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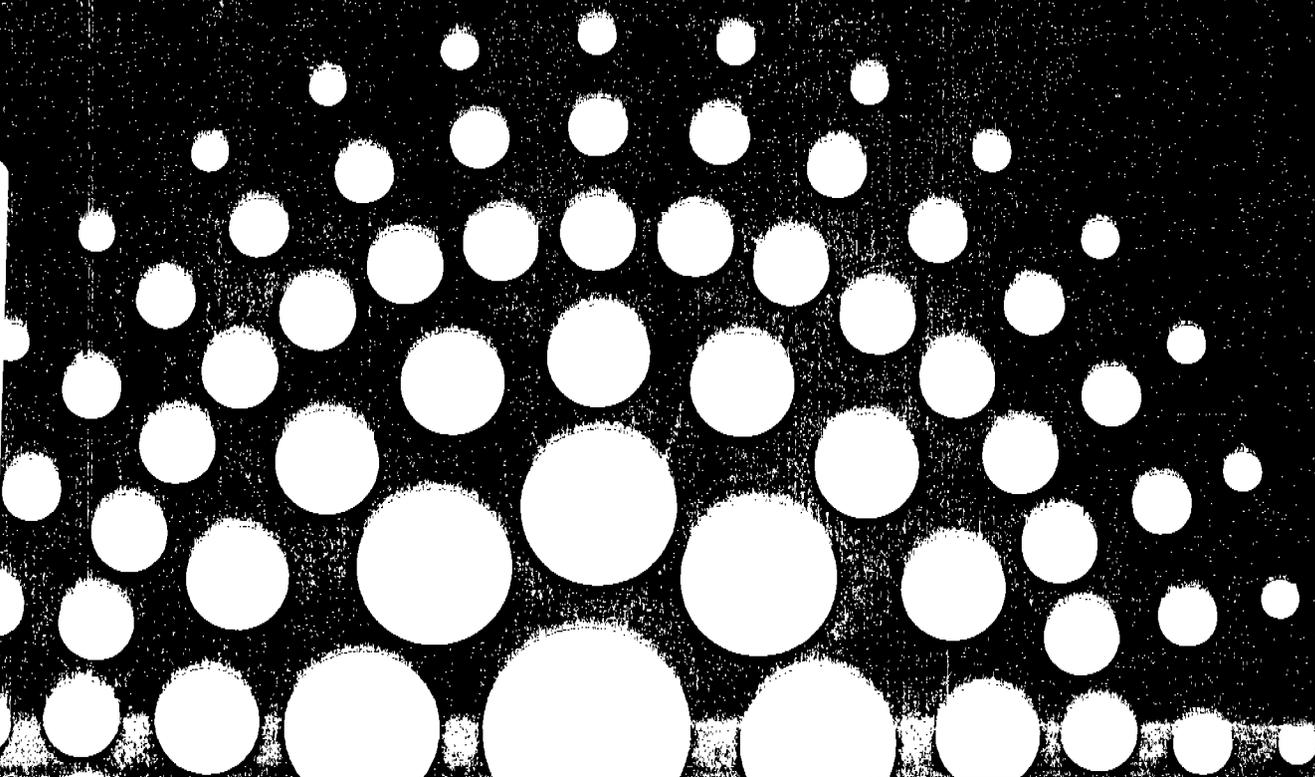


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# Fast Pyrolysis of Stored Biomass Feedstocks

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Biomass pyrolysis oils were produced from stored biomass feedstocks by rapid pyrolysis in a fluidized bed reactor. The feedstocks used for these studies were switchgrass, corn stover, and hybrid poplar. The woody and herbaceous feedstocks were stored in chip piles and bales, respectively, unprotected in an open field for 6 months. At the end of the storage period, biomass samples were taken from the interior of bales and the centers of chip piles for pyrolysis studies. The materials were ground to pass -20/+80 mesh and dried to less than 10% moisture content before pyrolyzing in the fluidized bed reactor. Pyrolysis was conducted at 500 °C and with less than 0.4 s apparent vapor residence time. Total liquid yields were as high as 66% for the hybrid poplar and as low as 58% for the corn stover. Moisture content of the oils was between 10 and 13%. Gas and char/ash yields were 10-15% and 12-22%, respectively. The char/ash yields were feedstock dependent, but storage influence was significant for only the corn stover feedstock. Gas and liquid yields were not influenced by storage time. The oils were highly oxygenated and had higher heating values (HHV) of 23-24 MJ/kg that decreased slightly with storage time for all the feedstocks except the switchgrass. The oils, as currently produced, are high in ash and alkali metals. Ultimately, they may be upgraded and used as boiler and turbine fuels.

