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Effects of Varying CDS, Drying and Cooling Temperatures on Glass Transition Temperature of DDGS

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Abstract. Distillers dried grains with solubles (DDGS), a co product of the corn-based fuel ethanol industry, is used widely as an animal feed. Due to increased demand for DDGS in livestock markets it has become essential to transport DDGS over long distances. Flowability problems in DDGS, due to particle caking, often create nuisance in storage and transportation. Materials above the glass transition temperature (Tg) can exist in a “rubbery state,” this condition can often be responsible for structural collapse, particle agglomeration, and caking of materials. This study investigated the effects of varying CDS (10, 15, and 20%, wb), drying (100, 200, and 300°C), and cooling temperature (-12 and 35°C) levels on the Tg of DDGS. Tg was found to range from 34 to 58°C and 41 to 59°C for cooling temperatures of -12°C and 35°C, respectively. Results indicated that there were significant differences due to the levels of CDS, drying, and cooling temperatures, individually as well as simultaneously. There were also significant interaction effects. Response surface regression yielded a predictive model with R² of 0.74 and SEM of 3.16. Using this regression equation, optimum ranges for drying and cooling temperatures were determined for various ambient conditions. These may be used to avoid flow problems.

Keywords. Caking, Distillers wet grains, Drying, Flowability
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 consumption will increase in coming years. To decrease our dependence on non-renewable fossil fuel sources, focusing on renewable energy sources like corn-based ethanol is important. With remarkable growth in the corn-based fuel industry, large amount of corn based Distillers Dried Grains with Solubles (DDGS) is being produced. The production of DDGS in the year 2007-2008 fiscal was calculated to be around 30.4 million metric tons and is projected to grow in the future (RFA, 2010). For over two decades, due to dense protein, fat, and energy content, DDGS has been used as livestock feed for cattle, swine, and poultry. 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). Due to a relatively high amount of protein and energy, DDGS is used as livestock feed for both ruminant and non-ruminant livestock (Ganesan et al., 2007a). To meet the high demand of DDGS in the livestock feed industry, transporting and handling of DDGS over long distances is important. DDGS is exposed to different environmental and physical conditions such as fluctuations in temperatures, humidity, etc.

Like many agricultural and food materials, DDGS is hygroscopic in nature, (i.e., it has the ability of absorbing moisture when exposed to moisture during the handling and storage). Due to these situations, DDGS particles tend to agglomerate to form solidified cakes or agglomerates. Caking or hardening of DDGS leads to difficulties during its unloading from rail cars and storage vessels, and ‘caking’ significantly contributes to economic losses and labor cost to break up the agglomerates (Rock and Schewedes, 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 to 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, and for the process to proceed, the surface of the particle or at least certain sites should become fluid. Fluidity among powder particles can be caused by the melting of fat molecules and addition of water molecules. During these conditions, the particles become sticky and caking occurs (Peleg, 1993).

Drying is one of the major food and biomaterial processing operations, and several drying operations like hot air (fixed or fluidized bed), freeze or spray drying is generally applied. For dried products, a significant amount of the product remains in the amorphous state, mainly due to a short residence time in the dryers. This mixture of crystalline and amorphous states can lead to a change in the physical state of the product and has the possibility to affect the physico-chemical characteristics of the material (Bhandari and Howes, 1999), especially changes in temperature. This change in the state of the matrix can lead to a phase transition of the amorphous state to a “rubbery state” which is also known as a glass-liquid transition state. This state is measured by the glass transition temperature (Tg). This can also used to predict the storage, flow, and processing condition of food and other biomaterials (Le Meste, 2002). The structural collapse of the product during air or freeze drying, or during the 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
Glass Transition Temperature (Tg)

Glass transition temperature (Tg) is specifically the property of an amorphous material. Amorphous materials are formed in unstable or non-equilibrium conditions where the solvent medium is removed by rapid supercooling or drying in a relatively short residence time. Thus, these materials are relatively not at thermodynamic equilibrium and behave like an extremely viscous “glass” having a viscosity above $10^{12}$ 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 transition temperature regions. First order transitions are those at which the first derivate of the thermodynamic functions suffer discontinuity in the heat capacities and the thermal expansion coefficients. They are the changes that take place between solid, liquid and gas states. At the second order transition temperature, a step change occurs in the properties that suffers discontinuity in the first order transition (Roos, 2003).

