Food Chemistry 116 (2009) 939–946

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Sorption isotherm of corn distillers dried grains with solubles (DDGS) and its prediction using chemical composition

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ARTICLE INFO

Article history:
Received 5 September 2008
Received in revised form 11 March 2009
Accepted 12 March 2009

Keywords:
Corn ethanol
Distillers grains with solubles (DDGS)
Heat of sorption
Moisture sorption isotherm

ABSTRACT

Corn distillers dried grains with solubles (DDGS) has high feed value due to its nutritive contents. The ratio of wet distillers grains (WDG) and condensed distillers solubles (CDS) added during the production process determines the chemical composition of DDGS. Effect of changing this ratio on water sorption behaviour of DDGS, at different temperature, was studied. Five mathematical models were evaluated to explain the sorption behaviour of DDGS. Prediction of sorption isotherm from chemical composition using a four-component model was also investigated. DDGS followed a BET Type III isotherm with higher equilibrium moisture content at increasing relative humidity. Difference in the sorption isotherm curves of DDGS samples reduced as equilibrium relative humidity increased. Equilibrium moisture content of DDGS samples reduced with lowering of CDS quantity added during production process. Modified Halsey equation was found suitable for mathematically explaining the sorption behaviour of DDGS. Binding energy of water molecule with DDGS increased with lowering of CDS level. Sorption behaviour of DDGS can be predicted from the chemical composition of protein, sugar, minerals, starch, fibre and glycerol. Increase in CDS level increased the percent relative deviation of predicted values calculated using the modified four-component model and might be due to the interaction between the chemical compounds present in the samples.

1. Introduction

Processing of ethanol from corn is mainly classified into three types namely dry grinding, wet milling and dry milling processes. In US, the dry grinding process is commonly used to produce ethanol from corn. This process is used in about 82% of fuel ethanol production plants (RFA, 2007). In 2006, a record 12 million tonnes of DDGS was produced in US (RFA, 2007). Production of ethanol by the dry grinding process results in distillers dried grains with solubles (DDGS); the primary coproduct. DDGS adds to the profitability of corn ethanol production since one-third of every gram of corn converted to ethanol produces DDGS. DDGS is sold primarily as a feed ingredient due to the presence of high nutritive components such as protein, fat, minerals, vitamins and starch (Belyea, Rausch, & Tumbleson, 2004).

DDGS is obtained from the non-fermentable residue of the corn to ethanol production process (wet distillers grain – WDG and condensed distillers solubles – CDS). CDS is obtained by increasing the solids content of thin stillage (from about 5–10% to 35–40%) using evaporators. After removing excess water from WDG by centrifugation, it is mixed with CDS and dried into a granular bulk in rotary drum dryers. For storage stability and long shelf-life, DDGS are usually dried to moisture of about 10–13% (wet basis). Process and operation parameters during drying, and moisture content of the final product will influence the physical characteristics and chemical composition which will in turn affect the quality and shelf-life of DDGS. The process parameters are primarily the amounts of WDG and CDS blended and how the blended feedstocks are dried to obtain DDGS – the final product. Variability in chemical composition during production and change in quality during transportation and storage have been found to impact the market value of DDGS (Belyea et al., 2004).

Moisture sorption isotherms are a useful tool for understanding the moisture relationship of a material and consequently its stability problems. Moisture sorption isotherms for bulk solids describe the equilibrium relationship between the moisture content and the relative humidity (RH) of the surrounding environment. Knowledge of the sorption isotherm of granular bulk solids of biological origin is important for transportation to longer distances and to know about moisture changes during storage. (Czepirski, Komorowska-Czepirska, & Szymonska, 2002). The isosteric heat of sorption is needed to provide information about the state of water present in DDGS and its dependence on temperature. Sorption isotherm will also give information about the mechanism behind interactions between components and their interaction with water in equilibrating to final moisture content. During transportation DDGS is exposed to various temperature

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doi:10.1016/j.foodchem.2009.03.050

and humidity environments. DDGS, being highly hygroscopic, has the tendency to cake and sorption isotherm can be used to predict the caking behaviour (Mathlouthi & Roge, 2003; Saragoni, Aguilera, & Bouchon, 2007). Caking and liquid bridging affects flowability and from an industry perspective, is one of the major hurdles in marketing of DDGS. In US, DDGS is primarily transported by rail from the Midwest (where majority of ethanol plants are located) to feedlots in the Southeast and Southwest, and transported to the coast for export via barges. For example, because of poor flowability of DDGS in hopper cars (caused by caking and bridging), two Class I railroad carriers have announced that they will not permit railroad-owned hopper cars to be used to haul DDGS (Ginder, 2007). Also, a third Class I carrier does not permit their cars to be used for hauling DDGS, even though the carrier did not make this explicit statement in its tariff (Ginder, 2007). Therefore, knowledge of the relationship between equilibrium moisture content (EMC) and relative humidity is important in establishing the critical moisture levels for DDGS at environmental conditions (air temperature and relative humidity) that may be encountered during their storage and transportation.

