CLEUBER RAIMUNDO DA SILVA

THERMODYNAMIC CHARACTERIZATION OF TWO PILOT SPRAY DRYERS AND EVALUATION OF THE EFFECT OF HIGH MOLECULAR WEIGHT COMPOUNDS ON TRADITIONAL AND LACTOSE-FREE DAIRY MIXES

Dissertation thesis presented to Universidade Federal de Viçosa as part of the requirements for the Postgraduate Program in Food Science and Technology to obtain the title of Doctor Scientiae.

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APROVED: February 20th, 2017

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To my parents Antônio Carlos, Maria de Fátima and my wife Sabrina

I dedicate

“It is not the strongest that survives, nor the smartest, but the one that best adapts to the changes.”

Charles Darwin

“Try to be a person of value instead of looking to be a successful person. Success is a consequence.”

Albert Einstein

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SUMMARY

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Publications (papers)

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LIST OF ABBREVIATIONS

T_g: Glass transition

ESC: Energy specific consumption

A_w: water activity

SD1: Spray dryer MSD 1.0, Labmaq, Brazil

SD2: Spray dryer Minor Production, Atomizer, GEA, Germany

$F_{h,air}$: Flow rate of humid air

$V_{a,out}$:Outlet air velocity

A_{out}: Area of the transversal section of outlet tubing

ρ: air density

$M_{wa,out}$: Mass of water contained in the outlet air

AH_{out}: Absolute humidity of the outlet air

$F_{d,air}$: Dry air flow rate

$M_{wa,in}$: Mass of water presented in the inlet air

AH_{in}: Absolute humidity of inlet air

$M_{w,inj}$: Mass water injected into spray dryer

$M_{tw,in}$: Total water mass entering the equipment

$M_{tw,out}$: Total mass of evaporated water

Δ_{mass}: Mass balance

$\varepsilon_{t,in}$: Total inlet energy

$\varepsilon_{a,in}$: Energy of the hot inlet air

$\varepsilon_{w,in}$: Energy of water entering the drying tower

$E_{a,in}$: Inlet air enthalpy

$T_{a,in}$: Inlet air temperature

Cp_w: Specific heat of water

$T_{w,inj}$: Temperature of injected water into spray dryer

$\varepsilon_{t,out}$: Total outlet energy

ε_{loss}: Energy loss

ε_{ef}: Energetic efficiency of the process

L_w: Latent heat of vaporization of water

$M_{ts,in}$: Total content of solids entering into drying tower

$F_{m,inj}$: Flow rate of concentrated milk

TS_m: Total solids of concentrated milk

$M_{ts,out}$: Total mass of solids after drying

M_p: Mass of powder milk recovered

TS_p: Percentage of total solids in the powder

T: Total time of the drying process

M_{loss}: Mass of milk powder lost

Cp_m: Specific heat of milk

$T_{m,inj}$: Temperature of concentrated milk

TS: Total solids

DE: Dextrose equivalent

B1: Initial soluble solids content (°Brix time zero)

B2: Final soluble solids content (°Brix after crystallization)

L =% lactose in the total solids;

ΔC_p: Change in heat capacity of each component in the glass transition

W: Mass fraction ($m \cdot m^{-1}$) of the component in the mix

L*: luminosity

a*: Hue

b* Saturation

C: Saturation index

H: Hue angle

ΔE: total or overall difference between the products

CRD: Complete Randomized Design

A: Ashes

TL: Total amount of lactose

LC: Lactose in the crystal form

LS: Lactose in solution

Ptn: Total amount of protein

F: Lipid content

Cs: Casein

WP: Whey protein

In: Inulin

Mt: Maltodextrin

MPC: Milk Protein Concentrate

DSC: Differential Scanning Calorimetry Analysis

St: Product without addition of maltodextrin or inulin

LCW: Percentage of lactose crystallization in the concentrated whey

ESC_{po}: Energy specific consumption for powder

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ABSTRACT

Silva, Cleuber Raimundo, D.Sc., Universidade Federal de Viçosa, February, 2017. **Thermodynamic characterization of two pilot spray dryers and evaluation of the effect of high molecular weight compounds on traditional and lactose-free dairy mixes.** Advisor: Antônio Fernandes de Carvalho. Co-advisors: Ítalo Tuler Perrone and Pierre Schuck.

The objective of this work is to develop a mathematical model that allows for thermodynamically evaluating of spray dryers through mass/energy balance, to elaborate products from mixing of the milk and whey and to evaluate the effect of compounds with high molecular weight in the physicochemical properties and drying characteristics of traditional and lactose-free dairy mixes. For the thermodynamic characterization, it has been utilized spray dryers with atomizer pressure nozzle (evaporation capacity: 1 kg of water/h) and with atomizer disc (evaporation capacity: 20 kg of water/h). For elaboration of the dairy mix, there have been used lactic bases (lactose containing and non-lactose containing bases), elaborated from different proportions of milk and whey, maltodextrin, inulin and soluble corn fiber. The mathematical model has been validated for the evaluation of mass and energy losses and allowed to compare the efficiency between spray dryers with different designs. The increase in whey content in dairy mix and, especially, the application of the lactose hydrolysis reduced both the quality of the powders (color, glass transition temperature, hygroscopy, etc) and drying properties (stickiness, caking and increased energy expenditure for water evaporation). The addition of the compounds with high molecular weight had a positive effect on the physicochemical properties and the drying of the powders, being maltodextrin the most efficient compound.

RESUMO

Silva, Cleuber Raimundo, D.Sc., Universidade Federal de Viçosa, fevereiro de 2017. **Caracterização termodinâmica de dois spray dryers pilotos e avaliação do efeito de compostos de alta massa molar em misturas lácteas tradicionais e deslactosadas.** Orientador: Antônio Fernandes de Carvalho. Coorientadores: Ítalo Tuler Perrone e Pierre Schuck.

O objetivo deste trabalho foi desenvolver um modelo matemático que permita avaliar termodinamicamente equipamentos de secagem, por meio de balanço de massa e energia, elaborar diferentes compostos lácteos a partir da mistura de leite/soro, e avaliar o efeito de compostos de alta massa molar nas propriedades físico-químicas e de secabilidade de compostos lácteos tradicionais e sem lactose. Para a caracterização termodinâmica foi utilizado um *spray dryer* com atomizador de bico de pressão com capacidade de evaporação de 1 kg de água/hora (SD1) e um *spray dryer* com atomizador de disco, (com capacidade de secagem de 20 kg de água/hora (SD2). Para a elaboração dos compostos lácteos, foram utilizadas bases lácteas, deslactosadas ou não, elaboradas a partir de diferentes proporções de leite e soro, além de maltodextrinas 10 e 20 DE, inulina e fibra solúvel de milho. O modelo matemático foi válido para avaliação de perdas de massa e energia e permitiu comparar a eficiência entre secadores por aspersão com diferentes desenhos. O aumento no teor de soro nos compostos lácteos e principalmente a aplicação do processo de hidrólise da lactose reduziram tanto a qualidade dos pós (cor, temperatura de transição vítrea, higroscopicidade, etc..), quanto sua secabilidade (ocorrência de adesão, empedramento e maior gasto energético para evaporação da água). A adição dos compostos de alta massa molar apresentou efeito positivo sobre as propriedades físico-químicas e de secabilidade dos pós, sendo a maltodextrina, o composto mais eficiente.

GENERAL INTRODUCTION

Spray drying allows the rapid dehydration of aqueous systems without having to apply high heat treatment hence it becomes the recommended technique for the drying of thermosensitive materials [1].

Although it is the most cost-effective drying technique applied in the dairy industry, spray drying demands high amounts of energy to promote water evaporation from food [2, 3], making it necessary for the development of methods and technologies to reduce the costs on the drying process itself. An interesting way to evaluate the process consists of determining the efficiency of the equipment from a mass/energy balance [4, 5]. This efficiency is dependent on the layout of the spray dryer, as well as on the characteristics of the processed product.

Among several dehydrated dairy products, there is the milk, which from the nutritional point of view, is considered one of the most complete foods, once it contains a high content of proteins, vitamins, minerals and an important source of calcium. World milk production totaled 802 million tons in 2014 and, in the same year, the milk production in Brazil was 35 million tons [6, 7].

Besides milk, whey has gained prominence in the dairy market and especially in the dehydrated products sector. This product represents about 80 to 90% of the total volume of milk used during cheese making [8]. Whey has been considered a costly by-product in the dairy industry, but due to its high nutritional value and to environmental consciousness, it has been treated as an important raw material.

The world production of whey has been of approximately 186 million tons in liquid form and 3 million tons in the dry form [6, 9].

Whey powder is a hygroscopic product with high tendency to absorb water from the air. This results in the agglomeration of particles and/or the adhesion of them inside the equipment during and after the drying process. These phenomena are known as stickiness and caking, respectively, and occur mainly due to the presence of whey lactose in the amorphous state [10–13].

The food dehydration by spray drying occurs very quickly not allowing the reorganization of the molecules in the amorphous state. This causes the molecule to remain in the gummy state, which is highly hygroscopic [14, 15]. The change from glassy to gummy is known as glass transition and occurs at a temperature called glass transition temperature (T_g), which is specific for each product and influenced by the composition and the water content in the final powder product [16, 17].

An alternative to minimize the stickiness and the caking is the previous crystallization of the lactose before drying. This strategy reduces the amorphous lactose content and avoids the occurrence of the cited drawbacks [18–20].

Controlled crystallization is unnecessary in free-lactose dairy products, since this sugar content is low and the risk of spontaneous crystallization is minimal. These products serve a wide range of lactose intolerant consumers who are characterized as unable or parcially unable to hydrolyze lactose in the small intestine [21].

The hydrolysis of lactose forms two reducing sugars (galactose and glucose) with low molecular weight that, when compared to lactose, present higher hygroscopy, higher reactivity (Maillard reaction) and lower glass transition temperature (T_g). These factors make the lactose-free products more difficult to dry and more prone to suffer stickiness and caking [22–24].

In order to improve the drying process and the final characteristics of the powder, the addition of compounds with high molecular weight has been a promising approach since carrier agents, encapsulants, body and texture improvers can increase the T_g of the food and reduce the occurrence of stickiness and caking [1, 11, 25, 26]. The addition of food substances to milk promotes changes in the physico-chemical properties and its drying. Under current Brazilian legislation, products produced from mixture of milk and other substances (dairy or non-dairy food) must contain at least 51% of dairy ingredients in the final product [27].

The objective of this work was to develop a mathematical model that allows for a thermodynamically evaluating of spray dryers, through mass and energy balance, to elaborate different products from mixing of the milk and whey and to evaluate the effect of compounds of high molecular weight in the physicochemical properties and the drying characteristics of traditional and lactose-free dairy mixes.

CHAPTER 1

BIBLIOGRAPHIC REVIEW

1.BIBLIOGRAPHIC REVIEW

1.1 Spray drying

Drying is one of the oldest methods of preservation which has among other advantages: to reduce the moisture and water activity of food, to increase the microbiological stability of products, to avoid the risk of chemical and biological degradation; and to reduce the storage and transportation costs [28].

In the manufacturing of dairy products some techniques can be applied such as freeze drying, roller drying and spray drying. Freeze drying has as advantages the recovery of volatiles and maintenance of the nutritional properties of products, however it does demand a high energy consumption (5000 to 10000 $KWh \cdot t^{-1}$ of removed water) and high costs of maintenance [29]. However, drum drying has a better energy efficiency (300 to 1000 $KWh \cdot t^{-1}$ of removed water) easy operation and maintainance [2]. On the other hand, some products, such as those rich in sugars may be damaged due to direct contact with the heating surface [30].

In dairy plants, spray drying is more widely applied because it presents better energy expenditure ratio when compared to freeze drying (up to 10 times lesser) and, differenly from drum drying, it does not show excessive heating of the product [28, 31].

Spray drying is a unitary operation in which a concentrated liquid (variable percentage of solids according to the product) is atomized and put in contact with a hot air flow also known as drying air. The characteristics of this product (temperature, viscosity and feed rate) together with the parameters used in the drying process (inlet air temperature, absolute air humity) determine the size of the powder particles, which may be varying from 10 μm to 3 mm [28]. The spray dried product is characterized as an amorphous liquid with high viscosity (η > 1014 Pa.s) and, in this state, the liquid has a relative viscosity similar to a solid. Therefore, the final product is more commonly referred to as powder [32].

The design of the spray dryer as well as the type of atomizer are directly related to the final quality of the powder. The main types of atomizers and their respective characteristics are shown in table 1.

Table 1 - Characteristics of atomization systems

Type of atomizer	Advantages	Disadvantages
Centrifugal atomizer or atomizing disk	Flexibility, high flow, possibility to work with high viscosity products	High investment and maintenance cost, increase the amount of occluded air and decrease the density of the powder
Pressure nozzle	Reduced amount of occluded air, higher powder density, better fluidity of the powder,	Elevated maintenance cost of the high pressure pump, wear of the parts that make up the nozzles (especially when working with lactose

	low investment in the nozzle	crystals), limitations on the viscosity and solids content of the product to be atomized
Two fluid nozzle	Suitable for sensitive products and high pressures	Increase the amount of occluded air and decrease of the dust density

Source: [33]; [34]; [35].

Despite the advantages, spray drying is one of the most costly unit operations of the dairy industry (1000 to 2000 Kwh·t^{-1} removed water) and, the main reason for this, is the need to provide latent heat of evaporation to remove water or other solvent [2, 3]. Thus, improvments in the operation of spray dryer must be performed in order to reduce the cost of production and improve the quality of milk powder [28].

According to [4], it is indispensable to know the energy consumption of the equipment and that this consumption is the key parameter in the evaluation of the efficiency of the spray dryer. The way to assess it can be by calculating the energy specific consumption (ESC in kg·kg^{-1}), which is defined as the amount of energy required to evaporate one kilogram of water. Another way to evaluate the efficiency of the process is to know the mass and energy losses of the equipment, the energy expenditure necessary to produce one kilogram of powder, or to evaluate the final cost of the product [5, 29].

In order to perform the dehydration of the food, it is important to effectively apply the steps that come prior to drying, such as membrane concentration and vacuum concentration in multiple stages, the choice of these techniques being dependent on the properties of the product to be subject to spray drying [29]. These techniques are responsible for significantly reducing energy costs in obtaining the powder, since the application of membrane may be up to 450 times lesser than in spray dryer (dependent on the kind of membrane) and vaccum evaporation up to 20 times [36–38].

Dairy products are considered thermally sensitive and their functional and nutritional properties can be negatively influenced by the processes applied in the evaporation of water [39]. In Brazil, professionals in the dairy sector obtained knowledge on drying from an empirical way, without a scientific basis involved in the process. Drying of milk is already well established by companies, however, the production of its derivatives and new products in general indicate the need for evaluation and modification of the process as well as greater control of the drying parameters. These actions aim to produce a good quality product, increase yield and reduce energy expenditure.

1.2 Milk

Globally, on the market, the demand for dairy products is constant throughout the year, causing surplus in times of high productivity to be sold at a lower price. As a result the excess of the raw material does not allows the productive growth for rural properties [40]. An alternative to generate greater profitability to it is the transformation of the product to its dehydrated form.

Milk is defined as the product of complete and uninterrupted milking, under hygienic conditions, of healthy, well fed and rested cows [41]. Milk nutritional quality as well as its derivatives is widely known, what makes it very important for human nutrition.

Milk is considered to be one of the most complete foods because it has a high content of proteins, vitamins and minerals as well as being an important source of calcium. This food is widely marketed and consumed by populations worldwide and is especially recommended for children and for the elderly [42, 43].

From a physico-chemical point of view, milk can be described as a colloidal system made up of proteins, or even a solution of lactose, soluble protein, minerals, vitamins and other components. In addition, the milk can be understood as an emulsion consisting of a dispersed phase (fat) and a continuous aqueous phase (whey) [44].

Brazil was the fifth largest producer of milk in the world in 2014, with a production of approximately 37.1 million tons, representing an increase of 5.1 % in production, compared to 2013 [6, 45]. Its processing and its transformation into derivatives (dairy) have been for ages alternatives to increase its shelf life. Among these alternatives is the drying process, which aims to increase the stability of the product.

1.3 Whey

Whey is another product that has gained interest in the world's dairy market, and yet until the mid-1990s was considered to be in some respects an undesirable by-product of the dairy industry. It is defined as the aqueous portion of milk, which separates from the clot during the manufacture of cheese or casein [6, 46, 47].

Whey is an opaque and greenish-yellow liquid containing about 55 % (w/w) of the solids and 80 to 90 % (w/w) of the milk volume used in the cheese making [8].

In the past, whey was considered an onerous by-product and was dispersed over the fields or used for animal feed. Due to the enforcement of stricter environmental laws, high nutritional quality of whey components (proteins, lactose, etc.) and the development of fractionation techniques, whey has been best used as an ingredient or an ingredient precursor [48].

Worldwide whey production amounted to about 186 million tonnes in net form or 12 million tonnes of solids [9].

Two types of whey are distinguished according to the procedure used for the separation of the curd: sweet whey derived from the enzymatic coagulation of milk (pH 6.3 - 6.6) and acid whey coming from the acidic coagulation of milk for the manufacture of casein or cheeses, such as Cottage, Creamy cheese, etc (pH 4.3 - 4.6) [46].

Serum proteins are also known for high nutritional value and applications in food products, such as β-lactoglobulin (β-Lg), α-lactalbumin (α-La) and bovine serum albumin (BSA) [49]. These proteins are commonly used in the food industry as ingredients, which have functional properties due to their high solubility, water absorption, gelation and emulsifying capacities [50–52].

Serum proteins also have nutritional functionality. They stand out for having in the structure, essential amino acids and bioactive peptides that confer several health benefits. Among other benefits, they help control muscle mass, reduce body fat, improve the intake process, act as insulin, reduce infection, healing, improve learning and reduce aging [53–55].

Several alternatives of use can be applied to whey by industries, including the preparation of whey powder. The main unit operations involved in the production are membrane separation, vacuum evaporation, crystallization and spray drying. Because it is a product which is difficult to dry (due to the presence of lactose in the amorphous phase), the crystallization process of this sugar, prior to the drying process is indicated, because it is related to the reduction of energy expenditure, quality and increase of final product yield, once this operation aims to decrease the problems of stickiness and caking [18, 56].

1.4 Dairy mixes

In the dehydrated dairy market, there is a range of products that have gained commercial attention. They have been referred to as milk powder analogues, or as a formulation, or as dairy mixes as is the case of Brazil. These products are usually made from the mixture of milk and other food substances and can be consumed directly or used as food ingredient applications [27, 57, 58].

