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Research Article

Moisture Sorption Characteristics of Corn Stover and Big Bluestem

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Moisture content is an important feedstock quality in converting it into energy through biochemical or thermochemical platforms. Knowledge of moisture sorption relationship is useful in drying and storage to preserve the quality of feedstocks. Moisture sorption isotherms for potential feedstocks such as corn stover and big bluestem are missing. EMC values of corn stover and big bluestem were determined using static gravimetric technique with saturated salt solutions (ERH 0.12–0.89) at different temperatures (20, 30, and 40°C). Depending upon the ERH values, EMC values were ranged from 8.0 to 19.6 and 8.8 to 19.2% db for corn stover and big bluestem, respectively, and they followed typical type II isotherm found in food materials. Nonlinear regression was used to fit five commonly used three-parameter isotherm models (i.e., modified Oswin model, modified Halsey model, modified Chung-Pfost model, modified Henderson model, and the modified Guggenheim-Anderson-de Boer (GAB) model) to the experimental data. Modified Halsey emerged as the best model with high F-statistic and R^2 values with low E_m and E_s and fairly random scattered residual plot for corn stover and big bluestem. These models can be used to predict the equilibrium moisture content of these feedstocks starting from harvesting, drying, preprocessing, transportation, storage, and conversion.

1. Introduction

The search for a renewable fuel resource has become a global priority due to obvious reasons such as declining fossil fuel resources and economic and environmental concerns. According to Demirbas [1], lignocellulosic biomass appears to be an attractive feedstock due to its renewability, positive environmental impacts resulting in no net release of carbon dioxide, and very low sulfur content, and they are cheap (compared to corn/sugarcane) and abundant [2]. Corn stover is considered as one of the potential feedstock and most studied materials towards biofuel too. Perlack et al. [3] estimated that approximately 256 million dry tons of corn stover will be available for conversion into fuel in the year 2030 due to collection technologies improvement and a steady yield increase. Several studies have shown that big bluestem has a great potential as a feedstock in the biofuel arena harvest years [4–6]. Moreover, the United States Department of Energy has also listed big bluestem as one of the herbaceous energy crops. Based on the previous facts, corn stover and big bluestem were selected for this study.

Moisture content is an important attribute of feedstocks in converting them in biochemical or thermochemical platforms into biofuels or bio-oil. Moisture content has a strong influence not only on harvesting and preprocessing/grinding but also on transportation, storage, conversion/processing, and the resultant products. There is always a trade-off between the feedstock production and its moisture content; for example, early harvest requires high drying cost [7]. According to Igathinathane et al. [8], safe storage and preprocessing of feedstock are important operations in supplying them to biorefineries. Feedstock is expected to be stored in ambient atmospheric conditions in an open field or in an enclosure due to bulky nature of it. The quality of stored feedstock is influenced by biological, microbiological, and organochemical reactions of the feedstock [9]. Deterioration of the feedstock depends on the moisture content and the types of storage. Nurmi [10] has reported that one of the challenging tasks in biomass harvesting is how to manage the storage of the feedstock. Several studies have revealed that the long-term storage results in dry matter loss, reduction in energy content, and causes health risk for the workers. In order to store the feedstock for long-term period, the moisture content should be below 17.65% db [7]. Feedstocks are subjected to different relative humidity (RH) and temperatures during harvesting, preprocessing, transportation, and storage in a wide variety of climates. Knowledge of the relationship between the temperature and RH of air is useful in selection of correct drying and storage operations to preserve the quality of feedstocks.

Most of the feedstocks are hygroscopic in nature, meaning that they may adsorb and desorb the moisture from surrounding atmosphere [11, 12] depending upon the environmental conditions. When the internal vapor pressure of the feedstock is equal to the vapor pressure of the surrounding air, the moisture content of the material represents the equilibrium moisture content (EMC). The internal vapor pressure depends upon the surrounding environment, that is, the temperature and RH, the characteristics of feedstock. EMC is useful to determine whether a feedstock will gain or lose moisture under a given set of temperature and RH conditions. Different feedstocks have different EMCs depending upon the temperature and RH of the environment as well as species, variety, maturity [13–15], porosity and microstructure [16], specific surface area [17], and amount of extractives and strength of feedstock/wood [18]. Recently, Jorgenson et al. [19] reported the monthly average EMC of woody biomass in the range of 4.9–21% db depending upon the locations (Fargo, North Dakota; Boulder, Colorado; Olympia, Washington; Phoenix, Arizona) within the US.

EMC can be determined through either static or dynamic method. In the static method, saturated salt solutions or acids of different concentrations are used for obtaining different ERH in a closed chamber. In the dynamic method, the various RHs are obtained by mixing fully dried air and fully saturated air at required proportions, or by conditioning the air by mixing with water vapor appropriately. In dynamic method, continuous recording of change in weight is technically more complicated than the static one. However, the main advantage of the dynamic method is that the sample reaches equilibrium more rapidly than with the static method. The principal static methods are gravimetric, manometric, and hygrometric. According to Aviara et al. [20], gravimetric technique has several advantages over the manometric and hygrometric techniques, and these are ability to determine the exact dry weight of the sample, minimization of temperature fluctuation between samples and their surroundings, recording the weight change in equilibrium with the respective water vapor pressures, and achieving hygroscopic and thermal equilibrium between samples and water vapor source. The advantage of the static method is its ability to maintain constant conditions easily [21–23]. Among static methods, gravimetric technique has been considered preferable/reliable to obtain complete sorption isotherms [20, 24] and has been recommended as the standard method [25]. Sometimes the weighing process may induce measuring errors [26], and mold may easily develop on samples in the high RH environment [27]. Therefore, these points should be addressed adequately while conducting an experiment. The method selection depends on the types of material, dynamic method is more suitable for pellets/briquettes, and static materials are suitable for powdery materials.

