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# Characterization of Bio-oils Produced from Fast Pyrolysis of Corn Stalks in an Auger Reactor

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**ABSTRACT:** Corn stalks were converted to bio-oils by fast pyrolysis in an auger fed reactor at 400 and 450 °C. Both acid-pretreated and untreated corn stalks were pyrolyzed. Proximate and ultimate analyses of the corn stalk feeds and bio-oils were performed, and the bio-oils were characterized by gas chromatography/mass spectrometry (GC/MS), gel permeation chromatography (GPC), <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, pH, ash, and viscosity measurements, and solids content and water analyses. Corn stalks have lower lignin content than wood, leading to lower bio-oil yields, more water produced and different chemical compositions than pine wood bio-oil generated in the same auger reactor. Acid pretreatment of stalks increased the bio-oil yields and decreased the char yields at both pyrolysis temperatures. Acid-treated stalks had lower water content, and pH, viscosity, and filterable solid values were lower than those of bio-oil from untreated stalks. Several compounds found in the bio-oil from untreated stalks were not detected in the bio-oil from acid-treated stalks. Thirty two compounds were quantitated in the GC/MS analysis of the two bio-oils. Gel permeation chromatography analysis indicated the presence of a significant fraction of high boiling point compounds that did not pass through the GC columns with bio-oils from both pretreated and untreated stalks. Weight averaged molecular weights of 490 and 530 for acid-treated and untreated stalks, respectively, were indicated by GPC. Portable auger reactors might be used for local production of corn stalk bio-oils during harvest, thereby avoiding the need to transport bulky, low density corn stalk or stover biomass to biorefineries or power generation units.

## 1.0. INTRODUCTION

Resource conservation, petroleum depletion, reduction of both CO<sub>2</sub> emissions and global warming, and generation of value-added products from biomass require the development of technologies to utilize biomass more efficiently. Considerable efforts have been made to convert renewable biomass to liquid fuels and chemicals since the oil crises in the mid-1970s.<sup>1,2</sup> Oil price increases and the accelerated growth rate of energy consumption in Asia, particularly China and India, raises the incentive to develop renewable fuels for all countries. In contrast to fossil fuels, the use of biomass is both renewable and more CO<sub>2</sub> neutral.<sup>3–5</sup> Furthermore, biomass represents, in countries like India or subtropical Africa, about 80% of energy resources (38% on a worldwide scale).<sup>6</sup> Biological and thermochemical conversion are now recognized as the most energy efficient ways to change biomass to fuels.

Fast biomass pyrolysis is a promising route to liquid fuels.<sup>1,7–10</sup> Virtually any form of biomass can be considered for pyrolysis, although most studies have been carried out on wood<sup>1,8,10</sup> due to its density and consistency. The majority of the pyrolysis papers have focused on the relatively new (25 years) field of “fast” or “flash” pyrolysis, which achieves about a 60% organic liquid yield at 400–500 °C with rapid heat transfer rates and short residence times. Fast pyrolysis-derived bio-oil is used as an energy source and for chemical production.<sup>11,12</sup> Fast heat transfer rates and very short vapor residence times in the absence of oxygen provide bio-oils that can be used as alternative fuels or chemical feed stocks.<sup>13–16</sup>

Corn is one of the most widely planted crops in the world. It is estimated that the total yield of corn in 2001 was  $6.1 \times 10^8$  Mt.<sup>17</sup> Corn demand resulting from the production of corn-derived ethanol has significantly increased corn yield since 2001. This demand causes a raising pressure on food costs.<sup>5,18,19</sup> Furthermore, the net CO<sub>2</sub>-lowering benefits and net energy benefits of using corn-derived ethanol are small, and serious doubt exists concerning the actual existence of such benefits.<sup>5,18–31</sup> Therefore, a more rational approach would be to use the corn stalks, leaves and cobs (lignocellulosic compositions) for energy production to increase the overall corn crop value while the kernels would be used for food production.

Graham et al.<sup>28</sup> estimated the total corn stover production in the Northern Iowa/Southern Minnesota region at 7.61 Mg ha<sup>-1</sup> and about two-thirds (5.16 Mg ha<sup>-1</sup>) could be collected in a sustainable manner. The cobs, stalks and leaves are an abundant resource. Therefore, it seems inevitable that the lignocellulosic parts of corn plants should be converted to fuels to enhance the total crop value per acre, while relieving some of the food price inflation pressure. Unfortunately, very little corn cob, stover, etc. is now converted to higher value-added products. Most is discarded as waste or as low-grade fuels.<sup>17,32</sup> For every 100 kg of corn grain, approximately 18 kg of corn cob is produced,<sup>33</sup> and this is only a small fraction of all corn plant biomass. Much of the cob generated remains unused

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as cellulosic wastes in fields and factories, posing a serious disposal/storage problem. This waste can be used as a renewable source for energy production,<sup>32</sup> extraction of xylan used in papermaking, textile printing, and the pharmaceutical industry,<sup>34</sup> production of fermentable hydrolysate,<sup>35</sup> and as carbohydrate source for producing bacterial protein.<sup>36</sup> Activated carbon from corn cobs was made with a BET specific surface area exceeding 1600 m<sup>2</sup>/g.<sup>37,38</sup>

Overall, corn stover is composed of several components with different characteristics.<sup>39</sup> Cobs represent only about 9% of the above ground biomass at physiological maturity while husks, shanks, silks, and cobs account for 30% of the stover mass. Stalks, tassels, leaf blades and leaf sheaths account for the remaining 70% in one study.<sup>40</sup> Pordesimo et al.<sup>41</sup> reported the stover dry mass is 15% cob while stalks (plus leaf sheaths and tassel), leaf blades, and husks (plus shank) accounted for 51%, 21%, and 13%, respectively.

Fast pyrolysis (500 °C and <0.4 s.) of corn stover to give 58% liquid yields was reported by Agblevor<sup>42,43</sup> in a fluidized bed reactor. Pyrolysis enthalpies for Northern Red Oak, Western White Pine, corn stover, and oat hulls were also reported.<sup>44</sup> Dry corn stalk pyrolytic liquefaction was investigated in a semicontinuous apparatus with a nonisothermal fluid extraction technique, both with and without sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) as a catalyst.<sup>45</sup> Corn stover pyrolysis yields and analytical and kinetic studies were reported<sup>46</sup> as were FT-IR studies.<sup>47</sup> Corn stalk and cob pyrolysis studies were conducted in a packed-bed pyrolyzer.<sup>48</sup> Pyrolytic-oil from corn stalk flash pyrolysis in a fluidized-bed reactor contained 27.3% acetic acid, 6.7% esters, 33.5% single ring aromatic compounds, and 1.32% multi-ring aromatic compounds.<sup>49</sup> Fast pyrolysis of corn straw produced up to 45% bio-oil yields.<sup>50</sup> Microwave pyrolysis of corn stover<sup>51</sup> and corn straw pyrolysis in a plasma-heated, laminar entrained flow reactor at a heating rate above 104 °C s<sup>-1</sup> was also reported.<sup>52</sup> Corn stalks were used for energy and carbon production employing rapid high temperature pyrolysis.<sup>53</sup> Bio-oil mass yields of 60% with heating values of ~20 MJ kg<sup>-1</sup>, and densities >1.0 Mg m<sup>-3</sup> were realized from fluidized bed pilot scale fast pyrolysis of both cobs and stover.<sup>54</sup> Corn stover pyrolysis at 400, 500, and 600 °C in a pressurized batch reactor<sup>55</sup> gave maximum biochar and liquid yields at 400 °C. A techno-economic study was conducted to examine the fast pyrolysis of corn stover to bio-oil at the 2000 dry tons/day scale with subsequent upgrading of the bio-oil to naphtha and diesel range fuels.<sup>56</sup> Two scenarios were considered where hydrogen was generated from a portion of the bio-oil or where merchant hydrogen was purchased for the upgrading steps.

