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Research Paper

The moisture sorption characteristics and modelling of agricultural biomass

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The moisture sorption properties of typical biomass samples (tobacco stem, rice husk, wheat straw, cotton stalk, corn straw and rice straw) were investigated under different conditions, and the adsorption kinetics was analysed with pseudo order models. The equilibrium moisture content (EMC) was simulated with different models based on biomass property and adsorption process. Results showed that the adsorption process of biomass can be divided into two ranges: rapid adsorption and slow adsorption process. A pseudo-second order model could better describe the moisture sorption process than a pseudo-first order model. Equilibrium moisture content (EMC) mainly depended on biomass type and environmental humidity. A modified Halsey model provided the best fit to EMC of biomass and this model can be used to predict EMC of biomass.

1. Introduction

Biomass has gained worldwide attention as a renewable energy source for thermochemical conversion (Aysu & Küçük, 2014; Damartzis & Zabaniotou, 2011; Wei et al., 2006). Biomass is hygroscopic in nature, and thus adsorbs moisture from its surroundings. The inherently high moisture content of biomass is a critical issue. However, when considering gathering and recycling these materials, it requires more energy for preprocessing, transportation, and conversion, and all of which can considerably increase the cost of utilisation (Kaewluan & Pipatmanomai, 2011; Medic, Darr, Shah, & Rahn, 2012; Serrano, Monedero, Lapuerta, & Portero, 2011). Further, water in biomass feedstock can affect the pyrolysis behaviour of biomass, e.g. the distribution of pyrolysis products, the physical and chemical properties of liquid oil and solid char, and the composition of gas (Burhenne, Damiani, & Aicher, 2013; Demirbas, 2004). To this effect, sufficient working knowledge of biomass moisture content is conducive to the

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Nomenclature

EMC, q_e, y	Equilibrium moisture content, %
TS	Tobacco stem
RK	Rice husk
WS	Wheat straw
CTS	Cotton stalk
CS	Corn straw
RS	Rice straw
$FTIR$	Fourier Transform Infrared spectroscopy
ERH	Equilibrium relative humidity, %
MC	Moisture content, %
W_t	Mass of the sample at time t, g
W_0	Initial mass of dried sample, g
q_t	Moisture content adsorbed (%) at time t, %
t	time, min
k_1, k_2	Rate constants
b_i	Regression coefficient
x_i	Experimental parameters
σ_i, σ_y	Standard deviation of x_i, y
T	Temperature, °C
A, B, C	Constants
RSS	Residual sum of squares
RMSE	Root mean squared error
MRE	Mean relative error
R^2	Coefficient of determination
EMC_C	Calculated value of EMC
n	Number of test data points
df	Degree of freedom

development of appropriate pretreatment methods and storage operations that support the material transportation and conversion, and, ultimately, increase the value of its utilisation. Equilibrium moisture content (EMC) is a vital parameter in evaluating the effect of external conditions on biomass moisture (Mohamed et al., 2005; Soysal & Öztekin, 1999). Moisture content of biomass that has reached a relatively steady state at certain relative humidity and temperature is known as EMC. The temperature and humidity of environmental conditions are key parameters determining EMC of biomass. Higher humidity results in a higher EMC under the same temperature, while lower temperatures lead to a higher EMC under constant humidity (Jamali, Kouhila, Mohamed, Idlimam, & Lamharrar, 2006; Karunanithy, Muthukumarappan, & Donepudi, 2013a). Arabhosseini, Huisman, and Muller (2010) found that EMC of miscanthus decreased with increasing temperature from 25 °C to 70 °C at constant humidity, and the typical S-shaped curves between EMC and equilibrium relative humidity were found for stems and leaves while the EMC values of stems were slightly lower compared to those of leaves. In addition to the temperature and humidity of the environment, EMC of biomass can be affected by its physicochemical properties. The EMC of biomass may depend on the composition, porosity, microstructure, specific surface area and other physicochemical properties (Arslan & Toğrul, 2005; Choudhury, Sahu, & Sharma, 2011; Karunanithy, Muthukumarappan, & Donepudi, 2013b). However, there little reported research on the effects of the physicochemical properties of biomass on EMC. It is important to study the physicochemical properties of biomass to better estimate the EMC of biomass.

Previous studies have investigated the EMC of different biomass such as flax straw, hemp stalk, and reed canary grass (Nilsson, Svennerstedt, & Wretfors, 2005), selected corn stover components (Igathinathane, Womac, Sokhansanj, & Pordesimo, 2005), miscanthus leaves and stems (Arabhosseini et al., 2010), amaranthus stems (Stencl et al., 2010), pine (Acharjee, Coronella, & Vasquez, 2011), aspen (He et al., 2013), corn stover and big bluestem (Karunanithy et al., 2013a). Agricultural biomass appears to be the most attractive feedstock due to its abundance, cheapness and renewability. However, relatively few studies have explored the moisture sorption process and EMC of agricultural biomass, such as wheat straw, cotton stalk, and rice straw. Different biomass materials display various moisture sorption characteristics. Therefore, it is necessary to study the moisture sorption process to better understand the hygroscopicity of biomass as a whole.

The physicochemical properties effect biomass EMC but the effect has been rarely discussed in the previous studies, therefore the mechanism of moisture sorption remains unknown. This research focusses on the effects of humidity, temperature and sample mass on the hygroscopicity of different agricultural biomass samples, and the impact of physicochemical properties on EMC of biomass. The aims of the study were to predict moisture sorption characteristics and mechanism of agriculture biomass and to explore the main influence factors that determine biomass EMC.