Glass transition is a property of a non-equilibrium system and cannot be classified as a pure phase transition, and should be rather be categorized as a state transition (Roos, 2003). For example, in a typical spray drying of milk powder, the solid particles are produced at high drying temperatures and in 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). The glass transition is often described with a single temperature value but can occur over a range of temperatures (Roos, 2003). At Tg, the viscous amorphous “glassy state” changes to a more mobile structure with less viscosity known as the “rubbery state” (Sá et al., 1998).

The glass transition can occur in both cooling and heating processes due to the removal of solvent (plasticizer), and it is a time-dependent phenomenon as it is a non-equilibrium state transition occurrence in amorphous powders (Roos, 2003). The Tg is characterized by an endothermal change in the apparent specific capacity that can be detected by using Differential Scanning Calorimetry (DSC) (Roos and Kharel, 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 (Sauerbrunn et al., 1992). Other manifestations of Tg are the sticky point temperature (Ts) and the collapse temperature (Tcot). All of these parameters measure the ability of the powder to cake at given temperature (Peleg, 1993).

Glass Transition Temperature in Food Applications

Food systems are complex mixtures of carbohydrates, proteins, lipids, water, variety of other minor components, and water. Use of DSC to observe thermograms and glass transition for protein denaturation or gelatinization of starch has been well established. Tg patterns are also extensively studied for melting and recrystallization of lipids, where there are complex polymorphic systems (Roos, 2003). There are changes related to glass transition temperature in food material like stickiness and caking in food powders, collapse in freeze dried food powders with sugars, 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). For example for the improved quality of freeze or air dried tomato and other fresh vegetables, glass transition temperatures have been used extensively to understand changes in the molecular mobility and preserves the original functionality of vegetables (Telis and Sobral, 2003). Tg evaluation for aqueous glucose-fructose solution gives an idea of storage and handling conditions for foods with high sugars components. Arvanitoyannis and Blanshard (1993) found the plasticizing effects of water molecules on sugar-rich food compounds by measuring Tg of the food samples. According to Dell Valle et al., (1999), shrinkage of food particles during high temperature drying not only affects the drying rate but also the physical and flavor characteristics of fruits. Also, correlation between shrinkage, food quality, and glass transition temperature was found for fruits and plant based materials (Dell Valle et al., 1999). According to Bellows and King (1973), the shrinkage of the fruits is minimal where the product is kept at a temperature below the Tg, and it favored better overall fruit quality.

Perishable and short shelf life fruits like strawberry, can be freeze-dried and then rehydrated before final use. Removal of water during processing often creates non-equilibrium amorphous state, and consequently changes the food material to a “glass transition state.” The “glassy state” creates dramatic changes in the physical and textural properties of the food materials (Moraga et al., 2004). There have been studies to examine the correlation between structural, functional, and textural properties of snacks or baked food materials vs. glass transition (Slade et al., 1993). Additionally, Tg applications have been found in research related to physiochemical properties of starch, gluten, and sucrose in food components (Slade, 1984). For baked cookies, state diagrams obtained from Tg and water activity data were used to study the water removal effect of sucrose, structural collapse, and textural properties (Slade et al., 1993). Sucrose dissolution and gelatinization of starch in cookie baking has been explained well with glass transition changes (Fuhr, 1962; Slade et al., 1993). Common sugars such as fructose, glucose, and sucrose inherently have a very low Tg, and their influence to depress the Tg is very significant in sugar rich food systems (Bhandari and Howes, 1999; Jouppila and Roos, 1994). Kasapis et al. (2004) found that for compound with high sugar levels, there were dramatic structural collapses of the food networks. The glassy behavior and stickiness was observed for low temperature food products, even though there was decrease in the overall sugar levels.