This paper examines the characterization of the first bio-oils from both acid-pretreated and untreated corn stalks produced by fast pyrolysis in an auger-fed pyrolysis reactor. This is an extension of our recent characterization of fast pyrolysis of wood and bark species in an auger reactor.<sup>57</sup> Corn bio-oils were characterized by water content, density, acid values, pH, viscosity, solids content, chemical analyses by gas chromatography/mass spectroscopy (GCMS), <sup>1</sup>H and <sup>13</sup>C NMR, and ash and elemental analyses. Bio-oil molecular weight analyses were studied by gel permeation chromatography (GPC). Acid washing of the feed has been used by others to raise liquid yields by reducing the biomass mineral content before pyrolysis.<sup>58–61</sup> Phosphoric acid-treated biomass is known to give enhanced 1,6-anhydrosaccharide yields in fast biomass pyrolysis.<sup>59,60</sup> Furthermore, the acid treatments of corn stalks were considered

as a way to increase the surface area of the biochar that resulted during fast pyrolytic bio-oil production.

Mohan and Pittman have demonstrated that fast pyrolysis biochars are promising adsorbents for water remediation.<sup>62</sup>

## 2.0. EXPERIMENTAL DESIGN

**2.1. Feed Preparation.** Bio-oils were produced by pyrolyzing treated and untreated corn stalks in an auger-fed reactor developed at Mississippi State University.<sup>1,57,63</sup> Corn stalks were collected from the State Farm, Starkville, MS. The stalks were crushed in a Bauer Mill (Bauer Brothers Co.) and densified under a pressure of 550 psi and 166 °C for 4 min using a Clifton Hydraulic press (Clifton Hydraulic Co.). This densified stalk material was crushed again in a Bauer Mill, ground in a Thomas Wiley Laboratory Mill, Model 4 (Arthur H. Thomas Co.), and screened (Universal Vibrating Screen) to a particle diameter of 0.5–5 mm. This particle size promotes fast heat transfer to the centers of the particles, allowing short pyrolysis times. Dry feeding was employed, and in other cases, additional water was added to the stalks to raise the moisture content to 18–20%. This assisted with certain gravity aided feeding modes to the reactor during pyrolysis runs. Another batch of corn stalks was also immersed and blended with 2 wt % aqueous H<sub>2</sub>SO<sub>4</sub> solutions, maintaining a stalk-to-water weight ratio of 1:6 in all the treatments. This mixture was placed in a Buchi water bath B-490 and heated to 100 °C for 1 h. The pretreated feed was then rinsed with water until pH ~7 was reached to avoid residual acid in the feed. Then, the stalks were dried to a 5–6% water content.

**2.2. Pyrolysis in the Auger Reactor.** Pyrolysis reactions of pretreated and untreated corn stalks were conducted at ~1–2.5 kg/h feed rates in a stainless steel proprietary auger reactor. This auger reactor was operated both with and without nitrogen purge gas. No added heat carrier was employed. The auger reactor pipe is 3 in. in diameter and 40 in. in length. A 12 rpm auger speed was applied at a pyrolysis temperature of 400 or 450 °C. The approximate time/temperature exposure profile employed for feed to traverse this reactor has been described previously.<sup>63</sup> The crushed, densified and ground corn stalks were fed to the reactor either dry (5–6% moisture content) or wet (18–20 wt % moisture). In the wet feeding, a substantially higher water content was present than that previously used when wood constituted the biomass feed.<sup>52</sup> Multiple band heaters along the reactor length were employed to supply heat. The feed was preheated to 110–120 °C prior to arrival in the pyrolysis zone to speed heat transfer.<sup>63</sup> Gas residence time in the reactor was calculated to be ~1 to 2 s. Solid feed takes about 30 s to traverse the 450 °C pyrolysis zone and a total of ~50 s to move to the char exit point. The majority of the pyrolysis forming the vapor and aerosol occurs in the first 4–5 s in the pyrolysis zone. Vapors passed into a condenser system to recover several liquid fractions. These auger-fed fast pyrolysis reactions involved longer residence times for the solid and somewhat slower heat transfer rates than occurs in typical fluidized bed reactors.

Bio-oil was collected after the pyrolysis reaction had been continuously generating bio-oil for 40–60 min to ensure steady state conditions had been reached.<sup>57</sup> Pyrolysis produced a mixture of gases, aerosols and some very fine char particles which entered the condensers. Noncondensed gases exited the condenser system at 24–25 °C. Most of the solid biochar was moved through the reactor by the rotating auger to a char removal pot. A total of three reactions were run for the treated and untreated stalks, and the bio-oils from each were combined for each reported analysis summarized in Tables 1–3.

Two basic methods were used to carry out these pyrolysis reactions. Both untreated and acid-treated stalks were soaked with excess water and dried to about 20 wt % water for “wet feeding” (entries 1 and 2 in Tables 2 and 3). These runs did not employ a preheated nitrogen gas purge, and the heating zone was held at 450 °C. The exiting vapors were fractionally condensed to separate a portion of the water from the major bio-oil fraction. These reactions were difficult to use for obtaining reasonable material balances due to viscous bio-oil holdup in the condensers and loss of organics to the separated water fractions. Therefore, a second method was employed for pyrolysis at 450 °C.

**Table 1. Proximate and Ultimate Analyses of Corn Stalks Used in Bio-oil Production**

item	as received	dried
Proximate Analysis (%)		
moisture	5.47	0.00
ash	4.49	4.75
volatile	73.46	77.71
fixed carbon	16.58	17.54
total	100	100
HHV (BTU/lb)	7522	7957
MMF (BTU/lb)	7905	8387
Ultimate Analysis (%)		
carbon	48.72	51.54
hydrogen	5.64	5.96
nitrogen	0.91	0.96
sulfur	0.09	0.10
oxygen	34.68	36.69
total	100	100

Nitrogen was purged throughout the reactions, and the stalks were fed into the reactor without added water (dry fed at 5–6 wt % moisture content). The residence time of the gases and aerosol formed in the reactor was reduced. This was accomplished by a variety of methods, some of which were proprietary. As in fluidized bed reactors, reducing the amount of time that vapors spend at high temperatures in general, and in contact with developing chars, will reduce subsequent unfavorable reactions. The vapors leaving the reactors were condensed and combined as a less viscous single fraction containing all the bio-oil and water (entries 3 and 4, Tables 2 and 3). Good material balances were achieved with these runs.