Early equilibrium moisture relations of biomass/feedstocks are limited and found for prairie hay, red clover hay, oat straw, and alfalfa hay in the 1940s [28, 29]. Due to high attention in biofuel research, once again researchers have started looking into EMC of different feedstocks such as wheat straw [30], pine [18], selected corn stover components [31], flax straw, hemp stalk, and reed canary grass [12], willow [32], amaranth stem [33], and miscanthus leaves and stem [7], and briquettes or pellets made from cotton stalk and sawmill waste [11], switchgrass [34], softwood [35], peanut hull [36], sorghum stalk, corn stover, wheat straw, and big bluestem [37]. Moisture sorption isotherms describe the relationship between the equilibrium RH (ERH) and the EMC at constant temperatures and pressures [38]. Several researchers have reviewed the suitability of isotherm models for various biological materials and concluded that no "universal model" adequately describes sorption behaviors over a broad range of temperature and RH [39, 40]. Therefore, for a specific feedstock, there is need to search for the most appropriate EMC/ERH equation [31, 39, 41, 42]. No literature on corn stover and big bluestem moisture sorption isotherm was found. However, Igathinathane et al. [31] studied EMC of selected corn stover components such as corn leaf, stalk skin, and stalk pith and estimated EMC of corn stalk based on their proportions. Recently, Theerarattananoon et al. [37] reported the EMC of pellets made from big bluestem, and they have not evaluated different moisture sorption isotherms. Therefore, the objectives of this study are to determine the moisture adsorption data of corn stover and big bluestem at different temperatures (20–40°C) and to evaluate the suitability of commonly used isotherm equations for predicting the EMC of these feedstocks at different ERHs.

2. Materials and Methods

2.1. Sample Preparation and Characterization. Corn stover and big bluestem were obtained from local farms (Brookings, SD, USA) and ground in a hammer mill (Speedy Jr, Winona Attrition Mill Co, MN) using 4 mm sieve. The ground feedstock was stored in sealed bins (0.68 m height and 0.47 m diameter) at room temperature (20 ± 1°C) until needed. The initial moisture content of the feedstocks was determined based on ASABE Standard S358.2 for forage moisture determination [53]. The amounts of extractives in these feedstocks were determined following NREL protocol [54].

2.2. Experimental Procedure. The moisture adsorption characteristics of feedstocks were determined at three different temperatures (20, 30, and 40°C) and at various RH conditions ranging from 12% to 89% using static gravimetric method (since feedstocks were in powdery form). Relative humidity conditions were maintained using different saturated salt

Table 1: ERH of the saturated salt solutions used in this study.

Saturated salt solution	Chemical formula	ERH (decimal)		
		20°C	30°C	40°C
Lithium chloride	LiCl	0.126	0.120	0.118
Magnesium chloride	$MgCl_2$	0.330	0.322	0.310
Potassium carbonate	K_2CO_3	0.451	0.434	0.420
Sodium bromide	NaBr	0.591	0.573	0.560
Sodium chloride	NaCl	0.752	0.740	0.730
Potassium chloride	KCl	0.853	0.830	0.821
Barium chloride	BaCl	—	0.890	—
Potassium nitrate	KNO_3	—	—	0.893

solutions which could give the respective humidity conditions at different temperatures. Various salt solutions and the experimental conditions maintained during this experiment are summarized in Table 1. ERH values were verified using a hygrometer (S 90191, Control Company, and Friendswood, TX, USA) and compared with the literature values [55–57]. The differences in the measured and the literature ERH values were negligible. The prepared saturated salt solutions and the weighed feedstock samples (0.5 g) in the aluminum cups were kept in the desiccators, which were sealed tightly using wax. Nalgene autoclavable plastic desiccators, with a 150 mm inner diameter and a 149 mm height, were used to provide the required environments. The lower portions of the desiccators, separated from the headspace by 140 mm aluminum plates, contained the specific salt solutions that had been prepared with distilled water. The salts used for preparing saturated solutions were of pure laboratory grade (Acros organics, NJ, USA). These desiccators were placed in the Fisher isotemp mechanical convection oven (Model 838F, Fisher Scientific, USA) and then exposed to varying temperatures. The change in moisture contents was observed by weighing the feedstock samples at regular intervals by taking them out (the room was also maintained the same temperature of the oven) and continued until there was no difference among the consecutive weights. In order to observe the experimental errors, the feedstock moisture readings were measured in triplicates.

2.3. Moisture Sorption Model Selection. Numerous models have been suggested in the literature to describe the relationship between EMC and ERH of biomaterials. In the late 1980s, Van den Berg [58] and Chen and Morey [39] listed the following five requirements for EMC equations: (1) the experimental curve should be described mathematically for practical applications such as drying and storing; (2) the equation should have a relatively simple form with a limited number of parameters; (3) the parameters should have a physical significance; (4) the parameters should include temperature dependence; (5) the equation should be able to correct for the influence of hysteresis. Several researchers have evaluated and found that no perfect model exists for describing sorption isotherms of biomaterials based on these criteria. Pfost et al. [59] used standard error of estimate as a criterion and compared the fit of five EMC/ERH models (with three and four parameters) to the published maize EMC data. They found that the residuals of the four-parameter equations were not significantly lower than those of the three-parameter equations. Further, it is easier to fit and use three-parameter equations without relying on tables or charts. Based on the results of this study, modified Henderson equation, modified Oswin equation, modified Chung-Pfost equation, and modified Halsey equation were adopted in ASAE standard D245.5 [60]. Most of the researchers, who studied different feedstocks such as wheat straw, selected components of corn stover, miscanthus, flax straw, hemp stalks, reed canary grass, and switchgrass pellets, used these four-three parameters equations. The Guggenheim-Anderson-deBoer (GAB) model has been recommended as the standard model for use in food laboratories in Europe [61] and the USA [62]. The temperature term was not incorporated in the GAB model; however, Jayas and Mazza [63] have incorporated the effect of temperature and developed a modified GAB model. The previous five moisture sorption models (Table 2) were selected for evaluation based on the facts presented earlier.