## Introduction

The potential for global warming and environmental degradation are key concerns for both the United States and the world community. These concerns have spurred interest in developing and using oxygenated fuels, especially in designated U.S. cities with severe pollution problems. Biomass is potentially the most attractive source of oxygenated fuels because it is widely dispersed, renewable, and could contribute zero net carbon dioxide to the atmosphere, if production and use are managed in a sustainable manner.

Biomass feedstocks vary considerably in source and composition. Some examples of biomass feedstocks are waste woods from the pulp, paper, and lumber industries; demolition wood from urban areas; agricultural residues; and cultivated herbaceous and woody energy crops. All of these feedstocks are susceptible to biological degradation. Because biomass feedstocks are diverse and biodegradable, thorough chemical characterization and storage studies are needed to assess the economic feasibility of producing fuels from these resources.

A major requirement for any large-scale production of biofuels is the long-term storage of feedstocks to ensure a continuous supply throughout the year. Long-term storage of organic materials has been shown to result in significant losses of extractives and fiber, as well as physical losses.<sup>1-3</sup> The main causes for these losses are (1) biochemical reactions produced by micro-

flora that proliferate in the suitable environment created by the stored biomass; (2) loss of water-soluble extractives during precipitation events; and (3) evaporative losses of volatile nonstructural cell wall components.<sup>4,5</sup>

In addition to feedstock quality, efficient conversion processes are vital for a successful biomass energy program. Several conversion technologies, including pyrolysis, gasification, liquefaction, and biochemical conversion, are currently under development. Fast pyrolysis technologies are receiving considerable attention because they can produce a more dense and easily transportable fuel compared to the original feedstock. The pyrolysis oils conceivably can be used as a chemical feedstock for other processes.

Although a number of studies have been conducted on storing biomass,<sup>4-7</sup> most of these studies were designed to determine the effects of storage on forage quality, pulping, or combustion characteristics of the feedstocks. The results of these studies provide some insight into the storage environment created by different storage procedures, but this information cannot be applied to pyrolytic conversion without considerable modifications. The objective of this paper, therefore, is to assess the effects of long-term storage on the thermochemical conversion of woody and herbaceous biomass feedstocks to oxygenated fuels.

\* Abstract published in *Advance ACS Abstracts*, June 1, 1995.

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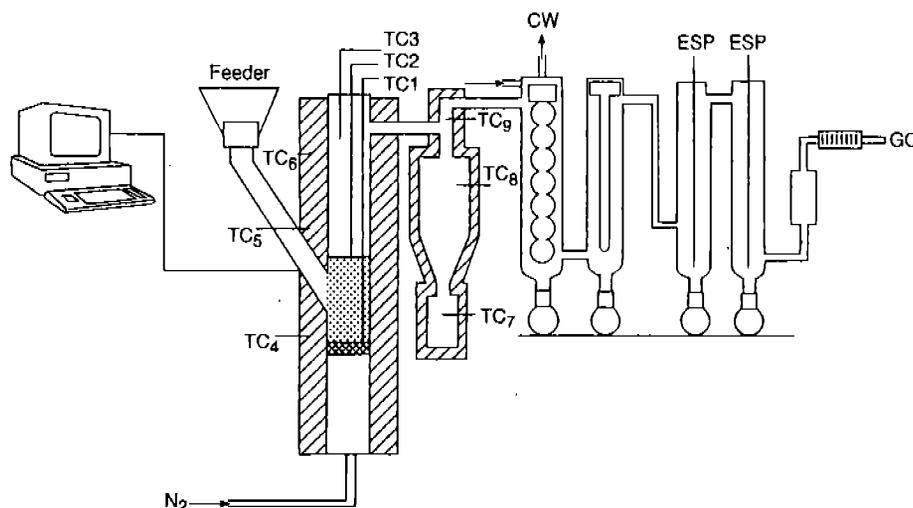
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**Figure 1.** Schematic diagram of the fluidized bed reactor showing the condensation train, feeder, and data acquisition units. TC1, TC2, ..., TC9 are thermocouples for the temperature controller; ESP = electrostatic precipitator; GC = gas chromatograph; CW = chilled water.