Several empirical models have been used to predict the sorption behaviour of hygroscopic materials which are either based on theories of sorption mechanism or purely empirical or semi-empirical. Ganesan, Rosentrater, and Muthukumarappan (2007) developed a new empirical model (GRM model), for prediction of isotherm behaviour of DDGS, by including the condensed distillers solubles content in the relationship between RH and EMC. Existing models are used to explain the sorption behaviour of various materials based on degree of fitting to actual data and the physical meaning of the model. However, the parameters of these models only account for physical changes in these materials. Finding a universal empirical model for the prediction of sorption behaviour of DDGS may not be applicable due to the physical and chemical variability of DDGS from different source and by the lack of uniformity in production process parameters across the industry.

Adsorption or desorption of moisture on exposure to humid environments is a complex phenomenon and it depends on carbohydrate, sugar, protein, fibre and mineral contents (Chen, 2000). Changes due to solubilisation and plasticisation of these chemical compounds affect the bulk properties of granular materials (Moreya & Peleg, 1981). Extensive studies on the influence of the chemical composition on moisture sorption behaviour have been documented (Iglesias, Chirife, & Boquet, 1980; Roman-Gutierrez, Mabille, Guilbert, & Cuq, 2003). Labuza (1968) suggested that water absorbed by any product may be derived by the weight percentage of each component times the amount it would absorb alone without considering the interaction between the components. Crapiste and Rotstein (1982) developed a four-component prediction model based on protein, sugars, fibre, starch and mineral contents, and the sorption behaviour of peas, white rice and beans were predicted reasonably well from the water chemical potential of the individual chemical components. The same method was successfully used to predict the sorption isotherm of corn (Ng, Morey, Wilcke, Meronuck, & Lang, 1995).

Ganesan, Muthukumarappan, and Rosentrater (2008) found that the sorption capacity of DDGS, at high RH (60–90%), increased with increase in temperature. It was similar to food material with high sugar content and followed Type III isotherm. Chemical composition, agglomeration pattern and particle size distribution of DDGS depends on the mass ratio of WDG and CDS blend, drying temperature and recycling pattern during the production process. The method of preparing DDGS in lab scale, as used by Ganesan et al. (2007, 2008), did not emulate the physical and chemical changes due to the mixing of WDG and CDS in industrial scale rotary dryers. This process inherently defines the bulk physical characteristics of DDGS that will affect its sorption behaviour. During transportation and storage, DDGS may also be exposed to low or high RH conditions or high RH fluctuating conditions which were not covered in the study by Ganesan et al. (2007, 2008).

The objectives of this study were to: (1) study the effects of temperature (10–40 °C) and processing conditions on the moisture sorption behaviour of DDGS, (2) fit an appropriate empirical equation to the sorption behaviour data, (3) quantify the isosteric heat of sorption of DDGS and (4) predict the EMC–ERH relationship of DDGS from its chemical composition.

2. Materials and methods

2.1. Production of DDGS samples

The DDGS samples were procured from The Andersons Clymers Ethanol LLC, Clymers, IN, USA. Four samples of DDGS were produced using four different process conditions by adjusting the total input quantity of CDS in two dryers connected in series (dryers 1 and 2) without changing the WDG input in dryer 1. In order to improve the efficiency of drying, about half of the hot product streams of DDGS exiting from dryers 1 and 2 were recycled back into both dryers, respectively. The base case process conditions was the plant's regular operating conditions, which blends about 212 l/min of CDS with WDG (~2500 l/min) and hot recycled DDGS added into dryers 1 and 2 at 60% of the maximum screw conveyor speed. The production process of DDGS was explained in detail by Ileleji, Prakash, Stroshine, and Clementson (2007). In this study, the four process conditions used to produce four different DDGS samples of varying chemical composition is described below in the order that they were produced:

1. 212 l/min CDS (7.4% of total inflow by volume) and hot recycled DDGS added at a rate of 60% of maximum recycle conveyor speed (Batch 1).
2. 98.4 l/min CDS (3.7% of total inflow by volume) and hot recycled DDGS added at a rate of 60% of maximum recycle conveyor speed (Batch 2).
3. 0 l/min CDS (0% of total inflow) and 60% of maximum recycle conveyor speed (Batch 3).
4. 98.4 l/min CDS (3.7% of total inflow by volume) and no recycled DDGS added (0% recycle) (Batch 4).

DDGS was produced using the process conditions for Batch 1 until about 9 tonnes of samples were produced. The process parameters were then changed to the next conditions for Batch 2 and the operating parameters of rotary dryer changed in increments to maintain safe conditions. At each set conditions, the dryers were allowed to run for 15 min to ensure steady-state and stability. After drying, DDGS was cooled using a rotary drum ambient cooler and conveyed to pile on a concrete pad where it was left to cool further for 3 days to ambient temperature conditions. During DDGS production, samples collected at each process conditions were transported to Purdue University, West Lafayette, IN, USA in plastic containers where they were cooled down in the lab before further analysis. About 40 g of the sub-samples from each of the DDGS batches were sent to a commercial analytical laboratory (Experiment Station Chemical labs, University of Missouri-Coulmbia, Columbia, MO) and analysed for crude protein, crude fat, crude fibre, minerals and ash (proximate analysis). Additionally, acid detergent fibre and neutral detergent fibre that are important for determining total digestible nutrients in feed were determined. The amount of total reducing sugars and glycerol were also determined as they have an effect on caking properties. The AOAC (2000) Official Methods for proximate analysis was used to analyse for these components.