**2.3. Bio-oil Characterization.** Liquid bio-oils obtained from treated and untreated corn stalk pyrolyses were stored in tightly sealed glass bottles in the dark at 4–5 °C.<sup>64–66</sup> Karl Fischer water analyses showed no changes in water content occurred over 8 months when stored at 4–5 °C. Immediately after production, the bio-oils were stored at 4–5 °C. They were then analyzed within 10 days because multiphase bio-oils can undergo reactions during storage at higher

temperatures. The corn stalk bio-oils were stored at 4–5 °C in sealed bottles that were kept in the dark. GC/MS analyses performed after approximately one year of storage were unchanged from GC/MS analyses performed shortly after bio-oil production. These analyses did not detect any major changes from GC/MS analyses conducted within 10 days of bio-oil production. Bio-oils contained aldehydes, carboxylic acids, hydroxyaldehydes, ketones, phenolics, levoglucosan, mono-, di-, and higher saccharides, etc. Some products are volatile. Lignin fragments are present including syringol and quaiacol structures and their monomeric, dimeric and trimeric analogs. Aging at ambient temperatures or heating typically produces some higher molecular weight compounds. Micro- and macrophase changes and loss of volatiles also can contribute to variations in the oil's chemical and physical properties. Stability of pyrolysis liquids have been previously monitored by following multiple parameters, which were all correlated.<sup>64,66,67</sup>

**2.3.1. Collective Properties: Density, Water Content, Solids, Ash, Acid Value, Heating Value, Elemental Analysis, and pH.** The pyrolysis oil liquid density was determined by picnometry according to ASTM standard.<sup>68</sup> This method is applied to oils that are liquids between 15 and 35 °C. Bio-oil density correlates well with its water content. The water content was determined by Karl Fischer titration.<sup>69,70</sup> Karl Fischer titrations were performed with a Cole-Parmer Model C-25800-10 titration apparatus. The heating values were measured as calorimetric values (higher heating value) in a Parr 1341 oxygen bomb calorimeter (Parr Instrument Co., Moline, IL).

The solids content was determined by the procedure of Oasmaa et al.<sup>71</sup> A Buchner filtration system and preweighed Whatman filter paper were used. Bio-oil (5 g) was dissolved in 100 mL of methanol and filtered. The filter paper was washed with methanol until the filtrate was clear. The solid obtained was oven dried (105 °C) for 1 h and stored in a desiccator prior to being weighed. The weight of the methanol insoluble solids divided by the weight of the bio-oil sample is the fractional solids content.

The acid value was determined by dissolving bio-oil (1 g) in 50/50 isopropanol/water, titrating with 0.1 M NaOH to a pH of 8.5 and calculated as the mg of KOH equivalent to one gram of sample. Bio-oil pH was determined in water. Bio-oil (1.00 g) was stirred with 50 mL of water and the pH of the water recorded using a calibrated model Orion EA 920 pH meter. Viscosities were obtained using both a BrookField model LV-DVI+ viscometer and a TA Instruments Model

**Table 2. Experimental Parameters for Corn Stalks Pyrolysis Runs in an Auger-Fed Reactor<sup>a</sup>**

entry	feed	moisture content (% wt)	feeding rate (kg/h)	pyrolysis temp. (°C)	bio-oil yield (% wt)	char yield (% wt)	gas yield (% wt)
1	untreated <sup>b</sup> (water added)	18–20	~1.0	450	35 <sup>b</sup>	23.5	32 <sup>c</sup>
2	acid-treated <sup>b</sup> (water added)	18–20	~1.0	450	46 <sup>b</sup>	20.4	23 <sup>c</sup>
3	untreated <sup>d</sup> (fed dry)	5–6	~2.5	400	35 <sup>d</sup>	29	13.5 <sup>e</sup>
4	acid-treated <sup>d</sup> (fed dry)	5–6	~1.8	400	51 <sup>d</sup>	23	4.4 <sup>e</sup>

<sup>a</sup>The ground and pressed stalk particle feed diameters were 0.5–5.0 mm. A nitrogen purge of 1.2 scfm was used in entries 3 and 4. <sup>b</sup>Bio-oil was collected by fractional condensation in a condenser train that separated a water fraction containing some organics. Bio-oil still contained significant amounts of water. <sup>c</sup>Estimated by difference, considering hold-up losses in condensers and organics lost to water fractions. <sup>d</sup>All condensables were collected as one fraction (water and bio-oil) to aid material balance determinations. The gas/aerosol residence time was kept to a minimum. The gas flow rates to the condensers were 19 L min<sup>-1</sup> for entry 3 and 13 L min<sup>-1</sup> for entry 4. <sup>e</sup>Directly measured. The untreated stalk pyrolysis gas contained 0.38% methane, 5.93% CO, 12.35% CO<sub>2</sub> and 66.27% nitrogen. The acid-treated stalk pyrolysis gas contained 0.11% methane, 1.31% CO, 4.69% CO<sub>2</sub>, and 75.81% nitrogen. No hydrogen or ethane was detected in either gas. Other components likely included oxygen.

**Table 3. Water Content, Acid Value, pH, Density, Percent Solids, and Viscosity of Each Bio-Oil Generated from Acid-Treated and Untreated Corn Stalks**

entry	feed	pyrolysis temp. (°C)	water content (% wt)	density (g/cm <sup>3</sup> )	acid value	pH	viscosity (cSt)	filterable solids (% wt)
1	untreated (water added)	450	27	1.17	81.7	3.29	41.4	2.25
2	acid-treated (water added)	450	21	1.18	87.8	3.09	50.6	1.42
3	untreated <sup>a</sup> (fed dry)	400	54.7	1.08	85.8	2.66	1.60	0.66
4	acid-treated <sup>a</sup> (fed dry)	400	41.6	1.17	72.2	2.87	3.31	0.70

<sup>a</sup>Elemental analysis untreated stalk bio-oil: 19.05% C, 9.31% H, 0.17% N, 71.46% remaining. Acid-treated stalk bio-oil: 24.88% C, 5.33% H, 0% N, 69.79% remaining. These analyses include the water present in the oil.



1000N rheometer. All viscosities were kinematic viscosities, obtained at 40 °C according to ASTM D445.<sup>72</sup>

**2.3.2. Gas Chromatography/Mass Spectrometry (GC/MS) Analysis.** Calibration standards were obtained from Sigma-Aldrich and used without further purification. Concentrated stock solutions were prepared by weighing 0.1 g of each individual compound to the nearest 0.1 mg, dissolving these standards in 2 mL of methanol, and quantitatively transferring each solution to a 100 mL volumetric flask. These solutions were diluted to 100 mL with dichloromethane. Aliquots of the 1000 µg/mL stock solutions were then diluted to concentrations of 20, 50, 80, 120, and 160 µg/mL in dichloromethane.

