Hydrothermal conversion of big bluestem for bio-oil production: The effect of ecotype and planting location

Jing Gan [a], Wenqiao Yuan [b,*], Loretta Johnson [c], Donghai Wang [a], Richard Nelson [d], Ke Zhang [a]

[a] Department of Biological and Agricultural Engineering, Kansas State University, Manhattan, KS 66506, United States
[b] Department of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC 27695, United States
[c] Department of Biology, Kansas State University, Manhattan, KS 66506, United States
[d] Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506, United States

ABSTRACT

Three ecotypes (CKS, EKS, IL) and one cultivar (KAW) of big bluestem (*Andropogon gerardii*) that were planted in three locations (Hays, KS; Manhattan, KS; and Carbondale, IL) were converted to bio-oil via hydrothermal conversion. Significant differences were found in the yield and elemental composition of bio-oils produced from big bluestem of different ecotypes and/or planting locations. Generally, the IL ecotype and the Carbondale, IL and Manhattan, KS planting locations gave higher bio-oil yield, which can be attributed to the higher total cellulose and hemicellulose content and/or the higher carbon but lower oxygen contents in these feedstocks. Bio-oil from the IL ecotype also had the highest carbon and lowest oxygen contents, which were not affected by the planting location. Bio-oils from big bluestem had yield, elemental composition, and chemical compounds similar to bio-oils from switchgrass and corncobs, although mass percentages of some of the compounds were slightly different.

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1. Introduction

Andropogon gerardii Vitman, commonly known as big bluestem, is a dominant grass in the tallgrass prairies of North America (Weaver and Fitzpatrick, 1932; Knapp et al., 1998). Big bluestem is widely distributed on loamy soils in Midwest United States grasslands and comprises up to 80% of prairie biomass (Knapp et al., 1998). Although photosynthesis in C_4 grasses is highly sensitive to water stress (Ghannoum, 2009), big bluestem is capable of maintaining high photosynthetic rates during periods of water shortage (Knapp, 1985) owning to its efficient water usage and resource allocation (Johnson and Matchett, 2001). Conversion of native perennial grasses such as big bluestem to biofuels offers major economic, environmental, and strategic benefits. Compared with switchgrass, the first-generation dedicated bioenergy species, big bluestem was found to produce three times more biomass (Epstein et al., 1998) with less (or no) irrigation or nitrogen fertilizers needed. Moreover, big bluestem was found to have higher cellulose and lignin contents and greater fermentability than switchgrass (Jung and Vogel, 1992), which are important qualities for biofuel conversion.

McMillan conducted early studies investigating the ecotype effects of several grasses, including big bluestem. Six ecotypes of big bluestem were collected across the United States from north to south and were planted in Texas (McMillan, 1965a) or in growth chambers with temperature and light-period controls (McMillan, 1965b). Results indicated that vegetation of big bluestem was affected by its ecotype and growth climate. Jefferson and co-workers (2002, 2004) also found that planting location had significant effects on big bluestem biomass production and its cellulose and hemicellulose contents in the Canadian prairie provinces. They found that big bluestem could not be well cultivated at sites above 51°N latitude in western Canada, and its cellulose and hemicellulose contents were lower than in lower latitude areas.

Cellulose, hemicellulose, and lignin are the three major compounds of lignocellulosic biomass. Higher cellulose content in biomass generally favors higher ethanol yield in biochemical conversion. Thermochemical conversion is another promising technology to convert lignocellulosic biomass such as big bluestem into bio-fuels. As one of the thermochemical conversion processes, hydrothermal conversion (HTC) has been extensively investigated for the production of bio-oil, which can be used as a fuel for stationary diesel engines, burners, boilers or turbines (Czernik and Bridgwater, 2004), or can be upgraded or further converted to transportation fuels (e.g., gasoline and diesel) and products such as polymers, aromatics, lubricants, and asphalt (Peterson et al., 2008). HTC is a chemical reforming process in which hot compressed water (or other solvents) is used as reaction medium with which biomass is depolymerized and reformed to gases, water-soluble matters, bio-oil, and char in an oxygen-absent enclosure.

* Corresponding author. Tel.: +1 9195156742; fax: +1 79195157760.
E-mail address: wyuan2@ncsu.edu (W. Yuan).

However, to the best of our knowledge, little information is available regarding the effect of ecotype and planting location of big bluestem on its chemical composition and consequent biofuel yield, and no information is available on converting big bluestem to bio-oil via HTC. The objective of this study was to understand the effects of big bluestem ecotype and planting location on its bio-oil yield and elemental composition. Four ecotypes of big bluestem reciprocally planted in three locations (Hays and Manhattan, KS, and Carbondale, IL) were used as the feedstock. For comparison purpose, switchgrass and corncobs were also tested.

