

**INVESTIGATIONS INTO PRACTICAL APPLICATIONS FOR THE CRITICAL WATER ACTIVITY FROM  
DYNAMIC DEWPOINT ISOTHERMS**

By

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**Abstract**

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Moisture plays an important role in the stability and storability of grain and grain based products. Stability factors such as microbial growth and texture are impacted by moisture and are well correlated to water activity, a measure of the energy status of water. The key to effectively using water activity as an indicator of product stability is to identify the critical water activity (RH<sub>c</sub>) where the rate of stability loss increases and shelf life ends. The RH<sub>c</sub> could be determined by interrogating pre-equilibrated samples at various water activities for quality performance and establishing the water activity where performance falls below acceptable levels. However, these types of studies tend to be labor and time intensive. A possible alternative that has shown promise is to identify the RH<sub>c</sub> by an inflection in the dynamic moisture sorption curve. Critical water activities determined using dynamic isotherms have been shown to be associated with glass transition in low molecular weight amorphous powders and could possibly be associated with other degradative change. The objective of this research project was to survey the dynamic isotherms of whole grain and grain-based products for an RH<sub>c</sub> that could be linked to a stability loss factor. Critical water activities were found in the dynamic isotherms of whole grain wheat and barley, oatmeal muffin premix, chicken gravy

premix, graham crackers, and shortbread cookies. The RHc of whole grain was found to be associated with the ideal water activity for tempered grain to produce flour whose water activity was below critical levels for microbial spoilage. The RHc of the premix powders was found to be associated with the wetting of the instant powders and initiation of dissolution. Finally, the RHc of the grahams and shortbread cookies was related to an abrupt loss of crispness. Comparison to previous studies and general practices indicated that the RHc values determined in this study were similar to those previously identified. Therefore, this study provides evidence that the RHc for the stability of grain based products can be determined from a dynamic isotherm rather than requiring a time and labor intensive study.

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## **Dedication**

This dissertation is dedicated to Shari, Joshua, Jacen, Jairden, Alexa, and Bethany who are my everything.

## GENERAL INTRODUCTION

The overall objective of the research presented in this dissertation is to investigate changes associated with the critical water activity (RH<sub>c</sub>) as identified by Dynamic Dewpoint Isotherms (DDI) of grain-based products. We wanted to know if complex stability studies could be replaced with a simple DDI analysis that identifies an RH<sub>c</sub>. The dissertation is divided into 5 sections. The first section presents a literature review of current information available on the topics of research presented in this dissertation, followed by four chapters structured as manuscripts for publication. The first chapter explores the connection between the critical water activity observed in the DDI curve of wholegrain wheat and barley to optimal tempering conditions for producing the most shelf stable flour. Chapter 2 further explores the relationship between the RH<sub>c</sub> of wholegrain wheat and barley and changes in water permeability of grain. Chapter 3 investigates the relationship between the RH<sub>c</sub> of oatmeal muffin and chicken gravy instant powders and physical properties of the powder. Finally, Chapter 4 looks at the connection between the RH<sub>c</sub> of graham crackers and shortbread cookies and changes in their crispness.

## LITERATURE REVIEW

For a grain-based food product to have value, it must have a shelf life long enough to allow for storage and distribution. Shelf life is the period after manufacture of a food product during which the product remains safe to consumers, retains desired sensory, chemical, physical and microbiological characters, and also complies with any label declaration of nutritional data [1]. Of the many factors, both intrinsic and extrinsic, that can influence shelf life, moisture is the most important and common to all products [2]. The impact of moisture on shelf life is best correlated to changes in water activity, and a key element to maximizing shelf life is to identify the water activity specification that maximizes shelf life [3]. Water activity changes can influence glass transition, lead to changes in the physical properties of powders, result in texture changes, and influence moisture permeability. Dynamic moisture sorption isotherms characterize changes in water activity due to moisture sorption and have the potential to identify water activity specifications that optimize shelf life.

### WATER ACTIVITY

The concept of water activity impacting stability has been known since the work of Scott [4, 5]. Water activity is derived from the 1<sup>st</sup> law of thermodynamics and is a measure of the energy of water as it is related to the relative activity of water in a system compared to that of pure water [6]. Under most conditions on earth, the activity of water in a sample, and hence the energy of the water, can be determined by dividing the partial pressure of water vapor in equilibrium with a sample by the saturated vapor pressure at the sample's temperature [6]. Water activity is equivalent to equilibrium relative humidity, but is typically reported as ratio between 0 and 1

instead of as a percentage. It is typically measured by placing a sample in a sealed chamber, allowing the water in the sample to come to vapor equilibrium in the headspace, and then measuring either the vapor pressure using chilled mirror technology or the equilibrium relative humidity using a humidity sensor [7].

## **MOISTURE SORPTION ISOTHERMS**

A moisture sorption isotherm characterizes the relationship between water activity, a qualitative measure of the energy of water, and moisture content, a quantitative measure of the amount of water in a system [8]. It provides a blueprint for water relations in a manufactured product and provides information about safety, quality, and shelf life. It is unique to the matrix of each product and is influenced by particle size, chemical makeup, and concentration of humectants such as salt or sugar [9]. There are two basic methods for determining moisture sorption isotherm characteristics, namely static and dynamic [10]. Traditional static methods for measuring moisture sorption isotherm properties rely on static equilibration to known water activity levels while tracking weight change. Newly developed dynamic methods directly measure water activity while gravimetrically tracking weight change, so there is no dependence on equilibration to known water activity levels to determine water activity [11].

Traditional isotherm methods depend on the equilibration of a sample to known water activity values and then measuring the equilibrium moisture content of the sample [8, 12-14]. This is most easily done by placing the sample in a sealed chamber over saturated salt slurries with



excess salt. Different water activity levels are achieved by using different salts. Adjusting a mixture of wet and dry air while monitoring the relative humidity with a sensor can also be used to control water activity. Different relative humidity levels are achieved by changing the proportion of dry to wet air. Some instruments are programmed to automatically change the water activity in a dynamic stepwise progression, usually referred to as Dynamic Vapor Sorption (DVS) [7]. The sample is held at each water activity level until weight levels off before moving to the next water activity. Common to all these isotherm methods is the dependence on equilibration to a known relative humidity level to determine each data point's water activity. True equilibration between the sample and the vapor source requires an infinitely long time. In practice, equilibrium is assumed when weight stops changing by a tolerable level. Increasing the tolerable weight change will speed up the equilibration process but water activity values become more uncertain.

Dynamic isotherm methods rely on direct measurement of water activity instead of equilibration to controlled water activity levels [11]. Weight change is still tracked gravimetrically by a balance in the controlled atmosphere, but samples are exposed to saturated wet air during adsorption and desiccated air during desorption instead of controlled humidity air. Samples exposed to wet or dry air will experience a change in water activity and moisture content. After roughly a 0.015 change in water activity ( $a_w$ ), air flow is stopped and the water activity and weight are measured. Water activity is typically determined using a chilled mirror method for highest accuracy [11]. Dynamic isotherm methods, while not a true measure of equilibrium conditions, provides considerable advantages in speed and data

resolution over static isotherm methods [11]. The Dynamic Dewpoint Isotherm (DDI) is an example of a dynamic isotherm method.

## **CRITICAL WATER ACTIVITY DETERMINATION USING DYNAMIC MOISTURE SORPTION**

### **ISOTHERMS**

The high resolution of dynamic isotherms makes it possible to visualize sudden changes in moisture sorption properties [11]. For many low water activity samples, initial water uptake is limited to adsorption on the surface of rigid glassy material. While not necessarily restricted to surface sorption, there are limited hydrogen binding sites for moisture sorption and the slope of the isotherm is relatively flat. If the sample experiences a matrix change, sorption switches to absorption as many more hydrogen binding sites become available in a now flexible, more mobile phase where the material and water can interact more freely [15-18]. Consequently, the slope of the isotherm curve steepens at the transition point as much more water is taken up with only a minor change in water activity, indicating a much more hygroscopic material. This drastic change in sorption properties results in a sharp inflection point in the isotherm curve [18, 19].

Efforts have been previously made to utilize the moisture sorption isotherm to identify matrix changes such as glass transition. Oksanen and Zografis [20] examined moisture sorption isotherms of poly(vinylpyrrolidone) (PVP K-30) at different temperatures to investigate the possibility of determining the glass transition using isotherm data. They used the traditional static saturated salt slurry method to produce the isotherms. In this method, samples are

equilibrated over salt slurries of various water activity values and then measured for moisture content. Because this method produces a limited number of data points, it requires empirical models for interpolation. Oksanen and Zografi [20] observed an upward trend in the isotherm curve where they measured the glass transition using DSC, but did not make an attempt to link the inflection point to the RHc. Bell [21], also working with static saturated salt slurry isotherms and limited data resolution, did not see any significant differences between the isotherms of PVP materials with different glass transitions and concluded that moisture sorption isotherms could not be used to determine the glass transition. Ubbink et al [17] also examined moisture isotherms of amorphous materials using static saturated salt slurry isotherm data. These authors identified the critical water activity corresponding to the glass transition as the intersection between two isotherm models. They postulated that water sorption characteristics should be different in the glassy state than in the rubbery state and consequently must be characterized using different models. Thus, they modeled the data in the glassy state using the Freundlich model, the data in the rubbery state using the Florry-Huggins model, and determined the critical water activity value where the two models intersected. Ubbink et al [17] compared the critical water activities they determined at 25°C with Tg data from DSC and found very good correlations ( $R^2 = 0.95$ ).

All of these investigators were hampered by limited data resolution. Dynamic isotherm methods now make it possible to observe real data points at each 0.01 change in water activity, eliminating the need to interpolate between data points with models [11]. Burnett et al. [22] modified static Dynamic Vapor Sorption (DVS) systems to produce dynamic isotherms by

flowing dynamically changing humidified air over amorphous samples. They observed sharp inflection points in the isotherm curve in the area of the glass transition, which they identified as the RH<sub>g</sub>. This inflection point was only visible with the higher resolution of the dynamic isotherm.

Carter and Campbell [10] investigated glass transition in spray dried milk powder using the DDI method. They discovered a sharp inflection point occurring at 0.43  $a_w$  when the isotherm temperature was 25°C. DD isotherms were generated for additional subsamples of spray dried milk powder (SDMP) and the inflection point appeared each time at the same water activity, indicating that the curve and the inflection point were repeatable. The water activity at which the inflection point in the curve occurred was identified as the RH<sub>c</sub> at the temperature of the isotherm. The isotherm curves were analyzed using a Savitzky-Golay [23] second derivative and the initial maximum in the second derivative curve was identified as the inflection point in the original curve. Changing the temperature of the isotherm changed the RH<sub>c</sub> where the inflection point occurred. At higher temperatures, the inflection point occurred at lower water activities (unpublished data). Carter & Campbell [10] determined that the relationship between isotherm temperature and RH<sub>c</sub> was linear and was in good agreement with T<sub>g</sub> as a function of  $a_w$  data determined using DSC on samples equilibrated to different water activities [24].

Yuan et al. [18] also investigated the glass transition using dynamic isotherms to identify RH<sub>c</sub> values for amorphous polydextrose. They chose to work with polydextrose because it is not susceptible to moisture-induced recrystallization. Using the DDI method, they generated DD

isotherms for polydextrose at temperatures ranging from 15°C to 40°C at 5°C intervals. As with the SDMP, they observed a distinct inflection point, representing the RHc for the glass transition, in the dynamic isotherm curve for polydextrose at each temperature. At 25°C, close to room temperature, they found the RHc for polydextrose to be 0.513  $a_w$  and the RHc decreased as temperature increased, similar to data shown for SDMP. As with the SDMP data, plotting RHc as a function of isotherm temperature was linear except at cold temperatures <20°C.

Yuan et al. [18] also obtained DD Isotherms at several different flow rates and found flow rate to have an influence on the RHc value. This would suggest that RHc is time dependent. The relationship between RHc and DDI flow rate was fairly linear, so they used regression analysis to extrapolate and predict RHc at a flow rate of zero (RHc<sub>0</sub>). They used both RHc and RHc<sub>0</sub> for further comparisons. They also compared various methods of finding the inflection point and found that the Savitzky-Golay [23] method was the easiest and provided similar results to other curve smoothing techniques, specifically an optimized MATLAB 2<sup>nd</sup> derivative algorithm and linear extrapolation.

Yuan et al. [18] determined Tg values for polydextrose at different water activity values using DSC and Modulated DSC (MDSC) and compared RHc values as a function of temperature to DSC first scan and MDSC Tg midpoint values. They found better than expected agreement between the two methods considering one method uses changes in heat capacity to determine the glass transition, whereas the other uses moisture sorption characteristics. At a constant

temperature, DDI RHc values were at higher water activity values and  $RHc_0$  values were closer in agreement with (M)DSC data than RHc values. These differences can likely be attributed to the time dependency of the measurements, where the RHc values from DD isotherms represent the time frame when the change in sorption properties due to a glass transition occur very quickly. This suggests that the inflection point in the dynamic isotherm curve representing the RHc will likely occur at lower water activity values if the samples are held at these water activity values long enough.

## **MOISTURE AND PHYSICAL STABILITY**

### **Glass Transition**

A glass transition can be described as a change that occurs in amorphous materials from a high viscosity, “frozen” glassy state to a lower viscosity, rubbery state [25]. A material in the glassy state behaves like a brittle solid, but without crystalline structure and only short ranges of order. The glass transition concepts that have long been understood in the field of polymer science can also be applied to food polymers [26, 27]. A phase transition from glassy to rubbery results in drastic changes in molecular mobility of food polymers, which has been linked to changes in product quality and can result in a loss of stability for low moisture amorphous foods [25, 28-30]. Foods in the glassy amorphous state exist in a metastable condition and remain stable for extended periods of time (months to years); however, once they have transitioned into the rubbery state, rates of degradative processes increase and shelf life decreases to weeks, days, or even hours [25]. Key physical stability factors identified to be linked to the glass

transition are an increased susceptibility to stickiness, caking, collapse and crystallization [31-37].

Common methods for investigating glass transitions have focused on identifying thermodynamic, mechanical, or dielectric changes while scanning temperature to identify the  $T_g$  [16]. This testing is done at constant moisture content. However, increased plasticization of amorphous glassy materials can also induce a glass transition even while temperature is held steady. Because moisture is the most common plasticizer in food materials, a critical moisture content, or more practically, a critical water activity or relative humidity ( $RH_c$ ) that results in a glass transition could plausibly be found by scanning water activity while holding temperature constant [18]. In theory, scanning temperature and scanning plasticizer level should lead to the same glass transition event. With the recent introduction of automatic isotherm generators capable of producing high resolution, dynamic moisture sorption isotherm curves, it is possible to observe glass transition events as sharp inflection points in the isotherm curve during dynamic moisture uptake.

A glass transition can be induced by increasing temperature until it exceeds  $T_g$  or by introducing increasing amounts of plasticizer. The addition of a plasticizer in the vicinity of an amorphous glass lowers viscosity, increases molecular mobility, and increases free volume [38]. As the amount of plasticizer increases, the glassy material experiences a change from the glassy to the rubbery state and then reaches a point where it can no longer support its own weight and collapses. Water is the main solvent and plasticizer in food ingredients and products [25, 39]. If

moisture continues to increase above the glass transition, molecular mobility continues to rise causing an increase in the rate of time dependent changes related to stability, such as stickiness, caking, collapse and crystallization [16].

The influence of moisture on T<sub>g</sub> can be easily examined by performing thermal analysis on samples that have been equilibrated to different water activities, and hence different moisture contents [25]. Multiple studies have shown a good correlation (R=0.98-0.99) between water activity and T<sub>g</sub> and this correlation is fairly linear over a water activity range of 0.1 to 0.7 a<sub>w</sub> [24, 31, 40]. Because T<sub>g</sub> values will change as water activity (and moisture content) changes, all T<sub>g</sub> studies should report the water activity or moisture content at which they were measured.

Low molecular weight amorphous materials such as amorphous simple sugars have very low T<sub>g</sub> values and are therefore susceptible to transitioning from a metastable glassy state to a less stable rubbery state under normal storage conditions. As the amount of plasticizer increases with increased water activity, the T<sub>g</sub> decreases until at some water activity it is equal to room, experimental, or storage temperature. The water activity value that decreases the T<sub>g</sub> to room temperature has been identified as the critical water activity or critical relative humidity (RH<sub>c</sub>) [18, 24, 32, 37, 41-43]. Like T<sub>g</sub>, RH<sub>c</sub> is unique to each material type and has been shown to increase with an increase in the molecular weight of the amorphous material [41]. As temperature increases, RH<sub>c</sub> decreases, just as T<sub>g</sub> decreases with an increase in relative humidity or water activity.



Since both temperature and moisture influence the glass transition, a  $T_g$  or  $RH_c$  should be reported with the corresponding water activity or temperature, respectively. Without these corresponding values,  $T_g$  and  $RH_c$  have limited usefulness in practical application. The interdependency of  $T_g$  and  $RH_c$  suggests that both temperature and humidity abuse can cause an amorphous food to experience a glass transition and in turn decreased stability. For amorphous glassy materials, such as dried powders stored in bulk and exposed to ambient relative humidity, a rise in ambient humidity above the  $RH_c$  will result in a glass transition and the powder will become susceptible to stickiness, caking, collapse and crystallization [25]. Water activity monitoring can be an effective tool to control loss of stability that can occur if these products experience a glass transition into the rubbery state. Conversely, glassy materials stored in good moisture barriers to prevent increases in water activity, but exposed to temperatures higher than the  $T_g$  for the product at its natural water activity will experience a glass transition and again will lose quality.

### **Caking of Powders**

Caking and stickiness of amorphous powders during handling, packaging and storage are ubiquitous problems in the food and pharmaceutical industries. Problems can happen both during the processing and storage of amorphous powders [16]. Stickiness refers to the tendency of a material to adhere to other surfaces or materials, which may or may not lead to caking [16]. Caking is the formation of permanent clumps due to the stickiness of particles which eventually can result in agglomerated solids, resulting in loss of functionality and lowered quality [44, 45]. Stickiness and caking reduce product recovery during drying, slow processing

time by clogging up hoppers and pipes, and reduce product shelf life. There are numerous proposed methods for ascertaining flow properties, from a simple test that consists of spinning a propeller in a test tube of powder to a complex flow testing rig fitted to a texture analyzer [46].

Caking and stickiness are water activity, time, and temperature dependent and are related to the collapse phenomena of the powder under gravitational force [47-50]. Stages in caking involve bridging, agglomeration, compaction, and liquefaction [49]. Factors known to affect caking kinetics may be divided into intrinsic properties of the powder itself (particle size distribution, hygroscopicity and charge of particles, state of the material, presence of impurities,  $T_g$ ) and external factors such as temperature, relative humidity and mechanical stress applied to the substance [49, 51]. If the powder is an amorphous glass, a transition from the glassy to rubbery state will cause the powder to become susceptible to caking and stickiness due to the increased mobility in the rubbery state [16, 30, 35, 52-54]. A glass transition can be induced by either temperature or moisture and protecting the powder against glass transition through packaging and storage conditions will help maintain its stability [16].

In addition to caking and stickiness, amorphous powders that have experienced a glass transition are much more susceptible to crystallization [16, 32-34, 36, 55, 56]. While amorphous glasses exist in a thermodynamically metastable condition, the state is not an equilibrium condition and they will move to the thermodynamically stable crystalline state. The kinetics of crystallization are determined by the glass transition properties of the material and its water

activity and temperature [16]. Crystallization, when not desired, results in loss of product quality and essentially will end the shelf life of the product, depending on the extent of crystallization.

Since the glass transition properties of amorphous materials, as identified by either RHc or Tg, determine susceptibility to physical stability loss, it would follow that the kinetics of the loss of stability also depend on RHc and Tg. Considerable research has been conducted to evaluate and model, using primarily WLF kinetics, the relationship between rate of loss of physical stability and T-Tg. Some researchers focused on determining the rate at different T-Tg [35, 40, 53, 57, 58] whereas others determined the T-Tg that resulted in instantaneous loss of stability [31]. It has further been shown that the actual value of the T-Tg determines the rate of loss, independent of the combination of water activity and temperature that combine to create that T-Tg value [35, 59]. Finally, the importance of T-Tg in determining the rate of crystallization has also been identified [34, 36].

