
Effects of varying condensed distillers solubles, drying and cooling temperatures on glass transition temperature of distillers dried grains

R. Bhadra¹, K.A. Rosentrater^{2*} and K. Muthukumarappan³

¹Department of Agricultural and Biosystems Engineering, South Dakota State University, 1400 North Campus Drive, Brookings, South Dakota, USA 57007; ²Department of Agricultural and Biosystems Engineering, Iowa State University, 3167 NSRIC Building, Ames, IA, USA 50011; and ³Department of Agricultural and Biosystems Engineering, South Dakota State University, 1400 North Campus Drive, Brookings, South Dakota USA 57007.

*Email: karosent@iastate.edu

Bhadra, R., K.A. Rosentrater and K. Muthukumarappan. 2011. **Effects of varying condensed distillers solubles, drying and cooling temperatures on glass transition temperature of distillers dried grains.** Canadian Biosystems Engineering/Le genie des biosystèmes au Canada. 53: 3.9–3.18. Distillers dried grains with solubles (DDGS), a coproduct of ethanol fuel production, is used as an animal feed and often must be transported long distances. DDGS flowability problems often create nuisance in storage and transportation. Materials above the glass transition temperature (T_g) can exist in a “rubbery state,” which is often responsible for particle agglomeration and caking. This study investigated the effects of varying condensed distillers solubles (CDS) (10, 15, and 20%, wb), drying (100, 200, and 300°C), and cooling temperature (–12 and 35°C) levels on the T_g of DDGS. T_g ranged from 34 to 58°C and 41 to 59°C for cooling temperatures of –12°C and 35°C, respectively. T_g data were used to develop an overall regression model, which yielded a predictive model with R² of 0.74 and SEM of 3.16. Using this model, optimum drying and cooling temperatures were determined. These conditions may be used to reduce flow problems. **Keywords:** caking, distillers dried grains with solubles (DDGS), drying, flowability.

Les grains séchés de distillerie qui contiennent des composants solubles (DDGS), un sous-produit de la production d'éthanol, sont utilisés comme aliment pour les animaux et doivent souvent être transportés sur de longues distances. Des problèmes d'écoulement liés aux DDGS créent des nuisances tant au niveau de l'entreposage que du transport. Des matériaux au-dessus de la température de transition vitreuse (T_g) peuvent exister dans un état caoutchouteux qui peut être à l'origine de la formation d'agrégats. Cette étude a vérifié l'effet de différentes concentrations de solubles condensés de distillerie (CDS) (10, 15 et 20% bh), de température de séchage (100, 200 et 300°C) et de niveaux de température de refroidissement (–12 et 35°C) sur le T_g des DDGS. T_g a varié entre 34 et 58°C et entre 41 et 59°C pour des températures de refroidissement de –12 et 35°C, respectivement. Les données de T_g ont été utilisées pour développer un modèle de régression global ayant un R² de 0,74 et un SEM de 3,16. En utilisant ce modèle, les températures optimales de séchage et de refroidissement ont pu être déterminées. Ces conditions peuvent être utilisées pour réduire les problèmes d'écoulement. **Mots clés:** agrégation, grains séchés de distillerie avec solubles (DDGS), séchage, écoulement.

INTRODUCTION

Research estimates that about 85% of all the energy consumption in the United States is from fossil fuel sources (USDOE 2008), and in order to meet the market demand, this percentage is anticipated to increase in coming years. To decrease dependence on non-renewable fossil fuel sources, focusing on renewable energy sources, like corn-based ethanol, is important. With the recent remarkable growth in the U.S. corn-based fuel ethanol industry, large amounts of corn based Distillers Dried Grains with Solubles (DDGS) are produced. The production of distillers grains in the fiscal year 2009–2010 was calculated to be around 30.4 million metric tons, and this is projected to grow in the future (RFA 2010). For over two decades, due to appropriate levels of protein, fat, energy, and mineral content, DDGS has been used as livestock feed for cattle, swine, and poultry (Ganesan et al. 2007a). DDGS typically contains 86 to 93% (db) dry matter, 26 to 34% (db) crude protein, 3 to 13% (db) fat, and important amino acids like methionine, leucine, arginine, and threonine (Rosentrater and Muthukumarappan 2006; Speihs et al. 2002). To meet the high demand for DDGS in the livestock feed industries, transporting and handling DDGS over long distances is increasingly important. DDGS is exposed to different environmental and physical conditions such as fluctuations in temperatures, humidity, etc.

Like many agricultural, biological, and food materials, DDGS is hygroscopic in nature, (i.e., it has the ability to absorb moisture during handling and storage). DDGS particles tend to agglomerate and form solidified cakes, and thus DDGS often has poor flow behavior. Caking or hardening of DDGS leads to difficulties during unloading from rail cars and storage vessels, and ‘caking’ significantly contributes to economic losses and labor cost to break up the agglomerates (Rock and Schwedes 2005). Stickiness in the particles (the “caking” phenomenon) causes poor flowability in the bulk material, and thus, makes it less efficient to handle during transportation and storage. Stickiness is often a problem for not only the quality of the end product, but also for the manufacturing

operations, equipment maintenance, and fire safety (Kudra 2002). Caking is considered to be a spontaneous agglomeration process between two previously fluid (or non-cohesive) particles, and for the process to proceed, the surface of particles or at least certain sites on those particles, become fluid. Fluidity among powder particles can be caused by the melting of fat molecules and the diffusion of water molecules. During these conditions, the particles become sticky and caking occurs (Peleg 1993).