All amorphous substances are metastable, and thus, can crystallize over time during storage. If a local portion of the product picks up moisture, Tg 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 resulting in caking (Jouppila and Roos, 1994; Pelleg and Hollenbach, 1984). The interaction of water with solids is a prime cause for food powders to stick together in low moisture food products. Properties like viscosity, surface tension, and solvation energy makes water a suitable catalyst for stickiness, caking, and collapse of food and particulate systems. Water acts as a plasticizer, helps in lowering the glass transition temperature for low-moisture foods and biological materials. Furthermore, water can exist on particles 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). According to Roos and Karel (1991), for lactose, sucrose, and fructose solutions the relation of Tg and crystallization rates can be stated as:
\[
\log_{10}\left(\frac{t}{t_g}\right) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}
\] (1)

Where, \( t \) is the time of crystallization, \( t_g \) is the time to crystallize at glass transition, \( C_1 \) and \( C_2 \) are the constants (17.44 and 51.6 K respectively), and \( T \) is the temperature (K). This equation (1), also known as William-Landel-Ferry (WLF) model, is based on the thermochemical mechanism theory developed for caking in amorphous powders by William et al. (1955). Jouppila et al. (1997) found significant effects of moisture, storage time, and \( T_g \) on lactose crystallization rates in skim milk powder. \( T_g \) studies have been done to evaluate recrystallization of starch, retrogradation of starch gels, and effect of lipid molecules by Farkas and Farkas (1996). \( T_g \) has also used to assess the effect of color change for wheat gluten. Moisture and different pretreatment conditions have been found to affect the browning and non-enzymatic reactions in food polymer, and thus, can affect the overall structural properties of food networks, which is detected by \( T_g \) measurements (Fujio and Lim, 1989). According to Moraga et al. (2004), there was a loss of crunchiness and quality of snack food items when the transition from the glassy to the “rubbery” state occurs. 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. Figure 1 represents the reduction of relaxation time and other change in mechanical properties in food materials, based on Roos (2003).

**Degree of Polymerization and Plasticization**

The glass transition temperature (\( T_g \)) is strongly dependent on the molecular weight of the material and is related as:

\[
\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{K}{DP}
\] (2)

Where, \( DP \) is the degree of polymerization, \( K \) is a constant, \( T_{g\infty} \) is the high molecular weight limit of \( T_g \) (used to describe the molecular weight dependence of \( T_g \) in a homogenous polymer series). \( T_g \) is related to moisture, increase in moisture will decrease the \( T_g \) (Slade and Levine, 1995). In amorphous complex food matrices, which contain carbohydrates and proteins, water acts as a plasticizer, (i.e, the free volume of the material increases with increasing water content) resulting in a decrease in the \( T_g \). The lowering of \( T_g \) will cause more stickiness in powders even at normal environmental conditions. Thus, changes in water content (and water plasticization) can affect food properties (Roos, 2003). Plasticization, or \( T_g \) decrease, mainly due to water molecules, but also other solutes can also act as plasticizers (Le Meste et al., 2002). For example, according to Bizot et al. (1992), depression of \( T_g \) due to the addition of glycerol in raisins was observed. Branching of polymers and internal plasticization took place due to the glycerol addition in raisins.

Water acts as a plasticizer enabling the mobilization of amorphous components. 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 the Gordon and Taylor (1952) equation. Finally, increase in the concentration of plasticizing agent (e.g. water) can decrease \( T_g \), and in turn will facilitate time-temperature dependent physical and chemical properties in food, affecting significantly product quality during storage and handling (Dell Valle et al., 1999; Roos and Karel,
According to Slade et al. (1993), the depression in Tg due to water or other plasticizing agents may be of advantage or disadvantage for variety of ingredients. Loss of crispiness and quality due to reduction in Tg values was found in Bhandari and Howes (1999). More details of water acting as a plasticizer in starch, starch hydrolysis products, and low molecular weight sugars can be found in Donald et al. (1993), Hemminga et al. (1993), and Joullioppa and Roos (1992).