2. Methods

2.1. Feedstock preparation

The feedstocks used in this study included big bluestem, switchgrass, and corncobs. Three ecotypes of big bluestem, Central Kansas (CKS, Kansas State University Agricultural Research Center–Hays, Hays, KS), Eastern Kansas (EKS, USDA Plant Material Center, Manhattan, KS), and Illinois (IL, Southern Illinois University Agronomy Center, Carbondale, IL) ecotypes were used. In Fall 2008, seeds of the ecotypes from these regions were collected by hand from pristine ungrazed prairie within 50 miles of their home sites (Table 1). Seeds of each ecotype were collected from two sites in the same region and separately planted in different blocks. The Kaw cultivar (KAW) was also used for comparison purpose. KAW is a cultivar bred by the USDA Plant Material Center (Manhattan, KS) that is widely used for restoration planting in Conservation Reserve Program lands throughout the Great Plains. All three ecotypes plus KAW were reciprocally planted in the three locations, Hays and Manhattan, KS, and Carbondale, IL, in August 2009 (Table 1) and were harvested in October 2010. For CKS, EKS, and IL ecotype of big bluestem, two samples were obtained for each ecotype. Switchgrass (*Panicum virgatum*-Kanlow) was grown and harvested at the Kansas State University Agronomy Farm in Manhattan, KS. For big bluestem and switchgrass, the entire plant except for the root was used in this study. Commercially available corncobs were obtained from Kaytee Products, Inc. (Chilton, WI). Each feedstock sample was ground in a Retsch SM2000 rotary cutting mill (Retsch Inc., Newtown, PA) with a 1.0-mm screen. After grinding, each sample was manually mixed using a glass rod. Samples were dried at 105 °C for 24 h before use in the experiments.

2.2. HTC apparatus and experimental procedure

A 1.8-L Parr model 4578 high-temperature, high-pressure reactor (Parr Instrument Company, Moline, IL) equipped with a magnetic stirrer, serpentine cooling coil, reflux/take-off condenser assembly, and bottom drain valve was used for all experiments. The reactor is made of T316 stainless steel with an extreme operation capability of 5000 psi and 500 °C. In a typical batch test, a 50-g dry sample with 2.5 g sodium hydroxide as the catalyst and 447.5 g deionized water were placed in the reactor. Air in the reactor was purged by flushing with nitrogen gas for five minutes. The

reactor was then pressurized to approximately 100 psi by using a high-pressure nitrogen gas cylinder and heated to 280 °C with a heating rate of approximately 5 °C/min. The desired temperature was kept for 20 min and the final gauge pressure at the end of the heating cycle was around 1100 psi. After the reaction, the reactor was cooled to room temperature with tape water and the gaseous products were vented from the gas outlet valve. The solid and aqueous products were collected from the reactor and separated by vacuum filtration with Whatman Grad No. 1 filter paper. Then, the water-insoluble fraction and the reactor were washed with acetone. The solvent-insoluble portion was separated through vacuum filtration, then dried to obtain the residual solid called bio-char. The solvent-soluble portion was then evaporated using a rotary evaporator (Buchi RE-111, Flawil, Switzerland) to remove acetone, and the remaining product was water-insoluble bio-oil. More details about the experimental apparatus and procedure can be found in one of our previous papers (Gan et al., 2010). All experiments were performed in duplicate, and data were expressed as average values. Bio-oil yield was defined as follows: Oil yield (%) = (weight of bio-oil)/(dry weight of feedstock) × 100%.

2.3. Analytical tests

Chemical composition of biomass was determined according to the laboratory analytical procedures developed by the National Renewable Energy Laboratory (Sluiter et al., 2005, 2008). Briefly, after water and ethanol extraction, the sample was soaked in 72% sulfuric acid at 30 °C for 1 h with constant stirring, followed by dilution to a 4% acid solution and heating for another hour at 120 °C. The aqueous products and solid residue of the pretreatment process were separated by vacuum filtration. The filtrate was adjusted to neutral by calcium carbonate, then the sugar contents of the filtrate were measured by high-performance liquid chromatography (Shimadzu, Kyoto, Japan), and acid-soluble lignin content in the filtrate was detected by a UV–visible spectrophotometer (BioMate 3, Thermo Electron Corporation, Madison, WI). The solid residue was dried and combusted. The weight difference between the dry residue and combustion residue was reported as acid-insoluble lignin.

The elemental compositions of feedstock and bio-oil products were analyzed by a CHNS/O elemental analyzer (PerkinElmer 2400, Shelton, CT). Each sample was placed in a tarred tin capsule (PerkinElmer N2411255) and precisely weighed using a PerkinElmer AD6 Autobalance. The weight of each sample tested was approximately 2 mg. Samples encapsulated in the tin were then loaded automatically by an integral 60-position autosampler (Perkin Elmer).

Bio-oil chemical compounds were analyzed by a gas chromatograph equipped with a mass selective detector (Agilent 5975C GC–MS with HP-5MS column, Agilent Technologies Inc., Santa Clara, CA). The temperature was kept at 40 °C for 1 min, then increased to 300 °C with 10 °C/min heating rate and held for 5 min. The inlet temperature of the GC–MS was 280 °C. Compounds in the bio-oil were identified using the NIST08 library (Agilent Technologies Inc., Santa Clara, CA).

Table 1
The seed collection site and planting location of big bluestem.

Location	Latitude (N)	Longitude (W)	Elevation (m)	2010 annual precipitation (cm/year)	Mean annual precipitation since 1961 (cm)	Growing degree days 2010	Soil type
Kansas State University Agricultural Research Center–Hays (Hays, KS)	38° 51′	99° 19′	603	50.11	58.22	4193	Roxbury slit loam
USDA Plant Material Center (Manhattan, KS)	39° 08′	96° 38′	315	67.82	87.15	4105	Sandy loam
Southern Illinois University Agronomy Center (Carbondale, IL)	37° 73′	89° 22′	127	66.95	116.73	4474	Stoy silt loam

All statistical analyses were performed using SPSS software (SPSS 17.0, SPSS Inc., Chicago, IL). Correlations among big bluestem characteristics (chemical and elemental compositions) and bio-oil properties (yield, carbon, and oxygen content) were determined using Pearson's correlation. Effects and interactions of ecotype/cultivar and planting location on bio-oil yield, carbon, and oxygen content were analyzed using the ANOVA test. Tukey's HSD test was used to check significant differences. For convenience, "cultivar" is not specifically differentiated from "ecotype" and are both described as "ecotype" thereafter in this article when the effect of ecotype/cultivar is discussed.