Drying is one of the processing operations involved in handling the biomass at the ethanol plant, and drying systems such as rotary drum, ring, and rotary steam tube dryers are most frequently used. For dried products, a significant amount of the product remains in the amorphous state, mainly due to short residence time in the dryers. A mixture of crystalline and amorphous states can lead to changes in the physical state of the bulk product and has the possibility to affect the physico-chemical characteristics of the dried material (Bhandari and Howes 1999). A change in the state of the matrix can lead to a phase transition from the amorphous state to a “rubbery state” which is also known as a glass-liquid transition state, technically called the glass transition temperature (T_g). T_g can be used to predict the storage, flow, and processing conditions of food and other biomaterials (Le Meste et al. 2002). Furthermore, structural collapse of the product during drying, or during storage of dried product, is responsible for the reduction in the volume and porosity, which results in the loss of desirable appearance and volatile substances. Powder stickiness and caking are related to this structural collapse, imposing important constraints on the drying and storage conditions of dried powders with a high content of sugars, minerals, and protein components (Le Meste et al. 2002).

Glass transition temperature (T_g, °C)

The glass transition temperature (T_g) is a key property of amorphous materials. Amorphous materials are formed in unstable, or non-equilibrium, conditions where the solvent medium is removed by rapid super-cooling or drying over a relatively short time. Thus, these materials are not at thermodynamic equilibrium and behave like an extremely viscous “glass” often having a viscosity above 10¹² (Pa)(s) (Downton et al. 1982; Wallack and King 1988). Carbohydrates and proteins in food systems are generally miscible with water and show both first-order phase transitions (e.g., melting, crystallization) and state transitions (e.g., denaturation, gelatinization, and glass transition) (Roos 2003). Phase transitions are traditionally classified according to the thermodynamic changes that occur in the various transition temperature regions. First order transitions are those at which the first derivative of the thermodynamic functions exhibit discontinuity in the heat capacities and the thermal expansion coefficients for solid, liquid and gas states. At the second order transition temperature, a step change occurs in the properties that show discontinuity in the first order transition (Roos 2003).

For example, in a typical spray drying of milk powder, the solid particles are produced at high drying temperatures during a short residence time in which particles fail to align themselves in a crystalline state and remain partially amorphous. On heating, only the amorphous solids undergo the second order phase transition (glass transition) where the “glass state” changes into a liquid “rubbery state.” Stickiness and lumpiness are often related to this “rubbery state” (Ozmen and Langrish 2002).

Glass transition can occur during either cooling or heating processes, or due to the action of a solvent (e.g., plasticizer), and it is a time-dependent phenomenon (Roos 2003). T_g is characterized by an endothermic change in the specific heat capacity, and can be detected using Differential Scanning Calorimetry (DSC) (Roos and Karel 1990). DSC is a thermal analysis technique which measures the temperature and heat flows associated with transitions in materials as a function of time and temperature (Gill et al. 1993). Other manifestations of T_g are the sticky point temperature (T_s) and the collapse temperature (T_{col}). All of these parameters measure the ability of a powder to cake at a given temperature (Peleg 1993).

There are many structural changes related to glass transition temperature. These include particle stickiness and caking, reduced bulk flowability, collapse in food powders with high sugar contents, crispiness of snack foods, crystallization of lipids and sugars, gelatinization of starch, and to some extent browning and enzymatic reactions (Slade and Levine 1991; Roos 1995).

Additionally, T_g applications have been found in research related to physico-chemical properties of starch (gelatinization), gluten, and sucrose in food components (Slade 1984). Furthermore, Kasapis et al. (2004) found that glassy behavior and stickiness were observed for low temperature food products, leading to structural collapse of the product. The changes in the mechanical properties of food materials are due to reduction in the relaxation time period, change in moisture content, water activity, and temperature.

Amorphous substances are metastable, and thus, can crystallize over time during storage. The William-Landel-Ferry (WLF) model is based on the thermochemical mechanism theory developed for caking in amorphous powders by Williams et al. (1955). If a local portion of a product picks up moisture, T_g is depressed and the rate of crystallization is accelerated (Bhandari and Howes 1999). This crystallization phenomenon tightly packs molecules, and results in loss of adsorbed water. The loss of water molecules leads to moisture migration in the food product, forming interparticle liquid bridges, which can lead to caking (Jouppila and Roos 1994; Peleg and Hollenbach 1984).

