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Effect of Torrefaction on Water Vapor Adsorption Properties and Resistance to Microbial Degradation of Corn Stover

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ABSTRACT: The equilibrium moisture content (EMC) of biomass affects transportation, storage, downstream feedstock processing, and the overall economy of biorenewables production. Torrefaction is a thermochemical process conducted in the temperature regime between 200 and 300 °C under an inert atmosphere that, among other benefits, aims to reduce the innate hydrophilicity and susceptibility to microbial degradation of biomass. The objective of this study was to examine water sorption properties of torrefied corn stover. The EMC of raw corn stover, along with corn stover thermally pretreated at three temperatures, was measured using the static gravimetric method at equilibrium relative humidity (ERH) and temperatures ranging from 10 to 98% and from 10 to 40 °C, respectively. Five isotherms were fitted to the experimental data to obtain the prediction equation that best describes the relationship between the ERH and the EMC of lignocellulosic biomass. Microbial degradation of the samples was tested at 97% ERH and 30 °C. Fiber analyses were conducted on all samples. In general, torrefied biomass showed an EMC lower than that of raw biomass, which implied an increase in hydrophobicity. The modified Oswin model performed best in describing the correlation between ERH and EMC. Corn stover torrefied at 250 and 300 °C had negligible dry matter mass loss due to microbial degradation. Fiber analysis showed a significant decrease in hemicellulose content with the increase in pretreatment temperature, which might be the reason for the hydrophobic nature of the torrefied biomass. The outcomes of this work can be used for torrefaction process optimization, and decision-making regarding raw and torrefied biomass storage and downstream processing.

1. INTRODUCTION

Lignocellulosic biomass has gained renewed attention in developed countries as a sustainable, abundant, and readily available energy and carbon source. Furthermore, public concern about the negative environmental impacts of fossil fuels use, energy dependence on foreign petroleum, and volatile oil prices have promoted the use of biomass feedstock in energy, fuel, and chemical production. Biomass has characteristics distinct from traditional, fossil energy/carbon sources that make its application more costly and complex than traditional fossil fuels. A number of factors increase the cost of biorenewables production, including the high oxygen content of biomass and products derived from it, the low energy and bulk density of biomass, a recalcitrant and heterogeneous nature, and high moisture content.[1] Unlike other unfavorable biomass characteristics, high moisture content is the parameter that affects multiple steps in a biorenewables production chain, such as transportation, storage, and upgrading of lignocellulosic biomass. Moisture increases the cost of transportation by increasing the amount of superfluous material that has to be transported.[2] Dry matter loss of wet biomass can be up to 30% depending on pretreatment and storage type, which increases overall production cost.[1,3] Furthermore, storage of large quantities of high moisture biomass represents a fire hazard due to spontaneous ignition.[4,5] The energy requirement for size reduction increases significantly as a consequence of the increase in moisture content of biomass.[6,7] Gasification of high moisture feedstock causes an increase in tar yield, a decrease in thermal efficiency of the system, and a decrease in operation temperature.[8] Moisture increases char yield and has a mixed effect on bio-oil yield and composition, depending on temperature and mineral matter content.[9] Moreover, the high water content decreases the heating value of biomass, causes ignition issues, demands large process equipment to handle large flue gas volume, and affects the overall combustion quality.[10]

Adsorption is a process of gas, liquid, or dissolved solid uptake by the surface of a solid phase, driven by minimization of the surface free energy. Desorption is a process opposite to adsorption. Adsorbed atoms or molecules leave the surface of the solid phase and return to gas or liquid phase as a result of desorption. It depends on temperature and pressure, as does adsorption.[11,12] Equilibrium moisture content (EMC) is established when the moisture content of material in question is in thermodynamic equilibrium with the relative humidity of the surrounding atmosphere at a particular temperature and pressure.[13] Therefore, change in the relative humidity of the environment affects the moisture content of any biological material at constant pressure and temperature.[7] The relationship between the EMC and the equilibrium relative humidity (ERH) at a constant temperature is expressed by moisture sorption isotherms.[14] The shape of isotherms gives insight into the mechanism of water adsorption and depends on structure and composition of material, in addition to pressure and temperature.[15] The desorption isotherm does not necessarily have to be the same as the adsorption isotherm. The former usually has higher values than the adsorption isotherm in the midrange levels of relative humidity. This is referred to as

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sorption hysteresis. Several theories have been developed to explain occurrence of hysteresis, such as capillary condensation, phase change of nonporous solids, and structural changes of nonrigid solids[11]. Understanding the relationship between EMC and ERH helps in designing drying, combustion, and thermochemical conversion systems; making decisions regarding storage methods for different biomass types; and improving product quality in general.[16]

More than 270 models have been used in the literature to predict water vapor sorption characteristics in materials of biological origin. According to Van der Berg and Bruin,[17] these models can be broadly classified into three categories: theoretical, semiempirical, and empirical. Theoretical models are based on a monolayer/multilayer sorption and a condensed film, and employ constants that have physical meaning. This is the opposite of empirical models, whose constants are not related to material properties.[18] Moreover, there is no single model that is capable of representing sorption behavior of every biological material over a wide range of temperatures and relative humidity levels.[19] Five isotherm equations, modified Henderson, modified Chung−Pfost, modified Halsey, modified Oswin, and modified Guggenheim−Anderson−deBoer (GAB), are accepted by the American Society of Agricultural and Biological engineers as standard models for describing the relationship between the ERH and the EMC of agricultural products.[20]