**State Diagrams**

Food processing and handling is often affected by fluctuations in temperature, moisture contents, and time (Slade et al., 1993). Biomaterials with a propensity to crystallize need to be examined critical water content and critical water activity, in order to avoid crystallization and improve shelf life (Moraga et al., 2004). The water content of the product, its physical state, temperature, and sorption isotherm is represented in state diagrams. State diagrams are useful tools in process optimization and formulation (Moraga et al., 2004). State diagrams show the critical water content and water activity, which is important in explaining changes in time-dependent mechanical and flow properties that are governed by Tg. Such state diagrams provide guidelines for handling powders. State diagrams are also referred to as stability/mobility diagrams. According to Jaya and Das (2007), the critical water activity was found to be lowest for pineapple powder 0.41 (moisture content is 5% db) and Tg at 43°C, and hence, it was first to pick up moisture (right after drying it had 0.1% db moisture content) and showed stickiness problems, compared to mango and tomato fruit powder. The schematic representation of a state diagram to represent the relationship between moisture content, water activity, Tg, and calculation of critical water content and critical water activity, is given in Figure 2. Usually, an increase in the water content leads to a decrease in Tg due to water absorption, and the biomaterial may change from the glass to the “rubbery state’ (Sá et al., 1998).

DDGS is commercially produced from corn-based ethanol plants, operated mostly using the dry milling process. In the production path of DDGS, wet distillers grains are mixed with condensed distillers solubles (CDS) and the dried in a drum dryer to produce DDGS. After fermentation of starch and other fermentable component to ethanol, the non-fermentable materials are divided roughly into two fractions - wet distiller’s grains and CDS (NCGA, 2008). In the industrial drying operation, often the drying temperatures range from 1000°F (inlet) to 300°F (outlet) (Bhadra et al., 2009a). Flowability and caking of DDGS particles are multivariate processes and depend on particle shape, size, chemical composition, and other physical properties (Bhadra et al., 2009b). Kleinschmit et al. (2005) reported that variation in DDGS physical, chemical and flow properties are mainly due to variation in operating parameters during DDGS formation and not due to the variation in corn quality. Therefore is it evident that for flowability of DDGS, drying temperature, and CDS levels are important factors that needs to be explored in depth. After production, DDGS is often transported over long distances through diverse ambient temperature conditions, Variations in ambient/storage temperature can interact with the relative humidity of the product. Water adsorption characteristics interact with humidity, which in turn affect the overall handling and flowability of DDGS. This was reported by Ganesan et al., (2007a).

Tg measurement to quantify stickiness and flow problems in DDGS with varying CDS and drying temperatures was done previously in Bhadra et al. (2009d). Ganesan et al., (2007b) also studied Tg with regular and reduced fat DDGS. However, the effect of Tg with varying CDS, drying temperatures, and cooling temperatures in DDGS has not yet been investigated was not done, until now. Thus, the main objectives of this paper were:
1) To evaluate the behavior of Tg 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 Tg = f (drying temperatures, cooling temperatures, and CDS levels).

3) To provide an optimum range of drying/cooling temperatures and CDS levels, in order to ensure safe handling and storage of DDGS.

Such broad spectrum work on Tg 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 distiller’s wet grains (DWG) and condensed distiller’s solubles (CDS) were collected from a commercial ethanol plant in South Dakota, and were stored under frozen condition (-10 ± 1°C). CDS was added to the DWG at levels of 10, 15, and 20% (wb) and then mixed thoroughly (Model no D300, Hobart Corporation, Troy, Ohio) for 5 min. 300 gm of combined samples were spread uniformly onto a thin steel plates which were 38 cm × 27 cm × 1 cm. They were dried in a laboratory scale (model no 838F, Fisher Scientific, Pittsburg, PA) oven. Drying was done at three selected temperatures (100, 200, and 300°C); temperature selection was based on interviews and discussions with industry experts, 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 ~ 8% (db) moisture content. After drying, the DDGS was cooled and stored in a refrigerator at -12°C or in an oven at 35°C. For both cases, the samples were stored for 3 months and then Tg measurements were carried out. Thus, in total we had 18 (3 drying temperature x 3 CDS levels x 2 cooling temperatures) experimental runs for Tg measurements, and each run was replicated three times.

Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) of the DDGS samples which were prepared with various conditions were evaluated using a differential scanning calorimeter (DSC) (Q series,™ Model Q200, TA Instruments, New Castle, DE). The DSC was equipped with an autosampler. The Tzero aluminum sample pan of 40 µl was subjected to a heating range of -20 to 100°C with a heating rate of 5°C/min; this was based on the previous literature on DDGS (Ganesan et al., 2007c and Bhadra et al., 2009). An empty Tzero aluminum pan of 40 µl was considered the reference cell. A refrigerated cooling system (RCS40), provided with DSC module, and has the ability to control the sample temperature from -40°C 400°C. Universal Analyzer software provided by TA instruments (New Castle, DE) was used to analyze Tg from the thermograms, using the half height integration method.
**Statistical Analyses**

For the 18 treatment combinations with 3 replications, a full factorial design (3 CDS x 3 drying temperature x 2 cooling temperature = 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 95% confidence level (i.e., \( \alpha = 0.05 \)), and were performed to determine main and interaction effects among the treatment combinations for each CDS levels, drying temperature, and cooling levels. TableCurve 3D v.4.0.01 (SYSTAT Software, Inc., San Jose, CA) was used to develop regression equations for 3D response surface modeling of \( \text{Tg} = f(\text{CDS}, \text{drying temperature}, \text{and cooling temperature}) \).

**Results and Discussion**

**Main Effects and Treatment Combination Effects**

Table 1 presents the main effects of CDS, drying temperature, and cooling temperature on Tg. A significant effect on Tg was observed for increase in drying temperature from 100 to 200°C, but a further increase of drying temperature to 300°C did not significantly impact the Tg. For CDS, a significant main effect was noticed when the CDS level was increased from 15 % (wb) to 20% (wb). Similarly, for cooling temperatures there was also a significant main effect on Tg, as indicated in Table 1. According to Bhadra et al. (2009d), there were significant effects on flow and physical properties due to varying drying temperature and CDS levels. Studies on the effect of drying temperature, CDS, and storage/cooling temperature on Tg were not reported. Thus, our results could not be compared. Tg is responsible for the dramatic changes in molecular structure of a material; it effects the stickiness of the product (Levine and Slade, 1988; Roos and Kharel, 1991a&b). Thus, it appears that varying CDS, drying, and cooling temperatures impacts the Tg of the material, which in turn significantly affects the physical behavior and overall flowability of DDGS. In a similar study by Bhadra et al. (2009d), for DDGS samples, it was found that \( \text{Tg} = f(\text{drying temperature}, \text{CDS}, \text{and moisture content}) \) was significant, and a predicted response surface plot with \( R^2 \) of 0.74 was established. Also, the above relationship yielded a regression equation of \( R^2 \) of 0.82, using a modified Gordon-Taylor model. More details on the parameter estimates and regression plots can be found in Bhadra et al. (2009d).

Table 2 indicates the treatment combination effects on Tg due to varying CDS levels, drying temperatures, and cooling temperatures. Significant treatment combination effects were found for all independent variables. For cooling temperature as -12°C, Tg was found to range from 34 to 52°C, while for +35°C (cooling temperature), the Tg was found from 41 to 59°C. Thus, there was a reduction in observed Tg for lower cooling temperatures. Depression of Tg due to plasticizing agents like water, sugars, etc. was seen other biomaterials such as air dried apple and strawberry samples (Dell Valle et al., 1998; Moraga et al., 2004). Water is the major plasticizing agent in biomaterials and it acts to lower Tg. Water itself has a very low Tg of -135°C (Johari et al., 1987). The reduction of Tg is responsible for structural collapse in food systems, loss of product quality during long term storage, and inefficient handling (Roos and Kharel, 1991; Roos 1987). Possibility of caking and agglomeration of DDGS increases if it is cooled at lower temperatures like -12°C, instead of +35°C. At freezing temperatures, the chance of moisture absorption and change in relative humidity is high. 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°C) would have revealed more changes in Tg, but this was beyond our experimental design. At low temperatures (~ -12°C), crystallization of water and fat molecules, and changes in relative humidity, can trigger caking and stickiness. For complex food materials like DDGS, hygroscopic products pick up moisture, and the Tg is locally depressed at a point, which in turn accelerates the rate of crystallization and thus there is an overall depression of Tg, loss of structure, and the flowability problems in food powders (Bhandari and Howes, 1999). For lactose samples, high moisture content increases water activity and crystallization rate, yielding more stickiness and further lowering of Tg (Senoussi et al., 1995). According to Bellows and King (1973), for most food materials, the structural collapse range from -5 to -60°C depending on the composition and amount of sugars present in the materials. During DDGS production at high drying temperatures, certain sites on the particle surface are exposed, causing fat molecules to melt, and can form solid bridges. Such changes could also trigger particle caking, even though the DDGS samples (stored at 35°C) showed better Tg values (Peleg, 1993).