Water acts as a plasticizer; it helps in lowering the glass transition temperature for low-moisture foods and biological materials. Furthermore, water can exist on particle surfaces as a monolayer, which can reduce the surface micro-roughness of the particles, thereby allowing the particles to stick on the basis of hydrophilic attraction (Adhikari et al. 2001).

Degree of Polymerization and Plasticization

T_g is strongly dependent on the molecular weight of the material, and is also related to moisture; an increase in moisture will decrease the T_g (Slade and Levine 1995). Changes in water content (and water plasticization) can affect food properties (Roos 2003). Plasticization, or T_g decrease, is often mainly due to water molecules; but also other solutes can also act as plasticizers (Le Meste et al. 2002).

Water acts as a plasticizer by enabling the mobilization of amorphous components. Water itself has a very low T_g of -135°C (Johari et al. 1987). Consequently as T_g is decreased, stickiness in food compounds can be seen (Fitzpatrick et al. 2007). The water and T_g relationship can be described by an equation given in Gordon and Taylor (1952). DDGS is also formed at high drying temperatures and short residence times, indicating that it is amorphous in nature. T_g of DDGS can be affected by cooling temperatures, process conditions, rate of crystallization, structural collapse of the bulk solid (Roos and Karel 1991a), and other physico-chemical changes that can indirectly affect flowability. Such in depth studies relating T_g and process parameters during drying of DDGS have not been done before and thus this study will establish for the first time some of those relations.

Application to ethanol coproducts

DDGS is commercially produced at corn-based ethanol plants, operated mostly using the dry milling process. After fermentation of starch and other fermentable component to ethanol, the non-fermentable materials are divided roughly into two fractions – wet distillers grains (DWG) and condensed distillers solubles (CDS) (NCGA 2008). In the production path of DDGS, wet distillers grains are mixed with condensed distillers solubles (CDS) and then dried in a drum dryer to produce DDGS. In the industrial drying operation, the drying temperatures often range from 538°C (inlet) to 148°C (outlet) (approximately) (Bhadra et al. 2009a). Particle flow and caking are multivariate processes which depend on particle shape, size, chemical composition, and other physical properties (Bhadra et al. 2009b). Kleinschmit et al. (2006) reported that variation in DDGS physical, chemical and flow properties are mainly due to variations in operating parameters during DDGS formation and not due to the variation in corn quality. Thus, we can say that for flowability of DDGS, operating parameters such as drying temperature and CDS levels are important factors that need to be studied. After production, DDGS is often transported over long distances through diverse ambient temperature conditions. Variations in ambient temperature and relative humidity can interact with the equilibrium moisture content of the product. Water adsorption characteristics interact with humidity, which in turn affect the overall handling and flowability of DDGS, as reported by Ganesan et al. (2007a).

T_g measurement to quantify stickiness and flow problems in DDGS with varying CDS and drying temperatures was done previously in Bhadra et al.

(2009c). Ganesan and Rosentrater (2007b) also studied T_g with regular and reduced fat DDGS. However, the change in T_g as affected by varying CDS, drying temperatures, and cooling temperatures in DDGS has not yet been investigated. Thus, the main objectives of this paper were:

1. To evaluate the behavior of T_g in DDGS samples prepared and stored under laboratory conditions using varying CDS (10, 15, 20%, wb), drying temperature levels (100, 200, and 300°C), and cooling temperature levels (-12°C and 35°C), including main and interaction effects.
2. To establish an overall model for $T_g = f(\text{temperature and CDS levels})$. T_g data for DDGS samples cooled at 25°C (Bhadra et al. 2009d) was evaluated and pooled with samples in this current study (cooling at -12°C and 35°C) for the overall modeling procedure.
3. To provide an optimum range of drying/cooling temperatures and CDS levels, in order to ensure safe handling and cooling of DDGS.

Such broad spectrum work on T_g has not yet been reported for DDGS, and may provide a detailed understanding about operation, handling, and flowability issues for DDGS.

MATERIALS and METHODS

Sample Collection and Preparation

Samples of distillers wet grains (DWG) ($\sim 60\%$ (db) moisture content) and condensed distillers solubles (CDS) were collected from a commercial ethanol plant in South Dakota, and were stored frozen ($-10 \pm 1^{\circ}\text{C}$). CDS was added to the DWG at levels of 10, 15, and 20% (wet basis-wb) and then mixed thoroughly (Model D300, Hobart Corporation, Troy, OH) for 5 min; 300 g of these combined samples were then spread uniformly onto thin steel plates (which were $38\text{ cm} \times 27\text{ cm} \times 1\text{ cm}$). They were dried in a laboratory scale (model no 838F, Fisher Scientific, Pittsburg, PA) oven. Drying was done at three temperatures (100, 200, and 300°C); temperature selection was based on non-published interviews and discussions with industry experts (data not presented here), and also based on our previous mathematical modeling of DDGS drying rate and moisture content with various drying temperature and CDS levels (Bhadra et al. 2009a).

