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Measurement and Comparison of Glass Transition and Sticky Point Temperatures of Distillers Dried Grains with Solubles (DDGS) with Varying Condensed Distillers Solubles (CDS) and Drying Temperature Levels

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ABSTRACT

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Distillers dried grains with solubles (DDGS) is the main coproduct of the U.S. fuel ethanol industry and has significantly impacted the livestock feed markets in recent years. Particle agglomeration and subsequent flowability problems during storage and transport are often a hindrance, a nuisance, and expensive. This paper aims at characterizing the glass transition (T_g) and sticky point (T_s) temperatures of DDGS samples prepared with varying condensed distillers solubles (CDS) levels (10, 15, and 20%, wb), drying temperatures (100, 200, and 300°C), and moisture contents (0, 10, and 20%, db), and it discusses implications on DDGS flowability behavior. Distillers wet grains were combined with specified levels of CDS and dried in a convection-style laboratory oven to produce DDGS.

Subsequently, predetermined amounts of water were added to the DDGS to achieve desired moisture content levels. To determine T_g (°C), a differential scanning calorimeter was used, whereas T_s (°C) was determined through a novel technique with a rheometer. Results indicated high correlations between observed T_s and observed T_g ($R^2 = 0.87$) data for DDGS samples. Also, the empirical model for predicted $T_g = f$(drying temperature, CDS level, and moisture content) based on the Gordon–Taylor model showed favorable R^2 (0.74). Stickiness of DDGS increased with an increase in moisture content, indicating flow problems resulting from moisture. It was found that drying temperatures and CDS levels each had significant effects on T_g and T_s as well.

Distillers dried grains with solubles (DDGS) is the primary coproduct from the corn-based fuel ethanol industry, which is mainly from dry-grind ethanol production plants across the Midwestern United States. It is commonly used as livestock feed for cattle, swine, and poultry. DDGS typically contains 86–93% (db) dry matter, 26–34% (db) crude protein, 3–13% (db) fat, and essential amino acids such as methionine, leucine, arginine, and threonine (Speihs et al 2002; Rosentrater and Muthukumarappan 2006). There has been enormous growth in the bioethanol industry in the last decade because of strong interest in alternative fuels, and therefore there is now substantial DDGS production. The production of DDGS is projected to have grown to nearly 40 million metric tons during 2013.

Like many agricultural and food materials, DDGS is hygroscopic in nature (i.e., it can absorb moisture from the surrounding atmosphere). Thus, DDGS particles may tend to agglomerate to form solidified masses (i.e., caking) by absorbing water or because of temperature differences. Caking, or hardening, of DDGS leads to difficulties during unloading from rail cars, bins, and other storage vessels, and it can result in economic losses to break up the agglomerates and discharge the storage vessels (Rock and Schwedes 2005). Stickiness in particles (or the caking phenomenon) causes poor flowability in the material and, thus, makes it less efficient to handle during distribution and storage. An understanding of properties affecting stickiness is crucial in defining appropriate processing, handling, and storage conditions for the material (Lazar et al 1956; Downton et al 1982; Wallack and King 1988).

Stickiness is often a problem that can impact both the quality of the product and manufacturing operations, and it can lead to equip-

ment wear and increased costs. Some have attributed it to adhesive and cohesive properties, effects of external factors, or the viscosity and viscoelasticity of the materials (Adhikari et al 2001). The cereal industry, the confectionary industry (because of sucrose or other sugar-based syrups), and the dairy industry (because of frequent caking of milk powders caused by milk proteins) (Hegg et al 1985) face stickiness issues in bulk handling. Some of the key factors that cause agglomeration of food and biological powders are viscosity (Simatos and Blond 1993), for which the governing model is the Williams–Landel–Ferry model (1955), plasticization of water (Adhikari et al 2001), temperature (Roos and Karel 1990), compaction because of load (Teunou et al 1999), and hygroscopic biological molecules such as glucose, fructose, and protein (Netto et al 1998).

Glass Transition Temperature (T_g, °C). Spray-dried or rotary drum dried products such as milk powders and fruit powders are amorphous solids. They are produced by a rapid drying process so that the food molecules do not have much time to align themselves and become crystalline. For DDGS, previous work has reported that the temperature of any typical drying operation ranges from 300 to 1,000°F, and the time taken to produce the dried DDGS is only a few seconds (Bhadra et al 2011a, 2011b). Therefore, like other food and milk powders, DDGS also has a high drying temperature and short drying time and, thus, forms an amorphous solid. The amorphous solid is often referred to as glass, a metastable supercooled liquid, with the typical range of viscosities of about 10^{12} Pa·s (Adhikari et al 2001). When an amorphous solid is heated, it undergoes a second-order phase transition known as the glass transition, in which the glasslike state assumes a more liquid form (rubbery) with lower viscosities of 10^6–10^8 Pa·s. Stickiness, caking, or the agglomeration of the powder are mostly associated with this rubbery phase (Downton et al 1982). The glasslike state will first be converted to a glass-rubbery phase transition state exactly at the glass transition temperature (T_g). After the phase transition period, the molecules will eventually be converted to crystals, whereas further heating of the product at increased temperature will melt the food powder. T_g is characterized by a change in the apparent specific heat capacity. This change takes place endothermically and is easily detected with a differential scanning calorimeter (DSC) (Roos and Karel 1990). T_g is affected by various factors, especially the composition of the material, molecular weight, and presence of plasticizers. Plasticiz-

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ers such as water can lower the T_g (°C) by diffusion of water molecules in the amorphous materials.

Sticky Point Temperature (T_s, °C). Researchers developed a way to measure the sticky point temperature (T_s, °C), aside from the most popular method of measuring T_g, for assessing stickiness in powders. T_s is defined as the given combination of temperature and moisture content at which a mass of powdery material resists movement and no longer flows freely. The moisture content–temperature graph is also known as the stickiness curve. T_s decreases as the moisture content increases, indicating more difficult flow behavior in the powders.