2. Materials and methods

2.1. Materials

Six different agriculture biomass products; tobacco stem (TS), rice husk (RK), wheat straw (WS), cotton stalk (CTS), corn straw (CS) and rice straw (RS) were selected in this study. Biomass samples were obtained from Wuhan, Hubei, China. The samples were firstly air-dried, and then ground to pass the sieves with 60 and 120 mesh. The particle size of biomass was 0.12–0.25 mm.

2.2. Biomass characterisation

The bulk density was the ratio of dry mass and volume. True density was determined by automatic true density analyser (Micromeritics, AccuPyc 1330, USA). Porosity was calculated on the basis of bulk density and true density (Githinji, 2014).

The surface organic functional groups of biomass were characterised by Fourier Transform Infrared spectroscopy (FTIR) analysis. To obtain FTIR spectra, samples were mixed with KBr (1:200, w/w) and ground, then the mixture was pressed into pellets. The biomass infrared spectra were recorded on a VERTEX 70 spectrometer (Bruker, VERTEX 70, Germany) at a resolution of 2 cm^{-1} and accumulation of 120 scans. Each spectrum was scanned from 400 cm^{-1} to 4000 cm^{-1} wave numbers.

2.3. Moisture sorption method

A hygroscopicity experiment for agriculture biomass was carried out in a constant temperature and humidity incubator (Shanghai, HWS-150, China) using the gravimetric method. The temperature and humidity of the incubator was adjusted to a specific value to study the effect of environmental conditions on hygroscopicity of biomass. The weighed sample was evenly spread over the bottom of a weighing bottle (diameter 50 mm and height 35 mm), and then dried in an oven at 105 °C for 12 h to prepare for the hygroscopicity test. The sample bottles, which were acclimatised to the chamber temperature, were weighed with their lids, uncovered and quickly transferred to the incubator when the given temperature and humidity remained stable. Each bottle with lid was weighed with time by analytical balance (max. capacity of 200 g, ±0.0001 g). The process of water absorption was considered to reach equilibrium when the mass difference of three consecutive masses was less than 1 mg. Each experiment was done in triplicate.

Moisture content (MC) of the sample at each environment condition was calculated as follows:

$$MC\ (\%) = (W_t - W_0)\ 100/W_t \quad (1)$$

where W_t is the mass of the sample at time t and W_0 is the initial mass of dried sample.

The effect of humidity on the hygroscopicity of biomass was conducted at different humidity levels ranging from 50% to 90% at the constant temperature of 30 °C. The temperature effect was done at 70% humidity and temperature settings of 20, 30 and 40 °C. The influence of sample mass was explored at 80% humidity and 30 °C.

2.4. Sorption kinetic models

To investigate the kinetics of moisture sorption process on biomass, pseudo-first-order and pseudo-second-order models were considered (Hamoudi & Belkacemi, 2012; Ho & McKay, 1999).

The pseudo-first order model was described by;

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (2)$$

the pseudo-second order model by;

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

where q_e and q_t are the moisture content adsorbed (%) at equilibrium and any time t (min) respectively, and q_e is equivalent to EMC where k_1 and k_2 are the rate constants.

2.5. Sensitivity analysis

Sensitivity analysis was used to evaluate the influence of experiment parameters on EMC of biomass. A multiple linear regression between the EMC (y) of the biomass and the experimental parameters (x_i) was established to obtain a standard deviation and a regression coefficient. Sensitivity indices was calculated by

$$\text{Sensitivity indices}\ (x_i) = \sigma_i b_i/\sigma_y \quad (4)$$

σ_i, σ_y − standard deviation of x_i, y, b_i − regression coefficient.

2.6. Moisture sorption isotherms

Equilibrium relative humidity (ERH) was defined in terms of EMC. A large number of EMC/ERH equations have been suggested in the literature to describe the EMC of biomass. Modified Henderson, modified Chung-Pfost, modified Halsey, and modified Oswin models (Eqs. (5)–(8)) are typically recommended to study the sorption isotherm (Igathinathane, Pordesimo, Womac, & Sokhansanj, 2009; Medic et al., 2012), detailed as follows.

$$\text{Modified Henderson equation}: \ EMC = \left[\frac{\ln(1-ERH)}{-A(T+B)}\right]^{\frac{1}{C}} \quad (5)$$

$$\text{Modified Chung-Pfost equation}: \ EMC = -\frac{1}{C}\ln\left[\frac{\ln(ERH)\cdot(T+B)}{-A}\right] \quad (6)$$

$$\text{Modified Halsey equation}: \ EMC = \left[\frac{-\exp(A+B\cdot T)}{\ln(ERH)}\right]^{\frac{1}{C}} \quad (7)$$

$$\text{Modified Oswin equation}: \ EMC = (A+B\cdot T)\left[\frac{ERH}{1-ERH}\right]^{\frac{1}{C}} \quad (8)$$

For each of these, *EMC* is the equilibrium moisture content (%), *ERH* is the relative humidity in decimal, T is temperature (°C), and A, B, and C are constants which can be calculated using a particular model according to existing experimental data.

These four equations (Eqs. (5)–(8)) were analysed by nonlinear regression to evaluate the fit quality of each model. The statistical parameter equations of residual sum of squares (*RSS*), root mean squared error (*RMSE*), mean relative error (*MRE*), and residual were calculated as follows (Eqs. (9)–(11)):

$$RSS = \sum_1^n (EMC_C - EMC)^2 \quad (9)$$

$$RMSE = \sqrt{\frac{RSS}{df}} \quad (10)$$

$$MRE = \frac{1}{n}\sum_1^n \frac{|EMC_C - EMC|}{EMC} \quad (11)$$

where EMC_C is the calculated value of *EMC*, n is the number of test data points, and *df* is the degree of freedom.