2.4. Analysis of Data and Model Evaluation. Parameter estimates of the models listed in Table 2 were determined with nonlinear regression procedure, using PROC NLIN of SAS version 9.2 (SAS Institute Inc, Cary, NC). The nonlinear regression procedure minimized the sum of squares of deviation between the predicted and observed isotherm data in a series of iterations to solve the model. The NLIN procedure used the Gauss-Newton method to solve the models. Input data to the NLIN procedure were a series of temperature, ERH, and corresponding EMC values for corn stover and big bluestem. The goodness of fit of each model was evaluated using performance/statistical parameters for nonlinear models, such as mean relative percent error (E_m), standard error (E_s) (% db), coefficient of determination (R^2), and F-statistic values. The F-statistic was directly obtained from the SAS output, and E_m, E_s, and R^2 were calculated using

$$E_m = \sum \frac{100}{N} \frac{\left(Y - \widehat{Y}\right)}{Y},$$

Table 2: The five most commonly used three-parameter isotherm equations for calculation of the equilibrium moisture content (EMC).

Model name	Equation	Eqtn no.
Modified Oswin	$M = (A + BT)\left[\dfrac{\mathrm{RH}}{1-\mathrm{RH}}\right]^{1/C}$	1
Modified Halsey	$M = \left[\dfrac{-\exp(A + BT)}{\ln(\mathrm{RH})}\right]^{1/C}$	2
Modified Henderson	$M = \left[\dfrac{\ln(1-\mathrm{RH})}{-A(T + B)}\right]^{1/C}$	3
Modified Chung-Pfost	$M = \dfrac{-1}{C}\ln\left[\dfrac{\ln(\mathrm{RH})(T + B)}{-A}\right]$	4
Modified GAB	$M = \dfrac{A(C/T)B\mathrm{RH}}{(1 - B\mathrm{RH})(1 - B\mathrm{RH} + (C/T)B\mathrm{RH})}$	5

M: moisture content, (% db); RH: relative humidity (decimal); T: temperature °C; A, B, and C: constants specific to each equation.

$$E_s = \sqrt{\frac{\sum\left(Y-\widehat{Y}\right)^2}{\mathrm{df}}},$$
$$R^2 = 1 - \frac{\text{Error } SS}{\text{Total } SS}, \tag{1}$$

where Y and $\widehat{Y}$ are the measured and predicted equilibrium moisture contents in % (db), N is the number of data points, and df is degree of freedom.

3. Results and Discussion

3.1. Observed EMC of Corn Stover and Big Bluestem. The experimental EMC values obtained for corn stover and big bluestem at various ERH and temperatures are shown in Figure 1. The plotted isotherms of corn stover and big bluestem followed type II isotherms for all three temperatures [7, 23]. Type II isotherms are more common in food materials, where an increase in temperature reduces the EMC. This EMC-reducing effect of the increased temperatures is in agreement with studies on various feedstocks [7, 12, 30, 31, 43] and pellets made from different feedstocks [11, 34–37]. The highest temperature (40°C) and the lowest ERH (0.12) combination produced the minimum EMC values, and the lowest temperature (20°C) and the highest ERH (0.89) combination produced the maximum EMC values for the feedstocks studied. Similar trends were reported for other feedstocks such as wheat straw [30], red clover leaves and stems [43], corn leaf, corn stalk skin and corn stalk pith [31], flax straw, hemp stalks, and reed canary grass [12], flax fibre [44–46], and miscanthus [7]. The observed minimum and maximum EMC values were 8.0 and 8.8 and 19.6 and 19.2% db for corn stover and big bluestem, respectively. The higher EMC values of these two feedstocks were lower than that of switchgrass (20.8% db) and prairie cord grass (21% db) [64]. Recently, Brown [65] reported that the typical EMC of biomass would be above 33.3% db if the RH exceeds 90%–95%. Considering this criterion, the feedstocks used in this study also confirm it; that is, maximum RH was 89% and the EMC was far lower than 33.3% db. Yan et al. [66] reported an EMC of 15.6% db for loblolly pine at a temperature of 30°C with RH of 83.6%, and this value was very close to 15.5 and 15.8% db, respectively, for corn stover and big bluestem. At 20°C and 90% RH, corn stover had a higher EMC than that of big bluestem, whereas at 30 and 40°C, big bluestem had a higher EMC than that of corn stover as evident from Figure 1. The EMC of corn stover in the present study was higher at lower range of ERH (0.12–0.50) when compared to corn leaf, stalk skin, and stalk pith [31], whereas the selected components of corn stover had a higher EMC at higher range of ERH (>0.5) than that of corn stover.

EMC values of different feedstocks and pellets made from different feedstocks were summarized in Table 3 for easy comparison. By comparing Figure 1 and Table 3, the present study EMC values for corn stover and big bluestem were higher at an ERH of 0.35 than that of other feedstocks. However, EMC values were well within the range of other feedstocks at ERH of 0.75 and 0.90 as listed in Table 3. EMC values for corn stover and big bluestem can be interpolated for 25°C using 20 and 30°C values. Interpolated (25°C) EMC values for corn stover and big bluestem were of 11.8 and 14.6 and 10.5 and 14.5% db with ERH of 0.35 and 0.75, respectively. These feedstocks had higher EMC values than that of pellets made from these feedstocks as reported by Theerarattananoon et al. [37]. Possible reasons for differences in EMC values might be due to high surface area of feedstocks [17], high strength of pellets [18], reactions during pelleting process due to high moisture and temperature [9], and feedstock geometry, morphology, and chemical composition including lignin content [46]. Amount of extractives varied from 8.5 to 12.5% and 12.5 to 19.2% for corn stover and big bluestem, respectively. There was no definite trend between amount of extractives and observed EMCs at different RH and temperatures. In general, common feedstocks starting from wheat straw to miscanthus had higher EMC values than that of natural fibres, wood, and pellets at 25°C with over the range of ERH as evident from Table 3.

3.2. Isotherms Fitting and Evaluation. Most researchers used the values of E_m and E_s to judge the adequacy of the models

Table 3: EMC (% db) of different feedstocks and pellets found in literature.