The proportion of each component in the food depends on the desired characteristics in the final product, the legislation of each country and the specific requirement of consumers.

In Brazil, dairy mixes are defined as a powder product resulting from the mixing of milk and dairy product(s) and; or food substance(s) suitable for feeding through a technologically appropriate process. Dairy ingredients must represent at least 51% of the total ingredients of the product [27].

Dairy mixes can basically be divided into three types: Infant formulas, which are those intended for children of different ages; the enriched mixes (products added with some health-promoting substance), which are intended for consumers with specific ingestion needs; and there are low-cost dairy mixes, which aim to serve a public of lower purchasing power and who are looking for a cheaper product. Some exemples of these products are present in the figure 1.

Several companies operating in Brazil are producers of these dairy mixes, such as Alibra, Aurora, Danone, Itambé, Nestlé, Piracanjuba, Rofran Foods e Tangará [60–67].

The production of dairy mixes in which occur addition of whey to milk is a challenge for industry since the presence of whey may negatively influence the behavior of the product during drying and storage process due to the presence of lactose in the amorphous form, which infers to the product increase in its hygroscopy capacity, increase of mass losses and energy expenditure, in addition to reducing the glass transition temperature [22, 68, 69].

Figure 1 - Dairy mixes with different formulations
1- infant formula for children in breastfeeding (DHA and AA added); 2- infant formula for children from 10 months (DHS and prebiotics added); 3- dairy mix containing maltodextrin enriched with iron and vitamins A, C and D; 4- Lactose-free dairy mix (added with vitamins and minerals). Source: [59–62]

1.5 Glass Transition

Most foods with reduced moisture content are in the amorphous or partially amorphous state. The amorphous matrix may exist as a highly viscous glassy structure or as a more liquid gummy structure [16].

The material in glassy state is in the metastable zone characterized by an unstable equilibrium region which can be permanently altered due to slightest disturbance [70, 71]. This alteration (from the glassy to the gummy state) is called glass transition and occurs at a determined temperature known as the glass transition temperature (T_g) [16, 72].

The T_g is specific to each product and is influenced by its composition and, mainly, by moisture content. Water acts as a plasticizer material increasing the intermolecular space or free volume, decreasing the local viscosity and increasing the mobility of molecules [73, 74].

The changes that occur in the product, due to T_g, can result in the phenomenon of stickness, collapse and crystallization during food processing and storage. These phenomena are described as dependent on time-temperature and on humidity [25, 75–77].

In a given product, the lower the T_g, the more likely it is to be subject to the phenomena of stickiness and caking that are directly associated with the tendency of some materials to agglomerate and, or to adhere when in contact with a surface [23, 24].

Stickiness often occurs in foods rich in sugars with low molecular weight, which, in the glassy state, are generally very hygroscopic and have low glass transition temperatures [11, 12].

For several reasons, it is essential that the sugar remain in the glassy state during handling and storage (T_g above room temperature) because the molecular mobility of the material in this state is extremely low [78, 79].

In the production of dehydrated dairy products, evaporation of water during spray drying is so rapid that, despite saturation, lactose can not crystallize, remaining therefore in the final product as amorphous lactose thus favoring the occurrence of problems during and after drying [80, 81].

To avoid stickiness and caking lactose must be pre-crystallized as α-lactose monohydrate, a non-hygroscopic form of lactose or may be added products with high molecular weight. Both actions are able to improve some properties of the powders such as hygroscopy, the final yield and to increase the glass transition temperature of the food [11, 19, 20, 82].

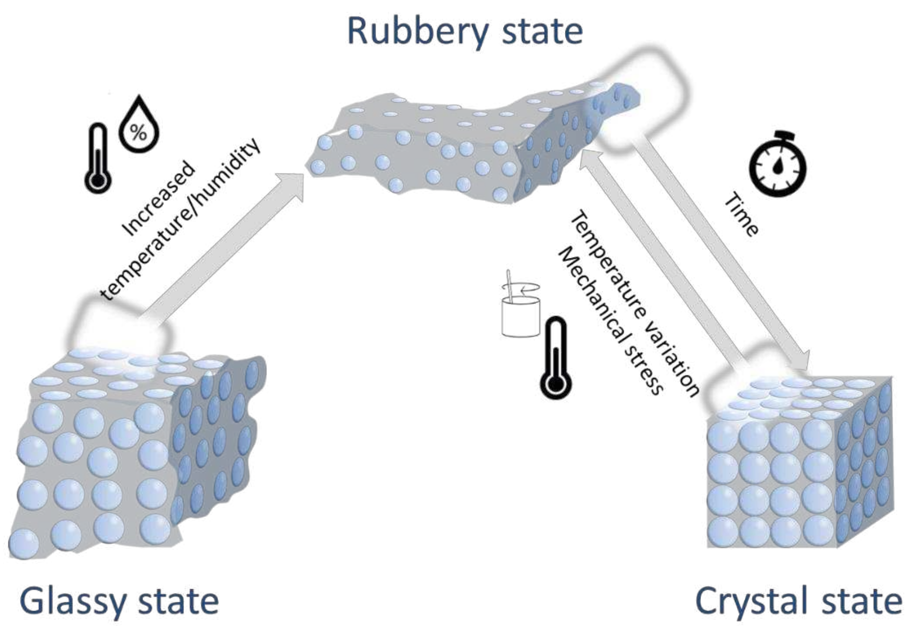

Figure 2 - Change from glassy to crystalline state through glass transition where the product is in the gum form. T = system temperature and T_g = glass transition temperature.

1.6 Lactose Crystallization

Lactose is a disaccharide consisting of one molecule of galactose and one of glucose linked together by a β-1,4 glycosidic bond and represents 70 % (w/w) of whey solids. Its presence contributes to the nutritional value of milk and dairy products and can affect the texture of certain frozen or concentrated products for being involved in changes in color, taste and texture of food [83].

Lactose has a low degree of sweetness compared to other sugars. A sucrose solution at 1, 5, 10 and 20 % (w/w) has the same sweetening power as a lactose solution at 3.5, 15, 30 and 33 % (w/w), respectively [2]. When in solution, it presents itself under two forms of diverse characteristics, alpha and beta in figure 3.

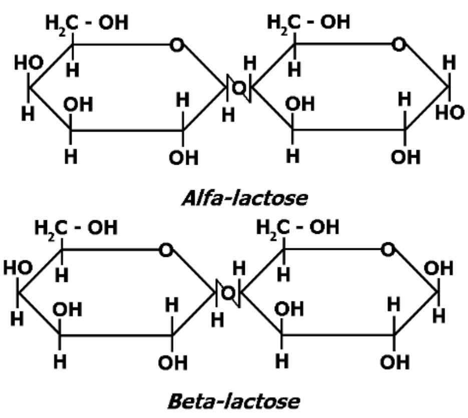

Figure 3 - Chemical structure of lactose isomers

From a technological point of view, what differs α-lactose from β-lactose is the distinct solubilities: where α-lactose and β-lactose show solubilities of 7 g/100 g and 50 g/100 g of solution, both at 15℃, respectively. This property is an important factor in the crystallization of lactose as far as milk or whey concentration goes, the alpha isomer is the first to reach the saturation condition [84].

After saturation, an imbalance occurs between the proportions of α- and β-lactose favoring the mutarrotation phenomenon. During this phenomenon, part of β-lactose is converted into α-lactose or vice versa, in order to restore the mutar-rotate balance between them [85].

Lactose can be found in the amorphous or crystalline state, the latter being characterized by its greater stability both for processing and shelf life [10, 86].

Crystal is one of the forms of space arrangement of an extremely regular substance, and this regularity at the molecular level gives rise to the polyhedral structure characteristic of each crystal. The size, shape and homogeneity of crystals are important in the technological aspect [87].

The crystallization process can be divided into three stages. The first phase is the generation of the motive force, which occurs due to supersaturation obtained by evaporation of the solvent or cooling of the system. The second step of the crystallization process is nucleation. This can occur occasionally as a result of the random association of solute molecules due to the chaotic movement of the solution. The third and final phase occurs due to the growth of the crystals. The increase in particle size (crystal) is related to two steps, the diffusion in which the solute migrates from the solution towards the interface of an adsorption layer, and the coupling of the molecules to the crystalline reticulum, in a First-rate reaction [88].

The crystallization is directly related to the final quality of this sugar-rich product like condensaded milk and whey powder. In spray drying, for example, the lactose molecule tends to change phase during the drying and storage process. As the evaporation of the water is fast, it does not give time for the molecule to be ordered, therefore, the product is subject to problems of stickiness and caking, that can occur during the processing and/or storage [14, 15].

One way to avoid these problems consists of reducing to the maximum the amount of lactose in its amorphous phase by controlling the crystallization process. By performing the controlled crystallization before the dehydration process drying properties can be improved and consequently reducing the problems already mentioned [18–20].

1.7 Maltodextrin

Another alternative that has been used to improve the drying process is the addition of high molecular weight compounds, being maltodextrin the most utilized for this purpose [89].

Maltrodextrins are products derived from the hydrolysis of starch, formed by linear amylose and branched chain amylopectins. They are considered to be D-glucose polymers, linked by α- (1,4) and α- (1,6) and are defined according to their degree of hydrolysis (DE = Dextrose equivalent). DE indicates the percentage of reducing sugars present in the maltodextrin estimated as dextrose based on dry matter [90, 91]. According to [92], maltodextrins have DE < 20, because above this value, the product is considered to be a syrup of solids or dextrose.

Maltdextrin is marketed in the form of a white powder or concentrated solutions being cheaper than other hydrocolloids added in food. Compared to native starches, it is more soluble in water and has a pleasant taste and a soft sensation in the mouth [93].

Maltodextrin performs multiple functions, in the texture, formation of films and in the improvement of the taste of foods. It is also used as an anti-oxidant, helper in the dispersion and solubility of powders, inhibitor of lactose crystallization by increasing of solids content and reducer of Maillard reaction [26, 94–96].

Maltodextrins are high molecular weight compounds and their presence in foods helps in the improvement of the drying process since the food hygroscopicity is reduced while the glass transition temperature is increased. It implies in the reduction of stickiness and caking problems that may occur during and after the drying process. Several studies have shown the beneficial effect of the addition of maltodextrins on the increase of T_g and on the improvement of drying process [11, 97–100].

1.8 Inulin

The addition of soluble fibers to foods has also been carried out in order to improve its nutritional and technological properties.Inulin that is a type of fructooligosaccharide (FOS) formed by fructose monomers containing a glucose unit at the endof chain linked by β-2-1 glycosidic bonds [101, 102].

Inulin has a high degree of polymerization (number of monomers in the chain) compared to other fructooligosaccharides and can contain up to 60 monomers [103] being considered an unconventional sugar and classified as food ingredient [104–106].

Inulin is naturally distributed in several foods of a balanced diet (garlic, banana, onion, etc.), however its amount in these foods is not significant enough to promote beneficial effects to health [107].

Commercially, this fiber has mainly been obtained from chicory (*Cichorium intybus*), Dahlia (*Dahlia pinuata*) and Jerusalem artichoke (*Helianthus tuberosus*) [102]. After extraction and drying, inulin appears as a white powder with a neutral taste and odor and can be added to foods without greatly modifying the viscosity, appearance and flavor [108].

Fibers are substances not digestible by the enzymes of the human organism, being classified as a prebiotic food since they serve as substrate to the microorganisms present in the large intestine [109]. Some health benefits have been reported as for the consumption of inulin, such as blood cholesterol reducer, glycemic index regulator, and anti-carcinogenic agent [110–112].

The relationship between food and health has been widely studied favoring the increase of commercial interest in this niche market (functional foods) [113, 114].

Not always the food consumed naturally contains the minimum amount of fibers to be ingested, which makes it interesting for the addition of these compounds as a food ingredient to reach the beneficial effects [107].

From the technological aspect, inulin has been used to replace sugar or fat, with the advantage that it does not result in caloric increase and alteration of taste [115].

Inulin has a positive effect on the texture of the food and when it is found in high concentrations presents gelation properties which reduces the process of syneresis in dairy products, the water activity and the phenomenon of crystallization in some types of products [116].

Since inulin is a high molecular weight compound and has high glass transition temperature, it can positively influence the drying of the food by reducing problems during the process. However, there are no reports studies evaluating the effect of the addition of fibers on the T_g and on the drying properties of foods.

1.9 Soluble corn fiber

Soluble fibers obtained by the partial hydrolysis of maize are also added to foods and consists of the mixture of α-1,4; α -1,6 and α-1,3 linked by glycosidic bonds [117].

As inulin, these substances have been reported as promoting health benefits and improving the technological properties of foods. The intake of soluble corn fibers can reduce the appetite by increasing the sensation of satiety; to acts in reducing the speed of the glicemic and insulinemic response to the stimuli based on carbohydrates [118, 119].

The fibers are directly related to the process of digestion and transport of food in the body and the increase of its consumption has been stimulated for the prevention and treatment of constipation and hemorrhoids. Supplementation with corn fiber in the diet, together with a controlled diet, is able to reduce the serum total cholesterol (TC), total triacylglycerol (T_g) and very low density lipoprotein cholesterol (VLDL-C) in the bodies of men with hypercholesterolemia [120]. These fibers were also tested in rat feeding and showed a significant effect on the reduction of plasma and liver cholesterol concentrations [121].

Solubles fibers are fermentables and, when ingested, reduce fecal putrefactive compounds, increase the fecal volume and increase the concentration of bifidobacterias, reducing intestinal discomfort [122].

In the technological point of view, soluble fibers have good appearance when used in different products and have good stability to heat, pH and processing stresses. They may exhibit different characteristics when it comes to the gelling ability and influence on viscosity. In this way, the choice of fiber type will depend on the characteristics desired in the final product [123]. The soluble fibers can present different weight molecular, according to their origin and the form of obtaining. The high molecular weights have the characteristic to replace the fat in food, improve its texture and increase the T_g of produtcs [11, 82].

Despite the great demand for different types of dairy mixes and severals the references made to the compounds of high molecular weight as drying process improvers, studies are still scarce with soluble fibers, which made it interesting to evaluate the use of these substances in traditional and free-lactose products.

CHAPTER 2

THERMODYNAMIC CHARACTERIZATION OF SINGLE-STAGE SPRAY DRYERS: MASS AND ENERGY BALANCES FOR MILK DRYING

Abstract

Spray drying requires high amount of energy for the preparation of dairy products. Even so, the wide majority of Brazilian industries do not know the efficiency of their equipment, as well as the final energy cost of production. In order to provide scientific material to these companies and the academic environment. This work aimed to create a mathematical model that allows to know the thermodynamic efficiency of spray dryers, through mass and energy balance. For this, the drying of whole milk in two different pilot single stage equipment was evaluated.

Thermodynamic characterization of single-stage spray dryers: mass and energy balances for milk drying.

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ABSTRACT

Spray drying is an efficient unit operation applied in food drying that demands a high amount of energy compared to vacuum evaporation and membrane filtration. The objective of this work was to present a mathematical model-like basis for the construction of mass and energy balances. For this purpose, milk drying in two lab-scale single spray dryers with different evaporative capacities have been used as examples. The values of the absolute humidity, the mass and energy losses, the ESC (energetic specific consumption) and the

efficiency of the process were obtained by calculations developed in this work. The mathematical model was valid for the evaluation of mass and energy losses, and it allowed us to compare the efficiencies of spray dryers with different designs. From this model, it is possible to compare different drying process and dryers.

Keywords: Mathematical modeling, mass and energy balances, energy consumption, spray drying.

1.INTRODUCTION

In 2014, the global milk production was 802 million tons, with an increase of 3.3% compared to the production in 2013 [6]. Since milk is perishable, the surplus production is designated for the fabrication of dehydrated dairy products in order to improve its conservation over time. However, in 2014, approximately 50 million tons of milk were designated for the production of whole milk powder [6].

In freeze drying the energy consumption is from 5000 to 10000 $KWh \cdot t^{-1}$ of removed water and in drum drying is from 300 to 1000 KWh. t^{-1} of removed water [2, 29, 30]. Although there are advantages to both techniques, spray drying is still the most used in the dairy industry for milk powder production. The energetic consumption of spray drying is approximately ten-fold lower than that of freeze drying, and contrary to the drum drying technique, the product does not reach high temperatures during water evaporation [28, 31].

In spray drying, milk is pulverized in droplets inside a drying tower where the product comes in contact with heated air. Due to an increase in the surface contact between the milk and the air, water is evaporated quickly without excessive heat treatment, during this operation [124]. Thus, milk powder with low water activity (a_w= 0.18 to 0.22) is formed without excessive losses of the nutritional and sensorial characteristics of milk [125].

Although spray drying is largely applied to the manufacturing of dried dairy products on an industrial scale, the energy consumption of this technique is still considerable (1000 to 2000 $Kwh \cdot t^{-1}$ removed water) [2]. Thus, the appropriate operation of spray dryer should be performed in order to reduce the cost of production and improve the quality of milk powder [33, 58, 124, 126]. Sustainability issues and reduction of energy costs are the next challenge for the dairy industry [127, 128].

The final cost of the milk powder formulas is associated with the losses (mass and energy) that occur during the drying process [129]. The mass losses are related to the adherence of milk particles on the internal surface of the drying tower or to transport of the particles by the air flow. In this study the thermal energy losses can be estimated as the sum of dissipated energy through the equipment surface and the energy not used in the conversion of water to vapor.

The mass and energy balance is a mathematical tool that allows the evaluation of the mass and the energy losses in the process of spray dryer dehydration. In addition, this tool makes possible the estimation of the production cost, the comparison of the efficiency of different equipment and the determination of the amount of energy necessary to evaporate 1 kg of water from the product. The application of the mathematical tool in dairy industry ensures the better control of the dairy powders technology [130, 131].

In this paper, we present a mathematical basis for construction of the mass and the energy balance for the milk drying process using single-stage spray dryer equipment. It aims to create a protocol that will work as a support for industries that plan to evaluate the production efficiency of their spray dryers. For this, we will use as an example the milk drying in two lab-scale spray dryers with different evaporative capacities.

2.MATERIAL AND METHODS

The experiments were performed using two lab-scale single-stage spray dryers. Table 1 summarizes the principal characteristics of each equipment.

