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# Prediction of storage stability parameters of spray dried powders of maltodextrins and corn syrups with different levels of hydrolysis (conversion)

# Predicción de los parámetros de estabilidad en el almacenamiento de polvos secados por aspersión de maltodextrinas y jarabes de maíz con diferentes niveles de hidrólisis (conversión)

A. Osorio-Tellez[1,2], R. Pedroza-Islas[2]*, C. Perez-Alonso[3]

[1] *Complementos Alimenticios, S.A. de C.V. Calz. de la naranja 157, C.P. 53370, Naucalpan, México.*
[2] *Departamento de Ingeniería Química, Industrial y de Alimentos, Universidad Iberoamericana, Prolongación de Reforma 880, Col. Lomas de Santa Fe, C.P. 01219, Ciudad de México, México.*
[3] *Departamento de Ingeniería Química, Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón esq. Paseo Tollocan s/n, Col. Residencial Colón, C.P. 50120, Toluca, Estado de México, México.*

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## Abstract

The aim of this work was to establish the maximum stability conditions of maltodextrins and corn syrups obtained by spray drying with different levels of starch hydrolysis as dextrose equivalent (***DE***) 10, 20, 30 and 40 from a thermodynamic study of sorption at 25, 35 and 40 ºC. These storage conditions were correlated with the hygroscopicity, glass transition temperature ($T_g$) and external morphology of these powders to minimize physical phenomena such as caking. The conditions of maximum stability according to the minimum integral entropy ($\Delta S_{int}$) for maltodextrins (***DE*** 10 and 20) fluctuated between $a_W$ of 0.12 to 0.25 at 25 ºC with hygroscopicity of 26% and $T_g$ of 112 ºC, while for corn syrups (***DE*** 30 and 40) $a_W$ between 0.03 to 0.05 at 25 ºC, with hygroscopicity of 36% and $T_g$ of 89 ºC; For the same value in ***DE*** as the temperature increases, the humidity ($M$) and the $a_W$ of maximum stability decrease, while for the same temperature, the increase in ***DE*** also decreases the humidity ($M$) and $a_W$ of maximum stability, maintaining their structural integrity without compaction; in extreme conditions, the powders showed a greater or lesser degree of caking.

*Keywords*: Hygroscopicity; sorption moisture; water activity; minimum integral entropy; glass transition temperature; maltodextrins; hydrolysis level.

## Resumen

El objetivo de este trabajo fue establecer las condiciones de estabilidad máxima de maltodextrinas y jarabes de maíz obtenidas mediante secado por aspersión con diferentes niveles de hidrólisis del almidón como dextrosa equivalente (***DE***) 10, 20, 30 y 40 a partir de un estudio termodinámico de adsorción a 25, 35 y 40 ºC. Estas condiciones de almacenamiento fueron correlacionadas con la higroscopicidad, temperatura de transición vítrea ($T_g$) y morfología externa de estos polvos para minimizar fenómenos físicos como el apelmazamiento. Las condiciones de máxima estabilidad de acuerdo con la mínima entropía integral ($\Delta S_{int}$) para maltodextrinas ***DE*** (10 y 20) fluctuaron entre $a_W$ de 0.12 a 0.25 a 25 ºC con higroscopicidad de 26% y $T_g$ de 112 ºC, mientras que para jarabes de maíz ***DE*** (30 y 40) $a_W$ entre 0.03 a 0.05 a 25 ºC, con higroscopicidad de 36% y $T_g$ de 89 ºC; para un mismo valor en ***DE*** conforme aumenta la temperatura, la humedad ($M$) y la $a_W$ de máxima estabilidad disminuyen, mientras que para una misma temperatura, el incremento en ***DE*** también disminuye la humedad ($M$) y $a_W$ de máxima estabilidad, manteniendo su integridad estructural sin compactación; en condiciones extremas los polvos presentaron en mayor o menor grado apelmazamiento.

*Palabras clave*: Higroscopicidad; humedad de sorción; actividad acuosa; mínima entropía integral; temperatura de transición vítrea; maltodextrinas; nivel de hidrólisis.

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* *Corresponding author. E-mail*: `rth.pdrz@gmail.com`

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# 1 Introduction

In the industry, the use of powder products obtained by spray drying is common, a process that contributes to preserving most of its components and extends the useful life by facilitating its handling (Macías-Cortés *et al*., 2020; Fitch-Vargas *et al*., 2019; Saavedra-Leoz *et al*., 2018) and protection of compounds (Luján-Hidalgo *et al*., 2019; Saavedra-Leoz *et al*., 2018). This technique is defined as the transformation of feed from a fluid state into a dried particulate form by spraying the feed into a hot drying medium (Macías-Cortes *et al*., 2019). In particular, the derivatives of corn starch with different levels of hydrolysis are produced via enzymatic or acidic starch and spray dried, which have various useful functionalities in food due to the fact that they exhibit a neutral and slightly sweet taste; they are composed of D-glucose units connected by glycosidic bonds (1-4) to give polymers of D-glucose of variable length and, therefore, with different molecular weight, since they are a mixture of saccharides (Castro *et al*., 2016).

The level of hydrolysis, also called conversion, is measured as equivalent dextrose (***DE***) and is determined using the reducing sugars method, expressed as dextrose (Castro *et al*., 2016; Descamps *et al*., 2013). Starch is associated with a zero ***DE*** value, maltodextrins between 3 and 20, corn syrups greater than 20, and glucose at a value of 100. Regarding the complexity of the molecules of maltodextrins and other derivatives of corn, they have been measured its molecular weights and related to its structure and functionality, reporting that as molecular weight decreases due to hydrolysis, some properties such as viscosity and plasticizing effect also decrease, while hygroscopicity and glass transition temperature ($T_g$) increase ( Castro *et al*., 2016).

On the other hand, powdered corn starch derivatives can form lumps, agglomerates or stones, phenomena where free-flowing particles unite to form aggregates or larger lumps through a process dependent on time, on the conditions of the product and the humidity of the environment, resulting in detriment to the quality of the product and hindering its use (Cano-Higuita *et al*., 2015; Descamps *et al*., 2013). Different authors have studied the effect of storage conditions in relation to the changes suffered in powdered products (Carvalho-Lago and Noreña, 2015; Da Costa *et al*., 2015). The water sorption isotherms analyze the degree of interaction of the water with the food and represent the relationship between the moisture content and the thermodynamic activity of the water in the product, in a given range of humidities (Hernández-Carrillo *et al*., 2019). If the food is not in thermodynamic equilibrium with its environment, it will gain or lose water until reaches it and during this process, the powdered food could tend to compaction (caking) or stone formation (Barbosa-Cánovas and Vega-Mercado, 2019).

Among the variables most studied as responsible for the caking phenomenon, are hygroscopicity, glass transition temperature and the phenomenon of moisture sorption in powders (Baptestini *et al*., 2020). Even though the water activity ($a_W$) and the glass transition temperature ($T_g$) have been used to predict the shelf life of food from a physical point of view (Barbosa-Cánovas and Vega-Mercado, 2019), the stability of food can also be determined by the thermodynamics of sorption water vapor, since it allows predicting the storage stability and shelf life of dehydrated foods from a physicochemical point of view (Baptestini *et al*., 2020).

Thermodynamic functions establish optimal storage and stability conditions. For example, the free energy necessary for the transfer of a water molecule, from the vapor state to the adsorbed state, is a quantitative measure of the affinity between the dry product and water and indicates the degree of spontaneity of the adsorption process (Guzmán-Hincapié and Zapata, 2018). The differential enthalpy of sorption is a differential molar quantity derived from the dependence of the temperature towards the isotherm, and represents the energies for the binding of water molecules at a particular hydration level, in contrast to the integral enthalpy, which is the average energy of all molecules already consolidated at that level (Schneider, 2013). Furthermore, entropy changes can define the degree of order or disorder existing in the adsorbent-adsorbate system. The minimum integral entropy is interpreted as the water activity in which a food product has the highest stability (Baptestini *et al*., 2020). This minimum occurs when strong bonds take place between the adsorbate (water) and the adsorbent (food) (Guzmán-Hincapié and Zapata, 2018).