The sticky point temperature measurement developed by Lazar et al (1956) was later used by several other researchers (Downton et al 1982; Wallack and King 1988). In the experimental setup for Lazar et al (1956), a sample in a glass tube was stirred manually. Figure 1 shows the concepts of the sticky region and the sticky point temperature (T_s) curve; more details on the sticky point method, the stickiness curve, the experimental setup, and the procedures can be found in Lazar et al (1956), Papadakis and Bahu (1992), and Wallack and King (1988). However, the traditional setup (Lazar et al 1956) and procedure of measuring T_s were modified several times by several authors (Pasley et al 1995; Hennigs et al 2001; Chegini and Ghobadian 2007). There are peer-reviewed articles comparing T_g with T_s and elaborately describing the phenomenon of stickiness or caking in food powders (Downton et al 1982; Chuy and Labuza 1994; Jaya and Das 2007).

With respect to the stickiness and flowability issues in DDGS with varying condensed distillers solubles (CDS) and moisture content, some work has been done with Carr (1965) and Jenike (1964) shear test properties (Ganesan et al 2007a, 2007b, 2008a, 2008b; Bhadra et al 2009a, 2009b). To date, only Ganesan and Rosentrater (2007) reported that T_g was correlated to stickiness and flowability issues of DDGS. However, this study was performed on a small scale, and more information is required to fully understand and quantify the cause of flowability problems in DDGS. Ganesan and Rosentrater (2007) reported T_g values for traditional DDGS, reduced-fat DDGS, dewaxed DDGS, and distillers dried grains (without solubles), but they did not perform any mathematical modeling for T_g. Also, no experiments were done to investigate T_s for DDGS samples and to correlate the results with DDGS caking problems.

Thus, the main objectives of this study were 1) to evaluate T_g and T_s for DDGS samples prepared under laboratory conditions with varying CDS (10, 15, and 20%, wb), drying temperature (100, 200, and 300°C), and moisture content (0, 10, and 20%, db) levels; 2) to develop an overall model based on varying drying temperature, CDS, and moisture content levels for predicting T_g (based on the Gordon–Taylor [1952] equation) and T_s (based on nonlinear regression analysis); and 3) to compare observed T_g and observed T_s values and examine the correlation between the corresponding dataset.

Such approaches have not yet been reported for DDGS, and they eventually may provide an understanding about how DDGS flowability and stickiness problems often occur.

MATERIALS AND METHODS

Sample Collection. Samples of distillers wet grains and CDS were collected from a commercial ethanol plant in South Dakota and were stored under frozen conditions (-10 ± 1°C) until needed. After thawing for 24 h, CDS was added to the distillers wet grains at levels of 10, 15, and 20% (wb) and then mixed thoroughly in a mixer (model D300, Hobart, Troy, OH, U.S.A.) for 5 min.

Sample Preparation. Combined samples (≈300 g) were spread uniformly on a thin steel plate with the dimensions of 38 × 27 × 1 cm and were dried in a laboratory-scale (model 838F, Fisher Scientific, Pittsburg, PA, U.S.A.) oven. The drying was done at three selected temperatures (100, 200, and 300°C). Temperature

range selection was based on interviews and discussions with industry experts and upon our previous drying studies (Bhadra et al 2011a, 2011b). For each temperature and CDS combination, the drying was done for a specified time limit to reduce all the experimental samples to 8% (db) moisture content, so that we had a common baseline in all the samples for moisture content to eliminate its possible influence on the measured properties. Commercial DDGS samples were found to be around 8% (db) moisture content. We had to dry each treatment combination with a different drying time so that the target value of 8% (db) moisture content was achieved. These dried samples were used partly to measure flow properties, as reported in Bhadra et al (2012b), and the other half were mildly dried in the oven for an additional 8 h at 50°C to reduce the moisture content to 0% (db), so that specific levels of water could be added to achieve the desired final moisture contents of 10 and 20% (db). Thus, in total we had 54 (three drying temperatures × three CDS levels × three final moisture contents × two replicate preparations) experimental runs for T_g and T_s measurements, and we implemented a full factorial randomized experimental design.

Measurement and Modeling of Glass Transition Temperature (T_g, °C). *DSC.* The glass transition temperature (T_g) of the DDGS samples was evaluated with a DSC (DSC822, Mettler Toledo, Schwerzenbach, Switzerland). Sample crucibles of 100 µL were subjected to a heating range of –20 to 100°C with a heating rate of 5°C/min. These conditions were based on the previous studies of DDGS by Ganesan and Rosentrater (2007). An empty aluminum crucible of 100 µL was the reference cell, and both the sample and reference cells were placed on their respective thermocouple sensors in the DSC. Liquid nitrogen was used as a dry gas to cool the furnace, and helium was used as the carrier gas or purge gas at 50 mL/min. T_g is indicated by the sudden change in the heat flow as temperature increases, and it was reported by using the STARe software provided with the DSC analyzer. Two replications for each run were carried out for each sample combination.