2.2. DDGS sample preparation for sorption studies

In this part of the study ground samples (1 mm size) were used for the experiments to overcome any variability due to particle size. The NFTA method (NFTA 2.2.2.5) of moisture determination, using 2 g of ground samples dried at 105 °C for 3 h which eliminates the particle size variation, was used for this study. Samples of DDGS for EMC measurements were drawn from the bulk after proper mixing because DDGS particles segregate during handling (Ileleji et al., 2007). Experiments were conducted within the moisture range of 6–25% (dry basis). Since the initial moisture content of samples from all batches were not equal and to treat all samples in similar manner, DDGS was rewetted to higher moisture level and then dried down to the required final moisture content (Ileleji, Wilcke, & Morey, 2003). To do this, samples were all rewetted to about 28% moisture (dry basis) by adding a predetermined amount of de-ionised water and then dried appropriately to the desired moisture level. To rewet the samples, water was sprayed on the samples using a handheld sprayer and mixed in a rotary tumbler for 1 h. To avoid agglomeration of DDGS at higher moisture levels, water was added in increments. After rewetting, the samples were stored at 4 °C for 72 h. Drying to desired moisture level was carried out on the lab bench in ambient conditions (22–25 °C) by spreading the samples in thin layer without any additional heat or airflow (drying time: 3–5 h).

2.3. EMC measurements

The rapid method suggested by Chen and Morey (1989) was used to measure the ERH of DDGS samples using temperature and relative humidity sensors (HMP 235, Vaisala Inc., Woburn, MA). The sensors were calibrated by the manufacturer and operated in the relative humidity range of 0–100% and temperature range of −40 to 180 °C. Experimentation was carried out at temperatures of 10, 20, 25, 30 and 40 °C. About 70 g of samples was placed in plastic sample containers and the containers were sealed with rubber caps leaving some headspace above the DDGS samples. Before sealing the container, the temperature and RH sensors were inserted through the rubber caps. The sample cups were then placed in a temperature controlled chamber thus making it possible to conduct experiments at different temperature levels. The sensors were connected to a data logger (2625 A Hydra Data Logger, Fluke Corp., Everett, WA) that recorded the RH and temperature of air in the headspace every 5 min. Temperature fluctuation inside the chamber was within ±0.5 °C limits. Temperature and RH inside the chamber was monitored using a HOBO temperature/RH data logger (Onset Computer Corporation, Bourne, MA). In the temperature controlled chamber, DDGS present in the sealed cup equilibrated to the temperature of the chamber. The temperature of the air in the headspace above the sample that was used as an indication of the temperature of DDGS was found to be within ±1 °C of the chamber temperature. Equilibrium conditions were deemed to have occurred when the variation in temperature and RH of head space air was within ±0.05% for at least 3 h. At this time, the measured temperature and RH were considered the equilibrium temperature and equilibrium RH at the set conditions (Chen & Morey, 1989). The chamber temperature was then increased to next level. To avoid condensation of moisture in the sensor, experiments were started at the lower temperature (10 °C) and increased to higher temperatures. After reaching equilibrium conditions, ~2 g of samples were removed and used to determine the equilibrium moisture content using the NFTA 2.2.2.5 method. Experiments were conducted in triplicates in order to conduct statistical analysis of the data. A randomized block design was used to assign sensors to the sample jars, so that the same sensor was not repeated for the same sample within replications at a particular moisture content, thus randomizing any biased errors in our measurements.

2.4. Sorption isotherm models

For prediction of the storage stability of products during storage, the sorption behaviour can be described mathematically. Equations used to explain the EMC–ERH relationship of corn, the feedstock of DDGS, were used in fitting the data (ASABE Standards, 2007). The GRM model, developed for predicting the EMC–ERH relationship of DDGS, was also tested. The equations are listed below:

Modified Henderson (MH) model : (1)

$$M = \left[\frac{\ln(1-\mathrm{RH})}{-A(T+B)}\right]^{\frac{1}{C}}$$

Modified Chung-Pfost (MCP) model : (2)

$$M = \left(\frac{-1}{C}\right)\ln\left[\frac{\ln(\mathrm{RH})(T+B)}{-A}\right]$$

Modified Oswin (MO) model : (3)

$$M = (A+BT)\left[\frac{\mathrm{RH}}{1-\mathrm{RH}}\right]^{\frac{1}{C}}$$

Modified Halsey (MHa) model : (4)

$$M = \left[\frac{-\exp(A+BT)}{\ln(\mathrm{RH})}\right]^{\frac{1}{C}}$$

Ganesan—Rosentrater—Muthukumarappan (*GRM*) model : (5)

$$M = \left[M_0 + \frac{tS}{At+BS} + CT\right]^{D*\mathrm{RH}}$$

where RH is the relative humidity (decimals); M is the moisture content (% dry basis); M_0 is the initial moisture content (% dry basis); T is the temperature (°C); S is the solubles content (% dry basis); A, B, C are the constants for the particular equation; t is the time (h).

Equation parameters were estimated by nonlinear regression using SAS v 9.1 (SAS Institute, Cary, NC).