Torrefaction is a thermochemical process conducted in the temperature range between 200 and 300 °C under an inert atmosphere and low heating rate. It is currently being considered as a biomass feedstock pretreatment, particularly for thermal conversion systems. The final solid product, referred to as torrefied biomass, is composed mainly of cellulose and lignin. It is characterized by increased brittleness, hydrophobicity, microbial degradation resistance, and energy density. Thus, torrefaction can play a significant role in decreasing the costs of transportation and storage of biomass in the large quantities needed to sustain biofuels production.[6,21]

A lot of research on the EMC−ERH relationship has been dedicated to fruits and vegetables, dairy, forage, grain, agricultural residues, and wood.[22−27] Several researchers investigated the water sorption of charcoal, coals, and activated carbon.[28−30] However, there have been only a few studies that investigated water adsorption properties of torrefied biomass.[21,31]

The objective of this work was to assess the hydrophobic nature of thermally treated biomass. Therefore, water adsorption characteristics of raw and torrefied corn stover were determined experimentally at four temperatures and five relative humidity levels. In addition, the suitability of five models for fitting ASABE accepted isotherms was evaluated. A microbial degradation test was conducted to assess dry matter loss due to microbial growth at high ERH. Furthermore, a fiber analysis test was performed to explain the lower water vapor adsorption onto torrefied corn stover.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Corn stover biomass was harvested in the fall 2010 from Iowa State University research fields located in Story County, IA. The bulk wet samples were stored in a cooling chamber at a temperature below 5 °C to preserve their original qualities and to prevent microbial degradation.

Subsamples of the wet material were dried at 60 °C for 72 h and stored in a desiccator until torrefaction or water vapor sorption experiments were conducted. The moisture content of samples before and after experiments was determined according to the ASAE standard for forage moisture measurement D358.2.[32] All samples were ground and sifted before the experiments to obtain physically uniform samples with a particle size less than 2 mm. Ground corn stover biomass was torrefied at 200, 250, and 300 °C according to the method employed by Medic and co-workers[33] with the modifications that all samples were dried before the processing and were torrefied for 20 min.

2.2. Water Vapor Adsorption Experiments. The EMC of biomass was determined at 10, 20, 30, and 40 °C using the static gravimetric method.[34] For this, 2 g (0.0001 g resolution) of samples were spread in a thin layer in Petri dishes and placed in hygrostats, which were sealed plastic containers. Duplicates of raw corn stover, and corn stover samples torrefied at 200, 250, and 300 °C were set in each hygrostat. Five saturated solutions of inorganic salts were used to control the ERH in the hygrostats, as shown in Table 1.[35]

Table 1. ERH of Saturated Solutions at Four Temperatures

salt	chemical formula	ERH (decimal) 10 °C	20 °C	30 °C	40 °C
lithium chloride	LiCl	0.113	0.113	0.113	0.112
magnesium chloride	$MgCl_2$	0.335	0.331	0.324	0.316
magnesium nitrate	$Mg(NO_3)_2$	0.574	0.544	0.514	0.484
sodium chloride	NaCl	0.757	0.755	0.751	0.747
potassium sulfate	K_2SO_4	0.982	0.976	0.970	0.964

All salts were reagent grade (Fischer Scientific, Pittsburgh, PA). Solutions were prepared at 50 °C with excess salt to ensure a saturation condition. Remote data loggers, to continuously measure and record temperature and relative humidity (HOBO U23 Pro v2, Onset Computer Corporation, Pocasset, MA), were placed in each hygrostat. An incubator with refrigeration capability (Isotemp incubator, Fischer Scientific, Pittsburgh, PA) was utilized to maintain different temperature levels (±1 °C) during experiments. Sample EMCs were assumed to be in equilibrium with the ERH when there was no difference (≤0.001 g) in three subsequent weight measurements. The weights of the biomass samples were measured every two days. The samples were covered with the lids immediately after removing them from the hygrostats. Only one sample at a time was outside the hygrostat. The duration of the whole process was less than 60 s per sample. Tukey−Kramer Honestly Significant Difference (HSD) procedure, available in the JMP Pro 9 statistical package (SAS Institute, Cary, CA) was used for pairwise comparison of all EMC means.

2.3. Adsorption Modeling. Relationships between ERH and EMC of raw and torrefied corn stover at four different temperatures and five different ERH levels were determined by fitting the experimental data, using five isotherm models (eqs 1−5) suggested in ASAE standard D245.6.[20] The GAB model is used in its adapted form to account for temperature influence.[36,13]

1. Modified Henderson model:

$$\mathrm{EMC} = \left[\frac{\ln(1 - \mathrm{ERH})}{-A\cdot(t + B)}\right]^{1/C} \tag{1}$$

2. Modified Chung−Pfost model:

$$\mathrm{EMC} = -\frac{1}{C}\cdot\ln\left[\frac{\ln(\mathrm{ERH})\cdot(t + B)}{-A}\right] \tag{2}$$

3. Modified Halsey model:

$$\mathrm{EMC} = \left[\frac{-\exp(A + B\cdot t)}{\ln(\mathrm{ERH})}\right]^{1/C} \tag{3}$$