For each temperature/CDS combination, drying was done for specified times in order to reduce all experimental samples to $\sim 8\%$ (dry basis-db) moisture content, and thus produce DDGS. After drying, the DDGS was cooled and stored in either a freezer at -12°C , or in an oven at 35°C . Thus, in total we had 18 (3 drying temperatures \times 3 CDS levels \times 2 cooling temperatures) experimental runs for T_g measurements, and each run was replicated three times, thus, $n = 18 \times 3 = 54$ for the study.

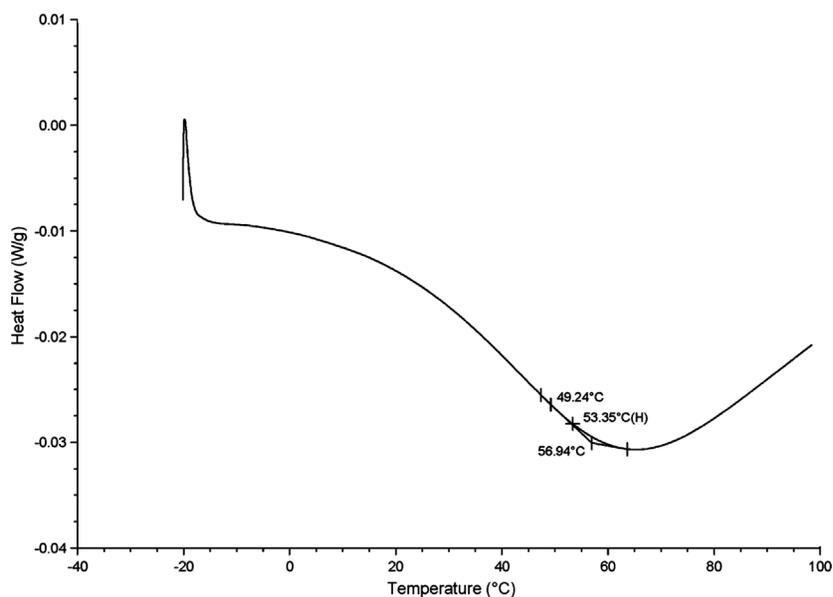


Fig. 1. Typical DSC curve generated during testing.

Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of the DDGS samples were evaluated using a differential scanning calorimeter (DSC) (Q series,TM Model Q200, TA Instruments, New Castle, DE). The DSC was equipped with an autosampler. An empty aluminum pan (40 μ l) was used as the reference cell to calibrate the instrument. Samples were subjected to a heating range of -20 to 100°C with a heating rate of $5^\circ\text{C}/\text{min}$; this was based on previous literature on DDGS (Ganesan and Rosentrater 2007b; Bhadra et al. 2009c). Universal Analyzer software provided by TA instruments (New Castle, DE) was used to analyze T_g (available after first scan data) from the thermograms, using the half height integration method.

Statistical Analyses

For the 18 treatment combinations (with 3 replications each), a full factorial design (3 CDS levels \times 3 drying temperatures \times 2 cooling temperatures = 54 runs) was performed. Formal statistical data analyses were completed using Microsoft Excel v.2003 (Microsoft Corp., Redmond, WA) and SAS software v.8 (SAS Institute, Cary, NC). Analyses included summary statistics, Analysis of Variances, and Least Significant Difference (LSD) testing at the 95% confidence level (i.e., $\alpha=0.05$); these were performed to determine main and interaction effects among the treatment combinations. TableCurve 3D v.4.0.01 (SYSTAT Software, Inc., San Jose, CA) was used to develop regression equations for 3D response surface modeling of $T_g=f$ (CDS, drying temperature, cooling temperature).

RESULTS and DISCUSSION

Main Effects and Treatment Combination Effects

Fig. 1 presents a typical DSC curve which was generated during the DDGS testing. Table 1 presents the individual

main effects due to CDS, drying temperature, and cooling temperature on T_g . A significant increase of T_g was observed for an increase in drying temperature from 100 to 200°C (indicating lower product stickiness), but a further increase of drying temperature to 300°C did not significantly further impact the T_g . For CDS, a significant T_g decrease (indicating possible product stickiness) was noticed when the CDS level was increased from

Table 1. Main effects due to CDS, drying temperature, and cooling temperature levels on DDGS glass transition temperatures. Values in the parenthesis are within ± 1 standard deviation.[†]

Independent Variable		T_g ($^\circ\text{C}$)
CDS (% , wb)	10	49.87 ^a (0.78)
	15	49.19 ^a (0.84)
	20	45.99 ^b (0.92)
Drying Temperature ($^\circ\text{C}$)	100	42.19 ^b (0.98)
	200	51.91 ^a (1.53)
	300	50.95 ^a (2.01)
Cooling Temperature ($^\circ\text{C}$)	-12	45.02 ^b (1.78)
	35	51.68 ^a (2.01)

[†] T_g is glass transition temperature ($^\circ\text{C}$); CDS is condensed distillers solubles (% , wb); Different letters indicate significant differences due to various levels of the given independent variable, LSD at $\alpha=0.05$.