Considering the importance of glass transition due to temperature or humidity abuse in reducing physical stability and ending shelf life, prevention is focused on controlling temperature and water activity by: (a) drying to low moisture content, (b) treatment of the powders at low humidity atmospheres and packaging in high barrier packages, (c) storage at low temperatures, and (d) in package desiccation [49]. If it is not possible to effectively control external factors, anticaking agents can be employed. Anticaking agents are food ingredients added to hygroscopic powders to improve their flowability and inhibit caking [51]. Main food-

grade anticaking agents are silicon dioxide, silicates and sterates, phosphates and polysaccharides [60]. An important class of anticaking agents are ones which can compete with the host powder for the available humidity due to their large water adsorptive capacity, thus reducing their hygroscopicity and the tendency to cake. Many of these ingredients are of porous nature and exert their protective action in foods first by preferentially adsorbing large amounts of water vapor onto specific sites with high binding energy, thus depressing  $a_w$  dramatically for relatively large moisture contents [51, 61].

### **Moisture and Texture**

Food texture is an important physical stability factor and perhaps the most common cause of end of shelf life. Texture has been described as a group of physical characteristics that are sensed by touch and are related to deformation and flow of food when a force is applied [62]. Moisture has been identified as having an important impact on food texture [62-69]. Katz and Labuza [65] specifically pointed out that water activity is a better predictor of quality than moisture content, and several subsequent papers were dedicated to the relationship between water activity and texture [62, 63, 65, 69-71].

Texture is typically measured using either sensory panels, texture analyzing equipment, or acoustics [72]. Terms commonly associated with texture are hardness, crispness, chewiness, bite, etc. In sensory panels, participants rate the texture based on how it performs in relation to their expectations. Texture analysis instruments attempt to mathematically quantify the biting and chewing process and by reporting relative values for hardness of bite, resistance to

snapping, and chewiness. These measurements are often combined in what is called a texture profile analysis (TPA). Often a blade or similar probe is attached to the instrument by a resistance arm that is very sensitive to changes in resistance or force. As the probe contacts and penetrates the sample, a time vs resistance plot is generated. Software is used to analyze these TPA curves to glean values for fracturability, hardness, cohesiveness, adhesiveness, springiness, gumminess, and chewiness [72].

The pioneering work investigating the relationship between water sorption and textural changes was by Katz and Labuza [65]. By equilibrating several crispy snack products with different water activities, they were able to investigate the relationship between water activity and crispness. They used both sensory and instrumental data. They found a linear relationship between water activity and the sensed crispness by the taste panel. The shift between like and dislike occurred at 0.4-0.5  $a_w$  and they determined this to be the critical water activity for texture. The instrumental results also showed a loss in crispness at the same water activity range. This study and other subsequent studies do not provide a clear explanation of why the relationship between water activity and texture exists but instead treat it as macroscopic relationship with practical utility [62, 63, 65, 69-71]. In some cases, it may be related to glass transition [29], but there are cases where the critical water activities identified are within the glass state [50].

While the relationship between water activity and texture was clear from Katz and Labuza [65], they did not identify an effective way to model the effect of water activity on texture. In follow

up articles, Bourne [62, 63] further emphasized the importance of water activity in determining texture but again did not discuss ways to model it. However, the shape of a curve of texture and  $a_w$  was sigmoidal with an abrupt drop over the critical  $a_w$  range. Peleg [73] showed that these types of sigmoidal relationships can be modeled using Fermi's equation, allowing for prediction of texture based on water activity. Several subsequent papers were able to successfully model the relationship between  $a_w$  and the texture of roasted coffee beans [71], biscuits [70], and breakfast cereals [64, 69, 73]. Tesch et al [69] also investigated water activity vs. acoustic crunch of cereal and while they did identify a relationship, the data was too scattered to model with Fermi's equation. It is worth noting that all of these papers considered the relationship between water activity and texture to be dynamic through the critical water activity range, but did not investigate the time dependency of loss of texture in relationship to a reference or critical water activity. They were also limited by water activity resolution due to the need to manually equilibrate samples to different water activities.

### **WATER DIFFUSION IN SEED GRAINS**

The rate of movement of water into seeds is dictated by the moisture diffusion resistance of multiple factors including the soil, seed coat, and seed composition [74, 75]. This movement of water has been modeled using Cranks solution to Fick's second law of diffusion [74-76], which assumes that combined resistance, or diffusivity of all of the factors is constant for a given seed genotype [75]. Of the factors listed, the moisture conductance (the inverse of the resistance) of the non-seed coat factors would be so high in comparison to the conductance of the seed coat that they should be able to be ignored and focus instead be placed on the seed coat

permeability as the most important determining factor for differences in water movement into seeds. When considering just the permeability of the seed coat and not the entire seed, diffusion of water can be modeled using Fick's first law of diffusion since there isn't a storage component and diffusion should be steady state, making calculations much easier [8]. Determining conductance using Fick's 1<sup>st</sup> law should also be possible when considering food materials with manufactured coatings such as shelled candy with coatings.

Fick's law determines the permeability of a seed coat at one set of environmental conditions. However, it seems likely that the permeability of seed coat would change as the environmental conditions change and water may only be able to penetrate the seed coat when the seed encounters a sufficiently high water activity [75]. Sen et al. [77] investigated the relationship between moisture content and seed diffusivity and modeled the relationship using constants specific to the seed species. They found that seed diffusivity increases with moisture or water activity. The permeability will also be influenced by temperature [75]. This makes sense, as there will be a water activity/temperature level where the resistance of the seed coat to water diffusion breaks down and allows water to move into and increase the water activity the germ, thereby stimulating germination. The water activity level where the rate of water diffusion into the seed coat increases would likely be genotype specific, hence the need for a species specific constant in the model used by Sen et al. [77]. A dynamic isotherm should be able to indicate the critical water activity where seed coat permeability increases as characterized by an inflection point in the isotherm curve [10]. If significant differences can be found between these germination critical water activities for different genotypes of important field crops such as

wheat, a dynamic isotherm may be an effective alternative to laborious germination testing in selecting genotypes with desirable germination characteristics.

As with seed coatings, the conductance of moisture through food coatings should vary with the water activity of the coating. While not looking specifically at coatings, Yu et al. [78] found that diffusivity values of corn starch was variable at different water activity levels. The inflection point in a dynamic isotherm curve of a coated food should be an indicator of the critical water activity where moisture begins to penetrate the coating rendering it ineffective. This critical water activity would be an important stability factor and could be used to compare the relative effectiveness of food coatings.

#### **MODELING CHANGES IN PHYSICAL STABILITY**

All manufactured products exist in a non-equilibrium condition that is at best metastable and with time, will undergo matrix changes leading to an end of shelf life [33, 44, 55, 79, 80].

Evidence presented in the previous section suggests that the rate of these degradative changes can be modeled based on the difference between the current temperature and some reference temperature [16, 25]. These degradative changes also have been linked to the glass transition [41, 57], leading to a preference for using  $T_g$  as the reference temperature [16, 29, 39, 81].

To create models that can track moisture and temperature induced changes, data sets are needed that track the rate of change on samples held under different conditions. The preferred method would be to conduct real-time acceptance testing as this would provide the most



accurate assessment of shelf-life. Unfortunately, for products whose shelf-life is months to years, the time required to complete this testing would be prohibitive when release of the product is desired as soon as possible [82, 83]. The best alternative option would then be to use Accelerated Shelf Life Testing (ASLT).

The idea of ASLT is to expose a product to extreme environmental conditions to speed up reactions and decrease the time to product failure [84]. The relationship between higher temperature and reaction rates is typically logarithmic making it possible to extrapolate shelf-life at normal conditions based on data collected under accelerated conditions. The first step of ASLT is to identify the event that ends shelf-life and determine an acceptable methodology for tracking the progress of the shelf-life ending event. Next, data that tracks the progress of the reaction over time under accelerated temperature and humidity are collected. Ideally, data will be collected on samples held at 3 temperatures and 3 water activities [85]. These data can then be used to extrapolate the reaction rate at non-accelerated conditions.

Several empirical models have been identified for modeling time dependency of degradative processes that can lead to an end of shelf life. The Arrhenius equation has traditionally been used to model the temperature dependence of chemical reaction rates [86]. For this relationship, a plot of rate vs. the reciprocal temperature (kelvin) takes on a typical logarithmic form of a decay process. Arrhenius, recognizing this shape, applied and adapted the traditional decay equation by introducing temperature and activation energy as controlling factors [87]. The equation is typically written as

$$k = k_a e^{\left(-\frac{E_A}{RT}\right)} \quad (1)$$

where  $k$  is the rate,  $k_a$  is the Arrhenius constant,  $E_A$  is the activation energy,  $R$  is the gas constant, and  $T$  is the kelvin temperature. The activation energy ( $E_A$ ) and the Arrhenius constant ( $k_a$ ) are unknown and are determined empirically using the ASLT data [86, 88]. The Arrhenius equation can be transformed into linear form

$$\ln k = \ln k_a - \left(\frac{E_A}{RT}\right) \quad (2)$$

where a plot of  $\ln(k)$  vs.  $1/T$  (called an Arrhenius Plot) is a straight line, with the slope providing the activation energy and the y intercept providing the Arrhenius constant needed for the Arrhenius model. With the activation energy and Arrhenius constant for the event of interest, the Arrhenius equation can now be used to predict the rate of reaction at lower temperatures.

While the Arrhenius equation has been effectively used to predict temperature effects for many product types, it is dangerous to use it with accelerated stability data and assume that predicted reaction rates and derived activation energies are correct [88]. There are several potential problems with the Arrhenius equation. First, the Arrhenius equation was originally derived to just deal with reaction rates in gases or solutions, not for solids [88]. Second, the Arrhenius equation assumes a linear relationship between the natural log of the rate and the reciprocal of kelvin temperature, which may or may not be the case and can only be verified by real-time data [82, 86, 88-90]. At elevated temperatures, changes in solubility can occur, proteins can be denatured, and starch may be gelatinized, all leading to a non-linear

relationship. This non-linearity can then lead to incorrect predictions of reaction rates at normal conditions.

Third, the derivation of the Arrhenius equation from ASLT data is only appropriate for the matrix phase in which it was derived and is not applicable for instance in the glassy state if it is derived in the rubbery state [82, 86]. In fact, it has been proposed that the Arrhenius relationship is not applicable at all in the rubbery state unless used over a limited temperature range [91].

Alternatively, it has been suggested that degradation rates in the rubbery state are more dependent on the difference between the ambient temperature (T) and glass transition temperature (T<sub>g</sub>) than on the actual temperature itself [92]. Consequently, alternatively models that base reaction rates on T-T<sub>g</sub> have been proposed as more appropriate in the rubbery state [91]. The Williams, Landel, Ferry (WLF) [81] equation has been used extensively to model time dependency based on T<sub>g</sub> [35-37, 91, 93, 94]. The WLF equation takes on the form of equation 3.

$$\ln t = \ln t_0 + \frac{-C_1(T-T_s)}{C_2+(T-T_s)} \quad (3)$$

Where t is time to the event, t<sub>0</sub> is the time to the event at the reference temperature, T is current temperature, T<sub>s</sub> is a reference temperature (T<sub>g</sub>) and C<sub>1</sub> and C<sub>2</sub> are empirical constants. The t term can be substituted for 1/rate or the magnitude of a mechanical property. In its original form, the WLF equation was used to model relaxation mechanisms [81], but it also has been used to model other physical stability factors such as crystallization and caking [34-36]. Universal constants are provided for C<sub>1</sub> and C<sub>2</sub>, but efficacy of the model is improved by

empirically deriving the constants specific to the data set [93]. The WLF equation is not appropriate for modeling the time dependency of all processes and is only applicable at a constant plasticizer or water activity level. In addition, the T<sub>g</sub> value must be determined for any products to be modeled with the WLF model. The applicability of the WLF model for a data set can be tested by determining if the plot of ln k (rate constant) as a function of T-T<sub>g</sub> produces a straight line [91].

The WLF model implies an upward concavity in the relationship between temperature and mechanical behavior and is not able to account for changes in plasticizer level [73]. A plot of T-T<sub>g</sub> may possess upward concavity at temperatures above T<sub>g</sub>, but a direct plot between mechanical properties in the region of the glass transition and temperature, at a constant plasticizer level, gives a sigmoidal shape [73]. This same sigmoidal shape is observed when mechanical properties are plotted as a function of water activity, at a constant temperature, in the region of the glass transition. This sigmoidal shape can be modeled using the Fermi relationship for either temperature or water activity, but not for the effect of both temperature and water activity simultaneously [73]. The form of the equation for modeling temperature effects is

$$Y(T) = \frac{Y_s}{\left[1 + \exp\left(\frac{T - T_c}{\alpha}\right)\right]} \quad (4)$$

and the form of the equation for modeling water activity effects is

$$Y(a_w) = \frac{Y_s}{\left[1 + \exp\left(\frac{a_w - a_{wc}}{\alpha}\right)\right]} \quad (5)$$

Where  $Y(T)$  and  $Y(a_w)$  are the rate or magnitude of some physical change at a corresponding temperature ( $T$ ) and water activity ( $a_w$ ), respectively.  $Y_s$  is the rate or magnitude of the physical change in the glassy state, whereas  $T_c$  and  $a_{wc}$  are the characteristic temperature and water activity where the first inflection point in the curve occurs. Finally  $\alpha$  is an empirical constant that characterizes the steepness of the curve in the region depicting loss of integrity and will likely be a different value for temperature and water activity. Equations 4 and 5 were found to be effective in the region of the transition, but the WLF equation is more appropriate for conditions far above  $T_g$  or  $RH_c$  [37, 73]. The WLF equation has only be utilized to model the effects of temperature on properties related glass transition and not water activity effects, whereas the Fermi model can be used to model either temperature or water activity effects [73].

Several researchers have recognized the limitations of existing models to account for both the water activity and temperature effect and have made modifications or created alternate models. Several alternative models were proposed in the 1970's that included both water activity and temperature, but they have not gained wide acceptance [95, 96]. Methods for combining the  $Q_{10}$  and  $Q_A$  factors to predict shelf-life based on both water activity and temperature are available, but do not combine the effects in one fundamental equation [85]. Multivariate empirically derived models that include both temperature and water activity, as well as other growth factors, have been developed to model microbial growth, but are very specific to the product, organisms, and humectant type [97-99].

Most recently, Waterman et al. [100] proposed a modified Arrhenius equation that attempted to decouple the water activity effect. They recognized a linear relationship between active ingredient degradation and water activity. This effect was in addition and separate from the temperature effect. They consequently included the empirically derived slope of the relationship between  $a_w$  and degradation as part of the Arrhenius equation, but did not derive the relationship using fundamental equations. The modified equation is

$$\ln k = \ln A + (E_A/RT) + B a_w \quad (6)$$

where  $k$  is the reaction rate,  $A$  is the Arrhenius constant,  $E_A$  is the activation energy,  $R$  is the gas constant,  $T$  is the temperature,  $a_w$  is the water activity, and  $B$  is the water activity factor. The  $A$ ,  $E_A$ , and  $B$  factors are empirically derived model fitting constants. This equation proved to work well for the specific study, but is still not based on fundamental equations. A survey of the literature indicates a need for the development of fundamental models that can account for both water activity and temperature effects on product quality and stability.

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**Chapter 1.**

**The Critical Water Activity from Dynamic Dewpoint Isotherms as a Specification for Wheat**

**Tempering and Flour Production**

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## **ABSTRACT**

Moisture plays an important role in processing wheat grain into flour, from proper grain tempering to the stability of the flour. Moisture of dry grain, tempered grain, and finished flour are currently tracked using moisture content. However, stability factors such as microbial growth, chemical stability, and texture are better correlated to water activity rather than moisture content. To determine if water activity could be utilized as a more effective specification for grain handling and milling as well as flour production, the water activity and moisture sorption properties of dry grain, tempered grain, farina, and flour were determined. The water activity of dry grain was found to be low enough for long term stability. Dynamic isotherms of dry grain indicated a critical water activity where the seed coat loses its resistance to water penetration, which corresponded with the water activity of tempered wheat. Finally, the water activity of finished flour and farina was found to typically be below the critical water activity for mold growth. Based on the results of the study, it would appear that the trial and error required to set current recommended moisture levels was simply identifying the moisture contents that correspond with water activity levels that prevent microbial spoilage and could have been avoided if water activity had been considered from the beginning. Consequently, it would be more effective to set specifications for grain handling and processing based on water activity rather than moisture content.

## INTRODUCTION

Wheat (*Triticum aestivum* L.) is one of the most widely produced grain crops in the world and wheat stores is considered an indicator of the economic stability of a country [1]. To produce a viable food ingredient, most wheat is milled into white flour. Wheat is typically classified as either hard or soft, each with unique end-uses. Hard wheat grain is typically higher in protein, requires a harder grind during milling, produces coarser particle sized flour, and is used for bread production [1]. Soft wheat grain is typically lower in protein, produces finer particle sized flour with less damaged starch, and is used for cookies and crackers [1, 2]. To have value as an ingredient, flour must perform well during processing, but it also must maintain its quality while being stored prior to use.

The milling process that transforms wheat grain into flour is multi-step, consisting of grinding grain into powder by passing it through a series of rolls, and then sieving the powder to separate the bran from the white flour [2]. White flour is primarily produced from the endosperm of the grain with the bran and germ removed, whereas whole wheat flour includes the bran and germ. Whole wheat flour is considered more nutritious, but white flour has a longer shelf life and is easier to work with as an ingredient due to less discoloration and easier processing [3]. Farina is a coarser milled product that consists of small amounts of the germ included with white flour and is commonly utilized as a breakfast hot cereal [4].

Prior to milling, grain must be tempered with moisture to soften the endosperm and toughen the bran, which facilitates grinding of the grain and separation of the bran and germ from white

flour [2]. Sufficient liquid water is added to raise the moisture level of the grain to 12-17% and then allowed to equilibrate for 16-24 hours before milling. However, standard practices do not include a test to determine if moisture equilibrium has been achieved, but instead depend on pre-set soaking times [2]. This variability necessitates tempering optimization for a given milling facility to maximize flour yield while maintaining flour quality. This requires careful balance as Kweon *et al.* [5] found that the tempering conditions impacted milling performance and flour functionality with flour produced from lower moisture tempering having greater flour yield, but poorer flour quality.

To have value as an ingredient, flour must possess good end-use quality that remains stable while the flour is stored prior to use [6]. The degradative reactions that could potentially end the shelf life of flour include: microbial spoilage, caking and clumping, nutritional loss, color loss, and rancidity [3, 7]. The two extrinsic influences that will most significantly impact the rate of shelf life loss of flour are temperature and moisture level [8, 9]. Moisture content is commonly required for any flour specification sheet, with 13.5% ideal for soft wheat and 14% ideal for hard wheat (Glen Weaver, Personal Communication). Moisture content provides useful information about the purity level of the flour and works well as a standard of identity, but unfortunately, is not very helpful in assessing the rate of shelf life loss [10]. The shelf life loss factors listed above are better correlated to water activity, a thermodynamic measurement of the energy of water [11]. Water activity measurement is typically accomplished in 3-5 minutes using easy to use instrumentation, is more repeatable than moisture content analysis, and can be verified using saturated or unsaturated salt solutions [12]. In addition, water activity

helps form the basis for the Food and Drug Administration's definition of potentially hazardous foods [13]. Consequently, including water activity in flour specifications is more critical to ensuring quality and shelf life than moisture content, yet water activity does not currently appear on any flour specification sheets.

The purpose of this study was to provide an argument for making water activity a commonly requested specification for flour. More specifically, the study investigated the impact of particle size, tempering conditions, and storage conditions on the water activity, moisture content, and moisture sorption properties of grain, flour, and farina. The information generated in this study should help explain some confusion over recommended moisture levels for flour, highlight the impact of storage conditions on flour moisture, and determine if water activity may be a preferable metric for tracking moisture in grain and grain-based products.

## **MATERIALS AND METHODS**

Commercial Hard Red Spring and Soft White Winter grain was obtained and processed by the USDA Western Wheat Quality Lab in Pullman, WA. Dry Whole Wheat (DWW) 50 gram samples were set aside for water activity and moisture sorption isotherm testing. The remaining hard and soft grain samples were tempered by adding enough water to raise the moisture level to either 15.5% or 17.0%, tumbling for 20 minutes, and then equilibrating for 16 hours. As with DWW, 50 gram samples of Tempered Whole Wheat (TWW) at each moisture level were set aside for water activity and moisture sorption isotherm testing. The rest of the tempered wheat was then milled using a modified Quadromat experimental mill [14]. Break flour and farina



samples were obtained from the mill (Figure 1) and turned over to Decagon Devices, Inc. in Pullman WA for analysis.

