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ABSTRACT

The objective of this work was to improve the drying of tomato juices after identifying the main parameters that are responsible for sticking during drying. Glass transition temperature (T_g) which is one of the key parameter, depends on the juice composition, mainly sugar. In order to reduce sugar, centrifugation was applied to the juices. T_g was determined by differential scanning calorimetry (DSC) for freeze-dried tomato juice and tomato pellet conditioned at various water activity (a_w) (0.1–0.5). The glass transition curve showed that T_g decreased with increasing of the moisture. Comparison of powders obtained by juice and pellet from centrifugation shows that the T_g of freeze-dried pellets is higher than that of juice at equal a_w values. Adsorption isotherms of freeze-dried tomato juice and pellet were determined at 25 °C and a relative humidity (RH) of 0–98% using a dynamic technique. The data obtained were fitted to GAB model that best fitted the experimental data. The equilibrium moisture content (X) value of the freeze-dried pellets are lower and had the same value of 8% dry mass. X is lower because the pellet powders are less hygroscopic than tomato juice powders because of the reduction of soluble compounds by centrifugation, notably sugars. Reducing the product sugar content by centrifugation enables to raise T_g without using carriers and obtain less hygroscopic powders, which is advantageous for product storage.

1. Introduction

Tomato is a widely cultivated fruit worldwide, with over 186 million tons produced per year (FAOSTAT, 2022). The biochemical composition of fresh tomatoes varies according to a number of factors, including cultivation practices, variety, irrigation, ripeness, soil and season. Tomato dry mass accounts for around 5–10% of the fruit total mass. Dry mass is composed of around 50% sugars (glucoses and fructose), 20% organic acids (citric and malic acids), 15% fibers, 8% minerals, 2% amino acids, carotenoids and other secondary metabolites (Davies et al., 1981). Tomatoes and tomato-based products are known to be rich in phytomicronutriments. Their consumption is associated with a reduced risk of cancer (Liu et al., 2010) and cardiovascular disease (Cheng et al., 2019). Increasing interest in the antioxidant activity of lycopene (the most common carotenoid in tomatoes) and other functional components has promoted the consumption of tomatoes and tomato products. Despite its high consumption, it is subject to numerous post-harvest losses each year due to its short shelf life and to the cost of storage. Thus, tomatoes can be processed into 2 main groups of products. One group contains whole or tomatoes in pieces, while the other is made up of crushed tomatoes in varying degrees of concentration. The first group includes: whole peeled tomatoes, non-whole peeled tomatoes and non-whole non-peeled tomatoes. The second group is made up of products distinguished by their level of concentration, expressed in Brix degrees. These include juice with the same water content as fresh fruit (5–6 °Brix); purees and "passata' (8–14 °Brix) and double and triple concentrates (28 and 32 °Brix respectively) (Vilas Boas et al., 2017). These products extend the shelf life of fruit and can be used as ingredients in the food industry.

The production of dried tomato products such as powders is another alternative to extend the shelf life, offering several advantages such as ease of storage, packaging, transport and mixing (Giovanelli et al., 2002). The drying process can be carried out by sublimation, evaporation or entrainment. Freeze-drying is a low-temperature drying process

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that removes water from a product. It consists of three stages: freezing, sublimation and desorption (Bhatta et al., 2020). Freeze-drying is a process used on a wide range of fruits. Indeed, it is difficult to dehydrate fruit or fruit products with a high water content using conventional drying techniques without risking damaging their nutritional and physical quality. This process allows the product to be dried while preserving its taste as much as possible. Sablani et al. (2011) asserted that, compared with air-drying, freeze-drying best preserves the anthocyanins, phenols and antioxidant activity of fruits such as blueberries and raspberries. However, this process is very costly because of the energy required to dry the product. In addition, it's a time-consuming process that lasts several hours. Spray-drying is an interesting alternative for producing fruit powders such as tomato powder, as it is a faster and less energy-intensive process than freeze-drying. It involves spraying the product to be dried, which is in liquid or suspended form, into a stream of hot air (Tontul and Topuz, 2017). Dehydration of the moist product takes place when it comes into contact with a sufficiently hot, dry stream of air or other gas. Today, this process is widely used in the production of milk powder in the food industry under well-controlled conditions (Schuck et al., 2012). However, during the spray-drying, sticking phenomena in the drying chamber and caking during storage of the powder are obtained when drying products such as fruit juices because of their high sugar content resulting in a low glass transition temperature (T_g) of the product. Hence, the importance of mastering the drying process by increasing T_g products while producing a product that preserves the nutritional quality of the powder obtained.

T_g is the temperature at which the product's state changes from glassy (amorphous) to rubbery (viscoelastic) through a thermal or water-plasticizing process. It is an important physical parameter in drying processes, but also in the properties of powders, as it is responsible for sticking, agglomeration and lump formation when temperature of the product is higher than T_g. Levine and Slade (1989) demonstrated that the "sticky point' temperature corresponds to T_g. Three factors influence T_g of a product: temperature, water activity (a_w) and product composition. Difficulties in drying sugar-rich products such as tomato juice stem from the high content of low-molecular-weight compounds (Sobulska et Zbicinski, 2021). These compounds include fructose (T_g = 5 °C), glucose (T_g = 31 °C), also some organic acids such as malic acid (T_g = 11 °C), citric acid (T_g = 16 °C) and tartaric acid (T_g = 21 °C) (Bhandari and Howes, 1999; Roustapour et al., 2006; Tontul and Topuz, 2017). Their presence causes a low T_g of the product and T_g transition during drying, which leads to sticking in the spray tower drying chamber and a significant reduction in drying efficiency because drying temperature is higher than T_g of the product.

