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Modeling the equilibrium moisture content (*EMC*) of *Miscanthus sinensis*, miscane, energy cane, and energy sorghum

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HIGHLIGHTS

- *Miscanthus sinensis*, miscane, energy cane, and energy sorghum were studied.
- Sorption behaviors of each crop were determined at 15, 25, and 35 °C.
- Modified Oswin model provided the best fit for the individual crop ($R^2 > 0.974$).
- A global isotherm model was developed for all four crops ($R^2 = 0.973$).
- The global model was further modified to include a sucrose content ($R^2 = 0.979$).

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ABSTRACT

Understanding of moisture sorption isotherms of bioenergy crops is critical to monitoring their stability and quality during harvest, handling, transportation, and storage. Relationships between the moisture content (*EMC*) and equilibrium relative humidity (*ERH*) of four biomass crops – *Miscanthus sinensis*, miscane, energy cane, and energy sorghum – were determined at 15, 25, and 35 °C. Type II and type III isotherm characteristics were observed in all samples. The Henderson, modified Henderson, modified Chung-Pfost, modified Halsey, modified Oswin, and modified GAB models were applied to the individual energy crop's sorption isotherm data and a global isotherm model for the four energy crops was developed. Results showed that the modified Oswin model best fit the sorption behavior of the individual crops ($0.974 \leqslant R^2 \leqslant 0.997$ and 0.72% wet basis (w.b.) $\leqslant$ standard error (*SE*) $\leqslant$ 1.91% w.b.) and for a global isotherm model of these crops ($R^2 = 0.973$ and $SE = 1.96\%$ w.b.). When the soluble sucrose content (0.00–15.9%) of the energy crops were included the global isotherm model based on the modified Oswin equation, overall performance improved ($R^2 = 0.979$ and $SE = 1.75\%$ w.b.).

1. Introduction

It has been estimated that to replace 30% of our current energy demand with fuels from renewable agricultural resources, the United States will need to produce one billion tons of biomass annually. Of these, 377 million tons needs to be dedicated lignocellulosic feedstock [1]. In order to make a change of this magnitude feasible, many obstacles need to be overcome including the ability to supply the processing facilities with a steady stream of feedstock with uniform composition, or potential sugar yield, throughout the year. Currently this is challenging as biomass composition varies based on inherent species variability, production practices, and multiple methods of harvest, collection, transportation, and storage. The "quality" of the biomass feedstock will likely degrade from the day of harvest and it is expected to undergo dry matter loss (*DML*) during storage. The rates of *DML* and quality degradation are expected to vary depending on weather conditions and material handling practices.

To properly store biomass feedstocks, their moisture sorption isotherms must be known. A moisture sorption isotherm describes the relationship between the equilibrium relative humidity (*ERH*) and the equilibrium moisture content (*EMC*) of a specific bioenergy crop at a given temperature [2]. Such *ERH*–*EMC* relationships are the key to understanding the water sorption properties of foods and agricultural products, predicting stability and moisture changes during harvest and storage, and selecting packaging materials. Several equations are used to describe these relationships [3]:

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Nomenclature

Symbols
°C degree Celsius
F *F*-statistic
R^2 coefficient of determination
% percentage
A, *B*, and *C* temperature dependent constants
T temperature
D regression coefficient of the energy cane and energy sorghum stalks which contained sucrose
SC sucrose content

Abbreviations
EMC equilibrium moisture content
ERH equilibrium relative humidity
MRE mean relative error
SE standard error
w.b. wet basis
DOE Department of Energy
DML dry matter loss
M. *Miscanthus*
USDA US Department of Agriculture
ARS Agricultural Research Service
MC_{wb} wet-basis moisture content
EBI Energy Biosciences Institute
ANSI American National Standards Institutes
ASABE American Society of Agricultural and Biological Engineers
M. modified

$$\text{Henderson}: \quad EMC = \left[\frac{\ln(1-ERH)}{-AT}\right]^{\frac{1}{B}} \tag{1}$$

$$\text{Modified Henderson}: \quad EMC = \left[\frac{\ln(1-ERH)}{-A(T+B)}\right]^{\frac{1}{C}} \tag{2}$$

$$\text{Modified Chung-Pfost}: \quad EMC = -\frac{1}{C}\ln\left[\frac{\ln(ERH)(T+B)}{-A}\right] \tag{3}$$

$$\text{Modified Halsey}: \quad EMC = \left[\frac{-\exp(A+BT)}{\ln(ERH)}\right]^{\frac{1}{C}} \tag{4}$$

$$\text{Modified Oswin}: \quad EMC = (A+BT)\left(\frac{ERH}{1-ERH}\right)^{\frac{1}{C}} \tag{5}$$