2.5. Isosteric heat of sorption

The net isosteric heat of sorption indicates the binding energy of water molecules with the material and it can be calculated from sorption isotherms measured at different temperature (Ruckold, Isengard, Hanss, & Grobecker, 2003). The isosteric heat of sorption (q_{st}) values was calculated using the following equation derived from Clausius–Clapeyron equation:

$$q_{\mathrm{st}} = -R\frac{\partial \ln(\mathrm{ERH})}{\partial(1/T)} \quad (6)$$

where q_{st} is the net isosteric heat of sorption (kJ/mol), R is the universal gas constant (kJ/mol K), ERH is the equilibrium relative humidity (decimals) and T is the absolute temperature (K). The net isosteric heat of sorption value is calculated, at a specific moisture content, by plotting the ln(ERH) against $1/T$ and determining the slope of this plot which equals $-q_{\mathrm{st}}/R$.

2.6. Prediction of EMC from chemical composition

Crapiste and Rotstein (1982) found that EMC of each component in a chemical composition can be calculated based on the equality of water chemical potential between the component and the surrounding air described by a four-component (FC) model. They suggested that total moisture content at equilibrium will be equal to the weighted sum of components EMCs given by the following relationship for prediction at 25 °C:

$$X_t = X_{\mathrm{v}} + W_{\mathrm{f}}X_{\mathrm{f}} + W_{\mathrm{s}}X_{\mathrm{s}} + W_{\mathrm{p}}X_{\mathrm{p}} \tag{7}$$

where X is the equilibrium moisture content, dry basis (decimal); W is the weight fraction of component, dry basis (decimal); t is the total (combined effect of all components); v is the vacuole (sugars and minerals); f is the fibre (cellulose); s is the starch; p is the protein.

The governing equations for calculation of individual components were adapted from Ng et al. (1995). The predicted EMC value was compared with the actual values from the experiments carried out at 25 °C. The weighted chemical fractions of DDGS used were crude protein, fibre, starch, residual sugars and minerals (Table 1). Glycerol is an important plasticizing component present in DDGS which can affect the bulk properties. The four-component model was modified (MFC) by including the water chemical potential of glycerol to assess the influence of this component in prediction (Eq. (8))

$$X_t = X_{\mathrm{v}} + W_{\mathrm{f}}X_{\mathrm{f}} + W_{\mathrm{s}}X_{\mathrm{s}} + W_{\mathrm{p}}X_{\mathrm{p}} + W_{\mathrm{g}}X_{\mathrm{g}} \tag{8}$$

where g is the glycerol, dry basis (decimal).

2.7. Data analysis

Statistical analysis was conducted using SAS v 9.1 (SAS Institute, Cary, NC). Nonlinear regression to fit experimental data was carried out using PROC NLIN procedure by Gauss–Newton method. *F*-statistic, Mean relative percent deviation (P), standard error (S.E) and residual plots were used to compare the performance of selected models. Mean relative percent deviation and standard error were calculated using the following equations:

$$P = \frac{100}{N} \times \sum \frac{|Y - Y_{\mathrm{p}}|}{Y} \tag{9}$$

$$\mathrm{S.E} = \sqrt{\frac{\sum (Y - Y_{\mathrm{p}})^2}{\mathrm{df}}} \tag{10}$$

where Y is the measured value, Y_{p} is the predicted value, N is the number of data points, df is the degrees of freedom.

3. Results and discussion

3.1. Sorption behaviour of DDGS

The composition of WDG and CDS are substantially different (Kim et al., 2008) and the ratio with which they are mixed during the production process significantly affects the chemical composition of final product (Table 1). Crude protein, acid detergent fibre (ADF) and neutral detergent fibre (NDF) of DDGS increased whilst fat, ash, sugars and glycerol content decreased with decrease in CDS level.

Table 1
Chemical composition of DDGS used for the EMC experiments.

Chemical Composition (% dry basis)	Batch 1	Batch 2	Batch 3	Batch 4
Crude protein	$29.67(0.15)^{a}$	$31.15(0.03)^{b}$	$34.40(0.85)^{c}$	$32.40(0.52)^{b}$
Crude fat	$12.00(0.18)^{a}$	$10.09(0.21)^{b}$	$8.26(0.22)^{c}$	$10.40(0.14)^{b}$
Crude fibre	$5.86(0.07)^{a}$	$7.26(0.21)^{b}$	$8.49(0.31)^{c}$	$6.91(0.31)^{b}$
Minerals				
Calcium (ppm)	$519.3(286.18)^{a}$	$208.7(24.70)^{ab}$	$127.3(7.37)^{b}$	$166.7(3.51)^{ab}$
Phosphorous	$0.78(0.03)^{a}$	$0.65(0.01)^{b}$	$0.47(0.01)^{c}$	$0.62(0.01)^{b}$
Sodium (ppm)	$1142.0(56.43)^{a}$	$845.0(9.54)^{b}$	$714.3(8.50)^{c}$	$411.6(11.24)^{d}$
Sulphur	$0.66(0.03)^{a}$	$0.60(0.01)^{b}$	$0.54(0.01)^{b}$	$0.60(0.01)^{c}$
Ash	$4.00(0.15)^{a}$	$3.12(0.05)^{b}$	$2.04(0.00)^{c}$	$2.97(0.02)^{b}$
Total reducing sugars	$5.98(0.30)^{a}$	$4.30(0.28)^{b}$	$2.34(0.13)^{c}$	$4.27(0.06)^{b}$
Glycerol	$8.45(0.30)^{a}$	$6.51(0.45)^{b}$	$3.28(0.07)^{c}$	$6.73(0.10)^{b}$
Acid detergent fibre	$11.17(0.30)^{a}$	$13.51(0.73)^{b}$	$17.00(1.11)^{c}$	$12.29(0.53)^{a}$
Neutral detergent fibre	$36.85(0.69)^{a}$	$43.26(0.64)^{b}$	$47.34(2.49)^{c}$	$39.76(2.23)^{a}$

$n = 3$; Values in parenthesis are standard deviation.
The same superscript letter within the same row indicates no significant difference $p \geqslant 0.05$.