Feedstocks	Temperature, °C									References
	15			25			35			
	ERH									
	0.35	0.75	0.90	0.35	0.75	0.90	0.35	0.75	0.90	
Wheat straw	8.0	14.5	28.5	7.5	14.0	27.0	7.0	11.5	24.0	Duggal and Muir, 1981 [30]
Red clover leaves				5.8	9.9	12.9	5.3	8.7	10.9	Stencl and Homola, 2000 [43]
Red clover stems				13.6	17.0	21.2	11.7	15.6	18.3	Stencl and Homola, 2000 [43]
Flax straw	9.5	15.0	25.5	9.0	14.5	24.0				Nilsson et al., 2005 [12]
Hemp stalk	9.0	14.5	22.5	7.0	13.0	21.0				Nilsson et al., 2005 [12]
Reed canary grass	10.0	15.0	22.0	7.0	13.5	20.0				Nilsson et al., 2005 [12]
Amaranth stem	9.9	16.2	25.8	8.5	13.7	22.8				Stencl et al., 2010 [33]
Corn leaves				7.5	15.0	28.1	5.7	12.7	22.7	Igathinathane et al., 2005 [31]
Corn stalk skin				6.5	15.1	27.0	5.4	13.5	20.7	Igathinathane et al., 2005 [31]
Corn stalk pith				5.8	13.1	37.6	3.6	10.9	24.0	Igathinathane et al., 2005 [31]
Corn stalk				6.4	14.6	29.8	4.9	12.8	21.6	Igathinathane et al., 2005 [31]
Miscanthus leaves				9.0	18.0	31.0				Arabhosseini et al., 2010 [7]
Miscanthus stem				8.5	16.5	30.0				Arabhosseini et al., 2010 [7]
Natural fibres										
Flax fibre	5.0	10.0	15.0	4.0	9.0	14.0				Hill et al., 2009; 2010 [44, 45]; Xie et al., 2011a [46]
Jute fibre				6.0–6.5	12.0–13.5	18-19				Hill et al., 2009 [44]; Xie et al., 2011a [46]
Hemp fibre				5.0	11.5	18.3				Xie et al., 2011a [46]
Sisal fibre				5.5	12.0	18.8				Xie et al., 2011a [46]
Wood										
Sapwood of Scots Pine				5.5–7.5	12.5–15.0	18.0–20.2				Xie et al., 2010; 2011b [47, 48]
Maple wood*				6.2	12.5	18.0				Papadopoulos, 2005 [49]
Elm wood				6.0	12.0	17.5				Papadopoulos, 2005 [49]
Balsa wood*				5.5	12.0	19.0				Wimmer and Schmid, 2010 [50]
Sapwood/softwood*				6.5–7.0	13.0–13.5	17.0–18.0				Papadopoulos and Hill, 2003 [51]; Mantanis and Papadopoulos, 2010 [52]
Pellets from										
Switchgrass				7.5	11.5	15.0				Colley et al., 2007 [34]
Peanut hull				9.0	14.0	22.5				Fasina, 2008 [36]
Corn stover				9.5	14.0	20.5				Theerarattananoon et al., 2011 [37]
Wheat straw				9.5	13.0	20.0				Theerarattananoon et al., 2011 [37]
Big bluestem				9.8	14.0	20.0				Theerarattananoon et al., 2011 [37]
Sorghum stalk				10.0	15.0	21.0				Theerarattananoon et al., 2011 [37]

Values were extracted either from table or figure from respective references.
*At 20°C.

to represent the relationship [7, 12, 31, 33, 34, 39, 67, 68]. Lower values of E_m and E_s indicate the better fit of the model compared with the other models. Chen and Morey [39] showed that low values of E_m and E_s were not sufficient criteria for evaluating the goodness of fit of isotherm equations; in addition, they recommended the use of residual plots. Accordingly, the residuals of EMC were plotted against independent variable (ERH) values and evaluated visually for randomness or pattern. A model was considered acceptable if the residuals were uniformly scattered about independent variable in x-axis, showing no systematic distribution or clear pattern of dependent variable residuals in the positive and negative directions of the y-axis. When a residual plot of a model indicated a systematic distribution or clear pattern, the model was not accepted [38, 39]. In this study, if a model has relatively small error terms (i.e., E_s and E_m), high F-statistic and R^2 values, and residual plots with randomly scattered points [31, 33, 34, 67], then it was considered as good/acceptable model.

The fitted isotherm constants and parameters indicating goodness of model fit are listed in Table 4. Out of five models used, modified GAB model did not fit well with

Table 4: Fitted isotherm parameters for corn stover and big bluestem.

Equation	Constants A	B	C	Performance/statistical parameters E_m	E_s	F	R^2	Residual
Corn stover								
Modified Oswin	15.41	−0.099	6.447	0.2476	1.455	1599	0.988	Random
Modified Halsey	13.04	−0.0402	4.8927	0.1310	1.384	1770	0.989	Random
Modified Henderson	1.604×10^{-7}	2.9404	4.6443	0.3754	1.616	1292	0.986	Systematic
Modified Chung-Pfost	2165	−1.4086	0.3834	0.0977	1.462	84	0.745	Random
Modified GAB	4.8372	2.011	1.177	3710	11.28	8	0.298	Systematic
Big bluestem								
Modified Oswin	15.7704	−0.1270	5.2686	0.6668	1.206	2269	0.992	Systematic
Modified Halsey	10.5023	−0.0427	3.9133	0.3607	1.062	2939	0.994	Random
Modified Henderson	2.63×10^{-6}	−0.3569	3.6383	0.9798	1.438	1515	0.988	Systematic
Modified Chung-Pfost	776.6	−3.7506	0.3184	0.3684	1.261	165	0.853	Systematic
Modified GAB	4.1221	2.0197	1.3465	2688	11.12	7.95	0.295	Systematic