Modeling of Glass Transition Temperature. A T_g prediction model for mixtures comprising amorphous polymers was first proposed by Gordon and Taylor (1952), which is mathematically described as follows:

$$T_g = \frac{X_s T_{gs} + K X_w T_{gw}}{X_s + K X_w} \tag{1}$$

where T_g is the glass transition temperature of the mixture (°C); T_{gs} and T_{gw} are the glass transition of the solid (in this case, it
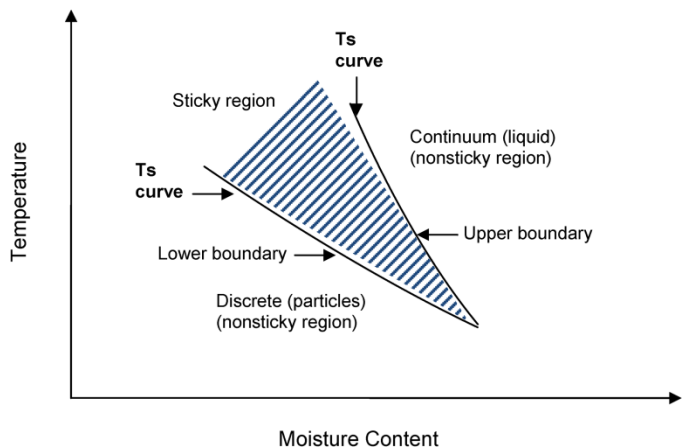

Fig. 1. Typical sticky region and sticky point temperature (T_s) curves, based on Kudra (2003). For this study, the nonsticky region lower boundary (T_s curve) was measured. More can be found in Papadakis and Bahu (1992).

refers to the observed glass transition temperature of DDGS with 0% [db] moisture, given a fixed CDS and drying temperature combination) and water in the sample, respectively; X_s and X_w are the mass fraction of solids and water (wet basis) in the sample; and K is the Gordon–Taylor (1952) parameter. The value of T_{gw} has been experimentally determined as –135°C (Gordon and Taylor 1952). For more details on how to calculate X_s and X_w for given binary system (water/solid), refer to Gordon and Taylor (1952).

The K parameter, which is dependent on the X_w, is different for individual materials and must be determined through regression analysis (Jaya and Das 2007).

Our goal was to create a single model for representing $T_g = f$(drying temperature, CDS level, and moisture content) for DDGS. According to Jaya and Das (2007), K is a function of X_w when moisture content is the only independent variable. However, for our samples, we had to modify K to incorporate X_w, CDS, and drying temperature as our independent variables. After various modifications of the base Gordon–Taylor model, we determined the modified K as follows:

$$K = (b1 \times X_w^2) + (b2 \times X_w) + (b3 \times X_w \times CDS/T) \quad (2)$$

Thus, the final modified Gordon–Taylor equation for this study is given as follows:

$$T_g = \frac{X_s T_{gs} + \left(b1X_w^2 + b2X_w + b3X_w CDS/T\right) X_w T_{gw}}{X_s + \left(b1X_w^2 + b2X_w + b3X_w CDS/T\right) X_w} \quad (3)$$

where T_g is the glass transition temperature of the mixture (°C); T_{gs} and T_{gw} are the glass transition temperatures of the solids and water, respectively; X_s and X_w are the mass fractions of solid and water (wb), respectively; K is the modified Gordon–Taylor parameter; CDS is the CDS addition level; T is the drying temperature (°C); and b1, b2, and b3 represent the model coefficients to be determined statistically from nonlinear regression.

Measurement of Sticky Point Temperature (T_s, °C). Traditionally, T_s is obtained with a glass apparatus with a stirrer embedded in the sample and with a mercury seal inserted between the glass and the rod. Details on this experimental setup and associated procedures were given in Wallack and King (1988), and it was widely used for food samples (e.g., fruit powders, dairy powders, coffee powder, etc.).

For our study, we did not use the traditional experimental setup to measure T_s, because of the hazardous nature of mercury, but instead developed a new approach with a rheometer (Visco-analyzer, ATS Rheosystems, Bordentown, NJ, U.S.A.) with a cup and vane tool arrangement. The vane tool was a four-blade stirrer made of stainless steel, with a stress coefficient of 4.151×10^4 Pa/N·m, strain coefficient of 0.926 1/s/rad, and inertia of 2.050×10^{-7} kg·mm. Figure 2 presents a pictorial view of the experimental setup of the rheometer and vane blade tool used to analyze T_s in this study.

The vane tool was inserted into the sample, which was regulated with a thermostat that maintained the sample at a constant set temperature from 20 to 85°C. The shear rate increased by increments of 2.5×10^{-1} 1/s, and the temperature increased by increments of 2°C every 3 min. This temperature and shear rate ramping were selected after several initial trials (data not shown). The specific temperature at which the torque (or force) showed a dramatic increase in value was identified as T_s. This experimental setup was developed and used for both validation of the Wallack and King (1988) T_s (°C) data with coffee samples (Bhadra et al 2012a) and the DDGS in this study.

For both T_s and T_g, the moisture content of the samples was controlled at 0, 10, and 20% (db) by adding required amounts of water and then equilibrating the samples for 24 h at room temperature prior to experimentation.

Experimental Design and Statistical Analyses. A full factorial design for three drying temperatures, three CDS levels, three moisture contents, and two replicate runs (thus, 54 experimental runs) was used. After all experiments were carried out, formal statistical data analyses with PROC GLM were conducted with SAS software version 8 (SAS Institute, Cary, NC, U.S.A.) and MS Excel (Microsoft, Redmond, WA, U.S.A.) to estimate regression coefficients. PROC NLIN was then performed, and Table-Curve 3D version 4.0.01 (SYSTAT Software, San Jose, CA, U.S.A.) was used to develop regression equations for response surfaces.