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Table 2. EMC of Raw and Torrefied Corn Stover

ERH[a]	t (°C)	samp.	EMC[b] (% db)	S.D.[c] (% db)	samp.	EMC (% db)	SD (%db)	samp.	EMC (% db)	SD (% db)	samp.	EMC (% db)	SD (% db)
0.113	10	raw	2.35	0.02	T200	2.13	0.19	T250	1.73	0.16	T300	1.86	0.04
0.335	10	raw	5.75	0.10	T200	4.98	0.14	T250	3.84	0.21	T300	4.34	0.04
0.574	10	raw	9.93	0.00	T200	8.53	0.16	T250	6.80	0.14	T300	6.84	0.13
0.757	10	raw	15.50	1.07	T200	12.35	0.45	T250	9.95	0.04	T300	9.76	0.01
0.982	10	raw	45.38	1.53	T200	42.88	0.91	T250	25.68	0.10	T300	26.13	0.86
0.113	20	raw	2.06	0.05	T200	2.03	0.04	T250	1.51	0.14	T300	1.67	0.19
0.331	20	raw	5.04	0.13	T200	4.31	0.05	T250	3.32	0.07	T300	3.90	0.01
0.544	20	raw	8.04	0.02	T200	6.76	0.14	T250	5.20	0.08	T300	5.87	0.02
0.755	20	raw	13.11	0.03	T200	11.20	0.04	T250	8.62	0.00	T300	8.90	0.06
0.976	20	raw[d]	41.48	0.94	T200	33.14	0.02	T250	24.00	1.03	T300	30.34	0.27
0.113	30	raw	1.99	0.02	T200	2.00	0.02	T250	1.70	0.09	T300	1.82	0.20
0.324	30	raw	4.86	0.00	T200	4.01	0.03	T250	3.25	0.03	T300	3.66	0.09
0.514	30	raw	7.41	0.05	T200	6.23	0.05	T250	4.84	0.01	T300	5.44	0.03
0.751	30	raw	12.22	0.10	T200	10.68	0.05	T250	8.34	0.13	T300	8.65	0.01
0.97	30	raw[d]	24.81	0.44	T200[d]	23.24	1.45	T250[d]	16.44	0.12	T300[d]	15.57	0.06
0.112	40	raw	1.77	0.27	T200	1.63	0.13	T250	1.18	0.00	T300	1.54	0.06
0.316	40	raw	4.66	0.26	T200	3.79	0.25	T250	2.92	0.05	T300	3.62	0.06
0.484	40	raw	6.41	0.08	T200	5.35	0.05	T250	4.07	0.00	T300	4.74	0.21
0.747	40	raw	10.94	0.40	T200	9.25	0.15	T250	7.30	0.09	T300	7.99	0.09
0.964	40	raw	18.17	2.38	T200	13.78	0.21	T250	10.16	0.47	T300	11.06	0.27

[a]Equilibrium relative humidity. [b]Equilibrium moisture content. [c]Standard deviation. [d]Growth of fungi observed.

4. Modified Oswin model:

$$\mathrm{EMC} = (A + B\cdot t)\cdot\left[\frac{\mathrm{ERH}}{1 - \mathrm{ERH}}\right]^{1/C} \tag{4}$$

5. Modified GAB (Guggenheim−Anderson−deBoer) model:

$$\mathrm{EMC} = \frac{A\cdot B_0\cdot C_0\cdot \mathrm{ERH}}{(1 - B_0\cdot\mathrm{ERH})\cdot(1 - B_0\cdot\mathrm{ERH} + B_0\cdot C_0\cdot\mathrm{ERH})} \tag{5}$$

$$B_0 = B\cdot\exp\left[\frac{H_1}{R\cdot T}\right]$$

$$C_0 = C\cdot\exp\left[\frac{H_2}{R\cdot T}\right]$$

where

EMC = equilibrium moisture content (% db).
ERH = equilibrium relative humidity (decimal).
A, B, C, B_0, C_0, H_1, H_2 = empirical constants. (Note: Their values are specific to particular model.)
t = temperature (°C).
T = absolute temperature (K).
R = universal gas constant (kJ kmol^{-1} K^{-1}).

Nonlinear regression was used to fit the aforementioned models into experimental results and obtain unknown coefficients. Regression analysis was done using JMP Pro 9 statistical package (SAS Institute, Cary, CA). The procedure employed the Gauss−Newton algorithm to minimize the residual sum of squares between predicted and observed data in an iterative way. The adequacy of tested models was evaluated using different statistical criteria, including mean percent relative error (MRE), residual sum of squares (RSS), root-mean-square error (RMSE), coefficient of determination (R^2), and plot of residuals.[19,37] Relations 6−9 were used to determine MRE, RSS, RMSE, and residuals, respectively.

$$\mathrm{MRE} = \frac{100}{n}\sum_{1}^{n}\frac{|\mathrm{EMC}_{\mathrm{expt}} - \mathrm{EMC}_{\mathrm{pred}}|}{\mathrm{EMC}_{\mathrm{expt}}} \tag{6}$$

$$\mathrm{RSS} = \sum_{1}^{n}(\mathrm{EMC}_{\mathrm{expt}} - \mathrm{EMC}_{\mathrm{pred}})^2 \tag{7}$$

$$\mathrm{RMSE} = \sqrt{\frac{\mathrm{RSS}}{\mathrm{df}}} \tag{8}$$

$$\mathrm{residual} = \mathrm{EMC}_{\mathrm{expt}} - \mathrm{EMC}_{\mathrm{pred}} \tag{9}$$

where

n = number of observations.
$\mathrm{EMC}_{\mathrm{expt}}$ = experimentally obtained equilibrium moisture content.
$\mathrm{EMC}_{\mathrm{pred}}$ = equilibrium moisture content predicted by the model.
df = degree of freedom.