Modified Guggenheim-Anderson-deBoer (GAB) :

$$EMC = \frac{A(C/T)B(ERH)}{[1-B(ERH)][1-B(ERH)+(C/T)B(ERH)]} \tag{6}$$

where *EMC* (% w.b.) and *ERH* (decimal form), *T* is the temperature (°C), and *A*, *B*, and *C* are temperature dependent constants. No perfect *EMC* model exists for description of sorption isotherms of biological materials [4]. In fact, Chen and Morey [5] found that the Modified Henderson and Chung-Pfost equations provided good models for starch grains and fibrous materials, the Modified Halsey equation was a useful model for high oil and protein products, and the Modified Oswin equation best fit the sorption–desorption behavior of popcorn, corncobs, and some corn varieties.

To date, moisture sorption isotherm relationships have been determined for a large variety of bioenergy crops: *Miscanthus* × *giganteus* [6], switchgrass [7,8], switchgrass pellets [9]; prairie cord grass [7], corn stover [10], energy sorghum [11], and aspen [12]. Each of the models (Eqs. (1)–(6)) has had different success in fitting the equilibrium moisture content of bioenergy crops at different ranges of equilibrium relative humidity. The difference in success is due to the fact that adsorption or desorption of moisture is a complex phenomenon and depends greatly on the composition of the material [13]. It is expected that physical and/or chemical interactions that occur during harvest, handling, transportation, and storage of biomass will induce changes on the sorption properties of its components. These changes, in turn, will affect the final moisture sorption isotherm of the biomass as it represents the integrated hygroscopic properties of all the components. When bioenergy crops contain soluble or residual sugars after preprocessing, these sugars will need to be accounted for in the isotherm model. Water sorption leads to phase transformations of sugars contained in the crop – sugars can be converted to an amorphous form during drying and slowly reconvert to the crystalline form during adsorption [14].

In this study, the sorption behavior of four bioenergy crops, including *Miscanthus sinensis*, miscane, energy cane, and energy sorghum, were determined. *Miscanthus* is a perennial C4 grass and widely distributed in eastern Asia and the Pacific islands. The ability to adapt to cold weather, water and fertility deficiency, heavy metals and low pH and the fact that it can grow in temperate and tropical areas offer advantages for this crop [15,16]. Unlike the widely studied variety, *Miscanthus* × *giganteus*, *M. sinensis* can produce seeds, does not need to use rooted plantlets or rhizome fragments for future growth [17,18], and can grow between 0.7–3 m height and yield 9.5–19.4 t ha^{-1} [16,19]. Miscane is a cross between sugarcane and miscanthus. The original purpose of cross breeding was to transfer the disease-resistance gene from miscanthus to sugarcane, but biomass production increases were evident for bioenergy applications. Miscanes present the best traits of its parents such as late flowering and high biomass content in sugarcane and low sugar, cold tolerance, dormancy and dry-down trait in miscanthus [16]. Energy cane is bred from wild cane and sugar cane to give lower sugar and higher biomass or fiber content. It has been reported that energy cane can grow double fiber contents than sugar cane [20]. Energy cane was developed in response to the US energy crisis in the 1970s as a way for breeders to transition sugarcane as an energy crop through biomass production. Several non-commercial energy cane varieties have been developed by the US Department of Agriculture – Agricultural Research Service (USDA ARS) in Houma, LA for enhanced biomass yields, adaptability to colder regions and fallow lands, and reduced production costs [21]. Sorghum is a C4 staple crop indigenous to Africa and is also categorized as one of the dedicated bioenergy crops [22]. There are several types of sorghum – grain sorghum, for human food consumption, comparable to corn; forage sorghum, for animal feed or silage; sweet sorghum, for sugar production; and energy sorghum, a feedstock developed for bioenergy applications [23,24]. Energy sorghum typically yields 15–20 tons per acre compared to forage sorghum and switchgrass, which yield 10 and 8 tons of biomass per acre, respectively [25]. Energy sorghum is highly tolerant to drought and has a much wider adaptation to different temperatures and soil types than sweet sorghum [23].

The objective of this study was to determine the sorption behavior of these four bioenergy crops at 15, 25 and 35 °C and relative humidity ranging from 0.118 to 0.907. Since the crops have varying levels of sucrose, the effect of sucrose content on their sorption characteristics was also investigated. All data were mod-