### Experimental Section

**Preparation of Feedstocks.** A detailed description of the methodology for storing and sampling herbaceous biomass bales and wood chip piles has been published elsewhere<sup>8</sup> and will not be described here. Samples of fresh and stored corn stover (*Zea mays* L), switchgrass (*Panicum virgatum* L), and hybrid poplar (*Populus deltoides* x *nigra* var. *Caudina*) were supplied to the National Renewable Energy Laboratory (NREL) researchers by the subcontractors of NREL's Terrestrial Biomass Feedstock Interface Project. The hybrid poplar feedstock was stored as conical whole-tree chip piles (3 m base diameter by 6 m high) constructed from 10 tonnes of chipped material. The corn stover and switchgrass feedstocks were stored as 500-kg square bales (1.52 × 1.52 × 2.44 m) and 320-kg (1.22 m diameter by 1.52 m) round bales, respectively. All biomass feedstocks (chip piles or bales) were stored unprotected in open fields for 6 months. One-kilogram samples were statistically sampled from the centers of the chip piles or interior of the bales after 0, 3.25, 6.5, 13, and 26 weeks of storage. Additionally, some corn stover bales were stored for 52 weeks; 1-kg samples were taken from the interior of these bales at the end of the storage period.

Only the fresh (0-week storage), the 26-week-old (6 months), and the 52-week-old feedstocks were used in this study. All samples were ground in a Wiley mill (Model 4) to pass a 2-mm screen and sieved to -20/+80 mesh size. Only samples of this mesh size were used in the data reported here. The Sauter mean diameters of the ground feed were 420 and 440  $\mu\text{m}$ , respectively, for the woody and herbaceous feedstocks. The moisture content of the feedstocks ranged from 5 to 6% (at high altitude and dry conditions in Golden, CO).

**Fluidized Bed Biomass Pyrolysis.** The fast pyrolysis studies were carried out in a bench-scale fluidized bed reactor (Figure 1). The reactor consisted of a 2-in. (50 mm) schedule 40 stainless steel pipe, 20 in. (500 mm) high (including a 5.5-in. (140 mm) preheater zone below the distribution plate), and was equipped with a 100  $\mu\text{m}$  porous metal gas distributor. The fluidizing medium was silica sand, and the bed was fluidized with nitrogen. The reactor was externally heated with a three-zone electric furnace. Biomass was fed into a feed hopper and conveyed by a twin-screw feeder into an entrainment zone where high-velocity nitrogen gas entrained the biomass feed

and carried it through a jacketed air-cooled feeder tube into the fluidized bed. The reactor tube contained a bubbling fluid bed with back-mixing of the feed and sand. The static sand bed height was 3.5 in. (90 mm), expanding to 4.7 in. (120 mm) when fully fluidized. The silica sand particles had a Sauter mean diameter of 350  $\mu\text{m}$ . To avoid feed-line blockage during the transport of the feed from the feed hopper into the pyrolysis zone, feed particle size, and moisture content were kept consistent, as described above.

The pyrolysis temperature was maintained at 500 °C and the apparent pyrolysis vapor residence time was about 0.4 s. The apparent vapor residence in the reactor was estimated using the Waterloo Fast Pyrolysis Process methodology.<sup>9</sup> In this approach, the residence time of gases and vapors is defined as the free reactor volume (the empty hot reactor volume minus the volume of hot sand) divided by the entering gas flow rate expressed at reactor conditions. Runs lasted from 1.5 to 3.5 h and the feed rate was 80–100 g/h. The feed rate, gas flow rate, and reactor temperature were kept constant during each run.

The nitrogen and pyrolysis gases and vapors exiting the reactor passed through a heated cyclone to separate char/ash and any entrained sand. The cyclone and char-pot temperatures were maintained at 400 °C to avoid condensation of the pyrolysis vapors in these units. The pyrolysis gases and vapors were then passed through a condensation train consisting of a chilled water condenser, an ice/salt mixture condenser, two electrostatic precipitators, and a cotton wool trap (all connected in series). The electrostatic precipitators were maintained at 13–15 kV.

The gaseous products were analyzed by gas chromatography using an on-line HP 5890 Series II instrument. Gaseous products were sampled and analyzed every 30 min during the run. Total gas volume was measured by a dry test meter. To ensure good mass balance, the entire setup (excluding the dry test meter) was weighed before and after each run.