**Interaction Effects**

The interaction effects for Tg with varying CDS, drying temperature, and cooling temperature levels are given in Table 3. Interaction between drying temperature*cooling temperature was not significant, as p-value (0.9157) was greater than \( \alpha = 0.05 \). Similarly, for the interaction between CDS and cooling temperature, p-value (0.1368) was greater than \( \alpha \). However, the interaction between drying temperature*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 among drying and cooling conditions, as well as CDS levels. This is responsible for changes in Tg, and thus, caking and agglomeration in DDGS. To further explain the effect of the interactions, relative contribution of the sum of squares for each interaction was determined. The SS were re-calculated to percentage basis (Figure 3) and it is evident that highest significant main effect was drying temperature (50.53) and the highest significant interaction effects was found for drying temperature*CDS (10.16).

**Response Surface Regression**

The overall response surface plot which represents Tg =f (drying temperature, cooling temperature, and CDS) is provided in Figure 4. For this overall modeling, we pooled our Tg 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 data from our previous samples using similar drying temperature and CDS levels, but cooled at 25°C (room temperature). The overall non-linear regression equation obtained from the response surface plot (Figure 4) with \( R^2 \) of 0.74, F-statistic of 47.37, and standard error of 3.15 is given below in equation 4 as:

\[
z = a + bx + cy + dy^2 + ey^3
\]

Where, z is Tg (°C), x is CDS (% wb), and y is cooling temperature/drying temperature (-). The parameter estimate values are as follows: a = 56.28, b = -0.28, c = 57.29, d = -370.12, and e = 433.56. Regression model with \( R^2 > 0.90 \) was not obtained due to scatter in the Tg data. The standard error was found to be low, which indicates that the overall response curve fit well to the observed Tg data.

Using equation 4, predicted Tg due different cooling temperature/drying temperature (-) ranges, for each CDS level can be predicted (Figure 5). From Figure 5, we can observe that for 10%
CDS, the predicted Tg was found to be slightly higher than the predicted Tg for 20% CDS. CDS, also known as “syrup” in the bioethanol industry, is found to contain relatively higher fat levels (Buchheit 2002; Cruz et al 2005). Thus, higher CDS levels indicate higher fat levels in DDGS. Typically, in commercial DDGS samples it has been found that the CDS levels often from 11% (db) to 15% (db) (Bhadra et al., 2009b). Higher fat levels will facilitate melting and solid bridges due to melting of fat molecules, which in turn can create flow problems in 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. For high summer temperatures (e.g. desert-like situations), where the ambient temperature is ~ 40-48°C, we want the Tg to be higher than this ambient temperature, so that there will be no collapse or stickiness. At Tg, the rubbery phase transition takes place, and structural collapse of the biomaterial takes place. Thus, stickiness and flow problems are mostly found near Tg. Thus, from Figure 5, in order to have Tg above 50°C for 20% CDS, we need to have the optimum range for cooling temperature/drying temperature (-) between -0.01 to 0.2, as indicated by dark gray color region, so that Tg occurs at 50°C. Furthermore, in order to have cooling temperature/drying temperature (-) below -0.01, the cooling temperature must be around -12°C, as indicated in Table 4. Having the cooling temperature <-12°C (i.e., cooling temperature/drying temperature (-) <-0.01) would enhance the crystallization of water particles. Also, lower temperature may also facilitate increase water plasticization effects due to changes in the relative humidity. Thus, due to combined effect of crystallization and plasticization there will be reduction of Tg. This transition and collapse at Tg would enhance and facilitate stickiness of any food/biomaterial (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 depress the Tg (Peleg and Hollenbach, 1984). Therefore, to have free flowing DDGS at hot conditions, where ambient temperature may rise around ~ 48°C we would need to have the optimum ranges of cooling temperature/drying temperatures (-) from -0.01 to 0.2, in order to avoid possible stickiness and flow problems.