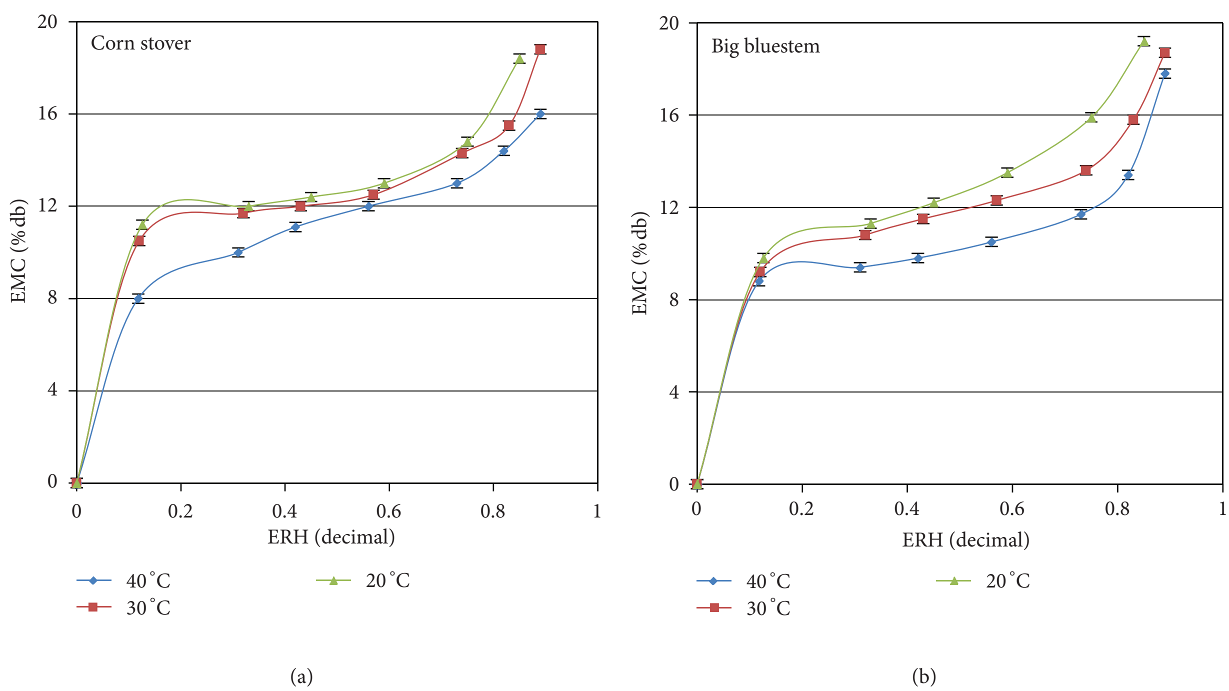

Figure 1: Moisture sorption of corn stover and big bluestem at indicated relative humidities and temperatures.

corn stover and big bluestem data; so this model will not be considered further. In this study, F-statistic value should make a better model performance parameter due to wide variation in the F-statistic values of the models. Considering F-statistic value, modified Halsey model had the highest for both the feedstocks and the second best was modified Oswin model. According to Wang and Brennan [69], a model can be acceptable if E_m values are below 10%, and based on this criterion, all the models are good except for modified GAB. However, other statistical parameters should be considered for proper selection of a model. As observed in Table 4, statistical parameters such as F-statistic, E_m, E_s, and R^2 followed a similar pattern among models and feedstocks. In general, the lower are the values of E_m and E_s, and the higher are the values of R^2 and the better is the goodness of fit. The coincidence of these parameters also indicates modified Halsey as the best and modified Oswin as the second best performing model for corn stover and big bluestem. Modified Chung-Pfost, modified Henderson, and modified GAB models did not perform well based on the criteria considered, and this observation was in agreement with Igathinathane et al. [31] and Nilsson et al. [12].

The next logical step in a model selection is to look into the residual plots of EMC versus ERH. Residual plots of modified Oswin, modified Halsey, modified Henderson, and modified Chung-Pfost for corn stover and big bluestem are shown in Figures 2 and 3, respectively. Among the models, modified Halsey and modified Oswin exhibited a fairly