Faced with these limitations, solutions have been found in industry to increase the product T_g. The objective is to increase the Tg of the product so that it will not be 10–20 °C below the drying outlet temperature. The most common method is to add additives such as starch hydrolysates, which have a high T_g (100–188 °C), in order to obtain a better drying yield (Sobulska and Zbicinski, 2021). They are produced by the hydrolysis of starch using acids or enzymes. They are cheap, odourless carriers and the most widely used in the food industry. Starch hydrolysates have also low viscosity at high concentrations in water. Hydrolysed starches are described by the dextrose equivalent (DE), which indicates the level of starch hydrolysis. Hydrolysed starch with a DE below 20 is called maltodextrine, which is the most used carrier for drying process (Shahidi and Xiao-Qing, 1993). However, there is disadvantages of maltodextrines used as a carrier agent as a high content of anti-caking agent in the product and reduced concentration of key bioactive nutrients. Furthermore, increased consumption of refined carbohydrates is undesirable for human health, since the glucose produced during digestion of refined carbohydrates is rapidly absorbed in the small intestine, thus increasing the glycemic load (Sobulska and Zbicinski, 2021). Other carriers are also used as alternatives to maltodextrines. These include Arabic gum, a natural gum derived from the exudate of the acacia tree. Its high solubility and low viscosity in water enable concentrations over 50% in the product. However, Arabic gum is expensive, has limited production potential and may contain impurities (Tontul and Topuz, 2017). Recent studies have also shown that proteins such as whey isolate, soy protein isolate and sodium caseinate are efficient in improving drying yield at low concentrations in the product. Fang and Bhandari (2012) increased drying yield by over 80% using protein concentrations of less than 5% from whey isolates.

In this study, we investigated the ways to improve the drying of tomato juice while avoiding carriers use. The approach used is to eliminate the sugars in the product, which are mainly responsible for the undesired effects during drying, with the particularity of using centrifugation as a process because it is not a process used to improve drying. As a first step, we are going to use freeze-drying as a drying process, which allows us to obtain tomato powder without encountering sticking problems. In order to understand how reducing sugar improve drying of tomato juice, the evolution of the T_g of the powder was studied in different a_w conditions. To understand the stability of tomato powder during storage and the diffusion of water vapour, the sorption isotherm was studied. The physico-chemical characteristics of the product obtained in this study enables us to anticipate how the product will behave during drying and storage. It enables us to optimize the spray-drying process with the aim of obtaining a high-quality powder with good nutritional quality by avoiding the use of carriers. The goal is to make the most of tomatoes' health benefits, particularly those of lycopenes as a dietary supplement.

2. Materials and methods

2.1. Tomato processing

2.1.1. Tomato juice production

Two varieties of processing tomatoes (H1311 and Terradou) were cultivated in 2020 in an open field near Avignon, France (44°11′22.4″N 4°48′11.7″E) (Vilas Boas et al., 2017). The fruits were processed in a pilot plant (CTCPA, Avignon, France) giving a tomato juice by cold-break (CB) or hot-break (HB) process to inactivate natural enzymes that degrades pectins. For CB juices, tomatoes were cleaned, shopped in a hammer mill (Electra F6N, Electra, France), heated for 2 min and 45 s at 50 °C in a scraped-surface heat exchanger (Thermorotor, Duprat, France) and directly refined at 0.8 mm. For HB, tomatoes were cleaned, juices were extracted and refined at ambient temperature in a turbo extractor equipped with 8/10 sieve (Giubillo short 55 KW, CFT, Italy), vacuum deaerated and immediately heated for 2 min at 95 °C under ohmic heating (Ohmico impianto pilota, CFT, Italy), then chambered for 5 additional minutes at 95 °C in a vapour exchanger, then homogenized and cooled down to 40 °C in a tank. Juices were canned, pasteurized for 25 min at 105 °C in a static autoclave (Lagarde, France) and cans were stored at 4 °C until analysis (Sinkora, 2022). In this study, all experiments were carried out with these four types of sample: H1311 CB juice, H1311 HB juice, Terradou CB juice and Terradou HB juice.

2.1.2. Centrifugation of tomato juice

Centrifugation was used in our study to separate the sugars present in the juice. The aim was to apply a centrifugal force that separates the juice into two fractions: pellet and supernatant. The supernatant is the aqueous fraction including the hydrophilic constituents like sugars of the juice suspension, while the pellet is the solid part corresponding to the sedimented particles, most of which contain the hydrophobic constituents of the suspension (Fig. 1). Since sugars (mainly fructose and glucose) are hydrophilic compounds and low weight particles, they are in the supernatant. Thus, centrifuging the juice results in a pellet reduced or even free in sugar. This would be advantageous for tomato juice drying, with improved drying behaviour. In order to determine the best centrifugation parameters, tomato juices were centrifuged using two centrifugation parameters: acceleration and centrifugation time. Pre-tests were carried out at 4000, 8000 and 13000 g at 5, 10 and 15 min in triplicate. Once centrifuged, the different fractions obtained were

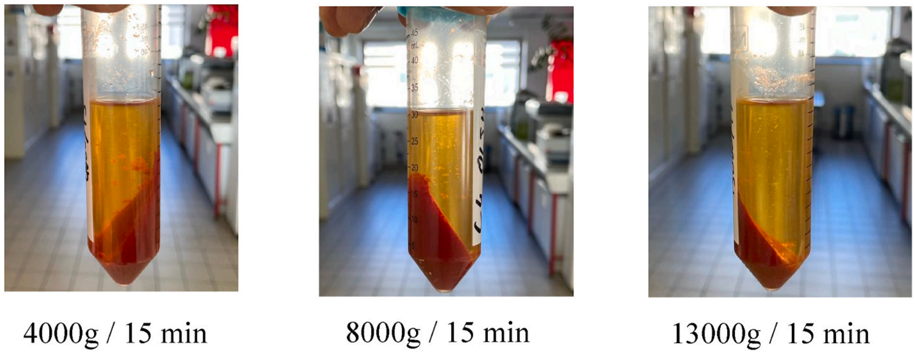

Fig. 1. Aspect of juice centrifuged at 4000, 8000 and 13000 g for 15 min.