3. Results and discussion

3.1. The effect of ecotype and planting location on bio-oil yield

Bio-oil yields were in the range of 19.5–27.2%, depending on big bluestem ecotype and planting location. The data were analyzed separately for each ecotype and planting location and are shown in Fig. 1. In Fig. 1, letters (a and b) above the standard deviation bars indicate that means of bio-oil yields are significantly different based on Tukey's HSD test ($p < 0.05$); e.g., bio-oil yield of group b is significantly higher than bio-oil yield of group a. We denote significant differences in the same manner for all remaining figures. As can be seen from Fig. 1, the effect of big bluestem ecotype on bio-oil yield is dependent on the planting location. When planted in Manhattan, KS, or Carbondale, IL, all ecotypes gave statistically similar bio-oil yield, indicating that the planting location rather than ecotype may influence bio-oil yield. When planted in Hays KS, slight differences in bio-oil yield were found, with KAW the highest and EKS ecotype the lowest. The average bio-oil yield at all three locations for each ecotype showed the same trend as in Hays, KS. In general, KAW and IL ecotype gave higher bio-oil yield, suggesting that they might be the advantageous ecotypes for bio-oil production.

The effect of planting location on bio-oil yield can be found in Fig. 2. KAW and IL had no significant differences in bio-oil yield regardless of where they were planted. From previous analysis, KAW and the IL ecotype were higher in bio-oil yield, which suggests that ecotype is the main factor influencing bio-oil yield for these two advantageous ecotypes in terms of bio-oil yield. However, for CKS and EKS ecotypes, Manhattan, KS, and Carbondale, IL, were significantly better planting locations than Hays, KS. These two ecotypes are considered relatively disadvantageous in terms of
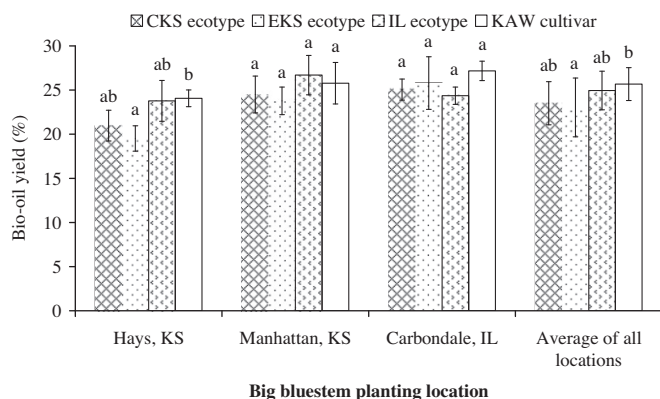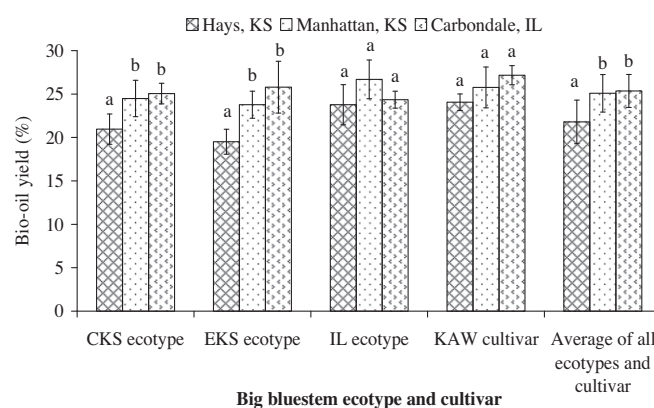

Fig. 2. Comparisons of bio-oil yield in different planting locations, grouped by ecotype. Different letters (a and b) above the standard deviation bars indicate that the means of bio-oil yield are significantly different (b > a), while the same letters indicate that the values are statistically the same, based on Tukey's HSD test ($p < 0.05$).
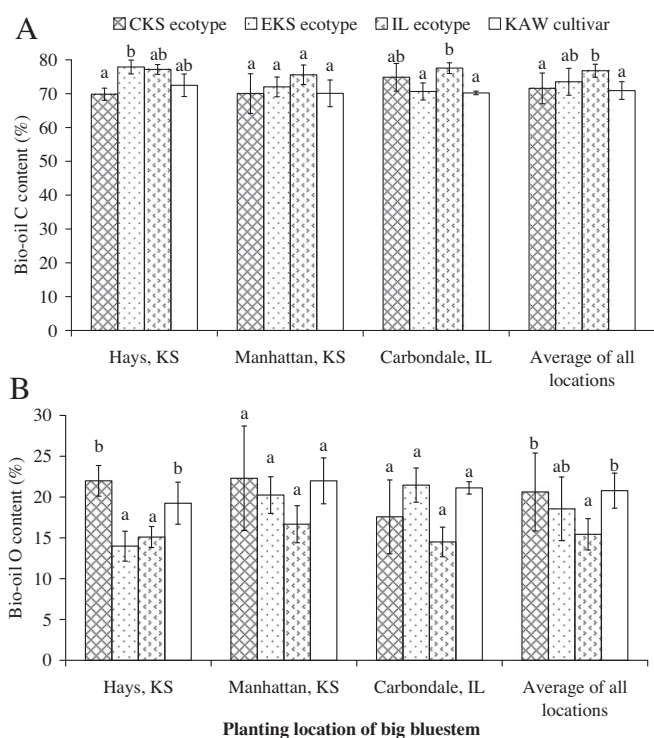
bio-oil yield from previous analysis; therefore, planting location became the dominant factor for bio-oil yield for these two ecotypes. These results indicate that local ecotypes did not show greater bio-oil production when they were planted in their home site. Furthermore, the average bio-oil yield of all ecotypes at each planting location also showed that the Illinois and Manhattan planting locations gave higher bio-oil yield than Hays. Thus, both ecotype and planting location can affect bio-oil yield. Because the sample size was small, looking at average values instead of individual ecotype or planting location would be more meaningful. With that in mind, KAW and IL planted in Manhattan or Illinois would be a better choice for higher bio-oil yield.