15% (wb) to 20% (wb). Similarly, for cooling temperatures (-12 and 35°C) there was also a significant difference in Tg (Tg for -12°C was lower than that at 35°C , suggesting possible stickiness and flow problems), as indicated in Table 1. Tg is often responsible for dramatic changes in molecular structure of a material and affects the stickiness of the product (Levine and Slade 1988; Roos and Karel, 1991a, b). Bhadra et al. (2009d) also found significant effects on DDGS flow and physical properties due to varying drying temperature and CDS levels. Studies on the effect of drying temperature, CDS, and cooling temperature on Tg were not reported, however. The various CDS, drying, and cooling temperatures in that study impacted the physical behavior and overall flowability of the DDGS. Bhadra et al. (2009c) found that

for various DDGS samples, $T_g = f(\text{drying temperature, CDS, and moisture content})$, and a predicted response surface plot with R^2 of 0.74 was established. Using a modified Gordon-Taylor model yielded a regression equation with R^2 of 0.82. More details on the parameter estimates and regression relationships can be found in Bhadra et al. (2009c).

Table 2 indicates the treatment combination effects on Tg due to simultaneously varying CDS levels, drying temperatures, and cooling temperatures. Significant treatment combination effects were found for all independent variables. For a cooling temperature of -12°C , Tg was found to range from 34 to 52°C , while for $+35^{\circ}\text{C}$ cooling temperature, the Tg was found to range from 41 to 59°C . Thus, there was a reduction in observed Tg for lower

Table 2. Treatment combination effects due to varying CDS, drying temperature, and cooling temperature levels on DDGS glass transition temperatures. Values in parentheses are within ± 1 standard deviation.[†]

Treatment	CDS (% , wb)	Drying Temperature ($^{\circ}\text{C}$)	Cooling Temperature ($^{\circ}\text{C}$)	Tg ($^{\circ}\text{C}$)
1	10	100	-12	42.46 ^{hi} (1.50)
2	15	100	-12	39.83 ⁱ (0.72)
3	20	100	-12	34.43 ^j (0.06)
4	10	200	-12	52.49 ^{cbd} (1.01)
5	15	200	-12	50.11 ^{ed} (1.03)
6	20	200	-12	43.34 ^h (0.95)
7	10	300	-12	46.13 ^g (1.42)
8	15	300	-12	47.74 ^{geg} (0.51)
9	20	300	-12	48.65 ^{fe} (0.84)
10	10	100	35	47.33 ^{fg} (0.51)
11	15	100	35	47.26 ^{fg} (1.21)
12	20	100	35	41.82 ^{ih} (1.08)
13	10	200	35	59.11 ^a (1.65)
14	15	200	35	53.07 ^{cb} (1.09)
15	20	200	35	53.31 ^{cb} (1.91)
16	10	300	35	51.69 ^{ed} (0.24)
17	15	300	35	57.11 ^a (0.31)
18	20	300	35	54.41 ^b (0.38)

[†]Tg is glass transition temperature ($^{\circ}\text{C}$); CDS is condensed distillers solubles (% , wb); Different letters indicate significant differences due to various combinations of independent variables, LSD at $\alpha = 0.05$.

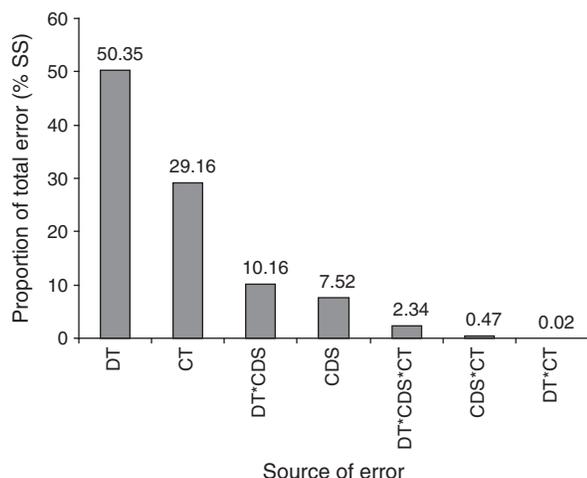


Fig. 2. Proportion of total error explained by interaction effects among CDS (% wb), drying temperature (DT, °C), and cooling temperature (CT, °C) levels.

cooling temperatures. Moreover, drying at higher temperatures ($>200^{\circ}\text{C}$) can give rise to higher degree of polymerization of the product, thus decreasing T_g . Depression of T_g due to plasticizing agents like water, sugars, etc. has been seen in other biomaterials such as air dried apple and strawberry samples (Dell Valle et al. 1998; Moraga et al. 2004). Water is often the major plasticizing agent in biomaterials, and it acts to lower T_g ; however, in our experiments, we kept moisture content constant at 8% (db), so we assume the change in T_g is mostly due to crystallization at sub-zero cooling temperatures, and polymerization at higher drying temperatures, not due to water plasticization.