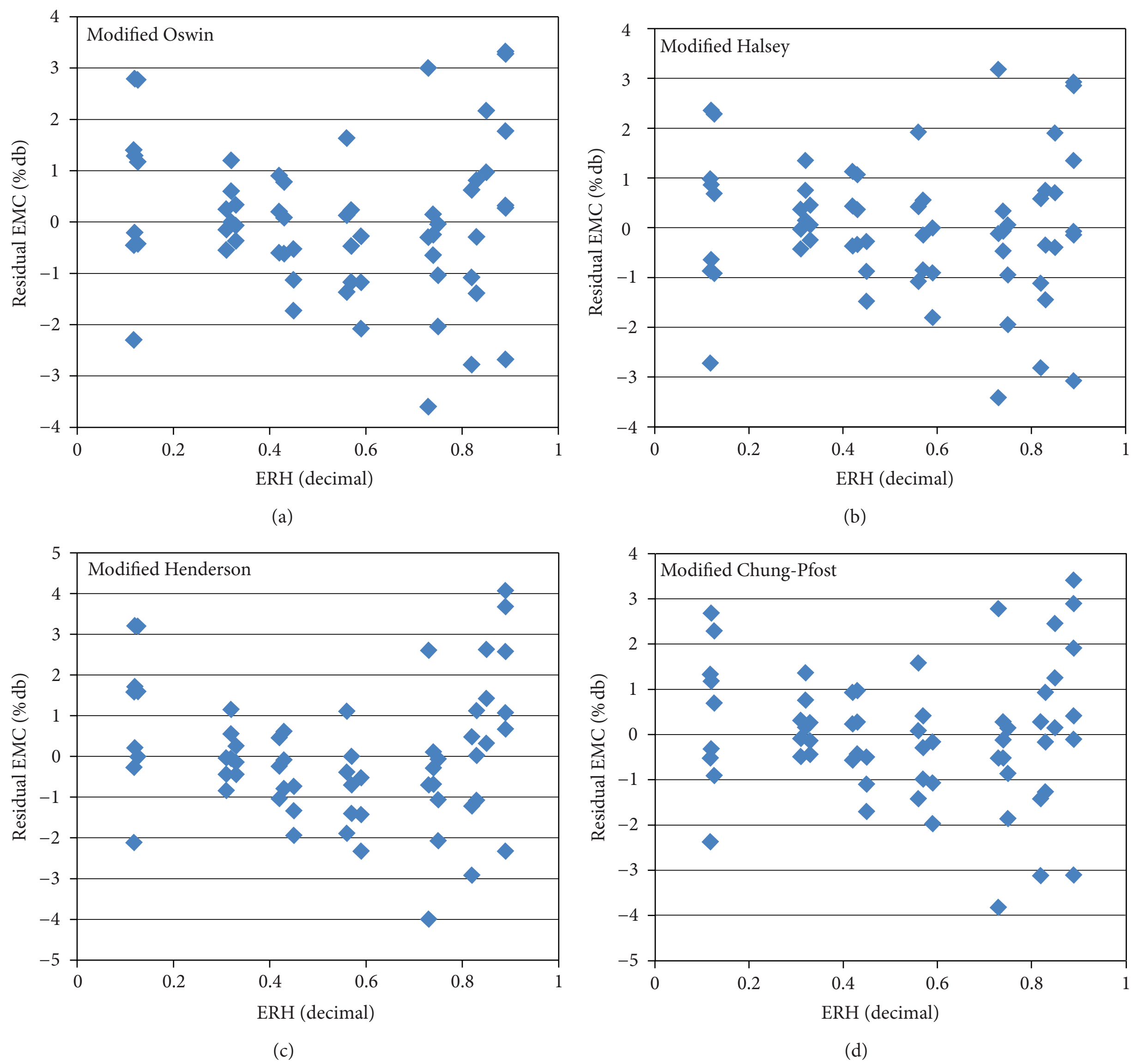

FIGURE 2: Residual plots of the fitted isotherm equations for the moisture isotherm data of corn stover at temperatures 20 to 40°C.

random distribution for both feedstocks when compared to modified Henderson and modified Chung-Pfost models. In addition to F-statistic, E_m, E_s, and R^2 values, residual plots also confirm modified Halsey as the best model for corn stover and big bluestem, and the second best model was modified Oswin for corn stover. In another study, a similar model selection was reported for switchgrass and prairie cord grass [64]. Nilsson et al. [12] also reported modified Halsey as the best model for flax and reed canary grass whereas modified Oswin as best model for hemp. The first and second models observed in this study were in reverse order of Igathinathane et al. [31]. Arabhosseini et al. [7] found modified Oswin as suitable model to describe the isotherm relation for miscanthus leaves and stem. Colley et al. [34] observed that modified Chung-Pfost model was the best and modified Oswin was the second best model predicted EMC of switchgrass pellets. According to ASAE standard D245.5 [70], modified Chung-Pfost model predicted the EMC of barely starw. In contrast to the previous studies including the current study, Duggal and Muir [30] reported modified Henderson as suitable model for wheat straw based on standard error of the estimate, and Stencl et al. [33] also reported modified Henderson as the best model for moisture adsorption and desorption of amaranthus stems. Similarly, Stencl and Homola [43] found that Henderson equation was the best model for red clover leaves, and Oswin equation was best for red clover stems.

3.3. Prediction of EMC by Modified Halsey and Modified Oswin Models. The best and second best models were used for generating moisture isotherm of corn stover and big bluestem. Figure 4 shows observed and predicted EMC at