Three replicates each of both hard and soft DWW, TWW, farina and flour at each tempering level (not DWW) were analyzed for moisture content using AACC method 44-15.02 [15] and water activity at 25°C using an AquaLab Series 4TE (Decagon Devices, Inc. Pullman, WA) .

Reported water activities and moisture contents were averaged across replicates. In addition, 3 replicates of each sample were analyzed for equilibration time and maximum moisture sorption when changing from 30% RH to 65% and 30% RH to 90% RH at 25 °C (weight change %dm/dt trigger setting 0.008/3 events) using the Dynamic Vapor Sorption (DVS) method in the AquaLab Vapor Sorption Analyzer (Decagon Devices, Inc. Pullman, WA). Equilibration time was identified as the time required in hours for the flour sample to move from the initial water activity to reach equilibrium, as indicated by meeting the weight change trigger, at the final water activity. Maximum moisture sorption was defined as the moisture content level achieved at either 65% or 95% relative humidity. Mean equilibration times and maximum moisture sorption values were averaged across triplicate analyses.

Whole grain, flour, and farina samples were also analyzed in triplicate using the Dynamic Dewpoint Isotherm (DDI) method in the AquaLab Vapor Sorption Analyzer at 25°C with an initial water activity of 0.10  $a_w$ , a final water activity of 0.90  $a_w$ , and a flow rate of 80 ml/min [16]. To compare the relative hygroscopicity of the hard and soft flour and farina samples, the linear slopes of the adsorption curves from 0.10  $a_w$  to 0.80  $a_w$  were compared. For whole wheat samples, the critical water activity (RH<sub>c</sub>) was identified as the water activity associated with a

sharp inflection in the DDI curve and was determined by finding the first maximum in the Savitsky-Golay 2<sup>nd</sup> derivative curve [16, 17]. Mean RHc values averaged across triplicate DDI curves were reported.

A two-way ANOVA was used to determine if particle size (whole wheat vs. farina vs. flour), hardness level, and tempering level, were significant sources of variation in moisture content, water activity, isotherm slope during adsorption, equilibration time, and maximum moisture sorption [18]. For treatments that were shown to be significant, Tukey's multiple means comparison were used to determine which treatment levels were significantly different.

## **RESULTS AND DISCUSSION**

As expected, the dry whole grain had the lowest water activity whereas the tempered wheat had the highest water activity (Table 1). The water activity of hard grain, flour, and farina was always higher than its soft counterpart regardless of the tempering level ( $p = 0.0001$ ) (Tables 1 and 2). The water activity of the 17% tempered whole wheat was above the RHc for mold (0.70  $a_w$ ) for both hard and soft wheat, but only for hard wheat at 15.5% [19]. The typical 16-24 hour hold time for tempered wheat should not be long enough for mold to grow. However, if the hold time was extended, any tempered wheat with water activity higher than 0.70 would likely experience mold growth.

The water activity and moisture content of flour and farina was always lower than the tempered whole wheat before milling due to removal of moisture during the milling process (Table 2). Based on Tukey's comparisons, flour and farina had similar ( $p > 0.05$ ) water activities

after milling for a given hardness and tempering level, with the exception of SWW farina at 15.5% tempering having a slightly lower water activity than flour. The water activities ( $<0.70 a_w$ ) and moisture contents (13.5% for soft, 14.0% for hard) of both flour and farina from 15.5% tempering were within acceptable limits. For 17.0% tempering, the water activity of the hard flour and farina was above the critical  $0.70 a_w$  value, but not the soft flour and farina. Still, the moisture content levels for all products at the 17.0% level would be considered too high. A suggested water activity specification for flour and farina would be  $0.62-0.68 a_w$ . As indicated in this study, this water activity range corresponds with ideal moisture levels for hard and soft flour. In addition, this water activity range would assure no mold growth and minimize the rate of rancidity development [19, 20].

The slopes of the dynamic isotherms for all flour and farina samples were not significantly different ( $p = 0.148$ ), indicating equivalent levels of hygroscopicity (Figure 2). The sorption curves were essentially linear up to  $0.75 a_w$ . The shape of the DDI curves of the whole grain samples were different from the flour and farina, and initially almost flat (Figure 2). This is typical of materials with hard coatings that limit the penetration of water into the interior. However, at higher water activities, the sorption isotherm curves of the whole grain samples experienced sudden changes in sorption properties where the samples began to absorb much more moisture, causing an inflection in the DDI curve. The water activity associated with this change was identified as the RHc and represents the point where water begins to penetrate the grain. This RHc occurred at a lower water activity for soft grain ( $0.743 a_w$ ) than for hard grain ( $0.795 a_w$ ) ( $p = 0.0001$ ), likely due to tighter adhesion between molecules in hard wheat. A

review of table 1 also indicates that these RHc values for the grain were similar to the water activities of the 17.0% tempered whole grain wheat.

Based on the connection between the RHc value of whole grain and current tempering moisture levels, it would be feasible to temper to a constant water activity rather than to a moisture level. Based on the preliminary results of this study, a recommended water activity specification for tempered wheat would be 0.75  $a_w$ . This water activity level would achieve tempering conditions similar to those currently being used, but with more consistency since water activity is more precise than moisture content and can be easily monitored with instrumentation to determine when tempering is complete. Finally, tempering the grain to 0.75  $a_w$  could be achieved by vapor equilibration to 75% RH (using saturated NaCl) which is more uniform than adding liquid water. If the grain mass is tumbled and provided with a constant source of 75% relative humidity air, the equilibration time should be similar to current tempering hold times, so mold growth shouldn't have time to begin. This process of tempering would have to be verified and could be hampered by slow movement of water vapor in the grain mass. However, if feasible, having a consistent starting water activity for tempered wheat should lead to more consistency in flour or farina water activity, making the flour more stable.

The DVS results in Figure 3 indicate that at 0.65  $a_w$ , there were not significant differences between hard and soft flour, as well as hard and soft farina ( $p = 0.798$ ). However, the 14.3% average moisture content of the hard and soft flour was significantly higher than the 13.6% average moisture content of the hard and soft farina samples ( $p = 0.009$ ). At 0.90  $a_w$ , the moisture content was roughly 20%, again with no significant differences between hard and soft

flour, as well as hard and soft farina ( $p = 0.441$ ). In addition, flour moisture was not significantly different from farina moisture ( $p = 0.488$ ). The time required to move to  $0.65 a_w$  from  $0.30 a_w$  was longer for hard flour at 15.1 hours, but not significantly longer ( $p = 0.471$ ) due to high variability in equilibration times for hard flour. The equilibration times were similar for soft flour, soft farina, and hard farina at around 5 hours, a further indication that the hard flour equilibration time was incorrect. The equilibration times at  $0.90 a_w$  were significantly different ( $p = 0.008$ ) among the sample types with hard farina at 23.4 hours longer than soft farina at 17.3 hours and hard flour at 14.5 hours, with soft flour the shortest at 11.0 hours.

Humidity levels of 60-70% should not be problematic since the water activity will be below the mold growth limit and moisture levels will be acceptable for both flour and farina. However, exposure to lower relative humidities will result in moisture loss to potentially unacceptable moisture levels. If flour or farina is exposed to high humidity (>70%), the water activity will be above the growth limit for microbial growth and the moisture levels will be unacceptable. Soft flour will reach unsafe water activity levels the fastest, but all products will have reached unacceptable water activities and moisture levels in only 24 hours (Figure 3). This change in water activity and moisture content only applies to product exposed to ambient conditions. Moisture movement through a mass of bulk stored product once the surface has come to equilibrium and the subsequent changes in water activity and moisture content are not part of this discussion.

## **CONCLUSIONS**

Observing the water activity changes of wheat as it was transformed from dry grain to tempered wheat, and then milled into flour provided insight into the basis for current handling practices. The current system is heavily dependent on tracking the moisture content change during milling rather than water activity. Considering that the currently suggested moisture content levels for flour and farina correspond with water activity levels right at the cutoff point for mold growth, it behooves the flour industry to consider including a water activity specification to ensure microbial safety. In addition, since lower water activities are better correlated with lower rates of rancidity than moisture content, it would make more sense to focus on optimizing water activity level and then confirm that the moisture content is acceptable rather than rely on just a moisture content specification.

The water activity of dry grain within acceptable moisture content levels is below the microbial growth limit and low enough that the seed coat effectively blocks out moisture penetration.

The water activity of tempered wheat is above the critical water activity of the seed coat causing a reduction in its resistance to water penetration and allowing softening of the grain in preparation for milling. Finally, the water activity of finished flour is just below the cutoff level for microbial growth. However, all flour types are equally hygroscopic and susceptible to moving to water activities above the growth limit if they are exposed to high humidity during storage and will do so in less than 24 hours.

Based on this survey of the water activity of wheat milling constituents, it appears that through trial and error, those who have set currently recommended moisture levels for grains and flour were fortunately, if unknowingly, finding the right water activity level to maximize stability.

Moisture content measurements in grain and flour certainly have their purpose as a standard of identity. However, logic suggests that since water activity is the parameter that is driving stability, directly measuring water activity would be a more effective way of ensuring a consistently stable product.

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## FIGURES



**Figure 1. Sample types utilized for this study including clockwise from the upper left: whole grain, farina, and break flour.**

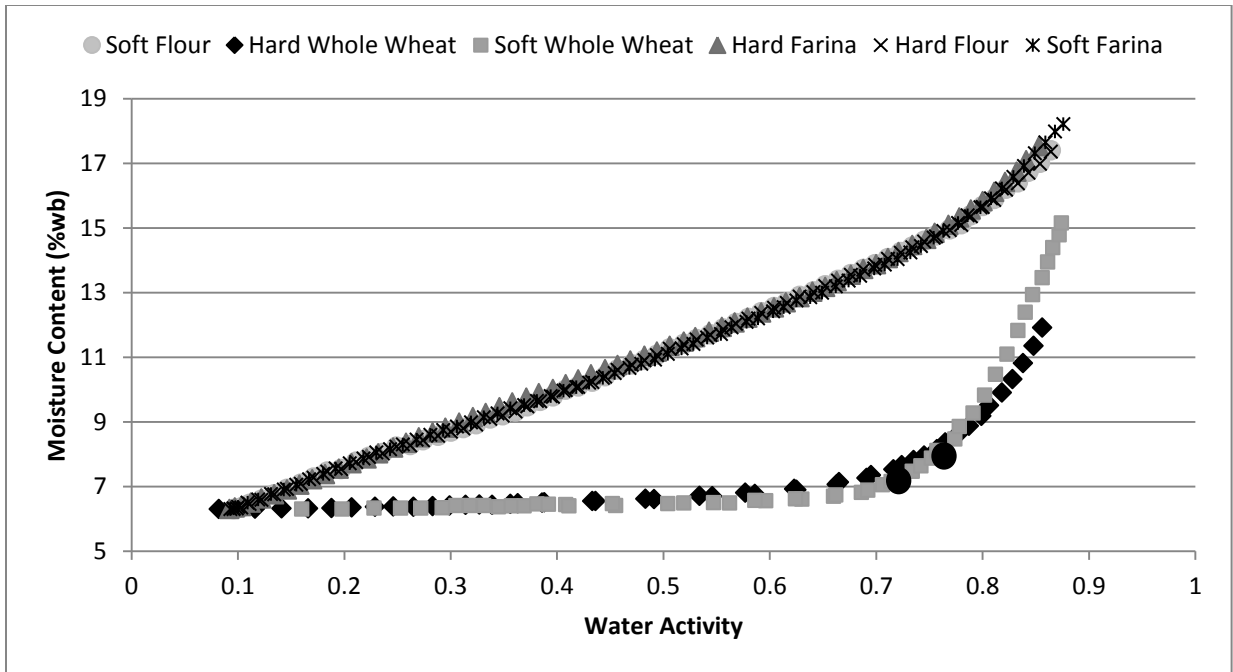


Figure 2. Dynamic isotherms for hard and soft grain, flour, and farina at 25 °C. Inflection points in the dynamic curves, highlighted by black dots, indicate the critical water activity (RH<sub>c</sub>) for whole wheat samples. The slopes of the dynamic curves of flour and farina indicate relative hygroscopicity.

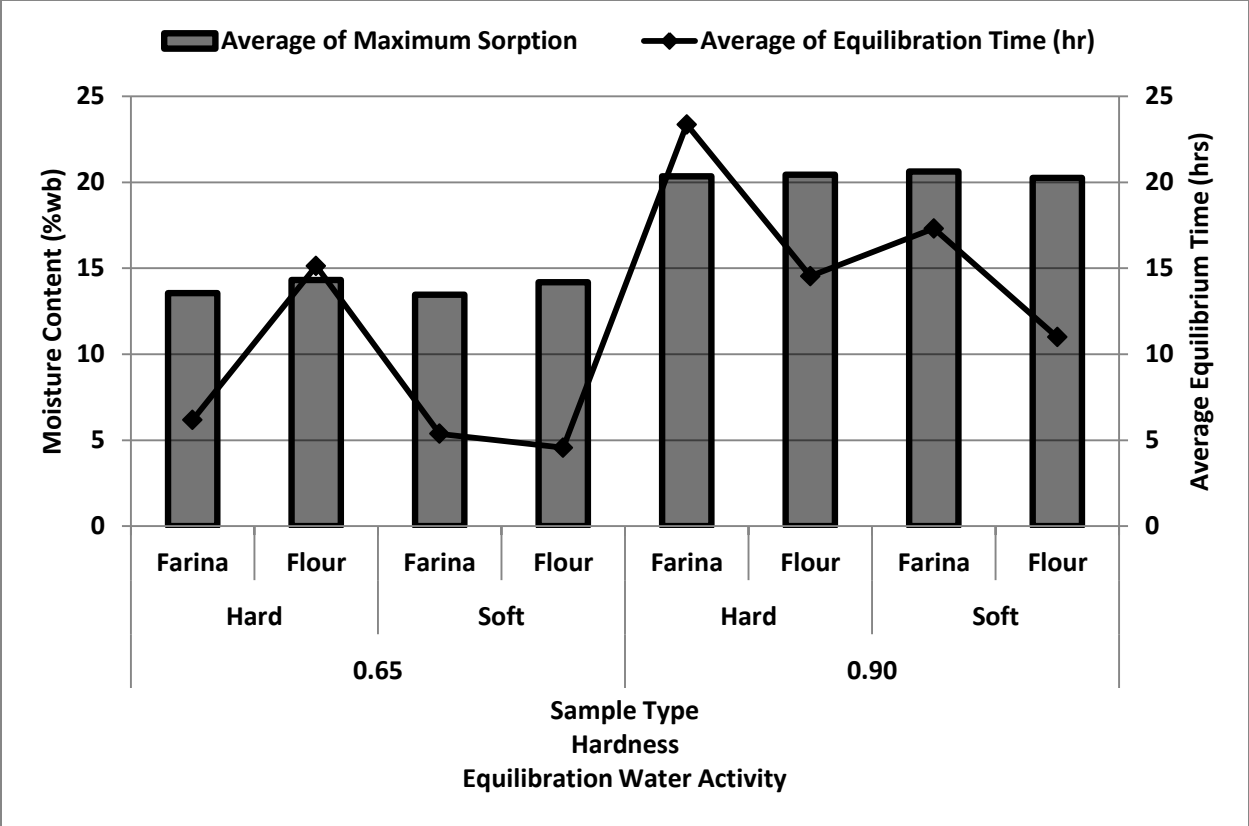


Figure 3. Average maximum moisture sorption and equilibration times for hard and soft flour and farina samples when equilibrating to 0.65  $a_w$  and 0.90  $a_w$ .

## TABLES

**Table 1. Water activity<sup>a</sup> and moisture content<sup>b</sup> of Hard and Soft whole wheat grain that is dry, tempered to 15.5%, and tempered to 17.0%.**

Parameter	Dry		15.5% Tempered		17.0% Tempered	
	Soft	Hard	Soft	Hard	Soft	Hard
Water Activity	0.410 <sup>F</sup>	0.502 <sup>E</sup>	0.660 <sup>D</sup>	0.707 <sup>C</sup>	0.749 <sup>B</sup>	0.794 <sup>A</sup>
Moisture Content (%)	6.20 <sup>E</sup>	7.91 <sup>D</sup>	10.38 <sup>C</sup>	10.94 <sup>BC</sup>	11.58 <sup>B</sup>	12.88 <sup>A</sup>

<sup>a</sup> Water activity values in a row followed by the same letter are not significantly different at  $p > 0.05$

<sup>b</sup> Moisture content values in a row followed by the same letter are not significantly different at  $p > 0.05$

**Table 2. Water activity<sup>a</sup> and moisture content<sup>b</sup> of hard and soft flour and farina tempered to 15.5% and 17.0%.**

	15.5%		15.5%		17.0%		17.0%	
	Tempered Soft		Tempered Hard		Tempered Soft		Tempered Hard	
Parameter	Flour	Farina	Flour	Farina	Flour	Farina	Flour	Farina
Water Activity	0.640 <sup>D</sup>	0.621 <sup>E</sup>	0.663 <sup>C</sup>	0.670 <sup>C</sup>	0.699 <sup>B</sup>	0.696 <sup>B</sup>	0.751 <sup>A</sup>	0.743 <sup>A</sup>
Moist Content	13.92 <sup>E</sup>	13.57 <sup>E</sup>	14.18 <sup>D</sup>	14.16 <sup>DE</sup>	14.98 <sup>B</sup>	14.66 <sup>C</sup>	15.65 <sup>A</sup>	14.75 <sup>BC</sup>

<sup>a</sup> Water activity values in a row followed by the same letter are not significantly different at

p>0.05

<sup>b</sup> Moisture content values in a row followed by the same letter are not significantly different at

p>0.05

**Chapter 2.**

**Changes in Grain Moisture Permeability at the Critical Water Activity from Dynamic Dewpoint Isotherms**

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## **ABSTRACT**

Moisture is an important external factor that impacts the stability and viability of grains. Movement of moisture through grain has been investigated, but not over a range of water activities and previous work did not use recently developed moisture sorption instrumentation. Moisture sorption isotherms can provide the information needed to determine moisture penetration rates into grain over different water activity ranges and can be simply generated automatically using instrumentation. The purpose of this study was to investigate moisture movement into grain using moisture sorption isotherms. Two methods for generating isotherms, static and dynamic, were utilized. The information provided by each method was unique and when combined, provided information about changes in moisture penetration into grain that occur as the water activity changes. Static isotherm data was utilized to calculate permeance values for the grain at different water activities whereas the dynamic isotherm data was used to determine a critical water activity (RH<sub>c</sub>) where the permeance of the grain underwent significant changes, causing an inflection in the dynamic isotherm. Comparing the permeance values generated from static isotherm data and the RH<sub>c</sub> from dynamic isotherm data confirmed that permeance does significantly change when the water activity is above the RH<sub>c</sub>. Generating DDI curves and finding the RH<sub>c</sub> for coated materials using automatic isotherm generators has the potential to provide a simple approach to finding the water activity level where the moisture barrier properties of the coating begin to breakdown.

## INTRODUCTION

The outer layers of grain serve as the primary defense mechanism against external factors that could impact seed viability or grain quality [1]. One of the most important external factors effecting grain stability is moisture. To maintain seed viability for germination, the internal moisture of the grain must be carefully controlled and premature penetration of moisture into the germ can trigger germination [2-4]. This premature germination can result in pre-harvest sprout where starch is broken down as part of the germination process before the grain is processed, rendering it unusable for typical postharvest applications [5]. In addition, high internal moisture due to penetration will cause it to be susceptible to microbial spoilage, impacting grain storability [5]. Finally, adequate penetration of moisture into the endosperm must be achieved prior to milling grain to ensure the production of high quality flour [6, 7]. This process, called tempering, is typically achieved by soaking the grain and waiting for enough moisture penetration to sufficiently raise the internal moisture level.

The rate of movement of water through seeds is dictated by the moisture diffusion properties of a complex mixture of grain components, each with their own diffusion properties [8]. This movement of water has been modeled using Cranks solution to Fick's second law of diffusion [9-11], which assumes that the combined diffusivity of all of the factors is constant for a given seed genotype [11]. The challenge posed by determining diffusion coefficients with the Crank equation is that it requires a geometric correction factor, and the geometry of a grain kernel is not straightforward. In early work, Babbit [12] assumed the grain to be a homogeneous sphere and this assumption was used in other research on moisture movement into wheat, which

indicated that the model was adequate in predicting moisture changes in the grain with time [13]. Kang and Delwiche [14] proposed that using a prolate spheroidal geometry correction provided a better estimation of the endosperm diffusion coefficient. While the movement of moisture through the grain is complex and challenging to model, the rate of moisture penetration through the outer layers is what actually determines if moisture will enter the grain. The slow diffusion rate through these outer layers becomes the determining factor for moisture movement into the grain [14, 15].