Pyrolysis oils were recovered (after weighing the pyrolysis unit) by rinsing the condensers and cotton wool trap with acetone. The oil-acetone mixture was filtered through 40–60- and 10–15- $\mu\text{m}$  fritted glass filters. The moisture content of the final filtrate was determined by Karl Fischer analysis. The weight of the acetone-insoluble fraction of the filtrate was added to the weight of the char/ash recovered from the char-

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**Table 1. Elemental Composition and Ash Analysis of Fresh and Stored Biomass Feedstocks<sup>a</sup>**

	HP0	HP26	SWG0	SWG26	CS0	CS26	CS52
% C	49.4	49.8	46.9	47.3	46.0	46.0	46.5
% H	6.0	5.9	5.8	5.9	5.9	5.4	6.1
% O	43.1	42.5	42.0	41.1	41.4	39.2	40.1
% S	0.05	0.06	0.11	0.09	0.12	0.07	0.09
% N	0.23	0.26	0.58	0.44	0.88	0.64	0.73
% ash	1.2	1.4	4.6	5.2	5.0	5.4	5.8
HHV (MJ/kg)	19.74	19.96	19.53	19.50	18.62	18.23	17.90
% Cl	<0.01	0.01	0.50	0.50	0.34	0.75	0.68
% K	0.33	0.29	1.08	1.30	0.67	0.62	1.60
% Ca	0.41	0.48	0.24	0.29	0.23	0.033	0.53
% Na	0.001	0.001	0.008	0.008	0.004	0.011	0.016
% Si	0.05	0.097	1.02	1.32	0.85	4.82	1.28
% P	0.08	0.08	0.31	0.22	na	na	na

<sup>a</sup> HP0 = fresh hybrid poplar; HP26 = 26-week-old hybrid poplar; SWG0 = fresh switchgrass; SWG26 = 26-week-old switchgrass; CS0 = fresh corn stover; CS26 = 26-week-old corn stover; CS52 = 52-week-old corn stover.

pot and the fluidized bed reactor, and these were recorded as total char/ash produced from each run. The acetone was evaporated under vacuum (40 °C and 61.3 kPa), and the recovered oils were analyzed for elemental composition and higher heating values, as well as chemical composition by gas chromatography/mass spectrometry (GC/MS). During the vacuum evaporation process, some of the volatile oil components such as acetaldehyde, methanol, and formaldehyde could have been lost, but these losses were not investigated. The oils from all feedstocks, and chars/ash recovered from the switchgrass feedstock oil filtration, were analyzed for trace inorganic elements.

## Results

The influence of storage time on the thermochemical conversion of biomass feedstocks was assessed by the following criteria: oil, char/ash, and gas yields; elemental composition of the oils; higher heating value (HHV) of the oils; and GC/MS analysis of the oils.

**Biomass Feedstock Composition.** The elemental compositions of the biomass feedstocks are given in Table 1. The ash content of the woody feedstock (hybrid poplar) was much lower than that of the corn stover and switchgrass; however, it was higher than that of debarked wood as reported in the literature,<sup>10</sup> because whole-wood hybrid poplar chips were used in this study. The corn stover had the highest ash content because the harvesting and baling processes invariably included extraneous soil materials that were analyzed as ash. The intrinsic ash content of this feedstock may therefore be lower than what is shown in the table. The ash content of the fresh and stored materials showed no significant differences within the experimental error of these measurements except the 52-week-old corn stover. The difference between the ash content of the stored 52-week-old corn stover feedstock and the fresh feedstock was statistically significant. The primary constituents of the ash were potassium, calcium, and silicon. Elemental composition and HHV of the stored and fresh feedstocks were similar, except that the corn stover feedstock showed differences between the fresh and 52-week-old samples.

**Char/Ash and Gas Production from Feedstock Pyrolysis.** Char/ash was defined as the nonvolatile

**Table 2. Material Balance for the Fluidized Bed Pyrolysis of Fresh and Stored (a) Hybrid Poplar, (b) Switchgrass, and (c) Corn Stover Feedstock**