Table 1 - Characteristics of spray dryers

Spray dryer	**Atomizer**	**Evaporative capacity (kg water·h^{-1})**	**Superficial area (m^2)**	**Model**	**Fabricator**
SD1	Pressure nozzle	1	0.51	MSD 1.0	Labmaq, Brazil
SD2	Rotating disc	20	7.54	Minor Production	Niro Atomizer, GEA, Germany

The relative humidities and temperatures were measured as presented in the scheme (Figures 1, 2 and 3) using a thermohygrometer (Rotronic, Hydropalm). The air velocity measurements were performed using an anemometer (Air Velocity Transducers, model TSI Alnor 84455) whose catheter was introduced in 5 different positions of the section of straight cylindrical ducts [35].

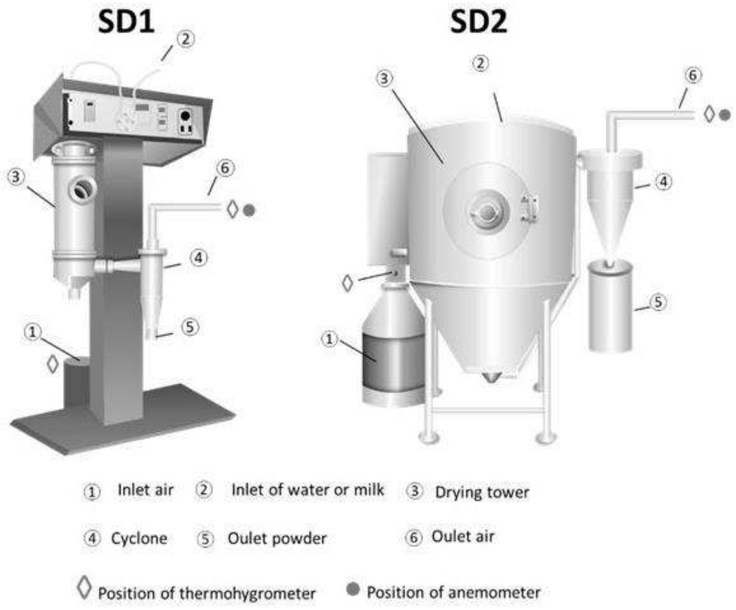

Figure 1 - Scheme of single stage spray dryers. SD1: Labmaq, Brazil; SD2: Niro Atomizer, GEA, Germany

2.1 Validation of mathematical models and evaluation of optimal efficiency of operation of spray dryers

2.1.1 Evaporation of water

Water heated at 40℃ was injected into SD1 or SD2 where it was evaporated in the presence of heated inlet air at 165 ± 5℃.

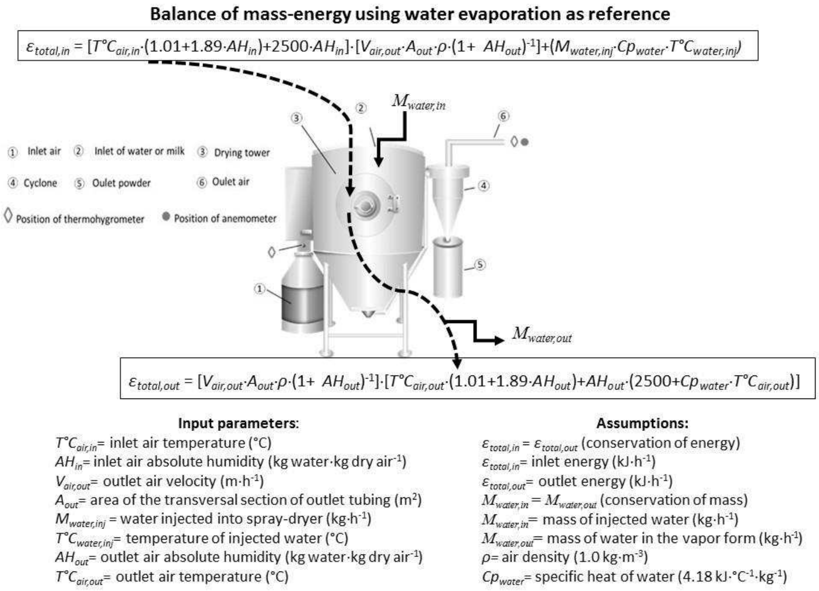

Figure 2 - Scheme of mass and energy balance calculations applied to water drying

The flow rate of the water was adjusted in order to maintain the outlet air temperature at approximately 90 ± 3℃. The process was executed with three repetitions on different days.

2.1.2 Drying of milk

Concentrated whole milk (40% dry material) at 40℃ was injected into SD1 or SD2 where it was dehydrated with inlet air at 165 ± 5℃.

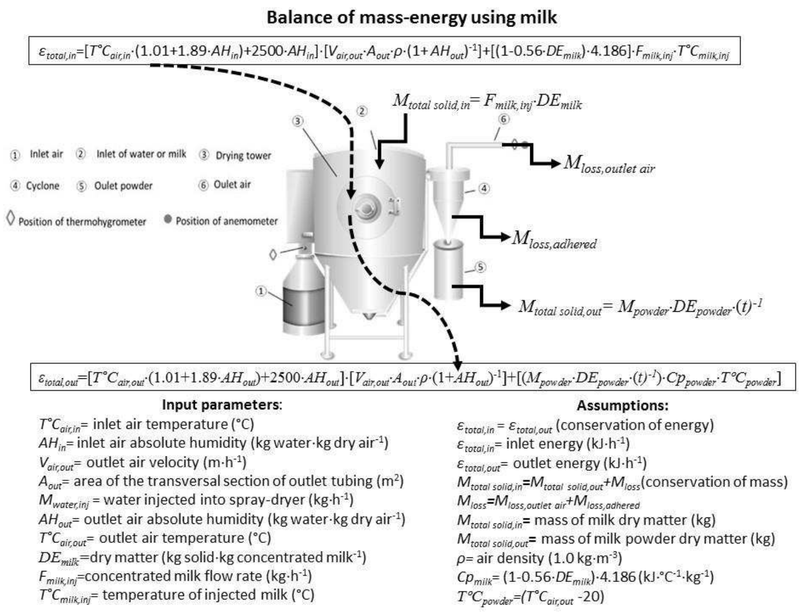

Figure 3 - Scheme of mass and energy balance calculations applied to milk drying

The flow rate of milk was adjusted in order to maintain the outlet air temperature at approximately 95 ± 3℃ to SD1 and 90 ± 3℃ to SD2. A ll experiments were carried out with three repetitions on different days.

3.RESULTS AND DISCUSSION

3.1 Balance of mass-energy using water evaporation as reference

3.1.1 Mass balance for water evaporation: validation of the mathematical model

To create a mathematical model for the evaporation process in spray dryers, the simpler condition will be tested. Before promoting the drying of dairy products, simple water evaporation will be performed. This means that in the equipment inlet, water will be injected, and only vapor will be recovered in the outlet of the spray dryers.

During the process of water evaporation, all water entering the equipment is assumed be converted to vapor, *i.e.,* no mass loss occurs. Thus, the mass balance under this condition has a finality to verify the accuracy of the mathematical equations and ensure that the measurements with the thermohygrometer and anemometer (temperature, relative humidity and air velocity) are consistent.

The first step of mass balance consists of calculating the flow rate of humid air ($F_{h,air}$; kg air·h^{-1}), which is similar in both the input and the output of the equipment. However, this parameter is preferably calculated from the outlet data since in some spray dryers, the air can enter by small slots or holes close to the atomizer, thus resulting in underestimation of the data.

$F_{h,air}$ is calculated from the air velocity measured by an anemometer in the outlet ($V_{a,out}$; m·h^{-1}), the area of the transversal section of outlet tubing (A_{out}; m^2) and the air density (ρ; kg·m^{-3}):

$$F_{h,air} = V_{a,out} \cdot A_{out} \cdot \rho \quad \text{eq. 1}$$

where ρ is assumed be constant and equal to 1.0 kg·m^{-3}.

The second step consists of determining the mass of water contained in the air ($M_{wa,out}$; kg·h^{-1}). $M_{wa,out}$ can be estimated from the absolute humidity of the outlet air (AH_{out}; kg water·kg dry air^{-1}) and the flow rate of humid air (eq. 2) [132].

$$M_{wa,out} = F_{h,air} \cdot AH_{out} \cdot (1 + AH_{out})^{-1} \quad \text{eq. 2}$$

The dry air flow rate ($F_{d,air}$; kg·h^{-1}) is calculated by subtraction of the flow rate of humid air and the water mass contained in the outlet air. By combining equations 1 and 2, $F_{d,air}$ can be written as:

$$F_{d,air} = F_{h,air} - M_{wa,out}$$

$$F_{d,air} = V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1} \quad \text{eq. 3}$$

The mass of water presented in the inlet air ($M_{wa,in}$; kg·h^{-1}) is the product of $F_{d,air}$ and the absolute humidity of inlet air (AH_{in}, kg $_{water}$·kg $_{dry\ air}$$^{-1}$):

$$M_{w,in} = F_{d,air} \cdot AH_{in}$$

$$M_{w,in} = AH_{in} \cdot V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1} \quad \text{eq. 4}$$

The total water mass entering the equipment ($M_{tw,in}$; kg·h^{-1}) is calculated by addition of the water injected into spray dryer ($M_{w,inj}$; kg·h^{-1}) and the amount of water carried from the inlet air ($M_{wa,in}$; kg·h^{-1}):

$$M_{tw,in} = M_{w,inj} + M_{wa,in}$$

$$M_{tw,in} = M_{w,inj} + [AH_{in} \cdot V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] \quad \text{eq. 5}$$

In the outlet, all water mass evaporated is eliminated by air in the vapor form. The total mass of evaporated water ($M_{tw,out}$; kg·h^{-1}) is determined by combination of equations 1 and 2:

$$M_{tw,out} = M_{w,out} = F_{d,air} \cdot AH_{out} \quad \text{eq. 6}$$

$$M_{tw,out} = V_{a,out} \cdot A_{out} \cdot \rho \cdot AH_{out} \cdot (1 + AH_{out})^{-1} \quad \text{eq. 7}$$

The final step for mass balance (Δ_{mass}; kg·h^{-1}) is performed by subtracting the total of the water exiting the spray dryer ($M_{tw,out}$; eq. 7) and the water total mass entering the equipment ($M_{tw,in}$; eq. 5), thus:

$$\Delta_{mass} = M_{tw,out} - M_{tw,in} \quad \text{eq. 8}$$

Using the mathematical treatment presented above, the mass balance (Δ_{mass} = 0) is according to the theoretical assumption for water evaporation. In other words, the mathematical model, as well as the measurements carried out with the anemometer and the thermohygrometer, were consistent with the reality of the drying procedure. In our case, the mass balance was equal to zero, but some variations can be found due to errors in measurements and numeric rounding.

Table 2 shows the parameters measured in the spray dryers during the water evaporation and the mass balance of process.

Table 2 - Inlet and outlet parameters used in mass balance for water evaporation

Equipment	*Inlet parameters*			*Outlet parameters*				
	AH_{in}* ($kg_{water} \cdot kg_{dry\ air}^{-1}$)	$M_{water,inj}$* ($kg \cdot h^{-1}$)	$M_{total\ water,in}$ ($kg \cdot h^{-1}$)	A_{out} (m^2)	AH_{out}* ($kg_{water} \cdot kg_{dry\ air}^{-1}$)	$V_{air,out}$* ($m \cdot h^{-1}$)	$M_{total\ water,out}$ ($kg \cdot h^{-1}$)	Δ_{mass} ($kg \cdot h^{-1}$)
SD1	1.63×10^{-2}	8.30×10^{-1}	1.69×10^{0}	9.62×10^{-4}	3.20×10^{-2}	5.65×10^{4}	1.69×10^{0}	0.00
SD2	1.34×10^{-2}	7.68×10^{0}	1.27×10^{1}	7.24×10^{-3}	3.39×10^{-2}	5.35×10^{4}	1.27×10^{1}	0.00

* Measurement performed in triplicate with standard variation inferior to 5 %.

3.1.2 Energy balance for water evaporation

Since the water is in a completely free state, meaning that it is not linked to any substrate, the energy balance has a finality, permitting the determination of the minimal energy consumed by each equipment. This approach allows a comparison of the energetic performance of spray dryers with different evaporative capacities and designs without the interference of the properties of a food matrix. In food, the water may be linked or partially linked to the main food components. This water does not act as a solvent; rather, it presents resistance to mechanical strength in addition to low molecular mobility and different dielectric properties of free water, thus making the drying process more difficult [133].

In addition to mass balance, in the energy balance, the calculation can be divided into energy entering and leaving the spray dryer.

The total inlet energy ($\varepsilon_{t,in}$; kJ·h^{-1}) is calculated by the addition of the energy of the hot inlet air ($\varepsilon_{a,in}$; kJ.h^{-1}) and the energy of water entering the drying tower ($\varepsilon_{w,in}$; kJ·h^{-1}):

$$\varepsilon_{t,in} = \varepsilon_{a,in} + \varepsilon_{w,in} \quad \text{eq. 9}$$

The energy of the hot air inlet ($\varepsilon_{a,in}$) is given by multiplication between the air enthalpy ($E_{a,in}$; kJ·kg^{-1}) and the flow rate of the air (from eq.3):

$$\varepsilon_{a,in} = E_{a,in}{\cdot}F_{d,air} \quad \text{eq. 10}$$

where $E_{a,in}$ is calculated from the temperature ($T_{a,in}$) and the absolute humidity (AH_{in}) of the inlet air:

$$E_{a,in} = T_{a,in}{\cdot}(1.01 + 1.89{\cdot}AH_{in}) + 2500{\cdot}AH_{in} \quad \text{eq. 11}$$

By substituting equations 3 and 11 into 10, the $\varepsilon_{a,in}$ can be rewritten as:

$$\varepsilon_{a,in} = [T_{a,in}{\cdot}(1.01 + 1.89{\cdot}AH_{in}) + 2500{\cdot}AH_{in}] \cdot [V_{a,out}{\cdot}A_{out}{\cdot}\rho{\cdot}(1 + AH_{out})^{-1}]$$

eq. 12

The second term of equation 9, *i.e.*, the energy of water entering into the drying tower ($\varepsilon_{w,in}$), is determined from the product of flow rate of water injected into spray dryer ($M_{w,inj}$; kg·h^{-1}), specific heat (Cp_w= 4.18 kJ·°C^{-1}·kg^{-1}) and its temperature ($T_{w,inj}$):

$$\varepsilon_{t,in} = M_{w,inj} \cdot C_{pw} \cdot T_{w,inj} \quad \text{eq. 13}$$

By substitution of equations 12 and 13 into equation 9, the total energy entering the system can be understood as:

$$\varepsilon_{t,in} = [T_{a,in} \cdot (1.01 + 1.89 \cdot AH_{in} + 2500 \cdot AH_{in}] \cdot [V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] + M_{w,inj} \cdot C_{pw} \cdot T_{w,inj} \quad \text{eq. 14}$$

The total outlet energy ($\varepsilon_{t,out}$; kJ·h^{-1}) is deduced analogously to that demonstrated for $\varepsilon_{t,in}$ using the outlet data. Therefore, $\varepsilon_{t,out}$ can be written as:

$$\varepsilon_{t,out} = \varepsilon_{a,out} + \varepsilon_{w,out}$$

$$\varepsilon_{t,out} = [\mathrm{T}_{a,out} \cdot (1.01 + 1.89 \cdot AH_{out}) + 2500 \cdot AH_{out}] \cdot [V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] + M_{tw,out} \cdot Cp_w \cdot \mathrm{T}_{a,out} \quad \text{eq. 15}$$

where $M_{tw,out}$ (kg·h^{-1}) denotes the mass of water in the vapor form.

Substituting equation 6 into 15 yields:

$$\varepsilon_{t,out} = [V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] \cdot [T_{a,out} \cdot (1.01 + 1.89 \cdot AH_{out}) + AH_{out} \cdot (250 + Cp_w \cdot \mathrm{T}_{a,out})] \quad \text{eq. 16}$$

From the inlet ($\varepsilon_{t,in}$; eq.14) and outlet ($\varepsilon_{t,out}$; eq.16) data, it is possible to determine the energy loss (ε_{loss}; in percentage):

$$\varepsilon_{loss} = \left(1 - \frac{\varepsilon_{t,out}}{\varepsilon_{t,in}}\right) \text{x } 100 \qquad \text{eq. 17}$$

This parameter allows evaluation of the amount of energy that is dissipated from spray dryer or simply wasted during drying process. Another parameter that allows comparison of the drying efficiency of different equipment is the energetic specific consumption (*ESC*; kJ·kg^{-1} evaporated water), which is defined as the amount of energy necessary to evaporate 1 kg of water [5]:

$$ESC = \frac{\varepsilon_{t,in}}{M_{tw,out}}$$

$$ESC = \frac{\varepsilon_{t,in}}{[V_{a,out} \cdot A_{out} \cdot \rho \cdot AH_{out} \cdot (1 + AH_{out})^{-1}]} \qquad \text{eq. 18}$$

The energetic efficiency of the process (ε_{ef}) can be estimated by division of the *ESC* value (eq. 17) by the latent heat of vaporization of water (L_w = 2337.46 kJ·kg^{-1}):

$$\varepsilon_{ef} = \frac{ESC}{L_w} \qquad \text{eq. 19}$$

This allows an estimation of how much more energy was expended in relation to the theoretical value (L_w). The higher the value of ε_{ef} is, the lower is the efficiency of the drying process.

All parameters necessary to calculate the energetic loss (ε_{loss}), the energetic specific consumption (*ESC*) and the energetic efficiency of the process (ε_{ef}) are displayed in Tables 2 and 3 for SD1 and SD2.

Table 3 - Energetic balance for water evaporation

	Inlet data			Outlet data				
Equipment	$T°C_{air,in*}$ (°C)	$T°C_{water,inj*}$ (°C)	$\varepsilon_{total,in}$ (kJ·h^{-1})	$T°C_{air,out*}$ (°C)	$\varepsilon_{total,out}$ (kJ·h^{-1})	ε_{loss} (%)	*ESC* (kJ·kg^{-1})	$\varepsilon_{efficiency}$
SD1	1.63×10^2	4.00×10^1	1.12×10^4	9.12×10^1	9.89×10^3	12.24	6.70×10^3	2.87
SD2	1.70×10^2	4.00×10^1	7.98×10^4	8.82×10^1	7.51×10^4	8.76	5.93×10^3	2.55

* Measurement performed in triplicate with standard variation inferior to 5 %.

The heat balance shows a difference between inputs and outputs (ε_{loss}) of approximately 12% and 9% for SD1 and SD2, respectively. This difference is related the heat loss from not insolated parts of equipment and probable errors of calculation and measurements. Although SD2 shows a superficial area (7.54 m^2) larger than SD1 (0.51 m^2), the non-insolated parts of each equipment present 100% and 20%, respectively. Additionally, SD2 shows the best value for ESC and ε_{ef}, indicating greater use of energy by this equipment.