One shortfall of many of the grain diffusion studies listed above is that grain diffusion was determined under a limited set of environmental conditions. However, since seeds will only germinate when they encounter an environment with a sufficiently high water activity, it is logical that the diffusion properties of the grain change with ambient relative humidity and temperature [11]. Sen et al. [16] investigated the relationship between moisture content and seed diffusivity and modeled the relationship using constants specific to the seed species. They found that seed diffusivity increases with moisture or water activity. Muthukumarappan and Gunasekaran [15] investigated the diffusion of moisture in corn and reported a reduction in moisture diffusion for corn pericarp at high humidity. However, Casada [17], using several thin layer diffusion models, found that diffusion increased when wheat and barley was exposed to higher relative humidities. Changes in moisture diffusion properties with water activity were also found in non-grain materials [18, 19].

A macroscopic evaluation of water uptake by grain at different water activities (equilibrium relative humidities) can be obtained through the moisture sorption isotherm. This relationship is unique to each type of material and to the temperature [16]. There are two basic methods for determining moisture sorption isotherms, namely static and dynamic. Both methods can presently be achieved using instrumentation that automates the process. Traditional static methods, often referred to as Dynamic Vapor Sorption (DVS), relies on equilibration to known water activity levels while tracking weight change [16]. If the time required to equilibrate to a given water activity is tracked along with the accompanying weight change, DVS information can be used to determine diffusion properties of grain [19]. Consequently, DVS investigations using automatic isotherm generators provide a convenient method for investigating changes in diffusion at various water activity levels. All previous methods manually controlled water activity, which is labor intensive and time consuming and may be why there are few studies that investigated diffusion over a range of water activities.

Dynamic sorption isotherm methods, such as the Dynamic Dewpoint Isotherm (DDI) method, differ from DVS methods in that they expose the sample to 100% relative humidity and then rely on direct measurement of water activity as it changes dynamically instead of equilibration to controlled water activity levels [18]. This makes DDI analyses faster and capable of much higher data resolution than DVS methods [18]. Because of the DDI method does not assure equilibrium, it does not provide the information needed to determine diffusion properties. However, the high resolution of the DDI method does make it possible to characterize abrupt changes in moisture sorption properties. Sharp inflections in the DDI curve have been used to

successfully determine moisture induced glass transition in milk powder [19], polydextrose, and cereal flakes [20]. The water activity associated with the inflection point in the DDI curve has been characterized as the critical water activity (RH<sub>c</sub>) at the temperature of the isotherm. If the DDI curve of whole grain similarly showed an abrupt change, it could indicate an RH<sub>c</sub> for changes in moisture diffusion properties of the grain.

The objective of this study was to investigate moisture penetration into grain using an automated isotherm generator. First, DDI curves of two grains, barley and wheat, were generated to look for inflection points that would identify an RH<sub>c</sub>. In addition, DVS data was utilized to determine if changes in the permeance of moisture into these grains could be observed as the water activity range over which there were calculated changed. Finally, permeance values from DVS data were compared to DDI curves to determine if changes in moisture penetration into the grain were more pronounced in the region of the RH<sub>c</sub>.

## **MATERIALS AND METHODS**

Whole grain samples of wheat for analysis were obtained from the USDA Western Wheat Quality Lab in Pullman, WA. Previous investigations into moisture sorption properties of wheat indicated non-significant differences between market classes, so only soft white wheat was used for analysis (unpublished data). Pearled barley samples with the outer layer removed were obtained from a bulk bin at a local grocery store. As-is moisture content for wheat and barley samples was 6.8% and 8.3%, respectively, whereas the as-is water activity was 0.30  $a_w$

for wheat and 0.45  $a_w$  for barley. Samples were stored in airtight plastic containers at room temperature prior to analysis.

To determine if wheat and barley grain experienced an inflection in the DDI curve, adsorption DDI curves were conducted at 25°C in triplicate on 1 gram subsamples of wheat and barley. The AquaLab VSA (Decagon Devices, Inc. Pullman, WA) was utilized for generating DDI curves with DDI settings of a minimum water activity of 0.03  $a_w$ , a maximum water activity setting of 0.90  $a_w$ , a flow rate of 80 ml/min, resolution setting of 0.01  $a_w$ , and starting sorption direction adsorption. Each triplicate DDI curve at each temperature was examined for the presence of an RHc, identified as the water activity associated with a sharp inflection in the DDI curve. The water activity of the RHc was determined by finding the first maximum in the Savitsky-Golay 2<sup>nd</sup> derivative curve [20, 21]. The RHc averaged across replicates was reported.

Static moisture sorption isotherm data at 25°C was generated on duplicate 1 gram samples of wholegrain wheat and barley using the DVS setting on the AquaLab VSA (Decagon Devices, Inc. Pullman, WA). To provide water activity levels both below and above the RHc, settings for the DVS test were an initial water activity 0.50  $a_w$  for wheat and 0.55  $a_w$  for barley; then stepped up at 0.10  $a_w$  intervals until reaching a final water activity of 0.90  $a_w$  for wheat and 0.95  $a_w$  for barley. The weight change data for the initial equilibration to 0.50  $a_w$  was utilized for moisture sorption isotherm, but not for determination of moisture permeability since the water activity interval was determined by difference between the as-is water activity and the starting water activity, making it not equivalent to the 0.10  $a_w$  interval used for the other equilibrium events.

This resulted in four water activity levels for determination of moisture permeability (Table 1.) Equilibration settings for all water activity levels were three successive events where the percent weight change was  $\leq 0.008$  %wt/hr. The instrument recorded water activity and weight readings at 5-6 minute intervals to create a weight change time series for each water activity level. For static isotherm data, equilibrium moisture contents averaged across replicates were reported for each water activity. This data was then modeled for best fit using the GAB equation, which is

$$m = \frac{m_o k_b c a_w}{(1 - k_b c)(1 - k_b a_w + k_b c a_w)} \quad (1)$$

Where  $m$  is the moisture in g/g solids,  $k_b$  is a constant in the range of 0.70 to 1 and  $c$  is a constant in the range of 1 to 2000,  $m_o$  is the monolayer moisture content in the same units as  $m$  and  $a_w$  is the water activity at moisture  $m$ .

As mentioned above, several studies have examined diffusion coefficients for grain using a variety of models [14, 15, 17, 22]. The purpose of this study was not to continue these investigations, but instead to determine if moisture penetration into grain changes significantly at specific water activity levels. For this macroscopic view of water movement into grain, only bulk mass transfer was considered important. In addition, relative changes in moisture penetration as water activity changed were more important than deriving actual diffusion coefficients. Specifically, permeance values derived from the integrated form of Fick's 1<sup>st</sup> law (eq 2) were assumed to be a good representation of the rate of moisture penetration and were used for comparisons between water activity levels [23].

$$m_r = \ln \frac{(m_e - m_i)}{(m_e - m_t)} = \frac{kt}{xC} \quad (2)$$

where  $m_r$  is the moisture ratio,  $m_e$  is the dry basis moisture content at equilibrium,  $m_i$  is the initial dry basis moisture content,  $m_t$  is the moisture content at a point in time  $t$ ,  $k/x$  is the permeance ( $\text{g} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{kPa}^{-1}$ ), and  $C$  ( $\text{g} \cdot \text{m}^{-2} \cdot \text{kPa}^{-1}$ ) is a constant for the given grain type. Permeance ( $k/x$ ) was determined by multiplying the constant  $C$  by the linear slope ( $\text{day}^{-1}$ ) from the plot of  $m_r$  vs  $t$ . The constant  $C$  is derived by

$$C = \frac{m_s s}{A e_s} \quad (3)$$

where  $m_s$  is the dry mass of the sample (g),  $s$  is the isotherm slope between the initial and final water activity,  $A$  is the sample surface area ( $\text{m}^2$ ), and  $e_s$  is the saturated vapor pressure (kPa).

To determine surface area of wheat and barley grains, a prolate spheroid shape was assumed.

The surface area of a prolate spheroid was determined according to equation 4 [24].

$$A = 2\pi b^2 \left( 1 + \frac{a}{be \sin e} \right) \quad (4)$$

where  $a$  is the length of the major semi-axis,  $b$  is the length of the minor semi-axis, and  $e$  is the eccentricity given by  $e = \sqrt{1 - (b/a)^2}$ . The average  $a$  value was 3.53 mm for wheat and 4.23 mm for barley. The average  $b$  value was 2.37 mm for wheat and 2.95 mm for barley. The surface area for wheat and barley were multiplied by 27, which was the average number of grains needed for a 1 gram sample. Permeance values were averaged across replicates for each water activity level and used for comparisons.

Analysis of Variance (ANOVA) was performed on permeance values with water activity considered a random factor using Minitab 16 Statistical Software [23]. Permeance values at



each water activity were compared using Tukey's multiple means comparison to determine if permeance values at water activities less than the  $RH_c$  were significantly different from those at water activities greater than the  $RH_c$ .

## **RESULTS AND DISCUSSION**

The DVS and DDI moisture sorption isotherm curves for both wheat and barley were similar at low water activities, but deviated as water activity increased until coming back in agreement at 0.90  $a_w$  and higher (Figure 1). The moisture contents for DVS data increased gradually as water activity increased, which was easily modeled using the GAB equation. In contrast, the shape of the DDI data was essentially flat until reaching water activities above 0.70  $a_w$ . At this point, sorption of moisture abruptly changes, resulting in an inflection in the DDI curve. The DVS and DDI methods are fundamentally different in how they obtain moisture sorption data [20, 25]. The DVS method requires holding the sample at a water activity until the sample has equilibrated, as indicated by the rate of weight change falling below some preset level, at which point the sample is assumed to be equivalent to the applied humidity. The DDI method relies on direct measurement of water activity using a chilled mirror measurement system as it dynamically takes up moisture and does not hold the sample until equilibrium. Consequently, the DVS curve represents the (near) equilibrium moisture sorption isotherm whereas the DDI data reflects the real-time changes in moisture sorption when exposed to high humidity [20, 25]. For many products, the moisture sorption isotherms from DDI and DVS coincide, except when a moisture barrier outer layer is present such as in wheat and barley [26].

For grain, moisture movement into the grain is a time-dependent process based initially on the permeance of the exposed surface. If given enough time, moisture will be able to move into the interior, at which point, the amount of moisture that can be absorbed is dictated by the water binding capacity of the bran and the endosperm. The endosperm is also the primary source of flour milled from grain, which is why the shape of the DVS wholegrain isotherms in Figure 1 are similar to that of flour milled from barley or wheat [27]. For the DDI curves, since the sample isn't held at a water activity for equilibration, enough time is not allowed for moisture to penetrate through the grain at water activities less than  $0.70 a_w$ , resulting in moisture sorption being limited to just the surface of the grain where there would be limited water binding sites. This limited sorption results in the generally flat DDI curve for both wheat and barley at water activities less than  $0.70 a_w$  (Figure 1). The deviation between the DVS and DDI curves represents the difference between absorption throughout the grain for DVS and limited surface adsorption for DDI.

The sharp inflection in the DDI curves of both wheat and barley that occurs at  $0.73 a_w$  for wheat and  $0.76 a_w$  for barley indicates a sudden change in moisture movement into the grain (Figure 1). These water activities were identified as the RHc values for moisture penetration into the grain. A macroscopic view of moisture movement doesn't allow for determining exactly what changes in the grain are responsible for the sudden increase in water penetration, but the RHc clearly identifies the point where the grain's resistance against moisture penetration begins to break down. Figure 2 provides additional evidence that the grain's permeance does indeed change at the RHc. For both barley and wheat, permeance values at water activities less than

the RHc were not significantly different ( $p>0.05$ ), but were significantly different from permeance values at water activities greater than the RHc (Table 2). Permeance values at both water activities above the RHc were similar for wheat, but significantly lower at 0.95  $a_w$  for barley. This loss in permeance at very high water activities could be the result of saturation of pores in the grain which would reduce the rate of moisture movement, but is inconclusive based on just the results of this study.

## **CONCLUSION**

The automated isotherm generator made generation of static and dynamic isotherm data for multiple samples of wheat and barley feasible in a reasonable amount of time. The static and dynamic moisture sorption isotherms each provided unique and valuable information. The static sorption curves provided the equilibrium moisture sorption properties of the grain and provided the data needed to determine permeance values at different water activities. The dynamic data does not facilitate calculation of permeance, but it does clearly indicate the point where moisture begins penetrating the grain.

Diffusion of moisture has been reported to be impacted by the water activity range over which the moisture is adsorbed. This study further identified that the permeance into the grain changes significantly when the water activity of the grain increases to values higher than the RHc. The DDI curve is able to dramatically illustrate this change with a relatively simple methodology if instrumentation is used. It would seem less than coincidental that the water activity associated with grain tempered to moisture levels needed for good milling performance

is just slightly higher than the RHc identified in this study (Brady Carter Dissertation Chapter 1). While the desirable moisture levels needed for milling were identified through trial and error, it appears that the RHc provides the reasoning behind these targeted moistures as they represent the water level needed for moisture to penetrate the grain so the endosperm can be softened.

It is assumed that other grains as well as other coated materials will likely have similar DDI curves to wheat and barley and that an RHc for moisture penetration of the coating can be identified. However, DDI analysis of these products would be needed to confirm. Previously, the time and labor required to investigate moisture penetration of coatings would be prohibitive for many investigators, but this study indicates that the availability of automated instrumentation makes it reasonable. The practical application provided by the RHc for coated products would be the safe storage humidity where the coating will still be an effective moisture barrier.

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FIGURES

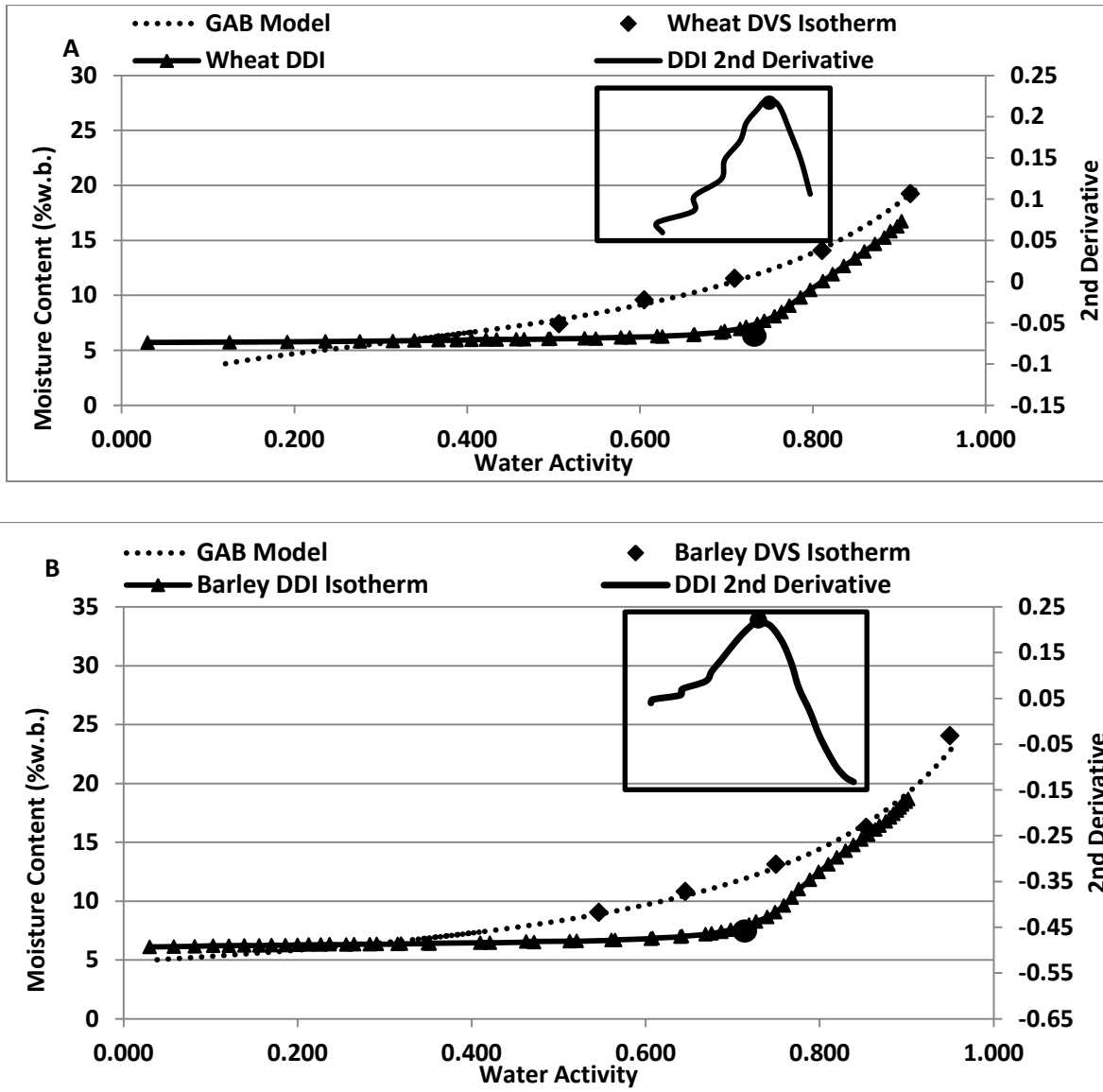


Figure 1. Static DVS and dynamic DDI moisture sorption isotherms for wheat (A) and barley (B), along with the GAB model for the DVS moisture sorption data. Within the superimposed solid box, the Savistky-Golay 2<sup>nd</sup> derivative plots are also shown on the secondary axis and the maximum in the curve identifies the inflection point in the original curve. The critical water activities associated with an inflection in the adsorption curve are identified as solid black circles.