characterized. We hypothesized that, for better centrifugation, the supernatant should not be visually red in colour, as this is an indicator of lycopene loss from the supernatant, a molecule of interest. They will be quantified to validate this hypothesis. The centrifugation yield must be above 50%, as sugars represent around 50% of the dry mass in tomato juice. Finally, the supernatant must be extracted as much as possible by evaluating the mass of each fraction. The centrifugation was done using an Avanti centrifuge (JE, Beckman Coulter) in 50 ml tubes. The centrifugation yield is calculated by Eq. (1):

$$\text{Centrifugation yield} = \frac{\text{Supernatant dry mass (g)}}{\text{Juice dry mass (g)}} \times 100. \tag{1}$$

2.1.3. *Freeze drying of tomato juice and pellet*

Tomato powders were produced by freeze-drying for 48 h tomato juice and pellet samples by using the same program on the freeze-drier (MUT 004 A, Cryotec). An initial freezing step was carried out at −40 °C. This was followed by a primary freeze-drying step at a pressure of 0.2 mBar to 1.995 mBar, with a temperature ramp-up from −30 °C to 20 °C. This cycle lasted 24 h. The final secondary freeze-drying stage was carried out at 0.001 mBar with a first ramp at 25 °C for 12 h, then at 30 °C for 12 h.

2.2. *Measurements*

2.2.1. *Dry mass content*

The dry mass content of tomato juice and pellet was measured by drying at 70 °C, at atmospheric pressure, for 48 h (Giovanelli et al., 2002). Measurements were carried out in triplicate. Dry mass contents are expressed in g of dry mass per 100 g of product.

2.2.2. *Analytical methods*

2.2.2.1. Sugar content. Extraction and determination of sugars (glucose, fructose and sucrose) were done by enzymatic method using a microplate reader (SAFAS FLX-Xenius Spectrofluorimeter) equipped with SAFAS automatic injection device. Experimentation was done on juice, supernatant or pellet samples stored at −20 °C in INRAE, Avignon (SQPOV unit). 5 g of product was weighed directly into the well, followed by 20 ml of distilled water using a dispenser. The whole was homogenized with the ultra Turrax for 1 min. The sample was then centrifuged at 9000 rpm at 4 °C; the supernatant was recovered by filtering through cheesecloth and stored at −20 °C until analysis, when it was thawed. Glucose, fructose and sucrose were quantified by enzymatic kits (D-Glucose and D-Glucose/D-fructose) for food analysis. The amount of Nicotinamide adenine dinucleotide phosphate (NADPH) formed during Hexokinase (HK) and glucose-6-phosphate dehydrogenase (G-6-*P*-DH) reactions is proportional to that of D-glucose and D-fructose. Measurements were carried out in triplicate and at 340 nm, maximum absorption of NADPH. Results are expressed in g/100 g dry mass (Trad et al., 2017). Apart from these experiments, the rest was carried out in the GEPEA laboratory (GPA Unit).

2.2.2.2. Carotenoids. Carotenoid extraction were done, using the micromethod described by Sérino et al. (2009) with some modifications described by Page et al. (2012). Sample were introduced into the HPLC. It equipped with diode array detector (SPD-M20A Shimadzu Inc., Kyoto, Japan). Column was Luna 3U (C8) 100 Å, 100 × 4.6 mm (Phenomenex, Torrance, CA, USA); mobile phase: solution A: 0.5 M ammonium acetate 30% – methanol, 70% v/v, solution B: methanol 100%.

Lycopene were extracted with four solvents: saturated aqueous NaCl solution, *n*-hexane, dichloromethane and ethyl acetate. Samples were analyzed on a HPLC with a diode array detector (SPD-M20A; Shimadzu, Kyoto, Japan) and a YMC C30 column (150 × 4.6 mm, i. d. 3 μm; YMC Co, Kyoto, Japan) as descrcribed by Yu et al. (2019).

2.2.2.3. Polyphenols. Phenolic compounds were extracted with the method described by (Yu et al., 2019). Phenolic compounds were analyzed on a ACQUITY UPLC© system coupled to a UV–visible diode-array detector (Waters Corp., Milford, USA) and a HCT Ultra Ion Trap mass spectrometer (Bruker Daltonics, Bremen, Germany). Authentic standards were used for calibration curves, in which quercetin (0.50–80.0 mg/L) and rutin (1.0–80.0 mg/L) were quantified at 360 nm, chlorogenic acid (0.30–20.0 mg/L) at 330 nm and naringenin (0.30–20.0 mg/L) at 280 nm, other flavonoids were quantified as quercetin equivalent at 360 nm.

2.2.3. *Measurement of glass transition temperature*

Samples of 1 g (±0.01 g) of freeze-dried tomato powders, in triplicate, were placed in pre-weighed aluminum cups. They were then placed in a desiccator at different relative humidity (RH) conditions using salt-saturated solutions. The solutions were prepared by adding salt to distilled water in a beaker under stirring at 25 °C until saturation. Water activity of the saturated salt solutions was determined for each in an aw-meter (AquaLab Pre, USA). Saturated solution are used at 25 °C: LiCl a_w 0.11, CH_3COOK at 0.23, $MgCl_2$ at 0.33, K_2CO_3 at 0.44 and $Mg(NO_3)_2$ at 0.53. The aim was to maintain a_w of powders between 0.11 and 0.53, according to the method for determining a sorption isotherm of Telis and Sobral (2001) which we have adapted. Once equilibrium has been reached (approx. 3 weeks), 3 mg (0.1 ± mg) of the samples was used to determine the T_g by differential scanning calorimeter (DSC Q100, TA Instruments, USA). The samples were heated at 10 °C/min between −80 °C and 100 °C in an inert atmosphere. The reference was an empty pan and the midpoint of the glass transition was considered as the characteristic temperature of the transition. All measurements were done in triplicate. The experiments were carried out on powders made from raw tomato juices and pellets samples.