3.2. Effects of ecotype and planting location on bio-oil carbon and oxygen content

In addition to yield, carbon (C) and oxygen (O) contents of bio-oil are also important. Bio-oil heating value increases as C content increases and O content decreases according to the Dulong formula (Minowa et al., 1998; Zhong and Wei, 2004). In addition, bio-oil containing less O is more stable, and vice versa. In this study, the bio-oil C content ranged from 69.8% to 77.9%, and O content was between 14.0% and 22.0%. This was consistent with reports from other researchers in which the typical C and O contents of HTC oil were 65–83% and 5–25%, respectively (Huber and Dumesic, 2006; Demirbaş et al., 2005; Demibaş, 2005; Wang et al., 2008; Gan et al., 2010; Zhang et al., 2011).

Bio-oil C and O contents are shown in Fig. 3. From Fig. 3A, ecotype seems to have affected C content of the bio-oil produced for certain locations; however, the trend was not consistent for individual ecotypes. For example, the CKS ecotype had the lowest C content in Hays, but not in the Illinois location. By averaging all three locations, IL ecotype gave the highest C content whereas CKS and KAW gave the lowest. O content showed a similar trend (Fig. 3B), but in an opposite way; that is, IL ecotype gave the lowest O content, and CKS ecotype and KAW gave the highest. This suggests a negative correlation between C and O contents of the bio-oil. The optimal ecotype of big bluestem to produce bio-oil with high C and low O content seems to be the IL ecotype.

The effect of big bluestem planting location on bio-oil C and O contents can be seen from Fig. 4. For all ecotypes except the EKS, no significant difference was observed in bio-oil C or O contents among different planting locations. Bio-oil produced from EKS ecotype planted in Hays, KS, contained more C and less O than that

Fig. 1. Comparison of bio-oil yields of different ecotypes in each planting location, grouped by planting location. Different letters (a and b) above the standard deviation bars indicate that the means of bio-oil yield are significantly different (b > a), while the same letters indicate that the values are statistically the same, based on Tukey's HSD test ($p < 0.05$).

Fig. 3. Comparisons of bio-oil carbon (A) and oxygen (B) contents of different ecotypes grouped by planting location. Different letters (a and b) above the standard deviation bars indicate that the means of C or O contents are significantly different (b > a), while the same letters indicate that the values are statistically the same, based on Tukey's HSD test ($p < 0.05$).

Fig. 4. Comparisons of bio-oil C (A) and O (B) contents in different planting locations, grouped by ecotype. Different letters (a and b) above the standard deviation bars indicate that the means of C or O contents are significantly different (b > a), while the same letters indicate that the values are statistically the same, based on Tukey's HSD test ($p < 0.05$).

planted in Manhattan, KS, or Carbondale, IL. The Hays planting site had significantly lower precipitation than Manhattan and Carbondale planting sites in 2010, which might have caused the differences in feedstock chemical composition (described in Section 3.3) and consequently different bio-oils. However, the other ecotypes planted in Hays did not yield significantly different bio-oils from other planting locations like the EKS ecotype, which suggests that interaction effects may exist between ecotype and planting location. In other words, different ecotypes might respond to climate changes in different ways. This conclusion might be biased due to small samples sizes in this study; therefore, looking at the average elemental compositions of all three ecotypes and KAW, which are statistically the same in the three planting locations (Fig. 4), would be more meaningful.

Effects of ecotype and planting location on bio-oil yield and bio-oil C and O contents were also analyzed by two-way ANOVA. Based on statistical results summarized in Table 2, bio-oil yield of big bluestem HTC was significantly affected by ecotype ($p < 0.05$) and planting location ($p < 0.01$), with the latter being more influential (greater F-value with smaller P-value). The interaction effect of ecotype and planting location on bio-oil yield was statistically insignificant ($p > 0.05$). Bio-oil C and O contents were significantly affected by both ecotype ($p < 0.01$) and the interaction between ecotype and planting location ($p < 0.05$); however, planting location alone had no significant effect on bio-oil C or O contents.

3.3. The effect of ecotype and planting location on big bluestem chemical and elemental compositions

It was hypothesized in this study that the yield and elemental compositions of bio-oil were determined by the chemical and elemental compositions of big bluestem feedstock (Table 3), which were influenced by ecotype and/or planting location. By averaging all ecotypes and cultivar in each planting location, big bluestem planted in Carbondale, IL and Manhattan, KS, contained higher cellulose and hemicellulose contents than in Hays, KS, whereas lignin contents of the three planting locations were statistically the same. A positive correlation between the total amount of cellulose and hemicellulose and bio-oil yield was found (described in Section 3.4, Fig. 5). Furthermore, big bluestem planted in Carbondale, IL and Manhattan, KS contained more C but less O than in Hays, KS, which may also explain the higher bio-oil yield in the two locations. A positive correlation between C content and bio-oil yield and a negative correlation between O content and bio-oil yield were found (described in Section 3.4, Fig. 6). The effect of big bluestem ecotype on its chemical and elemental compositions is dependent on the planting location. Generally, KAW and the IL ecotype had either higher cellulose content or lower O content; however, compared with planting location effect, ecotype effect on feedstock composition was not significant. Detailed analysis of the effect of ecotype and planting location on big bluestem chemical and elemental compositions will be reported in another article in our series (unpublished data).