Therefore, the main objective of this work was to establish the maximum storage stability conditions of maltodextrins and corn syrups obtained by spray drying with different levels of hydrolysis, through a thermodynamic sorption analysis and the evaluation of their hygroscopicity and glass transition temperature.

# 2 Materials and methods

## 2.1 *Materials*

Four spray-dried powders obtained from the company Complementos Alimenticios, S.A. de C.V. (Mexico City, México) were studied, that is, maltodextrins and corn syrups with different levels of hydrolysis measured as equivalent dextrose (***DE***): a) Corn maltodextrin with ***DE*** 10 (C1); b) Corn maltodextrin with ***DE*** 20 (C2), c) Corn syrup powder with ***DE*** 30 (C3); d) Corn syrup powder with ***DE*** 40 (C4). The reagents used were, in all cases, analytical grade obtained from SIGMA ALDRICH, Toluca, Estado de México, México, and the water used was double-distilled.

## 2.2 *Hygroscopicity*

Hygroscopicity was determined by the method proposed by Cai and Corke (2000). Two g of sample deposited in an aluminum tray placed in an airtight container containing a saturated solution of $Na_2SO_4$ (relative humidity of the order 81%) are placed for one week at 25 ºC. After this time, the amount of water gained by the material is determined by weight difference (Alpizar-Reyes *et al.*, 2017). Hygroscopicity was calculated using the equation of Jaya and Das (2004) and expressed in g $H_2O$ / 100 g dry sample:

$$\text{Hygroscopicity (\%)} = \left( \frac{\frac{b}{a} + W_i}{1 + \frac{b}{a}} \right) \times 100 \qquad (1)$$

where:
$b$ = Increase in the weight of the sample (g); $a$ = Amount of powder taken for measurement (g) (Original sample); $W_i$ = Free moisture present in the powder before measurement (g)

## 2.3 *Glass transition temperature ($T_g$)*

Glass transition temperature was obtained experimentally using a differential scanning calorimeter (DSC) TA-DSC Q20 (TA Instruments, New Castle, ***DE***, USA) equipped with a mechanical refrigeration system (RCS-refrigerated cooling accessory). Five mg of balanced sample were placed at different aqueous activities in the range 0.11-0.65 and three temperatures (25, 35 and 40 ºC), which were heated in hermetic aluminum bowls. The thermal program consisted of two cycles with a range of -80 ºC to 150 ºC heating at a ramp of 5 ºC / min in each of the two cycles, using an empty hermetic aluminum bowl as a reference. The calorimeter was calibrated for temperature measurement with indium standards and distilled water. The equipment purge was carried out using nitrogen at a flow rate of 50 mL / min. The data were analyzed using Analysis 2000 software version 4.7A (TA Instruments, New Castle, USA). The glass transition temperature was taken at the midpoint of the base line of variation obtained in the differential scan curve (Alpizar-Reyes *et al.*, 2017; Braga *et al.*, 2018).

## 2.4 *Scanning electron microscopy*

A Hitachi model SU3500 brand scanning electron microscope with GB-H mode at 2 kV voltage accelerator was used to investigate the microstructural properties of the maltodextrins and spray dried corn syrups stored in the temperature ranges and aqueous activities described above. Micrographs with different magnifications were obtained in order to appreciate details of the morphology of the powders studied. It was not necessary to metallize them because the electron microscope operates under low vacuum conditions.

## 2.5 *Sorption isotherms*

The spray-dried hydrolyzed carbohydrates were placed in inert plastic trays in several glass desiccators at room temperature containing $P_2O_5$ for 3 weeks to minimize the relative humidity of the interior environment of the desiccators, which upon reaching equilibrium with the powders obtained very low humidity (~0.5%). The water adsorption isotherms in maltodextrins and corn syrups were determined at 25, 35 and 40 ºC by the gravimetric method in the humidity range between 0.11 and 0.65 described by Lang *et al.* (1981). Approximately two grams of sample was weighed on an Ohaus brand analytical balance. These samples were placed in inert plastic trays on a perforated plate in small glass desiccators of 10 cm in diameter containing saturated solutions of different salts at the bottom of the desiccators in the range of water activity ($a_W$) of 0.11 to 0.65 (Alpizar-Reyes *et al.*, 2017; Labuza *et al.*, 1985) to allow the interaction of moisture from that environment with dust.

Subsequently, the desiccators were introduced into 3 stoves (Felisa brand) and kept at the study temperatures. The samples were weighed every 5 days on an Ohaus electronic balance until reaching the pseudo-equilibrium state (this was assumed when the difference between two consecutive weightings was less than 1 mg/g of solid). The moisture content of the samples was determined by weight difference after drying in a vacuum oven (Felisa brand) at 60 ºC for 24 h, using magnesium perchlorate as desiccant. All moisture adsorption experiments were carried out in triplicate, and the percentage difference in moisture content at equilibrium between replicates was on average less than 1% of the mean of the three values.

## 2.6 Sorption models

To predict the water sorption properties of the powders, the GAB model was used (Alpizar-Reyes *et al*., 2017; Zeimer *et al*., 2019). The Guggenheim-Anderson-De Böer (GAB) equation is a model with three parameters, each of which has a physical meaning. This model was used to adjust the data of the isotherms obtained and mathematically it is expressed as (Rizvi, 2014):

$$M = \frac{M_0 C K a_W}{(1 - K a_W)(1 - K a_W + C K a_W)} \tag{2}$$

where: $M$ = moisture content at equilibrium [kg $H_2O$ / 100 kg d.s.]; $M_0$ = moisture content of the monolayer [kg $H_2O$ / 100 kg d.s.]; $a_W$ = water activity; $C$ = Guggenheim constant, $K$ = constant that corrects the properties of the multilayer molecules.

The value of $M_0$ is the amount of sorbate adsorbed by one g of sorbent at one $a_W$ of the sorbate; C (Guggenheim's constant) is the energy constant related to the enthalpy difference (chemical potential std) and K is the measure of the enthalpy differences of the sorbate molecules but in these two layers, the pure liquid and its second state of sorption, the layers above the monolayer (Timmermann, 2003).

The values of the parameters of the GAB equation ($M_0$, $C$, $K$) were determined by a non-linear regression analysis with Polymath software version 6.1. To ensure that a good regression was performed, the percentage of error (average relative deviation modulus, $E$) between the experimental values and the estimated values of the moisture content was evaluated using the following equation (Zeymer *et al*., 2019):

$$E = \frac{100}{N} \sum \frac{|M_i - M_{Ei}|}{M_i} \tag{3}$$

where:
$M_i$ = experimental values of moisture content [kg $H_2O$/100 kg d.s.]; $M_{Ei}$ = moisture values [kg $H_2O$/100 kg d.s.] estimated by the GAB model; $N$ = number of experimental data. It is supposed to be a good fit when $E < 5\%$.