The equipment (SD1 and SD2) presented high energy loss compared to industrial spray dryers, which present losses between 3 and 5% [29]. In addition to the heat isolation capacity, the size of equipment may influence the energy loss and the efficiency [5].

3.2 Milk drying

In the previous section, the mathematical model and the measurements performed using an anemometer and a thermohygrometer were validated by mass balance. Furthermore, the ideal energetic operation of the spray dryers was evaluated using an energetic balance for water evaporation.

In this section, the mathematical approach used for water evaporation in spray dryer will be used for balance of mass and energy for milk drying.

3.2.1 Mass balance for milk drying

The total content of solids entering into drying tower ($M_{ts,in}$; kg·h^{-1}) is given by multiplication between the flow rate of concentrated milk ($F_{m,inj}$; kg·h^{-1}) and its total solids (TS_m, kg $_{solid}$·kg $_{concentrated\ milk}^{-1}$):

$$M_{ts,in} = F_{m,inj} \cdot \mathrm{TS}_m \quad \text{eq. 20}$$

In the outlet, the amount of solids after drying ($M_{ts,out}$; kg·h^{-1}) is calculated from the amount of powder milk recovered (M_p; kg), its total solids (TS_p; kg $_{solid}$·kg $_{concentrated\ milk}^{-1}$) and the total time of the drying process (t; h):

$$M_{ts,out} = \left(\frac{M_p \cdot \mathrm{TS}_p}{t}\right) \quad \text{eq. 21}$$

The mass balance is calculated as the difference between the amount of solids recovered after drying ($M_{ts,out}$; eq. 21) and the mass of solids injected into equipment ($M_{ts,in}$; eq.20):

$$\Delta_{mass} = M_{ts,out} - M_{ts,in}$$

$$\Delta_{mass} = \left(\frac{M_p \cdot TS_p}{t}\right) - F_{milk,inj} \cdot \mathrm{TS}_m \quad \text{eq. 22}$$

In an ideal drying process, all solids entering into system should be recovered after drying; however, in milk drying, a considerable part of the powder is lost in the air flow or adhered to the drying tower. The mass of milk powder lost (M_{loss}, in percentage) can be calculated as

$$M_{loss} = \left(1 - \frac{M_{ts,out}}{M_{ts,in}}\right) \cdot 100 \qquad \text{eq. 23}$$

Substituting equations 21 and 22 into 23, yields:

$$M_{loss} = \left(\frac{1 - M_p \cdot \mathrm{TS}_p}{t \cdot F_{m,inj} \cdot \mathrm{TS}_m}\right) \cdot 100 \qquad \text{eq. 24}$$

The negative sign of Δ_{mass} indicates that part of the milk solids were lost during drying. Another relevant factor for mass loss is the dissipation of powder together with the outlet air, and this loss increases based on how much finer the powder is. Lab-scale equipment produces finer particles then industrial equipment, and the spray dryers utilized in this experiment are compounds with a unique stage drying that increases the formation of these fine powders and consequently their loss [134, 135].

Table 4 shows the inlet and outlet data necessary to calculate the loss of mass for milk drying.

Table 4 - Mass balance for milk drying

	Inlet data		Outlet data				
Equipment	$F_{milk,inj*}$ (kg·h^{-1})	DE_{milk*} (kg·kg^{-1})	$M_{powder*}$ (kg)	DE_{powder}* (kg·kg^{-1})	t* (h)	Δ_{mass} (kg)	M_{loss} (%)
SD1	1.24 x10^{0}	3.83 x 10^{-1}	2.92 x 10^{-1}	9.55 x10^{-1}	6.67 x10^{-1}	- 0.06	12
SD2	1.83 x10^{1}	3.83 x 10^{-1}	1.46 x10^{0}	9.56 x10^{-1}	2.73 x10^{-1}	- 1.90	26

* Measurement performed in triplicate with standard variation inferior to 5 %.

3.2.2 Energy balance for milk drying

The energy balance for milk drying is very similar to that shown for water evaporation and it was previously described [136–138]. However, instead of the parameters for water, the data for concentrated milk will be used. Using equation 14 as a base, the energy entering during the drying process can be rewritten as:

$$\varepsilon_{t,in} = [\mathrm{T_{a,in}}\cdot(1.01 + 1.89\cdot AH_{in}) + 2500\cdot AH_{in}] \cdot [V_{a,out}\cdot A_{out}\cdot\rho\cdot(1 + AH_{out})^{-1}] + F_{m,inj}\cdot Cp_m\cdot T_{m,inj} \quad \text{eq. 25}$$

where Cp_m corresponds to the specific heat of milk in kJ·kg^{-1} and $T_{m,inj}$ is the temperature of concentrated milk in ℃.

Cp_m is estimated by follow relation [29]:

$$Cp_m = (1 - 0.56 \cdot TS_m) \cdot 4.186 \quad \text{eq. 26}$$

where Cp_m corresponds to the specific heat of milk in kJ·kg^{-1}, the equation 1- 0.56 x TS_m refers the mean specific heat of the milk solids components, which is established as 44% of the specific heat of water (4.186) and TS_m is the dry mass of the milk.

Substituting equation 26 into 25 yields:

$$\varepsilon_{t,in} = [\mathrm{T_{a,in}} \cdot (1.01 + 1.89 \cdot AH_{in}) + 2500 \cdot AH_{in}] \cdot [V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] + [(1 - 0.56 \cdot TS_m) \cdot 4.186] \cdot F_{m,inj} \cdot T_{m,inj} \quad \text{eq. 27}$$

The outlet energy (ε_{out}; kJ·h^{-1}) can be calculated from equation 15 by adapting the parameters for milk powder:

$$\varepsilon_{t,out} = \left[\mathrm{T}_{a,out} \cdot (1.01 + 1.89 \cdot AH_{out}) + 2500 \cdot AH_{out}\right] \cdot \left[V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}\right] + \left[\frac{M_p}{t} \cdot Cp_p \cdot \left(\mathrm{T}_{a,out} - 20\right)\right] \quad \text{eq. 28}$$

where M_p and Cp_p correspond to the rate of powder production in kg·h^{-1} and the specific heat of the powder (kJ·kg^{-1}·℃$^{-1}$), respectively. Note that the temperature of powder in the outlet of equipment was estimated as the temperature of outlet air ($T_{a,out}$) subtracted from 20℃. The temperature of the particle during spray drying is between the outlet air temperature and the wet-bulb temperature of the outlet air, which means 10 to 20℃ below the outlet air temperature [39, 139] .

Replacing Cp_p in equation 28 by its correspondent relation (eq. 26) yields:

$$\varepsilon_{t,out} = [\mathrm{T}_{a,out} \cdot (1.01 + 1.89 \cdot AH_{out}) + 2500 \cdot AH_{out}] \cdot [V_{a,out} \cdot A_{out} \cdot \rho \cdot (1 + AH_{out})^{-1}] + [(1 - 0.56 \cdot TS_p) \cdot 4.186] \cdot \frac{Mp}{t} \cdot (\mathrm{T}_{a,out} - 20) \quad \text{eq. 29}$$

The energy loss (ε_{loss}), energetic specific consumption for milk (*ESC*) and energetic efficiency of process (ε_{ef}) are also calculated for drying milk from equations 17, 18 and 19, respectively.

For spray dryers SD1 and SD2, the energetic losses (ε_{loss}) were approximately 1.1 and 1.2 times higher than the energetic losses for water evaporation (see table 3). These differences between milk drying and ideal drying (water evaporation) are directly related to powder mass lost during the process and the larger energy necessary to evaporate the water from food [89, 133].

Tables 4 and 5 list the parameters needed to calculate the energy balance for milk drying.

Table 5 - Energetic balance for milk drying

	Inlet data				Outlet data				
Equipment	$T_{a,in*}$ (℃)	AH_{in*} ($kg_{water} \cdot kg_{dry\ air}^{-1}$)	$T_{m,inj*}$ (℃)	$\varepsilon_{t,in}$ ($kJ \cdot h^{-1}$)	$V_{a,out*}$ (℃)	A_{out} (m^2)	AH_{out*} ($kg_{water} \cdot kg_{dry\ air}^{-1}$)	$T_{a,out*}$ (℃)	$\varepsilon_{t,out}$ ($kJ \cdot h^{-1}$)
SD1	1.62×10^{2}	1.59×10^{-2}	4.0×10^{1}	1.11×10^{4}	5.65×10^{4}	9.62 x 10-4	3.07×10^{-2}	9.76×10^{1}	9.68×10^{3}
SD2	1.70×10^{2}	1.36×10^{-2}	3.9×10^{1}	9.82×10^{4}	6.55×10^{4}	7.24×10^{-3}	3.80×10^{-2}	8.84×10^{1}	9.04×10^{4}

Equipment	ε_{loss} (%)	ESC ($kJ \cdot kg^{-1}$)	ε_{ef}
SD1	13.89	1.52×10^{4}	6.55
SD2	10.72	9.19×10^{3}	3.93

* Measurement performed in triplicate with standard variation inferior to 5 %.

4.CONCLUSION

The mathematical model was valid for evaluation of the mass and energy losses, and it allowed a comparison of the efficiency between spray dryers with different designs. Using this model, it is possible to compare different drying process and dryers. Spray dryer SD2 showed higher energy efficiency than SD1. Application of this protocol of calculus to industrial processes should measure the air flow rate, area of transversal section of outlet air tubing, air velocity, absolute humidity of the air (inlet and outlet), temperature (water or milk, inlet and outlet air) and mass (water or milk, powder).

CHAPTER 3

CHARACTERIZATION OF DAIRY MIX POWDERS WITH MALTODEXTRIN AND INULIN PRODUCED BY SPRAY DRYING

Abstract

Since the previous chapter it was demontrated a mathematical model for evaluation of energy efficiency of spray dryers with different designs. Taking into account that the drying process of milk is well established. This work had the objective to develop powder products to from the mixture of different proportions of milk and whey, in one of the spray dryers thermodynamically evaluated in chapter 2. Besides knowing the equipment efficiency, this new approach will assess the actual performance in terms of product quality. Thus, this work will evaluate the drying of dairy mixes containing or not high molecular weight compounds and will be evidenced the effect of these compounds over the physicochemical and drying properties of the dairy mixes.

CHARACTERIZATION OF DAIRY MIX POWDERS WITH MALTODEXTRIN AND INULIN PRODUCED BY SPRAY DRYING

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ABSTRACT

Dairy mix powders are mixtures of milk and whey subject to spray drying under regulation in many countries. In this work, dairy mix powders were manufactured from a combination of dairy bases (concentrated milk and whey) with or without maltodextrin and inulin. The effect of the formulation on the characteristics and drying properties of the products were evaluated. Higher whey concentrations reduced the proportion of protein and fat in the mixes, increased the carbohydrate concentration, decreased the mean hydrodynamic diameter of particles during the rehydration of powders in water, promoted greater particle agglomeration during drying, increased the browning saturation index and induced changes in the Raman spectrum profile with respect to the spectral contribution of lactose. The addition of maltodextrin and inulin reduced the powder agglomeration, increased the average hydrodynamic diameter of particles during rehydration in water, increased the theoretical glass transition temperature, reduced the browning of products and exhibted strong spectral contributions to Raman.

Keywords: spray drying; glass transition; size distribution of particles; whey; microscopy

1.INTRODUCTION

Dairy mix powders are defined as products of the mixture of milk with product(s), dairy food substance(s) or non-dairy product(s) or both, which are suitable for human consumption via a technologically appropriate process. Our objective is to determine the effect of the composition on the physico-chemical properties of dairy mix powders to provide a scientific basis to industries that are interested in developing dehydrated products from the mixture of milk and whey. Various formulations of dairy mix powders from concentrated milk, concentrated whey, inulin and maltodextrin were produced, and the drying characteristics, color, composition and microstructure of the powders were assessed.

2.MATERIAL AND METHODS

Nine different treatments were performed in duplicate (n = 2). Three formulations were used, which contained only milk concentrate and whey concentrate (dairy bases) in different proportions: 75/25 (A), 50/50 (B) and 25/75 (C). In other formulations, maltodextrin (A', B' and C') or inulin (A”, B” and C”) were added (Table 1).

Table 1 - Formulations of the treatments (n=2)

Treatments*	Dairy bases		Maltodextrin	Inulin
	Concentrated milk	Concentrated whey		
A	75	25	-	-
A’	60	20	20	-
A’’	60	20	-	20
B	50	50	-	-
B’	40	40	20	-
B’’	40	40	-	20
C	25	75	-	-
C’	20	60	20	-
C’’	20	60	-	20

*For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A’, B’ e C’: addition of maltodextrin. A’’, B’’ e C’’: addition of inulin.

2.1 Preparation of dairy mixes

Whole milk concentrate was obtained from the complete reconstitution of milk powder (25℃) to 40% total solids (TS). Maltodextrin 10 DE (Ingred ion) and inulin (Beneo) were used. The partially demineralized pre-concentrate whey (supplied by Porto Alegre dairy plant, Ponte Nova - MG) contained 36% soluble solids and were concentrated to 55% TS in a vacuum evaporator (Treu®). The whey concentrate was subjected to lactose crystallization in an open double-jacketed pan (Inoxul®), provided with a central stirrer. The soluble solids (°Brix) were determined in a digital refractometer (Biobrix® 2 WAJ-D model), and the percentage of crystallization was determined using equation 1 [140].

$$\%\ of\ cristalization = \frac{(B1-B2)\ X\ 9500\ X\ 100}{L\ X\ TS\ X\ (95-B2)} \quad \text{eq. 1}$$

where B1 = initial soluble solids content (°Brix time zero); B2 = final s oluble solids content (° Brix after crystallization); L =% lactose in the total solids; TS = % of total solids. After the percentage of crystallization reached 50% (mean 52.1% ± 1.6), the whey was divided into fractions according to Table 1 and added to the other ingredients. All treatments were subject to two-stage homogenization at 200 bar (Technohomo, Tecnolab model). Drying was performed in a single-stage spray dryer on a pressure nozzle spray system with a diameter of 1 μm (Labmaq, MSD 1.0 model), a water evaporation capacity of 1 $kg \cdot h^{-1}$, 30 $L \cdot min^{-1}$ compressed air flow, and 2.0 $m^3 \cdot min^{-1}$ blower air flow. The drying parameters were set at 170 ± 5℃ for the inlet air temperature and 90 ± 5℃ for the outlet air temperature.

2.2 Physico-chemical analyzes

The concentrations of total solids (TS), protein, ash, carbohydrates and lipids of the samples were analyzed. The TS concentration was determined by the gravimetric technique in an oven at 105℃. The total protein and ash conten t were determined using Micro-Kjeldahl method and the gravimetric method, respectively, to evaluate the weight loss of the material, which was incinerated in a muffle furnace at 550°C. These analyses were performed according to [14 1]. The fat content was determined using Gerber method [142], and the carbohydrate content was determined from the difference between total solids and the protein, lipid and ash content. The water activity (a_w) was measured using Aqualab (Decagon 3TE, Decagon Devices Inc., USA).

2.3 Evaluation of the microstructure

The morphology and agglomeration characteristics of the powders were evaluated without prior preparation using the Scanning Electron Microscope 2500x (Hitachi TM 3000, Hitachi Ltd., Tokyo, Japan). The size distribution of the particles during rehydration was obtained using the laser diffraction analyzer Beckman Coulter LS 13 320 (Beckman Coulter, Miami, FL, USA), which was coupled to the liquid analysis module (Aqueous Liquid Module, Beckman Coulter, Miami, FL, USA). Sufficient amounts of samples to generate turbidity readings were added to the liquid analysis module tank, which contained water at 25°C. The samples were slowly added to prevent the formation of agglomerates. The rehydration process in the equipment was supervised for 15 min (data collection interval of 3 minutes) to ensure complete rehydration, which was determined by the stabilization of the particle size distribution. Data were collected in the region of 0.04-2000 μm in 90 seconds. The refractive indices of 1.332 and 1.57 were used for the dispersing medium (water) and particles (casein micelles), respectively, according to [143] and are represented by % of volume occupied by the particles depending on their size.

2.4 Calculated glass transition temperature (Tg)

The glass transition temperatures were calculated from the extended equation of [144], which enables us to calculate the T_g values of systems with more than two components [145]. This equation was used by several authors [132, 146, 147].

$$Tg = \frac{W1\Delta Cp1Tg1 + W2\Delta Cp2Tg2 + W3\Delta Cp3Tg3}{W1\Delta Cp1 + W2\Delta Cp2 + W3\Delta Cp3} \qquad \text{eq. 2}$$

where T_g is the glass transition temperature (ºC) of the component; ΔCp is the change in heat capacity of each component in the glass transition ($J \cdot kg^{-1} \cdot ℃^{-1}$); W is the mass fraction ($m \cdot m^{-1}$) of the component in the mix.

For the calculation, the following values of T_g and ΔCp were used: lactose T_g 98°C, ΔCp 0,38 $J \cdot kg^{-1} \cdot ℃^{-1}$ [148]; casein T_g 132°C, ΔCp 0,26 $J \cdot kg^{-1} \cdot ℃^{-1}$ [69]; whey proteins T_g 127°C, ΔCp 0,09 $J \cdot kg^{-1} \cdot ℃^{-1}$ [69, 147, 149]; maltodextrin T_g 142°C, ΔCp 0,30 $J \cdot kg^{-1} \cdot ℃^{-1}$ [129, 150]; inulin T_g 120°C, ΔCp 0,65 $J \cdot kg^{-1} \cdot ℃^{-1}$ [151].

2.5 Color Analysis

The Mobile Colorimeter CR-10, L* a* b* system, luminosity, hue and saturation were used to calculate C, M, and ΔE. C and h are the saturation index and hue angle, respectively. ΔE is the total or overall difference between the products.

2.6 Raman spectra

The Raman spectra were obtained using an RFS 100 FT-Raman spectrometer (Bruker), which was equipped with a germanium detector, liquid nitrogen for cooling, an excitation line at 1064 nm, and Nd: YAG laser at 500 mW maximum. The conditions were electronically adjustable for each type of sample to be studied. In this work, the output power was set at 60 mW. This power level was selected to obtain the strongest Raman signal without overheating nor degrading the samples. The measurements were obtained at 4 cm^{-1} resolution in the spectral range of 3500-50 cm^{-1} with 512 accumulations every 15 minutes. The Opus 6.0 software (Bruker Optik Ettlingen, Germany) was used.

