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Thermal properties of big bluestem as affected by ecotype and planting location along the precipitation gradient of the Great Plains

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A B S T R A C T

The objective of this research was to study the effect of ecotype and planting location on thermal properties of big bluestem. Three big bluestem ecotypes (CKS, EKS, ILL) and a cultivar (KAW) were harvested in 2010 from four locations (Colby, Hays, and Manhattan, KS; and Carbondale, IL) and were evaluated for their specific heat, thermal conductivity, thermal stability, HHV (high heating value), and proximate contents. All populations revealed a large variation in specific heat (2.35–2.62 kJ/kg/K), thermal conductivity (77.85–99.06 $\times$ 10^{-3} W/m/K), thermogravimetric analysis as weight loss during the heating process (71–73%), and HHV (17.64–18.67 MJ/kg). Specific heat of the big bluestem was significantly affected by planting location, ecotype, and interaction between location and ecotype. Planting location had stronger influence on specific heat than ecotype. Specific heat increased as temperature increased, and a linear correlation model for specific heat prediction was developed as a function of temperature. Ecotype, planting location, and the interaction of ecotype and planting location did not have a significant effect on thermal conductivity; however, density and particle size showed a completely opposite relationship on thermal conductivity. Both planting location and ecotype significantly affected HHV. Among all environmental factors, potential evapotranspiration had the most significant effect on thermal properties.

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1. Introduction

Renewable energy has received growing attention as people have become more conscious of the fossil fuel shortage and greenhouse gas emissions have been related to global warming [1]. In 2010, renewable energy resources supplied 8% of the nation's total energy consumption and up to 8.05 quadrillion Btu (increased from 6% in 2009). Biomass led the other renewable energy resources (such as wind, solar, geothermal, and hydroelectric) by contributing 53% of the nation's renewable energy supply in 2010 [1]. Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, animal wastes, aquatic plants, algae, etc. [2]. Big bluestem (*Andropogon gerardii*) is regarded as second-generation biomass and recently has been proposed as promising energy crops because their growth requires few agricultural inputs (fertilizer and pesticides). Propheter and Staggenborg reported that only one-tenth of nitrogen filterlizers were required for big bluestem during the first two years comparing with annual biofuel crops such as corn, soybean and sorghum [3]. In addition, those annual biofuel crops had much higher soil nitrogen removal rate (~160 kg ha^{-1}) than big bluestem (~30 kg ha^{-1}) [3]. Lynd reported that perennial grasses such as big bluestem require substantially less fertilizer and pesticides than corn as biofuel feedstocks [4]. In the United States, big bluestem dominates the tallgrass prairie of North America and is a major component of prairie biomass [5,6]. Moreover, tolerance to heat and drought have enabled big bluestem to fill the deficiency in grasslands in the Midwestern U.S. when cool-season grasses (C3) are unproductive [7–9]. Recently research reported that successional herbaceous vegetation, such as big bluestem and alfalfa, on

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marginal lands in the Midwestern U.S. states can not only provide greenhouse gas emissions mitigation, but also produce substantial proportion of future biofuel energy target [10].

Thermal, biological, and physical processes are the three major technologies that help make use of a wide variety of biomass. In thermal conversion technologies, direct combustion and co-firing with coal were first utilized for electricity production and once were responsible for over 97% of the world's bioenergy production [11]. Pyrolysis has attracted the highest interest because it produces bio-oil, which can be used as a fuel in stable engines and converted into chemicals such as bio-lime nitrogen fertilizer [12]. Biomass gasification has been researched extensively due to its higher efficiencies compared with combustion, and fast pyrolysis is still at a relatively early stage of development [13]. Torrefaction, another promising thermal process, improves the quality of biomass in terms of heat content, physical properties, and chemical composition for combustion and gasification applications [14].

Understanding, predicting, and controlling these thermal processes and designing processing equipment require knowledge of the thermal properties of biomass, such as specific heat, thermal conductivity, thermal stability, HHV (high heating value), and proximate contents.

Specific heat of a substance (kJ/kg/K) is defined as the amount of heat required to increase the temperature of a unit of mass by one degree. Specific heat affects the total energy required for thermal conversion of biomass into biofuels. The specific heat of biomasses depends largely on their composition; using the specific heat of each component of a mixture and the mass fraction is usually sufficient to predict the specific heat of the mixture [15]. Although the method based on the specific heat of the components in the mixture is most widely used to predict specific heat because of its simplicity, experimentally determined value is usually higher than predicted value [16]. Koch utilized DSC (differential scanning calorimetry) as a convenient technique for measuring the specific heat of wood and bark of 72 spruce pine trees [17].