## 2.7 Thermodynamic properties of powders

### 2.7.1 Differential thermodynamic properties

The isosteric heat of adsorption is a thermodynamic parameter obtained from the equilibrium data; it represents the discrepancy between the latent heat of adsorption and the latent heat of condensation of pure water. Isosteric heat is determined by the following equation, which was derived from the Clausius-Clapeyron equation (Rizvi, 2014):

$$\left(\frac{\partial \ln(p/p_0)}{\partial(1/T)}\right)_M = \left(\frac{\partial \ln a_W}{\partial(1/T)}\right)_M = \frac{-H_i - h_1}{R} = -\frac{\Delta H_{dif}}{R} = -\frac{q_{st}}{R} \tag{4}$$

where:

$R$ = universal gas constant; $T$ = temperature on the absolute scale [$K$]; $p$ = pressure at equilibrium; $p_0$ = vapor pressure of pure water; $H_l$ = isosteric heat of adsorption; $h_l$ = heat of vaporization of pure water; $q_{st}$ = net isosteric heat of adsorption or enthalpy of adsorption. Using the Clausius-Clapeyron equation implies that at a specific moisture content of the system remains constant in the temperature range studied if a plot of ln($a_W$) versus ($1/T$) gives a straight line, and for it the enthalpy of vaporization of pure water (excess heat of adsorption) does not change with temperature (Rizvi, 2014). The change in adsorption molar differential entropy is calculated from the Gibbs-Helmontz equation (Rascón *et al*., 2015):

$$\Delta S_{dif} = S_1 - S_l = -\frac{\Delta H_{dif}}{T} - R \ln a_W \tag{5}$$

where:

$s_1 = \left(\frac{\partial S}{\partial N_1}\right)_{T,P}$ = molar differential entropy of water adsorbed on the material; $S_l$ = molar entropy of pure water in equilibrium with steam; $S$ = total entropy of water adsorbed on the material; $N_1$ = number of moles of water adsorbed on the material; $R$ = universal gas constant; $a_W$ = water activity; $T$ = temperature on the absolute scale [$K$].

### 2.7.2 Integral thermodynamic properties

Integral free energy ($\Delta G_{int}$) [kJ/mol] is calculated from the Gibbs equation (Guzmán-Hincapié and Zapata, 2018):

$$\Delta G_{int} = RT \ln a_w \tag{6}$$

Integral molar enthalpy [kJ/mol] is calculated with an equation similar to the equation (4), but keeping the diffusion pressure constant $\Phi$ (Guzmán-Hincapié and Zapata, 2018).

$$\left(\frac{\partial \ln(p/p_0)}{\partial T}\right)_{\Phi} = \frac{H_g - H_s}{RT^2} \tag{7}$$

Rearranging equation (4) and taking pure water at temperature **T** as the reference state:

$$\left(\frac{\partial \ln a_W}{\partial(1/T)}\right)_{\Phi} = \frac{-H_l - H_s}{R} = -\frac{\Delta H_{int}}{R} \tag{8}$$

where:
$H_s$ = molar integral enthalpy of water adsorbed on the material; $H_l$ = molar enthalpy of pure water in equilibrium with steam; $\Delta H_{int}$ = molar integral enthalpy; $\Phi$ = diffusion pressure or surface potential of the material. The diffusion pressure or surface potential of the material is determined as (Alpizar-Reyes *et al*., 2017): concept from which the following equation is obtained:

$$\Phi = \mu_{ap} - \mu_a = RT \frac{W_{ap}}{W_v} \int_0^{a_w} M d \ln a_W \tag{9}$$

$$\Phi = \alpha_1 T \int_0^{a_w} M d \ln a_W \tag{10}$$

where:
$\mu_{ap}$ = chemical potential of the pure adsorbent; $\mu_a$ = chemical potential of the adsorbent in the condensed phase; $W_{ap}$ = molecular weight of adsorbent; $W_v$ = molecular weight of water; $\Phi/\alpha_1$ = constant and similar to a process at $\Phi$ constant.

Once the values for ($\Delta H_{int}$) are obtained, changes of the integral molar entropy ($\Delta S_{int}$) [kJ/mol K] are evaluated as:

$$(\Delta S_{int})_T = S_s - S_L = -\frac{(\Delta H_{int}}{T} - R \ln a_W \tag{11}$$

where:
$S_s = (S/N_1)$ = integral entropy of water adsorbed on the material.

# 3 Results and discussion

## 3.1 Hygroscopicity

The hygroscopicity is the ability of the food powder to absorb moisture from high relative humidity environment and the degree of caking is expressed as percentage of powder, which will remain on a sieve of defined mesh size, after redrying and sieving the cake formed in the hygroscopicity test (Nurhadi *et al*., 2016; Martinelli *et al*., 2007). Castro *et al*. (2016) reported that maltodextrins are polysaccharides with low hygroscopicity, which increases as the ***DE*** value increases in a range between 10 and 20. Figure 1 shows the moisture gain due to the increase in hygroscopicity in maltodextrins and corn syrups. Hygroscopicity fluctuates in the order of 23.8 to 38.75%, the effect of temperature being significant. In this type of phenomena, water is first bound by most of the polar groups (which in this case are carbonyl groups at the end of the chain of polysaccharides) corresponding to the hydration of the monolayer, while it is superficially absorbed on the hydroxyl groups. As the polar sites are occupied, the water molecules are progressively linked to the monolayer through hydrogen bonds and / or Van der Waals interactions, leading to the formation of multilayers (Castro *et al*., 2016). These multilayers are more abundant to the extent that more reducing groups are present, as is the case of lower molecular weight chains (Descamps *et al*., 2013).

Likewise, this observed behavior indicates avidity towards ambient humidity, and a direct relationship between the level of conversion and hygroscopicity, a consequence of differences in the three-dimensional helical or branched structures of the carbohydrates generated during hydrolysis, which will be more complex in products of low conversion such as maltodextrins ***DE*** 10 and 20, and less complex as ***DE*** increases (Castro *et al*., 2016), and those structures of less complexity contribute to a higher hygroscopicity because they contain a greater amount of free reducing groups with the capacity to bind water, also because the glycosidic covalent bond at the primary level and the hydrogen bonds at the secondary level have an impact on the surface sorption behavior of these biomolecules (Saavedra-Leoz *et al*. 2018; Barbosa-Cánovas and Vega-Mercado., 2019).

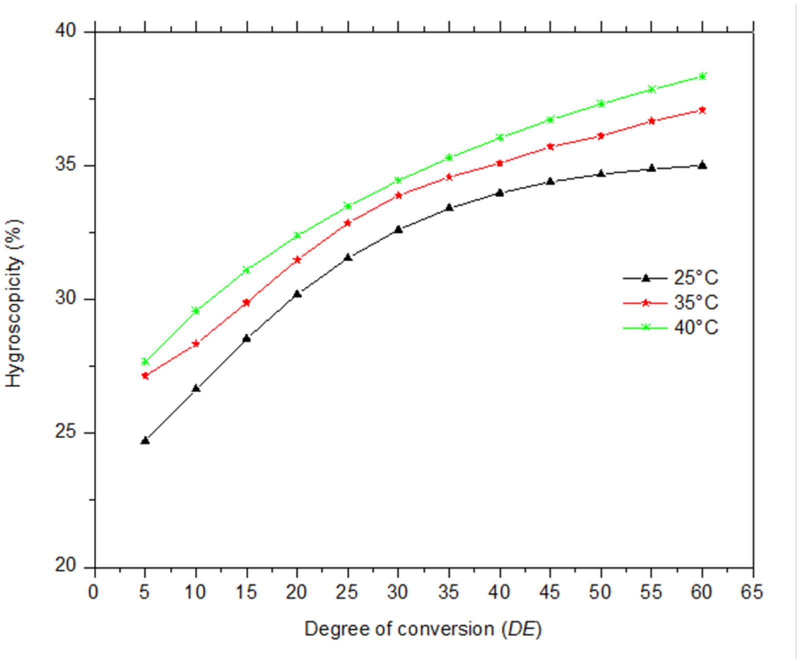

Fig. 1. Effect of the degree of conversion and temperature on the hygroscopicity of maltodextrins and corn syrups.

Zheng *et al*. (2007) studied the effects of cross-linking and esterification on the hygroscopicity and surface tension of cassava maltodextrins with different ***DE*** values (6.5, 8.0, 9.3, 10.2, and 11.8) were investigated. The hygroscopicities of all maltodextrins were gradually increased with the increase of ***DE*** and relative humidity (RH). Cross-linking and esterification decreased hygroscopicities by 26.5% and 12.1%, respectively. However, the combination of them reduced it by 33.7%. Higher RH greatly increases the hygroscopicity of maltodextrin and it is beneficial for maltodextrin product to store them at lower RH (11%).