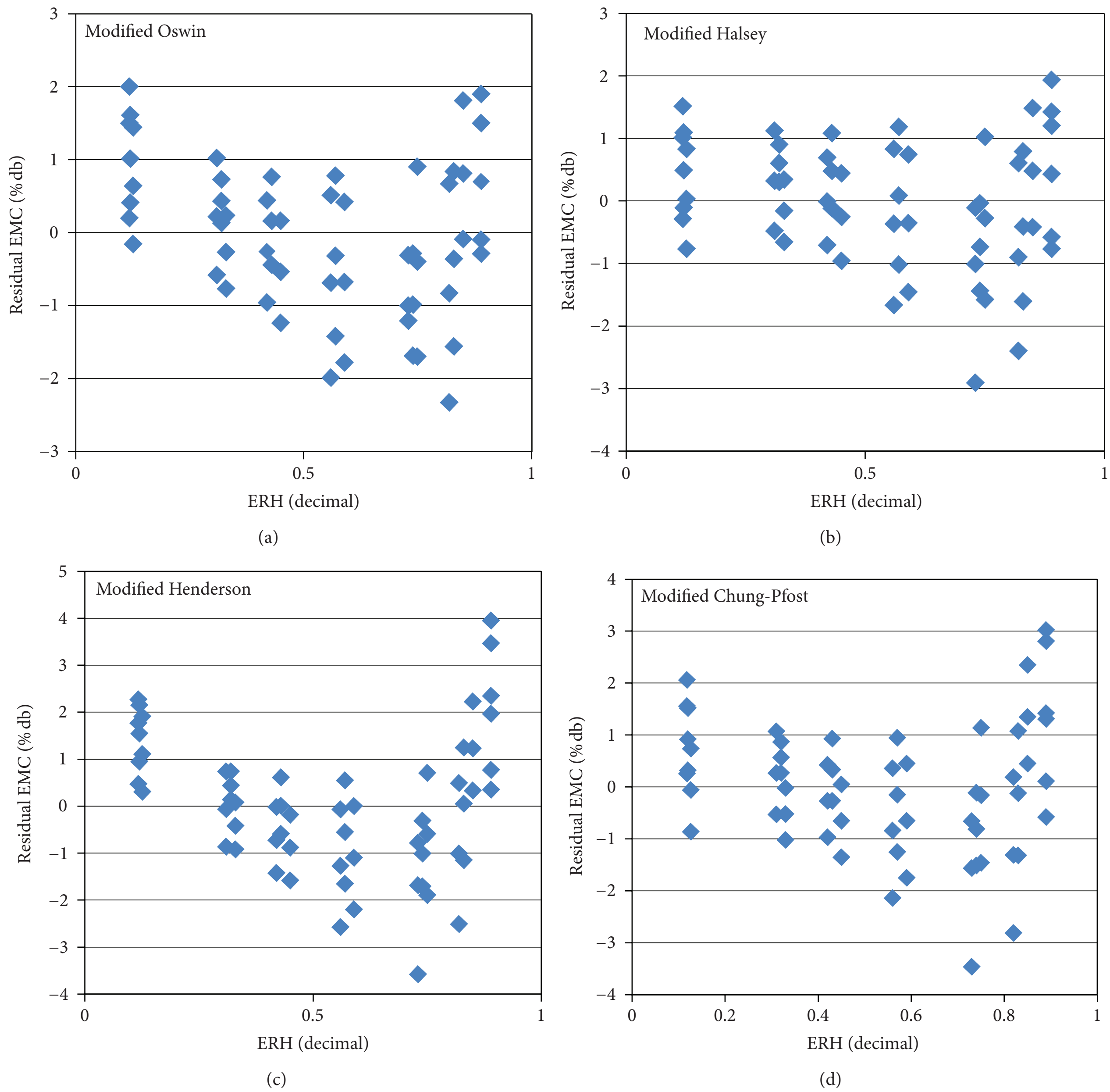

Figure 3: Residual plots of the fitted isotherm equations for the moisture isotherm data of big bluestem at temperatures 20 to 40°C.

different temperatures (20, 30, and 40°C). The closeness of observed EMC data (points) and predicted EMC (line) confirms the goodness of model fit for both feedstocks. As seen from these figures, model predicted isotherms follow type II isotherm, which was in agreement with flax straw, reed canary grass, hemp stalk, selected corn stover components, miscanthus leaves and stem, switchgrass, and prairie cord grass [7, 12, 31, 64]. A common feature in food material is a sharp increase in EMC greater than an ERH of 0.8 [31], which can be visualized in Figure 4 for corn stover and big bluestem, respectively. When comparing the three temperatures at constant RH, it can be seen that the EMC increases with decreasing temperature. From Figure 4, the predicted isotherms show a good fit of modified Halsey for corn stover and big bluestem, and the arrangement of curves also shows that increase in temperature decreased EMC. Considering the moisture content limit reported for long-term storage by Arabhosseini et al. [7], these feedstocks can be stored up to an ERH of 0.75 within the temperature range studied.

4. Conclusion

EMCs of corn stover and big bluestem were determined at three different temperatures with wide range of RH. The observed minimum and maximum EMC values were 8.0 and 8.8 and 19.6 and 19.2% db for corn stover and big bluestem,

