (2006). “Standard test method for bulk density of densified particulate biomass fuels,” ASTM International, West Conshohocken, PA.
- Benitez-Guerrero, M., Lopez-Beceiro, J., Sanchez-Jimenez, P. E., and Pascual-Cosp, J. (2014). “Comparison of thermal behavior of natural and hot-washed sisal fibers based on their main components: Cellulose, xylan and lignin. TG-FTIR analysis of volatile products,” *Thermochimica Acta* 581, 70-86.
- Borrega, M., Nieminen, K., and Sixta, H. (2011). “Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures.” *Bioresource Technology* 102(22), 10724-32.
- Bridgeman, T. G., Jones, J. M., Williams, A., and Waldron, D. J. (2010). “An investigation of the grindability of two torrefied energy crops,” *Fuel* 89(12), 3911-18. DOI: 10.1016/j.fuel.2010.06.043.
- Cameron, T. R. (2009). *Alaskan Timber Resources for Wood-Plastic Composite*, Master's Thesis, Washington State University Pullman, WA, USA.
- Chaffee, T. L. (2011). *Potential for Enhanced Properties of Wood Products by Hot Water Extraction of Low-Value, Endebarked Ponderosa Pine*, Master's Thesis, State University of New York, NY, USA.
- Chen, S., Liao, W., Liu, C., Wen, Z., Kincaid, R. L., Harrison, J. H., Elliott, D. C., Brown, M. D., Solana, A. E., and Stevens, D. J. (2003). *Value-Added Chemicals from Animal Manure* (PNNL-14495), Pacific Northwest National Lab., Richland, WA.
- Chen, Y., Stark, N. M., Tshabalala, M. A., Gao, J., and Fan, Y. (2014). "Properties of wood-plastic composites (WPCs) reinforced with extracted and delignified wood flour," *Holzforschung* 68(8), 933-940. DOI 10.1515/hf-2013-0175.
- Eder, A. and Carus, M. (2013). “Global trends in composites (WPC).” *Bioplastics Magazine* 8(4-13),16-17.
- Informa Economics (2013). “National market value of anaerobic digester products,” Prepared for Innovation Center for U.S. Dairy, Chicago, IL. (<http://www.usdairy.com/~media/usd/public/digestermarketpotentialoverview.pdf> as hx), Accessed on 01/21/2016.
- Kiguchi, M., Kataoka, Y., Matsunaga, H., Yamamoto, K., and Evans, P. D. (2007). “Surface deterioration of wood-flour polypropylene composites by weathering trials,” *Journal of Wood Science* 53(3), 234-38. DOI:10.1007/s10086-006-0838-8.

- MacConnell, C., Frear, C., and Liao, W. (2010). "Pretreatment of AD-treated fibrous solids for value-added container media market," CSANR Research Report 2010 – 001 (<http://csanr.wsu.edu/wp-content/uploads/2013/02/CSANR2010-001.Ch06.pdf>), Accessed on 01/21/2016.
- MacLellan, J., Chen, R., Kraemer, R., Zhong, Y., Liu, Y., and Liao, W. (2013). "Anaerobic treatment of lignocellulosic material to co-produce methane and digested fiber for ethanol biorefining," *Bioresource Technology* 130: 418-23. doi:10.1016/j.biortech.2012.12.032.
- Markets and Markets. 2014. "Wood plastic composite market by type (polyethylene, polyvinylchloride, propylene, and others), applications (building and construction products, automotive components, industrial and consumer goods, and others) and region-trends and forecasts (2014-2019)," (<http://www.marketsandmarkets.com/Market-Reports/wood-plastic-composite-market-170450806.html>), Accessed on 01/21/2016.
- Mohanty, A. K., Misra, M., and Drzal, L. T. (2005). *Natural Fibers, Biopolymers, and Biocomposites*, CRC Press, Boca Raton, FL.
- Morrell, J. J., Stark, N. M., Pendleton, D. E., and McDonald, A. G. (2010). "Durability of wood-plastic composites," 10th International Conference on Wood & Biofiber Plastic Composites, 71-76. Madison, WI.
- Panthapulakkal, S., Law, S., and Sain, M. (2006). "Effect of water absorption, freezing and thawing, and photo-aging on flexural properties of extruded HDPE/rice husk composites," *Journal of Applied Polymer Science* 100(5), 3619-3625. DOI:10.1002/app.23152.
- Pelaez-Samaniego, M. R., Yadama, V., Lowell, E., Amidon, T. E., and Chaffee, T. L. (2013a). "Hot water extracted wood fiber for production of wood plastic composites (WPCs)," *Holzforschung* 67(2), 193-200. DOI:10.1515/hf-2012-0071.
- Pelaez-Samaniego, M. R., Yadama, V., Lowell, E., and Espinoza-Herrera, R. (2013b). "A review of wood thermal pretreatments to improve wood composite properties," *Wood Science and Technology* 47(6), 1285-1319. DOI:10.1007/s00226-013-0574-3.
- Pelaez-Samaniego, M. R., Yadama, V., Garcia-Perez, M., and Lowell, E. (2015). "Abundance and characteristics of lignin liquid intermediates in wood (*Pinus ponderosa* Dougl. ex Laws.) during hot water extraction," *Biomass and Bioenergy* 81, 117-28. DOI:10.1016/j.str.2014.12.012.
- Pilarski, J. M., and Matuana, L. M. (2005). "Durability of wood flour-plastic composites exposed to accelerated freeze-thaw cycling. Part I. Rigid PVC matrix," *Journal of Vinyl and Additive Technology* 11(1), 1-8. DOI:10.1002/vnl.20029.
- Qian, Q., Machida, M., and Tatsumoto, H. (2008). "Textural and surface chemical characteristics of activated carbons prepared from cattle manure compost," *Waste Management* 28(6), 1064-71. DOI:10.1016/j.wasman.2007.03.029.
- Rangaraj, S. V., and Smith, L. V. (2000). "Effects of moisture on the durability of a wood/thermoplastic composite," *Journal of Thermoplastic Composite Materials* 13(2), 140-61. DOI:10.1177/089270570001300204.
- Ross, R. J. (ed.) (2010). *Wood Handbook: Wood as an Engineering Material* (General Technical Report FPL-GTR-190), U. S. Department of Agriculture, Forest Products Laboratory, Madison, WI.
- Rowell, R. M., O'Neill, E., Krzysik, A., Bossman, D., and Hemenover, M. (2007). "Incorporation of animal manures as reinforcing fillers in high-density polyethylene and high-density polypropylene composites," in: *9th International Conference on*