A commercial (US-108N, Ultra Scientific) mixture of six isotopically labeled compounds, consisting of 1,4-dichlorobenzene-*d*<sub>4</sub>, naphthalene-*d*<sub>8</sub>, acenaphthene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, chrysene-*d*<sub>12</sub>, and perylene-*d*<sub>12</sub>, at a concentration of 4000 µg/mL was used as an internal standard. The internal standard solution (10 µL) was spiked into each working standard to calculate a response factor over a five-point concentration range for each compound of interest.<sup>57</sup>

The GC/MS analysis of the pyrolysis oil from the untreated and treated corn stalks was performed with a Hewlett-Packard HP 5890-Series gas chromatograph equipped with a Hewlett-Packard HP 5971 series mass detector (MS). A representative sample (0.2 g) of each bio-oil was weighed to the nearest 0.1 mg and diluted to 10.00 mL with methanol. 1 mL of this solution was transferred to an autosampler vial and spiked with 10 µg/mL (ppm) internal standard just prior to analysis. A 1.00 µL volume of the diluted sample was injected into a fused silica capillary column coated with 5% phenylmethylpolysiloxane (DB 5, J&W Scientific) with dimensions of (30 mL × 0.32 mm ID × 0.25 µm film thickness). The initial oven temperature of the GC was 40 °C for 4 min, and the temperature was then programmed at a rate of 5 °C/min to 270 °C and held at 270 °C for 15 min. The injector and detector temperatures were 270 and 250 °C, respectively; the carrier gas was He of 99.99% purity. The *m/z* values, which represent the fragment ions of the compounds, were recorded for each compound. Full scan mass spectra were acquired from a 35 to 550 *m/z* at a scan rate of 0.2 s per scan, with an interscan delay of 0.1 s. The total time for each injection run was 67 min.

The mass spectrometer was configured for electron impact ionization at 70 eV, with an interface temperature of 225 °C and a source temperature of 210 °C. Prior to analysis, the spectrometer was mass-calibrated and abundance-tuned using heptacosfluorotributylamine CAS [311-89-7]. Full scan data were acquired and processed using Perkin-Elmer Turbomass software (2005 version 5.1.0.0944). Peak areas of the characteristic ions, usually the base peak, for the compounds of interest and a selected internal standard were used to calculate a response factor for each target compound.

A representative sample (0.2 g) of each bio-oil was weighed to the nearest 0.1 mg and diluted to 10.0 mL with dichloromethane. 1 mL of this solution was transferred to an autosampler vial and spiked with 10 µL of a 4000 µg/mL (ppm) internal standard just prior to analysis. A 2.00 µL injection was used to acquire GC/MS peak area data as described for the calibration standards. The concentrations in samples were determined by comparing the integrated peak areas of characteristic ions to responses generated with the working standards.

A list of target compounds for quantitative determination was compiled from previously published literature and from initial GC/MS analysis of bio-oil, followed by the qualitative identification based on mass spectral library matches.

**2.3.3. Nuclear Magnetic Resonance Analysis.** <sup>13</sup>C NMR spectra of whole bio-oils obtained at 450 °C from both treated and untreated corn stalks were recorded in DMSO-*d*<sub>6</sub> solutions at 600.13 MHz and 60 °C using a Bruker AMX-600 spectrometer. <sup>1</sup>H NMR spectra were also obtained on this Bruker AMX-600 600-MHz spectrometer with *z*-gradient, inverse, and heteronuclear capabilities, respectively. 18–20 wt % solutions of bio-oil were employed. About 105 scans were accumulated for each sample <sup>13</sup>C spectrum using a 90°-pulse width together with broadband proton decoupling using 5 mm diameter tubes. Inverse gated decoupling was applied to void Nuclear Overhauser Effect (NOE) effects in the <sup>13</sup>C spectra. Tip angles of 45° for <sup>1</sup>H and 30° for <sup>13</sup>C were used.

The integrated <sup>13</sup>C spectra were divided into five general chemical shift ranges for analysis: 215–163 ppm (carbonyl carbons), 163–110 ppm (total aromatic carbons), 110–84 ppm (carbohydrate-type carbons), 84–54 ppm (methoxy- or hydroxy-bound carbons), 54–1 ppm (primary, secondary, tertiary, and most quaternary alkyl carbons). The aromatic region was further subdivided into 125–112 ppm (guaiacyl carbons) and 112–110 ppm (syringyl carbons). The alkyl region was also subdivided into 34–24 ppm (mostly secondary and tertiary carbons) and 24–6 ppm (most primary and some secondary carbons). These areas were also selected because the integral curves were flat at each of these breaks, facilitating more precise measurements, allowing accurate integrations as a fraction of the total carbons present. This protocol is similar to that developed by Bozell at the National Renewable Energy Laboratories<sup>73</sup> and McKinley at B.C. Research.<sup>74</sup> These assignments are also consistent with the bio-oil and model compound studies reported by Breitmaier and Voelter.<sup>75</sup> <sup>1</sup>H NMR spectral integrations were divided into the following ranges: 10.0–8.0 ppm, 8.0–6.8 ppm, 6.8–6.4 ppm, 6.4–4.2 ppm, 4.2–3.0 ppm, 3.0–2.2 ppm, 2.2–1.6 ppm, and 1.6–0.0 ppm.<sup>57</sup> An excellent in-depth use of <sup>1</sup>H and <sup>13</sup>C NMR to characterize biomass pyrolysis oils from several sources including corn stover has been reported.<sup>76</sup>

**2.3.4. Gel Permeation Chromatography Analysis (GPC).** Six polystyrene standards with peak molecular weights of 2900, 1990, 1200, 1050, 580, and 162 were used for molecular weight calibration. Each standard (0.5 g) was weighed (analytical balance) into a beaker (50 mL), dissolved in tetrahydrofuran (THF), quantitatively transferred to a Class-A 10 mL volumetric flask, and diluted to volume. Standards were filtered through a 0.45 µm Millex syringe driven filter unit into a 4 mL vial, and capped for analysis.

Homogeneous bio-oil samples (from treated and untreated corn stalk oils pyrolyzed at 450 °C) were each weighed (~0.3 g) in a beaker (50 mL), dissolved in THF, quantitatively transferred to a 50 mL volumetric flask, and diluted to volume. All samples were filtered through a 0.45 µm Millex syringe driven filter unit into a 4 mL vial and capped for analysis. GPC analyses were performed on a Waters HPLC (high pressure liquid chromatography) system, consisting of a Waters 600E system controller and a Waters 410 differential refractometer. Approximately 80 µL aliquots of each standard and sample were individually flushed through a 20 µL sample loop and injected for analysis. A Varian Polymer Laboratories Plgel 3 µm, 100 Å, 300 mm × 7.5 mm analytical column and a 100% THF mobile phase with a flow rate of 1 mL/min were employed. The total sample run time was 16 min. Data was acquired and processed using PC-based Viscotek GPC Software, Version 2.61.