The model with the smallest values of MRE, RMSE, and RSS, as well as the largest value of R^2 was considered to be the best fit for the experimental data, and the most accurate description for the relationship between a sample's EMC and ERH. Furthermore, a model was considered acceptable only if its plot of residual vs predicted EMC showed no systematic spread or pattern.[19]

2.4. Microbial Degradation Experiment. The microbial degradation test was conducted using the same equipment and experimental set up that was used for water vapor adsorption tests. The duration of the test was 30 days. During the experiment, temperature was maintained at 30 °C with the help of incubator. Relative humidity was maintained at 97% (saturated solution of K_2SO_4 salt). These parameters were chosen to promote natural microbial growth without any attempt to inoculate material with specific fungi species. Dry matter content of samples was determined before and after the experiment, according to ASAE standard method D358-2.[32]

2.5. Fiber Analysis. Fiber analysis was done according to the National Renewable Energy Laboratory procedure.[38] In short, carbohydrates present in the biomass were dissolved in two stage sulfuric acid hydrolysis, and the resulting monomers were analyzed by means of high performance liquid chromatography (HPLC) with refractive index detector (Varian ProStar 355/356, Varian Inc., Palo Alto, CA) and a column (Bio-Rad Aminex HPX-87P, Hercules, CA). Solid residual was weighed and considered to be acid insoluble lignin, while acid soluble lignin in hydrolysate was determined spectrometrically.

Table 3. Water Vapor Adsorption Parameters for the Raw and Torrefied Corn Stover

samp.	model	A	B	C	H_1	H_2	R^2	MRE (%)	RSS	RMSE
raw	MCP[a]	80.3430	12.9223	0.1395			0.8942	44.01	3.028	0.0422
	MHa[b]	4.7831	−0.0358	2.1794			0.9645	31.39	1.017	0.0245
	MO[c]	10.6784	−0.1340	2.4557			0.9766	20.02	0.671	0.0199
	MH[d]	0.0018	26.4117	1.0734			0.9686	17.99	0.899	0.0230
	MGAB[e]	3.8848	0.3849	47.3216	2090.335	45000	0.9594	30.14	1.162	0.0278
T200	MCP	70.4461	9.3173	0.1601			0.8740	48.19	2.835	0.0408
	MHa	4.4186	−0.0420	2.1203			0.9783	25.45	0.489	0.0170
	MO	9.3512	−0.1311	2.3795			0.9875	15.44	0.281	0.0129
	MH	0.0027	20.9265	1.0297			0.9748	22.72	0.568	0.0183
	MGAB	3.2719	0.3362	47.6590	2427.192	42356.11	0.9749	25.37	0.565	0.0194
T250	MCP	93.4331	13.4685	0.2416			0.9106	32.11	0.836	0.0222
	MHa	4.1963	−0.0353	2.3710			0.9548	29.51	0.423	0.0158
	MO	6.9828	−0.0826	2.6851			0.9712	18.92	0.270	0.0126
	MH	0.0022	26.6979	1.1954			0.9661	14.32	0.317	0.0137
	MGAB	2.6351	0.3527	61.0000	2256.327	41223.2	0.9529	27.73	0.440	0.0171
T300	MCP	107.560	18.4000	0.2239			0.8551	31.15	1.663	0.0313
	MHa	4.2505	−0.0321	2.3463			0.9076	27.49	1.060	0.0250
	MO	7.3975	−0.0848	2.6590			0.9223	18.38	0.891	0.0229
	MH	0.0019	32.5443	1.1756			0.9072	19.47	1.064	0.0250
	MGAB	2.7887	0.3993	39.1527	1965.523	44322	0.9016	24.27	1.129	0.0274

[a]Modified Chung–Pfost. [b]Modified Halsey. [c]Modified Oswin. [d]Modified Henderson. [e]Modified GAB.