Thermal conductivity of a material (W/m K) is a measure of its ability to conduct heat. Thermal conductivity of biomass depends mostly on composition and the characteristics of the biomass that affect the heat flow paths through the material. Mohsenin reviewed thermal conductivity measurement techniques for both steady-state and transient-sate transfers [18]. The heated probe method is simple, fast, and requires only a small sample, and it has been widely used for thermal conductivity determination [19]. Thermal stability, the ability of a material to resist changes in physical shape or size as its temperature changes, is essential to understand and predict the reactions and kinetics during biomass thermal conversion. TGA (thermogravimetric analysis) is the usual technique for determining thermal stability by quantitative measurement of weight changes (loss/gain) associated with thermally induced transition as a function of temperature or time [20]. High heating value (MJ/kg) is an important thermal parameter to characterize the amount of energy produced by the combustion of a unit mass of a material. Proximate analysis is a simple and rapid procedure for defining the substance energy content and determining how clean and efficient the substance is for the purpose.

Our recent research on big bluestem showed that planting location and ecotype as well as interaction of planting location and ecotype had significant effects on chemical and elemental composition of big bluestem [21]. In addition, our study also showed that bio-oil yield from big bluestem through hydrothermal conversion was significantly affected by both ecotype and planting location [22]. However, we found no research on the thermal properties of big bluestem, especially the effects of ecotype and planting location on the thermal properties of big bluestem. Therefore, the objectives of this research were to characterize the thermal properties of big bluestem and to study the effects of ecotype and planting location on thermal properties of big bluestem and thus, fill a critical gap in fundamental knowledge of thermal properties of a valuable bioenergy grass.

2. Materials and methods

2.1. Materials

Three big bluestem ecotypes, CKS (Cedar Bluffs [CDB]), EKS (Konza [KON]), and ILL (12Mile [12M]), and the KAW cultivar, which is widely planted to restore marginal lands, were harvested from reciprocal garden plots in four planting locations (Colby, Hays, and Manhattan, KS; and Carbondale, IL) in 2010. Among the four locations, the Colby planting site was used to test the threshold of drought tolerance and the possibility for planting in drier Great Plains locations. Two populations from each ecotype were evaluated for thermal properties. No nitrogen fertilizers and pesticides were applied to the big bluestem. Details of seed collection and planting location have been described previously [21]. The big bluestem samples were ground into powder using a RetschSM2000 cutting mill (Haan, Germany) with a 1.0-, 2.0-, and 4.0-mm sieve, respectively. For thermal conductivity measurement, only 2.0- and 4.0-mm particle sizes were used. After grinding, each sample was fully mixed in sealed plastic storage bags. To eliminate any error that might be caused by water, samples were dried at 45 °C for 24 h and saved in the plastic bag before measuring specific heat, thermal conductivity, high heating value, and proximate content. All measurements were carried out in short time at room temperature of 22 °C and 40% humidity.

2.2. Specific heat by differential scanning calorimetry (DSC)

Specific heat of big bluestem was measured with DSC Q200 V24.4 instrument (TA Instruments, New Castle, DE) calibrated with indium and zinc. An empty sealed pan was used as a reference for every measurement. Three-step scans were carried out in this study. The first scan was conducted with an empty hermetic pan to determine the baseline background heat flow, which was subtracted from subsequent measurements. Next, sapphire was weighed and sealed in a pan for determination value of E. E was the calibration constant and calculated by using Equation 1:

$$E = \frac{C_{ps} \times H_r \times M}{H \times 60} \tag{1}$$

where C_{ps} is specific heat of sapphire, which was standard and obtained from the literature (kJ/kg/K); H_r is heating rate, which was 10 in this study (K/min); M is sapphire mass (mg); H is measured heating value (mW); and 60 is conversion constant (minute to second).

For the sample run, an empty pan and a pan with a 5-mg sample were placed into the DSC. The specific heat of the sample is calculated by transposition equation and substituting E. Large-volume stainless steel pans were used. All measurements were held at 323 K for 10 min, scanned from 323 K to 473 K at a heating rate of 10 K/min, and then held at 473 K for another 10 min. The sample was characterized in an inert environment by using nitrogen with a gas flow rate of 50 ml/min.

2.3. Thermal conductivity by probe method

Fig. 1 shows a diagram of the experimental apparatus for measurement of thermal conductivity using the heated needle probe. The container is filled with biomass with a confined particle size