3.4. Correlations between feedstock compositions and bio-oil yield

A positive linear relationship between bio-oil yield and the total amount of cellulose and hemicellulose in the feedstock is shown in Fig. 5. Bio-oil yield generally increased as the total amount of cellulose and hemicellulose increased. Cellulose and hemicellulose were found to be able to convert to bio-oil in hot-compressed water at relatively low temperatures (260–300 °C) by some other researchers (Minowa et al., 1997; Pińkowska et al., 2011). The relatively low coefficient of determination ($R^2 = 0.63$) of the linear regression in Fig. 5 suggests that bio-oil yield was probably affected by other factors besides the total amount of cellulose and
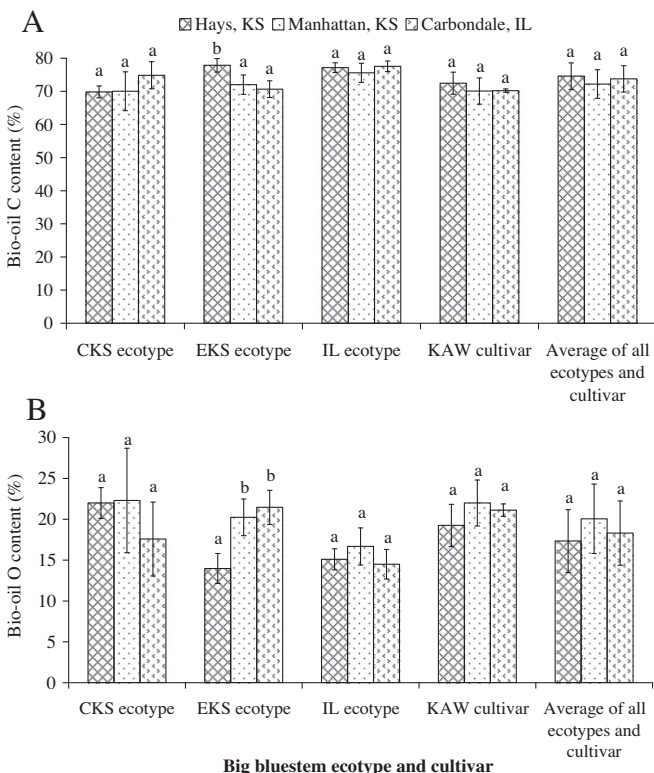
Table 2
Two-way ANOVA test of the effect of ecotype and planting location on bio-oil yield and elemental composition.

Source of variation	Bio-oil yield			Bio-oil carbon content			Bio-oil oxygen content		
	df	F	P	df	F	P	df	F	P
Ecotype	3	3.83	.020	3	7.42	.001	3	7.17	.001
Location	2	13.12	.000	2	2.11	.140	2	2.59	.092
Ecotype × location	6	1.83	.127	6	2.71	.032	6	2.68	.033

Table 3
Chemical and elemental compositions of big bluestem (wt.% db).