On the other hand, the maltodextrins are mainly used in materials that are difficult to dry−such as fruit juices, flavorings, and sweeteners−and to reduce stickiness and agglomeration problems during storage, thereby improving product stability (Plazola-Jacinto et al, 2019; Carrillo-Navas *et al*., 2011; Martinelli *et al*., 2007). The hygroscopic moisture of spray-dried betacyanin powders with 15 ***DE*** maltodextrin at various drying temperatures (150 - 210 ºC) ranged from 45.4 g/100 g to 49.2 g/100 g (Cai and Corke, 2000). The hygroscopicity of spray-dried cactus pear juice powder with 10 and 20 ***DE*** maltodextrins varied from 36.30 to 48.93 g water/100 g dry solid. The values of hygroscopicity obtained in this product no significant effect of the type of maltodextrin on the hygroscopicity of the powder was found (Rodríguez-Hernández *et al*., 2005).

### *3.2 Glass transition*

The glass transition is the passage of a metastable thermodynamic state, characterized by high molecular order and aggregation, to another thermodynamic state, known as rubbery state, where there is more molecular mobility and thus lower stability (Luján-Hidalgo *et al*., 2019). In the spray drying process, during the feeding of the fluid to the drying chamber and dehydration, the injected solids, maltodextrins and / or corn syrup are in an amorphous state; After drying, these biomaterials acquire a glassy or rubbery state depending on the drying temperature and the drying mechanism itself, and some simple components such as contained low molecular weight carbohydrates make the powders obtained have low temperature values of glass transition ($T_g$). Additionally, these powders present relatively low values in water content, which predisposes them to have high percentages of hygroscopicity, making them less stable (Braga *et al*., 2018).

Figure 2 shows the glass transition temperatures of maltodextrins and corn syrups at different degrees of conversion and storage temperatures. $T_g$ of the amorphous matrix decreases with the water content due to plasticizing effects of the water due to structural changes and the fusion phenomenon when the $a_W$ increases (Guadarrama-Lezama *et al*., 2014), this behavior matches that described by Nurhadi *et al*. (2016) for maltodextrin 10 ***DE***, which in the case of complex carbohydrates is related to the interaction of water with three-dimensional structures of greater or lesser molecular weight depending on the level of conversion and the structural transformation due to changes in the vitreous state into a less viscous one, which allows the flow of the liquid and the formation of bridges between particles (Barbosa-Cánovas and Vega-Mercado, 2019), which are more abundant as the degree of conversion increases. Similar findings that show this behavior were also reported for starch and starch derived products such as native rice starch, acidic hydrolyzed potato starch, breakfast cereals and wheat gluten due to maltodextrin as a starch derived product still showed the same phenomenon as shown by starch system (Nurhadi *et al*., 2016; Carlstedt *et al*., 2014).

On the other hand, this behavior of change of state from vitreous to rubbery is related to the observed hygroscopicity, since to the extent that the polar sites available for water absorption are more abundant, the possibility of water diffusion and its effect plasticizer is greater, promoting said change of state (Barbosa-Cánovas and Vega-Mercado, 2019). Water sorption relates water content and water activity across food solids while the relationship among water content and glass transition temperature of an amorphous phase describe water plasticization. The correlation between water sorption and water plasticization is often used to determine the critical water content and critical water activity of materials at a chosen temperatures. The materials with water contents lower than their respective critical water content show enhanced stability especially in terms of physical stability (Nurhadi *et al*., 2016).

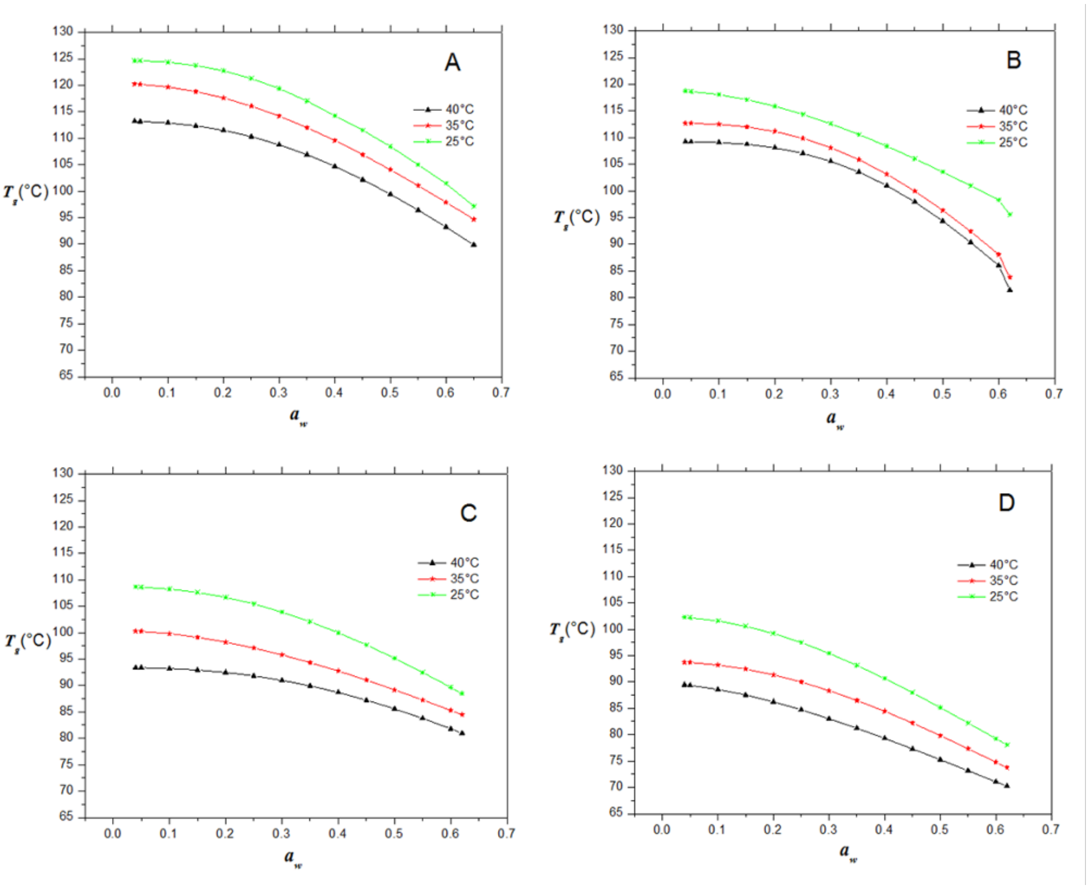

Fig. 2. Glass transition temperature as a function of aw for maltodextrins and corn syrups with different levels of conversion. A) ***DE*** 10; B) ***DE*** 20; C) ***DE*** 30; D) ***DE*** 40.

Table 1. Sorption-related properties in equilibrium with relative humidity conditions of the environment in free-flowing powders.

| ***DE*** | **Hygroscopicity** *(%)* | $T_g$ (°C) | $a_W$ |
|---|---|---|---|
| **10** | 26.6 | 124 | < 0.30 |
| **20** | 30.2 | 118 | < 0.15 |
| **30** | 32.6 | 108 | < 0.10 |
| **40** | 34.0 | 102 | < 0.05 |

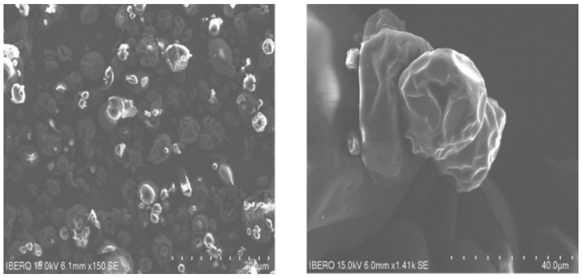

Fig. 3A. Appearance at the microscopic level of dust particles in equilibrium with relative humidity conditions of the environment. Free-flowing powder. Maltodextrin with ***DE*** 10 at 25 °C, $a_W < 0.4$.