The models that had the largest R^2 and F value and the lowest *RSS*, *RMSE*, and *MRE* values are considered the best fit for experimental data.

3. Results and discussion

3.1. Physicochemical properties of biomass

3.1.1. Physical characteristics of biomass

The bulk density, true density and the porosity of biomass are shown in Table 1. Tobacco stem and rice husk had higher bulk density and true density than other biomass while the porosity of tobacco stem and rice husk were relatively low. Wheat straw and cotton stalk had similar true density while wheat straw had much lower bulk density and higher porosity than cotton stalk. Corn straw had the highest porosity followed by wheat straw, when significant differences existed between the true density of corn straw and wheat straw. No significant differences in porosity and bulk density were observed between cotton stalk and rice straw, while the true density of rice straw was significantly higher than that of cotton stalk. The physical characteristics of wheat straw and rice straw were significantly different, and cotton stalk and corn straw also had different physical properties.

3.1.2. *Chemical properties of biomass sample*

The FTIR spectra of six biomass samples are shown in Fig. 1. It shows that the samples of biomass consisted of alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups observed, such as O–H stretching vibration (3000–3700 cm^{-1}), C=O and (1600–1800 cm^{-1}) and C–O stretching vibration (1000–1350 cm^{-1}) with some C–H bending vibration (1360–1480 cm^{-1}), C=C stretching vibration and C–H stretching vibration (2800–3000 cm^{-1}), etc.

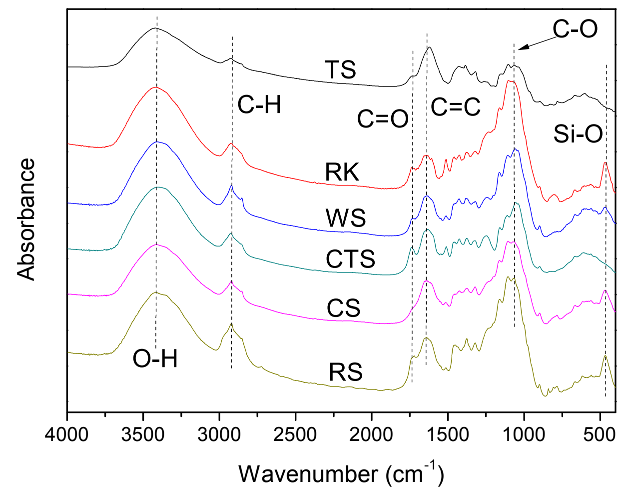
The peaks of the functional groups in the region of 3750–3000 cm^{-1} and 3000–2800 cm^{-1} for each biomass sample existed with the same wavenumber, and the peak areas were calculated for quantitative analysis. Rice husk had the largest peak area (68.99% cm^{-1}) in the region of 3750–3000 cm^{-1}, followed by wheat straw (66.98% cm^{-1}), cotton stalk (65.93% cm^{-1}), rice straw (62.75% cm^{-1}), corn straw (54.41% cm^{-1}) and tobacco stem (37.98% cm^{-1}). Rice straw had the largest peak area (9.03% cm^{-1}) in the region of 3000–2800 cm^{-1}, followed by wheat straw (5.74% cm^{-1}), rice husk (4.74% cm^{-1}), cotton stalk (4.57% cm^{-1}), corn straw (4.29% cm^{-1}) and tobacco stem (1.81% cm^{-1}). Alkyl groups with C–H stretch in the region 3000–2800 cm^{-1} and are strongly correlated with hydrophobicity (Kinney et al., 2012), while the C=O peak (1680–1730 cm^{-1}) primarily represents ionisable carboxyl groups, signifying hydrophilic surface functionality (Gray, Johnson, Dragila, & Kleber, 2014). These groups indicated that the samples may have different hygroscopicity. High moisture content in biomass can result in higher transportation costs and lower conversion efficiency, hence the hydrophobicity is critical to the efficient utilisation of biomass resources.

With respect to the various biomass samples, because of the inherent properties of the original agricultural product, their main compounds are also slightly different. Tobacco stem showed lower hydroxyl groups (3700–3000 cm^{-1}) and $-CH_3$ and $-CH_2$ groups (2922 cm^{-1}), while rice straw had higher C–O and $-CH_3$ and $-CH_2$ groups (Uzunov, Uzunova, Angelova, & Gigova, 2012). As there was high Si content in rice husk, some Si–O peaks were also found. Rice straw, cotton stalk and wheat straw, also showed similar Si–O structures to rice husk.

Table 1 – Density and porosity of biomass.

Sample	Bulk density ($kg\ m^{-3}$)	True density ($kg\ m^{-3}$)	Porosity (%)
TS	427.22 ± 9.69	1645.77 ± 3.49	74.04 ± 0.64
RK	497.85 ± 11.39	1536.27 ± 0.45	67.59 ± 0.73
WS	182.29 ± 5.61	1478.20 ± 1.25	87.67 ± 0.37
CTS	223.34 ± 5.92	1479.53 ± 2.61	84.90 ± 0.41
CS	169.73 ± 5.10	1505.37 ± 3.18	88.73 ± 0.33
RS	217.33 ± 8.63	1497.17 ± 2.76	85.48 ± 0.58

TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw.



TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw

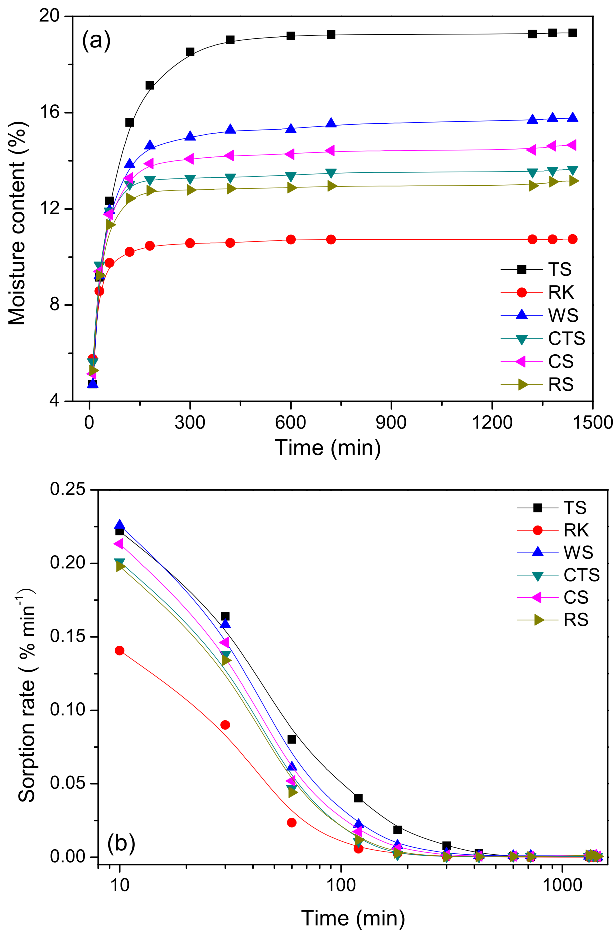
Fig. 1 – FTIR spectra of different biomass samples.

3.2. *Moisture sorption characteristics of biomass*

3.2.1. *Moisture sorption process of biomass*

The moisture content and sorption rate of the biomass samples at 30 °C and 70% humidity are shown in Fig. 2. It can be seen that biomass samples adsorbed water quickly in the first 100 min, and the moisture content increased linearly. However, with time, the water adsorption velocity decreased rapidly, and the moisture content increased slightly as adsorption time approached 420 min. The moisture sorption rate of the samples followed the same trend as that reported by Yu, Cannayen, Hendrickson, and Sanderson (2014). After that the adsorption velocity diminished almost to zero, and biomass reached the equilibrium moisture content. The moisture sorption process of biomass may be described as: rapid absorption of water followed by slow water absorption in the later stages. The moisture differential between biomass and the environment was the greatest during the inception phase, and moisture diffusion was more rapid via physical adsorption. Biomass easily absorbs moisture from the environment, therefore, the water absorbing capacity increased with high absorption rate. As the moisture content gradually reached saturation, chemical adsorption with a low absorption rate became the main process.

As shown in Fig. 2, where similar water absorption trends were observed, the final moisture content differed greatly, with tobacco stem having the highest moisture content (19.03%), followed by wheat straw (15.69%), corn straw (14.69%), cotton stalk (13.61%), rice straw (13.12%), and rice



TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw

Fig. 2 – Moisture sorption curves and rate of biomass at 30 °C and 70% humidity.

husk (10.74%). This might be related to their physical-chemical structure as tobacco stem showed the highest true density and lowest hydrophobicity. Also, tobacco stem took longer to achieve EMC. It can be concluded that the moisture content of biomass with higher hygroscopicity may need longer to reach its equilibrium value.

Tobacco stem had the highest sorption rate, followed by wheat straw, corn straw, cotton stalk and rice straw, while rice husk had the lowest sorption rate. Within the first 300 min, the sorption rates of cotton stalk, rice straw and rice husk almost reached their final stable values. It took about 420 min for the sorption rates of wheat straw and corn straw to reach steady state, and tobacco stem needed 600 min. The sorption rate of biomass with higher hygroscopicity may need longer time to decrease to zero. The initial high sorption rate indicated that biomass will absorb moisture at a more rapid rate when they are drier.

The moisture sorption process of wheat straw at 30 °C under different humidity is shown in Fig. 3. It can be seen that moisture content of wheat straw increased with the humidity increased from 50% to 90%. With time, the moisture content at higher humidity became much higher than that at lower humidity. The water adsorption rate decreased rapidly at all values of humidity, and eventually reached a relatively stable state. The adsorption rate diminished almost to zero in 300 min at 50%–70% humidity while at 80%–90% humidity it became relatively stable in 24 h. It took a long time for moisture content of wheat straw to reach equilibrium at 80%–90% humidity. The moisture content and water adsorption rate of wheat straw were both higher at 90% humidity, followed by those at 80% and 70% humidity. There were more water molecules available under conditions of high humidity environment, and the moisture differential between biomass and environment was greater during the initial period resulting in more rapid moisture diffusion. Higher humidity had a greater impact on the moisture content and water adsorption rate of wheat straw.