2.2.4. *Determination of sorption isotherms*

The sorption characteristics of powders is an important parameter studied in order to understand the stability of powders during storage and the diffusion of water vapour (Al-Muhtaseb et al., 2002). The state of water in foods has long been studied with the aim of understanding their chemical and microbiological stability. Determination of the sorption isotherm explains the state of water within the food in three main regions (Fig. 2). The first region corresponds to strongly bound water, with an enthalpy of vaporization higher than that of pure water. The moisture content theoretically represents the adsorption of water molecules in the first layer. This water is not free and available for chemical reactions or plasticizing. The second region corresponds to water molecules that are less bound and are above the monolayer. This water is available for low molecular weight and biochemical reactions. The third region contains excess water in the form of fluid in the macro-capillaries. It has almost all the properties of water in bulk and therefore can act as a solvent. It is generally believed that water extending beyond the monolayer helps the mobility of solute molecules and act as solvent (Yanniotis and Blahovec, 2009). The sorption isotherm can be presented by mathematical models according to theoretical or empirical criteria. Numerous models are proposed in the literature, such as those based on monolayer water absorption (Langmuir model); the GAB and BET model, which is based on multilayer absorption; semi-empirical models such as Halsey's model; or empirical models such as those of Oswin and Smith (Goula and Konstantinos, 2005).

Around 10 mg of powder sample was taken to determine the sorption isotherm. It was done in a Dynamic Vapour Sorption (DVS) (Surface Measurement Systems, UK). Test were done at an air temperature of 25 °C and a relative humidity range of 0–98%. Due to the duration (1 week) and high precision of the equipment, the experiment was carried out once for each sample. The steps of humidity were set to around 10% and the mass changes were recorded once every minute. Whenever the control program detects a mass change of less than 0.002% per minute, the relative humidity automatically changes by approximately 10% (Garbalińska et al., 2017; Yin et al., 2018; Kelly et al., 2016). The data obtained were fitted to several models (BET, GAB, Oswin and Halsey). By comparing the R-square statistics and the mean relative percentage deviation (P), the GAB model has given best results. The sorption isotherms data were fitted in Microsoft Excel software (Microsoft, USA) with the GAB Eq. (2) (Van den Berg and Bruin, 1981):

$$X = \frac{XCka_w}{(1 - ka_w)(1 - ka_w + Cka_w)} \tag{2}$$

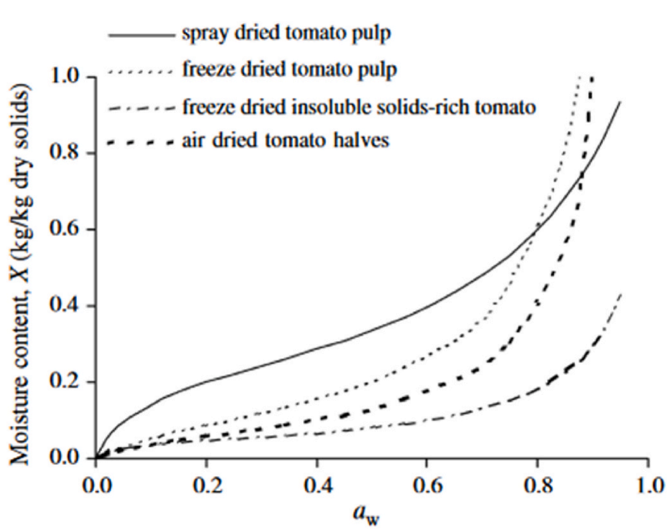

Fig. 2. Water sorption isotherms (20 °C) modeled by the GAB equation for various dry tomato products by Giovanelli et al. (2002). The dotted lines are based on data.

Where X is the equilibrium moisture content on dry mass; C is the Guggenheim constant; k is a factor for multilayer molecules with respect to the bulk liquid. The GAB constant equation were estimated by a direct non-linear regression analysis method.

2.3. Statistical analysis

Statistical analysis was performed with Statgraphics Stratus software (Statgraphics Technologies, Inc. USA). The mean value for the triplicate of each sample was used for the comparison. One-way analysis of variance (ANOVA) and Tukey tests were used to discern the significant differences at a level of $p < 0.05$. The aim is to identify the difference between samples (juice, supernatant or pellet) according to variety and process (HB/CB).

3. Results and discussion

3.1. Impact of centrifugation on dry matter and sugar content

The hypothesis in this study is that reducing the sugar content in the product to be dried could improve its capacity for drying, particularly by spray-drying. It was shown in the pre-study of centrifugation that the best parameter for extracting sufficient sugars from the juice is 13000 g at 15 min with a yield of over 58% of the dry mass in the supernatant based on dry mass (Table 1).

Based on these yields, the rest of the results were obtained by centrifuging at 13000 g for 15 min. Applying this to the Terradou and H1311 (CB and HB) juices, which have a dry mass content of 6%, supernatants of around 5% of dry mass and pellets of 9% of dry mass were obtained (Table 2). The different sugar composition of juices are glucose, fructose and sucrose, with a higher fructose content, characteristics of ripe tomato products (Agius et al., 2018). Terradou tomato varieties contain more soluble sugars than H1311 varieties, as confirmed by Sinkora (2022). These varietal characteristics would explain the higher amount of sugars in Terradou products and its ability to release more dry mass and sugars. We also noted that there are fewer sugars present in HB samples than CB. This could be explained by the fact that HB products are processed at higher temperatures, resulting in increased viscosity and larger particles (Sinkora, 2022), making centrifugation more difficult. Centrifuging removes more than 69%–77% of sugars, demonstrating that it is an effective process for reducing sugar in the pellet.