## *3.3 Scanning electron microscopy*

From the microscopic observation of the samples subjected to the relative humidity conditions of the studied environment, it is observed that as part of the water sorption phenomenon, the dust particles present three states:

1.- State of free flow.- Powder particles flow freely (free-flowing powders). Microscopically (Figure 3A) they are formations that tend towards sphericity with little surface deformation and few "sticky" contact points, reflecting a minimum state of wetting; figure on the right shows in greater detail the sphericity and smaller contact area between the particles. Table 1 shows the properties studied and that are related to the compaction phenomenon at different levels of conversion. According with literature, powders in that conditions show no cohesion of the particles because the moisture adsorbed on the surface generates a high viscosity that does not allow it to acquire the necessary mobility to act as a plasticizer for its diffusion through the particle, the high $T_g$ maintains the vitreous state and low hygroscopicity prevents the acquisition of humidity and prevents the formation of a sticky surface and the subsequent establishment of bridges that lead to the agglomeration of the particles (Barbosa-Cánovas and Vega-Mercado, 2019), this behavior was observed both in Maltodextrins 10 and 20 ***DE***, as well as corn syrups 30 and 40 ***DE*** at 25 ºC and low which is verified with a low $a_W$ in equilibrium with the environment, these variables are reached in low temperature conditions (25 ºC).

2.- Crystalline appearance.- The particles show a slight agglomeration. Macroscopically they are observed with a crystalline appearance (Figure 3B) with structures of certain sphericity but attached or agglomerated to a larger matrix. Table 2 shows the properties mentioned and that correspond to the state of crystalline appearance.

Correlating the reported values that show a decrease in $T_g$ of maltodextrins 10 and 20 ***DE***, and corn syrups 30 and 40 ***DE*** at 35 ºC with the micrographs shown, it is observed that lower values in $T_g$ has a relevant contribution to the change from glassy to rubbery state, while higher hygroscopicity reported increases the acquisition of moisture that favors the plasticizing activity of water on the surface, observing the generation of isolated agglomerates without reaching the collapse of the particles.

Table 2. Sorption-related properties in equilibrium with ambient relative humidity conditions in crystalline-looking powders.

| ***DE*** | **Hygroscopicity** *(%)* | $T_g$ (°C) | $a_W$ |
|---|---|---|---|
| **10** | 28.3 | 120 | > 0.30 < 0.40 |
| **20** | 31.5 | 112 | > 0.15 < 0.20 |
| **30** | 33.9 | 100 | > 0.12 < 0.14 |
| **40** | 35.0 | 93 | > 0.05 < 0.11 |

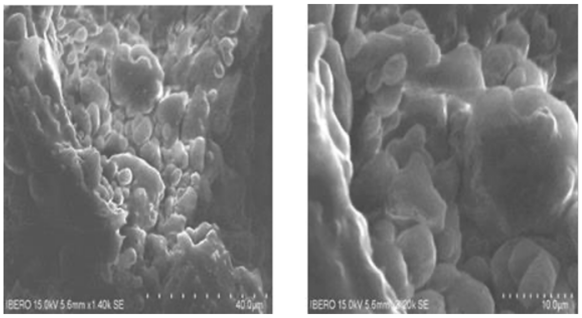

Fig. 3B. Appearance at the microscopic level of dust particles in equilibrium with relative humidity conditions of the environment. Crystal appearance. Corn syrup DE 30 at 35 °C, $a_W = 0.2$.

Table 3. Properties related to sorption in equilibrium with conditions of relative humidity of the environment in powders with complete agglomeration (liquefaction, fusion and / or plasticization).

| ***DE*** | **Hygroscopicity** *(%)* | $T_g$ (°C) | $a_W$ |
|---|---|---|---|
| **10** | 29.6 | 96 | > 0.30 < 0.40 |
| **20** | 32.4 | 95 | > 0.15 < 0.20 |
| **30** | 34.4 | 88 | > 0.12 < 0.14 |
| **40** | 39.0 | 78 | > 0.05 < 0.11 |

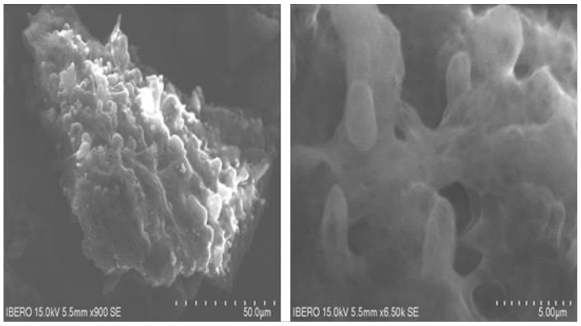

Fig. 3C. Appearance at the microscopic level of dust particles in equilibrium with relative humidity conditions of the environment. Liquefaction, fusion and / or plasticization. Corn syrup ***DE*** 40 at 40 °C, $a_W$= 0.2.

3.- Liquefaction, fusion and / or plasticization of the particles.- The agglomerated powder particles, macroscopically form a mass of plastic appearance (Figure 3C), structures without sphericity are observed, united or agglomerated to each other or in a continuous matrix. Table 3 shows the properties mentioned and that correspond to the state of complete agglomeration with liquefaction, fusion and / or plasticization of the particles.

When complete agglomeration occurs, the particles have completely collapsed due to the double plasticizing effect due to high hygroscopicity (up to 39% for ***DE*** 40) and low $T_g$ (up to 78 ºC for ***DE*** 40) at elevated temperatures (40 ºC ), in this state, the interparticle bridges have disappeared due to the high moisture content (also high $a_W$), involving the solubilization of low molecular weight fractions (as is markedly in the case of ***DE*** 30 and 40) causing a hygroscopic behavior. At this point, the lumps can be few or numerous, of different size and varying in the degree of hardness (Barbosa-Cánovas and Vega-Mercado, 2019). Images of maltodextrins 20 and 30 ***DE*** are not shown because there were no significant differences between the samples in the morphological appearance of the maltodextrins regardless of their level of conversion.

## *3.4 Sorption isotherms*

The experimental isotherms obtained are shown in Figure 4, said data adequately respond to the modeling postulated by the GAB equation, with a typical sigmoidal shape; according with the literature, food systems composed mainly of crystalline components such as sugars and salt are represented by this kind of isotherms (Villegas-Santiago *et al*., 2020), with the determined parameters shown in Table 4, being the modulus of the relative mean deviation ($E$) less than 5.0, which are considered as indicators of the goodness of the fit (Zeymer *et al*., 2019). The sorption phenomenon is a function of the level of conversion of carbohydrates derived from starch and the storage temperature; this follows the GAB model due to the existence of surface multilayers of the material (Pérez-Alonso *et al*., 2006), where the presence of reducing groups modifies the way in which the multilayers are accommodated on the material.

Temperature is acknowledged as a dominant factor with respect to moisture sorption phenomena. Moisture content is expected to decrease with increasing temperature at a specific water activity (Iglesias and Chirife, 1982). This behavior is consistent with the thermodynamics of sorption, and is indicative of the impaired hygroscopic nature of the material (Rizvi, 1986). This trend has been observed for different biopolymers of a different chemical nature such as chitosan, starches, mesquite gum, Prosopis alba exudate gum, xanthan gum, among others (Rosa *et al*., 2010; Pérez-Alonso *et al*., 2006; Vasile *et al*., 2020; Basu *et al*., 2007). However, an opposite trend was found in this work by maltodextrins (***DE*** 10 and 20) and by corn syrups (***DE*** 30 and 40), where moisture content increased with the temperature. This behavior has been observed by gum Arabic, blend of biopolymers (gum Arabic - mesquite gum - maltodextrin ***DE*** 10, GA17%-MG66%-MD-17% w/w), microcrystalline cellulose and fish protein myosin (Pérez-Alonso *et al*., 2006; Cadden, 1988; Das and Das, 2002). Unfortunately, the complex nature of the adsorption phenomena in food materials makes difficult to explain this adsorption behavior. For biopolymers, the process not only involves adsorption but also structural changes of the polymer matrix due to swelling.