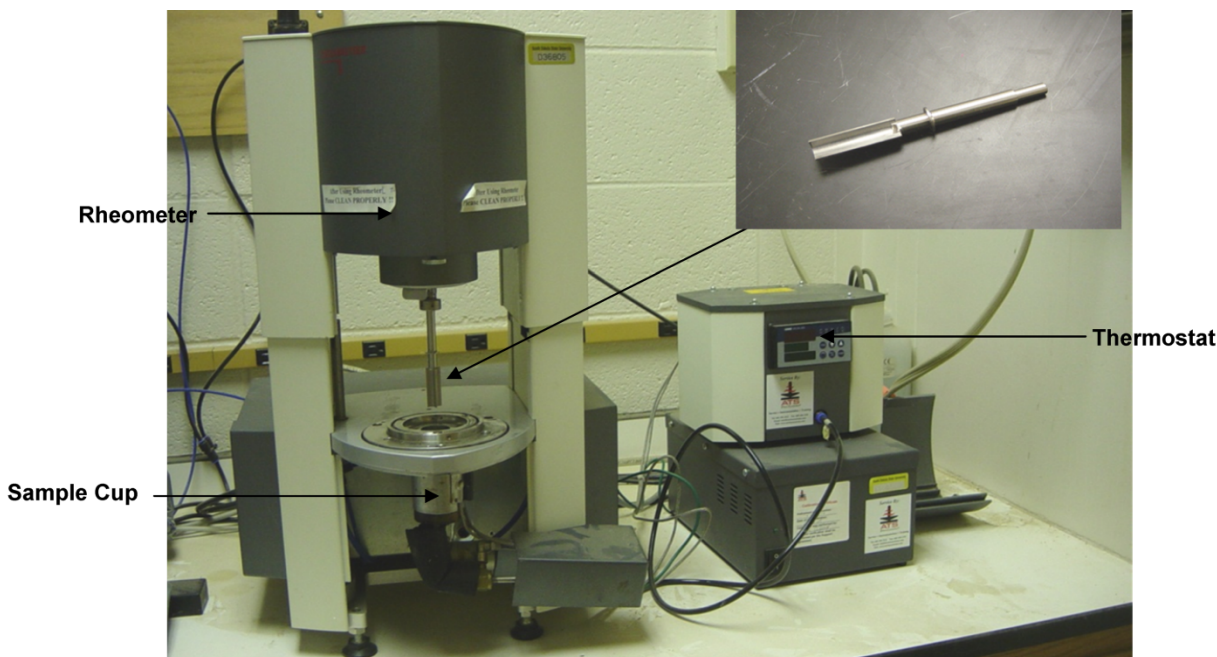
Fig. 2. Experimental setup used to measure the sticky point temperature (T_s, °C) using a rheometer. The four-blade vane stirring tool (36.79 mm in length, 6.78 mm in width, and propeller shaft 105.63 mm in length) is enlarged in the inset.

RESULTS AND DISCUSSION

Glass Transition Temperature Measurement and Modeling.

Tables I and II illustrate the various nonlinear regression equations tried for modeling K (also known as the Gordon–Taylor [1952] parameter) as a function of moisture, drying temperature, and CDS level for DDGS samples used in this study. From Table II, we can clearly see that model 11 (equation 2) yielded the highest R^2 of 0.8232 and F value of 78.82 out of 24 modified equations. Even though only five modified equations showed no convergence criteria in the nonlinear modeling process, because of the lower ranges of R^2 and F values we did not consider it to be possible

TABLE I
Parameter Estimates from Nonlinear Regression Modeling of K as a Function of CDS, Drying Temperature, and Moisture Levels in DDGS[a]

Number	Model	b1	b2	b3	b4
		Parameter Estimates			
1	$K = b1 \times X_w^{b2} + b3 \times X_w/(T + CDS)$	4.34×10^{-3}	-7.75×10^{0}	-7.42×10^{-1}	…
2	$K = b1 \times X_w^{b2} + b3 \times T^{CDS}$	-1.72×10^{-3}	7.91×10^{7}	1.47×10^{-52}	…
3	$K = b1 \times X_w^{\wedge}(b2 \times CDS) + b3 \times T$	…	…	…	…
4	$K = b1 \times X_w^{\wedge}(b2 \times T) + b3 \times CDS$	-9.19×10^{-3}	5.17×10^{0}	3.70×10^{-4}	…
5	$K = b1 \times X_w^{\wedge}(b2 \times T/CDS)$	…	…	…	…
6	$K = b1 \times X_w^{\wedge}(b2 \times T \times CDS)$	3.17×10^{8}	1.00×10^{0}	…	…
7	$K = b1 \times X_w^{\wedge}(b2 \times T \times CDS)$	…	…	…	…
8	$K = b1 \times X_w^{2} + b2 \times X_w/T + b3 \times X_w \times CDS/T$	8.30×10^{-3}	-5.52×10^{-1}	7.95×10^{-3}	…
9	$K = b1 \times X_w^{2} + b2 \times X_w/CDS + b3 \times X_w \times T/CDS$	1.00×10^{0}	-1.32×10^{-2}	1.88×10^{-4}	…
10	$K = b1 \times X_w^{2} + b2 \times X_w + b3 \times X_w \times T/CDS$	-8.73×10^{-2}	8.48×10^{-1}	1.05×10^{-2}	…
11	$\mathbf{K = b1 \times X_w^{2} + b2 \times X_w + b3 \times X_w \times CDS/T}$	$\mathbf{-8.73 \times 10^{-2}}$	$\mathbf{8.88 \times 10^{-2}}$	$\mathbf{-2.69 \times 10^{-2}}$	…
12	$K = b1 \times X_w^{2} + b2 \times X_w \times T + b3 \times X_w \times CDS$	-3.00×10^{-4}	2.10×10^{-5}	5.30×10^{-5}	…
13	$K = b1 \times X_w^{2} + b2 \times X_w \times T + b3 \times CDS$	-5.78×10^{-1}	2.30×10^{-5}	2.91×10^{-4}	…
14	$K = b1 \times X_w^{b4} + b2 \times X_w \times T + b3 \times X_w \times CDS$	…	…	…	…
15	$K = b1 \times X_w^{b4} + b2 \times X_w \times T + b3 \times CDS$	-5.74×10^{-1}	2.30×10^{-5}	3.21×10^{-4}	1.54×10^{-2}
16	$K = b1 \times X_w^{\wedge}(b2 + CDS + T)$	…	…	…	…
17	$K = b1 \times (X_w/(T + CDS))^{b2}$	-2.98×10^{-1}	7.50×10^{-1}	…	…
18	$K = b2 + b1 \times X_w^{b4} + b3 \times T/CDS$	-1.00×10^{0}	1.00×10^{0}	1.03×10^{-4}	6.92×10^{-2}
19	$K = b1 \times X_w^{b3} + b2 \times T/CDS$	-4.89×10^{39}	4.36×10^{-3}	3.46×10^{-3}	…
20	$K = b1 \times CDS \times X_w^{b3} + b2 \times T$	-2.36×10^{-1}	3.50×10^{-5}	2.34×10^{2}	…
21	$K = b1 \times X_w^{b4} + b2 \times CDS + b3 \times T$	-3.96×10^{-1}	2.71×10^{-4}	2.10×10^{-5}	1.45×10^{-2}
22	$K = b1 \times X_w^{b3} + b2 \times CDS \times T$	-1.06×10^{9}	2.189×10^{-6}	9.31×10^{-2}	…
23	$K = b1 \times X_w + b2 \times CDS + b3 \times T$	4.56×10^{-3}	-4.00×10^{-5}	6.75×10^{-6}	…
24[b]	$K = b1 + b2 \times X_w^{2} + b3 \times (X_w \times CDS)/T$	0.0409	−0.0392	−0.0269	…