(a) Hybrid Poplar <sup>a</sup>					
material balance	HP0	HP26		run 2	
	run 1	run 1	run 2		
gas (%)	15.5	15.7	14.9		
char/ash (%)	14.0	13.8	14.2		
water (%)	4.9	6.4	na		
organics (%)	57.3	52.1	66.0 <sup>b</sup>		
total	91.7	88.0	95.0		
gases					
CO	na	5.4	4.7		
CO <sub>2</sub>	14.3	9.5	9.3		
CH <sub>4</sub>	0.1	0.3	0.3		
C <sub>2</sub> H <sub>4</sub>	1.2	0.5	0.6		
(b) Switchgrass <sup>c</sup>					
material balance	SWG0		SWG26		
	run 1	run 2	run 1	run 2	
gas (%)	11.0	10.4	11.4	12.9	
char/ash (%)	20.3	21.6	18.4	20.5	
water + organics (%)	61.5	63.4	57.8	60.2	
total	92.8	95.4	87.6	93.6	
gases					
CO	3.4	3.2	2.5	3.9	
CO <sub>2</sub>	7.1	7.1	8.6	8.4	
CH <sub>4</sub>	0.2	0.1	na	0.2	
C <sub>2</sub> H <sub>4</sub>	na	na	na	0.1	
C <sub>4</sub> H <sub>6</sub>	0.3	na	0.3	0.2	
(c) Corn Stover <sup>d</sup>					
material balance	CS0		CS26		CS52
	run 1	run 2	run 1	run 2	
gas (%)	15.1	14.6	14.3	11.7	13.2
char/ash (%)	15.9	15.0	19.4	19.5	19.9
water (%)	7.2	6.9	4.9	7.9	na
organics (%)	52.7	54.2	57.6	55.0	58.1 <sup>c</sup>
total	90.9	90.7	96.2	94.1	91.2
gases					
CO	3.7	3.3	4.0	2.1	2.5
CO <sub>2</sub>	9.9	7.2	9.9	9.1	9.0
CH <sub>4</sub>	0.4	na	0.2	0.3	0.4
C <sub>2</sub> H <sub>4</sub>	1.2	4.1	0.2	0.1	1.3

<sup>a</sup> Temperature = 500 °C and apparent vapor residence time <0.4 s. All data are on moisture-free basis. Moisture content of HP0 run 1 and HP26 run 1 and run 2 are 5.0, 4.0, and 4.5, respectively. <sup>b</sup> Organics + water. <sup>c</sup> Temperature = 500 °C and apparent vapor residence time <0.4 s. All data are on moisture-free basis. Moisture content of SWG0 = 5.0%; SWG26 run 1 = 6.0; SWG26 run 2 = 3.2%. <sup>d</sup> Temperature = 500 °C and apparent vapor residence time <0.4 s. All data are on moisture free basis. Moisture content of CS0 run 1 = 5.2%; CS0 run 2 = 5.6%; CS26 run 1 = 5.3%; CS26 run 2 = 5.1%; and CS52 = 5.3%.

pyrolysis residue collected from the fluidized bed reactor, the char-pot, and the acetone-insoluble material collected after filtration of the oils through 40–60- and 10–15- $\mu$ m filters. Most of the char/ash (~90%) was collected in the cyclone separator and 0.5–1% was recovered from the filtration of the oils. Char materials contained mostly carbon, oxygen, and hydrogen. The char/ash yields are shown in Table 2. A comparison of the char/ash yields from various feedstocks indicates that the intrinsic ash content of the feedstocks has a significant influence on char formation. The fresh corn stover feedstock, which had ash content similar to the fresh switchgrass (Table 1) had a lower char/ash yield compared to the switchgrass, apparently because a large proportion of the ash was extraneous material. Statistically significant differences exist between the char/ash yields of fresh and stored corn stover, but no significant

**Table 3. Trace Inorganic Analysis of Chars Recovered from the Pyrolysis of Switchgrass Feedstock**

source of char	K (ppm)	Na (ppm)	Ca (ppm)	P (ppm)	Cl (%)	ash (%)
run 1: 40–60- $\mu$ m filter	7700	225	5600	2700	1.02	9.5
run 1: 10–15- $\mu$ m filter	8500	690	7100	3600	1.06	15.3
run 1: char pot	24000	155	7300	2700	na	na

differences exist between the char/ash yields of the fresh and stored poplar and switchgrass. It is apparent from the char/ash data that storage effects are only significant for the corn stover feedstock.

The ash contents of the switchgrass chars recovered from filtration of the pyrolysis oils was relatively high compared to the starting feedstocks and the pyrolysis oils (Table 3). This suggests that the inorganic species are sequestered in the char fraction of the pyrolysis products. The potassium and calcium contents of these chars were consequently very high compared to the pyrolysis oils and the starting feedstocks.

Material balance for the inorganic constituents in the feedstocks and pyrolysis products appear very poor because analysis of char/ash samples by ASTM standard methods were extremely difficult and had poor repeatability.