3. RESULTS AND DISCUSSION

3.1. Experimental Results. The EMCs of raw and corn stover torrefied at 200 (T200), 250 (T250), and 300 °C (T300) are included in Table 2. EMC of all four types of biomass decreased with an increase in temperature during water adsorption experiments. The minimum and maximum EMC, with temperature in parentheses, of raw, T200, T250, and T300 samples were 1.77 (40 °C) and 45.38 (10 °C) % db; 1.63 (40 °C) and 42.88 (10 °C) % db; 1.18 (40 °C) and 25.68 (10 °C) % db; and 1.54 (40 °C) and 30.44 (20 °C) % db; respectively. This phenomenon is typical for biological products and might be a consequence of the enhanced excitation states of water molecules at higher temperatures, which lowers cohesive forces between them.[36] The Clausius–Clapeyron equation predicts a shift of adsorption isotherms downward as a result of an increase in temperature, which is a consequence of more energy available for water vaporization and decrease in moisture binding energy.[39,40] As expected, the EMC of biomass increased with an increase in ERH, and with no exception, samples exposed to the lowest and highest ERH also respectively had the lowest and highest EMC, regardless of pretreatment temperature. Dry raw corn stover had the highest EMC values at all temperatures for ERH above 0.4. There was no significant difference between samples below 0.4, according to Tukey–Kramer HSD test, regardless of environmental temperature. Furthermore, EMC of thermally treated samples decreased with the increase in torrefaction process temperature. This is mainly a consequence of a decrease in the number of water adsorption sites and changes in the material structure due to cleavage of hydroxyl groups from biomass polymers and the formation of nonpolar unsaturated structures.[6,41,42] Moreover, hemicellulose fraction in biomass is degraded to different extents during torrefaction, depending on temperature.[21] Since the main mechanism of water adsorption onto biomass is binding to polar sites, such as hydroxyl groups in sugar molecules, elimination of hemicellulose also increases hydrophobicity.[43] The difference between hydrophobicity of corn stover torrefied at 250 and 300 °C is not statistically significant. Tukey–Kramer HSD test revealed that differences between ERH levels for the same sample and environmental temperature are all significant (not shown in Table 2). This is true regardless of sample type. If the samples of the same kind and ERH, but different environmental temperature, are compared to each other, no straightforward conclusion could be established. Moreover, the only exception is the highest ERH value at which all samples were significantly different. Therefore, hydrophobicity of thermally treated material was clearly expressed only at the highest ERH level, regardless of environmental temperature, with raw and samples torrefied at 250 °C having highest and lowest EMC, respectively.

Growth of fungi colonies was observed at the highest ERH values on raw samples at 20 and 30 °C and on T200 and T250 samples only at 30 °C. This might affect the EMC of the samples. However, samples with mold contamination did not show any abnormally high EMC values caused by dry matter loss due to microbial degradation. Hence, the aforementioned samples were also included in the statistical analysis and fitting of water adsorption isotherms.

3.2. Fitting Sorption Models to Experimental Results. Five water sorption isotherms, selected according to the ASABE standards, were used to fit the experimental data presented in Table 2. Nonlinear regression was used for fitting yielded unknown model parameters that are shown in Table 3. Statistical criteria for model performance characterization (MRE, RMSE, RSS, and R^2) are also given in Table 3. These were used for the selection of the model that described the relationship between ERH and EMC most accurately. The lowest MRE, RMSE, and RSS values are used to indicate the best model for fitting experimental data. The modified Oswin model represented the best model for fitting raw and torrefied biomass, as with this model lowest values of the aforementioned three parameters were obtained. The modified Henderson was the second best performing model.

In addition to previously discussed statistical parameters used for model performance characterization, a residual plot is often used as a main criterion for model acceptance or rejection. Residual plots for all five selected models are shown in Figure 1.