It was also found that the pellet obtained was red in colour, indicating that a good proportion of the lycopenes had been preserved after centrifugation. To confirm this, a test of the impact of centrifugation on lycopenes and polyphenols, tomato molecules of interest, was carried out in the different fraction (Table 3). For all samples, supernatant had very low lycopene levels, as lycopenes are not water-soluble compounds (Story et al., 2010). Supernatants from H1311 juices have higher lycopene levels. As shown above (Table 2), H1311 varieties centrifuge less well, which induces the loss of lycopene. Pieces of pellet may end up in the supernatant. The same phenomena can be observed for carotenoid content. These results show that centrifugation retains over 94% of the lycopenes in the initial juice. The impact of centrifugation on polyphenols content is different. More than 57% of total polyphenols are present in the supernatant after centrifugation of the different tomato

Table 1
Centrifugation yield (dry mass) of supernatant of Terradou HB juice at the four faster and longer parameters. [a, b, c] denotes a statistically significant difference.

	8000 g	13000 g	8000 g	13000 g
	15 min	15 min	10 min	10 min
Centrifugation yield (% dry mass)	57.54 ± 0.14[b]	58.42 ± 0.05[a]	56.19 ± 0.27[c]	57.98 ± 0.42[ab]

Table 2
Dry mass, glucose, fructose and sucrose matters in dry mass (d.m) juices, supernatant a pellet obtained by centrifugation at 13,000 g during 15 min ^{a} to ^{7} denotes a statistically significant difference.

			Dry mass *(g/100g)*	Glucose *(g/100 g d.b)*	Fructose *(g/100 g d.b)*	Sucrose *(g/100 g d.b)*
Terradou	**HB**	**Juice**	6.21 ± 0.08^{a}	19.18 ± 0.37^{j}	30.93 ± 0.29^{s}	15.18 ± 1.25^{1}
		Supernatant	5.00 ± 0.00^{d}	16.90 ± 0.51^{m}	27.75 ± 0.79^{v}	14.03 ± 0.79^{34}
		Pellet	9.26 ± 0.08^{g}	3.33 ± 0.66^{p}	5.43 ± 0.55^{y}	3.07 ± 0.54^{6}
	CB	**Juice**	6.17 ± 0.04^{a}	20.57 ± 0.11^{i}	33.26 ± 0.79^{r}	14.23 ± 0.69^{12}
		Supernatant	5.36 ± 0.03^{c}	16.96 ± 0.23^{L}	26.27 ± 0.59^{u}	10.09 ± 0.28^{45}
		Pellet	9.11 ± 0.13^{f}	4.58 ± 0.53°	7.02 ± 0.94^{x}	2.59 ± 0.91^{67}
H1311	**HB**	**Juice**	5.77 ± 0.04^{b}	17.49 ± 0.38^{k}	24.28 ± 1.12^{t}	12.46 ± 0.25^{12}
		Supernatant	4.47 ± 0.03^{e}	15.63 ± 0.34^{n}	21.13 ± 1.37^{w}	9.83 ± 1.25^{5}
		Pellet	8.80 ± 0.07^{h}	3.70 ± 0.23^{q}	4.39 ± 0.98^{z}	2.30 ± 1.46^{67}
	CB	**Juice**	5.69 ± 0.04^{b}	14.52 ± 0.18^{k}	22.92 ± 0.33^{t}	11.77 ± 0.48^{2}
		Supernatant	4.52 ± 0.15^{e}	15.57 ± 1.40^{n}	29.08 ± 0.76^{w}	14.82 ± 1.29^{3}
		Pellet	8.98 ± 0.05^{h}	2.74 ± 0.51^{q}	3.84 ± 0.52^{z}	1.88 ± 0.37^{7}

Table 3
Polyphenols, lycopenes and carotenoids in dry mass (d.m) of juices, supernatant a pellet obtained by centrifugation at 13,000 g during 15 min ^{a} to ^{x} denotes a statistically significant difference.

			Polyphenols (µg/g d.m)	Lycopene (µg/g d.m)	Total caretonoids (µg/g d.m)
Terradou	**HB**	**Juice**	474.94 ± 30.31^{c}	2688.89 ± 377.70^{L}	2912.35 ± 448.79^{u}
		Supernatant	481.60 ± 0.09^{f}	70.16 ± 2.53°	70.16 ± 2.53^{w}
		Pellet	456.50 ± 17.99^{i}	7127.17 ± 1657.5^{r}	8042.16 ± 1685.30^{z}
	CB	**Juice**	463.12 ± 15.46^{c}	3620.37 ± 133.63^{k}	4045.21 ± 152.80^{u}
		Supernatant	471.24 ± 1.97^{f}	90.40 ± 21.47°	90.40 ± 21.47^{w}
		Pellet	358.13 ± 7.72^{j}	8665.62 ± 970.88^{r}	9768.62 ± 1083.05^{z}
H1311	**HB**	**Juice**	1378.22 ± 22.51^{b}	4995.90 ± 322.18^{m}	5696.87 ± 363.42^{t}
		Supernatant	1498.90 ± 15.25^{e}	302.57 ± 39.30°	383.97 ± 39.81^{w}
		Pellet	1233.23 ± 44.33^{h}	19,123.35 ± 2271.46^{q}	21,272.81 ± 2444.91^{y}
	CB	**Juice**	1778.75 ± 21.01^{a}	9014.13 ± 720.13^{m}	10,051.23 ± 746.39^{s}
		Supernatant	2124.00 ± 11.56^{d}	1001.9 ± 448.43^{n}	1219.61 ± 498.42^{v}
		Pellet	1478.65 ± 39.53^{g}	27,241.70 ± 1825.09^{p}	30,167.72 ± 2076.22^{x}

juices. This is due to their water-soluble nature. Under the effect of centrifugal force, the polyphenols migrate with the water in the supernatants.