Gas yields were not significantly affected by storage of the materials; however, there appear to be slight differences in gas yields due to biomass species variation. Surprisingly, the hybrid poplar feedstock produced the highest gas yield (15%), apparently because of the high bark content of the feedstock. The gas yield of the switchgrass feedstock was lowest (11%). The major product gases were carbon dioxide, carbon monoxide, methane, ethane, and propane. Hydrogen, water vapor, and other minor hydrocarbon components were not quantified. The composition of the gaseous products were similar for the multiple samples taken at 30-min intervals during the run and these were similar to sawdust pyrolysis results reported in literature.<sup>11</sup> This suggests that very little cracking of the pyrolysis products took place on the surface of the residual char/ash in the fluidized bed reactor. Further, for processes where fresh char had catalyzed the cracking of the newly formed volatiles, the carbon monoxide and carbon dioxide contents of the gaseous products were reported to have increased significantly.<sup>12</sup>

**Pyrolysis Oils Production.** The condensable pyrolysis products (pyrolysis oils) were single-phase, brownish, viscous, acidic liquids that contained 10–13% moisture. The moisture contents of these pyrolysis oils were relatively low compared to what has been reported in the literature,<sup>9</sup> probably because some of the moisture was entrained in the fluidizing gas and could not be captured and analyzed. We noticed a significantly large water peak in the chromatogram of the pyrolytic permanent gases, but this was not quantified.

The pH of the pyrolysis oils ranged from 2.5 to 3.0. The physical properties of the pyrolysis oils appeared to be feedstock dependent: the corn stover and switchgrass oils were more sticky and very viscous compared to the hybrid poplar oils. The pyrolysis oil (organics +

water) yields, determined gravimetrically, ranged from 58 to 66% for the three feedstocks (see Table 2). The pyrolysis oil yields appeared to be unaffected by the storage of the feedstocks but were influenced by the biomass species.

The pyrolysis oil yields were also influenced by the collection efficiency of the electrostatic precipitators because about 50% of the pyrolysis vapors were aerosols. This effect is evidenced by the poor mass closure for some of the runs shown in the tables. For runs where the electrostatic precipitator voltage was steady at 15 kV throughout the run period, pyrolysis oil yield was very high (73% for hybrid poplar feedstock) and the mass closure was very good (98%). At very high biomass feed rates ( $\geq 100 \text{ g h}^{-1}$ ), viscous pyrolysis oils tend to accumulate rapidly on the electrodes and this caused voltage leakage and loss of pyrolysis products. For relatively low biomass feed rates ( $\leq 80 \text{ g h}^{-1}$ ), this problem is minimized.

The collection efficiency of the electrostatic precipitator also was feedstock dependent. The corn stover and switchgrass pyrolysis oils were more difficult to condense by the electrostatic precipitator, probably because these oils were more viscous than the hybrid poplar pyrolysis oils and therefore oil built up more rapidly on the electrodes and caused voltage leakage. Further, the potassium content of the corn stover and the switchgrass pyrolysis oils are 4–6-fold higher than that of the hybrid poplar pyrolysis oil (Table 4) and with 1–2% ash in the unfiltered oil, it is possible that this also contributed to the arcing of the precipitator during the condensation process.

**Composition of Biomass Pyrolysis Oils.** Table 4 shows the elemental compositions of the pyrolysis oils from the various feedstocks. The HHVs were similar for all fresh feedstock pyrolysis oils, but these were slightly higher than HHVs for the stored feedstocks in the case of the hybrid poplar and corn stover. For the switchgrass feedstock pyrolysis oil, the HHVs for the fresh and stored materials were similar.

The ash contents of all the pyrolysis oils were very low (<0.05%), probably because the oils were filtered through the 40–60- and 10–15- $\mu$ m filters before the analysis. As expected, the sulfur contents of these oils were low compared to fossil fuels. However, the chlorine and nitrogen contents of these oils were higher than those from fossil-derived fuels.<sup>13</sup> The corn stover and switchgrass feedstock pyrolysis oils had higher chlorine and nitrogen contents than the hybrid poplar feedstock pyrolysis oil. This is because the original feedstocks had higher concentrations of these elements compared to the hybrid poplar, probably because more fertilizer was required for good growth of the corn and switchgrass. The storage time of feedstocks appeared to have some influence on the sulfur, chlorine, and nitrogen content of these oils.

Trace inorganic analysis of the pyrolysis oils showed relatively high concentrations of potassium, sodium, phosphorus, calcium, and silicon in the oils. Storage appears to have some slight influence on these constituents in the oils.