2.7 Statistical Analyses

The Complete Randomized Design (CRD) was used with 9 treatments and 2 replications (Table 1). The Analysis of Variance and Tukey's test were conducted for multiple comparisons of the means at 5% significance level. The Linear Correlation Analysis was applied except for the calculated values. The SAS software (SAS Institute Inc., 2008) version 9.1 was used.

3.RESULTS AND DISCUSSION

3.1 Physico-chemical characterization and microstructure of dairy mix powders

There was no significant difference ($p > 0.05$) for the total solids (TS), which indicates that the differences in compositions of the products are not related to the moisture content, and there is regularity during drying. There is a significant difference ($p < 0.05$) in the protein, fat, and carbohydrate contents of 9.7-21.2 $g \cdot 100\ g^{-1}$, 3.0-19.2 $g \cdot 100\ g^{-1}$ and 53.1-79.9 $g \cdot 100\ g^{-1}$, respectively. Mixes that contained only milk and whey in the formulation (A, B and C) had different protein, fat and carbohydrate contents ($P < 0.05$). A decrease in amount of milk in the milk and whey mixture resulted in lower protein/fat content and greater carbohydrate content. Table 2 shows that the dairy mixes with maltodextrin and inulin (A', A'', B', B’’, C' and C'') showed a reduction in protein and fat and an increased concentration of carbohydrate compared with the respective reference treatments in the proportion milk/whey of the dairy basis (A, B and C).

Table 2 - Composition of the dairy mix powders (n=2*)

	TS	CS[3]	WP[3]	A	TL[1]	LC	LS	T_g[4] (ºC)	T_g[5] (ºC)	a_w	AS
A	98.3±0.2[a]	13	8	5.8±0.0[ab]	52.1	6.5	45.6	104.4	72	0.13±0.01[bc]	2.277
B	96,7±0.9[a]	8,1	10	6.1 ± 0.3[a]	60.8	15.2	45.6	102.8	44.9	0.21± 0.02[a]	0.639
C	97.1±0.1[a]	4	10,4	5.6±0.2[ab]	70.9	26.6	44.3	101.3	46	0.19±0.03[a]	0.553
A'	97.8±0.5[a]	8,5	5,1	4.0±0.4[ab]	34.5	4.3	30.2	120.1	81.5	0.13±0.02[bc]	5.516
B'	97,8±0.1[a]	5,5	6,7	4.5±0.5[ab]	41.8	10.5	31.4	118.8	79.4	0.16±0.02[ab]	9.017
C'	97.7±0.5[a]	2,7	7	4.5±1.5[ab]	48.2	18.1	30.1	118.5	75.4	0.18±0.03[ab]	8.385
A''	97.8±0.3[a]	8,6	5,1	4.1±0.2[ab]	38.3	4.8	33.5	113.4	87.7	0.12±0.03[c]	5.553
B''	97.8±0.3[a]	5,4	6,7	3.3±0.1[b]	42.6	10.7	32	113.0	85.7	0.11±0.01[c]	7.128
C''	97.4±1.0[a]	3	7,9	3.6±0.1[b]	48.7	18.3	30.4	112.8	79.7	0.12±0.01[bc]	8.650

A represents dairy bases prepared by 75% of concentrated milk and 25% concentrated whey; B prepared by 50% of concentrated milk and 50% concentrated whey; and C prepared by 25% of concentrated milk and 75% concentrated whey. A', B' and C': addition of maltodextrin. A'', B'' and C'': addition of inulin., TS = total solids ($g\cdot100g^{-1}$), A = ash (g·100g-1) TL = total lactose amount, LC = lactose in crystal form is the crystallized lactose in the concentrated whey, LS = lactose in solution is the amount of non-crystalized lactose in concentrated whey, Cs = casein, WP = whey protein, T_g = Glass transition temperature, a_w = water activity, S_A = average size distribution (% volume) of the dairy mix powders after rehydration(µm), [1]Determied by difference, [2]Determined by mass balance, [3]determined by considering 80% of the milk protein is casein and 90% of the whey proteins are whey proteins. [4] considering a_w = 0, [5] determined considering the moisture of the products. Same letters do not differ significantly by Tukey test ($p < 0.05$).

The final composition of the products in relation to the primary source of the present solid constituents is shown in 7.

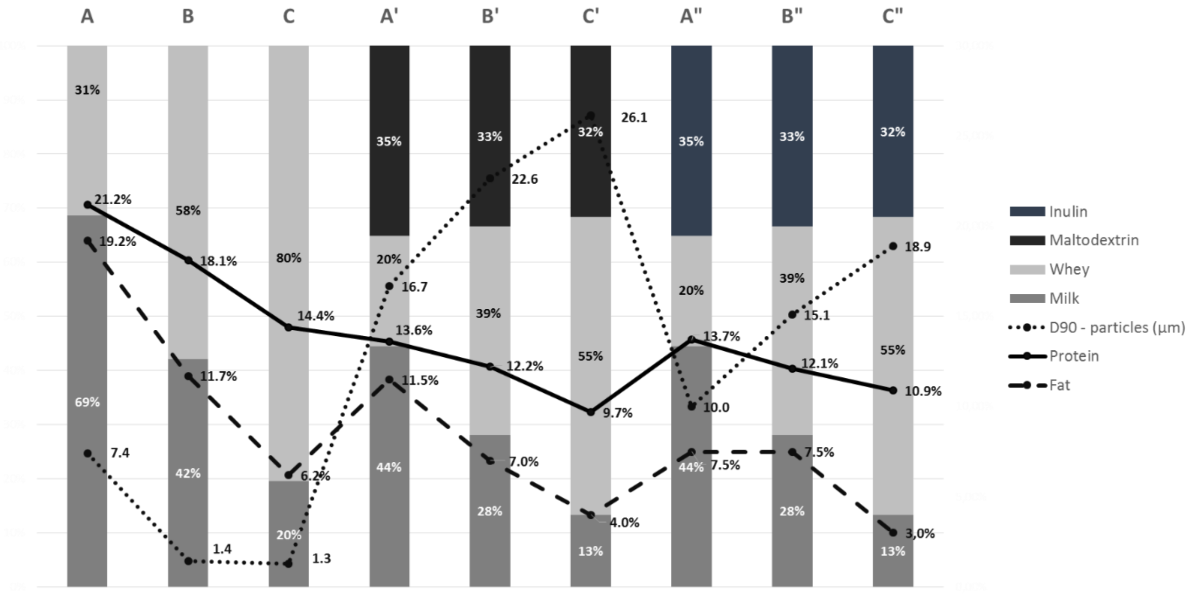

Figure 1 - Final composition according to the source of solids

For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A’, B’ e C’: addition of maltodextrin. A’’, B’’ e C’’: addition of inulin.

D_{90} = represents the hydrodynamic diameter in which 90% of the particles has lesser size

The microstructure evaluation of the products using scanning electron microscopy is shown in Figure 2. Comparing images A, B and C, we observe an increase in agglomeration (A <B <C) with the increase in amount of whey in the mix formulation.

The products with added maltodextrin and inulin (A', A'', B', B’’, C' and C'') had lower incidence of particle agglomeration. According to [11], maltodextrin is a low hygroscopic product by nature, and adding it to food induces a less hygroscopic property.

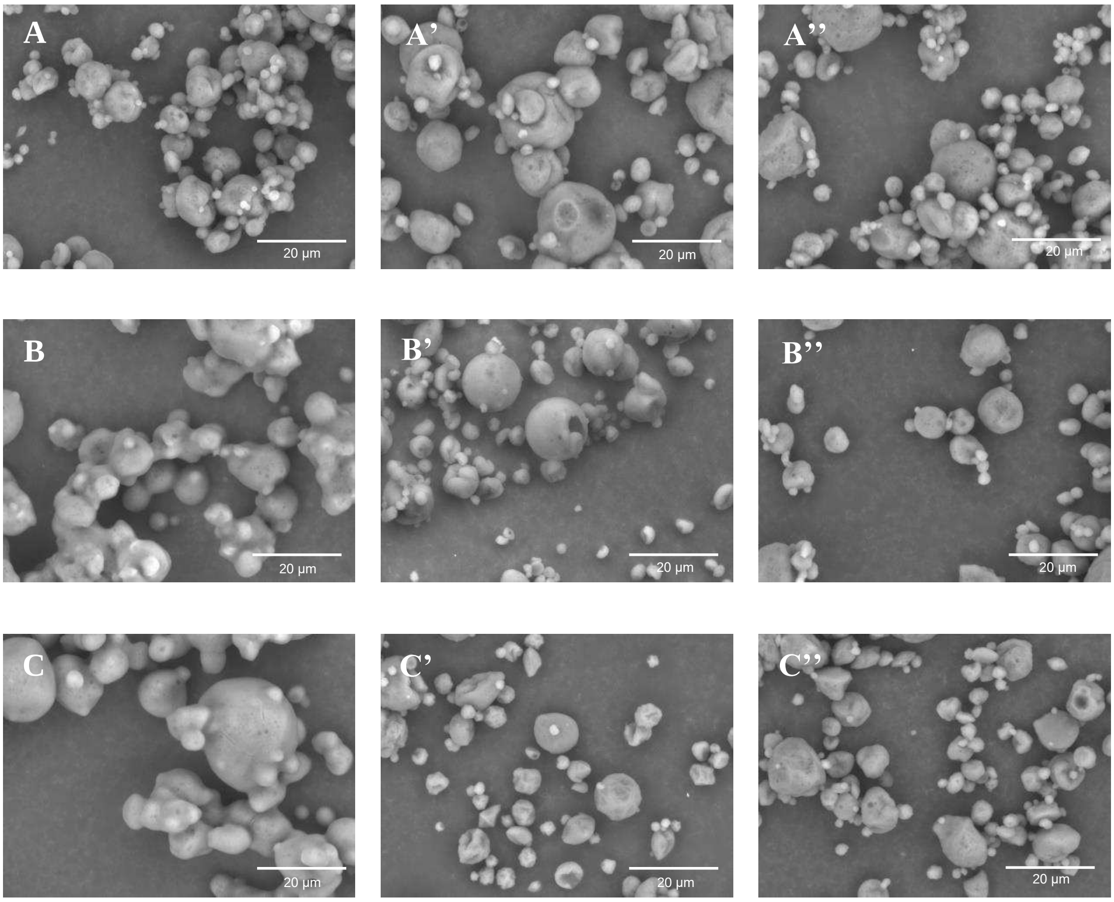

Figure 2 - Images of the dairy mix powders (2.500x) showing the agglomeration of the particles
For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A', B' e C': addition of maltodextrin. A'', B'' e C'': addition of inulin.

During the initial phases of the rehydration, different particle size distributions were obtained as shown in Figure 3, and the data are summarized in Table 3.

Figure 3 shows the distribution of the volume percentage occupied by the particles according to their hydrodynamic diameters. Typically, the distribution of particle size in fluid milk shows two populations: casein micelles (150-200 nm) and fat globules (5 µm). All samples showed a population of particles centered at approximately 200 nm, which could correspond to the casein micelles such as in fluid milk.

The intensity of this population decreased in all maltodextrin- (A', B' and C') and inulin-added treatments (A", B" and C") in comparison with their references (A, B and C). Thus, these ingredients strongly interact with the milk constituents and hinder the dispersion of caseins. In addition, the increase in whey proportion in the formulation directly affects the particle size. The obtained D_{90} values were 7.401, 1.425 and 1.304 micrometers for A, B and C, respectively, as shown in Table 3. In addition to the population centered at 200 nm, the samples exhibited other peaks at 0.5-60 micrometers.

All other samples with inulin (A", B" and C") showed a large population in the region of 6 microns, which features the behavior of this ingredient. Similarly, the three products with maltodextrin (A', B' and C') showed highly populated particle areas with maximum sizes of 17-20 micrometers.

Considering the described rehydration process in two steps by [143], different morphologies of the powder particles in Figure 3 can explain the different observed hydration capacities. These authors described the rehydration process of MPC (Milk Protein Concentrate) powder in two simultaneous steps: the rupture of particle agglomerates into individual particles and the release of particulate matter into the aqueous phase [143].

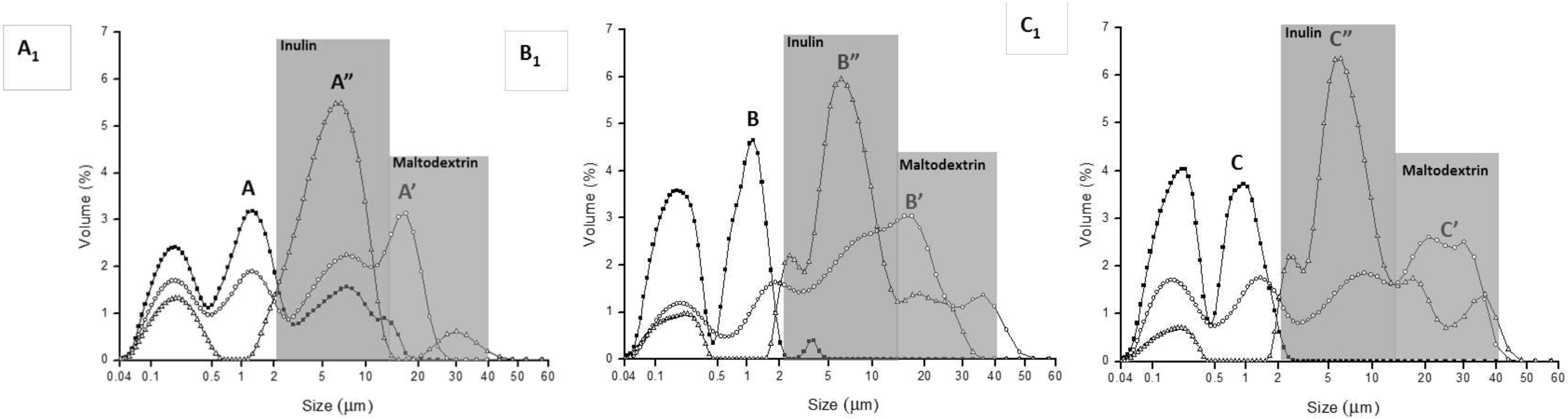

Figure 3 - Size distributions of the particles after rehydration

Figure A1 represents dairy bases prepared by 75% of concentrated milk and 25% concentrated whey; B1 prepared by 50% of concentrated milk and 50% concentrated whey; and C1 prepared by 25% of concentrated milk and 75% concentrated whey. Where (n) = no addition of maltodextrin or inulin, (o) = addition of 20% of maltodextrin, (Δ) = addition of 20% of inulin.

Table 3 - Size distribution (% volume) of the dairy mix powders after rehydration

Treatments[1]	Average (µm)	Standard deviation (µm)	Particle size (µm) D_{90}[2]
A	2.277	3.374	7.401
A’	5.516	6.549	16.68
A”	5.553	5.806	10.00
B	0.639	0.632	1.425
B’	9.017	10.16	22.64
B”	7.128	6.282	15.10
C	0.553	0.500	1.304
C’	8.385	10.59	26.14
C”	8.650	8.389	18.90

[1] For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A’, B’ e C’: addition of maltodextrin. A’’, B’’ e C’’: addition of inulin.

[2] D_{90} represents the hydrodynamic diameter in which 90% of the particles has lesser size.

3.2 Evaluation of color

The color parameters are shown in Table 4. This system enables the specification of color perceptions in terms of a three-dimensional space. The axial component L* is the luminosity and ranges from 0 (black) to 100 (white), a* (blue to yellow) and b* (green to red) [152]. The attributes of a* and b* show specific values in the plan. However, to better understand and analyze the results, the values should be replaced by vectorial forms (C and h) that represent the saturation index and hue angle, respectively [153].

The results of 9 treatments in Table 4 show that the color parameters L*, a*, b* and C showed significant differences ($p < 0.05$) according to the dairy mix formulations, which were not noticed for parameter h ($p > 0.05$). Evaluating parameter L* for products A, B and C (mixes without drying agents, maltodextrin and inulin), we observed that product C (product with a lower milk concentration) had the highest brightness value of 54.4 ± 2.6. Milk is a white translucent liquid [154, 155]. The replacement of milk for whey in dairy mixes reduces the level of these components and may reduce its whiteness and increases its luminosity [156–158].

For a* of A, B and C, the samples became red, whereas mix C showed a value of 10.2 ± 0.9 for this parameter. For b*, the product became strongly yellow, and product C had the highest saturation index of 36.6 ± 1.1. These treatments (A, B and C) showed h values between 73.5° ± 1.1 to 76.0° ± 0.9, which indicates that they were yellow [153]. Although milk is white, it has carotenoids, which are yellowish. This product also contains reducing sugars and amino groupings, which can react with each other and promote non-enzymatic browning (Maillard reaction). Maillard reaction can be accelerated when the temperature increases, such as in the case of evaporation and drying in this work [159].

The products that contained the dairy basis in the proportion of 75% milk concentrate and 25% whey concentrate, i.e., A, A' and A'' (group A), showed no significant difference ($p > 0.05$) in luminosity (brightness). Although inulin and maltodextrin can provide a degree of opacity, their addition could not change the brightness of the mixes [160]. This effect is attributed to the higher proportion of milk in these products because milk has opaline characteristics [155]. It is believed that the added concentration of drying agents is not sufficient to change the brightness of the product in the proportion of 75% milk concentrate and 25% whey concentrate.

The dairy mix powders with 50% milk concentrate and 50% whey concentrate, i.e., B, B' and B'' (group B), showed no significant difference (p> 0.05) in the analyzed attributes. Thus, the addition of maltodextrin and inulin to these products with this proportion of milk and whey does not interfere with the objective color of the products.