Similarly, for normal ambient temperature in the Midwest US, where the summer temperatures can go high ~ 35°C, for 20% CDS, the cooling/drying temperature should be in the range from -0.105 to 0.33 or >0.33, so that the Tg for DDGS is at 40°C. This range of cooling temperature/drying temperature is indicated by light gray color region in Figure 5. For a lower Tg value (40°C), there is more flexibility in the cooling temperature/drying temperature range than for a higher Tg value (50°C), as predicted in Figure 5.

Conclusion

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 multiple regression analysis could predict Tg model with R²= 0.74. For each CDS level, the optimum range of cooling temperatures/drying temperatures (-) were calculated so that DDGS should not show caking problems when shipped across the country under very hot conditions (ambient
temperatures ~ 45°C). Additionally, for average summer temperatures in South Dakota (ambient temperature ~ 35°C), the optimum ranges of cooling temperature/drying temperature were calculated. Thus, this research is an important step to understand the role of processing conditions on DDGS stickiness. The response surface plot and the overall global model for Tg=f (drying temperature, cooling temperature, and CDS level) was useful in predicting safe ranges of cooling/drying temperatures (-) for DDGS production and storage. 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 (Tg) and flowability issues in DDGS.

Acknowledgements

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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.

References


Bhadra, R., K., Muthukumarappan, and K. A. Rosentrater. 2009c. Measurement and comparison of glass transition and sticky point temperatures for DDGS as affected by
CDS and drying temperature levels. ASABE International Conference, 21-24 June, Reno, NV. Paper No. 096614, St. Joseph, MI: ASABE.


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

<table>
<thead>
<tr>
<th>Independent Variable</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CDS (%, wb)</strong></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>49.87a</td>
</tr>
<tr>
<td></td>
<td>(0.78)</td>
</tr>
<tr>
<td>15</td>
<td>49.19a</td>
</tr>
<tr>
<td></td>
<td>(0.84)</td>
</tr>
<tr>
<td>20</td>
<td>45.99b</td>
</tr>
<tr>
<td></td>
<td>(0.92)</td>
</tr>
<tr>
<td><strong>Dry Temperature (°C)</strong></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>42.19b</td>
</tr>
<tr>
<td></td>
<td>(0.98)</td>
</tr>
<tr>
<td>200</td>
<td>51.91a</td>
</tr>
<tr>
<td></td>
<td>(1.53)</td>
</tr>
<tr>
<td>300</td>
<td>50.95a</td>
</tr>
<tr>
<td></td>
<td>(2.01)</td>
</tr>
<tr>
<td><strong>Cooling Temperature (°C)</strong></td>
<td></td>
</tr>
<tr>
<td>-12</td>
<td>45.02b</td>
</tr>
<tr>
<td></td>
<td>(1.78)</td>
</tr>
<tr>
<td>35</td>
<td>51.68a</td>
</tr>
<tr>
<td></td>
<td>(2.01)</td>
</tr>
</tbody>
</table>

†Tg is glass transition temperature (°C); CDS is condensed distillers solubles (% wb); Different letters indicate significant differences due to various levels of the given independent variable, LSD at α=0.05.
Table 2: Treatment combination effects due to varying CDS, drying, and cooling temperature levels on DDGS glass transition temperatures.†