3.2. Glass transition temperature (T_g) evolution

Freeze-dried powders thermograms obtained in a_w between 0.11 and 0.53 shows the existence of two T_g (Fig. 3). According to Telis and Sobral (2002) the lowest T_g correspond to the glass transition of a matrix formed by water and sugar, and the highest T_g which is less visible and less water plasticized could be attributed to macromolecular constituents of tomato. This phenomenon is due to a separation of the phase of polymers and between proteins and plasticizers, respectively, which is typical of systems formed by blends of polymers. Luque et al. (1997) obtained for isolated tomato fruit cuticules a composite of polymerized cutin (a biopolymer composed of waxes, phenols, pectin, and cellulose) and various monomeric waxes, that also shows a lower temperature T_g at – 30 °C and additional one around 30–45 °C.

Fig. 4 shows the evolution of T_g for CB Terradou juice and pellet in function of a_w. A decrease in T_g of CB Terradou powders is observed as a_w and water content increases. This phenomenon is explained by the plasticizing effect of water on T_g. Numerous studies have demonstrated this phenomenon, as in the case of Telis and Sobral (2001), who studied the state diagram of freeze-dried pineapple. They state that at a_w values < 0.90 (hygroscopic domain), the plasticizing effect of water is evident, whereas for water activities above 0.90, the T_g curve shows a discontinuity, with a rapid increase in T_g approaching a constant value. This plasticizing activity of water can be explained by the weakening of hydrogen bonds and intra- and inter-macromolecular dipole-dipole interactions due to the shielding of these mainly attractive forces by water molecules. The low T_g of water may also be a cause of the observed decrease. In fact, water is the lowest molecular weight solvent with a T_g of −135 °C, and this difference in the T_g with macromolecules in foods reduces the viscosity of water-biopolymer mixtures over a wide range of temperatures (Goula et al., 2008).

In this study, we first planned to make a comparison between the different varieties and processes and see which product has the highest T_g, to be able to then carry out a more study on the most interesting samples, modeling included. Comparison of juice and pellet powders shows that the T_g of freeze-dried pellets is higher than that of freeze-dried tomato juice at equal a_w values. It is more accentuated at low a_w values (0.1 and 0.2), with T_g differences between 3 and 8 °C. The difference in T_g decreases at a_w values of 0.3 and 0.4 (below 3 °C), then rises to 4 °C at $a_w = 0.5$. It has been shown in the literature that other components present in the product, in addition to water, can influence the product's T_g (Bhandari et al., 1997). Depending on their proportion and interaction in the product, they can considerably reduce it. These include soluble components like fructose, glucose and sucrose. In our study, when we apply centrifugation to tomato juice, the majority of soluble compounds end up in the supernatant. At the end, sugar content is reduced by more than 65% for H1311 varieties and 75% for Terradou varieties in the pellet compared with the initial juice. Centrifuging reduces the fraction of low molecular weight molecules. It has been shown in the literature that the glass transition temperature decreases with the increase in low molecular weight solutes. Thus, by reducing the sugar content in the product, an increase in T_g is observed at low a_w.

Terradou freeze-dried powders have higher T_g values than those of the H1311 variety (Fig. 5). Results shows that Terradou CB pellet powder has higher T_g values than the other powders. H1311 HB powders have the lowest T_g values. This could be explained by the behaviour of the juices during centrifugation. Studies by Sinkora (2022) showed that H1311 varieties led to products with higher apparent viscosity than Terradou because of the highest alcohol insoluble solids content (AIS). This explains the lower centrifugation yield for the H1311 variety. When

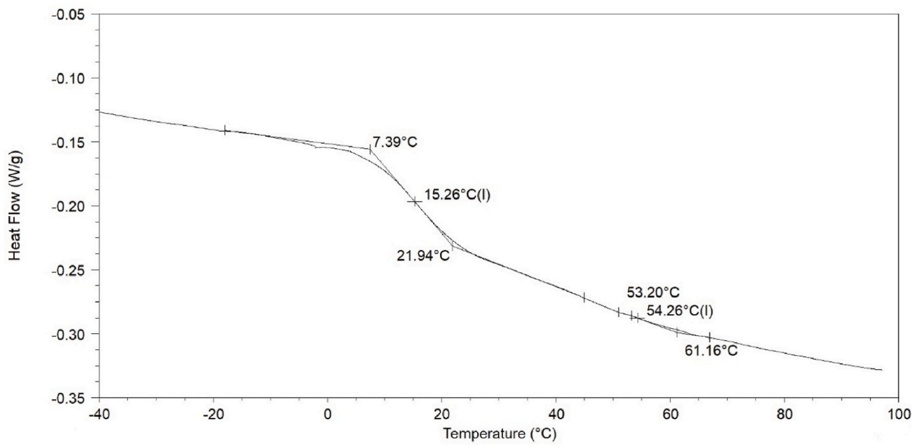

Fig. 3. CB Terradou pellet thermogram.