Table 4 - Results for the parameters L*, a*, b*, C e h of the dairy mix powders (n=2)

Treatments[2]	L*	a*	b*	C	H
A	47.1 ± 1.6^{bcd}	7.5 ± 0.5^{d}	30.2 ± 0.8^{b}	$31.1 \pm 0{,}8^{b}$	$76{,}0 \pm 0.9^{a}$
A’	50.9 ± 1.1^{abc}	8.5 ± 0.5^{bcd}	31.5 ± 0.3^{ab}	32.6 ± 0.2^{b}	$75{,}0 \pm 0.9^{a}$
A’’	52.2 ± 2.8^{ab}	9.6 ± 0.9^{ab}	31.9 ± 1.3^{ab}	33.4 ± 1.4^{ab}	$73{,}3 \pm 0{,}9^{a}$
B	49.6 ± 3.8^{abc}	9.4 ± 0.3^{abc}	31.7 ± 2.6^{ab}	33.0 ± 2.5^{ab}	$73.5 \pm 1{,}1^{a}$
B’	46.2 ± 3.7^{cd}	8.6 ± 1.2^{abc}	30.7 ± 2.6^{b}	31.8 ± 2.8^{b}	$75{,}1 \pm 1{,}3^{a}$
B’’	49.7 ± 2.4^{abc}	9.2 ± 0.9^{abc}	31.5 ± 1.1^{ab}	32.8 ± 1.0^{ab}	$73{,}8 \pm 1{,}8^{a}$
C	54.4 ± 2.6^{a}	10.2 ± 0.9^{a}	34.5 ± 1.4^{a}	$36{,}0 \pm 1.1^{a}$	$73{,}6 \pm 2.1^{a}$
C’	45.6 ± 2.4^{cd}	8.2 ± 0.4^{bcd}	29.4 ± 0.5^{b}	30.6 ± 0.5^{b}	$74.5 \pm 0{,}9^{a}$
C’’	45.0 ± 1.8^{d}	7.8 ± 0.8^{cd}	29.5 ± 1.1^{b}	30.5 ± 1.0^{b}	75.3 ± 1.3^{a}

[2] For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A’, B’ e C’: addition of maltodextrin. A’’, B’’ e C’’: addition of inulin.
L* = luminosity; a* = hue; b* = saturation; C = saturation index and h = hue angle. Same letters do not differ significantly by Tukey test (p <0.05).

It is imperative to note that the behavior of the saturation index parameter of products with higher whey concentration in dairy-based C, C' and C'' (group C) enables the effect of drying agents in the browning saturation. Product C displayed a value of 36.0 ± 1.1, where C' and C'' had values of 30.6 ± 0.5 and 30.5 ± 1.0, respectively, (p <0.05). Similar results were found by [161], who replaced the fat in the preparation of ice cream by various substances and noted that maltodextrin could maintain the white color of the product [162] used inulin as a replacement for sucrose in chocolate production and observed that the samples with higher inulin concentrations had lower saturation indices (C).

Another important parameter in the color analysis is the total or overall difference (ΔE), which enables us to determine how much the impression of the overall color of a sample differs from a standard and whether this difference is sensory noticeable [163]. The ΔE values for the dairy mix powders obtained from the nine treatments are shown in Table 5. The subjective perception of color with respect to these values was determined by [164].

Comparing the mixes with only milk and whey in the formulation (A, B and C), we found that the following overall differences: ΔE of 4.1 for A and B and 5.7 for B and C. Both differences were classified as clear perception [164, 165]. However, ΔE of 8.5 for products A and C shows a pronounced difference, which is classified as a very clear perception.

The results show that the change in proportion of milk and whey in the mixes changes the product color, and this change becomes more noticeable with the greater difference between the quantities of milk and whey in the dairy base.

For ΔE of Group A (A - A’ and A - A’’), the addition of maltodextrin and inulin changed the color of the products, and both differences were classified as very clear perception. For Group B, B' and B’’ showed overall differences that were classified as very clear and clear perception, respectively. This result indicates the effect of the addition of maltodextrin and inulin on the product color.

Table 5 - Results for ΔE considering A, B e C as standard samples

Treatments*	ΔE**								
	A	A'	A''	B	B'	B''	C	C'	C''
A	-	4.2^{2}	5.5^{2}	4.1^{2}	-	-	8.5^{3}	-	-
B	-	-	-	-	3.1^{2}	2.8^{1}	5.7^{2}	-	-
C	-	-	-	-	-	-	-	10.7^{3}	10.6^{3}

* For all treatments the dairy bases were prepared keeping the same ratio of concentrated milk and concentrated whey respectively 75% and 25% (A), 50% and 50% (B); 25% and 75% (C). A', B' e C': addition of maltodextrin. A'', B'' e C'': addition of inulin.
** ΔE = total or global difference: [1] clear perception (1.5 to 3.0); [2] very clear perception (3.0 to 6.0); [3] extremely clear perception (6.0 to 12.0), according to [164].

In Group C, the differences between mix C and the ones with drying agents C' and C'' were defined as clear.The observed difference in Group C is the largest among all groups seemingly because of the higher concentration of whey in the mix formulations. This feature was also observed in [166]. In another food matrix, when the effect of whey added to ham on color was assessed, it is worth noting that over 25% addition of whey to the matrix made the color change sensory noticeable.

3.3 Theoretical calculations of T_g

To evaluate the effect of different dairy formulations in the glass transition temperature (T_g) in relation to the variation of the milk base composition and the addition of drying agents, T_g was calculated for the products of nine treatments. The data are summarized in Table 6. The theoretical T_g may be different from (generally higher than) those obtained using the Differential Scanning Calorimetry Analysis (DSC) [129].

The theoretical values are not always accurate, and not all elements are considered in the calculation [132]. However, the application of the formula enables the correlation between the calculated and measured results to understand the product behavior in drying and storage. In addition, it helps to evaluate the effect of food composition on the glass transition temperature and provide a comparative and not absolute analysis of temperatures. In the studied formulations, three main factors contribute to the value of T_g: milk/whey ratio, percentage of lactose crystallization in whey and presence of maltodextrin and inulin.

The data in Table 6 shows that the increase in whey content in the mixes from 25% to 75% causes a decrease in T_g from 0.6 to 3.6℃. The crystallization of lactose in whey concentrates of 0-75% causes a variation in the calculated T_g value from 1.0 to 2.3 °C.

The addition of inulin promotes an increase in calculated T_g from 9.6 to 12.6 ° C, whereas maltodextrin increase T_g from 16.3 to 18.3℃. From these results, one can conclude that in the formulation of dairy mixes, the addition of maltodextrin has the largest contribution to the product stability by causing greater relative increase in T_g, and the addition of inulin has the second largest contribution. The development of these formulations should consider the desired balance between T_g increase and particle size of the powders with respect to the addition of maltodextrin and inulin.

Table 6 - Effect of the composition and the crystallization rate on calculated glass transition temperature (Tg)

Atributes	75 milk +25 whey	50 milk +50 whey	25 milk +75 whey	ΔT_g max Effect of whey addition
St LCW 0	103.8	101.8	100.2	3.6
St LCW 25	104.1	102.2	100.6	3.5
St LCW 50	104.4	102.8	101.3	3.1
St LCW 75	104.8	103.6	102.5	2.3
St LCW 90	105.1	104.2	103.8	1.3
Inulin	113.4	113.0	112.8	0.6
Mt	120.1	118.8	118.5	1.6
ΔT_g max Effect of the crystallization rate	1.0	1.8	2.3	
ΔT_g max Effect of inulin addition	9.6	11.2	12.6	
ΔT_g max Effect of maltodextrin addition	16.3	17.0	18.3	

Where: St = dairy mix powder without maltodextrin and inulin, LCW = percentage of lactose crystallization in the concentrated whey before mix to milk, Mt = maltodextrin.

The addition of whey and lactose crystallization shows no significant relative increase in T_g. Thus, these attributes are less important to the design of dairy mix powders than the addition of maltodextrin and inulin. The formulations with the highest calculated glass transition temperatures also had lower particle adhesion as shown in Figure 2 and during the experiments. These results are consistent with the increase in molecular mass of the soluble compounds in the powders [11]. The increase in T_g resulted in the reduced adhesion of particles on the equipment surface and agglomeration of molecules [23, 24]. [167, 168] assessed the effect of the maltodextrin addition in mango fruit pulp preparations and observed an increase in T_g when the maltodextrin concentration increased.

The glass transition values for inulin in anhydrous form and solution were presented by others [151]. However, no work evaluated the effect of the inulin addition on T_g of other products.

3.4 Raman spectra and principal component analysis of dairy mixes

Raman spectroscopy was used to evaluate the formulations in the production of dairy mixes. The Raman spectra of milk powder, whey powder and maltodextrin were separately discussed in previous studies of the group [169, 170].

In the Raman spectra of the mixes without high molecular weight compounds (A, B and C), the vibrational modes of the asymmetrical CH_2 stretching were observed at 2930 cm^{-1}. This band was assigned to the CH bonds of proteins and carbohydrates. In the region of the CH bond stretching, there was a band with weak intensity at 2850 cm^{-1}. This spectral region was assigned to the CH_2 symmetric stretching of lipids.

The Raman spectrum at 1800-400 cm^{-1} showed many bands and was rich in structural information. The low-intensity band at 1750 cm^{-1} was assigned to the C = O stretch vibrational mode of fatty acids in milk [171]. At 1660 cm^{-1}, there was a medium-intensity band related to the C = O stretching of protein molecules, which is denominated as the amide I mode. The amide II vibration mode, which is related to the N-H deformation coupled modes and C-N stretching of protein molecules, appeared at 1550 cm^{-1}. The intense band at 1440 cm^{-1} was attributed to the CH bond deformation modes and is related to lipid molecules, carbohydrates and aliphatic amino acids in milk protein [171, 172].

The region of 1200-800 cm^{-1} was dominated by bands that mainly involved the vibrational modes of the chemical bonds of carbohydrates. The main vibrational modes are C-O stretching, C-C stretching and C-O-H deformation at 1120-1060 cm^{-1} and C-O-C deformation at 950-870 cm^{-1}.

Because there is a large amount of lactose in whey, its Raman spectra bands were characterized by the presence of this compound; the main bands were located at 2978, 2888, 1087 and 850 cm^{-1}. This band increased in intensity when the whey content increased in the mix formulation (B and C).

The addition of maltodextrin (A', B' and C') changed the spectral profile of the milk base (Figure 4). The maltodextrin Raman spectrum showed different bands from other components in the mixes. The literature shows the band at 477 cm^{-1} as a marker to identify maltodextrin in milk samples [173]. Strong couplings between the vibrational modes were found in this region of the vibrational spectrum. Such modes are mainly related to the deformation of the skeleton of the glycoside ring [δ (C-C-C + C-C-O)]. Other regions with observed changes are 1340 cm^{-1} [ν(C-O) + δ(C-O-H)] and 1080 cm^{-1}, which involve the coupled mode ν(C-O) + ν(C-C) + δ(C-O-H).

Inulin is a polysaccharide composed of fructose; the changes in the Raman spectrum because of its addition are similar to the spectra of whey and maltodextrin.

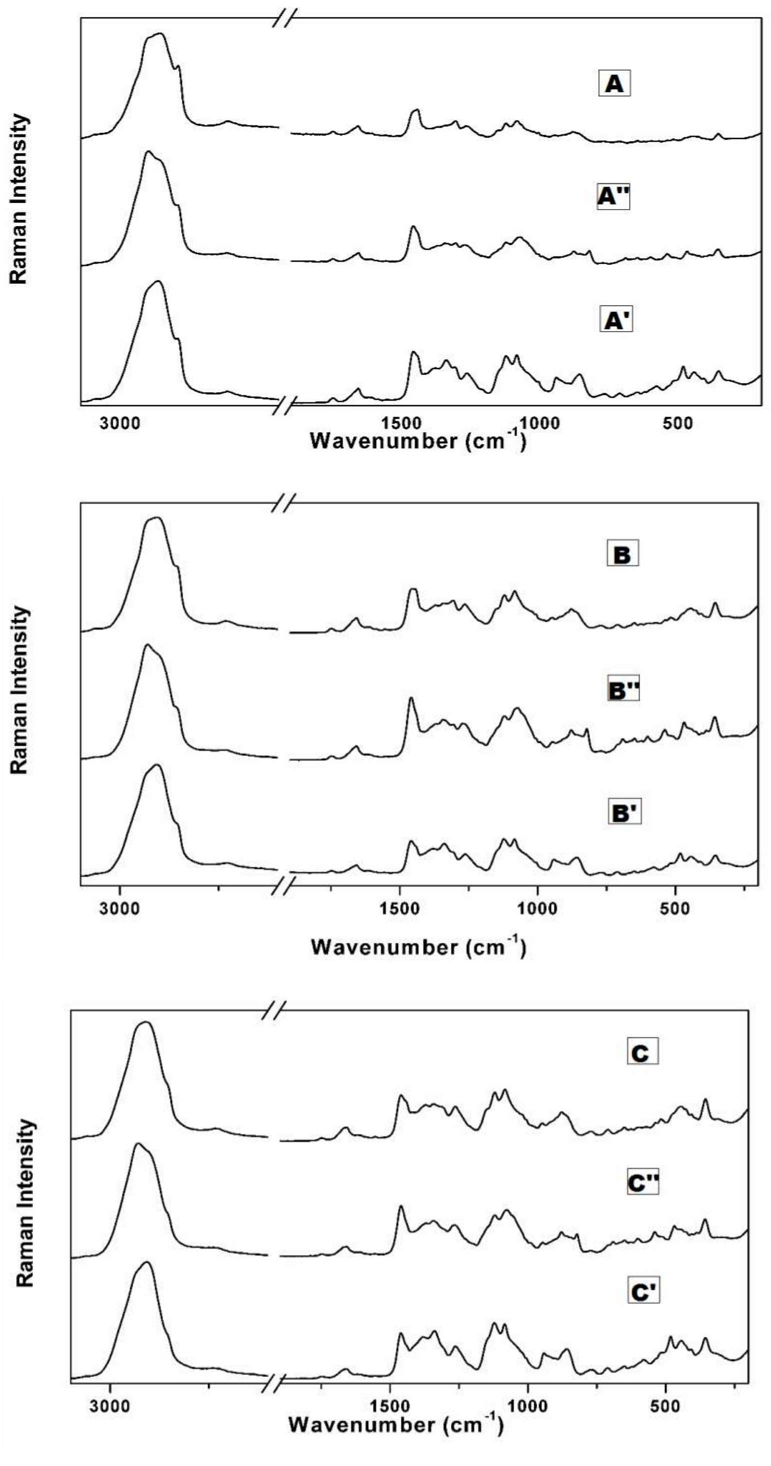

Figure 4 - Results of Raman Spectroscopy

Figure A represents dairy bases prepared by 75% of concentrated milk and 25% concentrated whey; B prepared by 50% of concentrated milk and 50% concentrated whey; and C prepared by 25% of concentrated milk and 75% concentrated whey. A’, B’ and C’: addition of maltodextrin. A’’, B’’ and C’’: addition of inulin.

The presence of inulin in dairy mixes (A'', B'' and C'') after drying can be confirmed by the bands in the Raman spectrum at 1450 cm^{-1} (δCH_2), 1333 cm^{-1} (δCH_2), 1270 cm^{-1} (δCH), 1059 cm^{-1} (νCOC), 867 cm^{-1} (δCOC) and 813 cm^{-1} (νCC). The Raman spectroscopy technique can be used to assess the qualitative composition of mixes. This analytical approach does not require separation methods and other sample preparation steps. Thus, the analysis can be quickly performed, is consistent and does not generate waste.

4.CONCLUSION

The development of dehydrated dairy products from a mixture of milk and whey may have different final compositions, i.e., variations in protein and fat content, and various properties, such as adhesion, color and particle size. The conditions studied in this paper show that the addition of maltodextrin and inulin favorably contribute to the conservation and drying of powders; however, such addition increases the hydrodynamic particle size during rehydration. The increased whey proportion in the mix contributes to a minor brightness and more pronounced yellow color (browning) probably because of the increased incidence of Maillard Reaction.

CHAPTER 4

DEVELOPMENT AND EVALUATION OF THE PHYSICO-CHEMICAL PROPERTIES OF A LACTOSE-FREE, MALTODEXTRIN AND SOLUBLE FIBER ADDED DAIRY PRODUCT

Abstract

In the last study, it was found that the addition of maltodextrin and inulin improved the drying properties of dairy mixes containing whey. In this chapter, it is intend evaluate the effect of addition of high molecular weight compounds on physicochemical and drying properties of dairy mixes. The mathematical model developed in the chapter 2, will be here applied in the drying of free-lactose dairy mixes. For this purpose, lactose-free dairy mixes containg or not maltodextrin or soluble corn fiber, will be dried in spray dryer and evaluated in relation of phisical chemical characteristics.

DEVELOPMENT AND EVALUATION OF THE PHYSICO-CHEMICAL PROPERTIES OF A LACTOSE-FREE, MALTODEXTRIN AND SOLUBLE FIBER ADDED DAIRY PRODUCT

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ABSTRACT

Products made from the mixing of milk and other food substances have been gaining ground in the dairy market due to their nutritional characteristics and the need to meet the specific necessities of some types of consumers and applications in the food industry as in chocolate and ice cream production. The alteration in the composition of the food changes its physico-chemical and drying properties. The addition of whey makes the food more difficult for drying, mainly because of the concentration of lactose in the product, which is responsible for making it more conducive to problems of stickiness and caking, during and after the drying process. These problems are even more evident in lactose-free products, since the hydrolysis of lactose releases sugars of low molecular weight, low glass transition temperature and more hygroscopic, compared to lactose. The objective of this work has been to evaluate the effect of the addition of maltodextrin 20 DE (Dextrose equivalent) and soluble corn fiber on the physico-chemical and drying properties of lactose-free dairy product. The centesimal compositions, the particle agglomeration profiles of the powders, degree of hygroscopy, particle size during the hydration process, objective color, spectroscopic profile and mass and energy balance have been evaluated. The hydrolysis of lactose increased the degree of agglomeration of the particles of the powders, increased the hygroscopicity, reduced the rate of hydration of the proteins, increased the saturation index of the yellow color, promoted a change in the profile of the Raman spectrum in relation to the control product, besides greater mass loss and greater energy expenditure. The addition of high molecular weight compounds reduced the tendency to agglomeration of the particles, altered the profiles of the Raman spectra and in the case of matodextrin, there has been reduction of mass loss and energy expenditure.

Keywords: spray drying; whey; lactose-free; mass and energy losses

1.INTRODUCTION

The world production of milk powder was approximately 8 million tons in 2014, with skim milk powder being the largest dairy product in relation to the previous year [6]. Other dehydrated products that have gained commercial attention are the analogues of skim milk powder, which are products usually made from the mixture of milk and other food substances and can be consumed directly or used as food ingredient applications [57, 58]. The proportion of each component in the food depends on the desired characteristics in the final product, the legislation in force in each country and the specific need of the consumers to whom the food will be destined.

The alteration in the composition of the food changes its physico-chemical properties, which impacts its drying characteristics [174]. The addition of whey to milk, for example, may negatively influence the behavior of the product during drying and storage process, due to the reduction of the casein concentration and the increase in the proportion of lactose, which has a higher hygroscopic capacity and lower glass transition temperature than casein [22, 69, 175].

Another factor that may hinder the drying process is the hydrolysis of lactose, whose final product is sugars of low molecular mass (galactose and glucose). These sugars have a lower glass transition temperature, are highly hygroscopic, and are more amenable to Maillard reaction compared to the lactose molecule [22, 176].