[a] K = the Gordon–Taylor parameter in equation 2; X_w = the mass fraction of water (wb); CDS = the condensed distillers solubles addition (%, wb); T = the drying temperature (°C); b1, b2, b3, and b4 = the parameter estimates of the model determined statistically; and DDGS = distillers dried grains with solubles. Model 11, indicated in bold, represents the best overall model for K.

[b] This is the general linear model obtained from stepwise regression procedure in SAS.

TABLE II
Model Performance of Nonlinear Regression Modeling of K as a Function of CDS, Drying Temperature, and Moisture Levels in DDGS[a]

Number	Model	F Statistic	R^2	Model SS	Error SS	Total SS	SEM
		Model Performance					
1	$K = b1 \times X_w^{b2} + b3 \times X_w/(T + CDS)$	33.85	0.6724	0.0006	0.0003	0.0009	0.0371
2	$K = b1 \times X_w^{b2} + b3 \times T^{CDS}$	2.16	0.0586	0.0001	0.0017	0.0018	0.0072
3	$K = b1 \times X_w^{\wedge}(b2 \times CDS) + b3 \times T$	NC	…	…	…	…	…
4	$K = b1 \times X_w^{\wedge}(b2 \times T) + b3 \times CDS$	21.4	0.558	0.001	0.0008	0.0018	0.0064
5	$K = b1 \times X_w^{\wedge}(b2 \times T/CDS)$	NC	…	…	…	…	…
6	$K = b1 \times X_w^{\wedge}(b2 \times T \times CDS)$	0	0.0001	0	0.0018	0.0018	0.0073
7	$K = b1 \times X_w^{\wedge}(b2 \times T \times CDS)$	NC	…	…	…	…	…
8	$K = b1 \times X_w^{2} + b2 \times X_w/T + b3 \times X_w \times CDS/T$	14.68	0.4646	0.0008	0.001	0.0018	0.0054
9	$K = b1 \times X_w^{2} + b2 \times X_w/CDS + b3 \times X_w \times T/CDS$	14.71	0.4641	0.0008	0.001	0.0018	0.8808
10	$K = b1 \times X_w^{2} + b2 \times X_w + b3 \times X_w \times T/CDS$	68.6	0.8011	0.0015	0.0004	0.0018	0.0033
11	$\mathbf{K = b1 \times X_w^{2} + b2 \times X_w + b3 \times X_w \times CDS/T}$	**78.82**	**0.8232**	**0.0015**	**0.0003**	**0.0018**	**0.0031**
12	$K = b1 \times X_w^{2} + b2 \times X_w \times T + b3 \times X_w \times CDS$	16.82	0.4989	0.0009	0.0009	0.0018	0.0052
13	$K = b1 \times X_w^{2} + b2 \times X_w \times T + b3 \times CDS$	40.95	0.7901	0.0014	0.0004	0.0018	0.5069
14	$K = b1 \times X_w^{b4} + b2 \times X_w \times T + b3 \times X_w \times CDS$	NC	…	…	…	…	…
15	$K = b1 \times X_w^{b4} + b2 \times X_w \times T + b3 \times CDS$	40.32	0.7901	0.0014	0.0039	0.0018	0.005
16	$K = b1 \times X_w^{\wedge}(b2 + CDS + T)$	NC	…	…	…	…	…
17	$K = b1 \times (X_w/(T + CDS))^{b2}$	−10.64	−1.6796	−0.003	0.0049	0.0018	0.0119
18	$K = b2 + b1 \times X_w^{b4} + b3 \times T/CDS$	23.74	0.5899	0.0005	0.0004	0.0009	0.729
19	$K = b1 \times X_w^{b3} + b2 \times T/CDS$	27.65	0.6188	0.0011	0.0007	0.0018	0.0835
20	$K = b1 \times CDS \times X_w^{b3} + b2 \times T$	39.59	0.7017	0.0013	0.0005	0.0018	6.332
21	$K = b1 \times X_w^{b4} + b2 \times CDS + b3 \times T$	42.58	0.7956	0.0014	0.0004	0.0018	0.0065
22	$K = b1 \times X_w^{b3} + b2 \times CDS \times T$	33.55	0.663	0.0012	0.0006	0.0018	0.0068
23	$K = b1 \times X_w + b2 \times CDS + b3 \times T$	16.53	0.4945	0.0009	0.0009	0.0018	0.0148
24[b]	$K = b1 + b2 \times X_w^{2} + b3 \times (X_w \times CDS)/T$	28.23	0.6311	0.0006	0.0063	0.0009	0.03

[a] K = the Gordon–Taylor parameter in equation 2; X_w = the mass fraction of water (wb); CDS = the condensed distillers solubles addition (%, wb); T = the drying temperature (°C); SS = sum of squares; SEM = the standard error of the mean; NC = no convergence; and DDGS = distillers dried grains with solubles. Model 11, indicated in bold, represents the best overall model for K.