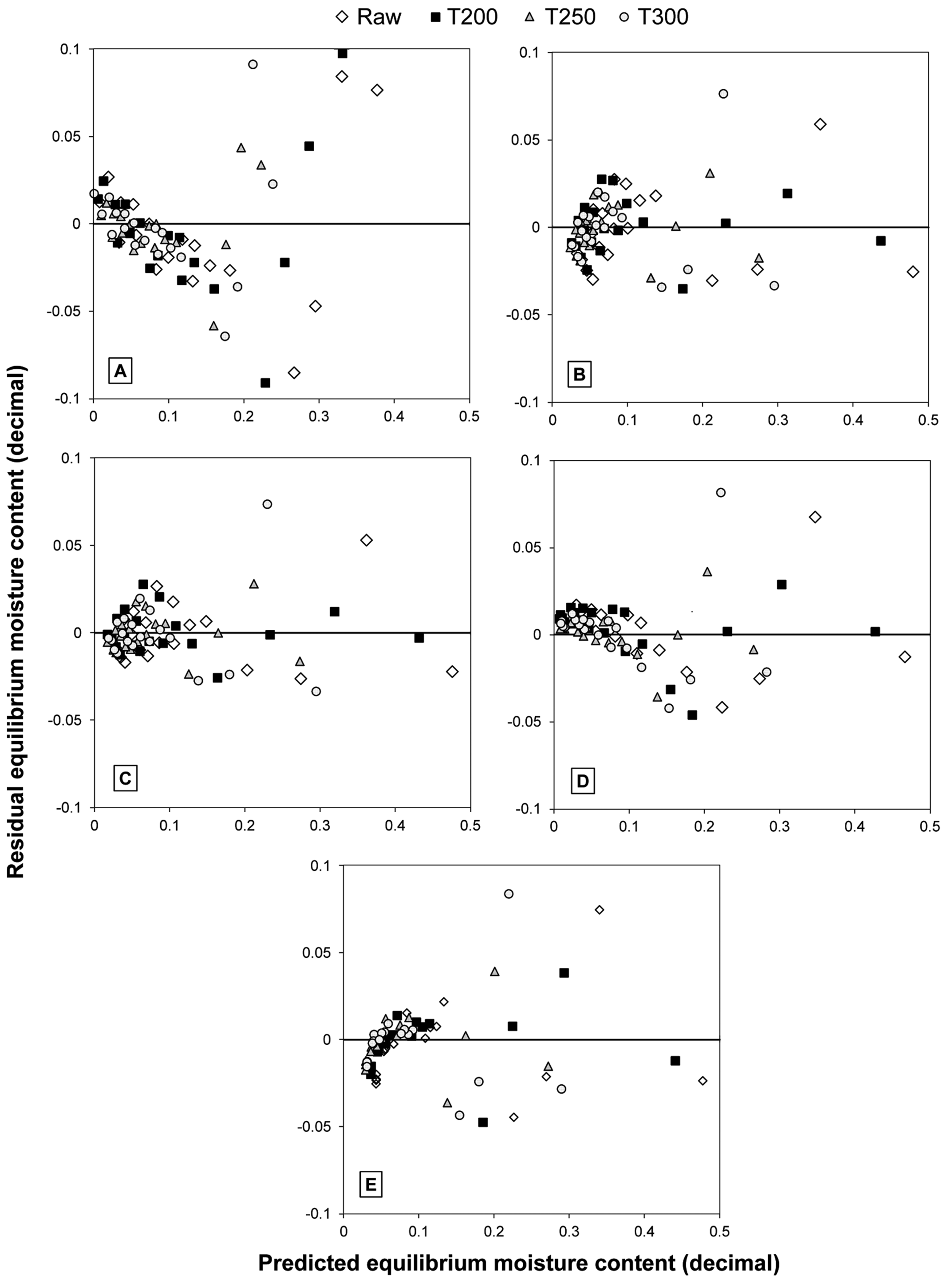

Figure 1. Residual plots of the water vapor adsorption isotherms for raw and torrefied corn stover: (A) modified Chung−Pfost, (B) modified Halsey, (C) modified Oswin, (D) modified Henderson, (E) GAB.

As can be seen in the figure, modified Chung-Pfost, modified Henderson, and modified GAB models show a systematic distribution of residuals. Therefore, these were poor models for describing the correlation of ERH and EMC of corn stover and had to be rejected. Modified Oswin and Halsey models had a random distribution of residuals, but because the former has better statistical parameters, it has been accepted as the best among five investigated models. The modified Oswin model provided the best fit not only for raw corn stover, but also for torrefied corn stover. Igathinathane and co-workers[27] investigated the EMC of three corn stover components and concluded that the modified Oswin and Halsey isotherm models performed best based on prediction capabilities and randomized residuals.

As can be seen in Figures 2−5, the fitted modified Oswin equation shows that EMC data of raw and torrefied corn stover follow a sigmoidal curve, typical for most agricultural products.[44] This type of curve represents a type II isotherm, according to Brunauer and Emmet's classification (BET).[45] This family of isotherms describes multilayer adsorption with

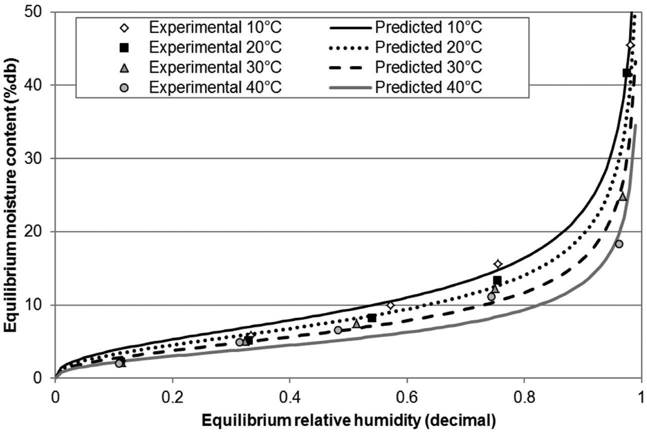

Figure 2. Experimental results and isotherms predicted by the modified Oswin model of raw corn stover.

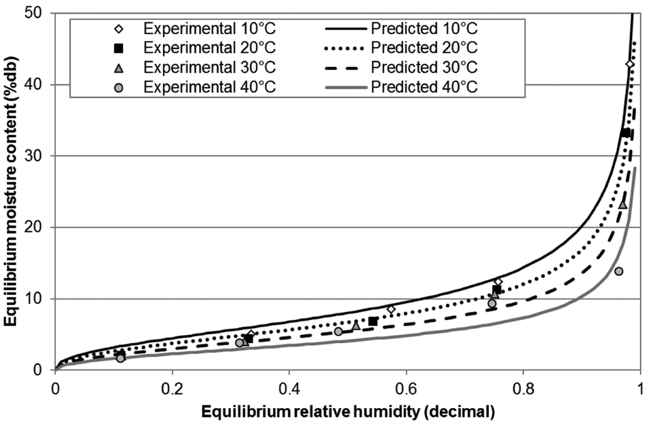

Figure 3. Experimental results and isotherms predicted by the modified Oswin model of corn stover torrefied at 200 °C.