### 3.0. RESULTS AND DISCUSSION

**3.1. Corn Stalk General Properties.** Proximate and ultimate analyses of the corn stalks used for bio-oil production are reported in Table 1. The bulk density of corn stalk was 0.26 g/cm<sup>3</sup>. Lignin expressed as Klason lignin was 18.1 wt %. Holocellulose, estimated according to the method of Wise et al.,<sup>77</sup> was 70.00 wt %. Carbon, hydrogen, nitrogen, sulfur, ash, oxygen, determined on as-received dry and air-dried stalks, are also reported in Table 1. This lignin content of corn stalks is far lower than the lignin content of softwoods, which typically range from 26 to 37%.<sup>78</sup>

**3.2. Corn Stalks Pyrolyses.** Bio-oil yields and compositions are sensitive to processing conditions. Scott and co-workers<sup>79</sup> demonstrated that alkali and alkaline earth cations in the biomass serve as catalysts that promote lignocellulose degradation to char. Removal or reduction in amount of these cations by soaking in dilute acid before fast pyrolysis enhances anhydrosugar yields from lignocellulose. Anhydrosugars can be a platform for chemical synthesis or a substrate for fermentation. Brown and co-workers evaluated the effect of alkali removal on the pyrolytic products of herbaceous biomass.<sup>80</sup> Similarly, biomass pretreated with phosphoric acid prior to fast

**Table 4. GC/MS Analysis of 32 Quantitated Compounds in the Bio-oils Produced by Fast Pyrolysis of Acid-Pretreated and Untreated Corn Stalks at 450 °C<sup>a</sup>**

quantitated compounds in whole bio-oils	retention time (min)	quantitation ion ( <i>m/z</i> )	concn (wt %)	
			acid-pretreated stalks	untreated stalks
furfural	4.19	96	1.60	0.70
furfuryl alcohol	5.00	98	0.04	0.06
2-methyl-2-cyclopentenone	6.39	96	0.07	0.08
2 (5H)-furanone	6.70	84	0.67	0.41
5-methylfurfural	8.34	110	3.69	2.59
3-methyl-2-cyclopentenone	8.35	96	0.11	0.12
phenol	9.38	94	0.94	0.83
3-methyl-1,2-cyclopentanedione	10.58	112	0.35	0.42
2-methylphenol	11.63	108	0.24	0.28
3-methylphenol	12.33	108	0.61	0.59
2-methoxyphenol	12.49	124	0.19	0.21
2,6-dimethylphenol	13.07	122	0.02	0.03
2,4-dimethylphenol	14.51	122	0.11	0.14
3-ethylphenol	15.10	122	0.35	0.44
2,3-dimethylphenol	15.37	122	0.04	0.04
naphthalene	15.19	128	0.03	0.06
2-methoxy-4-methylphenol (4-methylguaicol)	15.68	138	0.17	0.19
1,2-benzenediol	15.68	110	0.41	1.42

quantitated compounds in whole bio-oils	retention time (min)	quantitation ion ( <i>m/z</i> )	concn (wt %)	
			acid-pretreated stalks	untreated stalks
4-methyl-1,2-benzenediol	18.02	124	0.10	0.16
4-ethyl-2-methoxyphenol (4-ethylguaicol)	18.17	137	0.05	0.07
3-methyl-1,2-benzenediol	18.90	124	1.02	0.89
2,6-dimethoxyphenol	20.19	154	0.13	0.14
eugenol	20.31	164	0.03	0.05
2-methoxy-4-propylphenol	20.57	137	0.01	0.01
vanillin	21.44	151	0.29	0.33
<i>cis</i> -isoeugenol	21.64	164	0.03	0.04
3,4-dimethylbenzoic acid	22.69	105	0.09	0.14
<i>trans</i> -isoeugenol	22.70	164	0.07	0.13
4-ethylbenzenediol	22.42	123	0.01	0.02
levoglucosan and other anhydrosugars <sup>a</sup>	24.25 <sup>a</sup>	60	32.2	16.4
acetovanillone	23.65	166	0.07	0.06
oleic acid	37.29	55	0.08	0.59
total wt % of the injected bio-oil from all 32 of these cmpds (approximation; see text)			43.83	27.65

<sup>a</sup>The levoglucosan peak was broad, and it merged with (and was overlapped by) some other anhydrosugar peaks. Thus, the entire area of this peak group was taken, and the concentration was approximated by using the levoglucosan ion current quantitation for the entire peak region. Compounds not quantitated in the table above that have been identified in all four bio-oils include: acetic acid, 5-methylfurfural, 1-hydroxy-2-propanone, 2,3-dihydrobenzofuran, 2-methoxy-4-vinylphenol, 1,6-anhydro- $\beta$ -D-glucopyranose, hexadecanoic acid, octadecenoic acids (6 and 9), 2-methylimino-perhydro-1,3-oxazine, 4-methylphenol, 3,4-dimethylphenol, and 2-methoxy-4-(1-propenyl)phenol (e.g., 4-(1-propenyl)guaicol). Compounds identified in untreated cornstalk bio-oil but not found in acid-treated corn stalk bio-oil formed at 450 °C include: methylglyoxal, 4-propylphenol, 2-propylphenol, abietic acid, 2-hydroxy-3-methyl-2-cyclopenten-1-one, 1-hydroxy-2-butanone, butyrolactone, 2,5-furandione, 5-methyl-2,5-furandione, 1,2-propadienylbenzene, 4-ethyl-2-methoxyphenol, indene, 2-methoxy-4-(1-propenyl)phenol, and 3,4,4'-trimethoxy-6'-methyl-1,1'-biphenyl, 1-nonadecene, hexadecanoic acid. Samples of acid-pretreated and untreated stalk bio-oils formed at 400 °C were also examined by GC/MS and gave similar results. About three times more anhydrosugars appeared in the MS for the acid-pretreated samples (versus twice as much for the sample formed at 450 °C). At the lower pyrolysis temperature, chemical differences in the bio-oils would be expected. The relative formation of the following compounds dropped sharply upon lowering the pyrolysis temperature from 450 to 400 °C in both acid-pretreated and untreated samples: furfural 2(SH)-furanone, 5-methylfurfural, 3-methylphenol, 3-ethylphenol, 1,2-benzenediol, 3-methyl-1,2-benzenediol, vanillin, and oleic acid. Conversely, the relative amounts of 3-methyl-1,2-cyclopentanedione, 2-methoxyphenol, and 3-ethylphenol increased upon lowering the pyrolysis temperature to 400 °C for both acid-treated and untreated samples. Many other compounds were only tentatively identified in both of the bio-oils, and the confidence level in these assignments was not high enough to list here.

pyrolysis gave increased liquid yields and less char production.<sup>59</sup> Therefore, acid-treated and untreated corn stalks were separately pyrolyzed at both 400 and 450 °C in the auger reactor in our work. The feeding rate was ~1–2.5 kg/h, with particle diameters of 0.5–5.0 mm (Table 2).