Water sorption behaviour of DDGS at different temperatures (10, 20, 25, 30 and 40 °C) is presented in Fig. 1. The sorption isotherm of DDGS followed BET Type III isotherm with an asymptotic growth at high RH levels which is typical for any product containing sugar and glycerol (Mathlouthi & Roge, 2003). A similar trend has been reported for DDGS at various CDS levels (Ganesan et al., 2008). This indicates that moisture exists as free molecule in DDGS and therefore can lead to mold growth during storage (Debnath, Hemavathy, & Bhat, 2002). It was also noted that moisture sorption of DDGS increased with increase in temperature. For corn, the feedstock from which corn DDGS is made, temperature was negatively correlated with EMC (Chen, 2000). However, in our study, temperature was positively correlated with EMC for all the batches of DDGS. Due to this, at higher ERH (approximately >75%), the difference between isotherms generated at different temperatures decreased. This may be due to the high protein content (Sopade, Ajisegiri, & Badau, 1992), especially when protein in DDGS is concentrated three folds after removal of starch during fermentation. Considerable increase in EMC was noted after 60% RH and the rise was steep above 70% RH. For storage stability of DDGS, optimum conditions with EMC <15% corresponding to <50–60% RH in the sorption isotherm can be considered safe in the temperature range of 20–30 °C.

Fig. 2 shows that condensed distillers solubles (CDS) added during the production of DDGS influenced the sorption behaviour. Affinity for water decreased with decrease in CDS level which is seen in the DDGS samples with no CDS (Batch 3) to DDGS samples with 7.4% by volume of CDS (Batch 1). This may be due to the change in chemical composition of DDGS based on the amounts of CDS added during the production process (Table 1), which were significantly different from Batches 1–3 with decreasing CDS levels from 7.4% by volume to zero. The finding was supported by the results reported by Godbillot, Dole, Joly, Roge, and Mathlouthi (2006) that decrease in glycerol content reduces the EMC, but contradicts the results reported by Pollio, Resnik, and Chirife (1987) that decrease in fat and increase in protein content increases the EMC. This may be due to the higher plasticizing effect of glycerol present in the DDGS. It can also be noted that change in recycle conveyor speed which is indicative of the amount of recycled DDGS put back during drying did not influence the sorption behaviour of DDGS. The crude protein, fat, sugar and glycerol contents were not significantly different for the samples produced with and without recycling (Batches 2 and 4).

Modified Henderson (MH), Modified Chung-Pfost (MCP), Modified Oswin (MO), Modified Halsey (MHa) and Ganesan–Rosentrater–Muthukumarappan (GRM) equations were used to fit the experimental data. The estimated model parameters and the various comparison criteria used for selecting best fit equation are given in Table 2. MH, MO and MHa models gave high *F*-statistic values, p-value <0.001 with low relative percentage deviation and standard error. In comparison, Modified Halsey model gave low percentage deviation (2.63–3.96%) and standard error (0.38–0.55). The GRM model developed by Ganesan et al. (2007) for DDGS with varying CDS levels did not fit the moisture sorption data from our experiments as the model coefficients failed to converge during nonlinear regression process. This is because GRM model does not fit the type of sorption curve for DDGS and hence a poor fit or non-convergence fit was obtained. Some contributing factors might have been the addition of an internal parameter (syrup content) in the model as a variable, and the range of CDS content used in obtaining the empirical data from which the model was devel-

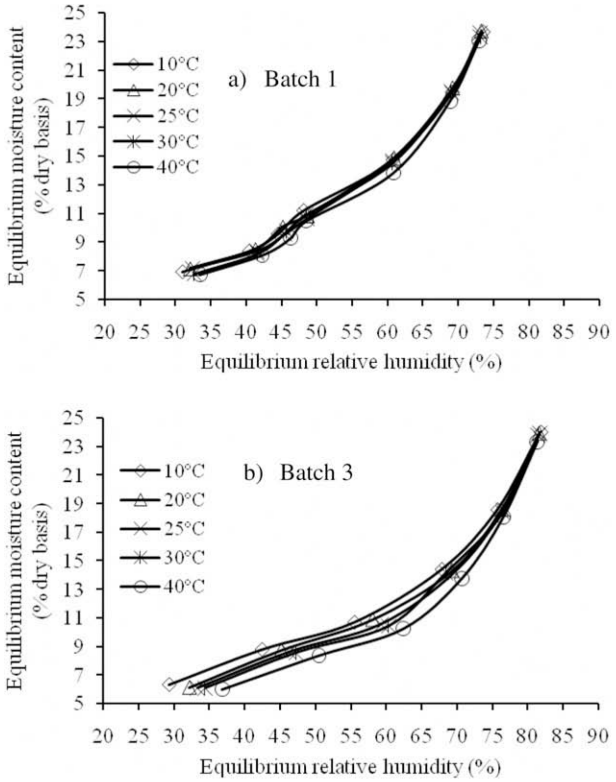

Fig. 1. Moisture sorption isotherm of DDGS for samples of Batches 1–4.