Ecotype	Planting location	Cellulose	Hemicellulose	Lignin	Cellulose and hemicellulose	
CKS	Hays, KS	30.02 ± 0.46[a]	22.79 ± 0.77[a]	18.17 ± 0.53[a]	52.81[a]	
	Manhattan, KS	30.03 ± 1.03[a]	24.73 ± 0.66[ab]	17.72 ± 0.15[a]	54.76[ab]	
	Carbondale, IL	30.55 ± 0.88[a]	26.55 ± 1.63[b]	17.45 ± 0.90[a]	57.1[b]	
EKS	Hays, KS	27.80 ± 0.35[a]	22.03 ± 0.47[a]	17.33 ± 0.13[a]	49.83[a]	
	Manhattan, KS	29.53 ± 0.37[b]	25.01 ± 0.64[b]	17.17 ± 0.50[a]	54.54[b]	
	Carbondale, IL	29.46 ± 1.17[b]	26.33 ± 0.80[c]	18.05 ± 0.62[a]	55.79[b]	
IL	Hays, KS	28.96 ± 1.64[a]	21.99 ± 0.60[a]	16.51 ± 0.33[a]	50.93[a]	
	Manhattan, KS	29.96 ± 1.49[a]	25.20 ± 1.23[b]	16.27 ± 1.20[a]	55.06[b]	
	Carbondale, IL	29.71 ± 0.38[a]	25.54 ± 1.11[b]	17.47 ± 0.90[a]	55.25[b]	
KAW	Hays, KS	29.38 ± 0.00[a]	22.31 ± 0.32[a]	16.92 ± 0.20[a]	51.69[a]	
	Manhattan, KS	32.28 ± 0.48[ab]	24.10 ± 0.37[b]	17.62 ± 0.05[b]	56.38[b]	
	Carbondale, IL	33.25 ± 0.33[b]	26.30 ± 0.10[c]	19.35 ± 0.17[c]	59.55[c]	
Average of all ecotypes and cultivar	Hays, KS	29.0 ± 1.17[a]	22.3 ± 0.61[a]	17.28 ± 0.71[a]	51.3 ± 1.50[a]	
	Manhattan, KS	30.19 ± 1.28[ab]	24.85 ± 0.83[b]	17.13 ± 0.88[a]	55.04 ± 1.50[b]	
	Carbondale, IL	30.39 ± 1.48[b]	26.16 ± 1.10[c]	17.90 ± 0.96[a]	56.55 ± 2.17[b]	
CKS	Average in all locations	30.20 ± 0.79[ab]	24.69 ± 1.89[a]	17.78 ± 0.63[b]	54.89 ± 2.29[a]	
EKS		28.93 ± 1.07[a]	24.45 ± 1.97[a]	17.52 ± 0.58[b]	53.38 ± 2.9[a]	
IL		29.55 ± 1.25[a]	24.24 ± 1.91[a]	16.75 ± 0.97[a]	53.79 ± 2.77[a]	
KAW		31.64 ± 1.82[b]	24.24 ± 1.80[a]	17.96 ± 1.13[b]	55.87 ± 3.56[a]	
	Location	**Carbon**	**Hydrogen**	**Nitrogen**	**Sulfur**	**Oxygen[a]**
Elemental composition (wt.% db)						
CKS	Hays, KS	50.11 ± 1.27[a]	4.18 ± 0.04[a]	1.08 ± 0.07[a]	0.65 ± 0.45[a]	43.99 ± 0.79[a]
	Manhattan, KS	50.66 ± 0.97[a]	4.15 ± 0.04[a]	0.83 ± 0.01[a]	0.51 ± 0.27[a]	43.86 ± 0.73[a]
	Carbondale, IL	53.16 ± 0.56[a]	4.26 ± 0.21[a]	0.76 ± 0.18[a]	0.75 ± 0.03[a]	41.08 ± 0.61[a]
EKS	Hays, KS	48.66 ± 0.78[a]	4.11 ± 0.04[a]	1.15 ± 0.12[a]	0.34 ± 0.01[a]	45.76 ± 0.68[b]
	Manhattan, KS	49.92 ± 0.11[ab]	4.11 ± 0.42[a]	0.90 ± 0.07[a]	0.46 ± 0.30[a]	44.61 ± 0.17[b]
	Carbondale, IL	53.12 ± 1.13[b]	4.39 ± 0.12[a]	0.97 ± 0.54[a]	0.75 ± 0.04[a]	40.78 ± 0.43[a]
IL	Hays, KS	50.09 ± 0.33[a]	4.43 ± 0.40[a]	0.99 ± 0.21[a]	0.30 ± 0.06[a]	44.21 ± 0.20[c]
	Manhattan, KS	51.62 ± 0.02[b]	4.31 ± 0.18[a]	0.91 ± 0.21[a]	0.54 ± 0.29[a]	42.63 ± 0.28[b]
	Carbondale, IL	53.15 ± 0.10[c]	4.34 ± 0.01[a]	0.92 ± 0.01[a]	0.74 ± 0.01[a]	40.86 ± 0.06[a]
KAW	Hays, KS	50.78 ± 0.57[a]	4.41 ± 0.60[a]	0.84 ± 0.13[a]	0.27 ± 0.51[a]	43.70 ± 0.67[c]
	Manhattan, KS	51.22 ± 0.62[a]	4.46 ± 0.46[a]	0.69 ± 0.19[a]	0.74 ± 0.16[a]	42.89 ± 0.20[b]
	Carbondale, IL	53.65 ± 0.14[b]	4.42 ± 0.01[a]	0.63 ± 0.14[a]	0.75 ± 0.01[a]	40.55 ± 0.02[a]
Average of all ecotypes and cultivar	Hays, KS	49.78 ± 1.02[a]	4.26 ± 0.23[a]	1.04 ± 0.15[a]	0.40 ± 0.25[a]	44.52 ± 0.97[c]
	Manhattan, KS	50.80 ± 0.82[a]	4.23 ± 0.23[a]	0.85 ± 0.12[a]	0.54 ± 0.22[a]	43.58 ± 0.93[b]
	Carbondale, IL	53.21 ± 0.55[b]	4.34 ± 0.12[a]	0.85 ± 0.27[a]	0.75 ± 0.02[a]	40.85 ± 0.36[a]
CKS	Average in all locations	51.31 ± 1.64[a]	4.19 ± 0.11[a]	0.89 ± 0.17[a]	0.64 ± 0.26[a]	42.98 ± 1.57[b]
EKS		50.57 ± 2.15[a]	4.20 ± 0.24[a]	1.00 ± 0.27[a]	0.52 ± 0.23[a]	43.71 ± 2.36[b]
IL		51.62 ± 1.38[a]	4.36 ± 0.21[a]	0.94 ± 0.14[a]	0.52 ± 0.24[a]	42.57 ± 1.51[a]
KAW		51.88 ± 1.55[a]	4.43 ± 0.03[a]	0.72 ± 0.11[a]	0.59 ± 0.27[a]	42.38 ± 1.64[a]

Different letters (a, b, and c) indicate that the means of composition are significantly different in the order of c > b > a based on Tukey's HSD test ($p < 0.05$). The same letters indicate that the values are statistically the same.
   [a] Calculated by the difference between 100% and the total amount of carbon, hydrogen, nitrogen, and sulfur.