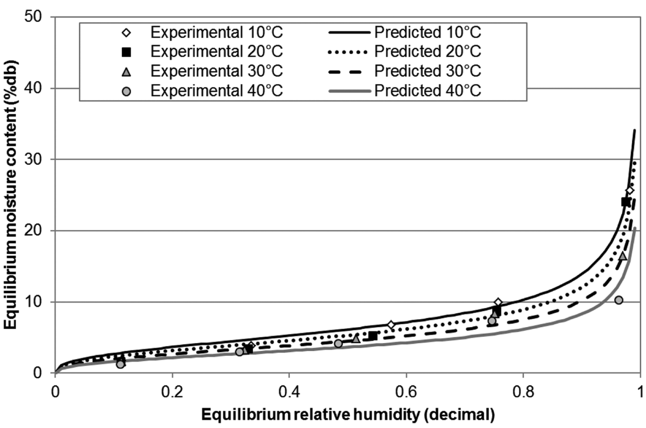

Figure 4. Experimental results and isotherms predicted by the modified Oswin model of corn stover torrefied at 250 °C.

an asymptotic trend as water activity approaches 1.0. The type II isotherm is concave downward in the low RH region and concave upward in the high RH region. It represents isotherms typical for BET adsorption mechanism that allows infinite adsorption for RH values close to 1. The concavity in the low RH range is considered to represent the end of formation of monomolecular layer and the beginning of the development of the multilayer of water molecules.[46] In case of lignocellulosic

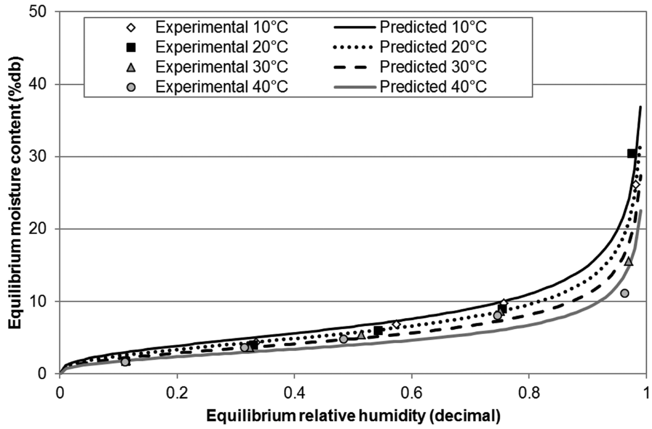

Figure 5. Experimental results and isotherms predicted by the modified Oswin model of corn stover torrefied at 300 °C.

material, the monolayer is created via strong hydrogen bonding of single molecules in amorphous regions of plant fiber matrix. The almost linear midportion of the isotherm corresponds to weak bonds between multiple layers of water molecules or to the filling of the fine capillaries. The steep portion of the isotherm beyond concavity in the high RH region is a consequence of the swelling of the cellulose and of the condensation of free water in coarse capillaries where they exist in a bulk state.[47,48] The previously discussed trend of decreasing EMC with increasing environmental temperature, regardless of sample type, is clearly depicted in these figures. However, this trend is less expressed in the case of corn stover torrefied at 250 (T250) and 300 °C (T300). It can be seen in the figures that increasing ERH causes increasing EMC of all samples. This is especially pronounced at ERH values above 0.9. The abrupt increase in EMC at ERH above 0.9 is larger for raw (45% db) and T200 (40% db) than for T250 (25% db) and T300 (25% db). As already stated, the difference between raw and corn stover torrefied at higher temperatures may be due to degradation of hemicellulose. Moreover, the elimination of hemicellulose leads to the elimination of monosaccharides and hydroxyl moieties that served as water binding sites. Curves show a sharp increase at about 0.8−0.9 ERH, which is characteristic for type II isotherms.[49]

As can be seen in Figure 6, torrefied biomass has distinct water vapor adsorption properties from raw biomass. There-

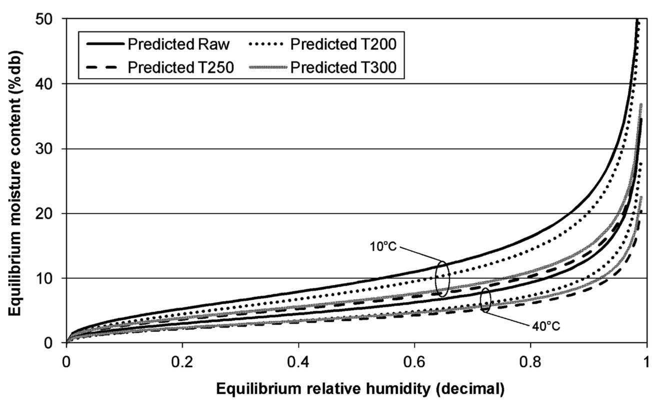

Figure 6. Comparison of raw and torrefied corn stover isotherms at 10 and 40 °C.

fore, all predicted isotherms of torrefied samples are grouped together at 40 °C. However, raw corn stover at 10 °C and corn

Table 4. Fiber Analysis of Raw and Torrefied Corn Stover[a]

samp.	ASL (%)[b]	AIL (%)[c]	glucan (%)	xylan (%)	arabinan (%)
raw	2.6 ± 0.14[a]	19.4 ± 0.37[a]	45.7 ± 0.14[a]	27.8 ± 0.07[a]	4.6 ± 0.01[a]
T200	2.6 ± 0.14[a]	22.9 ± 0.25[b]	44.9 ± 0.31[a]	25.5 ± 0.04[b]	4.0 ± 0.23[b]
T250	2.7 ± 0.21[a]	33.3 ± 0.55[c]	46.0 ± 0.41[a]	15.8 ± 0.70[c]	2.3 ± 0.05[c]
T300	1.0 ± 0.04[b]	75.1 ± 0.49[d]	19.9 ± 0.27[b]	3.6 ± 0.27[d]	0.4 ± 0.01[d]

[a]Note: Values (mean ± standard deviation of two measurements) are on dry basis (db) and ash- and extractives-free basis Samples marked with different letters in superscript are significantly different at $\alpha = 0.05$ according to the Tukey−Kramer pair-wise mean comparison test. Different fiber categories were not compared to each other. [b]Acid soluble lignin. [c]Acid insoluble lignin.

stover torrefied at 200 °C had a similar predicted EMC, but they were significantly different from samples torrefied at 250 and 300 °C, which had similar behavior at this environmental temperature.