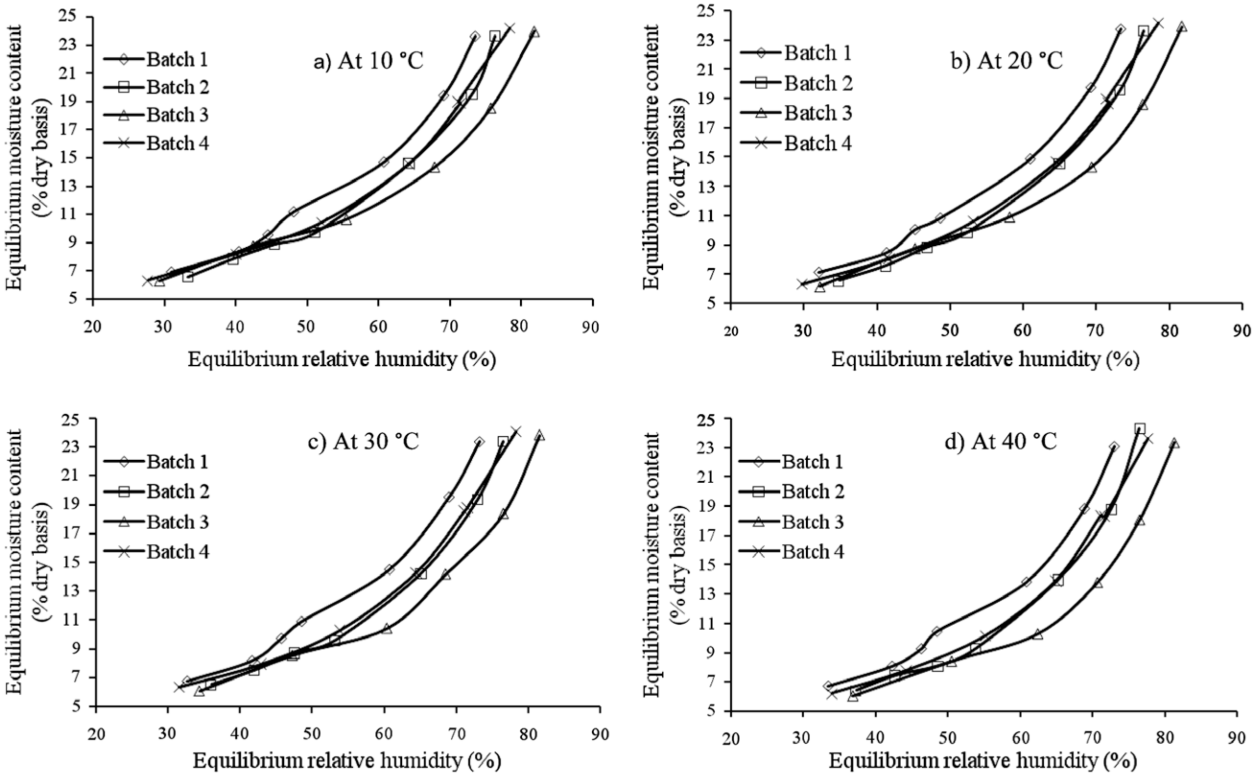

Fig. 2. Effect of chemical composition on sorption isotherm of DDGS at different temperature.

oped. The methodology used by Ganesan et al. (2007) in determining the CDS content is different from the volumetric addition of CDS during DDGS production practiced by commercial fuel ethanol plants. From the five models evaluated, Modified Halsey model was found to predict the sorption behaviour of DDGS better than the other models. This model is being used to predict the sorption

Table 2
Estimated parameters and comparison criteria for select EMC models.

Models	Estimated parameters and comparison criteria						
	A	*B*	*C*	*D*	*F*-statistic	*P* (%)	Standard error
Batch 1							
MH	1×10^{-4}	727.7	0.92	–	4517.46	11.96	0.74
MCP	765.4	415.4	0.08	–	479.80	12.84	1.07
MO	11.37	-14.8×10^{-3}	1.37	–	9566.48	3.44	0.51
MHa	2.17	-1.29×10^{-3}	1.05	–	16718.0	2.65	0.38
GRM	1.02×10^{-4}	-1.7×10^{-4}	−27.59	0.37	420.00	17.02	2.03
FC	–	–	–	–	–	17.37	0.066
MFC	–	–	–	–	–	6.86	0.032
Batch 2							
MH	1.32×10^{-4}	748.1	0.85	–	2553.34	7.40	0.96
MCP	513.1	300.9	0.08	–	347.10	9.80	1.33
MO	9.67	-12.9×10^{-3}	1.31	–	5067.36	5.07	0.68
MHa	1.96	−0.00133	1.03	–	9012.85	3.41	0.51
GRM	8.78×10^{-7}	-3.13×10^{-6}	40800.9	0.25	828.38	12.69	1.43
FC	–	–	–	–	–	13.80	0.050
MFC	–	–	–	–	–	6.54	0.022
Batch 3							
MH	2.48×10^{-4}	309.0	0.97	–	1825.65	8.73	1.11
MCP	293.5	135.5	0.10	–	324.34	9.60	1.40
MO	9.41	-24.9×10^{-3}	1.54	–	4330.21	5.30	0.72
MHa	2.38	-3.23×10^{-3}	1.23	–	7575.12	3.96	0.55
GRM	0.01	0.1	0.48	1.10	287.81	30.63	3.41
FC	–	–	–	–	–	12.55	0.028
MFC	–	–	–	–	–	16.34	0.013
Batch 4							
MH	1.16×10^{-4}	694.7	0.92	–	4064.37	6.30	0.83
MCP	532.6	273.1	0.09	–	379.49	8.91	1.26
MO	10.17	-13.2×10^{-3}	1.44	–	10779.1	3.84	0.51
MHa	2.26	-1.38×10^{-3}	1.14	–	18149.2	2.63	0.39
GRM	9.4×10^{-5}	-2.3×10^{-4}	−6.53	0.37	783.68	13.52	1.61
FC	–	–	–	–	–	16.29	0.061
MFC	–	–	–	–	–	6.04	0.033