The moisture adsorption property of wheat straw at different temperatures with 70% humidity is shown in Fig. 4. A rapid initial moisture absorption process, followed by a slower increase in the later stages, was also observed in wheat straw at 20 °C and 40 °C. It was found that moisture content of wheat straw at 20 °C was the lowest, and it was significantly less than those at 30 °C and 40 °C. This indicates that higher environment temperatures result in higher moisture contents of biomass. Igathinathane et al. (2009) also found that the

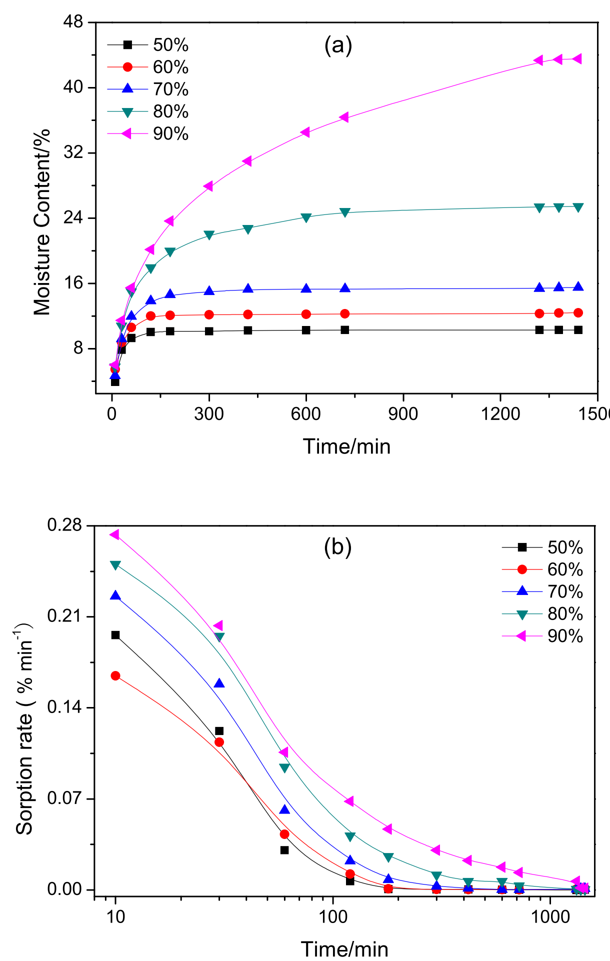


Fig. 3 – Profile of moisture sorption process of wheat straw with humidity at 30 °C.

increase of temperature could contribute to the variation in moisture content and EMC of agricultural materials. The sorption rate of wheat straw at 20–40 °C had the same trend, and the sorption rate of wheat straw at 20 °C was the lowest. Within the first 60 min, the sorption rate of wheat straw at 30 °C was the highest but it subsequently fell between 20 °C and 40 °C. A suitable temperature may be conducive to moisture transfer in the initial period of moisture sorption process. It can be seen that the variation of sorption rate was similar and reached a minimum after 3 h of sorption when the sorption rate was <0.011% min^{-1}. The higher sorption rate had the most rapid moisture diffusion but the process of moisture transfer appeared to reach an equilibrium as the sorption rate reduced. Low temperatures are advantageous for low moisture sorption content and biomass.

3.2.2. *Sorption kinetics*

The typical kinetic results at 30 °C and 70% humidity by pseudo-first order and pseudo-second order kinetic models are shown in Fig. 5, and the kinetic parameters for moisture sorption process of biomass at 70% humidity and different temperatures are given in Table 2. Typical observed and predicted characteristics illustrated that the pseudo-second order model fitted better than the pseudo-first order model. Similar predictive behaviour of the kinetic models was also observed at other temperatures (20 °C and 40 °C) of moisture sorption (not shown) but the kinetic parameters are also given in Table 2.

Both the selected kinetic models adequately described the observed moisture sorption characteristics of each biomass (Table 2). The pseudo-second order model better described the kinetic results with R^2 greater than 0.99 for all biomass samples than the pseudo-first order model. The q_e value calculated by pseudo-second order model for each biomass was higher than that obtained by the pseudo-first order model. Both sorption constants (k_1 and k_2) of the kinetic models of RK were the largest followed by WS and CS, and those of TS were the smallest. The higher constants values indicated the more rapid moisture uptake signifying a shorter time to reach equilibrium.

3.3. *Biomass EMC and model fit*

3.3.1. *EMC of biomass at different humidity*

The EMC of six biomass samples under different humidity at 30 °C are shown in Fig. 6a. EMC increased with humidity, and it

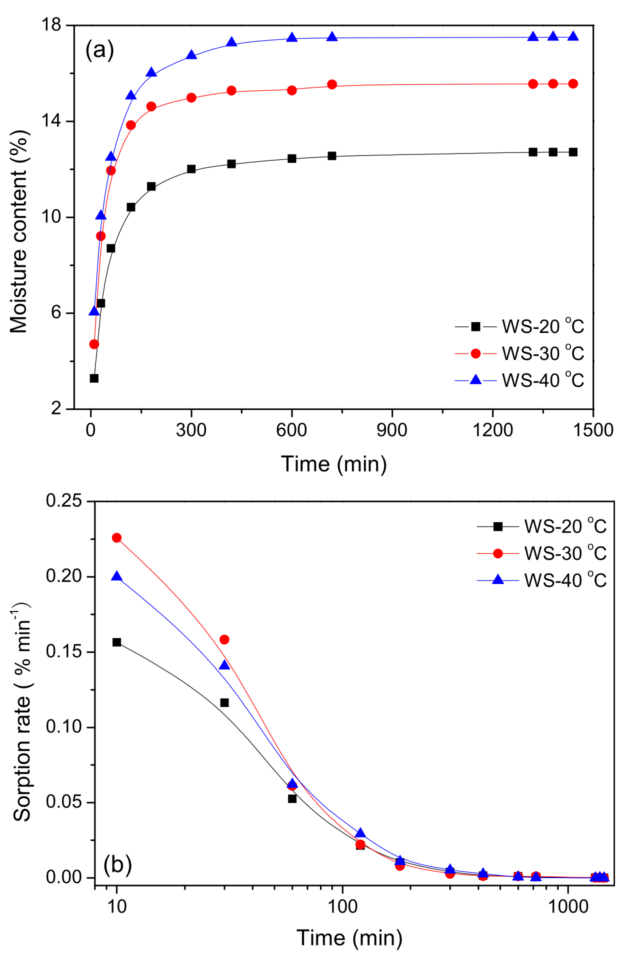


Fig. 4 – Moisture sorption curves and sorption rate of wheat straw (WS) at various temperatures at 70% humidity.