Products rich in amorphous lactose and in sugars derived from their hydrolysis are subject to problems of agglomeration of the powders and adhesion to the wall of the equipment, besides being propitious to caking after the drying process [12, 174, 177].

As an alternative to reduce the problems that occur in the drying process, the addition of high molecular weight compounds has been carried out since this maneuver reduces the hygroscopicity and increases the T_g of the product [25, 168].

Knowing the composition of the food as well as the dynamics of its constituents is of great importance, both from the nutritional and the technological aspects. Among the technologies applied in food analysis, Raman spectroscopy is a very effective tool in the characterization of materials, is a versatile technique, which allows analyzing several components at the same time requiring no preparation step (mandatory in other conventional analyzes), besides being a non-destructive technique, suitable for online processes. Studies with traditional or lactose-free dairy products as well as high molecular weight added products have been reported by different authors [170, 173, 178–180].

The objective of this work has been to evaluate the effect of the addition of maltodextrin 20 DE and soluble corn fiber on the physico-chemical and drying properties of a lactose-free dairy product.

2.MATERIAL AND METHODS

For the experiment, four different dairy products containing 50% milk and 50% whey were produced in duplicate (n = 2) and identified as: T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

For the preparation of the dairy mix were used fluid skim milk, fluid whey obtained from the production of mozzarella cheese, maltodextrin 20 DE (Ingredion) and soluble corn fiber (Tate & Lyle). Milk and whey mixtures were subject to concentration process up to 35% (m / m) of total solid in vacuum evaporator (Treu®), under boiling temperature of 60 °C. To concentrated m ixs T2, T3 and T4 were added the enzyme lactase (Prozyn) and then subject to refrigeration process (5 °C for 12 hours) until > 90%lactose hydrolysis occurred. The degree of hydrolysis of lactose was obtained according to the methodology used by [173].

After the hydrolysis process, the mix was dried in a single-stage spray dryer with disk atomizer (Niro Atomizer®) model Minor Production with a drying capacity of 10 kg of water per hour. The drying parameters used were 163 ± 2 ° C temperature for inlet air and 85 ± 3 °C for outlet air.

2.1 Physico-chemical analyzes

The concentrations of total solids (TS), protein, ash, carbohydrates and lipids of the samples have been determined. The TS concentration was determined by the gravimetric technique in oven at 105℃. The total protein and ash content were determined using Micro-Kjeldahl method and the gravimetric method, respectively, to evaluate the weight loss of the material, which was incinerated in a muffle furnace at 550℃. These analyses have been performed according to [141]. The fat content was determined using Gerber method [142], and the carbohydrate content was determined from the difference between total solids and the protein, lipid and ash content. The water activity (a_w) was measured using Aqualab (Decagon 3TE, Decagon Devices Inc., USA).

2.2 Evaluation of the microstructure

The morphology and agglomeration characteristics of the powders were evaluated without prior preparation using the Scanning Electron Microscope 1000x (Hitachi TM 3000, Hitachi Ltd., Tokyo, Japan). The size distribution of the particles during rehydration was obtained using the laser diffraction analyzer Beckman Coulter LS 13 320 (Beckman Coulter, Miami, FL, USA), which was coupled to the liquid analysis module (Aqueous Liquid Module, Beckman Coulter, Miami, FL, USA). Sufficient amounts of samples to generate turbidity readings were added to the liquid analysis module tank which contained water at 25℃. The samples were slowly added to prevent the formation of agglomerates. The rehydration process in the equipment was supervised for 15 min (data collection interval of 3 minutes) to ensure complete rehydration which was determined by the stabilization of the particle size distribution. Data were collected in the region of 0.04-2000 μm in 90 seconds. The refractive indices of 1.332 and 1.57 were used for the dispersing medium (water) and particles (casein micelles), respectively, according to [143] and are represented by % of volume occupied by the particles depending on their size.

2.3 Hygroscopicity analysis

The moisture gain and the hygroscopicity of the powders were determined by weighing the samples and analyzing their water activities according to the method used by [181], and some modifications were made. Approximately 3.0g of samples were weighed in Petri dishes, which were placed in a desiccator at 25 °C containing saturated $CaCO_3$ solution (44.1% RH). The mass and a_w of the samples were evaluated for 132 hours, this process being repeated every 12 hours.

2.4 Color Analysis

The products were evaluated for their colorations, using ColorQuest XE HunterLab colorimeter, system L* a* b*, being, respectively, luminosity, hue and saturation. From the obtained results with the colorimeter, the values of C and h, representing, respectively, saturation index and pitch angle were calculated.

2.5 Raman spectra

The Raman spectra have been obtained using an RFS 100 FT-Raman spectrometer (Bruker), which was equipped with germanium detector, liquid nitrogen for cooling, an excitation line at 1064 nm, and Nd: YAG laser at 500 mW maximum. The conditions were electronically adjustable for each type of sample to be studied. In this work, the output power was set at 60 mW. This power level was selected to obtain the strongest Raman signal without overheating nor degrading the samples. The measurements were obtained at 4 cm^{-1} resolution in the spectral range of 3500-50 cm^{-1} with 512 accumulations every 15 minutes. The Opus 6.0 software (Bruker Optik Ettlingen, Germany) was used.

2.6 Mass and energy balance

The mass balance was calculated by the difference between the total mass inserted in the system minus the mass obtained at the output of the system, while the energy balance was calculated by the difference between the total input energy minus the output energy.

The calculated parameters were mass loss, energy loss and specific energy consumption (ESC_{po}), which is the amount of energy required to obtain 1kg of powder according to the mathematical model developed by [182].

The mass loss was calculated by the difference between the mass of solids recovered after drying and the mass of solids injected for a certain time:

$$\Delta_{mass} = \left(\frac{M_p \text{ x } TS_p}{t}\right) - F_{m,inj} \text{ x } \mathrm{TS}_m \qquad \text{eq.1}$$

Where Δ_{mass} is the mass loss (kg); M_p is the mass of powder obtained in the process (Kg); TS_p is the total solids of the powder ($kg_{solid} \cdot kg_{powder\ milk}^{-1}$); T is the time (h); $F_{m,inj}$ is the mass of concentrate product injected into the equipment (kg) and TS_m is the total solids of the concentrate product ($kg_{solid} \cdot kg_{concentrated\ milk}^{-1}$).

The energy loss was obtained by the difference between the total input energy and the total output energy:

$$\varepsilon_{loss} = \left(1 - \frac{\varepsilon_{t,out}}{\varepsilon_{t,in}}\right) \text{x } 100 \qquad \text{eq.2}$$

Where ε_{loss} is the energy loss; $\varepsilon_{t,out}$ is the total energy exiting the system and $\varepsilon_{t,in}$ is the total energy injected into the system.

The ESC_{po} was obtained by the ratio between the amount of total energy that entered the system and the mass of powder obtained after the drying process:

$$ESC_{po} = \left(\frac{\varepsilon_{t,in}}{M_p}\right) \qquad \text{eq.3}$$

where, ESC_{po} is the energy consumption spent to obtain one kilogram of powder recovered from the system; $\varepsilon_{t,in}$ is the total energy that enters the system; M_p is the total mass of powder recovered in the process.

2.7 Statistical Analyses

The Complete Randomized Design (CRD) was used with 4 treatments and 2 replications. The Analysis of Variance and Tukey's test were conducted for multiple comparisons of the means at 5% significance level. The Linear Correlation Analysis was applied except for the calculated values. The SAS software (SAS Institute Inc., 2008) version 9.1 was used.

3.RESULTS AND DISCUSSION

3.1 Centesimal composition of dairy mixes

According to the results, there was no significant difference ($p > 0.05$) between ESTs nor between a_w concerning all treatments. In relation to protein, fat and ash, when the products T1 and T2, products containing only the milk base (milk and whey), were compared, they did not present any difference between themselves. This same relationship occurred between the mix containing in addition to the dairy base, maltodextrin and soluble corn fiber (T3 and T4).

Addition of the high molecular weight compounds reduced the proportion of proteins, fat and ashes in the dairy mixes and increased the carbohydrate concentration (Table 1).

Table 1 - Physical chemical analysis data of the products

Treatments	Total solids ($g \cdot 100g^{-1}$)	Protein ($g \cdot 100g^{-1}$)	Fat ($g \cdot 100g^{-1}$)	Carbohydrates ($g \cdot 100g^{-1}$)	Ashes ($g \cdot 100g^{-1}$)	A_w
T1	96.90 ± 0.45^a	24.68 ± 0.26^a	3.15 ± 0.19^a	60.82 ± 0.20^b	8.25 ± 0.06^a	0.17 ± 0.03^a
T2	96.93 ± 0.30^a	24.49 ± 0.57^a	3.38 ± 0.14^a	60.90 ± 0.48^b	8.16 ± 0.05^a	0.16 ± 0.02^a
T3	96.20 ± 0.45^a	19.14 ± 0.21^b	2.13 ± 0.14^b	68.52 ± 0.38^a	6.42 ± 0.05^b	0.16 ± 0.03^a
T4	97.00 ± 0.67^a	19.31 ± 0.39^b	2.21 ± 0.19^b	69.29 ± 0.43^a	6.39 ± 0.05^b	0.14 ± 0.03^a

A_w = Water activity. T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

3.2 Scanning Electron Microscopy

Figure 1 shows less agglomeration of the particles of the powder in T1, compared to other treatments. This was probably due to the lactose hydrolysis process applied to T2, T3 and T4 treatments. Lactose hydrolysis increases the concentration of monosaccharide sugars (galactose and glucose) in the product, which have a lower glass transition temperature (T_g) than lactose [132].

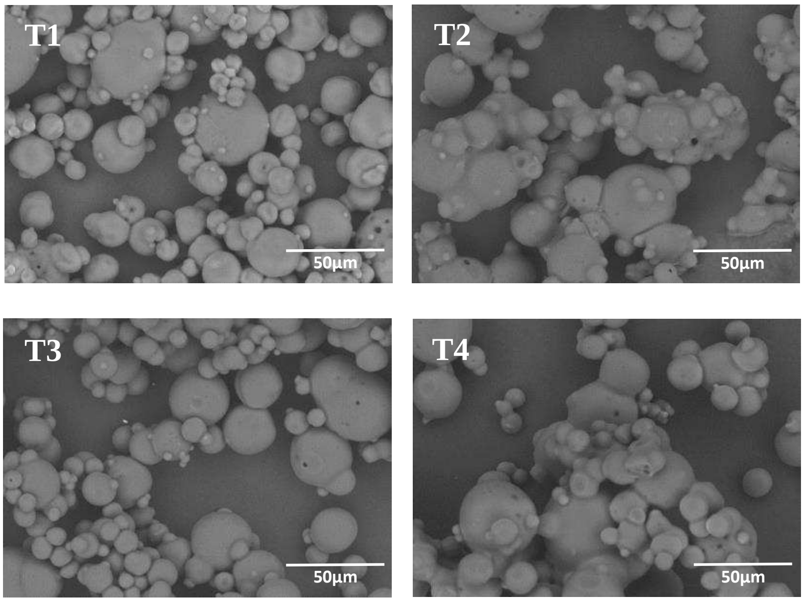

Figure 1 - Scanning electron microscopy images of milk powder mixes, on 1,000x magnification, showing the trends of the particles of the powder for agglomeration

T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

Addition of the high molecular weight compounds reduced the degree of agglomeration of the powder particles, with maltodextrin having a better effect in this regard. Maltodextrin is not hygroscopic, compared to low molecular weight sugars and its presence in the food matrix tends to reduce the degree of particle agglomeration [11]. Characteristic that can be presented by the soluble fiber, depending on its form of obtaining [123].

3.3 Hygroscopicity

Lactose-free products absorbed more water than the traditional one and the addition of maltodextrin and soluble corn fiber was not able to reduce the mass gain. In addition, the soluble fiber-containing compound was the one that most absorbed water. This same behavior has been observed in the variation of a_w for all the treatments.The degree of hydrolysis of the starch influences the properties of the product, the higher the hydrolysis, the greater its hygroscopicity and the more conducive to problems in drying and storage, which may be the case of this product [89, 183].

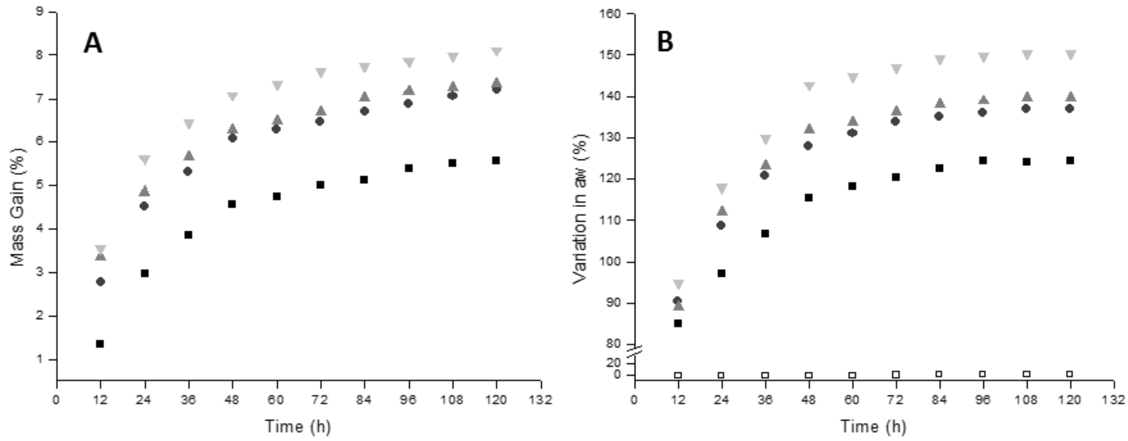

Figure 2 - *Hygroscopicity data of the products: graph of the mass gain of the powders at different times*
(A); Graph of the variation of a_w at different times (B). T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added (■);T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added (●); T3, product submitted to the hydrolysis process and maltodextrin added (▲); T4, product submitted to the hydrolysis process and soluble maize fiber added (▼).

3.4 Adhesion of the powders in the drying chamber

According to figure 3, the treatments submitted to lactose hydrolysis process (T2, T3 and T4) showed a higher degree of adhesion of the powders to the equipment wall during the drying process. This is because galactose and glucose monomers, formed from the hydrolysis of lactose, are compounds of low molecular weight, therefore they act to reduce the glass transition temperature of the product [22]. Low molecular weight sugar-rich products are more amenable to adhesion problems and product stability during storage [75].

The treatments T2, T3 and T4 absorbed more water (figure 2). The water has significant plasticizing power over the amorphous lactose and the products derived from its hydrolysis, having a negative effect on the T_g of the product. The increase in the water content of the food implies in the reduction of glass transition temperature [184, 185].

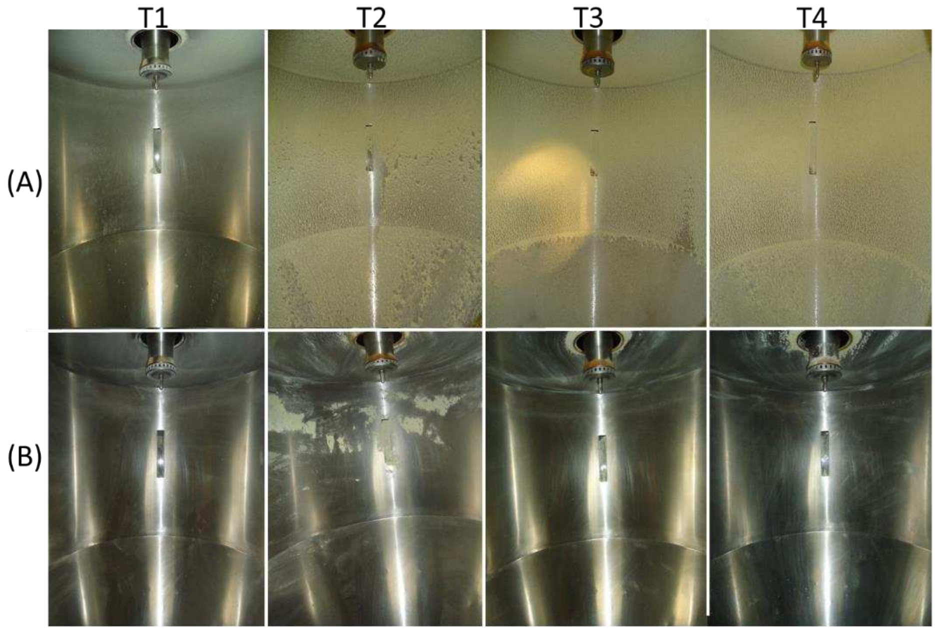

Figure 3 - Drying chamber images before and after the dust collection process: image of the chamber immediately after drying
(A); Image after removal of dust (B). T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

The addition of maltodextrin and soluble corn fiber present in mixes T3 and T4 reduced the degree of adhesion of the powders to the wall of the equipment in relation to T2. This fact can be noticed in the images of the chamber after the process of removal of the powders and of the difficulty of withdrawal of the product that has been observed experimentally.The addition of high molecular weight compounds increases the final T_g of the products and may imply in improvement in the drying process and storage conditions [89, 132].

Product T2 showed greater adhesion of the powder to the wall of the chamber, presented caking during the drying process. This problem may have occurred because the temperature of the powder during the dehydration process was greater than the T_g of the product, which is low when compared to the other treatments [22].

The hydrolyzed product tends to absorb more water than the traditional one and this absorption can result in collapse and agglomeration of the powder and formation of hard mass. Physical changes (viscosity and collapse) have been described as time-temperature and humidity-dependent phenomena [75, 76, 186].

3.5 Particle size after rehydration

After the rehydration process of the dairy mixes in water, different particle size distributions have been obtained as shown in figure 4 and data summarized in table 2.

Figure 4 shows the distribution of the percentage of the volume occupied by the particles according to their hydrodynamic diameters. Particle size distribution of two major populations is characteristic for fluid whole milk: one corresponding to the casein micelles (50 to 400 nm) and one corresponding to the fat globules (1 to 10 μm).

The dairy mix powder T1, after rehydration, showed a population of particles centered at approximately 141 nm, which corresponds to the casein micelles as in the fluid milk. A second region above 800 nm was also observed with a population of particles of 11.1% of the volume for T1, being attributed to the possible protein aggregates still in solubilization process, associated with the residual lipid fraction of the products, having their particles centered at approximately 2 μm.