- Wood and Biofiber Plastic Composites*, 371-374. Madison, WI: Forest Products Society (http://www.fpl.fs.fed.us/documnts/pdf2007/fpl_2007_rowell003.pdf?) Accessed on May 10 2016.
- Rowell, R. M., O'Neil, E., Krzysik, A., Bossman, A. D., Galloway, D. F., and Hemenover, M. (2008). "Industrial applications of animal manure filled thermoplastics." *Molecular Crystals and Liquid Crystals*, 484: 616-22. DOI 10.1080/15421400801904609.
- Sandoval-Torres, S., Jomaa, W., Marc, F., and Puiggali, J-R. (2010). "Causes of color changes in wood during drying," *Forestry Studies in China* 12(4), 167-175. DOI:10.1007/s11632-010-0404-8.
- Sannigrahi, P., Kim, D. H., Jung, S., and Ragauskas, A. (2011). "Pseudo-lignin and pretreatment chemistry," *Energy and Environmental Science* 4(4), 1306. DOI:10.1039/c0ee00378f.
- Schirp, A., Loge, F. J., Englund, K. R., Wolcott, M. P., Hess, J. R., Houghton, T. P., Lacey, J. A., and Thompson, D. N. (2006). "Pilot-scale production and material properties of extruded straw-plastic composites based on untreated and fungal-treated wheat straw," *Forest Products Journal* 56(10), 90-96.
- Selig, M. J., Viamajala, S., Decker, S. R., Tucker, M. P., Himmel, M. E., and Vinzant, T. B. (2007). "Deposition of lignin droplets produced during dilute acid pretreatment of maize stems retards enzymatic hydrolysis of cellulose," *Biotechnology Progress* 23(6), 1333-39. DOI:10.1021/bp0702018.
- Singh, O. V., and Harvey, S. P. (2010). *Sustainable Biotechnology: Sources of Renewable Energy*, Springer, New York, NY. DOI:10.1007/978-90-481-3295-9_1.
- Slaughter, A. E. (2004). "Design and fatigue of a structural wood-plastic composite," Washington State University. DOI:10.1017/CBO9781107415324.004.
- Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D., and Templeton, D. W. (2010). "Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods," *Journal of Agricultural and Food Chemistry* 58(16), 9043-9053. DOI:10.1021/jf1008023.
- Stark, N. (2001). "Influence of moisture absorption on mechanical properties of wood flour-polypropylene composites," *Journal of Thermoplastic Composite Materials* 14(5), 421-32. DOI:10.1106/UDKY-0403-626E-1H4P.
- Stokke, D. D., Wu, Q., and Han, G. (2014). *Introduction to Wood and Natural Fiber Composites*. Chichester, UK: John Wiley and Sons Ltd.
- Streubel, J. D., Collins, H. P., Tarara, J. M., and Cochran, R. L. (2012). "Biochar produced from anaerobically digested fiber reduces phosphorus in dairy lagoons," *Journal of Environmental Quality* 41(4), 1166-1174. DOI:10.2134/jeq2011.0131.
- Várhegyi, G., Antal, M. J., Jakab, E., and Szabó, P. (1997). "Kinetic modeling of biomass pyrolysis," *Journal of Analytical and Applied Pyrolysis* 42(1), 73-87. DOI:10.1016/S0165-2370(96)00971-0.
- Winandy, J., and Cai, Z. (2008). "Potential of using anaerobically digested bovine," *BioResources* 3, 1244-55.

Yue, Z., Teater, C., MacLellan, J., Liu, Y., and Liao, W. (2011). "Development of a new bioethanol feedstock-anaerobically digested fiber from confined dairy operations using different digestion configurations," *Biomass and Bioenergy* 35(5), 1946-53.
DOI:10.1016/j.biombioe.2011.01.035.

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