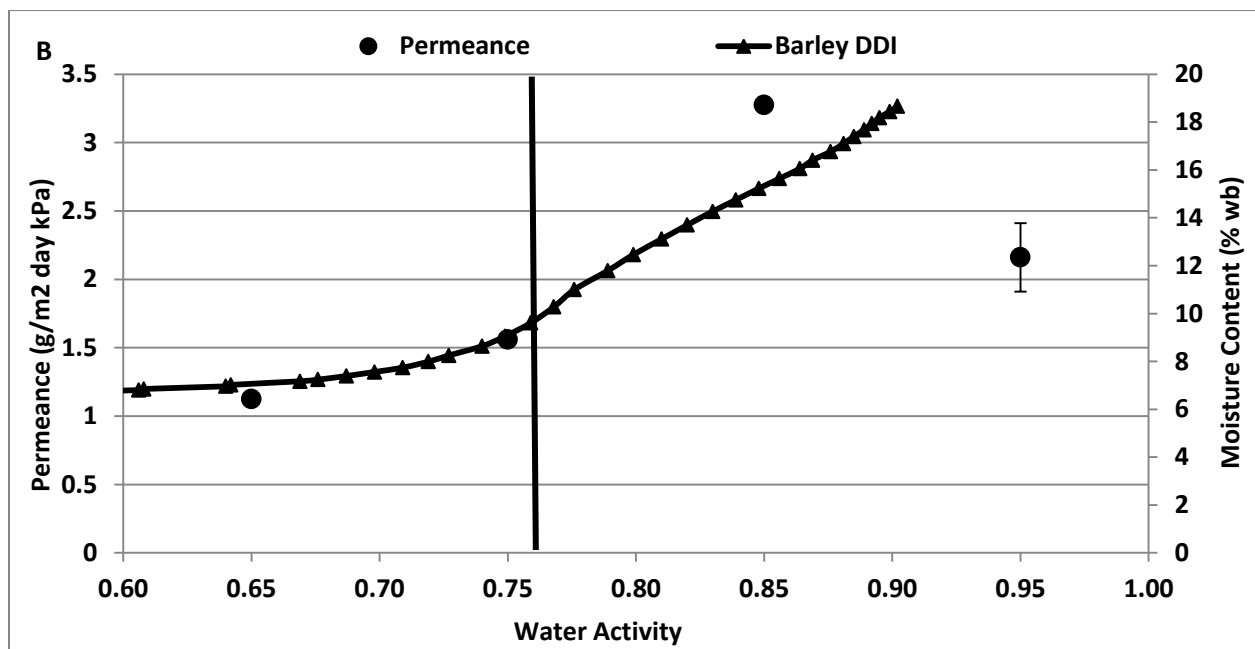
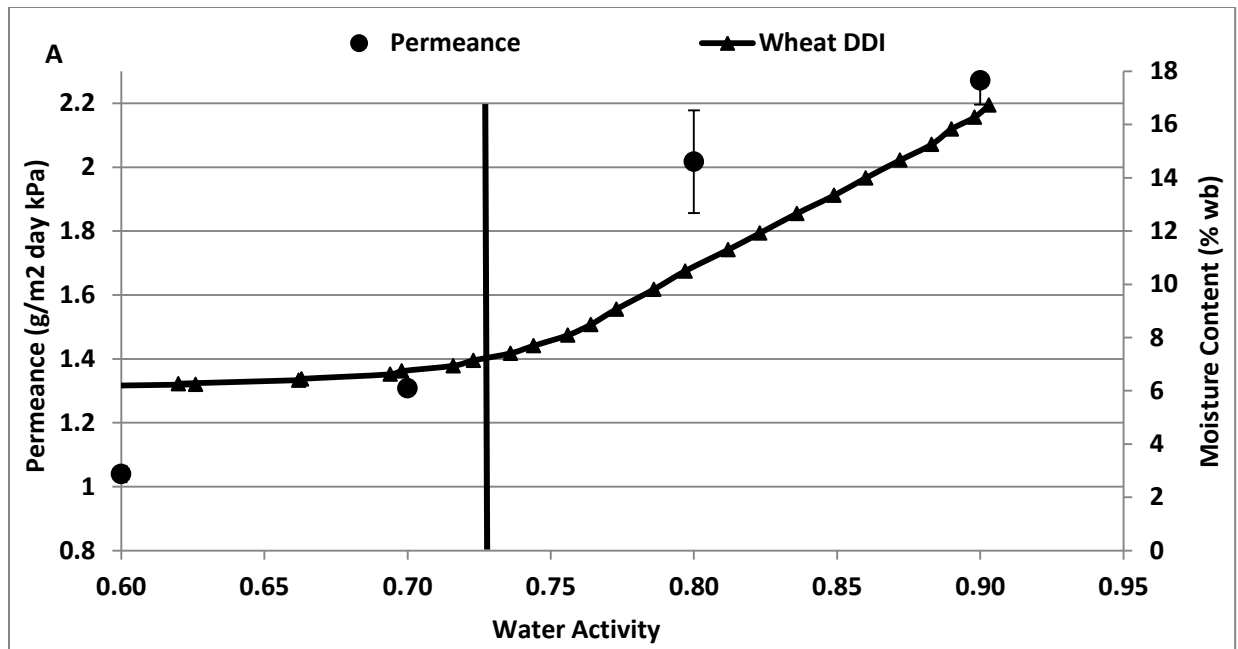


Figure 2. Permeance values and DDI isotherm data for wheat (A) and barley (B). Solid vertical black lines represent RH<sub>c</sub> values obtained from DDI analysis.

## TABLES

**Table 1. Water activity levels investigated for moisture permeability.**

<b>Grain</b>	<b>1<sup>st</sup> Water Activity</b>	<b>2<sup>nd</sup> Water Activity</b>	<b>3<sup>rd</sup> Water Activity</b>	<b>4<sup>th</sup> Water Activity</b>
Wheat	0.60	0.70	0.80	0.90
Barley	0.65	0.75	0.85	0.95

**Table 2. Permeance values<sup>a</sup> ( $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}\cdot\text{kPa}^{-1}$ ) at each water activity level for wheat and barley.**

<b>Grain</b>	<b>1<sup>st</sup> Water Activity</b>	<b>2<sup>nd</sup> Water Activity</b>	<b>3<sup>rd</sup> Water Activity</b>	<b>4<sup>th</sup> Water Activity</b>
Wheat	1.040 <sup>A</sup>	1.308 <sup>A</sup>	2.017 <sup>B</sup>	2.271 <sup>B</sup>
Barley	1.124 <sup>A</sup>	1.561 <sup>A</sup>	3.276 <sup>C</sup>	2.161 <sup>B</sup>

<sup>a</sup> Permeance values followed by the same letter in a row are not significantly different ( $p>0.05$ ).

**Chapter 3.**

**The Critical Water Activity from Dynamic Dewpoint Isotherms as an Indicator of Pre-mix  
Powder Stability**

**Brady Carter  
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## ABSTRACT

Premix instant powders offer quick, easy alternatives for making common food products such as gravy, muffins, and beverages. To remain viable and be considered stable, all powders must remain free flowing. The problem of caking and stickiness in powders is ubiquitous across industries. Premix instant powders must be free of caking, but must also maintain their wettability, solubility, and dissolution properties. The main extrinsic factors that influence the caking and general stability of powders are temperature and water activity. More specifically, for amorphous powders, maintaining stability requires avoiding a glass transition from the metastable glassy state to the rubbery state. Dynamic isotherms are an effective way to investigate the critical water activity for glass transition in low molecular weight amorphous powders. This critical water activity can be used as a specification to maintain the stability of glassy powders. Premix instant powders are often primarily wheat flour, which has a high glass transition, so it is questionable if a critical water activity associated with stability can be found. The purpose of this study was to determine if a critical water activity can be determined for premix instant powders using dynamic isotherms and if this critical water activity is associated with product stability. Instant oatmeal muffin powder and instant chicken gravy powder were analyzed by dynamic isotherms and found to have a critical water activity at approximately 0.70  $a_w$ . Samples of the premix powders were then equilibrated to water activities above and below the critical water activity and examined for changes in caking strength over time. It was determined that there was no trend in changes in caking strength over time at the various water activities, likely because the samples were analyzed at constant water activity instead of allowing water activity to vary with time as in previous studies. However, the mean caking

strengths at water activities less than the critical water activity were significantly higher than at higher water activities. The premix samples also experienced color and other appearance changes above the critical water activity. The changes in the premix powders' matrices that occurred at the critical water activity impacted their performance and are more likely associated with the initiation of dissolution than with glass transition. Regardless of their cause, these changes did result in degradation of the powder, indicating that a critical water activity from dynamic isotherms provides a specification to prevent product loss for premix instant powders without an extensive stability study.

## INTRODUCTION

Caking and stickiness of powders during handling, packaging and storage are ubiquitous problems in the food and pharmaceutical industries. Problems can happen during both processing and storage of amorphous powders [1]. Stickiness refers to the tendency of a material to adhere to other surfaces or materials, which may or may not lead to caking [1].

Caking is the formation of permanent clumps due to the stickiness of particles which eventually can result in a loss of functionality and lowered quality [2, 3]. Stickiness and caking reduce product recovery during drying, slow processing time by clogging up hoppers and pipes, and reduce product shelf life. There are numerous proposed methods for ascertaining flow properties, from a simple test that consists of spinning a propeller in a test tube of powder to a complex flow testing rig fitted to a texture analyzer [4].

Caking and stickiness are water activity, time, and temperature dependent and are related to the collapse phenomena of the powder under gravitational force [5-8]. Stages in caking involve bridging, agglomeration, compaction, and liquefaction [7]. Factors known to affect caking kinetics may be divided into intrinsic properties of the powder itself (particle size distribution, hygroscopicity, charge of particles, state of the material, presence of impurities, and glass transition temperature) and external factors such as temperature, relative humidity and mechanical stress applied to the substance [7, 9]. If the powder is an amorphous glass, a transition from the glassy to rubbery state will cause the powder to become susceptible to caking due to increased molecular mobility in the rubbery state [5, 10-18]. A glass transition can be induced by either temperature or moisture and protecting the powder against glass



transition through packaging and storage conditions will help maintain its stability [1]. The temperature at which a glass transition occurs at a given water activity has been identified as the glass transition temperature ( $T_g$ ) [19, 20]. The water activity where the glass transition occurs at a given temperature has been identified as the critical water activity (RHc) [21]. The plasticization of particle surfaces and drastic reduction in surface viscosity that occurs at the glass transition is thought to be the main contributor to the resulting increased caking rate [22]. Specifically, the rate of caking has been related to the difference between storage temperature ( $T$ ) and  $T_g$  ( $T-T_g$ ), which can be modeled using the Williams, Landel, and Ferry (WLF) relationship [10, 14, 16, 17].

The rate of caking of food powders is also related to moisture sorption and changes in water activity. As the storage humidity is increased, the rate of changes in caking strength and caking index increases significantly [7, 11-13, 15, 18, 23]. Similar to the effect of increasing  $T-T_g$  on caking, the increase in caking rate related to increased water activity likely is a result of moving above the RHc for glass transition. Traditionally, this RHc value would have to be determined by running  $T_g$  analyses at multiple water activity levels. However, recently developed Dynamic Dewpoint Isotherms (DDI) have made it possible to directly determine the RHc for glass transition in low molecular weight amorphous powders at a given temperature [24, 25]. A sharp inflection point in the DDI curve due to sudden changes in sorption properties at the glass transition identifies the RHc. If both an increase in caking rate and the RHc determined by DDI analysis are related to the glass transition, it is logical that there should be significant

differences in the caking rate at water activities below and above the RHc. This would mean that the RHc could be used as a specification to maintain powder stability.

While many food powders are utilized as ingredients, instant premix powders are purchased directly by consumers and used as a convenient way to quickly make products such as gravy, sauces, and baked products [26]. Like any powder, these premix powders must stay free flowing and maintain an acceptable level of wettability and solubility to be acceptable to the consumer [26]. Premix powders are typically complex combinations of multiple ingredients each with a different glass transition temperature, so it is unknown if the DDI curves for these powders will show an RHc. Even if they do, it is unclear if the RHc can be used as a specification to maintain product acceptability. Premix powders whose main ingredient is flour, which is primarily starch, are especially unlikely candidates for exhibiting a DDI RHc because the glass transition for the amorphous region of starch occurs at water activities greater than 0.95 at room temperature [1]. The purpose of this study was to determine if an RHc from the DDI method could be determined for premix instant powders whose main ingredient is flour. If an RHc could be determined, a further objective was to determine if the rate of change in caking strength is different at water activities below and above the RHc, indicating that the RHc from DDI could be used as a stability control specification for premix powders.

## **MATERIALS AND METHODS**

Premix instant oatmeal muffin mix (OM) and chicken gravy mix (CG) were obtained from a local grocery store. Both of these instant powders have wheat flour as their top ingredient. The

powders were then sieved to create uniform particle size. Powders were placed on an 850  $\mu\text{m}$  and 150  $\mu\text{m}$  sieve and shaken for 5 minutes. Any powder remaining on the 150  $\mu\text{m}$  sieve was retained for analysis. The sieving process resulted retention of 24% of the total initial oatmeal muffin mix on the 850  $\mu\text{m}$  sieve, which consisted primarily of the oats and was removed. For chicken gravy, none of the sample was retained on the 850  $\mu\text{m}$  sieve and less than 1% passed through the 150  $\mu\text{m}$  sieve. The powder was then divided into subsamples to be used for water activity testing, DDI analysis, and caking analysis.

The initial water activity of OM and CG was determined at 25°C using an AquaLab Series 4TE (Decagon Devices, Inc. Pullman, WA). Adsorption DDI curves were conducted in triplicate on subsamples of OM and CG to determine if an RHc could be identified. The AquaLab VSA (Decagon Devices, Inc. Pullman, WA) was utilized for generating DDI curves with DDI settings of a minimum water activity of 0.03  $a_w$ , a maximum water activity setting of 0.90  $a_w$ , a flow rate of 80 ml/min, resolution setting of 0.01  $a_w$ , and starting sorption direction adsorption. DDI curves were generated at 25°C, 35°C, and 40°C. Each triplicate DDI curve at each temperature was examined for the presence of an RHc, identified as the water activity associated with a sharp inflection in the DDI curve. The water activity of the RHc was determined by finding the first maximum in the Savitsky-Golay 2<sup>nd</sup> derivative curve [24, 27]. The mean RHc from triplicate DD isotherms was utilized for additional analysis. One replicate of OM and CG at 25°C was subjected to a 2<sup>nd</sup> adsorption and desorption DDI event to determine if the resorption curve matched the initial adsorption curve.

Subsamples of OM and CG were equilibrated to water activity levels higher and lower than the RHc to examine the impact of the RHc on caking strength. Samples were placed in sealed chambers over saturated slurries and controlled to 25°C, 35°C, and 40°C in an oven until the samples had reached equilibrium. Progression to equilibrium of samples was tracked by measuring the water activity of 1 subsample. Equilibrium was assumed when the water activity of sequential readings were within +/- 0.003 of the expected water activity. For OM, 4 water activity levels were used: 0.649  $a_w$  (CoCl<sub>2</sub>), 0.689  $a_w$  (KI), 0.753  $a_w$  (NaCl), and 0.810  $a_w$  (KBr). For CG, since its mean RHc was lower at 0.70  $a_w$ , 4 lower water activity levels were used: 0.576  $a_w$  (NaBr), 0.649  $a_w$  (CoCl<sub>2</sub>), 0.689  $a_w$  (KI), and 0.753  $a_w$  (NaCl).

The equilibrated subsamples of OM and CG were then subjected to caking strength analysis over time. Readings were taken at equilibrium as time zero and then 5 days, 11 days, 14 days, and 21 days after equilibrium. A unique subsample was used for caking strength analysis at each time interval. Caking strength was assessed according to the methodology of Wang et al. [28] with some slight modifications. Five gram subsamples of OM and CG were placed in 4 cm diameter plastic cups and compacted with a 1.3 kg load force for 30 seconds. The cups with the sample were then placed on a TA-TX2 Texture Analyzer (Stable Microsystems Ltd, Godalming, UK) with the sample offset from center toward the edge of the cup to eliminate the impact of any center dimples in the plastic cup. A 1.5 cm cylinder probe was then used to compress the samples at 1.0 mm/s to a depth of 5 mm into the sample. The peak force (N) achieved during compression was reported as the caking strength.

Analysis of Variance (ANOVA) was performed on caking strength values with temperature, water activity, time, and their interaction considered random factors using Minitab 16 Statistical Software [29]. For comparisons of caking strength, since time was not a significant source of variation, measurements taken across time intervals were combined as replicates and averaged, excluding those lying outside of the 95% confidence interval for the mean. RHc values at each temperature, as well as caking strength values at each water activity and temperature were compared using Tukey's multiple means comparison. Finally, discriminant analysis was used to determine if caking strength values above and below the RHc compiled two distinct statistical groups.

## **RESULTS AND DISCUSSION**

Figure 1 shows the DDI curves for OM and CG at 25°C, 35°C, and 40°C. In the water activity range of 0.10  $a_w$  to 0.7  $a_w$ , OM and CG samples took up only a small amount of moisture resulting in a relatively flat curve. Then, at water activities higher than approximately 0.70  $a_w$ , a sudden change in sorption properties occurred resulting in steepening of the slope as the uptake rate increased. The result is the appearance of an inflection point in the sorption curve associated with the RHc. The specific RHc value was identified as the water activity associated with a maximum in the Savitsky-Golay 2<sup>nd</sup> derivative curve (Figure 1). Such a sudden increase in the rate of moisture uptake experienced at the RHc would require the sudden availability of many previously inaccessible binding sites for water, which would only be possible if the matrix experienced substantial property changes at this water activity. The extremely high data resolution of DDI isotherms makes it possible to identify the RHc associated with these changes.

Previous studies reported that these inflection points could be observed in low molecular weight amorphous powders, but it was unclear if the inflection point would appear for premix powders whose primary ingredient is flour (19, 20).

The RHC values for both OM and CG were in the range of 0.70-0.75  $a_w$  (Table 1). These RHC values are higher than those seen for other amorphous powders, but not unexpected since the primary ingredient in both products is wheat flour [24]. It is not clear if the transition that occurred and resulted in a change in sorption properties was a glass transition event, since the glass transition of wheat flour is expected to occur at water activities greater than 0.95  $a_w$  when the temperature is 25°C [1]. The 2<sup>nd</sup> most prominent ingredient in the ingredient list for OM is brown sugar. Figure 2 shows the DDI curve of brown sugar with the DDI curve of flour. Brown sugar's DDI curve has an inflection point at 0.74  $a_w$  at 25°C, while the DDI curve of flour does not have an inflection point. Since brown sugar's RHC value matches the RHC for OM at 25°C (Table 1), it appears that the shape of the DDI curve for oatmeal is being strongly influenced by the brown sugar. The 2<sup>nd</sup> and 3<sup>rd</sup> most prominent ingredients in CG are dextrose and sodium chloride. The DDI curves of these two ingredients at 25°C are shown with the DDI curve for flour in Figure 3. The DDI curve for sodium chloride is typical for a crystalline salt and undergoes deliquescence into a saturated slurry at 0.75  $a_w$ . The DDI curve for dextrose is more typical of an amorphous material that is experiencing a glass transition at an RHC of 0.716  $a_w$ . As with OM, the RHC of dextrose, the 2<sup>nd</sup> most prominent ingredient matches the RHC for gravy at 0.72  $a_w$ , while the flour DDI curve shows no inflection point. Consequently, dextrose is likely the primary contributor to the shape of the gravy DDI curve. Sodium chloride may be having some

modifying effect as well, but its concentration is likely low enough to limit its impact. The RH<sub>c</sub> value of OM did not change at different temperatures, but decreased significantly at higher temperatures for CG (Table 1). This is likely the result of differences in the temperature sensitivity of brown sugar and dextrose.

For this study, time was not a significant source of variation in caking strength for either OM (p value 0.08) or CG (p value of 0.007) at the 0.001 level. This is not in agreement with previous studies that found that caking strength increased over time when exposed to higher humidities [7, 11-13, 15, 18, 23]. However, these studies did not equilibrate the samples to a water activity and then start tracking caking strength, but instead tracked changes from the moment the sample was exposed to high humidity. This confounds the effect of water activity and time since water activity is not constant. The different rates of change in caking strength at different humidity levels would then be the result of creating different driving forces for water activity change with time. The caking strength then increases more quickly over time because the water activity is increasing more quickly. The lack of association of caking strength changes and time for this study was then likely due to the samples being already equilibrated and any changes in the strength of the powder would have already occurred. In addition, the significant changes in caking strength with time is typically associated with the rubbery state and the samples in this study were both above and below the RH<sub>c</sub>, resulting in 2 different matrix phases.

When caking strength values at a given water activity and temperature are averaged and plotted for both OM and CG, there is a clear indication that the strength properties of the

powders decreased above the RHc (Figure 4). When the caking strength values above and below the RHc are grouped into 2 distinct groups, discriminate analysis confirms the grouping with 100% assurance for both OM and CG. These results would indicate that a significant change in the properties of the powders is occurring at the RHc. In previous studies, a matrix transition was typically associated with an increase in caking strength [7, 11-13, 15, 18, 23]. Conversely, the instant powders analyzed in this study lost strength at water activities higher than the RHc, which would indicate that instead of tracking caking strength, the analysis was measuring the wetting level of the powders. Since these premix powders are intended to be instant, they must possess good wettability and solubility characteristics. It is likely that the RHc identified for these instant powders is indicating the onset of dissolution, which would explain the sudden changes in sorption properties as portions of the powder began to dissolve, making additional water binding sites available. Samples of both OM and CG at the highest water activities had a moist appearance, experienced some shrinkage, and experienced color changes, losing their identity as instant powders (Figure 5). The change of color would be expected if the instant powders were beginning to go into solution resulting in dilution of the color pigments and fading of the colors.

Exposure of products to abuse conditions is usually temporary and only impacts portions of the product before normal storage conditions are restored. This raises the question of the permanency of the changes that occur at the RHc. Will the product be restored once its water activity is reduced back to values below the RHc? Figure 6 indicates that the inflection in the DDI adsorption curve did not occur during a second adsorption event for either OM or CG. The



subsequent adsorption curve did experience a large increase in moisture, but uptake was more consistent and smooth rather than abrupt at the RHc. This would suggest that the change that occurred during the initial adsorption at the RHc was an irreversible change and the product could not be put back into its original condition simply by desiccation. This lack of reversibility is a clear indication that a significant change has occurred in the matrix of these powders due to wetting. A similar lack of reversibility in the DDI adsorption curve was seen with low molecular weight amorphous samples experiencing glass transition [24]. This irreversible change in these powders as a result of wetting would be expected to result in changes in attributes of the portion of the product that experienced the change even when its water activity drops to levels below the RHc. From a practical standpoint, the consequence of this irreversibility would be that if the water activity of the powders is allowed to exceed the RHc, at least some portion of the product will be permanently altered and could only be returned to its original condition through reprocessing.