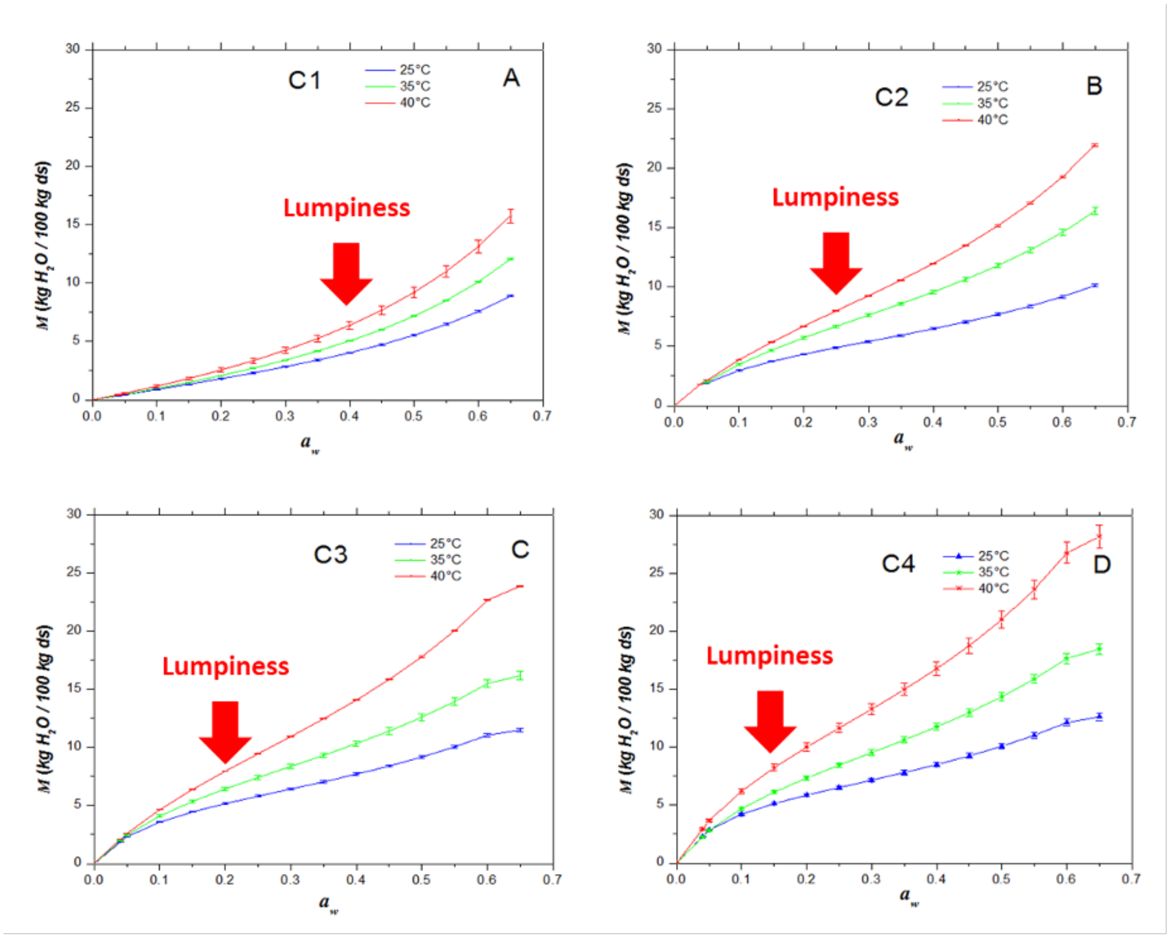

Fig. 4. Sorption isotherms for spray dried powders of maltodextrins and corn syrups at different levels of conversion. A) ***DE*** 10 (C1); B) ***DE*** 20 (C2); C) ***DE*** 30 (C3); D) ***DE*** 40 (C4).

The internal structure such as the porosity and tortuosity of the biomaterial is another factor that leads to this behavior in the adsorption process; as well as the drying process that was used to obtain the maltodextrins and the corn syrups. The conformation and topology of the molecule and the hydrophilic/hydrophobic sites adsorbed at the interface is highlighted (Pérez-Alonso *et al*., 2006).

The constants of the GAB equation obtained by the non-linear regression of the experimental data at 25, 35 and 40 ºC are shown in Table 4. The humidity value of the monolayer ($M_0$) is of interest because it is an indicator of the amount of water that is strongly adsorbed to specific sites on the surface of powders, and is indirectly considered as the value at which the powder is most stable (Carrillo-Navas *et al*., 2011; Alpizar-Reyes *et al*., 2017). It has been assumed that the value of the monolayer represents the saturation of polar groups corresponding to the water adsorbed in the most active sites (Barbosa-Cánovas and Vega-Mercado, 2019; Pérez-Alonso *et al*., 2006; Carvalho Lago and Noreña, 2015); and that is also where the product is most stable against microbial attack (Rahman and Labuza, 2009; Sablani *et al*., 2007). Sorption moisture values are similar to those reported for maltodextrin (***DE*** 10) in the range of 4.4-12.5, which are slightly lower than those reported in the literature (Perez-Alonso *et al*., 2006) for ***DE*** 10, who determined $M_0$ in the range of 6.96 and 7.35; For the case of ***DE*** 20, (Descamps *et al*., 2013) reported $M_0$ values of 4.63 for maltodextrin 21 ***DE***, similar to the 5.0 determined.

$M_0$ increases its value as the temperature increases, which is attributed to the formation of new available sites where water can bind due to morphological, topological and structural changes on the surface of the powder (Rizvi, 2014), since for biopolymers, The sorption process also involves changes in the polymer matrix due to the fusion of the material (Perez-Alonso *et al*., 2006), this fusion contributes to the irreversible formation of clumps of material that, when consolidated, take on a compact and hard texture that gives rise to stone formation.

High values of $M_0$ in the materials (as in the case of ***DE*** 40) may be due to the improvement in the sorption capacities through the fusion of the protective layer of the hydrocolloid and the increase in the number of polar sites, just where the water could have a higher affinity for the hydrocolloid (Guadarrama-Lezama *et al*., 2014), the foregoing agrees with what was observed in the determination of the hygroscopicity of powders, in which high hygroscopicity and low $T_g$ favor the solubilization of fractions of low molecular weight that lead to collapse and in extreme cases the plasticization of the powder, indicating a direct relationship between the dependence of hygroscopicity, the state of the solid (rubbery when the $T_g$ is exceeded), the humidity of the monolayer and the level of equivalent dextrose (degree of conversion expressing free reducing groups) of maltodextrins and corn syrups.

Regarding the Guggenheim constant ($C$), for $C >$ 2.0 the GAB equation expresses a sigmoidal curve with an inflection point (type II equation in Brunauer's classification) (Blahovec and Yanniotis, 2010) for maltodextrins and corn syrups; On the other hand, it is assumed that since the interactions between the adsorbent and adsorbate are endothermic, the value of C decreases with respect to temperature, an effect related to the heat of adsorption of the water that binds to the material through strong interactions (Carrillo-Navas *et al*., 2011; Rizvi , 2014), behavior that can be observed in the powders studied in this section.

The multilayer correction constant ($K$) is a measure of the difference in the free enthalpy (standard chemical potential) of the molecules of the adsorbed material in these two states: pure liquid and its sorption state (Timmermann, 2003), thus such as the interactions of the molecules in the multilayers with the adsorbent, which tend to be between the value of the energy of the molecules in the monolayer and the value of liquid water (Castro *et al*., 2016). Values of $K < 1.0$ have been found especially when water sorption is influenced by polymers; and as temperature increased, $K$ values also increased (Table 4) indicating multilayer molecules became more entropic (Pavón-García *et al*., 2015). Timmermman (2003) and Conegero *et al*. (2017) report that the addition of maltodextrin strongly reduces the interaction between water vapor and the matrix of solids, compared to materials that do not contain them.