hemicellulose of the feedstock, such as lignin content. Compared with cellulose, lignin is more readily hydrolyzed to liquid organic compounds (Tymchyshyn and Xu, 2010), but the decomposition of pure lignin favors the formation of water-soluble organic compounds and solid residue rather than heavy bio-oil. Furthermore, solid residue is formed by condensation reactions of the liquid organic compounds (Bobleter and Concin, 1979). Luo and co-workers (2010) found that the liquid products from Pubescens hydrothermal reaction at 300 °C for 15 min contained largely phenol derivatives (decomposed from lignin) and around 50% lignin was left in the solid residue. Demirbaş (2000) also reported that free phenoxyl radicals derived from lignin decomposition had a random tendency to form bio-char via condensation or repolymerization; however, bio-oil produced from real biomass HTC contained significant

quantities of phenolic compounds and their derivatives (Bhaskar et al., 2008; Tymchyshyn and Xu, 2010; Sun et al., 2011), which indicated that lignin in real biomass contributed greatly to bio-oil production. Roberts and co-workers (2011) reported that boric acid inhibited the condensation reaction in pure lignin base-catalyzed HTC. Significant interactions between the biomass chemical compounds in the HTC process may occur because acetic acid and other organic acids were produced from cellulose and hemicellulose in HTC. Weak correlation between lignin content and bio-oil yield was found in this study, perhaps because of the complex reactions in biomass HTC. Minowa and coworkers (1998) also found that the bio-char yield increased as the biomass lignin content increased, but the correlation between lignin content and bio-oil yield was weak. The other reason for the weak correlation might
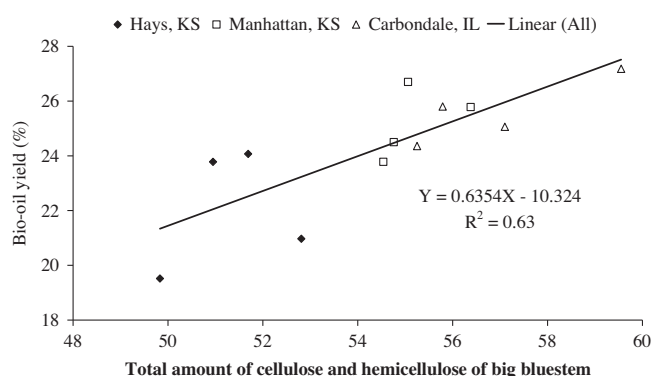
Fig. 5. Effect of the total amount of cellulose and hemicellulose in big bluestem on bio-oil yield.
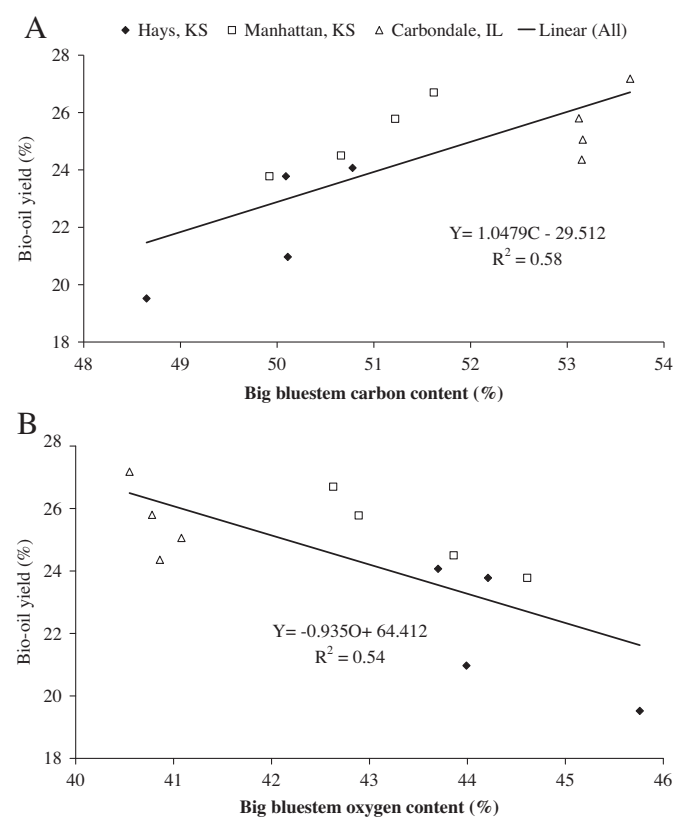
Fig. 6. Effect of big bluestem C content (A) and O content (B) on bio-oil yield.

be the narrow lignin content range (16.3–19.6%) of big bluestems in this study. The effect of lignin content on bio-oil production is difficult to distinguish clearly in such narrow range.

The effect of big bluestem C and O contents on bio-oil yield is evident in Fig. 6. Higher C content or lower O content, which usually correlate with each other, gave higher bio-oil yield. Similar phenomena were observed in microalgae HTC at 300 °C for 30 min. Bio-oil yield increased with increasing microalgae C content, but decreased as microalgae O content increased (Vardon et al., 2012; Garcia Alba et al., 2012). Heavy bio-oil produced from biomass HTC mainly consists of high molecular weight organic compounds such as phenolic compounds and their derivatives, long-chain carboxylic acids/esters, and long-chain hydrocarbons (Bhaskar et al., 2008; Sun et al., 2011). Biomass C is the main source of produced heavy bio-oil.

Correlations between bio-oil yield and the contents of cellulose, hemicellulose, and lignin, as well as C and O contents of the feed-stock were also analyzed by SPSS Pearson's correlation. Correlations between bio-oil yield and the contents of cellulose and hemicellulose were significant at the 0.05 level, and the correlation coefficients (r) were 0.67 and 0.70, respectively. Furthermore, a strong positive correlation between bio-oil yield and the total amount of cellulose and hemicellulose was found ($r = 0.79$, significant at the 0.01 level), which is consistent with Fig. 5. The correlation between bio-oil yield and lignin content is weak and insignificant with a correlation coefficient of 0.14; however, considering the narrow range of lignin content in the selected big bluestem samples (16.3% to 19.4% in Table 3), the correlation is not reliable enough to exclude the effect of lignin content on bio-oil yield. The positive correlation between big bluestem C content and bio-oil yield ($r = 0.75$, significant at the 0.01 level) and the negative correlation between big bluestem O content and bio-oil yield ($r = -0.72$, significant at the 0.01 level) are also consistent with the findings from Fig. 6.