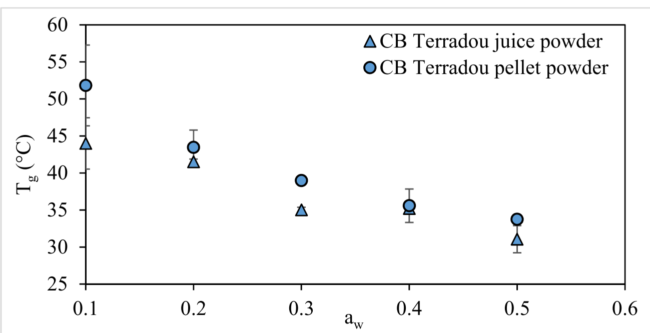

Fig. 4. Evolution of T_g as a function of a_w for CB Terradou juice and pellet powder.

centrifuging products from this variety, fewer soluble compounds with low T_g, such as sugars and organic acids, are removed in the supernatant. Moreover, the Terradou variety contains the most soluble sugars, resulting in a greater reduction in sugars. The effect of centrifugation is therefore more pronounced for Terradou powder. There was no significant effect of the HB/CB process on T_g. Based on the value of the second T_g peak, the Terradou CB pellet powder sample seems to be the most interesting for drying. Indeed, Bhandari et al. (1997) have stated that to avoid wall sticking and caking phenomena, the spray-drying outlet temperature should be lowered to a temperature 10–20 °C higher than the product's Tg. However, it is not always possible to guarantee a product temperature at the end of the process, or during storage, that is lower than it. This problem can be partly solved by raising the product's glass transition temperature.

3.3. Sorption isotherms

Water sorption from food is a complex phenomenon; the most important water-absorbing components in food are various polymers (protein, starch, cellulose, hemicellulose, sugars etc.). Fig. 6 shows the experimental moisture sorption data for HB H1311 powder and HB H1311 pellet powder, at a temperature of 25 °C. There is an increase of the equilibrium moisture content with an increasing of a_w. A sigmoid shape is noticed for all the samples, which is characteristic of amorphous materials. At low and intermediate a_w, a linear increase of the moisture content with a_w is noticed in the multilayer sorption region, whereas at a higher a_w levels, the water content increases quickly with a_w in the capillary condensation region. It could be explained by the fact that at low a_w, physical sorption occurs at strongly active protein sites, since water can only be adsorbed at OH sites on the crystalline sugar sites. In the intermediate a_w range, sorption takes place at less active sites and, from there, there is a gradual dissolution of sugars, culminating in complete exudation of sugars into solution when a_w is high.

A direct regression method was used to fit the GAB equation to water vapour adsorption data for freeze-dried tomato powder. The results are shown in Table 4. Considering the values of the mean coefficient of determination (R^2) and the mean relative percentage deviation (P) (<2.5%), it can be considered that the GAB equation is satisfactory for

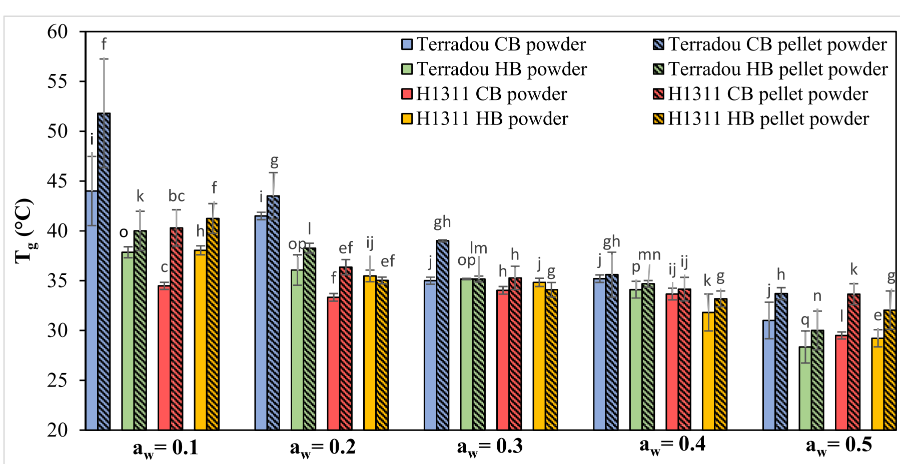

Fig. 5. Glass transition temperature of freeze-dried tomato powder.

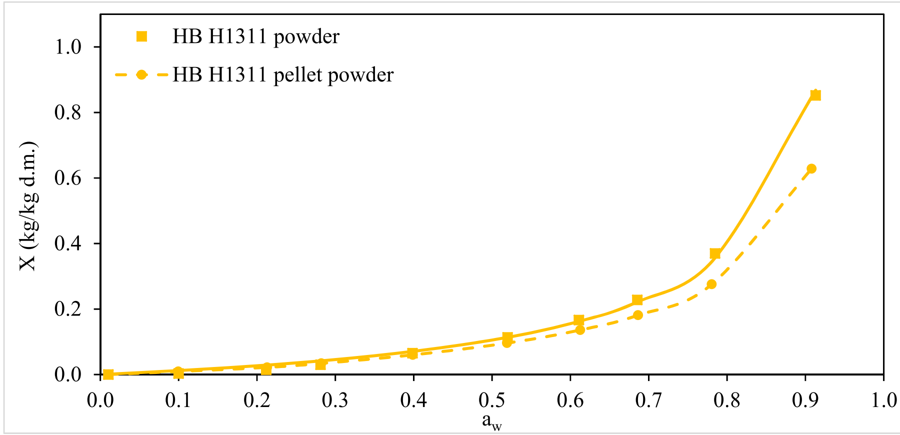

Fig. 6. Sorption isotherms of freeze-dried tomato juice and pellet at 25 °C, experimental (symbols) and predicted by the GAB model (lines).

modeling the adsorption effect of tomato powder. Values of the monolayer moisture content X is known to be the moisture content affording the longest duration with a minimum loss of quality at a given temperature. Below that value, there is a minimal deteriorative reaction except oxidation of unsaturated fats. In the literature X of fruits are between 10% and 15% dry mass (Goula and Konstantinos, 2005). Only the estimated value of X of the freeze-dried tomato juice are within those values. X value of the freeze-dried pellet are lower and had the same value of 8% dry mass. X is lower because the pellet powders are less hygroscopic than tomato juice powders. This could be explained by the reduction of soluble compounds by centrifugation, notably glucose and fructose. Similar results were found by Giovanelli et al. (2002), who studied the sorption isotherm of freeze-dried insoluble solids-rich tomato. They noticed that the monolayer moisture content of the insoluble solids-rich tomato are lower than those of freeze-dried tomato pulp. The value for is lower than 1 as dictated by GAB equation. In view of these results, we can conclude that powders derived from pellets are less hygroscopic, which is of interest for storage. This would enable the T_g to fall less rapidly, and the product to become caked less quickly.