The "stickiness", caking and collapse point of the powders increases as the degree of conversion and the temperature increase, from $a_W = 0.5$ for ***DE*** 10 and 20, 0.45 for ***DE*** 30 and 0.4 for ***DE*** 40, and is associated with changes in hydration and physical composition of the biopolymeric matrix (Castro *et al*., 2016).

Table 4. Sorption isotherm constants for spray dried maltodextrins and corn syrups with different conversion levels (***DE*** 10, 20, 30 and 40).

| ***DE*** | **T (ºC)** | $M_0$ Monolayer moisture | $C$ Guggenheim constant | $K$ Multilayer correction constant | $E$ Relative mean deviation modulus (%) |
|---|---|---|---|---|---|
| **10** | 25 | 4.48 | 8.56 | 0.79 | 1.05 |
| | 35 | 6.07 | 5.94 | 0.86 | 0.51 |
| | 40 | 8.05 | 4.74 | 0.89 | 3.55 |
| **20** | 25 | 5 | 13.37 | 0.82 | 1.29 |
| | 35 | 7.92 | 7.06 | 0.87 | 1.68 |
| | 40 | 10.13 | 5.3 | 0.91 | 0.37 |
| **30** | 25 | 5.77 | 14.08 | 0.85 | 1.14 |
| | 35 | 8.13 | 8.89 | 0.87 | 2.3 |
| | 40 | 11.59 | 5.64 | 0.92 | 0.26 |
| **40** | 25 | 6.18 | 17.66 | 0.86 | 2.39 |
| | 35 | 9.18 | 9.09 | 0.88 | 2.37 |
| | 40 | 12.58 | 7.69 | 0.95 | 3.41 |

### *3.5 Thermodynamic properties*

The thermodynamic properties are useful to establish the condition of maximum food stability based on the interpretation of processes such as dissolution, crystallization and fusion of powdered products (Rascón *et al*., 2015; Alpizar-Reyes *et al*., 2017). The graph of differential enthalpy ($\Delta H_{dif}$) as a function of the moisture content $M$ (kg $H_2O$ / 100 kg d.s.) at 25, 35 y 40 ºC is shown in Figure 5, which is similar in form to that reported by Carrilo-Navas *et al*. (2011) for microencapsulates of passion fruit juice (23-26 kJ / mol), and lower in magnitude than maltodextrins and corn syrups (30-45 kJ / mol), it establishes that all values of the differential enthalpy are negative within the ranges studied humidity; negative enthalpy values confirm that there are strong attractive forces between the surface of the powders and the water (Pérez-Alonso *et al*., 2006). The maximum values in $\Delta H_{dif}$ for its different water contents are shown in Table 5, they are in the range of 32.81 and 46.37 kJ/mol, that are above the reported values of 15.52, 12.79 and 10.53 kJ / mol for soy protein isolate, whey protein isolate and mesquite gum respectively (Bonilla *et al*., 2010); in it becomes evident that the values of $-\Delta H_{dif}$ increase as the level of conversion (***DE***) in the starch hydrolysates increases, since they exhibit active sites with different binding energies on their surface, but water molecules preferentially adsorb at active sites where the forces exhibit the most negative values of differential enthalpy.

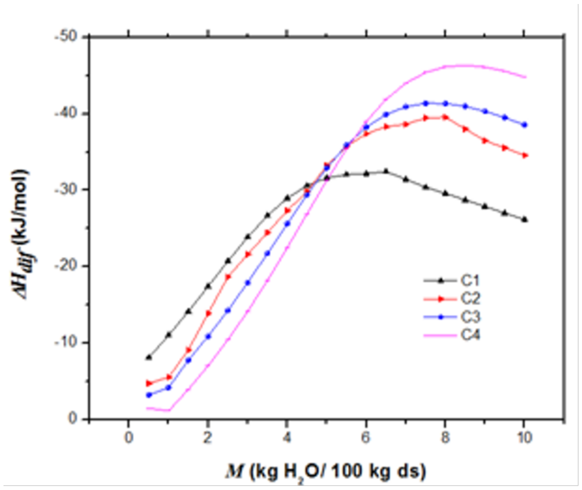

Fig. 5. Isosteric heat of water adsorption as a function of moisture content for spray-dried powders of carbohydrates derived from corn starch with different levels of hydrolysis (C1 = ***DE*** 10, C2 = ***DE*** 20, C3 = ***DE*** 30, C4 = ***DE*** 40).

Table 5. Maximum differential enthalpy and moisture content for maltodextrins and corn syrups with different conversion levels (***DE*** 10, 20, 30 and 40).

| ***DE*** | $-\Delta H_{dif}$ **(kJ/mol)** | **M (kg H2O/100 kg d.s.)** |
|---|---|---|
| **10** | 32.81 | 7.0 |
| **20** | 39.56 | 8.0 |
| **30** | 41.36 | 8.0 |
| **40** | 46.37 | 8.5 |

The maximum enthalpy value indicates the coverage of the most powerful binding sites and the largest water-solid interactions (Rizvi, 2014). Increases in $-\Delta H_{dif}$ could be associated with melting of the carbohydrate polymer matrix that expose new active sites, where new water molecules can be adsorbed by an exothermic process that compensates for endothermic heat. In this sense, the maximum value obtained agrees with the values reported for maltodextrin (Pérez-Alonso *et al*., 2006), these values being higher as the level of conversion increases, which also agrees with the measurement of hygroscopicity and $T_g$.

The differential entropy $\Delta S_{int}$ represents the algebraic sum of the molar differential entropy and the total entropy of water absorbed into the solid at a particular level of hydration, plus the change in order or disorder after new water molecules are absorbed by the system at the same level of hydration. The available number of available sorption sites corresponding to a specific level is proportional to the differential entropy, which describes the degree of disorder of the water molecules (Cano-Higuita *et al*., 2015); these values for maltodextrins and corn syrups correspond to a range of 7.0-8.5 kg $H_2O$ / kg d.s., which are higher than those reported by Bonilla *et al*. (2010) for canola oil microcapsules using different wall materials (whey protein concentrate, in a range of 4.0-7.9 kg $H_2O$ / kg d.s.) (Bonilla *et al*., 2010), which is due to higher hygroscopicity and lower $T_g$ that generate a greater sorption effect in maltodextrins and corn syrups.

Figure 6 represents the graph of the differential entropy $\Delta S_{int}$ as a function of the moisture content $M$ (kg $H_2O$ / 100 kg d.s.) at 25 ºC, this graph shows similar behavior to that reported by Bonilla *et al*. (2010) for isolates of soy protein, whey and mesquite gum and give an indication that the minimum entropy values are located at moisture contents between 7.0 and 8.0, a range similar to that found for the differential enthalpy (Bonilla *et al*., 2010).

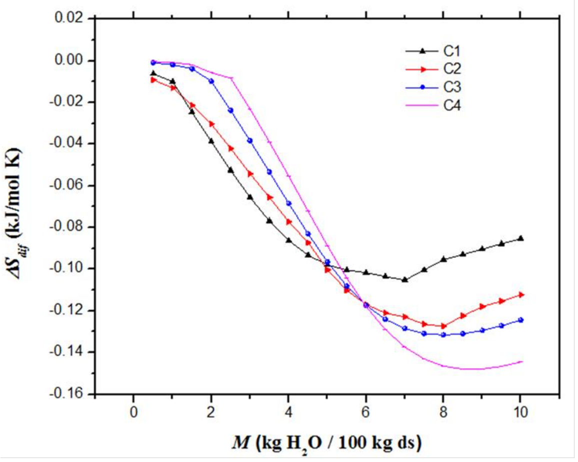

Fig. 6. Differential entropy as a function of moisture content at 25°C for maltodextrins and corn syrups with different levels of conversion (C1 = ***DE*** 10, C2 = ***DE*** 20, C3 = ***DE*** 30, C4 = ***DE*** 40).

This behavior can be explained by the fact that in this range of moisture content the maximum value of differential enthalpy is reached and indicates the covering of the strongest binding sites and greater water - biopolymer interactions, while at this same level of hydration, the minimum value of differential entropy was reached, indicating the change in order or disorder of the system after new water molecules were adsorbed by the biopolymer surface (Bonilla *et al.*, 2010; Pérez-Alonso *et al.*, 2006).