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Table 4. Elemental and Ash Analysis of Filtered Fluidized Bed Pyrolysis Oils of Fresh and Stored Biomass Feedstocks<sup>a</sup>

	HP0	HP26	SWG0	SWG26	CS0	CS26	CS52
% C	57.0	55.0	55.8	54.7	57.4	55.3	55.2
% H	6.6	6.6	6.9	6.8	6.9	6.6	6.6
% O	36.1	38.1	36.3	37.5	34.2	36.6	37.0
% S	0.01	0.01	0.03	0.04	0.04	0.06	0.04
% N	0.34	0.31	0.79	0.77	1.33	0.97	1.09
% ash	<0.05	<0.05	<0.05	<0.05	0.08	<0.05	0.13
HHV (MJ/kg)	24.3	23.3	23.8 ± 0.1	24.0 ± 0.1	24.7	23.5	22.5
% Cl	<0.1	<0.1	0.19	0.23	0.20	0.26	0.18
K (ppm)	26 ± 1	37 ± 3	115 ± 2	158 ± 3	157 ± 1	144 ± 1	206 ± 8
Ca (ppm)	9.8 ± 0	23.5 ± 1.5	8.2 ± 0.2	6.9 ± 0.2	3.1 ± 0.1	5.6 ± 0.4	10.4 ± 0.6
Na (ppm)	14.1 ± 0.1	11.4 ± 0.9	12.6 ± 1.3	13.2 ± 0	12.2 ± 2.8	22.2 ± 1	60.0 ± 2.4
Si (ppm)	1.1 ± 0.4	2.1 ± 0.4	2.1 ± 0.5	2.4 ± 0	1.8 ± 0.3	1.5 ± 0.4	na
P (ppm)	1.4 ± 0	2.3 ± 0.2	3.4 ± 0.2	3.5 ± 0.2	1.2 ± 0.1	1.0 ± 0	2.2 ± 0.2

<sup>a</sup> Temperature = 500 °C and apparent vapor residence time <0.4 s. All data are on moisture free basis. HP0 = fresh hybrid poplar; HP26 = 26-week-old hybrid poplar; SWG0 = fresh switchgrass; SWG26 = 26-week-old switchgrass; CS0 = fresh corn stover; CS26 = 26-week-old corn stover; CS52 = 52-week-old corn stover. The errors are standard deviations of multiple determinations.

GC/MS analysis of the chemical components of oils from the stored and fresh feedstocks (for all biomass species) did not reveal any significant qualitative differences due to storage. It must be pointed out that only about 20% of the total pyrolysis oil injected unto the column eluted and these were very difficult to quantify because the identity of most of the compounds were unknown. However, the oils from the corn stover and the switchgrass were different from the hybrid poplar pyrolysis oils with respect to their chemical composition. The switchgrass and corn stover oils had lesser amounts of phenolic components compared to the hybrid poplar oils, especially the syringyl-derived pyrolysis components. Pyrolysis molecular beam mass spectrometry and nuclear magnetic resonance spectroscopic analyses of the oils also revealed similar trends in their qualitative compositions.<sup>14</sup>

## Discussion

**Influence of Storage on Pyrolysis Products.** The influence of storage on feedstock pyrolysis products can be evaluated in terms of microbial and weathering activities while the feedstocks were stored in the open, as well as the morphology of the individual biomass species. During storage in the open, both the bales and the chip piles were exposed to precipitation, heat from the sun, wind, and other environmental factors. These factors, particularly precipitation, could result in leaching of the water-soluble nonstructural cell wall components of the feedstocks (e.g., starch). Exposure to heat from the sun could also lead to evaporative loss of some volatile nonstructural cell wall components of the feedstocks. These losses were indicated by a decrease in the extractives contents of the feedstocks, especially switchgrass.<sup>8</sup> The weathering also discolored the outer layers of the stored feedstocks bales, but the interior of the bales were not discolored.

The extractives of woody biomass are known to contain polyphenolic materials that have higher HHVs than the structural components of the cell wall.<sup>10</sup> Therefore, the loss of some of these components will invariably result in the loss of HHV of the feedstocks, accounting for some of the loss in HHV of the pyrolysis

oils. This was clearly shown by the lower HHV of the poplar pyrolysis oils made from stored feedstock.

Alternatively, herbaceous feedstocks such as switchgrass are known to contain significant amounts of nonstructural carbohydrates in their extractives.<sup>15</sup> The loss of some of these components should either increase the HHV of the stored feedstock pyrolysis oil or have no effect. In this study, we observed no significant difference between the HHV of the stored and fresh switchgrass pyrolysis oils.