Bio-oil, char, and gas yields for treated and untreated corn stalks are reported in Table 2. Acid treatment of corn stalks increased the bio-oil yields and decreased the char yields in both 400 and 450 °C pyrolyses runs. Thus, corn stalk bio-oil yields can be increased by acid treating before fast pyrolysis. The bio-oil obtained from acid-treated stalks contained less water at both temperatures providing increased organic content in the bio-oil. Similar results were reported earlier for cellulose fast pyrolysis where acid treatment was carried out before thermochemical conversion into bio-oil.<sup>59,60</sup>


**3.3. Collective Properties: Density, Water Content, Solids, Ash, Acid Value, Heating Value, Elemental Analysis, pH, and Viscosity.** Acid pretreatment removes a significant fraction of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> salts from the stalks prior to pyrolysis. Lowering the salt content lowers the weight of char produced. These salts may play a role in

**Table 5. <sup>13</sup>C NMR Integrations of Specific Chemical Shift Regions of Whole Corn Stalk Bio-oils Formed at 450 °C Compared to Pine Wood Bio-oil<sup>a</sup>**

type of carbon	chemical shift region (ppm)	carbon content (% of all carbon in each spectrum)		
		acid-treated corn stalks oil	untreated corn stalks oil	pine wood oil <sup>b,57</sup>
carbonyl	215–163	18.5	19.6	11.8
aromatic	163–110	29.9	38.0	48.4
carbohydrate	110–84	5.9	2.2	5.8
methoxy/hydroxy	84–54	26.5	19.3	16.1
Alkyl carbons	54–1	19.2	20.9	17.9
	34–24	3.9	0	8.5
	24–6	15.3	20.9	9.4

<sup>a</sup>Spectra were obtained at 60 °C in DMSO-*d*<sub>6</sub> at 600.13 MHz at 60 °C on a Bruker AMX 600 spectrometer using inverse gated decoupling to avoid NOE effects. <sup>b</sup>Pine wood bio-oil at 450 °C was prepared in the same auger reactor by a similar procedure at the same 450 °C temperature.

Table 6.  $^1\text{H}$  NMR Integrations of the Whole Corn Stalk Bio-oils Formed at 450 °C versus Specific Chemical Shift Ranges<sup>a</sup>

Chemical shift region (ppm)	Type of protons	Hydrogen content (% of all hydrogen)		
		Acid-treated Corn Stalks oil	Untreated Corn Stalks oil	Pine wood oil <sup>b,57</sup>
10.0–8.0	-CHO, -COOH, downfield ArH	5.49	2.36	2.63
8.0–6.8	ArH, HC=C (conjugated)	12.35	13.32	4.35
6.8–6.4	HC=C (nonconjugated)	0.95	0.98	5.30
6.4–4.2	-CHO, ArOH, HC=C (nonconjugated)	17.61	12.07	16.54
4.2–3.0	CH <sub>3</sub> O-, -CH <sub>2</sub> O-, -CHO	24.68	17.44	37.56
3.0–2.2	 CH <sub>3</sub> C-, CH <sub>3</sub> -Ar, -CH <sub>2</sub> Ar	22.16	22.48	9.04
2.2–1.6	-CH <sub>2</sub> -, aliphatic OH	10.25	16.59	13.69
1.6–0.0	-CH <sub>3</sub> -, -CH <sub>2</sub> -	6.58	15.26	10.88

<sup>a</sup>No resonances were observed for either sample between 13.5 to 10.7 ppm. The chemical shift regions for some classes of protons overlap somewhat the OH protons from water, alcohols, and carboxylic acids. These values are pH-dependent and can be found over a wide range. -CO<sub>2</sub>H protons can exist from 13 to 10 ppm, phenolic protons from 8.0 to 4.0 ppm and water, hydroxyaldehyde, hydroxyketone, and alcohol can vary widely with pH. The pH values of the bio-oil samples before dissolution in DMSO-d<sub>6</sub> were 2.8–3.0, but the actual pH in the DMSO-d<sub>6</sub> solutions was not measured. <sup>b</sup>Pine wood bio-oil was prepared in the same auger reactor at 450 °C by a similar procedure.

catalyzing dehydration reactions of cellulose and hemicelluloses in the 350–500 °C temperature region. However, any detailed explanation is not warranted at this time.

Various collective properties including density, water content, pH, acid value, viscosity and filterable solids are presented in Table 3. Bio-oil from acid-treated corn stalks had a lower water content than bio-oil from untreated corn stalks. This can be most clearly illustrated by entries 3 and 4 in Table 3, where all the condensate was collected as a single fraction. Acid-treated stalks gave a 51% yield of which 41.6% was water, corresponding to a 29.8 wt % yield of organic chemical components. Untreated stalks gave a 35% yield of condensed product of which 54.7% was water. Thus, the yield of organic compounds in this bio-oil was only 15.9 wt %. Bio-oil obtained from acid-treated corn stalks had a modestly lower acid value (72.2 compared to 85.8) than bio-oil generated from untreated stalks at 400 °C. At 450 °C the acid-treated stalks had a larger acid value. Bio-oil from treated corn stalks contained less filterable solid. pH values from acid-treated corn stalks were lower than those from untreated stalks for the bio-oils produced at both temperatures. Kinematic viscosities of bio-oil are sharply dependent on their water content, as seen in Table 3. As the water content was raised from 27% for untreated bio-oil made at 450 °C to 54.7% for bio-oil made at 400 °C, the viscosity dropped from 41.4 to 1.60 cSt. A similar drop was seen for the acid-treated bio-oils. While the oil compositions are dependent on pyrolysis temperature, the percent water is by far the major factor in these observed viscosity changes. These oils have low heating values due to the substantial amounts of water present. Their heating values are calculated by two different methods in Table 8, both with and without water present.

**3.4. Gas Chromatography/Mass Spectrometry (GC/MS) Analysis of Bio-oils.** Approximately  $1/4$  of the identified compounds found in the bio-oil samples were furfural or glucose derivatives formed by dehydration of glucose or the monosaccharides that occur in hemicellulose. Unidentified anhydrosugars and their decomposition products were also present. Many of the compounds observed by GC/MS in corn stalk oils reported here were also seen in wood bio-oils.<sup>1,57</sup> Representative examples include acetic acid, hydroxyacetaldehyde, acetal, ethyl acetate, 1-hydroxy-2-butanone, 5-hydrox-

ymethylfurfural, levoglucosan, 2-methoxyphenol, 1,2-benzenediol, eugenol, and oleic acid. Substantial amounts of acetic acid, formic acid, and hydroxyacetone are produced but appear near or under the solvent peak and the carboxylic acids appear as somewhat broadened peaks, making quantification less accurate.