<table>
<thead>
<tr>
<th>Treatments</th>
<th>CDS (%, wb)</th>
<th>Drying Temperature (°C)</th>
<th>Cooling Temperature (°C)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>100</td>
<td>-12</td>
<td>42.46</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
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<td>-12</td>
<td>39.83</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>100</td>
<td>-12</td>
<td>34.43</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>200</td>
<td>-12</td>
<td>52.49</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
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<td>-12</td>
<td>50.11</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>200</td>
<td>-12</td>
<td>43.34</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>300</td>
<td>-12</td>
<td>46.13</td>
</tr>
<tr>
<td>8</td>
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<td>300</td>
<td>-12</td>
<td>47.74</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>300</td>
<td>-12</td>
<td>48.65</td>
</tr>
<tr>
<td>10</td>
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<td>100</td>
<td>35</td>
<td>47.33</td>
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<td>41.82</td>
</tr>
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<td>200</td>
<td>35</td>
<td>59.11</td>
</tr>
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<td>15</td>
<td>200</td>
<td>35</td>
<td>53.07</td>
</tr>
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<td>20</td>
<td>200</td>
<td>35</td>
<td>53.31</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>300</td>
<td>35</td>
<td>51.69</td>
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<tr>
<td>17</td>
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</tr>
<tr>
<td>18</td>
<td>20</td>
<td>300</td>
<td>35</td>
<td>54.41</td>
</tr>
</tbody>
</table>

†Tg is glass transition temperature (°C); CDS is condensed distillers solubles (% wb); Different letters indicate significant differences due to various combinations of independent variables, LSD at α=0.05.
Table 3: Interactions effects due to CDS, drying, and cooling temperature levels on DDGS glass transition temperatures.†

<table>
<thead>
<tr>
<th>Source</th>
<th>p-values</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>CT</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>CDS</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>DT*CT</td>
<td>0.9157</td>
</tr>
<tr>
<td>DT*CDS</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>CT*CDS</td>
<td>0.1368</td>
</tr>
<tr>
<td>DT<em>CT</em>CDS</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

† Tg is glass transition temperature (°C); CDS is condensed distillers solubles (% wb); DT is drying temperature (°C); CT is cooling temperature (°C); α=0.05.
Table 4: Predicted glass transition values for varying CDS, cooling, and drying temperatures using equation 4 (obtained from response surface modeling, Figure 4).†

<table>
<thead>
<tr>
<th>Cooling Temperature (°C)</th>
<th>Drying Temperature (°C)</th>
<th>Cooling Temperature/drying Temperature ratio (-)</th>
<th>CDS (%) , wb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>-12</td>
<td>100</td>
<td>-0.12</td>
<td>40.48</td>
</tr>
<tr>
<td>-12</td>
<td>200</td>
<td>-0.06</td>
<td>48.57</td>
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<td>300</td>
<td>-0.04</td>
<td>50.52</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
<td>0.25</td>
<td>51.40</td>
</tr>
<tr>
<td>25</td>
<td>200</td>
<td>0.13</td>
<td>55.66</td>
</tr>
<tr>
<td>25</td>
<td>300</td>
<td>0.08</td>
<td>55.89</td>
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<td>35</td>
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<td>0.35</td>
<td>46.73</td>
</tr>
<tr>
<td>35</td>
<td>200</td>
<td>0.18</td>
<td>54.45</td>
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<tr>
<td>35</td>
<td>300</td>
<td>0.12</td>
<td>55.77</td>
</tr>
</tbody>
</table>

† Tg is glass transition temperature (°C); CDS is condensed distillers solubles (% wb).
Figure 1: Effect of temperature, water activity, or water content on relaxation times and relative rates of mechanical changes in amorphous biological materials, based on Roos and Kharel (1991a).
Figure 2: State diagram representing the relationships between water content, water activity, and glass transition temperature for amorphous biological materials (based on Roos and Kharel, 1991a).
Figure 3: Proportion of total error explained by interaction effects among CDS (% wb), drying temperature (DT, °C), and cooling temperature (CT, °C) levels.
Figure 4: Best fit response surface relationship for glass transition temperature (Tg, °C) as a function of CDS (% wb), drying temperature (°C), and cooling temperature (°C).
Figure 5: 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 ~ 48°C (desert like); light gray region indicates the optimum temperature range for DDGS when the ambient temperature ~ 35°C (summer in South Dakota). As a worst case scenario for flowability, 20% (wb) CDS levels were used for all predicted ranges.