3.5. Comparison of bio-oil production from big bluestem, switchgrass, and corncobs

Table 4 summarizes the yield and elemental composition of bio-oils generated from big bluestem, switchgrass, and corncobs. When the highest-yielding big bluestem (KAW planted in Carbondale, IL) was used in statistical analysis, big bluestem had bio-oil yield similar to corncobs, and yield was significantly higher than that from switchgrass. However, bio-oil from KAW big bluestem planted in Carbondale, IL, had the lowest C and the highest O contents compared with those from switchgrass and corncobs. When the average bio-oil yield and elemental composition of all big bluestems were used, bio-oil yield of big bluestem and switchgrass had no significant difference, but both were lower than that of corncobs. Bio-oils produced from the three types of biomass were statistically the same in both C and O contents. This is the first data set, to the best of our knowledge, that provides fundamental information about the potential of big bluestem to be developed as a bio-fuel feedstock and how it compares with more widely used crops such as switchgrass.

The main chemical compounds of bio-oils produced from big bluestem (KAW planted in IL), switchgrass, and corncobs are summarized in Table 5. Bio-oils from the three biomass contained similar chemical compounds, such as ketones (3-Penten-2-one, 4-methyl- and 2-Pentanone, 4-hydroxy-4-methyl-), alcohol (1-Hexanol, 2-ethyl-), esters (2-Ethylhexyl mercaptoacetate and Diethyl Phthalate), and long-chain alkane hydrocarbons (Hexadecane and Nonadecane), but area percentages varied by biomass. Among the many chemical compounds in the bio-oils, 2-Ethylhexyl mercaptoacetate and 1-Hexanol, 2-ethyl- were the dominant compounds. The highest concentrations of 2-Ethylhexyl mercaptoacetate and 1-Hexanol, 2-ethyl- were observed in corncob-based bio-oil, whereas bio-oils from big bluestem and switchgrass had similarly lower concentrations, perhaps because corncobs have higher cellulose (35.6%) and hemicellulose (30.0%) contents than big bluestem (31.2% cellulose, 26.2% hemicellulose) and switchgrass (31.0% cellulose, 20.4% hemicellulose). In HTC, cellulose and hemicellulose are believed to make short- and straight-chain hydrocarbons such as -Ethylhexyl mercaptoacetate and 1-Hexanol, 2-ethyl-. Small percentages of 2-Pentanone, 4-hydroxy-4-methyl- were observed in all three bio-oils and were considered the decomposed product of benzene derivatives from lignin (Bhaskar et al., 2008). Neither phenol nor its derivatives were found in the bio-oils produced in this study. Bhaskar and coworkers (2008) reported that phenolic derivatives could be concentrated in aqueous products with strong alkali solution, which was the case for this study.

Table 4
Comparison of bio-oil production between big bluestem, switchgrass, and corncobs.

Biomass	Bio-oil yield (%)	Bio-oil C content (%)	Bio-oil O content (%)
Best big bluestem-KAW	27.2 ± 1.1[b]	70.2 ± 0.5[a]	21.12 ± 0.76[b]
Switchgrass	23.6 ± 0.2[a,A]	75.5 ± 0.2[b,A]	15.77 ± 1.29[a,A]
Corn cobs	29.9 ± 0.5[b,B]	74.8 ± 0.08[b,A]	16.76 ± 0.64[a,A]
Big bluestem-Average	24.1 ± 2.7[A]	73.5 ± 4.1[A]	18.6 ± 4.1[A]

Lowercase letters (a and b) indicate whether the means of yield or elemental composition of the best yielding big bluestem-KAW, switchgrass, and corncobs are significantly different based on Tukey's HSD test ($p < 0.05$). Uppercase letters (A and B) were used to indicate the difference among the average bio-oil yield and elemental composition of all big bluestems, switchgrass, and corncobs. The same letter means they are not significantly different, whereas different letters mean they are significantly different in the order of b > a or B > A.

Table 5
Identification of compounds by GC–MS in bio-oil from big bluestem, switchgrass, and corncobs.

No.	RT (min)	Name of compound	Molecular formula	Area (%) Big bluestem	Switchgrass	Corncobs
1	5.8	3-Penten-2-one, 4-methyl-	$C_6H_{10}O$	1.5	4.6	–
2	6.4	2-Pentanone, 4-hydroxy-4-methyl-	$C_6H_{12}O_2$	3.7	5.8	3.6
3	9.3	1-Hexanol, 2-ethyl-	$C_8H_{18}O$	21.1	20.9	30.1
4	15.0	2-Ethylhexyl mercaptoacetate	$C_{10}H_{20}O_2S$	33.0	25.6	48.3
5	17.1	Diethyl Phthalate	$C_{12}H_{14}O_4$	2.05	0.55	0.51
6	22.8	Hexadecane	$C_{16}H_{34}$	–	3.36	–
7	22.9	Nonadecane	$C_{19}H_{40}$	8.93	–	3.19

4. Conclusions

Bio-oil yield of big bluestem HTC was significantly affected by both ecotype and planting location, but the latter was more influential. The interaction effect between ecotype and planting location on bio-oil yield was statistically insignificant ($p > 0.05$). Bio-oil C and O contents were significantly affected mainly by ecotype ($p < 0.01$) and sometimes by the interaction between ecotype and planting location ($p < 0.05$); however, planting location alone had no significant effect on bio-oil C or O contents. Big bluestem and switchgrass have similar potential for bio-oil production via HTC.

Acknowledgements

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