To verify that permanent differences had occurred in samples exposed to water activities higher than the RHc, additional caking strength tests were performed on duplicate samples of oatmeal and gravy at 25°C. OM samples were equilibrated to 0.81  $a_w$ , above the RHc, and then re-equilibrated to 0.65  $a_w$ , lower than the RHc. CG samples were equilibrated to 0.75  $a_w$ , above the RHc, and then re-equilibrated to 0.57  $a_w$ , lower than the RHc. The caking strengths of these samples are shown with the original caking strengths at low water activity in Table 2. A Student's T-test revealed that the strength of the samples that were exposed to water activities higher than the RHc and then brought back below the RHc were significantly lower than those

held at low water activity for both OM ( $p = 0.005$ ) and CG ( $p = 0.042$ ). This change in the physical strength of the powders provides further evidence that the change experienced by these instant powders when exposed to water activities greater than the RHc is both significant and permanent.

## **CONCLUSION**

The DDI curves of both OM and CG powders experienced sudden changes in sorption properties indicating an RHc, but unlike in earlier studies, this RHc was likely not associated with a glass transition. Instead, it is more likely that the RHc indicated the onset of dissolution of the instant powders. The samples held at water activities less than the RHc did not show any differences in caking strength, indicating that caking may not be the most likely or important stability loss factor for these premix powders. The expected trend of increased caking strength as water activity increased above the RHc was not seen in this study, likely because the RHc indicated the wetting of the instant powder and changes to the solubility and dissolution properties of the product instead of more susceptibility to caking.

The RHc of these powders was still a clear indicator of loss of stability and they would need to be processed to water activity levels below the RHc, and then protected from high storage humidity by a packaging with good moisture barrier properties. Any product exposed to water activities higher than the RHc will undergo irreversible changes and will not have the same properties even if the water activity is reduced to levels below the RHc. The approach of identifying the RHc presented in this study provides a straightforward method for identifying

the optimal water activity ranges for instant powders using a DDI curve from an automated vapor sorption analyzer without the need for a time and labor intensive full caking strength study.

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FIGURES

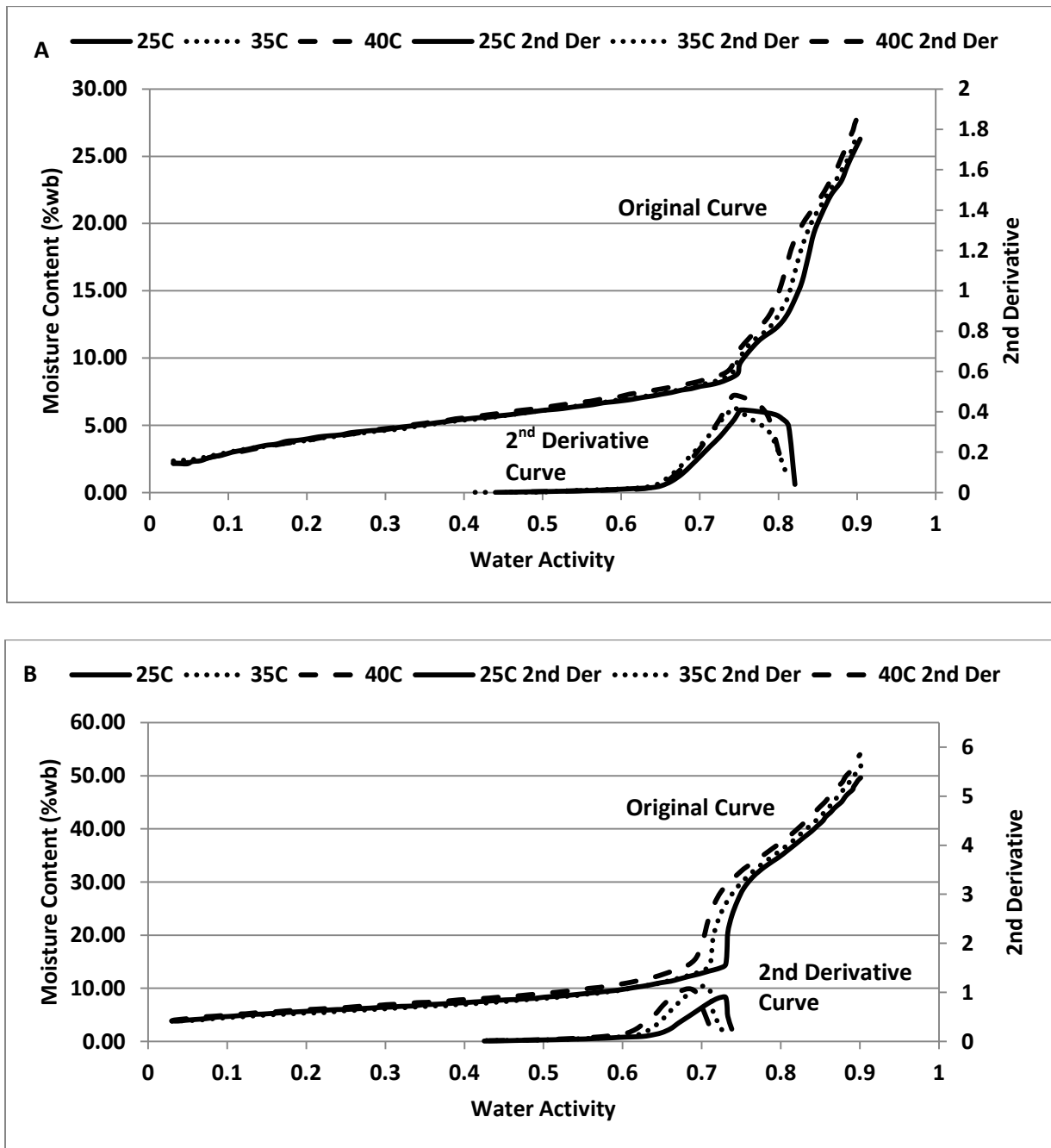


Figure 1. Dynamic dewpoint adsorption isotherms for oatmeal (A) and gravy (B) premix powders at 25°C, 35°C, and 40°C. The Savistky-Golay 2<sup>nd</sup> derivative plots are also shown on the secondary axis and below the original curve. The maximum in the 2<sup>nd</sup> derivative curve identifies the inflection point in the original curve.



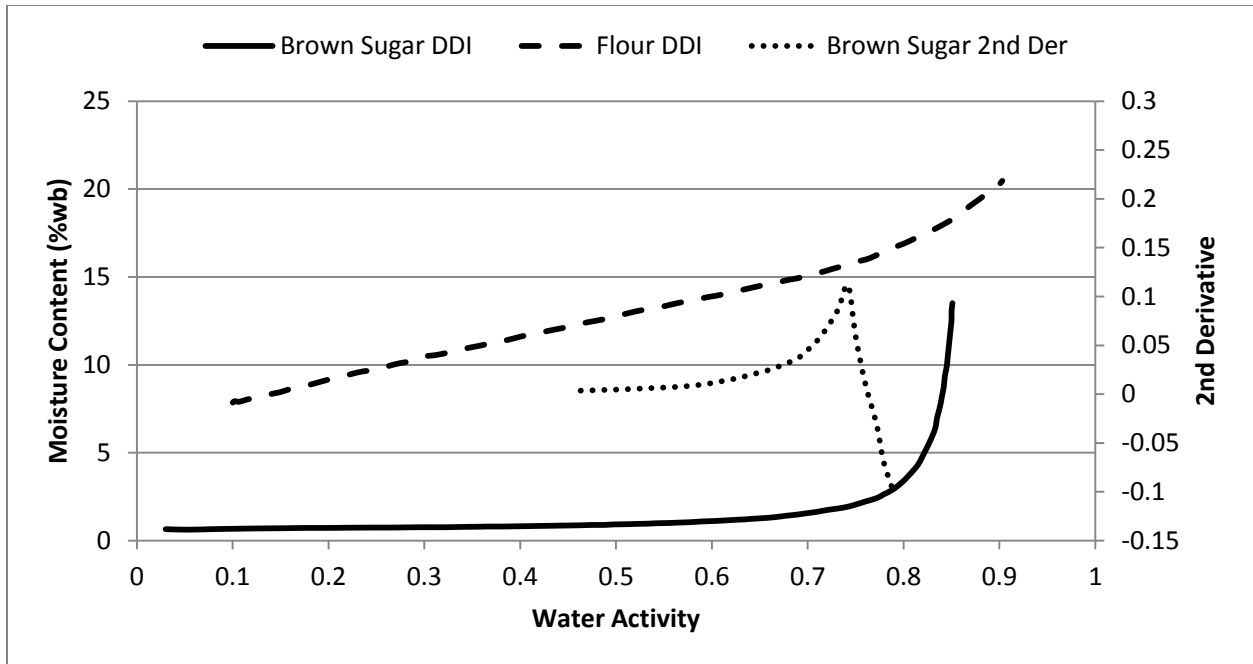


Figure 2. DDI Curve (—) for Brown Sugar, the 2<sup>nd</sup> most prominent ingredient in oatmeal premix. The 2<sup>nd</sup> derivative curve (···) is also shown and the maximum in the 2<sup>nd</sup> derivative curve at 0.742  $a_w$  indicates an inflection point in the original curve. The DDI curve for flour (---) is also shown for comparison.

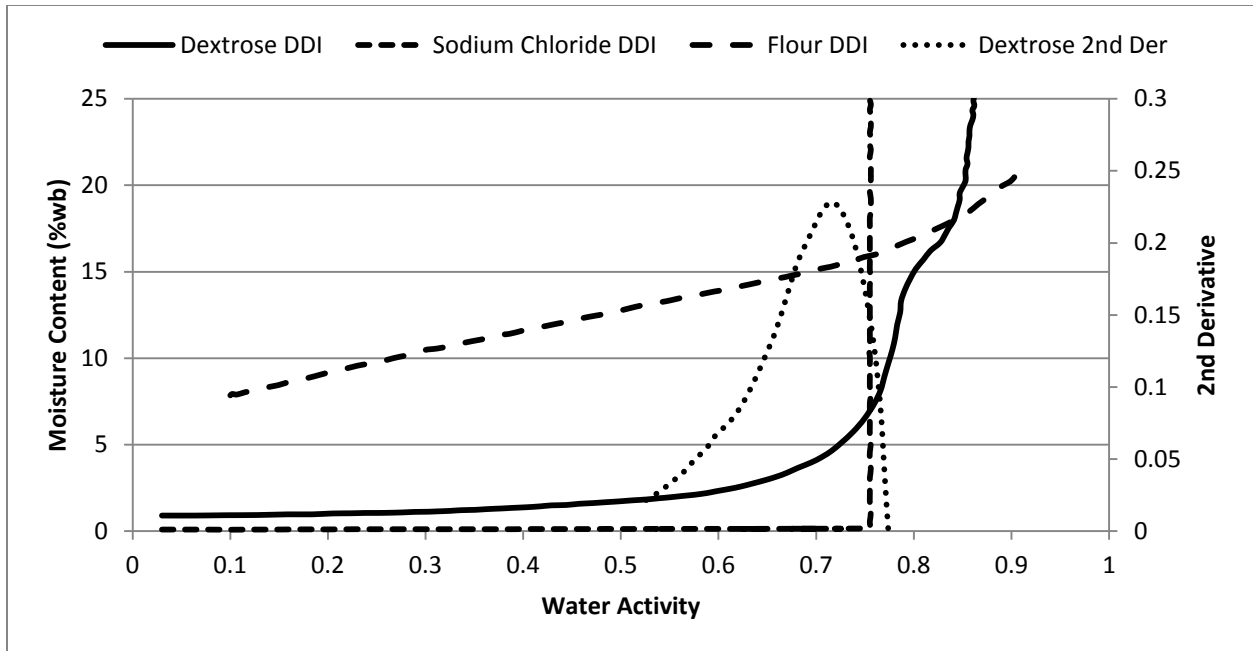


Figure 3. DDI Curve (—) for Dextrose, the 2<sup>nd</sup> most prominent ingredient in gravy premix, and Sodium Chloride (---), the 3<sup>rd</sup> most prominent ingredient. The 2<sup>nd</sup> derivative curve (····) for dextrose is also shown and the maximum in the 2<sup>nd</sup> derivative curve at 0.716  $a_w$  indicates an inflection point in the original curve. Sodium Chloride experiences deliquescence at 0.753  $a_w$ . The DDI curve for flour (— · —) is also shown for comparison.

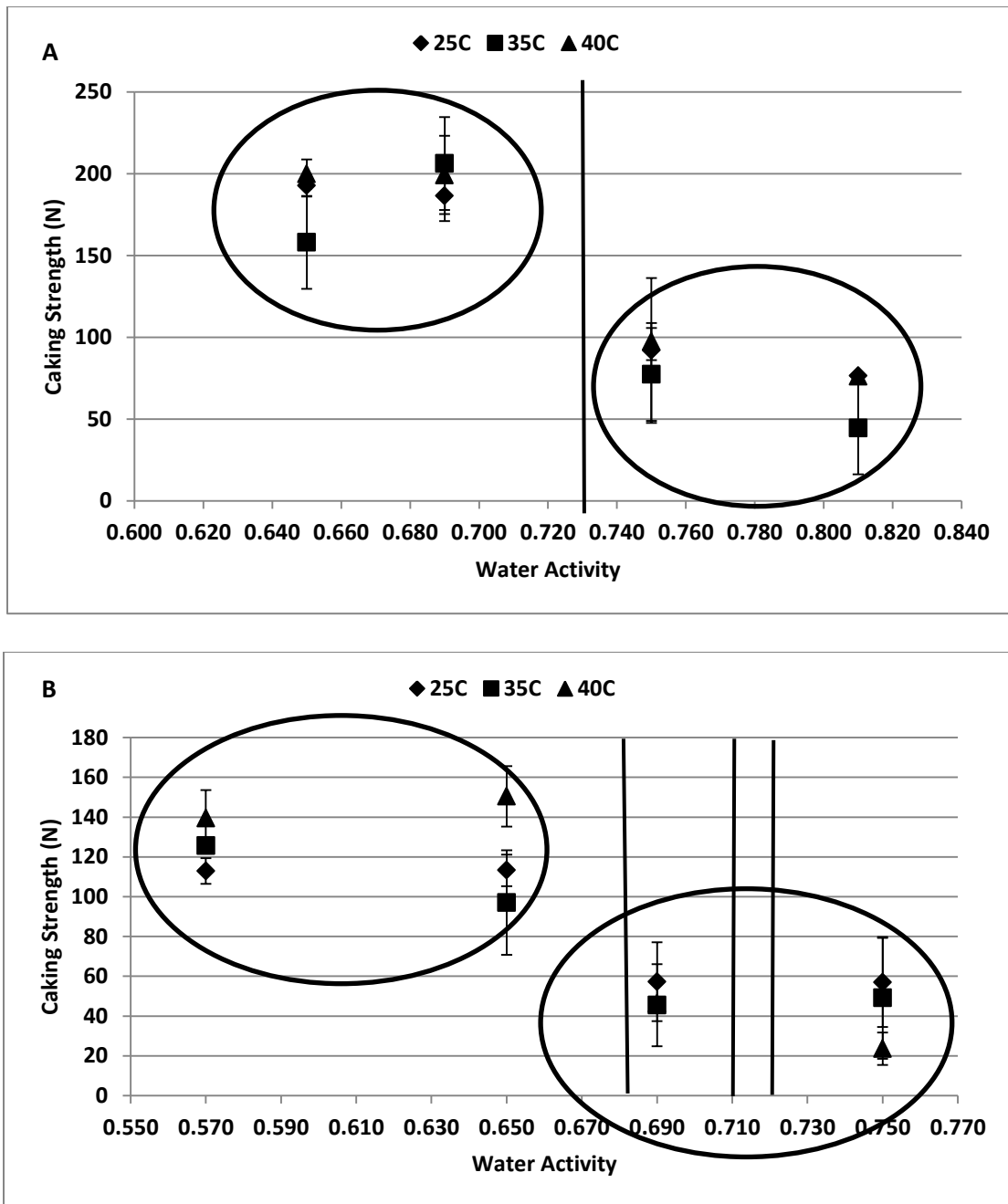
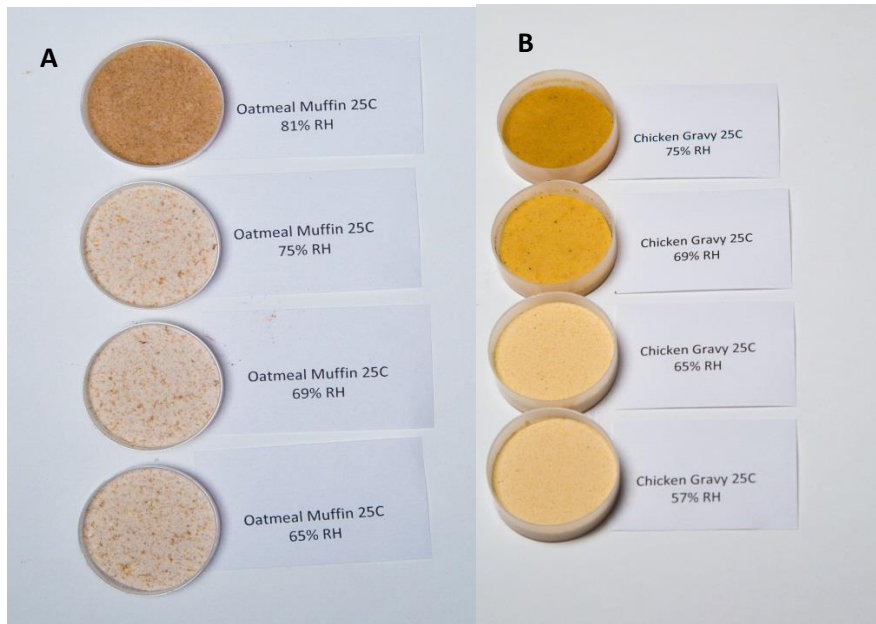


Figure 4. Average caking strength of oatmeal (A) and gravy (B) premix as water activity increases at 25°C, 35°C, and 40°C. Caking strength values within a circle are not significantly different ( $p < 0.05$ ). Vertical solid lines indicate the critical water activity from DDI analysis averaged across temperature for oatmeal (0.73 $a_w$ ) and shown separately at each temperature for gravy.