The possibility of caking and agglomeration of DDGS increases if it is cooled at low temperatures (such as -12°C), rather than at higher temperatures (i.e., at $+35^{\circ}\text{C}$). Moreover, cooling temperature at 35°C is just 10°C higher than room temperature, and major impacts of cooling temperatures on structural collapse and caking was not noticed at 35°C . Higher cooling temperature ($>35^{\circ}\text{C}$) could have revealed more changes in T_g , but this was beyond our experimental design. It appears that sorption capacity of the particles is affected by both temperature and the interstitial relative humidity level (see for example, Ganesan et al. 2007a). At low temperatures ($\sim -12^{\circ}\text{C}$), crystallization of water and fat molecules combined with changes in relative humidity can trigger caking and stickiness. For complex food materials like DDGS, hygroscopic products pick up moisture (due to changes in relative humidity), and the T_g is locally depressed at a point, which in turn accelerates the rate of crystallization, and thus there is an overall depression of T_g , loss of structure, and flowability problems in the powders (Bhandari and Howes 1999).

During DDGS production at high drying temperatures, certain sites on the particle surfaces are exposed, causing fat molecules to melt, and can form solid bridges upon cooling and solidification. Such changes could also trigger particle caking (Peleg 1993), even though

Table 3. Interactions effects due to varying CDS, drying temperature, and cooling temperature levels on DDGS glass transition temperatures.[†]

Source	p-values
CDS	<0.0001
DT	<0.0001
CT	<0.0001
DT*CDS	<0.0001
CT*CDS	0.1368
DT*CT	0.9157
DT*CT*CDS	0.0015

[†] T_g is glass transition temperature ($^{\circ}\text{C}$); CDS is condensed distillers solubles (% wb); DT is drying temperature ($^{\circ}\text{C}$); CT is cooling temperature ($^{\circ}\text{C}$); $\alpha=0.05$.

the DDGS samples (stored at 35°C) showed better T_g values in this study. The T_g was relatively higher (average = 51.67°C), thus, transportation during summer should not be affected because the product will have higher T_g than ambient temperature. Product collapse and molecular levels changes (brought about by glass transition) will be avoided. Hence, reduced stickiness should occur.

Interaction Effects

The interaction effects for T_g with varying CDS, drying temperature, and cooling temperature levels are given in Table 3. The interaction between drying and cooling conditions was not significant, as the p-value (0.9157) was greater than $\alpha=0.05$. Similarly, for the interaction between CDS and cooling temperature, the p-value (0.1368) was greater than α . However, the interaction between drying temperature and CDS was significant. Also, the overall interaction among drying temperature, CDS, and cooling temperature was significant (p-value = 0.0015, $p < \alpha$). This indicates that there was a simultaneous interaction between drying and cooling conditions, as well as CDS levels. This interaction is thus responsible for changes in T_g and caking and agglomeration in DDGS. To further explain the effects of the interactions, the relative contribution of the sum of squares (SS) for each interaction was determined. The SS were recalculated as a percentage basis of total error (Fig. 2), and it is evident that the most important effect was due to drying temperature (50.35), and the highest interaction effect was drying temperature and CDS (10.16).

Response Surface Regression

An overall response surface plot which represents $T_g = f$ (drying temperature, cooling temperature, and CDS) is provided in Fig. 3. For this overall modeling, we pooled all T_g data for DDGS samples prepared at varying CDS levels (10, 15, and 20%, wb), drying temperatures (100, 200, and 300°C), cooling temperatures (-12 , and 35°C), with T_g data from our previous samples (Bhadra et al. 2009d) using similar drying temperatures and CDS levels, but cooled at 25°C (room temperature only). The moisture contents of the DDGS samples from Bhadra et al. (2009d)

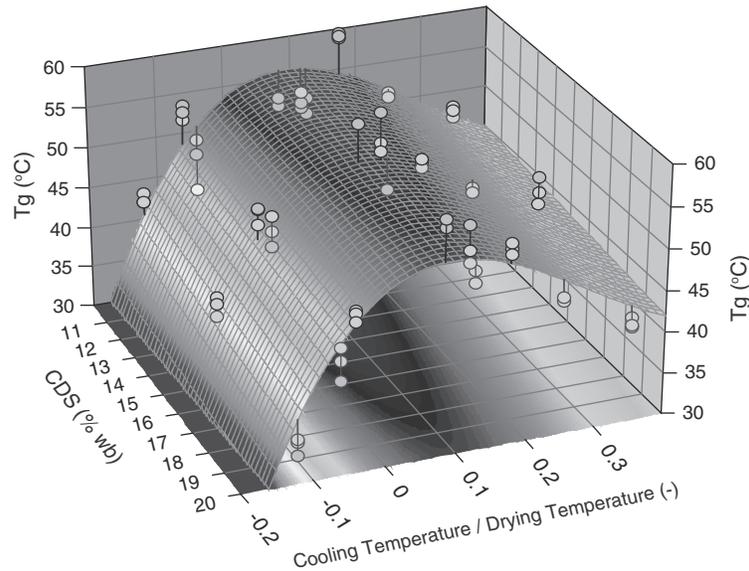


Fig. 3. Best fit response surface relationship for glass transition temperature (T_g , °C) as a function of CDS (% wb), drying temperature (°C), and cooling temperature (°C).