behaviour of soybeans (Chen, 2000). But for corn, feedstock of DDGS, modified Chung-Pfost and Modified Henderson models are used to predict the sorption behaviour.

The isosteric heat of sorption calculated at different moisture content is given in Fig. 3. Isosteric heat of sorption values were high at low moisture content and decreased with increase in moisture content. After certain moisture content, the heat of sorption values became negative. This may be due to increase in EMC by endothermic dissolution of sugars at higher temperature (Kaymak-Ertekin & Gedik, 2004). Also, at increasing moisture content, the available sorption sites become occupied and moisture sorption occurs on less active sites giving lower heats of sorption (Iglesias & Chirife, 1976). The difference in chemical composition, by change in CDS added during production process, influenced the isosteric heat of sorption of DDGS. Decrease in CDS quantity added increased the heat of sorption. The isosteric heat of sorption values reached zero at 15%, 17% and 22% (dry basis) moisture contents for the CDS inflow of 212 l/min (7.4% by volume), 106 l/min (3.7% by volume) and 0 l/min, respectively. Negative heat of sorption values has no physical meaning and might be within the error of determination (Kaymak-Ertekin & Gedik, 2004). The magnitude of change due to the difference in percent recycle was not significant (Fig. 2).

3.2. Prediction of sorption from chemical composition

The equation by Crapiste and Rotstein (1982) (Eq. (7)) was used to predict the sorption behaviour of DDGS from its chemical composition. DDGS components protein, starch, fibre, sugar and mineral were used for prediction. Sugars and minerals were combined as the vacuole component (Crapiste & Rotstein, 1982; Ng et al., 1995). Equations used by Ng et al. (1995) were used to calculate the EMC of the components.

Comparison between predicted and actual sorption isotherm at 25 °C is shown in Fig. 4. The percent relative deviation, of the predicted values by four-component model, was higher than 10% for all sample batches of DDGS and ranged from 12.55% to 17.37% and the standard error ranged from 0.028 to 0.66 (Table 2). The difference in predicted and actual EMC values increased with increase in CDS quantity added during the drying process of DDGS. It can be assumed that other than protein, fibre, starch and sugar, the pres-

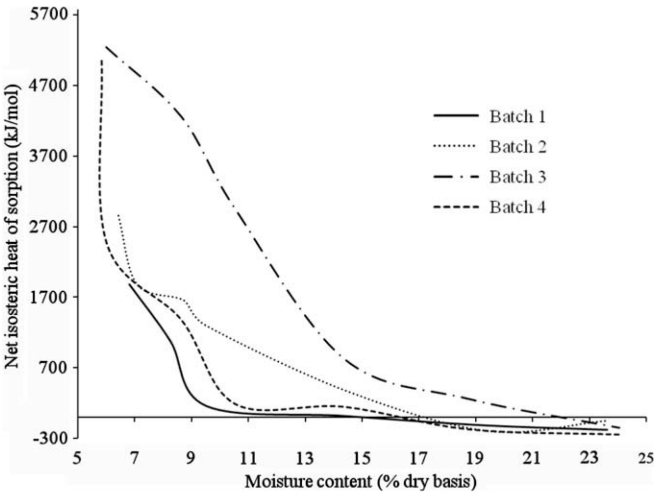

Fig. 3. Net isosteric heat of sorption of DDGS samples.

ence of glycerol, a humectant also influenced the sorption behaviour of DDGS. The amount of glycerol present in DDGS can affect the sorption process and can lead to change in flow properties due to caking. Glycerol is normally produced as a by-product of yeast metabolism during conversion of sugars to ethanol, and the levels of glycerol production increases with increasing stress levels (Hallsworth, 1998). Godbillot et al. (2006) reported that the presence of glycerol changes the sorption process at around 50% RH. Below this RH value, glycerol is less hygroscopic and when the RH increases above 50%, adsorbed water increases with glycerol content (Enrione, Hill, & Mitchell, 2007; Godbillot et al., 2006). The four-component model was therefore modified by including the glycerol content in the prediction (Fig. 4). The percent relative deviation and standard error reduced due to inclusion of glycerol in the prediction equations for Batches 1, 2 and 4. In the case of Batch 3, in which CDS was not added during production and had the lowest glycerol content, the modified four-component model increased the relative deviation. Therefore the four-component model and modified four-component model can be used to predict the sorption behaviour of DDGS produced with and without addition of CDS, respectively.