Corn stalk bio-oils also contained phenolic structures derived from its lignin content. Phenyl rings with only one methoxy group predominated. These are guaiacyl lignin components. 4-Methylguaiacol, 4-ethylguaiacol, 4-(1-propenyl)guaiacol, vanillin, and both *cis*- and *trans*-isoeugenol were most abundant (all shown in Table 4). Methylphenols and dimethylphenols were also observed. Phenol was the most abundant phenolic compound present, occurring at concentrations close to 1% for untreated and treated corn stalks. Smaller amounts of dimethoxyphenols originating from syringyl lignin components were observed in bio-oils from both treated and untreated stalks.

The 32 compounds in Table 4 were quantitated. However, they represent only a fraction of all the peaks observed and only a portion of those identified, but not quantitated, by GC/MS. Other compounds identified in these two bio-oils are listed in a footnote. The sum of the 32 quantitated compounds in Table 4 represented an estimated 43.8 and 27.7% by weight of the acid-treated and untreated corn stalk bio-oils, respectively, formed at 450 °C. This corresponds to about 55 and 38% by wt of the organic compounds' mass in these oils, respectively, when compensating for the water present in each sample. The weight percent values of 31 of the 32 quantitated compounds listed in Table 4 are considered accurate. However, the broadened levoglucosan peak blended into, and was overlapped by, that of other anhydrosugars. This peak grouping ran from retention times of 24.2 to 26.8 min for the acid-pretreated stalk bio-oil sample and from 23.9 to 25.5 min for the untreated stalk bio-oil sample. By examining the full mass spectral fragmentation patterns throughout these regions, it was clear that both levoglucosan and other related anhydrosugars constituted the compounds in this region.

To estimate the weight percent of the injected bio-oils that these "levoglucosan" regions represented, the integrated areas of these regions were assumed to have levoglucosan's ion



**Table 7. Molecular Weight Analysis of Corn Stalk Bio-oils, Prepared at 450 °C, by Gel Permeation Chromatography (GPC) in Tetrahydrofuran<sup>a</sup>**

feed stock	$M_w$	$M_n$	$M_p$	$M_w/M_n$
treated corn stalks	490	280	220	1.75
untreated corn stalks	530	290	250	1.83

<sup>a</sup>Where  $M_w$  is the weight-averaged molecular weight,  $M_n$  is the number-averaged molecular weight

current quantitation. This approximation gave wt percentages of 32.2% and 16.4% for the acid-pretreated and untreated stalk bio-oils, respectively. All the remaining 32 compounds constituted only 11 to 12% wt. of the two bio-oil samples (considered reasonably accurate). However, the levoglucosan anhydrosugar region quantitations are only crude estimates. Since these estimated regions represent significantly more of the bio-oils' mass than all of the other 32 of the compounds, the total percent by weights of the two injected samples (mentioned above) made up by all 33 compounds is only an approximation. However, it is clear that acid pretreatment of the stalks promoted anhydrosugar formation in the bio-oil isolated at both 450 and 400 °C.

Oleic acid was observed in bio-oil samples from both feeds (Table 4). Oleic acid originated from a triglyceride extractive component, known to occur in hardwoods and softwoods. A major difference in the product distributions, versus those from wood, was the absence of 2,6-dimethoxyphenol in the bio-oil from acid-treated corn stalks. GC/MS analysis of the bio-oils showed these and other changes in the relative product distributions caused by acid pretreatment (Table 4).

The quantitated compounds plus other unidentified peaks from GC/MS in total, still represent only a portion of the total bio-oil. The highest molecular weight species (dimer, trimer, and oligomeric cellulose/hemicellulose and lignin pyrolysis products) would not get through the injector and GC-column. It is likely that 20 to 30 wt % of the bio-oil contents could be higher molecular weight compounds. This concurs with the GPC analysis discussed below.

### 3.5. Gel Permeation Chromatography Analysis (GPC).

The weight-averaged molecular weights ( $M_w$ ) for the bio-oils obtained from treated and untreated corn stalks were 490 and 530, respectively, while the number averaged molecular weights ( $M_n$ ) were 280 and 290. Thus, the molecular weight was slightly higher for the bio-oil from untreated corn stalks. The polydispersities ( $PD = M_w/M_n$ ) were 1.75 and 1.83 for the bio-oils obtained from treated and untreated corn stalks, respectively. These weight-averaged molecular weights are substantially higher than any of the compounds identified by GC/MS (Table 4) such as oleic acid (280), 4-propylquiocol (166), or 5-methylfurfural (110). Even if the GPC molecular weight data has error biased in the high molecular weight direction, it is obvious that dimeric and oligomeric remnants of cellulose and lignin decompositions are present, which do not pass through the GC column. These products form during incomplete pyrolytic degradation to monomeric components and make up part of the aerosol swept into the condensers. This fraction can be greatly reduced with proprietary changes to the reactors.

### 3.6. <sup>13</sup>C and <sup>1</sup>H Nuclear Magnetic Resonance Analysis.

NMR analysis examines the entire bio-oil sample, unlike GC/MS, which can only identify components that can pass through the GC column to the MS detector. Therefore, any direct comparison of

**Table 8. Percent Ash, Elemental Analysis, and BTU Content of Composite Bio-oil Samples from Treated and Untreated Corn Stalks Feed Stocks<sup>a</sup>**

properties	acid-treated corn stalks bio-oil formed at 450 °C	acid-treated corn stalks bio-oil formed at 400 °C	untreated corn stalks bio-oil formed at 450 °C	untreated corn stalks bio-oil formed at 400 °C
water (wt %) <sup>b</sup>	21.0	41.6	27.3	54.7
carbon (wt %)	43.17	24.88	51.59	19.05
hydrogen (wt %)	7.03	8.63	7.19	9.31
nitrogen (wt %)	<0.6	0	<0.5	0.17
sulfur (wt %)	0.35		0.12	
ash (wt %)	0.19		0.26	
heat value (BTU/lb)	7310 <sup>c</sup>	3807 <sup>d</sup>	9191 <sup>c</sup>	3007 <sup>d</sup>
heat value calcd with 0% H <sub>2</sub> O (Btu/lb)	10 050 <sup>d,e</sup>	6534 <sup>d,e</sup>	11 110 <sup>d,e</sup>	7482 <sup>d,e</sup>
heat value (BTU/lb)	7878 <sup>f</sup>	5150 <sup>f</sup>	9597 <sup>f</sup>	4397 <sup>f</sup>
heat value calcd with 0% H <sub>2</sub> O (Btu/lb)	9527 <sup>g</sup>	7624 <sup>g</sup>	12,548 <sup>g</sup>	7682 <sup>g</sup>
fixed carbon (by diff)	5.65		6.47	
volatile matter	66.88		75.98	