[b] This is the general linear model obtained from stepwise regression procedure in SAS.

model for K. Convergence criteria should be met in nonlinear regression modeling (Sharma 1996). Model 24 was obtained after applying stepwise regression modeling techniques, and it yielded a lower R^2 value (0.6311) compared with the final selected nonlinear model (model 11). From Table II, we can also conclude that the standard error of the mean showed low values for most of the trial models. However, some of those were not considered as the potential model for DDGS samples with varying drying temperature, CDS, and moisture levels because they had negative predicted K values and, therefore, yielded unreasonable predicted T_g values.

Previous research on T_g with various food and fruit powders predicted the T_g for varying moisture contents, but there have been no studies done (prior to this paper) that examined DDGS, specifically the effects of drying temperature, CDS, and moisture content factors on the Gordon–Taylor (1952) equation. So it was not possible to directly compare the final predicted model for K (equation 2), and hence the final predicted model for T_g (equation 3), with previous literature. Model 11 (also equation 2) was selected as the best possible equation to predict K (Gordon–Taylor parameter) for varying CDS, drying temperature, and moisture contents in DDGS. We incorporated the equation of predicted K (equation 2, model 11 in Tables I and II) in the base Gordon–Taylor model (equation 1), which yielded the final single comprehensive model (equation 3) for predicted T_g (°C) with varying CDS, temperature, and moisture contents in DDGS. Research on

mango, pineapple, and tomato powders by Jaya and Das (2007) was able to construct a power law type of equation for predicted K parameter, but there was only moisture content as the independent variable, unlike our research design. Similar to this study, Sablani et al (2007) was able to calculate predicted K and T_g values for different types of salt with low moisture contents by using the Gordon–Taylor model (1952).

A study by Bhandari et al (1997) with sugar-rich food materials mentioned clearly that the Gordon–Taylor model (1952) is best suited for a binary mixture in which one component is water and the other is a single solute. Couchman and Karasz (1978) reported for tertiary mixtures of water, sucrose, and fructose, and the equation was more complicated. For DDGS samples, we can assume it to be a binary mixture of DDGS powders and water molecules, and therefore we used the Gordon–Taylor model (equation 2) as the base model for modeling purposes.

In DDGS, we observed a nonlinear relationship with varying moisture content and T_g (Table III). As the moisture content increases, T_g decreases, which indicates more flow problems owing to possible stickiness. Similar results were found by Lloyd et al (1996) for milk powders. Roos and Karel (1991) also predicted similar effects of moisture contents on T_g values in maltodextrin. With DDGS samples prepared at different drying temperature and CDS levels, we achieved similar trends in T_g as we increased the moisture contents. Only one instance was contrary to this trend: the T_g value at 100°C with 20% (wb) CDS level and 20% (db) moisture content showed a slightly higher T_g value ($\approx$47.05°C) than 10% (db) moisture content ($\approx$43.00°C), indicating that there were less caking problem for DDGS at 20% (db) moisture content. It may be because at a lower drying temperature (100°C) the highest CDS level (20%, wb) had lubricating effects and, thus, showed slightly less cohesive problems (indicated by higher T_g). CDS or syrups (solubles) are high in vitamins, fat, and protein but low in fiber content. Syrup also yields a digestible energy value approximately 91% of that of raw corn (Cruz et al 2005).

In this study we could analyze the individual effects of T_g on the various CDS levels and drying temperatures, and it is also stated that T_g is one of the most important factors in determining the stickiness in DDGS. More detailed kinetic studies on the viscosity and T_g in low-moisture food components, as done by Le Meste et al (2002), were not considered here. For our research design we did not consider such analysis and focused more on obtaining the overall comprehensive model for $T_g = f$(drying temperature, CDS level, and moisture content).

In a study by Chuy and Labuza (1994) with milk powders and commercial infant formula, the T_g was predicted to have a strong linear correlation with water activity. However, for our samples, we could observe a nonlinear relationship between T_g and moisture content (R^2 from 0.89 to 0.99). Moisture content and water

TABLE III
Prediction Models for T_g and T_s by Response Surface Regression[a]

Parameter	Prediction of T_g	Prediction of T_s
Dependent variable		
z	Predicted T_g (°C)	Predicted T_s (°C)
Independent variables		
x	Temp (°C)/CDS (% wb)	Temp (°C)/CDS (% wb)
y	Moisture content (% db)	Moisture content (% db)
Predicted model	$\ln z = a + b/x^2 + cy^{0.5}$	$\ln z = a + b/x^2 + cy^{0.5}$
Model performance		
R^2	0.701	0.727
Adjusted R^2	0.683	0.711
F statistic	59.784	68.083
Standard error	3.722	3.766
Parameter estimates		
a	4.126	4.128
b	–4.543	–5.573
c	–0.051	–0.055
Figure number	5	6

[a] T_g = glass transition temperature (°C); T_s = sticky point temperature (°C); Temp = the drying temperature (°C); CDS = condensed distillers solubles addition rate (% wb); and a, b, and c = parameter estimates determined statistically.

TABLE IV
Parameter Estimates for Linear Regression Modeling Between Predicted and Observed T_g (°C) as a Function of CDS and Drying Temperature Levels[a]

Drying Temperature (°C)	CDS (% wb)	a	b	R^2	SEM
100	10	1.4129	–21.313	0.8676	2.47
	15	0.8262	7.7766	0.5470	2.61
	20	1.6663	33.146	0.9088	3.41
200	10	0.7913	13.4520	0.9948	2.46
	15	0.5244	32.744	0.9751	7.30
	20	0.7202	18.108	0.8393	4.51
300	10	0.5895	23.4300	0.5936	4.88
	15	0.7876	12.4080	0.7909	2.96
	20	1.0051	–0.2785	0.9731	0.78

[a] T_g = glass transition temperature (°C); CDS = condensed distillers solubles addition rate (% wb); predicted T_g was determined using equation 3: predicted T_g = (a)(observed T_g) + b; and SEM = standard error of the mean.