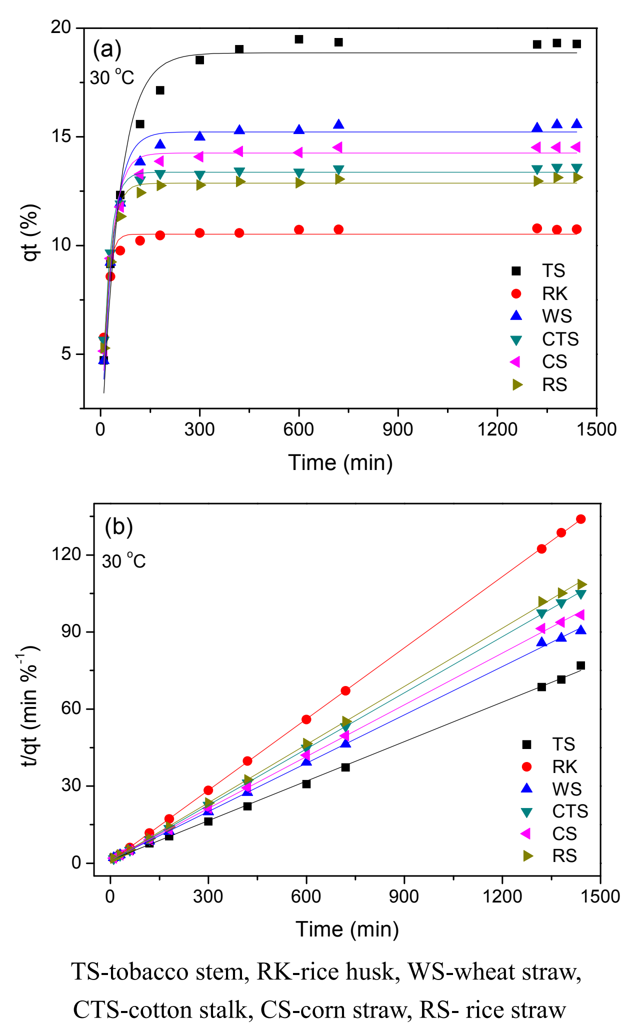


Fig. 5 – The adsorption kinetics of pseudo-first order model (a) and pseudo-second order model (b), solid lines show kinetic model at 30 °C and 70% humidity.

Table 2 – Kinetic constants for moisture sorption process of biomass at 70% humidity.

Sample	T (°C)	Pseudo-first order model			Pseudo-second order model		
		q_e	k_1	R^2	q_e	k_2	R^2
TS	20	16.57	0.0143	0.97553	17.51	0.0015	0.99977
	30	18.86	0.0187	0.96834	19.50	0.0022	0.99903
	40	25.50	0.0232	0.94973	27.03	0.0014	0.99975
RK	20	9.10	0.0483	0.96725	9.37	0.0106	0.99998
	30	10.53	0.0680	0.93723	10.81	0.0131	0.99998
	40	10.48	0.0933	0.89362	10.84	0.0112	0.99986
WS	20	12.29	0.0217	0.96359	12.99	0.0028	0.99998
	30	15.23	0.0292	0.97107	15.94	0.0031	0.99960
	40	17.11	0.0271	0.92606	18.07	0.0024	0.99990
CTS	20	11.26	0.0270	0.95289	11.80	0.0040	0.99996
	30	13.37	0.0456	0.97709	13.72	0.0071	0.99992
	40	13.40	0.0480	0.91751	13.97	0.0054	0.99992
CS	20	11.31	0.0240	0.96118	11.82	0.0038	0.99992
	30	14.25	0.0355	0.96563	14.87	0.0039	0.99970
	40	16.28	0.0288	0.92023	17.28	0.0024	0.99981
RS	20	10.95	0.0332	0.94922	11.39	0.0055	0.99997
	30	12.87	0.0441	0.97592	13.23	0.0068	0.99981
	40	13.80	0.0406	0.93136	14.43	0.0045	0.99990

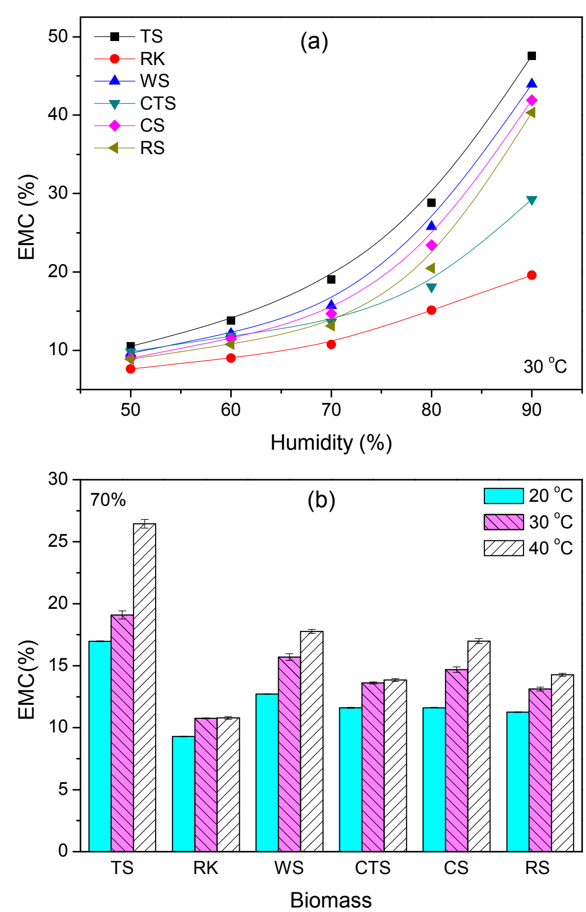
TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw.