**Figure 5. Images of oatmeal (A) and gravy (B) premix powders exposed to different relative humidities until equilibrium at 25°C indicating a color change and product change at higher water activities.**

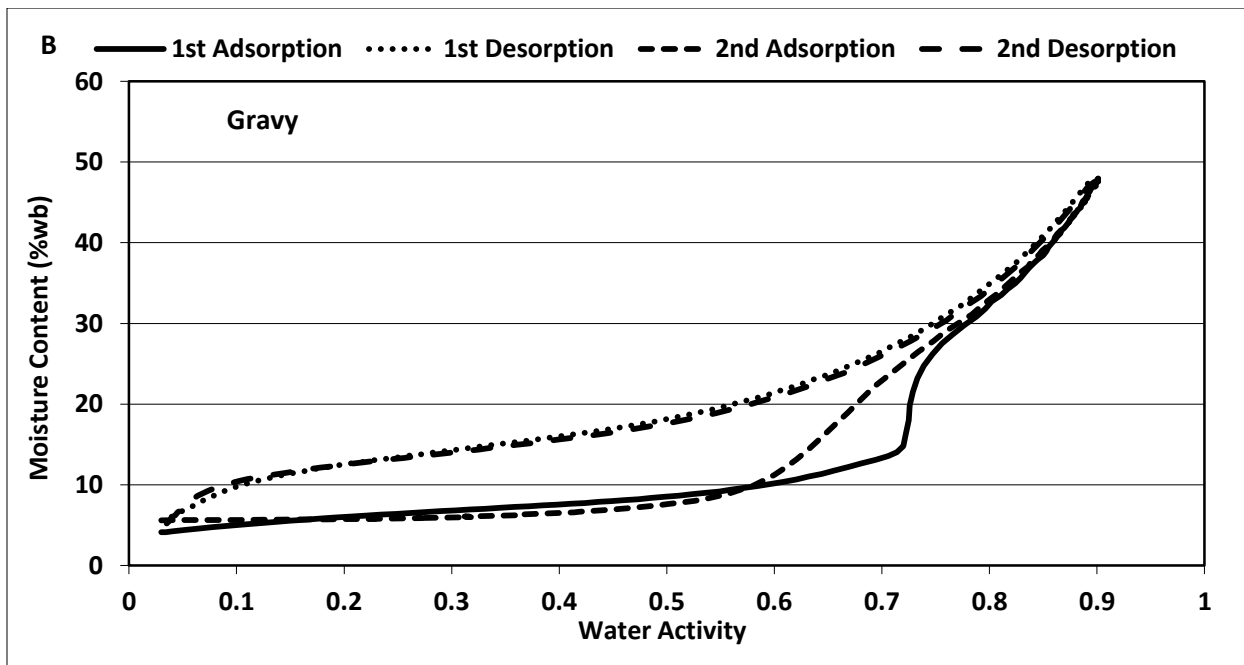
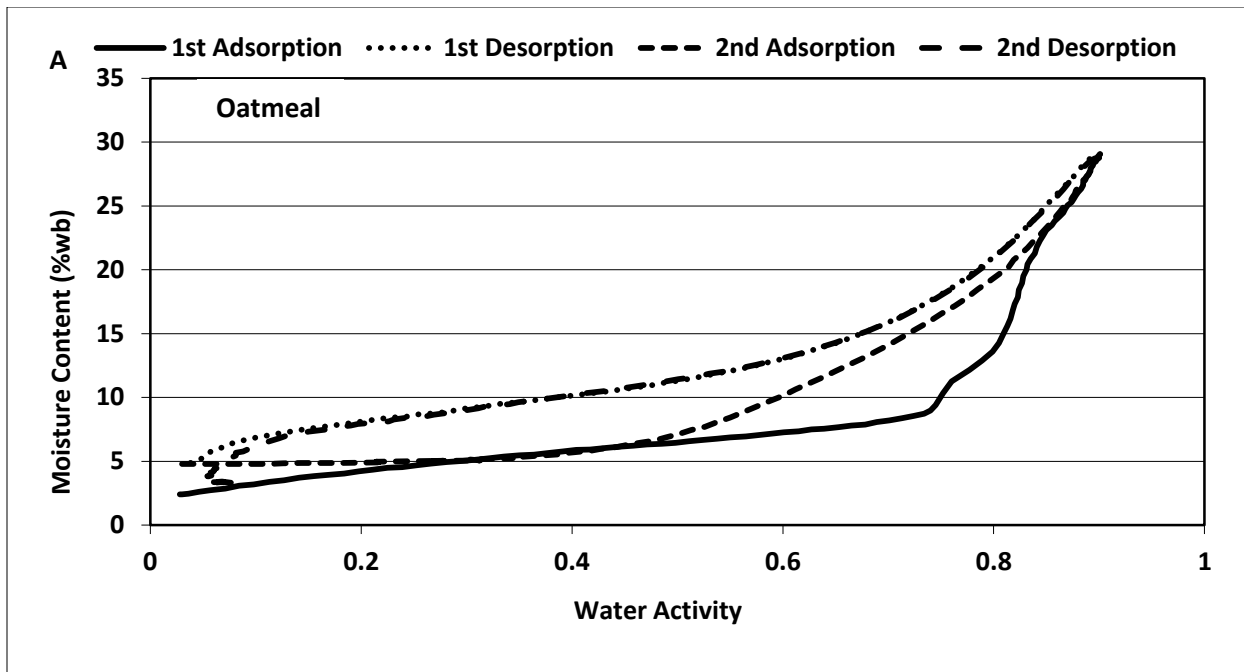


Figure 6. Dynamic dewpoint isotherms for oatmeal (A) and gravy (B) premix powders at 25°C.

The samples were subjected to an initial adsorption (—), then desorption (····), a 2<sup>nd</sup> adsorption (---), and a final desorption event (----).

#### TABLES

## TABLES

**Table 1. Critical water activities<sup>a</sup> of oatmeal and gravy premix at three different temperatures.**

<b>Sample</b>	<b>25°C</b>	<b>35°C</b>	<b>40°C</b>
Oatmeal Premix	0.740 <sup>A</sup>	0.730 <sup>A</sup>	0.730 <sup>A</sup>
Gravy Premix	0.720 <sup>A</sup>	0.705 <sup>AB</sup>	0.680 <sup>B</sup>

<sup>a</sup> Critical water activities in a row followed by the same letter are not significantly different ( $p>0.05$ ).

**Table 2. A comparison of average caking strengths (N) of oatmeal and gravy samples that were held at water activities below the RHc to samples held at water activities higher than the RHc, and then returned to a water activity below the RHc.**

<b>Sample</b>	<b>Held Below RHc</b>	<b>Above RHc to Below RHc</b>
Oatmeal Premix	192.8 <sup>A</sup>	164.2 <sup>B</sup>
Gravy Premix	112.9 <sup>A</sup>	60.6 <sup>B</sup>

<sup>a</sup> Hardness values in a row followed by the same letter are not significantly different ( $p>0.05$ ).

**Chapter 4.**

**The Critical Water Activity from Dynamic Dewpoint Isotherms as an Indicator of Crispness in  
Low Moisture Cookies**

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Washington State University**



## ABSTRACT

Low moisture cookie snacks are expected to possess a crisp texture when consumed. If this crispness is lost, the product is deemed unacceptable to the consumer. The most important factors influencing the crispness of low moisture cookies are moisture and temperature. Studies have shown that there exists a critical water activity where desirable crispness will be lost. Typically, this critical water activity would be obtained through an extensive texture study. However, high resolution dynamic isotherm curves have recently been shown to identify critical water activities (RH<sub>c</sub>) by sharp inflections in the adsorption curve. The purpose of this study was to determine if the RH<sub>c</sub> from dynamic isotherms of low moisture cookie snacks provided the critical water activity for texture as well. Dynamic isotherms were developed for two low moisture cookies at three different temperatures and used to determine the RH<sub>c</sub>. Then, samples preconditioned to various water activities and temperatures were analyzed for crispness. The effect of water activity on crispness was more important than temperature. Cookie samples at water activities less than RH<sub>c</sub> maintained their crispness, but suffered an abrupt loss in texture at water activities higher than RH<sub>c</sub>, giving a sigmoidal shaped response. Fermi's equation for sigmoidal response was used to model the data and estimate a critical water activity for texture. Both the RH<sub>c</sub> and Fermi's critical water activity were found in the range of texture loss, but the RH<sub>c</sub> corresponded with the initial loss in texture while Fermi's critical water activity was at the center of the texture loss. Since the RH<sub>c</sub> can be obtained with much less labor and time than a texture study and provides an effective indication of the loss of crispness, it was concluded that the RH<sub>c</sub> provides a viable alternative for determining the critical water activity for crispness.

## INTRODUCTION

Food texture is an important physical stability factor and gives an identity to a product. When the texture of a product is correct, it receives little notice, but when it is not, the product is rejected immediately [1]. Since textural properties result from the often complex interactions of multiple factors, it is desirable to focus in on a limited number of texture attributes [2]. The most common texture attribute associated with low water activity products, such as cookies and crackers, is crispness, which has been described as being sensed by both touch and sound [3, 4]. When a force is applied to a crisp product, it should fail abruptly with a distinct high pitched sound [4]. Relative levels of crispness can be measured using either sensory panels, texture analyzing equipment, or acoustics [5]. Texture analysis instruments attempt to mimic the sense of crispness by applying a perpendicular force to the sample, typically using some type of blade. This method is called a three point bend and force is applied until the sample fails and the maximum force achieved prior to failure is recorded [6].

The crispness of low moisture products can be impacted by moisture changes [1, 3, 7-10]. The pioneering work investigating the relationship between water sorption and textural changes was by Katz and Labuza (9). They focused on water activity, the energy of status of water, as a better predictor of crispness than moisture content, a quantitative measure of the amount of moisture. By equilibrating crisp products to various water activities and then evaluating the samples for crispness, they were able to track changes in crispness due to water activity changes. Using both sensory panel data and instrumentation, the relationship between

crispness as sensed by the panel and water activity was essentially linear, allowing identification of a water activity range where crispness changed from acceptable to unacceptable. A specific explanation of the reason for the change in crispness at these water activity values was not provided, but was treated as a macroscopic observation with practical utility. In some cases, loss of crispness may be related to glass transition [11], but there are cases where the critical water activity for crispness has been identified within the glassy state [12].

With the work of Katz and Labuza (9) as a foundation, subsequent studies of crispness using either sound or force, found a sigmoidal relationship between crispness and water activity [1, 3, 7, 8, 10]. This sigmoidal shape was successfully modeled using the Fermi model, allowing for prediction of texture based on water activity and provided an estimation of the critical water activity for texture. [1, 3, 7, 13]. Subsequent papers were also able to successfully model the relationship between  $a_w$  and the texture of roasted coffee beans [14], biscuits [1], and breakfast cereals [10, 13, 15]. These studies provided evidence that the uptake of moisture during storage by a product is a primary contributor to loss of crispness.

The sorption of water that can lead to a loss in crispness can be characterized through the relationship between water activity and moisture content. This relationship is called the moisture sorption isotherm and is unique to each type of material [16]. The nature of the sorption isotherm is determined by particle size, chemical makeup, and concentration of humectants such as salt or sugar [17]. There are two basic methods for determining moisture sorption isotherm characteristics, namely static and dynamic. Traditional static methods for

measuring moisture sorption isotherm properties, often referred to as Dynamic Vapor Sorption (DVS), rely on equilibration to known relative humidity levels while tracking weight change [16]. Newly developed dynamic methods such as the Dynamic Dewpoint Isotherm (DDI) method, directly measure water activity while gravimetrically tracking weight change, so there is no dependence on equilibration to known humidity levels to determine water activity [18]. Since dynamic isotherm methods rely on direct measurement of water activity, they are faster and capable of much higher data resolution than DVS methods [18].

The high resolution of the DDI method makes it possible to characterize abrupt changes in moisture sorption properties resulting from moisture induced matrix changes. Repeatable sharp inflections in the DDI curve have been used to successfully determine moisture induced glass transition in milk powder [19], polydextrose, and cereal flakes [20] The water activity at which the inflection point in the curve occurred was identified as the critical water activity (RH<sub>c</sub>) at the temperature of the isotherm. Due to its association with glass transition, this RH<sub>c</sub> has been identified as the critical water activity level for the loss of stability in amorphous powders [21]. Since previous studies investigating water and crispness identified a critical water activity range, there is the possibility that an RH<sub>c</sub> identified from a DDI curve for a crisp product could be an alternative option for finding the critical water activity for texture without an extensive texture study. The objective of this work was to determine if the DDI curves for low water activity snack cookies could be used to identify an RH<sub>c</sub> and if this RH<sub>c</sub> was also related to the loss of crispness.

## MATERIALS AND METHODS

Graham crackers (GC) and shortbread cookies (SC) were obtained from a local grocery store with a sample being 1 precut rectangle for GC and 1 whole cookie for SC. The 'as is' water activity was determined using an AquaLab Series 4TE at 25°C (Decagon Devices, Inc. Pullman, WA). To determine the RHc, triplicate dynamic adsorption isotherms using the Dynamic Dewpoint Isotherm (DDI) method were conducted on out of package samples of GC and SC. The AquaLab VSA (Decagon Devices, Inc. Pullman, WA) was utilized with DDI settings of minimum water activity of 0.03  $a_w$ , a maximum water activity setting of 0.90  $a_w$ , a flow rate of 80 ml/min, resolution setting of 0.01  $a_w$ , and starting sorption direction adsorption. DDI curves were generated at 25°C, 35°C, and 40°C. The RHc for each triplicate DDI curve at each temperature was identified as the water activity associated with a sharp inflection in the DDI curve and was determined by finding the first maximum in the Savitsky-Golay 2<sup>nd</sup> derivative curve [21, 22]. The mean RHc from triplicate DD isotherms was utilized for additional analysis. One replicate for each cookie at 25°C was subjected to a 2<sup>nd</sup> adsorption and desorption DDI event to determine if the resorption curve matched the initial adsorption curve.

To investigate the relationship between RHc and quality loss, 4 replicates of each cookie type were controlled to water activity levels higher and lower than the RHc. Samples were placed in sealed chambers over saturated slurries and controlled to 25°C, 35°C, and 40°C in an oven until the samples had reached equilibrium. Containers for all water activity levels at a given temperature were controlled in the same oven. Equilibrium of samples was identified when the water activity of duplicate cookies was within +/- 0.003 of the expected water activity. For GCs,

5 water activity levels were used: 0.328  $a_w$  ( $MgCl_2$ ), 0.382  $a_w$  (NaI), 0.529  $a_w$  ( $Mg(NO_3)_2$ ), 0.576  $a_w$  (NaBr), and 0.649  $a_w$  ( $CoCl_2$ ). For SC, 4 water activity levels were used: 0.432  $a_w$  ( $K_2CO_3$ ), 0.576  $a_w$  (NaBr), 0.649  $a_w$  ( $CoCl_2$ ), and 0.753  $a_w$  (NaCl).

Once the samples were equilibrated to the different water activities, the 4 replicate samples of each cookie were subjected to crispness testing using a TATX2i Texture Analyzer (Stable Microsystems Ltd, Godalming, UK). A three point bend test using a TA-92 three point rig and a TA-42 knife probe was used to snap the cookie samples. Crispness was determined as the maximum force (N) applied at failure of the sample. The settings for the texture analyzer were a trigger force of 5g, test speed of 2.0mm/sec, travel distance of 5.0 mm, and a return speed of 10 mm/s. Average crispness values for each cookie type at each temperature and water activity were reported.

Analysis of Variance (ANOVA) was performed on crispness values with temperature, water activity, and their interaction considered random factors using Minitab 16 Statistical Software [23]. In addition, variance components for each factor were determined to compare relative contribution to variation [24]. RHc values at each temperature, as well as crispness values at each water activity and temperature were compared using Tukey's multiple means comparison. Finally, the impact of water activity on texture was modeled using Fermi's model for a sigmoidal response [13].

## **RESULTS AND DISCUSSION**

The high data resolution offered by the DDI method provides the opportunity to visualize sudden changes in sorption properties that likely are associated with changes in the properties of the product. While these inflection points have been observed in low molecular weight amorphous powders, it was unclear if they would appear in the DDI curves for other types of products (19, 20). Figure 1 shows the DDI curves for GC and SC run at 25°C, 35°C, and 40°C. The initial slope of the adsorption curve is flat with very little gain in moisture as water activity increases for both product types. Then a sharp inflection point in the curve can be observed at all 3 temperatures at specific water activities. This inflection point indicates a sudden change in sorption properties associated with reaching a specific water activity where the slope steepens and more moisture is taken up as water activity increases. An increase in the rate of moisture uptake as water activity changes would require the sudden availability of many previously inaccessible binding sites for water. Such an event would be similar to a glass transition where mobility and free volume suddenly increase making polar materials such as sugar and starch more available to water than in the previous low mobility state.

Figure 2 indicates that the sudden change in the product observed as an inflection in the DDI adsorption curve does not occur during a second adsorption event for either GC or SC. Instead, the subsequent adsorption curve is both shifted up due to hysteresis and is smoothly concave, lacking the distinct inflection point of the first adsorption curve. This would suggest that the change that occurs during the initial adsorption at the  $RH_c$  is an irreversible change and the product cannot be put back in its original condition simply by desiccation. Such a distinct

change that results in a matrix with new and unique sorption properties would suggest concurrent changes in physical attributes such as texture at the RHc.

The RHc values for GC were significantly lower than those for SC indicating that the RHc for each product is unique to the matrix (Table 1). This is not unexpected since the water activity level that would be needed for a matrix to no longer be able to support its structure, resulting in changes in mobility, would be dictated by its unique internal chemistry. For GC, the RHc value decreased significantly with temperature, but not for SC. RHc values associated with the glass transition of low molecular weight, amorphous carbohydrates typically reduce as temperature is increased, but the level of temperature response is matrix specific (20). GC and SC are complex products with both amorphous and non-amorphous ingredients, making it difficult to pinpoint exactly which components of the matrix are changing to lead to the sharp inflection in the DDI curve. Consequently, the matrix changes occurring in the GC and SC are unique to each product and dependent on their particular matrix chemistry, with the RHc temperature sensitivity of the GC matrix more closely resembling glass transition.

Table 2 shows the crispness values at each water activity and temperature for GC whereas Table 3 provides the crispness values for SC. In general, changes in crispness are more pronounced at a given temperature as water activity changes than at a given water activity as temperature changes. For GC, crispness values at the lowest water activity averaged 15 N across all 3 temperatures, but reduced to approximately 4 N at the highest water activity for all temperatures. Similarly, SC crispness averaged 24 N at the lowest water activity and



approximately 3 N at the highest water activity across all temperatures. Analysis of variance with temperature, water activity and their interaction as factors indicated that all 3 factors were significant for GC whereas just water activity and temperature and not their interaction were significant for SC. To identify the relative contribution of each variation source, variance components (VC) for each factor were also determined. For GC, water activity (VC=21.21) was a larger source of variation than temperature (VC=0.04) and the interaction term (VC=2.37). Similarly for SC, water activity (VC=90.66) was a larger variation source than both temperature (VC=5.97) and the interaction term (VC=0.70). These results suggest that water activity is the main control factor for crispness and further investigations into crispness in this study will focus on water activity with temperature as a secondary factor.

The GC and SC samples equilibrated to different water activities and temperatures experienced losses in crispness as water activity increased at all temperatures (Figure 3). Superimposing a line representing the RHc determined by the DDI curves indicates that the crispness values are similar at water activities lower than the RHc, but are significantly (Table 2) reduced at water activities higher than the RHc (Figure 3). This sigmoidal response of texture to increased water activity was also reported in previous studies and the water activity associated with the downward inflection in texture was identified as the RHc for texture [1, 3, 7, 14]. These studies further modeled the sigmoidal response of texture to water activity using the Fermi equation, except that the characteristic water activity of Peleg (13) was replaced with the critical water activity, giving equation 1.

$$C_{(a_w)} = \frac{c_0}{\left(1 + \exp\left(\frac{a_w - a_{wc}}{b}\right)\right)} \quad (1)$$

where  $C(a_w)$  is the crispness at a given water activity,  $C_0$  is the initial crispness,  $b$  is a constant describing the slope of the transition, and  $a_{wc}$  is the critical water activity at the inflection point (3).

The crispness values determined in this study were modeled for response to water activity at each temperature and the resulting smooth curves from the model have been placed over the data points in Figure 3. The Fermi models verified the sigmoidal response of texture to increasing water activity and the models differed slightly for each temperature. The Fermi models for SC indicated a more abrupt loss in texture at the RHc than GC. Tables 4 and 5 list the model coefficients and the  $R^2$  values for the Fermi models for GC and SC, respectively. The overall higher  $R^2$  values for SC than GC would indicate a better fit by the Fermi model, but the generally high  $R^2$  values indicates good agreement for both products. The RHc lines superimposed on Figure 3 provide evidence that the RHc values obtained from DDI curves match up well with the texture loss inflection point in the Fermi model.

Previous studies of texture and water activity identified the  $a_{wc}$  of the Fermi model to be the upper water activity limit to maintain desired textural properties [1, 3, 7, 14]. To obtain this value required completion of a full examination of texture vs. water activity including equilibration to various temperature and water activities and conducting texture analysis, either instrumental or sensory. The results of this study also enabled the determination of an  $a_{wc}$  using Fermi's model of texture data collected at various water activities and temperatures. However, RHc values obtained from DDI curves also matched well with a loss in crispness. A

comparison between RH<sub>c</sub> values from Table 1 and the a<sub>wc</sub> values from Tables 4 and 5 indicate that while the a<sub>wc</sub> values tend to be higher, the two values, determined using very different techniques, fall into a similar range. The difference can be explained by the RH<sub>c</sub> agreeing more with the start of the downward trend in texture while the a<sub>wc</sub> corresponds with the midpoint of the downward trend and so is found at higher water activities (Figure 3).

## **CONCLUSION**

Adsorption of moisture by both GC and SC caused changes in texture as expected. Moisture acts as a plasticizer which lowers viscosity and provides an overall softening effect. Moisture adsorption is characterized using moisture sorption isotherms. Using recently developed DDI curves to track adsorption makes it possible to observe inflections in the curve corresponding with distinct changes in sorption properties associated with irreversible changes in the product matrix. The water activity associated with this inflection point, identified as the RH<sub>c</sub>, can be obtained in typically 24-48 hours using an automated instrument.