were constant at 8% (db) for all the DDGS samples at 25°C. The overall non-linear regression equation obtained from the response surface plot (Fig. 3) had an R^2 of 0.74, F-statistic of 47.37, and standard error of 3.15, and is given below as:

$$z = a + bx + cy + dy^2 + ey^3 \quad (1)$$

where z is T_g (°C), x is CDS (% wb), and y is cooling temperature/drying temperature ratio [– (which denotes a dimensionless quantity)]. The parameter estimate values are as follows: $a = 56.28$, $b = -0.28$, $c = 57.29$, $d = -370.12$, and $e = 433.56$. The TableCurve 3D software (v.4.0.01) can only model if there are two axes of independent variables. Thus, we combined cooling temperature/drying temperature to produce a dimensionless ratio. We had CDS and cooling temperature/drying

temperature as our two independent variables of the model (Eq. 1). A regression model with $R^2 > 0.90$ was not obtained due to scatter in the T_g data. The standard error was found to be low, which indicates that the overall response curve fit well to the observed T_g data.

Using Eq. 1, $T_{g\text{predicted}}$, which is due to different cooling temperature/drying temperature (–) ratios, for each CDS level, can be predicted (Fig. 4). From Fig. 4, we observe that for 10% CDS, $T_{g\text{predicted}}$ was found to be slightly higher than the $T_{g\text{predicted}}$ for 20% CDS. CDS, also known as “syrup” in the ethanol industry, contains relatively high fat levels (Buchheit 2002; Cruz et al. 2005). Thus, greater CDS addition levels result in higher fat levels in the final DDGS. Typically, in commercial DDGS samples, it has been found that CDS levels often range from 11% (db) to 15% (db) (Bhadra et al. 2009b).

Table 4. Predicted glass transition ($T_{g\text{predicted}}$) values for varying CDS, cooling temperature, and drying temperature levels using Eq. 1 (obtained from response surface modeling, Fig. 3).[†]

Cooling Temperature (°C)	Drying Temperature (°C)	Cooling Temperature/Drying Temperature ratio (–)	CDS (% wb)		
			10	15	20
			$T_{g\text{predicted}}$ (°C)		
–12	100	–0.12	40.48	39.06	37.64
–12	200	–0.06	48.57	47.15	45.73
–12	300	–0.04	50.52	49.10	47.68
25	100	0.25	51.40	49.98	48.56
25	200	0.13	55.66	54.24	52.82
25	300	0.08	55.89	54.47	53.05
35	100	0.35	46.73	45.31	43.89
35	200	0.18	54.45	53.03	51.61
35	300	0.12	55.77	54.35	52.93

[†] T_g is glass transition temperature (°C); CDS is condensed distillers solubles (% wb).

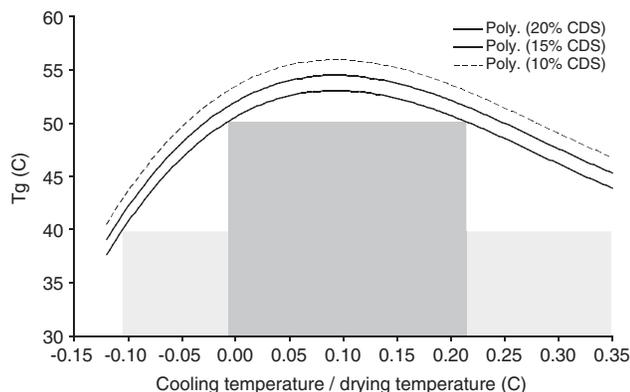


Fig. 4. Predicted optimum cooling temperature/drying temperature ranges for glass transition temperature. Dark gray region indicates the optimum temperature range for DDGS when the environmental temperature is $\sim 48^{\circ}\text{C}$ (desert like); light gray region indicates the optimum temperature range for DDGS when the ambient temperature is 35°C (summer in US Midwest). As a worst case scenario for flowability, 20% (wb) CDS levels were used for all predicted ranges.

Higher fat levels facilitate liquid melting, flow, and solid bridge formation, which in turn can create flow problems in the DDGS (Adhikari et al. 2001).

DDGS is usually shipped under varied ambient temperature conditions, and it is sometimes kept in the rail car for weeks before it is finally delivered to the consumer and unloaded. According to Fig. 4, for high summer temperatures (e.g. desert-like situations), where the ambient temperature is often $\sim 40\text{--}48^{\circ}\text{C}$, the Tg should be higher than this ambient temperature, so that there will be no structural collapse or stickiness. At Tg, a rubbery phase transition takes place, and the biomaterial can become very sticky. In fact, stickiness and flow problems are mostly found near Tg. Thus, from Fig. 4, in order to have Tg above 50°C for 20% CDS (as worst case scenario), the optimum range for cooling temperature/drying temperature