Microfloral activity is another important factor in the quality of biomass feedstocks. Solid-state nuclear magnetic resonance and pyrolysis molecular beam mass spectrometric studies of samples taken from the centers of the stored hybrid poplar chip piles showed that all the piles were colonized by microflora.<sup>16</sup> This microfloral colonization resulted in a significant decrease in the lignin content of the feedstock. A similar observation was noted for the corn stover feedstock. Because the lignin component of the feedstock is highly aromatic, it has a higher HHV than the carbohydrate component of the feedstock.<sup>10</sup> The loss of some of the lignin component caused by microfloral activity will partially account for the reduced HHV of the pyrolysis oil produced from the stored feedstock.

Our studies also showed that switchgrass samples taken from the centers of the bales were neither weathered nor microbially degraded, while material on the surface was weathered as well as microbially degraded. Because the samples for the pyrolysis studies were taken from the centers of the bales, it is not surprising that the HHV of the stored and fresh switchgrass feedstock pyrolysis oils were similar.

The loss of both structural and nonstructural cell wall components of the biomass feedstocks implies a relative increase in the inorganic or ash content of the feedstocks. Intrinsic inorganic species, especially potassium, are known to catalyze char formation reactions.<sup>17</sup> There-

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fore, relative increased concentrations of this element will promote increased char formation reactions. This is probably responsible for the increase in the char/ash yield of the stored corn stover feedstock. Although the ash contents of both the stored and fresh corn stover were similar, the true intrinsic ash content of the feedstocks may have been confounded by the extraneous material in this feedstock. For the switchgrass and hybrid poplar feedstocks, which were relatively clean with respect to extraneous material, no statistically significant increases in ash content or char/ash formation were observed.

**Inorganic Constituents of Pyrolysis Oils and Char.** The potential applications of pyrolysis oils include feedstocks for high-value products; feedstocks for catalytic upgrading to gasoline-like products or oxygenate additives for gasoline; fuel for turbine generation of electrical power; and fuel for steam boilers and diesel engines.

Although the ash contents of the pyrolysis oils for both the fresh and stored feedstocks were relatively low, and consequently, the level of primary inorganic species (potassium and calcium) in the oils was low in absolute terms, the content is relatively high for practical applications in combustion processes. Turbine fuel applications require the total alkali metals concentration to be less than 1 ppm, and similar specifications apply to the other inorganic species.<sup>13</sup> It must be pointed out that these specifications apply strictly to petroleum-derived fuels where the sulfur content of the fuels is relatively high and the potential for the formation of alkali metal sulfates during the combustion of such fuels is also very high. In the turbine power generation industry, alkali metal sulfates are known to cause hot corrosion problems on turbine blades. Because pyrolysis oils are new fuels that have not been tested for any length of time, no independent standards exist for them. Therefore, these fuels must meet the existing specifications for fossil fuels.

Furthermore, the relatively high alkali metals content of pyrolysis oils could contribute to fouling of heat exchanger tubes in steam boilers. Any large-scale application of these fuels will require the inorganic species content to be reduced several fold.

The high concentration of ash in the chars of switchgrass and perhaps other feedstocks precludes their use in certain applications. The maximum ash content in chars for use as charcoal briquettes is 12% compared

to 15% in switchgrass pyrolysis chars.<sup>18</sup> However, these chars may be suitable for application as soil conditioners because of their high potassium and calcium contents. For woody feedstocks, even though the inorganics may be concentrated in the chars, the overall ash content is low. They may therefore find a wider application compared to the herbaceous biomass pyrolysis chars.

Of equal importance for the application of these liquids is the development of suitable analytical methods for the determination of trace alkali metal contents in the oils and chars/ash. The current ASTM standard methods appear to be inadequate for the analysis of these materials because they were primarily developed for petroleum fuels and have been adopted for pyrolysis oils and char/ash analysis.

## Conclusions

Properly stored feedstocks appear to show little degradation of properties in the pyrolysis products. Microbial attack and weathering of the stored feedstocks appear to have contributed to a decrease in the higher heating value (HHV) of the pyrolysis oils produced from some of the biomass feedstocks. In cases where there appear to be very little microbial attack or weathering of the feedstocks, no significant changes were observed in the HHV of the pyrolysis oils. Therefore, it is very important to reduce the loss of both the structural and nonstructural cell wall components of the feedstocks by reducing outside storage time.

Because these pyrolysis oils contain relatively high inorganic constituents, they cannot meet current turbine fuel specifications unless there is some reduction in the content of the inorganic species in the fuels. These new fuels need extensive testing to establish appropriate standards for their applications in turbines, diesel engines, and steam boilers.

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