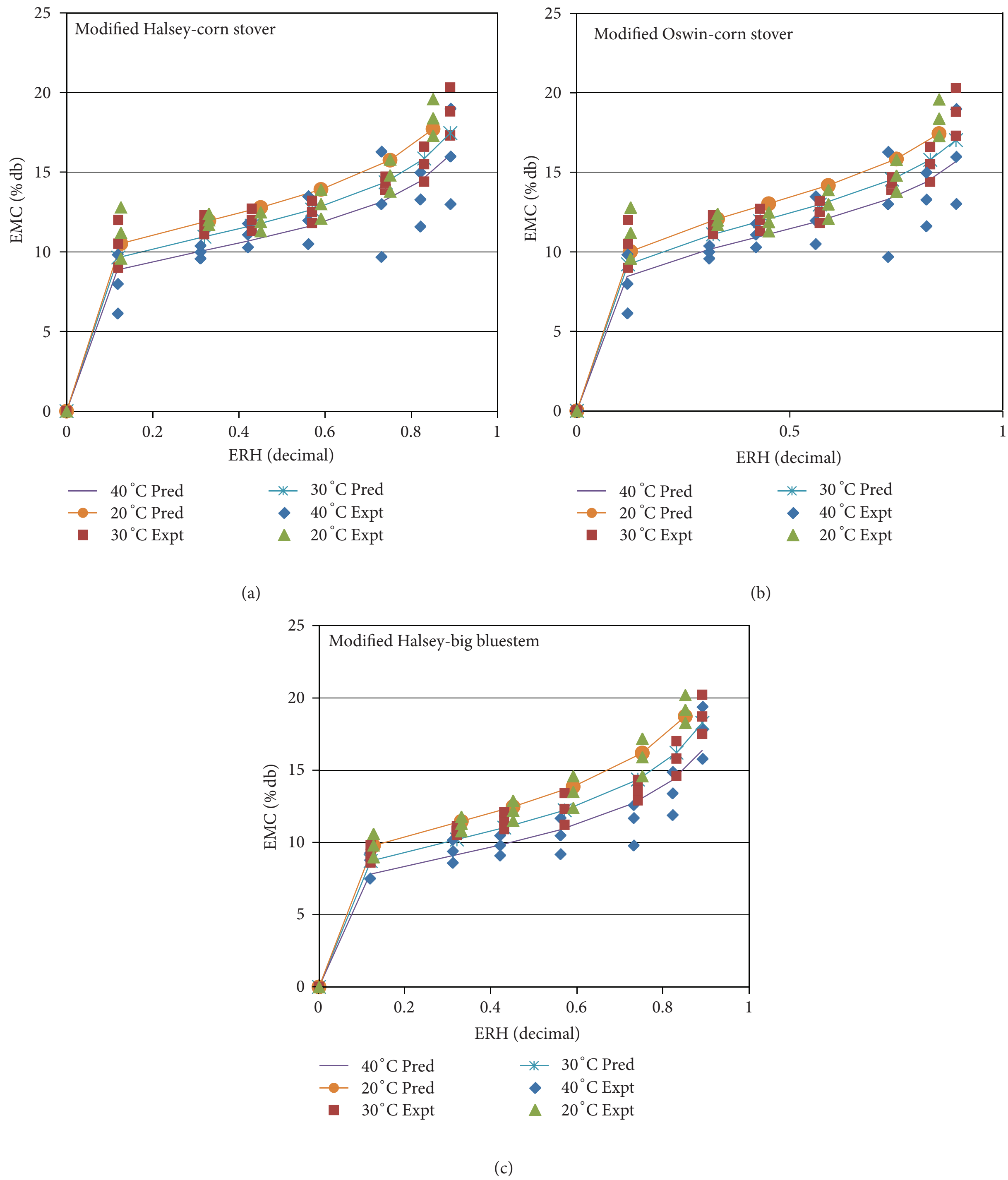

FIGURE 4: Comparison between observed and modified Halsey and modified Oswin equations predicted sorption isotherms of corn stover and big bluestem at indicated temperatures (Expt: experimental: Pred; predicted).

respectively. Corn stover had a higher EMC than that of big bluestem at high RH across the temperature. Among the models applied to fit experimental data of corn stover and big bluestem, modified Halsey model fits very well followed by modified Oswin model. The constants of these equations can be used to estimate the EMC of these feedstocks within the temperature range.

Nomenclature

Symbols

df: Degree of freedom
E_m: Mean relative percent error
E_s: Standard error

N: Number of data points
R^2: Coefficient of determination
Y: Experimental equilibrium moisture content % (db)
$\widehat{Y}$: Predicted equilibrium moisture content % (db)
%: Percentage
$^{\circ}C$: Degree Celsius.

Abbreviations

ASAE: American Society of Agricultural Engineers
ASABE: American Society of Agricultural and Biological Engineers
db: Dry basis
ERH: Equilibrium relative humidity
EMC: Equilibrium moisture content
exp: Experimental
GAB: Guggenheim-Anderson-deBoer
m: Metre
mm: Millimetre
NLIN: Nonlinear
NREL: National Renewable Research Laboratory
Prd: Predicted
RH: Relative humidity
SS: Sum of squares.

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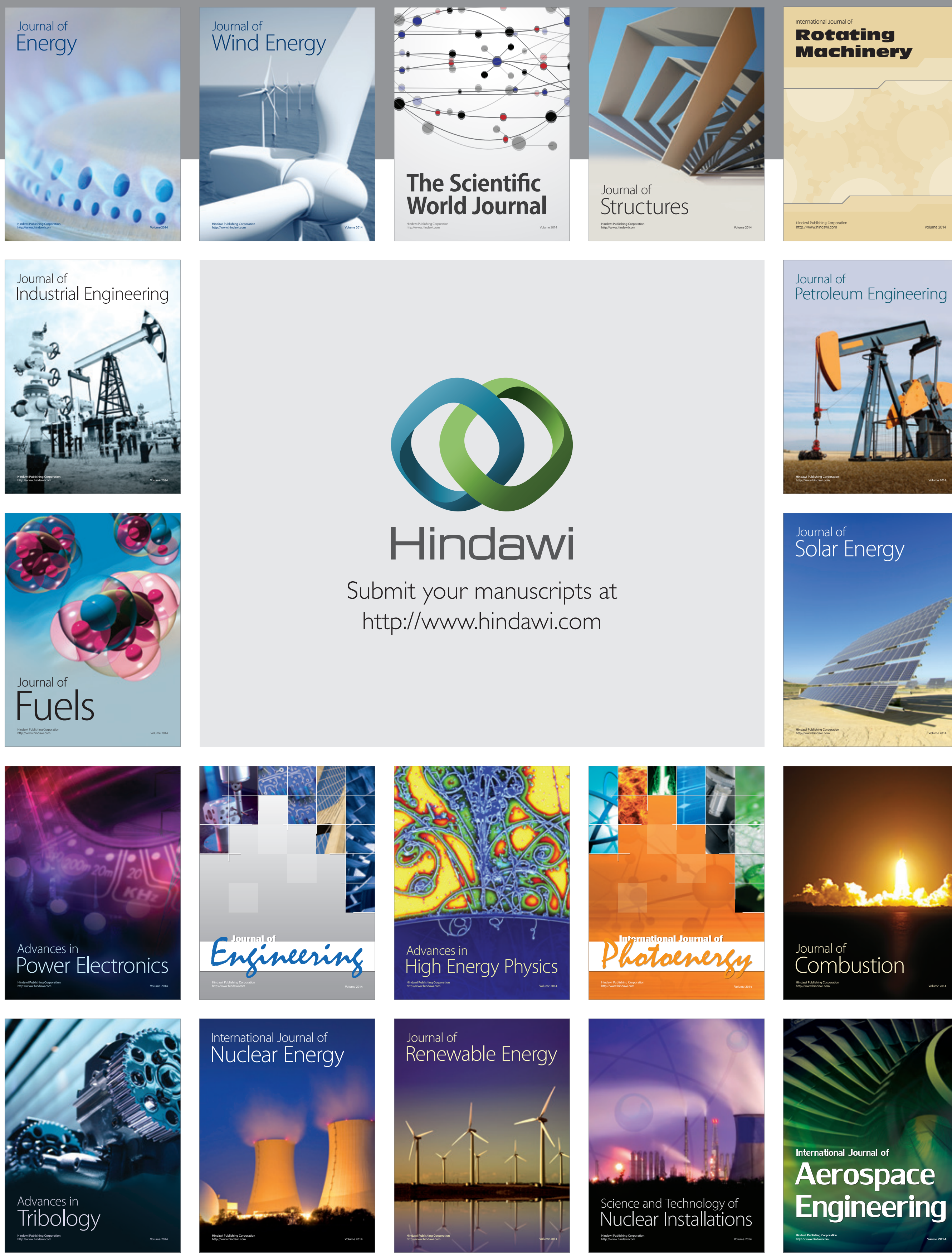
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