TABLE V
Parameter Estimates for Linear Regression Modeling Between Observed T_g (°C) and Observed T_s (°C) as a Function of CDS and Drying Temperature Levels[a]

Drying Temperature (°C)	CDS (% wb)	a	b	R^2	SEM
100	10	0.7216	14.7000	0.4729	2.17
	15	0.7709	8.8596	0.9836	2.17
	20	1.4253	–21.3500	0.9324	2.42
200	10	1.2280	–9.8290	0.9898	3.24
	15	0.8690	6.3340	0.9896	1.74
	20	0.9166	2.6581	0.8511	3.84
300	10	1.1337	–9.4237	0.9427	2.77
	15	0.7829	10.1060	0.8284	2.29
	20	0.7615	11.2760	0.9458	1.86

[a] T_g = glass transition temperature (°C); T_s = sticky point temperature (°C); CDS = condensed distillers solubles addition rate (% wb); observed T_s = (a)(observed T_g) + b; and SEM = standard error of the mean.

activity are considered effective factors to measure food properties and showed high correlation ($R^2 = 0.969$) between each other (Chirife et al 2006). Ganesan and Rosentrater (2007), the only study for T_g with DDGS (so far), predicted the range of T_g to be around 20°C for regular, reduced-fat, and dewaxed DDGS. Our study with DDGS samples, prepared under varying drying temperatures and CDS levels, produced a T_g range from 42 to 68°C and showed the trends of decreasing T_g as we increased the moisture content, indicating more flow problems and caking in the particles with higher moisture contents. In Ganesan and Rosentrater (2007), no predictive modeling for T_g (based on the Gordon–Taylor equation) as a function of moisture content, CDS, and drying temperature was done. Moreover, the T_g was reported in temperature ranges; specific T_g values were not reported in that paper.

Table IV represents the parameter estimates for predicted T_g, based on our developed model (equation 3) versus observed T_g values. From Table IV, we can observe the R^2 values were in general above 0.79, and many of the treatment combinations showed

higher R^2 values, indicating that our proposed model (equation 3) did fairly well for DDGS samples in predicting T_g values with varying CDS and drying temperature levels.

Correlation Between Glass Transition Temperature (T_g, °C) and Sticky Point Temperature (T_s, °C). Table V represents the correlation of T_g versus T_s, both popularly used to measure the stickiness, caking, or flow problems in food powders. From Table V, we can observe that except for drying temperature 100°C and 10% CDS levels, all the other regression coefficients were above 0.82, indicating strong linear correlation between T_g and T_s. This trend was also found in previous research with other biomaterials and fruit powders (Jaya and Das 2007; Ozmen and Langrish 2006). For DDGS, as the moisture levels increased, T_s increased, signifying higher flow problems at higher moisture levels. Similar trends in T_s values were found in coffee powders and maltodextrins (Wallack and King 1988). Also, Downton et al (1982) showed a sharp decrease in T_s as the moisture content increased for the sucrose–fructose binary amorphous mixtures.

In Werner et al (2006), corn syrup solids with different dextrose equivalents were studied, and they confirmed that T_s and T_g are

Fig. 3. Relationship between predicted T_g (°C) and observed T_g (°C) for distillers dried grains with solubles samples prepared with varying condensed distillers solubles (CDS), drying temperature, and moisture content levels, using the entire experimental data set (i.e., three CDS and three drying temperature levels).
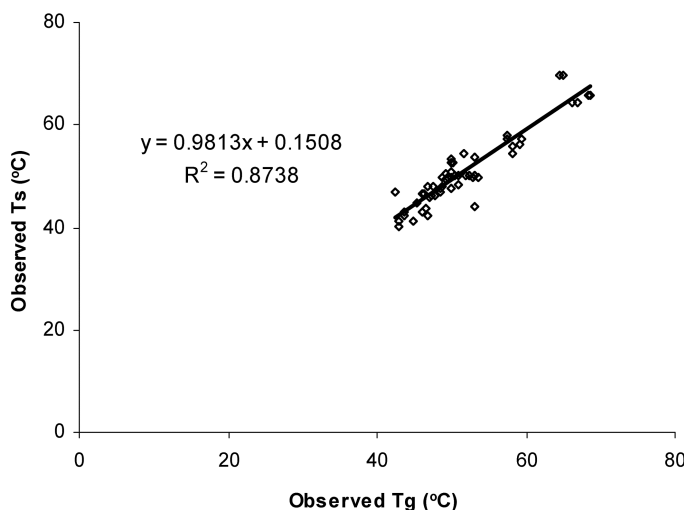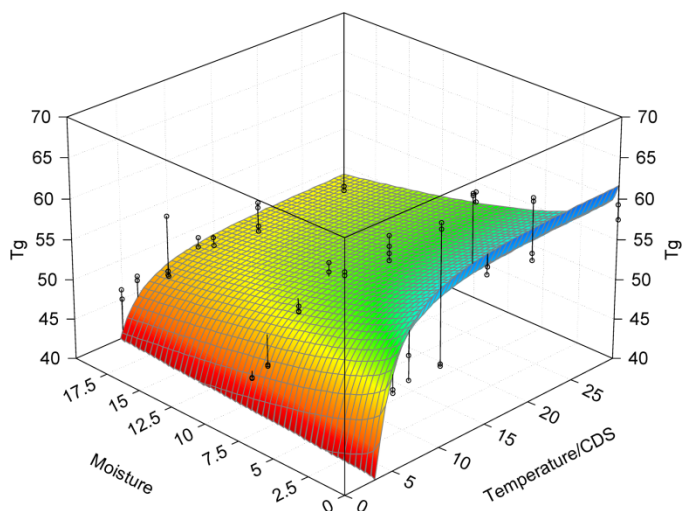