The values for Gibbs free energy at 25 ºC shown in Figure 7 were -9.95 kJ / mol for C1, -11.22 kJ / mol for C2, -11.87 kJ / mol for C3 and -12.79 kJ / mol for C4, respectively at 25 ºC. Those values are close to each other and less than zero. Gibbs free energy is related to the reaction process in the sorption layers of the material, and the values of $\Delta G < 0$ indicate that the sorption of water is a spontaneous process (Rizvi, 2014), showing that the reaction that occurs in the microstructure of the product it could remain stable at 25 ºC. Additionally, given that the $\Delta G_{int}$ value tends to 0 as the water content increases, it is possible to conclude that there will be few sites available for the sorption of higher levels of water content (Cano-Higuita *et al.*, 2015). On the other hand, the fact that the value of $\Delta G_{int}$ decreases as the level of conversion increases in starch derivatives indicates that this is a variable that increases the sorption of water in the product, a situation that agrees with the observations made regarding the hygroscopicity of powders of different degrees of conversion.

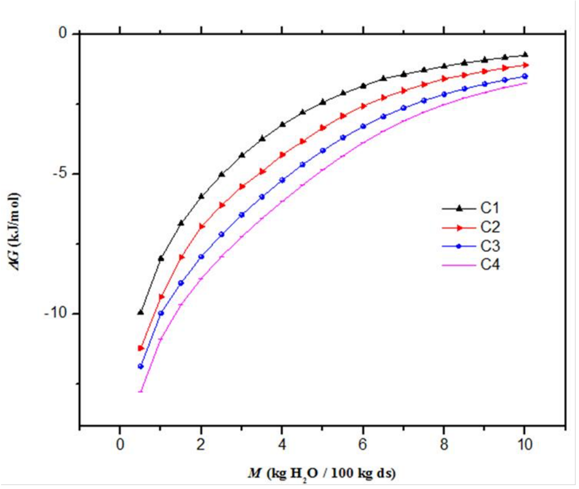

Fig. 7. Gibbs Free Energy as a function of moisture content at 25°C for maltodextrins and corn syrups with different conversion levels (C1 = ***DE*** 10, C2 = ***DE*** 20, C3 = ***DE*** 30, C4 = ***DE*** 40).

According to Rizvi (2014), negative values of $\Delta G_{int}$ show strong intermolecular interactions or bonds (related to enthalpy), which generate a large reduction in the freedom of the configuration of the water molecules and therefore a greater degree of order in the system (related to entropy) (Cano-Higuita *et al.*, 2015).

Figure 8 shows the relationship of the integral entropy ($\Delta S_{int}$) with respect to the moisture content ($M$) at 25 ºC. As the powders adsorb moisture, the entropy decreases to a minimum point that is considered the maximum stability, because it is where the water molecules reach a more ordered arrangement within the solid. The conditions of minimum integral entropy ($\Delta S_{int}$) related to the maximum stability of the powders and their corresponding moisture content ($M$) and $a_W$ are shown in Table 6, for the same value in ***DE*** as the temperature increases (from 25 to 40 ºC), humidity ($M$) and $a_W$ of maximum stability decrease, while for the same temperature, increasing ***DE*** to achieve maximum stability decreases humidity ($M$) and $a_W$. The minimum integral entropy for tamarind seed mucilage was found at 2.29 kg $H_2O$/100 kg d.s. ($a_W = 0.11$) at 20 ºC, 2.18 kg $H_2O$/100 kg d.s. ($a_W = 0.17$) at 30 ºC and 2.17 kg $H_2O$/100 kg d.s. ($a_W = 0.21$) at 40 ºC. Velázquez-Gutiérrez *et al.* (2015) established minimum integral entropy for chia mucilage at 7.56 kg $H_2O$/100 kg d.s. ($a_W = 0.34$) at 25 ºC, 7.59 kg $H_2O$/100 kg d.s. ($a_W = 0.41$) at 35 ºC and 7.63 kg $H_2O$/100 kg d.s. ($a_W = 0.53$) at 40 °C.

Table 6. Conditions of maximum stability for maltodextrins and corn syrups with different levels of conversion (C1 = ***DE*** 10, C2 = ***DE*** 20, C3 = ***DE*** 30, C4 = ***DE*** 40).

| **SAMPLE** | ***DE*** | **TEMPERATURE (ºC)** | ***M*** **(kg $H_2O$/ 100 kg d.s.)** | $a_W$ |
|---|---|---|---|---|
| C1 | 10 | 25 | 3.88 | 0.25 |
| | | 35 | 3.6 | 0.17 |
| | | 40 | 3.41 | 0.12 |
| C2 | 20 | 25 | 3.43 | 0.13 |
| | | 35 | 3.11 | 0.09 |
| | | 40 | 3.02 | 0.07 |
| C3 | 30 | 25 | 3.19 | 0.08 |
| | | 35 | 3.03 | 0.06 |
| | | 40 | 2.62 | 0.05 |
| C4 | 40 | 25 | 3.15 | 0.06 |
| | | 35 | 2.99 | 0.05 |
| | | 40 | 2.91 | 0.04 |

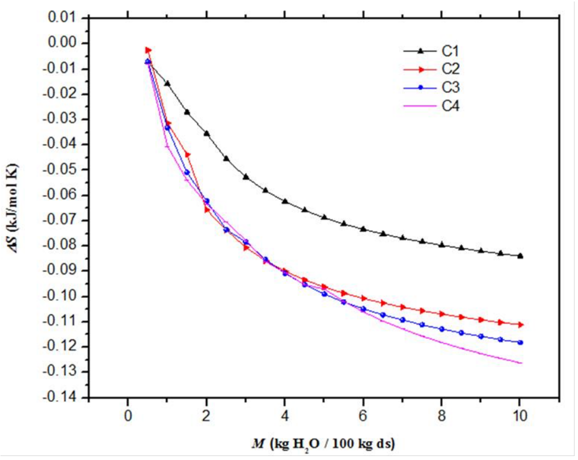

Fig. 8. Differential entropy as a function of moisture content at 25°C for maltodextrins and corn syrups with different levels of conversion (C1 = ***DE*** 10, C2 = ***DE*** 20, C3 = ***DE*** 30, C4 = ***DE*** 40).

Torres *et al*. (2012) determined the minimum integral entropy for carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums, finding that the highest stability occurred at an interval of moisture contents of 2.00-9.00 kg $H_2O$/100 kg d.s. at 20 ºC for the hydrocolloids studied. In another study, the conditions for maximum stability of faba bean protein were 4.33 kg $H_2O$/100 kg d.s. ($a_W$ = 0.40) at 25 ºC, 4.37 kg $H_2O$/100 kg d.s. ($a_W$ = 0.36) at 35 ºC, and 4.44 kg $H_2O$/100 kg d.s. ($a_W$ = 0.24) at 40 ºC (Alpizar-Reyes *et al*., 2018).

## Conclusions

The phenomenon of caking, agglomeration or stone formation in spray-dried powders of maltodextrins and corn syrups with different degrees of hydrolysis (***DE*** 10, 20, 30 and 40) is a thermodynamic process that depends on the temperature and humidity of the environment. The GAB equation was useful for modeling the water vapor sorption phenomenon between dust and the environment. The conditions of maximum stability according to the minimum integral entropy ($\Delta S_{int}$) for maltodextrins with lower ***DE*** (10 and 20) fluctuated between $a_W$ of 0.12 to 0.25 at 25 ºC with a hygroscopicity of 26% and $T_g$ of 112 ºC, while for corn syrups with higher ***DE*** (30 and 40) $a_W$ between 0.03 to 0.05 at 25 ºC, with a hygroscopicity of 36% and $T_g$ of 89 ºC, maintaining its structural integrity without compaction, and therefore its stability; in extreme conditions the powders showed a greater or lesser degree of caking.

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