increased rapidly above 70% humidity. Tobacco stem had the highest EMC while rice husk had the lowest from 50% to 90% humidity. The EMC of tobacco stem was about 10.5% at 50% humidity, then rose to 47.6% at 90% humidity. The EMC of rice husk increased from 7.6% at 50% humidity to 19.6% at 90% humidity. Cotton stalk had higher EMC than wheat straw, corn stalk and rice straw at 50% humidity while EMC of these three biomass samples became higher than that of cotton stalk at the humidity of 60%, 70% and 80%. Rice straw had lower EMC at 50%–70% humidity while its EMC was much higher than cotton stalk at 80%–90% humidity. At higher humidity, wheat straw had the highest EMC, followed by corn stalk, rice straw and cotton stalk.

The EMC data of biomass plotted against humidity followed a sigmoidal curve, typical for most agricultural products (Karunanithy et al., 2013a; Nilsson et al., 2005). The monomolecular layer of moisture sorption plays a major role in low humidity environments while the multilayers of water molecules are much more important at high humidity (Rouquerol, Rouquerol, Llewellyn, Maurin, & Sing, 2013). The monolayer is created by the strong hydrogen bonding of single molecules in biomass. The bonds become weak between multiple layers of water molecules with humidity and the fine capillaries become full of water molecules in high humidity. The condensation of free water in coarse capillaries results in higher EMC in higher humidity environments. The EMC of different biomass were different at the same humidity, probably because some biomass contains more hydrophilic functional groups and fewer hydrophobic groups than others. It may be that the inherent properties of the biomass source determine the EMC of biomass under the same environmental conditions.

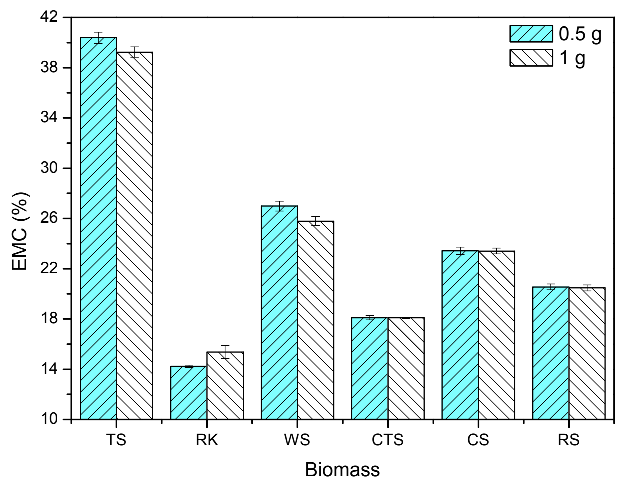
3.3.2. EMC of biomass at different temperature

The EMC of each biomass was higher than the q_e obtained by the pseudo-first order model and lower than q_e calculated by pseudo-second order model (Table 2 and Fig. 6(b)). However, the difference between EMC of each biomass sample from the



TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw

Fig. 6 – Effects of humidity (a) and temperature (b) on EMC of biomass.



TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw

Fig. 7 – EMC of biomass with different sample mass at 80% humidity and 30 °C.

experiment and its fitted value was <5%. The EMC of each biomass increased with the increasing temperature from 20 °C to 40 °C at 70% humidity in Fig. 6b. Except for the EMC of cotton stalk and rice husk at 30 °C and 40 °C, the effect of temperature on EMC of each biomass was significantly different. The change of EMC in tobacco stem from 30 °C to 40 °C was much higher than that from 20 °C to 30 °C which is contrary to the trend found for other biomass samples. Hence, the higher temperature had relatively reduced impact on the EMC of biomass with lower hygroscopicity. The high temperature generated, made the biomass particle swell, and the biomass with higher hygroscopicity absorbed more moisture.

3.3.3. *EMC of biomass with different sample mass*

The effect of sample mass on EMC of biomass is shown in Fig. 7. Except for rice husk, the EMC of tobacco stem and wheat straw decreased with the increasing sample mass, and had almost no influence on the EMC of cotton stalk, corn straw and rice straw. There was an 8.04% increase in EMC of rice husk, and EMC of tobacco stem and wheat straw fell by 2.81% and 4.44% respectively. Tobacco stem also had the highest EMC, followed by wheat straw, corn straw, rice straw, cotton stalk and rice husk at 80% humidity and 30 °C when the sample mass was reduced by half. For small samples it was easy for each particle to absorb moisture quickly from the environment. Hence, a cohesive force was formed within the wetted biomass with higher hygroscopicity which absorbed much moisture and reached equilibrium. More biomass in the same weighing bottle increases its thickness which makes it difficult to form strong cohesive force. Tobacco stem was observed to bond together, while rice husk loosened and gathered at the lowest point in the inclined bottle as it was vibrated. This confirmed that a cohesive force existed in the biomass samples with higher hygroscopicity.