3.3. Microbial Degradation Results. Microbial degradation tests were conducted at 30 °C and 0.97 ERH. These values were chosen because they were the only conditions that sustained fungi growth on all four samples. The results are presented in Figure 7. Dry matter loss (DML) of the raw corn stover sample was about 17% after 30 days and was the highest among all samples (Figure 7).

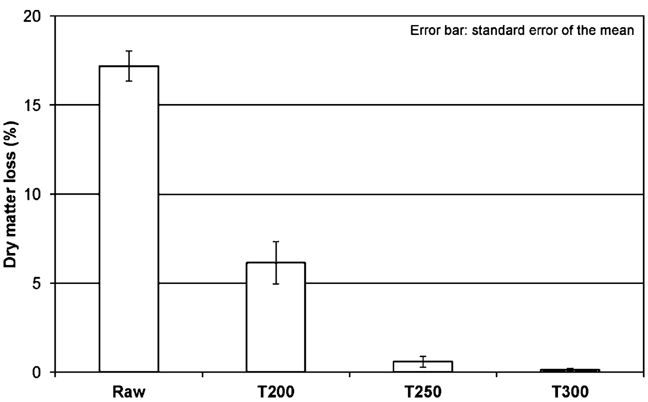

Figure 7. Dry matter loss due to microbial degradation at 0.97 ERH and 30 °C.

This value was about 3 times higher than the dry matter mass loss of the T200 sample. DMLs for corn stover torrefied at 250 and 300 °C were less than 1%.

As discussed in sections 3.1 and 3.2, even though torrefied biomass is comparatively more hydrophobic in nature than raw biomass, it still adsorbs a relatively significant amount of water vapor. At the temperature and ERH used in the microbial degradation experiment, raw and T200, and T250 and T300 samples had EMC values of about 25 and 15% db, respectively. However, the DMLs were significantly lower in the cases of corn stover torrefied at 250 and 300 °C than that in the case of raw biomass. This might be due not only to the elimination of hemicellulose and an increase in hydrophobicity but also to the formation of sugar and lignin degradation products toxic to microorganisms, such as furan and phenol derivatives that are trapped in the pores of torrefied material.[50−53]

3.4. Fiber Analysis Results. Results of the fiber analysis are shown in Table 4. There was an overall trend of decrease in both xylan and arabinan quantity with increase in torrefaction temperature. In this work, these two compounds are considered to represent the hemicellulose fraction of corn stover, because other minor components, such as galactan and mannan, were present only in traces. As expected, raw and biomass pretreated at 300 °C had respectively the highest (28%) and the lowest (4%) amount of hemicellulose. A similar trend was also observed by several other researchers.[6,22] Increasing the torrefaction temperature from 250 to 300 °C caused cellulose degradation and a decrease in its content from about 45 to 20%, respectively. Nevertheless, there was no significant difference between raw, T200, and T250 in regard to cellulose content, which was expressed as a glucan percentage. Relative total lignin content increased from 20 to 75% with the temperature increase, probably due to carbohydrate elimination and conversion to acid insoluble products during the thermal pretreatment.

4. CONCLUSION

The EMC of raw and thermally pretreated corn stover was measured at ERH and temperature ranging from 10 to 98% and 10 to 40 °C, respectively. Except at the highest ERH value, the sample torrefied at 200 °C did not have water adsorption properties different from the raw biomass. However, the adsorption properties of samples torrefied at 250 and 300 °C were significantly different from the raw biomass. Torrefaction may have increased hydrophobicity of biomass through the elimination of the hydrophilic carbohydrate fraction and its partial conversion into nonpolar, hydrophobic degradation products. Five isotherms were fitted to the experimental data to obtain the EMC−ERH prediction equations. Isotherms of all samples belong to type II. The modified Oswin model, followed by the modified Halsey model, showed the best performance and was recommended for the characterization of water vapor sorption behavior of raw and torrefied corn stover. The modified Chung−Pfost, modified Henderson, and modified GAB models were not recommended because their residual plots were systematic. Degradation test at highest ERH and 30 °C showed that raw biomass had about 17% dry matter loss due to microbial degradation. Samples torrefied at 250 and 300 °C had negligible dry matter loss when compared to raw and samples torrefied at 200 °C. This might be predominantly due to higher hydrophobicity and probably the formation of degradation products toxic to fungi. Fiber analysis showed a significant decrease in hemicellulose content and a relative increase in the lignin content of torrefied corn stover. Optimal torrefaction temperature was found to be 250 °C, since higher process temperatures cause excessive dry matter loss during the torrefaction process without significantly enhancing hydrophobicity and resistance to microbial degradation of torrefied corn stover.

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Notes

The authors declare no competing financial interest.

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