In this study, the RH<sub>c</sub> obtained from DDI curves was compared with data on crispness obtained through an extensive texture study at various water activities and temperatures. The RH<sub>c</sub> obtained from DDI curves matched with the initiation of a loss in crispness in GC and SC. While it would have been possible to determine a critical water activity by modeling the texture data with the Fermi model as done in previous studies, the results of the study indicate that it would not be necessary. Using the RH<sub>c</sub> obtained from DDI analysis as the upper limit specification for water activity would be even more conservative than using the a<sub>wc</sub> from the Fermi model and it

actually represents a value where verifiable changes in the matrix occurs as opposed to obtaining the value through modeling. The greatest advantage of using the RHc is that it provides the necessary information to set a water activity specification to maintain desirable texture, but does not require a time and labor intensive texture study to obtain the value. It is true that the DDI curve for every product type will not necessarily show a distinct RHc value. However, if equipment is available for conducting DDI analysis, its speed and ease would merit a first look before taking on a more extensive texture study.

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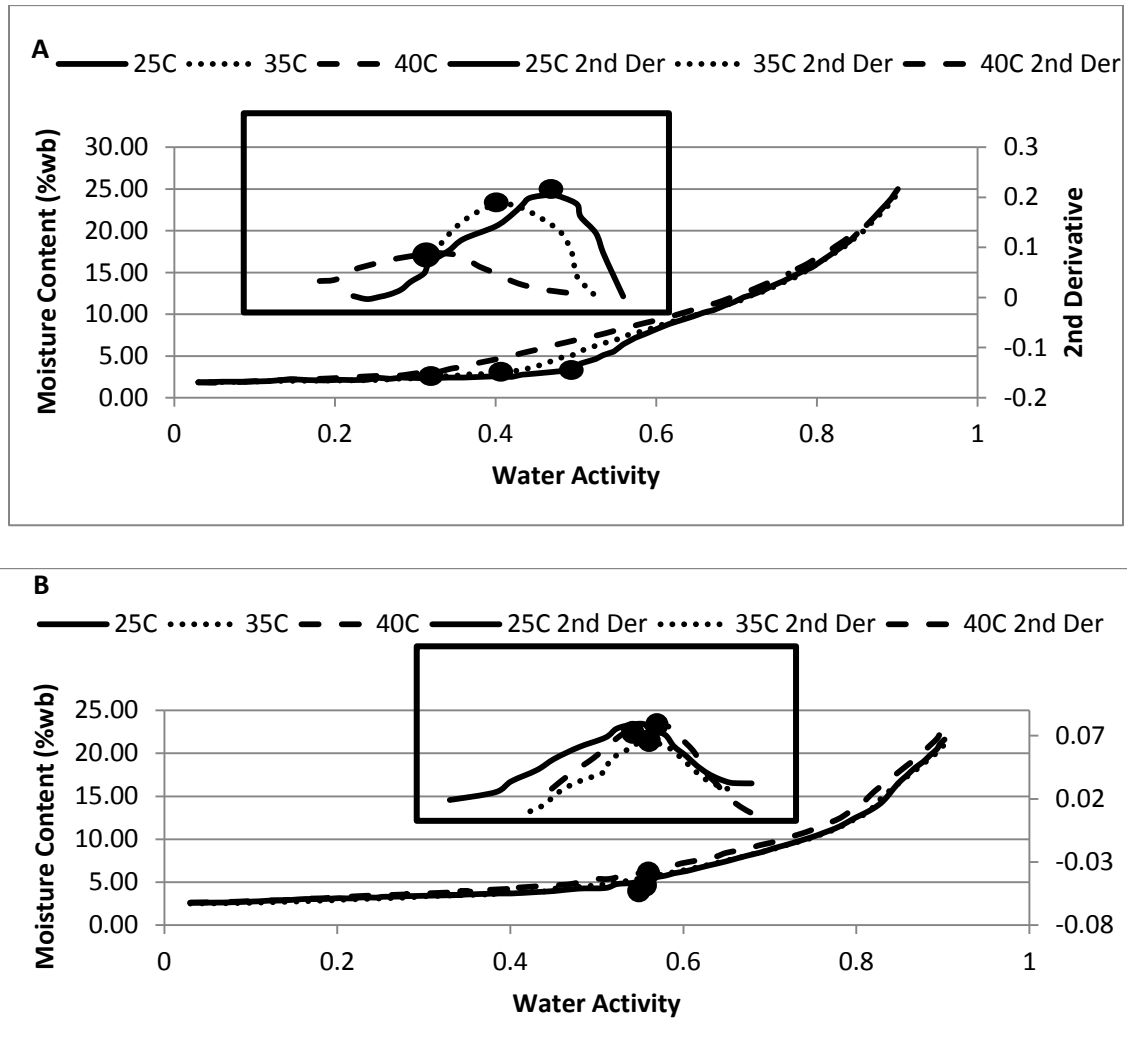
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**FIGURES**



**Figure 1. Dynamic dewpoint adsorption isotherms for graham cracker (A) and shortbread cookie (B) at 25°C, 35°C, and 40°C. Within the superimposed solid box, the Savistky-Golay 2<sup>nd</sup> derivative plots are also shown on the secondary axis and the maximum in the curve identifies the inflection point in the original curve. The critical water activities associated with an inflection in the adsorption curve are identified as solid black circles.**

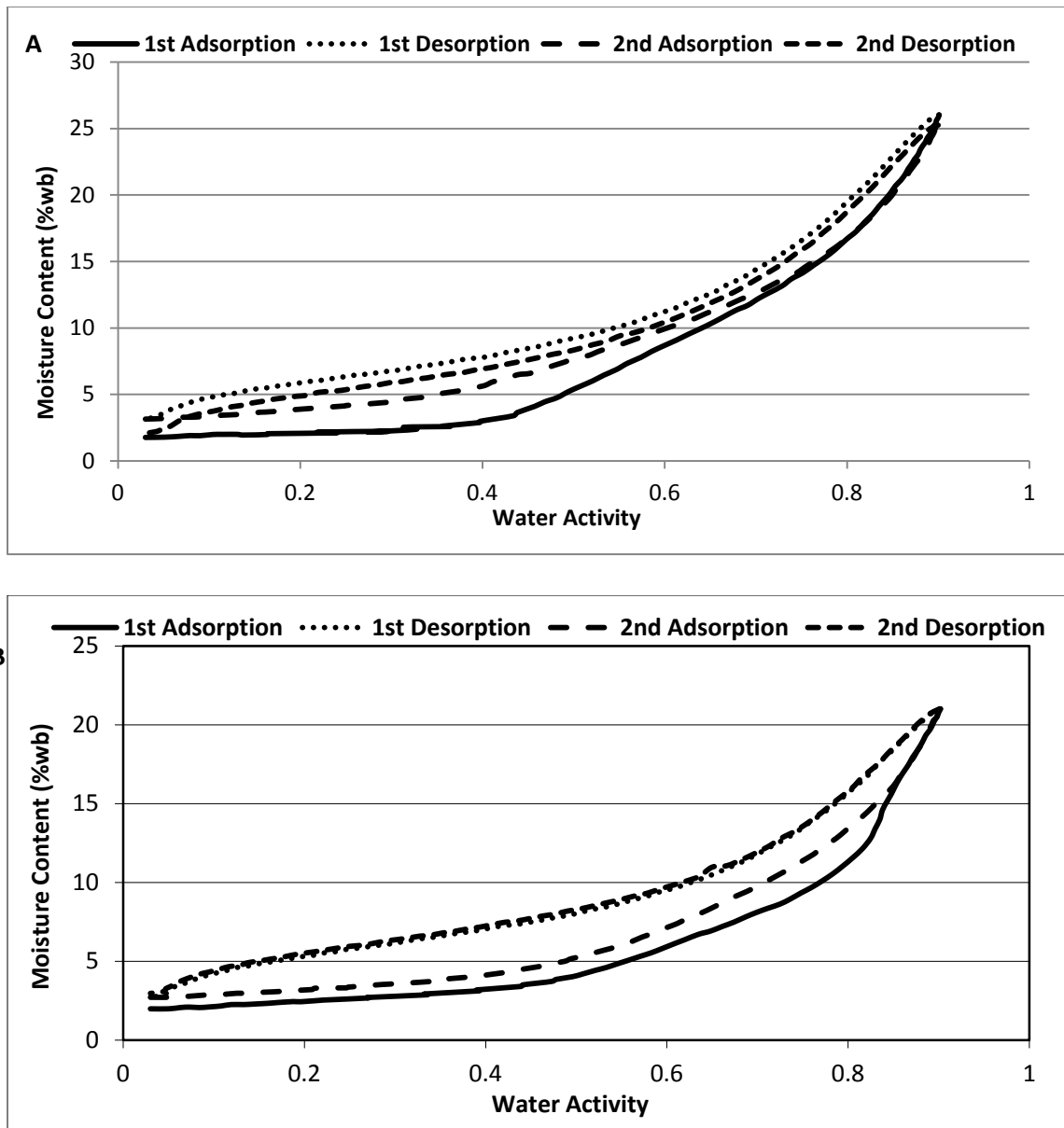


Figure 2. Dynamic dewpoint isotherms for Graham Crackers (A) and Shortbread Cookies (B) at 25°C. The samples were subjected to an initial adsorption (—), then desorption (·····), a 2<sup>nd</sup> adsorption (---), and a final desorption event (---).

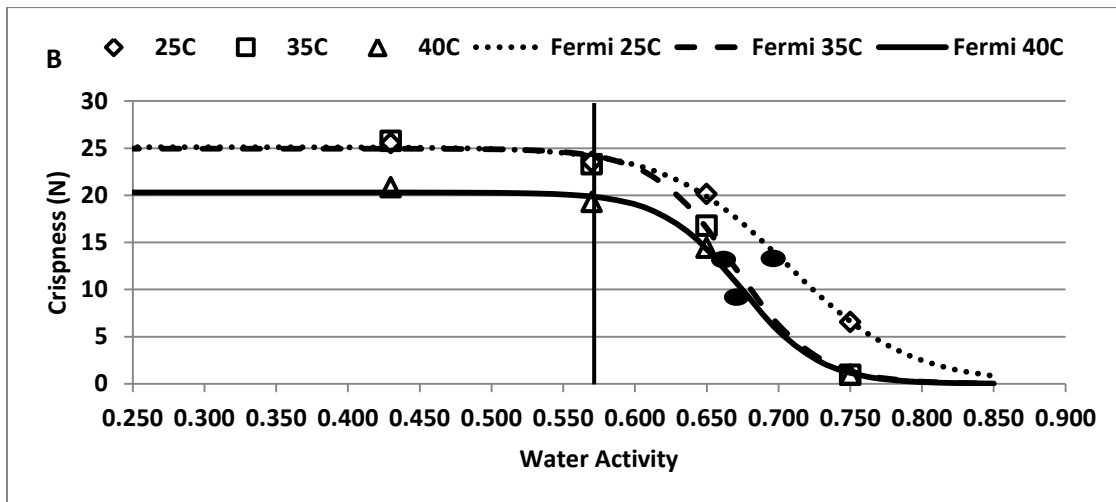
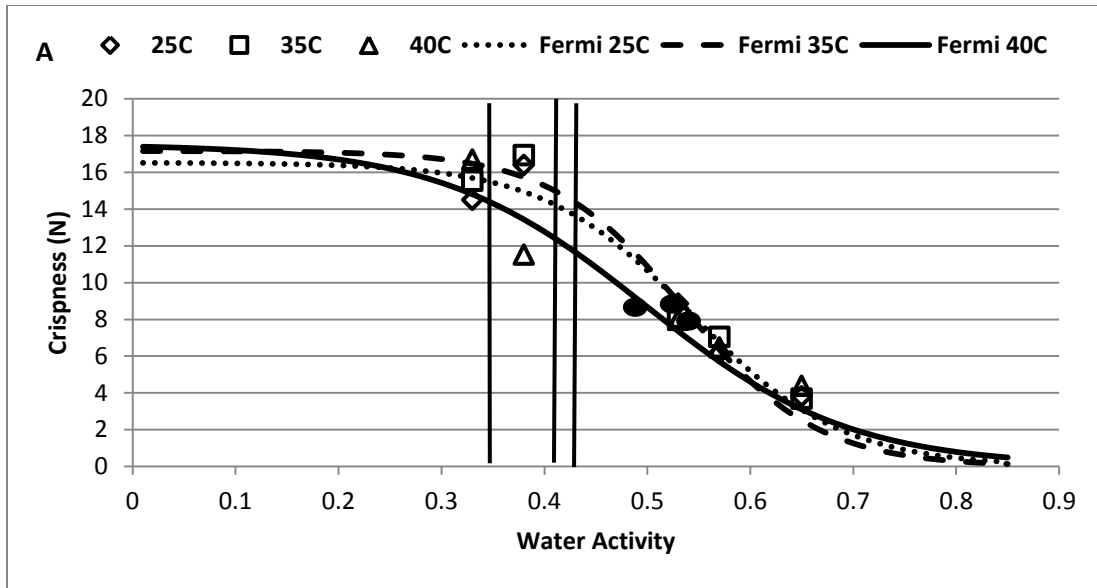


Figure 3. Average crispness of Graham Crackers (A) and Shortbread Cookies (B) as water activity increases at 25°C, 35°C, and 40°C. Smooth curves representing Fermi models at each temperature are included and solid circles represent  $a_{wc}$  values from Fermi modeling. Solid vertical black lines represent average RHc values obtained from DDI analysis for each temperature.

## TABLES

**Table 1. Critical water activities<sup>a</sup> from dynamic dewpoint isotherms of graham crackers and shortbread cookies at three different temperatures.**

<b>Sample</b>	<b>25°C</b>	<b>35°C</b>	<b>40°C</b>
<b>Graham Crackers</b>	0.435 <sup>A</sup> (0.01)	0.410 <sup>B</sup> (0.01)	0.35 <sup>C</sup> (0.01)
<b>Shortbread Cookies</b>	0.550 <sup>A</sup> (0.01)	0.565 <sup>A</sup> (0.01)	0.565 <sup>A</sup> (0.01)

<sup>a</sup> Critical water activities in a row followed by the same letter are not significantly different

( $p > 0.05$ ).

**Table 2. Average crispness<sup>a</sup> of graham crackers at three different temperatures as measured on a texture analyzer using three point bend.**

Sample	25°C	35°C	40°C
0.328	14.502 <sup>A</sup>	15.533 <sup>A</sup>	16.689 <sup>A</sup>
0.382	16.398 <sup>A</sup>	16.934 <sup>A</sup>	11.524 <sup>B</sup>
0.529	8.859 <sup>BC</sup>	8.09 <sup>C</sup>	7.969 <sup>C</sup>
0.576	6.162 <sup>CDE</sup>	7.048 <sup>CD</sup>	6.476 <sup>DE</sup>
0.649	3.808 <sup>E</sup>	3.681 <sup>E</sup>	4.380 <sup>DE</sup>

<sup>a</sup> Crispness values followed by the same letter are not significantly different ( $p>0.05$ ).

**Table 3. Average crispness<sup>a</sup> of shortbread cookies at three different temperatures as measured on a texture analyzer using three point bend.**

<b>Sample</b>	<b>25°C</b>	<b>35°C</b>	<b>40°C</b>
0.432	25.515 <sup>A</sup>	25.737 <sup>A</sup>	20.815 <sup>ABC</sup>
0.576	23.504 <sup>AB</sup>	23.274 <sup>AB</sup>	19.118 <sup>BCD</sup>
0.649	20.118 <sup>ABCD</sup>	16.744 <sup>CD</sup>	14.415 <sup>D</sup>
0.753	6.537 <sup>E</sup>	0.931 <sup>E</sup>	0.972 <sup>E</sup>

<sup>a</sup> Crispness values followed by the same letter are not significantly different ( $p>0.05$ ).

**Table 4. Fermi model coefficients applied to the relationship between crispness and water activity for GC crackers at three different temperatures.**

Temperature	$C_0^a$	$b^b$	$a_{wc}^c$	R2
25°C	16.527	0.073	0.543	0.962
35°C	17.163	0.065	0.536	0.972
40°C	17.52	0.099	0.498	0.917

<sup>a</sup> $C_0$  is the initial crispness,

<sup>b</sup> $b$  is the slope of the transition,

<sup>c</sup> $a_{wc}$  is the critical water activity at the inflection point

**Table 5. Fermi model coefficients applied to the relationship between crispness and water activity for shortbread cookies at three different temperatures.**

Temperature	$C_0^a$	$b^b$	$a_{wc}^c$	R2
25°C	25.106	0.042	0.707	0.997
35°C	24.943	0.028	0.669	0.996
40°C	20.298	0.027	0.674	0.997

<sup>a</sup> $C_0$  is the initial crispness,

<sup>b</sup> $b$  is the slope of the transition,

<sup>c</sup> $a_{wc}$  is the critical water activity at the inflection point



**Executive Summary and Future Work**

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## **SUMMARY**

The research presented in this dissertation was focused on investigating the breadth of applications for the critical water activity (RH<sub>c</sub>) from dynamic moisture sorption isotherms (DDI). In Chapter 1, the RH<sub>c</sub> for wheat grain was shown to correspond with the recommended moisture levels for grain tempered for milling. Whole wheat equilibrated to the RH<sub>c</sub> was sufficiently tempered to produce high quality flour and farina. Additionally, grain tempered to the RH<sub>c</sub> produced flour and farina with water activity less than the growth limit for microorganisms.

In Chapter 2, the RH<sub>c</sub> was identified as the point at which moisture began penetrating wheat and barley grain. These findings clarified the results from Chapter 1, that the tempering moisture level corresponded with the RH<sub>c</sub> because it is the point at which moisture will penetrate the grain, thereby facilitating softening of the endosperm. It also highlighted that moisture permeability is influenced by water activity and that the inflection point that occurs at the RH<sub>c</sub> is the result of changes in water permeability.

Chapter 3 identified that the RH<sub>c</sub> in premix powders is associated with the onset of dissolution as the instant powder goes into solution. It was also found to be influenced by phase transitions of secondary amorphous ingredients in the products. Powders at water activities higher than the RH<sub>c</sub> softened due to the phase transitions and did not return to their original state when dried back to water activities below the RH<sub>c</sub>. Consequently, premix powders need to be maintained at water activities less than their RH<sub>c</sub> to remain stable.

Chapter 4 highlighted a loss in crispness associated with the RHc of grahams and shortbread cookies. This sigmoidal change in texture at the RHc corresponded with previous textural studies in other products, but was able to determine the RHc for texture loss without a full texture study. To maintain acceptable crispness levels, the water activity of these products needs to be maintained at levels lower than the RHc.

The results presented in this dissertation provide evidence that links the RHc from DDI to important quality and stability factors in a variety of products, thereby enhancing its practical usefulness. A DDI curve is easily generated for most product types in several days using instrumentation, with very little setup or oversight. Consequently, when attempting to identify the ideal specifications for the optimization of a product, running a DDI test and looking for an RHc appears to be a reasonable first step. If the DDI curve does not show an inflection in the adsorption curve, additional study would be needed. However, for those products whose DDI curve does identify an RHc, a water activity release specification could be set based on the RHc with the expectation that if the water activity of the product is maintained below (or above) the RHc, the utility of the product will be maximized. Additional factors effecting utility may also need to be evaluated, but at least the ideal water activity range would be known from DDI analysis without the need for complex experimentation, thus avoiding the expense and time loss typically associated with research studies.

## **FUTURE WORK**

The research presented in this study showed a connection between the RHc from DDI with key stability factors. However, it did not investigate all possible mechanisms for stability loss and used mechanical assessments of quality instead of sensory analysis. In addition, assumptions were made that the quality assessment being investigated was the key factor that would end stability for the product. Additional research is needed to determine if products processed to the RHc identified for these products does correspond with an acceptable product during daily production. Additional work would also be needed to determine if the RHc could be linked to additional important quality factors. Further, the proposal to temper to a water activity rather than a moisture level would need to be verified.

In addition, the link of the RHc to changes in permeability that lead to inflections in the DDI curve were investigated on a macroscopic level. To determine the actual changes that are occurring in the matrix at the RHc would require tracking water behavior at the molecular level. Finally, this study investigated specific products whose DDI curves did show an RHc, but did not serve as an extensive survey of DDI curves for a variety of products. DDI analysis of a wide variety of products will be necessary to determine the range of products that do exhibit an RHc and if it could be used as an indicator of the stability of those products.