3.3.4. *Isotherms fitting*

The R^2 values fitted by modified Henderson and modified Chung-Pfost models were all negative, and the models were not suitable for fitting EMCs of the biomass samples. The modified Halsey and modified Oswin models successfully fitted the EMC data for biomass. Their fitting parameters are presented in Table 3. The modified Halsey and modified Oswin models showed a random distribution of residuals confirming that the models can be used to fit EMC of the biomass.

The modified Halsey model was found to provide a better fit to the EMC of each biomass, as it had the higher R^2 and F values and the lower values for RSS, RMSE, and MRE than the modified Oswin model. The biomass samples used in this study used the same EMC fitting model as those used for switchgrass and prairie cord grass by Karunanithy et al. (2013b). The EMC of biomass at different humidity and temperatures within the experiment ranges can be calculated using the fitted constants of the modified Halsey model.

3.4. *Sensitivity analysis*

3.4.1. *Effect of external conditions*

A sensitivity analysis between EMC of biomass and experiment parameters is shown in Table 4. The R^2 (0.5925) indicated that there was a multiple correlation relationship between the

Table 3 – Fitted isotherm parameters for biomass.

Biomass	Model	Constants			Statistical parameters				
		A	B	C	R^2	RSS	RMSE	MRE	F
TS	Modified Halsey	1.566	0.030	1.170	0.963	5.707	1.902	0.052	434
	Modified Oswin	3.248	0.260	1.410	0.949	7.835	2.612	0.059	316
RK	Modified Halsey	2.399	0.010	1.572	0.900	1.999	0.666	0.053	342
	Modified Oswin	5.513	0.048	1.905	0.878	2.433	0.811	0.059	281
WS	Modified Halsey	1.436	0.016	1.058	0.955	4.397	1.466	0.060	369
	Modified Oswin	4.458	0.129	1.270	0.945	5.392	1.797	0.067	301
CTS	Modified Halsey	3.357	0.014	1.849	0.895	2.518	0.839	0.046	426
	Modified Oswin	7.045	0.077	2.246	0.881	2.877	0.959	0.049	373
CS	Modified Halsey	1.403	0.019	1.110	0.963	2.973	0.991	0.052	470
	Modified Oswin	3.742	0.143	1.336	0.957	3.440	1.147	0.057	406
RS	Modified Halsey	1.829	0.013	1.248	0.931	3.407	1.136	0.061	326
	Modified Oswin	5.204	0.086	1.505	0.914	4.262	1.421	0.067	261

TS-tobacco stem, RK-rice husk, WS-wheat straw, CTS-cotton stalk, CS-corn straw, RS- rice straw.

Table 4 – Sensitivity analysis results of experiment parameters.

Parameters (x_i)	Sensitivity indexes	Sensitivity sequence
Humidity	0.7699	1
Temperature	0.1108	2
Sample mass	0.0093	3

Multiple correlation coefficient: $R^2 = 0.5925$.

Table 5 – Sensitivity indexes of physicochemical properties.

Humidity/%	True density	Bulk density	Porosity	PA1	PA2	R^2
50	5.3589	−36.8423	−33.5741	−0.3538	0.9458	0.9864
60	2.9618	−10.2766	−8.4098	−0.3406	1.0190	0.9996
70	−0.1875	25.9928	25.8739	−0.2422	1.2411	0.9943
80	−3.9278	70.4397	68.1771	−0.0888	1.7607	0.9957
90	−3.1088	54.9846	53.4218	0.2347	1.0491	0.9969

PA1: the peak area in the region of 3000–2800 cm^{-1}, PA2: the peak area in the region of 3750–3000 cm^{-1}.

EMC and experimental parameters. Results showed that humidity had the greatest influence on the EMC of biomass, followed by temperature and sample mass. The humidity had a greater impact on the EMC of biomass than temperature. This may be due to the higher hygroscopicity of biomass at 80–90% humidity.

3.4.2. *Effect of physicochemical properties on biomass EMC*

The sensitivity indexes between EMC of biomass and physicochemical properties at different humidity are given in Table 5. The higher R^2 indicates the better multiple correlation between EMC and physicochemical properties. Results showed that the OH group in the region of 3750–3000 cm^{-1} was correlated with hygroscopicity at different humidity. The very high sensitivity indexes indicated that the porosity and bulk density had a great influence on EMC of biomass. True density was beneficial to moisture sorption of biomass at 50–60% humidity, while it was not conducive to moisture sorption at 70–90% humidity. The porosity and bulk density had the opposite effect. The EMC of biomass was negatively correlated with the alkyl groups in the region of 3000–2800 cm^{-1} at 60–80% humidity, while it was positively correlated at 90% humidity. It could be that the 90% humidity had a great impact on EMC of biomass.

4. Conclusions

The moisture sorption process of biomass with time can be broadly divided into two phases, including rapid adsorption at first, then slow adsorption. A pseudo-second order model better fits the moisture sorption process of biomass than a pseudo-first order model. The initial 100 min of sorption process was critical to the storage and processing of biomass, as the biomass absorbed moisture at the highest rate. EMC of biomass was within 7.63%–47.56% in this study. EMC of biomass increased with the increase of humidity and temperature. The modified Halsey model is recommended as the best effective predictors of EMC for biomass used in this study. EMC of biomass can be estimated by the constants of the modified Halsey model within humidity and temperature ranges. The inherent characteristics (porosity and bulk density) of biomass have a great influence on EMC, and humidity can play an important role in moisture sorption of biomass. Other physicochemical properties of biomass may also have impact on its hygroscopicity, and further research should focus on these physicochemical characteristics.

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