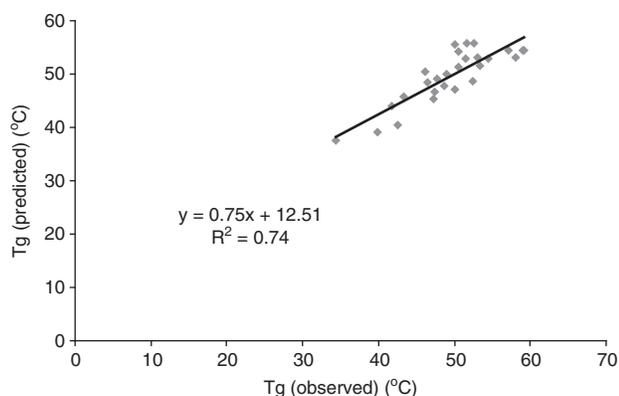


Fig. 5. Plot of predicted Tg vs. observed Tg for the entire DDGS samples prepared at varying CDS, drying temperature, and cooling temperature.

ratio (—) should be between -0.01 to 0.22 , as indicated by the dark gray color region in Fig. 4, so that Tg occurs at or above 50°C . Furthermore, in order to have the cooling temperature/drying temperature (—) below -0.01 , the cooling temperature must be around -12°C , as indicated in Table 4. Having the cooling temperature at sub-zero range (-12°C) could enhance the crystallization of water particles. Thus, due to the effect of crystallization there will be reduction of Tg. This transition and collapse at Tg can enhance and facilitate stickiness of foods and biomaterials (Bhandari and Howes 1999). Amorphous food powders (like DDGS) are extremely hygroscopic in nature, and they pick up moisture even at small temperature and relative humidity changes, which increases the rate of crystallization of the overall product and depresses the Tg (Peleg and Hollenbach 1984). Therefore, to have free flowing DDGS at hot conditions, where ambient temperatures may rise to $\sim 48^{\circ}\text{C}$, the optimum ratios of cooling temperature/drying temperatures (—) from -0.01 to 0.2 would have to be achieved, in order to avoid possible stickiness and flow problems.

Similarly, for normal ambient temperatures in the Midwest US, where the summer temperatures can reach $\sim 35^{\circ}\text{C}$, for 20% CDS (as worst case scenario), the cooling/drying temperature should be in the range either from -0.105 to 0.33 , or even greater than 0.33 , so that the Tg for DDGS is at or above 40°C . This wide range of cooling temperature/drying temperature is indicated by the light gray color region in Fig. 4. When a lower Tg value (i.e., 40°C) is acceptable, more flexibility is allowed in the range of cooling temperature/drying temperature ratio than for a higher Tg value (50°C), as predicted in Fig. 4.

Fig. 5 presents a plot of Tg predicted obtained from Eq. 1 (Fig. 3) vs. observed Tg values for DDGS samples prepared with varying CDS, drying temperature, and cooling temperature levels. Overall we can observe that the regression line fitted the data points well ($R^2 = 0.74$). However, the deviation of some data points may be due to inherent variability in the dataset. Also, DDGS samples were prepared in two sets, one set with cooling temperatures at -12 and 35°C and the other set with cooling temperature at 25°C , leading to variability in the overall dataset.

CONCLUSIONS

Glass transition temperature can influence stickiness in bulk solids such as DDGS. From this study, we found the effect of drying temperatures, cooling temperatures, and CDS levels on Tg values. Our results indicated that there were interaction effects between all the independent variables. Samples cooled at -12°C showed slightly lower Tg compared to samples cooled at 35°C , indicating more stickiness in DDGS cooled at -12°C . Non-linear regression analysis could predict Tg with $R^2 = 0.74$. For each CDS level, the optimum range of cooling temperatures/drying temperature ratio (—) was calculated so that DDGS should not show caking problems when shipped across the country under very hot conditions (ambient temperatures $\sim 45^{\circ}\text{C}$). Additionally, for average

summer temperatures in the Midwest (ambient temperatures $\sim 35^{\circ}\text{C}$), the optimum range of cooling temperature/drying temperature ratio was calculated. Thus, this research is an important step toward understanding the role of processing conditions on DDGS stickiness. The response surface and the overall global model for $T_g = f$ (drying temperature, cooling temperature, and CDS level) was useful in predicting safe ranges of cooling/drying temperature ratio (–) for DDGS production and cooling. More studies with wider ranges of CDS levels, cooling conditions, and drying temperatures would be a future step to increase understanding of glass transition temperature (T_g) and flowability issues in DDGS.

DISCLAIMER

Mention of trade name, propriety product or specific equipment does not constitute a guarantee or warranty by the United States Department of Agriculture and does not imply approval of a product to the exclusion of others that may be suitable.

ACKNOWLEDGEMENTS

The authors would like extend gratitude to Dakota Ethanol, LLC (Wentworth, SD) who contributed coproduct samples for this study; and the South Dakota Corn Utilization Council (SDCUC), South Dakota Agricultural Experimental Station, and USDA-ARS for providing facilities, equipment, and financial support.

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