Fig. 5. Best fit response surface relationship between predicted T_g (°C) and condensed distillers solubles (CDS, % wb), drying temperature (°C), and moisture content (% db) levels (refer to Table III for the appropriate regression equation).
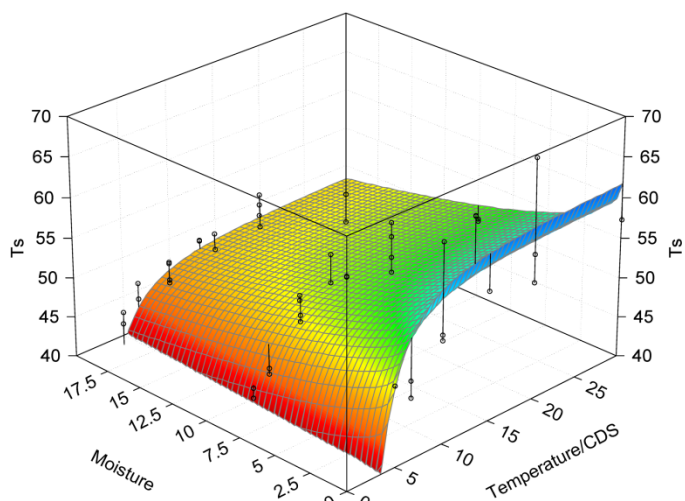

Fig. 4. Relationship between observed T_g (°C) and observed T_s (°C) for distillers dried grains with solubles samples prepared with varying condensed distillers solubles (CDS), drying temperature, and moisture content levels, using the entire experimental data set (i.e., three CDS and three drying temperature levels).

Fig. 6. Best fit response surface relationship between predicted T_s (°C) and condensed distillers solubles (CDS, % wb), drying temperature (°C), and moisture content (% db) levels (refer to Table III for the appropriate equation).

closely related. Jaya and Das (2007) also showed correlation between T_g and T_s values, indicating that T_s and T_g are both similar parameters with different experimental techniques to measure them. According to Ozmen and Langrish (2006), in skim milk powder T_g and T_s were highly correlated, and they are virtually the same measurement with different experimental approaches. Our findings in Table V showed similar results for DDGS samples. From Table V we could observe that the R^2 for T_g versus T_s relation was above 0.85 (very favorable), and it showed a linear relationship between T_g and T_s. No prior study in this context was done before, so it was not possible to compare the R^2 values of this study with relevant literature.

Figures 3 and 4 represent the overall global plots for observed T_g versus predicted T_g and observed T_g versus observed T_s for DDGS samples with varying CDS (10, 15, and 20%, wb), moisture content (0, 10, and 20%, db), and drying temperature levels (100, 200, and 300°C), respectively. We could clearly observe that the R^2 was above ≈0.75 for both the cases. The R^2 value for Figure 4 (plot of observed T_g versus observed T_s) was slightly higher (0.8738), indicating better correlation between T_s and T_g. The accuracy and appropriateness of our rheometer-based approach to measure T_s for DDGS samples is discussed in detail later, in regard to the validation to determine the accuracy of the method.

Predicted T_g (°C) and T_s (°C) for Varying CDS Levels, Temperatures, and Moisture Contents. Table III illustrates the best possible nonlinear regression equation for T_g and T_s = f(drying temperature, CDS level, and moisture content) with TableCurve 3D software. The R^2 values for both regression equations were around 0.72. Favorable higher R^2 values (>0.90) were not achieved; however, the predicted regression equations were simple and easy to implement. It could provide a vital tool for DDGS samples to predict T_g and T_s with different operating conditions in industrial applications. Figures 5 and 6 represent the corresponding response surface 3D plots of T_g = f(moisture content, drying temperature/CDS level) and T_s = f(moisture content, drying temperature/CDS level), respectively. Such multiple regression analyses were not previously done for DDGS samples; this study is the first of its kind that could incorporate the effects of drying temperature, CDS levels, and moisture contents simultaneously for T_g and T_s evaluation, hence predicting caking and flow problems in DDGS.

Validation of Sticky Point Temperature (T_s, °C) Measurement by a Rheometer Procedure. In this study with DDGS samples, T_s was calculated with a rheometer with a vane tool and cup arrangement, as discussed in the Materials and Methods section. However, to observe the appropriateness of the T_s measurement procedure, we carried out a validation study with commercial-grade coffee powder. The original T_s data for coffee powder (reported by Wallack and King [1988]) was validated by the T_s obtained from the rheometer in the current study. Our results clearly showed that the T_s data obtained from Wallack and King (1988) for coffee powder, which used the traditional glass and tube experimental setup, and the rheometer-based T_s analysis were very close. More details on validation can be found in Bhadra et al (2012a).

CONCLUSIONS

This study determined the effect of drying temperature and CDS levels on DDGS T_g and T_s (°C), thus improving understanding of stickiness in DDGS particles. Similar to previous research on other biomaterials, DDGS also showed a strong correlation between T_s and T_g, with R^2 = 0.87. Based on the Gordon–Taylor model, a global comprehensive model (R^2 = 0.74) was developed for predicting T_g = f(moisture content, drying temperature, and CDS level). Stickiness in the DDGS samples increased as the moisture content increased, and it showed potential flow problems. For varying CDS levels, there were some slight changes in

T_g values: average T_g for 20% (wb) CDS (51.05°C) was slightly lower than average T_g for 10% (wb) CDS (51.81°C), indicating better flow at the 10% (wb) CDS level. Response surface regression provided nonlinear regression surfaces that can be used to predict T_s and T_g for various drying temperatures, CDS levels, and moisture contents. T_g and T_s are both considered vital parameters that quantify the stickiness and caking behavior of powders. Thus, this research is a crucial step toward understanding phase transitions and DDGS stickiness. Because no previous studies have yet examined DDGS T_s and T_g, this research forms part of crucial evidence for alleviating flowability issues in DDGS, apart from flow property data analysis.

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