In Figure 4, it is possible to observe that, unlike T1, the T2 dairy mix presented, besides the two regions found in T1 (<500 nm and> 800 nm), a population of particles in the intermediate region (between 500 nm and 800 nm), corresponding to 3.1% of the volume. Considering that there is no significant difference in composition between T1 and T2 (Table 1), and due to the observation of a larger agglomeration of particles in T2 powder by scanning electron microscopy in figure 1, it can be inferred that the obtaining of this population of particles identified in the region between 500 nm and 800 nm (after hydration) is directly related to the lactose hydrolysis process, which provides greater agglomeration of T2 particles, and, in this situation, decreases in the rehydration capacity of the powder. [187] correlated the decrease in the solubility of whole milk powder during its aging with the evolution of the Maillard reaction and the cross-linking of caseins. Later, this same team demonstrated the action of the products of Maillard reaction as promoters of cross-linking between caseins [187]. In this context, the fact that the product is subject to the hydrolysis process of lactose may provide an increase in the non-enzymatic browning reaction (Maillard reaction) of the powders, which could therefore contribute to the reduction of its rehydration capacity as shown in Table 2 of the particle distribution.

Considering the two-step rehydration process as described by [143], the different morphologies of the dust particles could explain the different rehydration capacities observed. These authors described the process of rehydration of powdered MPC (milk protein concentrate) as occurring in two simultaneous steps: breaking particle agglomerates into individual particles and releasing the particle material into the aqueous phase [143]. Correspondingly, populations of particles in the intermediate region have also been identified for T3 and T4, these being in addition to the hydrolysis of lactose, the addition of maltodextrin and soluble fiber, respectively. In Table 3, it is possible to observe the distribution of the particles of the four rehydrated dairy mixes in the three regions of interest.

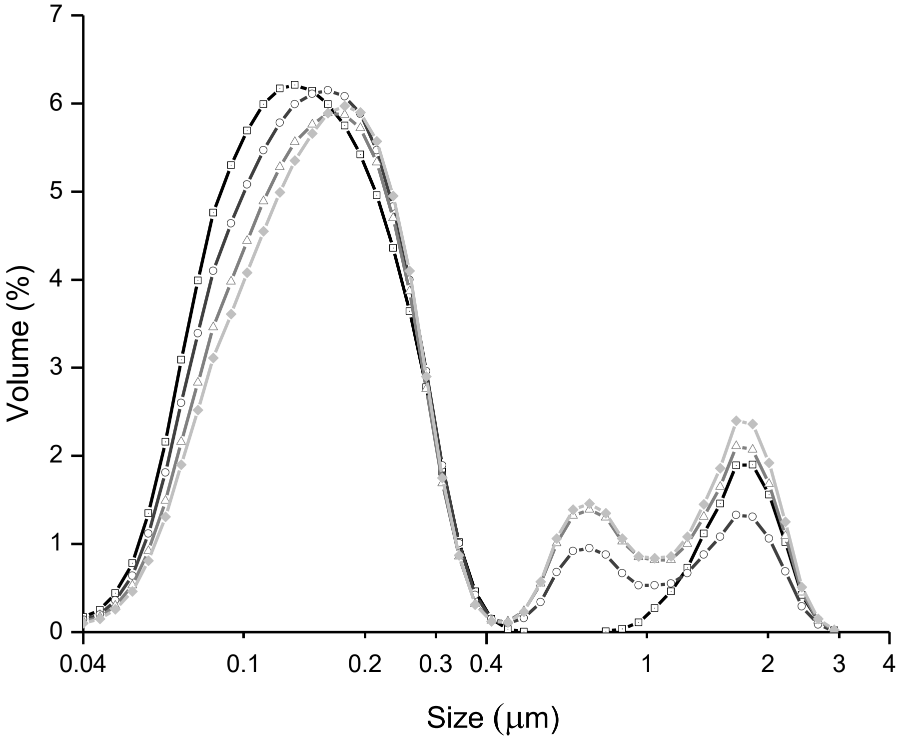

Figure 4 - Distribution of particle size of powdered dairy mixes after rehydration in water

T1 (□), control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2 (○),product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3 (Δ), product submitted to the hydrolysis process and maltodextrin added; T4 (♦), product submitted to the hydrolysis process and soluble corn fiber added.

A decrease in the population observed in the region <0.5 μm is accompanied by an increase in populations in the two other regions, leading to the conclusion that the addition of maltodextrin and soluble corn fiber leads to a decrease in hydrolyzate powders rehydration capacity, in detriment to the improvement of the drying capacity.

Table 2 - Statistical data of particle size analyzes (% volume) of dairy mixes after water hydration

Treatments	Volume of particles per region of size		
	< 0.5 μm (%)	0.5 – 0.8 μm (%)	> 0.8 μm (%)
T1	88.9	0	11.1
T2	86.4	3.1	10.5
T3	79.2	4.6	16.2
T4	77.3	4.9	17.8

T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

3.6 Objective color

The products in general presented a high luminosity compared to that of the powdered milk. This is due to the addition of whey to the mix and, consequently, to the reduction of milk constituents which are responsible for its white coloration and low luminosity [156–158].

According to the results, the hydrolysis process was not sufficient to alter the luminosity of the blends. The soluble fiber, according to the manufacturer, should have a neutral coloration in the formulations [188]. However, its addition significantly reduced ($p < 0.05$) this parameter. Therefore, the brightness of the product should not be evaluated on an isolated basis.

In relation to the parameter a*, T3 presented the lowest value, tending slightly to the blue coloration. For the value of b*, all treatments showed a significant difference between themselves ($p > 0.05$). The hydrolysis process increased the tendency of the product to yellow, with this tendency being greater in those added with drying improvers, where T4> T3.

The results for the hue angle (h) and the saturation index (C) showed that all products are yellow, and T2, T3 and T4 show a more pronounced staining than the traditional mix (T1). Glucose and galactose, the main products of lactose hydrolysis, are reactive and at elevated temperatures can react with the protein present in the mix, causing non-enzymatic browning [22].

The addition of maltodextrin and soluble fiber increased the degree of color saturation even further, and this effect was greater for fiber addition. The hydrolysis of the starch releases sugars, which are low in molecular weight and more susceptible to non-enzymatic browning, the greater the latter, the higher the degree of hydrolysis [90].

Table 3 - Values of the parameters L*, a*, b*, C and h of the dairy powder mixes (n = 2)

Tratamentos	L*	a*	b*	C	H
T1	93.26 ± 1.34 [a]	-2.70 ± 0.02[a]	10.77 ± 0.29[d]	11.10 ± 0.29[d]	-75.91 ± 0.28[a]
T2	92.65 ± 0.89 [a]	-2.81 ± 0.03[b]	12.34 ± 1.15[c]	12.66 ± 1.13[c]	-77.09 ± 1.04[b]
T3	91.75 ± 1.50 [a]	-3.04 ± 0.02[c]	13.77 ± 0.16[b]	14.10 ± 0.16[b]	-77.54 ± 0.06[b]
T4	89.92 ± 0.39[b]	-2.70 ± 0.04[a]	15.58 ± 0.47[a]	15.81 ± 0.47[a]	-80.16 ± 0.15[c]

Where: L* = Luminosity; a* = Tonality; b * = Saturation; C = Saturation index and h = hue angle. T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

3.7 Raman spectroscopic characterization

Raman spectroscopy has been used in this work to evaluate the effect of hydrolysis of lactose and the addition of the high molecular weight compounds in the produced dairy mixes.

Raman spectra of milk powder, whey powder and maltodextrin have already been discussed separately in previous studies of the group [169, 173], however, the study of dairy products with lactose hydrolyzate which were obtained by liquid mixture of milk and whey for later concentration and drying, if necessary, aimed to evaluate the behavior of the spectroscopic properties of the products.

Figure 5 shows the Raman spectra of the four products after production. The Raman spectrum region of 1500 to 300 cm $^{-1}$ presented a large number of bands and is rich in structural information. The intense band at 1460 cm^{-1} is attributed to the modes of deformation of the CH bond with contribution of the carbohydrate molecules and the aliphatic amino acids present in milk proteins [171, 172].

The region of 1200 to 800 cm^{-1} is dominated by bands which mainly involve the vibrational modes of chemical bonds of carbohydrates. The main vibrational modes are the stretches C-O, C-C and C-O-H deformation in the region between 1120 and 1060 cm^{-1}; C-O-C deformation between 950 and 870 cm $^{-1}$.

The main alterations in the spectra can be observed as a result of the hydrolysis of lactose and are located in the region of 1350 cm^{-1}, from 1200 to 800 cm^{-1} and in the low 480-410 cm^{-1} wave number. As lactose band intensities decrease accordingly with hydrolysis, the bands at 525 and 424 cm^{-1} refer to increased spectral contribution of glucose and galactose [189]. An important observation is that carbohydrates are present in amorphous form in dairy mixes immediately after production.

The addition of maltodextrin (T3) caused changes in the spectral profile of the milk base. The Raman spectrum of maltodextrin presented bands that distinguish it from other components present in the mix. The literature shows the band in 477 cm^{-1} as a marker in the identification of maltodextrin in milk samples [173]. Strong couplings between the vibrational modes were found in this region of the vibrational spectrum, such modes are mainly related to the deformation of the skeleton of the glycosidic ring [δ(C-C-C + C-C-O)]. Other regions where changes have been observed are in the region of 1340 cm^{-1} [ν(C-O) + δ(C-O-H)], and of 1080 cm^{-1}, which involves the coupled mode of ν(C-O) + ν (C-C) + δ(C-O-H).

The Raman spectroscopy technique can be used to evaluate the qualitative effect of lactose hydrolysis on dairy mixes as well as the addition of maltodextrin. The presence of the soluble fiber in the dairy mixes (T4) after drying moderately modified the spectroscopic properties of the product, mainly in bands in the Raman spectrum in the region of 950 and 850 cm^{-1} (δC-O-C + δC-C-H + νC-O).

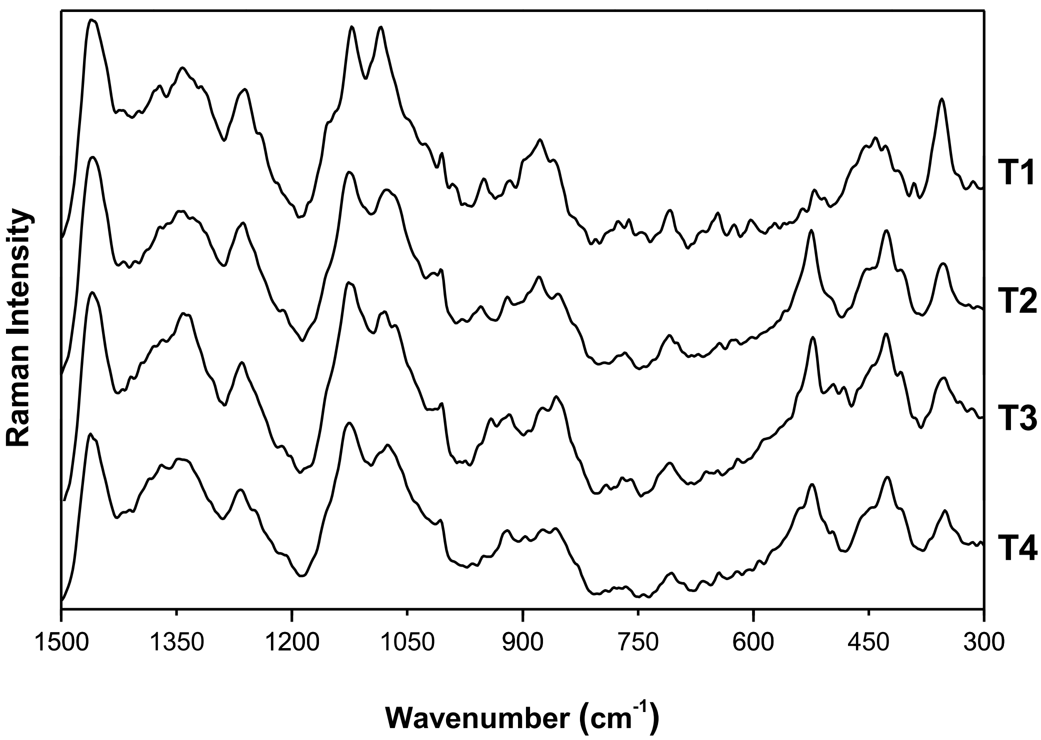

Figure 5 - Raman spectra obtained from milk mixes

T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

3.8 Mass and energy balance

The mass loss was different ($p < 0.05$) among all treatments, with the traditional product presenting the lowest loss. The treatments subject to hydrolysis of lactose had the glass transition temperature reduced which favored the increase of stickiness on the walls of the equipment and consequently led to loss of yield [24, 190]. [22], dried lactose-free milk and obtained only 50% of the final yield.

Table 4 - Mass and energy balance of dairy products

Treatments	Mass loss (%)	Energy loss (%)	ESC_{po}^{*} ($kJ \cdot kg^{-1}$)	Efficiency (-)
T1	6.80 ± 076^{a}	17.21 ± 0.79^{a}	21123 ± 876^{ab}	4.67 ± 0.55^{a}
T2	20.76 ± 0.54^{c}	16.90 ± 1.5^{a}	23854 ± 145^{c}	4.49 ± 0.29^{a}
T3	14.12 ± 3.18^{b}	21.07 ± 0.27^{b}	19926 ± 474^{a}	4.99 ± 0.39^{a}
T4	24.33 ± 0.24^{d}	19.03 ± 1.75^{ab}	21301 ± 151^{b}	4.65 ± 0.08^{a}

ESC_{po} = Energy specific consumption to produce 1 kilogram of powder. T1, control product without lactose hydrolysis and without maltodextrin nor soluble corn fiber added; T2, product submitted to the process of hydrolysis of lactose and without maltodextrin nor soluble corn fiber added; T3, product submitted to the hydrolysis process and maltodextrin added; T4, product submitted to the hydrolysis process and soluble corn fiber added.

The high weight compounds presented opposite results among themselves. Maltodextrin proved to be efficient in reducing the mass loss. However, the soluble corn fiber- containing product was the one that presented the highest loss. Maltodextrin reduced the adhesion of the powder to the walls of the equipment and consequently increased the yield of the product [98, 191]. [72] also observed an increase in the production yield of blackberry juice promoted by maltodextrin addition.

In relation to energy data, the hydrolysis process had no influence on energy loss, since there was no significant difference (p> 0.05) for this parameter, between the traditional (T1) and the lactose-free (T2). The presence of maltodextrin increased the energy loss compared to products containing only milk and whey. However, when the specific energy consumption for each kilogram of powder produced was evaluated, this treatment was the one that spent the least energy among lactose-free products. In addition, their expenditure was equal (p> 0.05) to that of T1 (traditional product). Results that can be explained by the mass yields obtained for the four products.

4.CONCLUSION

Because it is a whey added product, the hydrolysis process implied a greater reduction in the quality of the physicochemical characteristics and drying, since it favored the darkening of the product, made it more hygroscopic, with greater tendency to adhesion of the particles and also increased the mass and energy losses in the drying process. The matodextrin was the high molecular weight compound that presented better performance in improving the drying process. It was able to reduce the hygroscopicity and adhesion of the powder in the drying chamber and also implied in the increase the yield of the product and reduces the energy expenditure required for its manufacture.

CHAPTER 5

GENERAL CONCLUSION AND PERSPECTIVES

1.GENERAL CONCLUSION

The knowledge of the efficiency of the spray dryer in the food drying is of paramount importance, since this is a technique that demands high amount of energy. The efficiency may be obtained by means of mass and energy balance, using the mathematical model developed in the present work. The model allows to evaluate the efficiency of equipment with different designs and the processing of different products, such as the dairy mixes elaborated from the milk and whey mixture.

The addition of whey to milk changes the final composition of the product and influences various properties, such as adhesion, color and particle size. The addition of maltodextrin and inulin favorably contributed to the conservation and drying of powders. However, such addition increases the hydrodynamic particle size during rehydration.

The lactose hydrolysis is another factor that hinders the drying process, and this difficulty is most evident in dairy mixes, since they are products rich in lactose. Among the high molecular weight compounds added, maltodextrin has been shown to be more efficient as it improves the the physicochemical and drying properties.

2.PERSPECTIVES

This work allowed to create a mathematical model that presented an efficient tool in the thermodynamic characterization of equipment with different designs and in the elaboration of different products. The professionals in the drying sector acquired skills in milk drying and, empirically, whey drying processes, without a scientific knowledge of the process. Due to the variety and complexity of products to be elaborated, such as dehydrated dairy mixes, more rigorous methods based on their thermodynamic and physico-chemical properties are necessary. Therefore, it is interesting to apply the mathematical model in industrial equipment, in the most diverse types of products, since the evaluation of the efficiency of the equipment will allow industries to understand their processes and consequently to know effectively the mass and energy yields of their equipment.

The efficiency of the drying process, the maintenance of the nutritional and sensorial properties of the product, depends on several factors, such as the characteristics of the food matrix and drying parameters (flow rate of the concentrate product, inlet and outlet air properties). These parameters should be specific to each type of food, and the more difficult it is to dry the product, the greater the need to respect the parameter values, since variations in them may imply problems in the characteristics of the food or in the low Mass and energy yield. In this way, it is interesting to perform a work by varying the drying conditions and applying the mass and energy balance, in order to understand the influence of this variation on the physical-chemical and drying properties of the product, as well as the thermodynamic properties of the process. The results of the mass and energy balance will allow to know the best drying parameters for the elaborated product.

This work also verified that the addition of maltodextrin has been shown to be advantageous in the preparation of powdered milk products, since it was capable of modifying its physicochemical and drying properties. It reduced the degree of adhesion and agglomeration of the powder, reduced the effect of the Maillard reaction on the color of the product and increased the glass transition temperature. However, the concentration of this compound in dairy mixes and the effect of this concentration on the process and product are not presented in the literature, which makes interesting to develop a work that shows the effect of the variation in the proportion of maltodextrin on the properties of elaborated dairy mixes from milk and whey, and that allows to discover what the ideal concentration for the product developed.

Maltodextrin is obtained by partial hydrolysis of the starch, and its degree of hydrolysis is expressed as equivalent dextrose (DE). The degree of DE is largely responsible for the physico-chemical properties of maltodextrin, hence the final characteristics of the added products of that compound. Although increasing the Tg of the product, reducing the degree of agglomeration and increasing the energetic and mass yields, maltodextrin implies in increasing the hydrodynamic size of the particle and may present difficult solubilization, which may be a problem in some types of product. It is therefore necessary to carry out a work by applying maltodextrins with different degree of DE in dairy mixes made from milk and whey. This study aims to show the effect of degree of DE on these products and to define the best maltodextrin in each situation.

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