<sup>a</sup>These analyses give the wt % found in the whole bio-oil produced at 450 °C in the auger reactor, including the water contents. <sup>b</sup>The amounts of water reported here were produced using identical condensing conditions but small feed rate changes can vary the efficiency of water removal from the bulk of the bio-oil. The amounts of water in these bio-oils could be equalized by appropriate condenser and feed ratio settings. <sup>c</sup>Determined by oxygen bomb calorimetry for bio-oil samples made at 450 °C. <sup>d</sup>Values for bio-oils made at 400 °C were calculated from elemental analyses using the Dulong equation.<sup>83</sup> HHV (Btu/lb) = 14 544 × (C wt fraction) + 62 028 × (H wt fraction – O wt fraction/8) + 4050 × (S wt fraction), with 54.7% (untreated) and 41.6% (treated) water present. <sup>e</sup>The values were calculated from elemental analyses as per the Dulong's equation in footnote d. These values are extremely sensitive to the weight fraction of hydrogen and should be considered as approximations. As water content increases and is subtracted to give the bases for these calculations, sensitivity to errors in hydrogen analyses is substantial. The calculated heating values for oils with 0% water (HHV) for the two bio-oils made at 400 °C are probably lower than the true values. Given all the possible errors that enter these calculations, we would estimate that the HHVs for all four oils are likely between 8000 and 10 500 Btu/Lb. <sup>f</sup>Values for bio-oils made at 400 and 450 °C were calculated from elemental analyses using the equation given by Channiwalla and Parikh specifically designed for biomass fuels.<sup>84</sup> HHV(MJ/kg) = 0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0151N – 0.0211A, where C, H, O, N, S, and A represent carbon, hydrogen, oxygen, nitrogen, sulfur, and ash contents of material, respectively, expressed as mass percent on a dry basis. Further conversion to Btu/kg was achieved using the conversion factor: 1 MJ/kg = 429.92 Btu/lb. <sup>g</sup>These values were calculated using the Channiwalla and Parikh equation (footnote f) employing the elemental composition of each bio-oil sample computed after removing the water contents that are given in the first row of data in this table. Again these values are extremely sensitive to the weight fraction of hydrogen and should be considered as approximations.

the GC/MS analysis with either <sup>13</sup>C or <sup>1</sup>H NMR spectra could be misleading since a fraction of all the bio-oil samples are not represented in GC/MS output data. Both acid-pretreated and untreated corn stalks produced bio-oils with a lower aromatic content than that of pine wood bio-oil produced in the same reactor at 450 °C under similar conditions (see Tables 5 and 6). This is evident in the 163–110 ppm region of the <sup>13</sup>C spectra and in the greater methoxy content in the 4.2–3.0 ppm range of the <sup>1</sup>H spectra. This likely reflects the higher lignin content (27–29%) in pine wood<sup>78</sup> than in corn stalks, which exhibited



only 18% lignin. Differing amounts of water in each bio-oil sample represented in Tables 5 and 6 do not distort the NMR analyses because the spectra were obtained with water suppression.

A major effect of acid pretreatment on the chemical composition of the bio-oils was observed. Acid pretreatment produced corn stalk bio-oil with more than twice the aldehyde and carboxylic acid content of bio-oil from the untreated stalks, which had amounts of these compounds similar to pine wood bio-oil.<sup>57</sup> Both corn stalk bio-oils have substantial contributions from vinyl protons on the  $\beta$ -carbon of  $\alpha,\beta$ -unsaturated acids, aldehydes, and ketones. This contribution greatly enhances the  $^1\text{H}$  integrations between 8.0 and 6.8 ppm, a region that also includes aromatic protons. The acid-treated stalk bio-oil exhibits a substantially higher fraction of protons with chemical shifts from 6.8 to 2.2 ppm (64.5%) than the untreated stalk bio-oil (52.0%). This indicates that a greater portion of the total products from corn stalk pyrolysis originates from cellulose and hemicelluloses. Lignin-derived methoxy groups and benzylic protons also occur in this region, but untreated stalk bio-oil has a higher aromatic carbon content ( $^{13}\text{C}$  163–110 region) than the acid-treated stalk oil. Thus, the clearly greater fraction of protons from 6.8 to 2.2 ppm in the acid-treated sample can only mean that a higher fraction of cellulose/hemicelluloses decomposition products appear in the bio-oil from the stalks that had been pretreated with acid. This suggests that acid treatment, which removes alkali and alkaline metal cations, enhances the cellulose pyrolytic cleavage/decomposition rates to volatile products. This is also in accord with the higher fraction of aliphatic protons in the bio-oil from the untreated stalks. If both samples produced the same absolute amounts of products with aliphatic regions, the higher yields of cellulosic volatile decomposition products from acid-pretreated stalks would lower that sample's fraction of aliphatic contents. At a higher heat-transfer rate (fluidized bed reactor), this product distribution difference may no longer occur. However, at the lower heat-transfer rates used (versus most fluidized bed reactions) in the 450 °C auger reactor runs, acid pretreatment may beneficially enhance cellulose fragmentation relative to that in untreated stalks. Perhaps, this is why the molecular weight of the acid-treated stalk bio-oil (Table 7) was somewhat lower than that from untreated stalks. While these bio-oil samples were not studied by NMR, their GC/MS analyses were similar, suggesting the chemical compositions are dominated by the low lignin content of the stalks.

## CONCLUSIONS

Acid washing biomass is a method to enhance fast pyrolysis liquid yields from corn stalks. Sulfuric acid-treated corn stalks gave increased liquid yields because alkali and alkaline metal cation content in the biomass was reduced prior to pyrolysis. Compaction of the stalks into pellets is needed for smooth feeding. These factors cause changes in product distribution. In general, the corn stalk bio-oils are formed with higher water contents than those formed from wood. Wood bio-oil from the same reactor also had a higher content of pyrolytic lignin components because wood has a higher lignin content than corn stalks. Corn stalk bio-oils are highly oxygenated, low heating value liquids containing a lot of water (Table 8). The water content remaining in the pyrolysis oil will vary with fractional condensation, the amount of free moisture content present in the feed and pyrolysis temperature. However, no matter how the stalk pyrolysis is conducted, it will generate

more water overall than that of wood under identical conditions. Removal of more water by careful fractional condensation lowers the overall yield of stalk bio-oil because some water-soluble organic components are lost in the water fraction. Water removal raises the heating value of the oil obtained, but even when water is partially removed (see samples made at 450 °C in Table 8), the heating values are modest. However, per unit mass of stalks fed to the pyrolytic process, more water is formed from corn stalks than from wood, an apparently unavoidable consequence of the high cellulosic and low lignin content (18%) of the stalks.

This work demonstrated that corn stalks can be successfully converted to bio-oil in a continuous auger fed reactor that has slightly slower rates of heat transfer to the biomass than fluidized bed reactors. Significant further optimization may be possible. A portable auger reactor system used in tandem with a combine during corn harvesting could convert stalks, leaves, etc. to a more energy dense bio-oil for transport to a biorefinery along with residual char. The char could be deposited back on the land as an effective way to sequester this carbon in soil for a  $10^2$ – $10^3$ -fold longer period than leaving the stalks behind.<sup>81,82</sup> For this to be practical, continuous stover grinding, densification/compaction, and pelletization methods should be developed to allow seamless feeding of auger-fed pyrolyzers. This approach provides a way to use the enormous corn harvest to provide renewable energy while improving the overall energy output per energy input without competing with food security.

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### Notes

The authors declare no competing financial interest.

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