Though modification of prediction equation improved the performance of model, the difference between predicted and actual value was high at high RH. The deviation might have resulted from the interaction between chemical components present in DDGS. Further modification of the model by including interaction terms may reduce the deviation and error of prediction. It is evident that the prediction of sorption process in the presence of glycerol and its interaction with other components is important to the development of good predictive models describing DDGS sorption behaviour. To understand this effect, studies on the effect of glycerol on sorption behaviour of DDGS is being pursued.

4. Conclusions

The effect of change in process variables on water sorption behaviour of DDGS was studied in the moisture content range 6–25% at five temperature levels (10, 20, 25, 30 and 40 °C). The EMC of DDGS was higher at higher RH and the EMC increased with temperature. CDS added during the production process influenced the sorption behaviour of DDGS and the EMC reduced with reduction in CDS content. The Modified Halsey model suitably predicted the sorption isotherm but the DDGS specific Ganesan–Rosentrater–Muthukumrappan model did not perform well. Net isosteric heat of sorption value ranged from 5245 to −245 kJ/mol with higher values occurring at lower moisture range. Reduction in quantity of CDS added lowered the heat of sorption of DDGS. Change in recycled amount of DDGS during the drying process had an insignificant effect on the sorption behaviour of DDGS at different RH environments. The four-components model used for prediction of EMC from chemical composition performed well for the samples produced with reduced CDS level. Inclusion of water chemical potential of glycerol improved the performance of prediction model. It can be summed up that chemical composition highly influence the water sorption behaviour of DDGS and refinement of prediction models based on chemical composition will help the industry in formulating storage, transportation and processing strategy for DDGS. This would be especially necessary due to the variable chemical composition of DDGS produced in the industry nationwide.

Acknowledgements

The authors express thanks to Indiana State Department of Agriculture (ISDA) and the Agricultural Research Programs of the

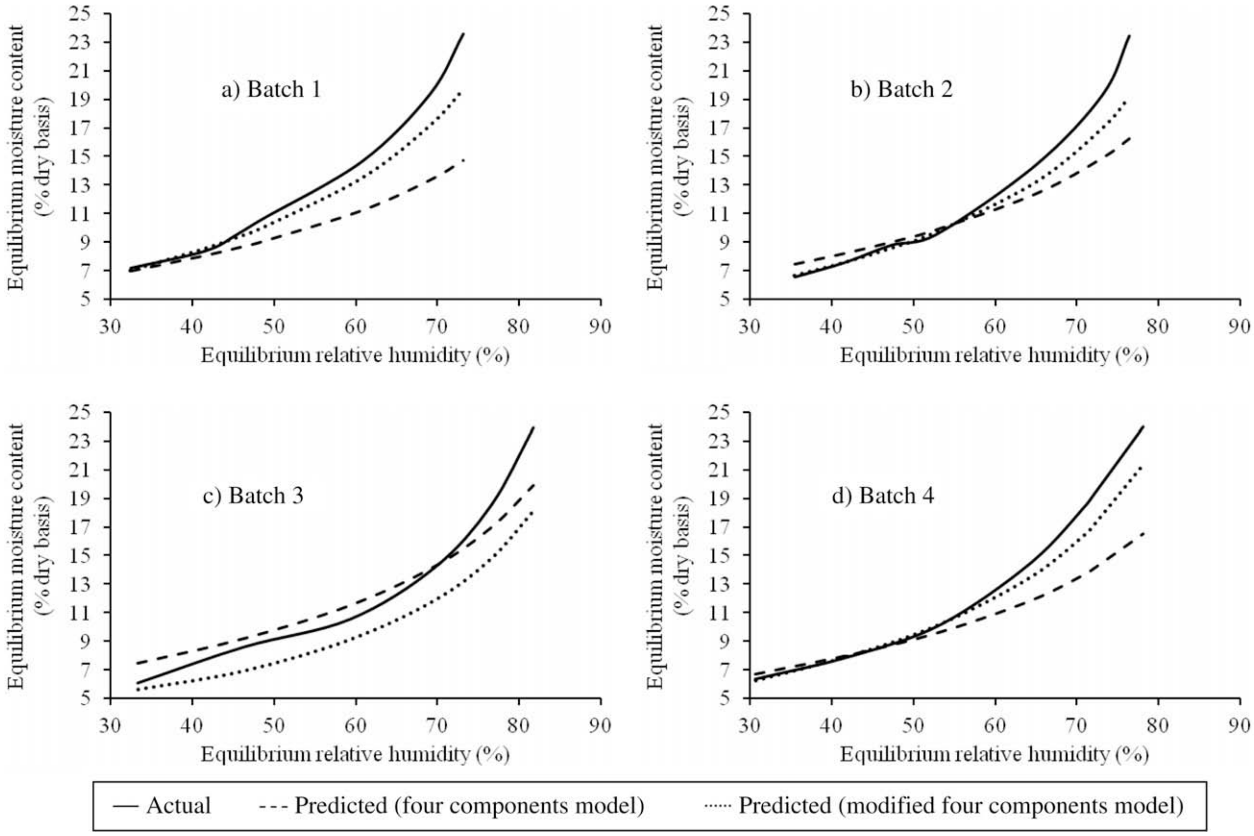

Fig. 4. Predicted moisture sorption isotherm of DDGS using chemical composition.

College of Agriculture, Purdue University, USA for their financial support and to The Andersons Clymers Ethanol LLC, Clymers, IN, USA for their cooperation in using their facility for preparing the DDGS batch samples as well as its donation.

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