Terradou powders appear to be more hygroscopic than H1311 powders (Fig. 7). This behaviour of Terradou powders can be explained by their higher sugar composition and lower insoluble solids-rich tomato. At low a_w there is no major difference in the sorption isotherm due to the process (CB or HB). Differences started in the multilayer sorption region where the CB powder of the same product are more hygroscopic than HB powder. According to the isotherms, powders from the pellets appear to be more stable during storage due to their low hygroscopicity. H1311 HB pellet powders appear to be the most stable in storage. However, freeze-drying prevented thermal degradation and changes in the physical structure of the material. Dried samples would therefore appear to be more stable than they actually are, as they would be less sensitive to variations in humidity. Powders may be less stable when spray-dried.

Table 4
GAB model parameters.

	X	C	k	Mean coefficient of determination (R^2)	Mean relative percentage deviation (P) (%)
H1311 CB powder	0,12	0,75	0,98	0,9997	1.94
H1311 CB pellet powder	0,08	1,50	0,98	0,9999	1.40
Terradou CB powder	0,11	0,94	0,99	0,9998	1.30
Terradou pellet CB powder	0,08	1,55	0,99	0,9998	1.39
H1311 HB powder	0,11	1,00	0,97	0,9993	1.44
H1311 HB pellet powder	0,08	1,60	0,98	0,9998	1.34
Terradou HB powder	0,12	0,81	0,97	0,9993	1.44
Terradou pellet HB powder	0,08	1,43	0,98	0,9998	1.35

4. Conclusions

Determining the Glass transition temperature (T_g) of freeze-dried tomato powders allows studying how reducing sugars composition could improve drying. T_g is a parameter that is studied to anticipate undesirable phenomena such as sticking. A product with a low T_g is difficult to spray-dry. To overcome this, tomato juices from the H1311 and Terradou varieties produced either by Cold Break or Hot Break process are centrifuged to obtain a sugar-reduced pellet. Supernatants obtained from Terradou variety extract more than 70% of the sugar, while those from H1311 extract 60%. This is due to the higher initial soluble sugar content of Terradou tomato varieties. Centrifugation of CB juices extracts more sugars in the supernatant than HB ones. Indeed, HB products are processed at higher temperatures, resulting in increased viscosity and larger particles making centrifugation more difficult. Powder made from Terradou CB pellet seem to be interesting for their higher T_g. It is related to the reduction in sugars which is more pronounced for this sample. H1311 HB pellet powders are also interesting for their low hygroscopicity. Their higher insoluble solids can explain this behaviour. Lowering the product sugar content enables to raise T_g without using an anti-caking agent. This could be a good alternative in order to optimize spray drying. Reducing the sugar content also allows obtaining less hygroscopic powders, which is advantageous for product storage. However, an initial study using freeze-dried samples may not accurately describe the properties of spray-dried powders, since freeze-drying does not bring any major changes in the physical structure of the material in the product, unlike spray drying. The next step will be to study the impact of sugar reduction on the quality of the spray drying and the tomato powder obtained, in order to compare with the results obtained with freeze-drying. Another main objective will be to verify that centrifugation does not decrease the amount of interesting microphytonutriments in the same way as it decreases the sugar content in the final powders.

CRediT authorship contribution statement

Robert Thierry Malomar: Writing – review & editing, Writing –

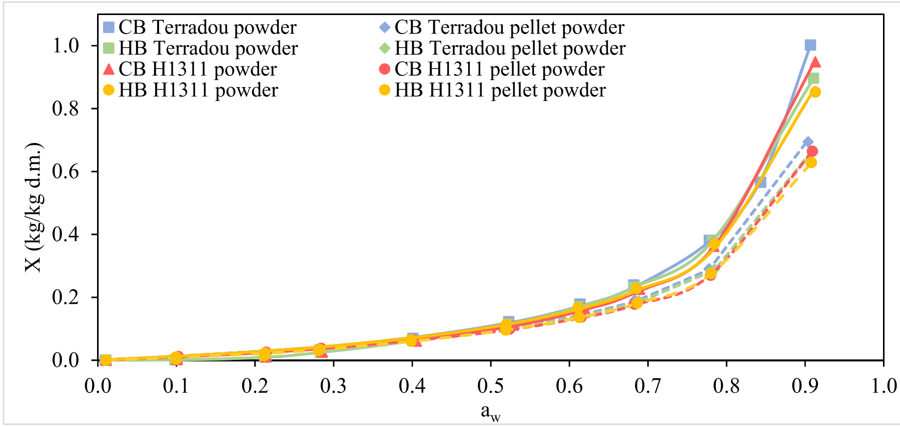

Fig. 7. Sorption isotherms of freeze-dried tomato juice and pellet at 25 °C, experimental (symbols) and predicted by the GAB model (lines).

original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Caroline Garcia:** Formal analysis. **Béatrice Gleize:** Formal analysis. **Vanessa Jury:** Validation, Supervision, Methodology. **Emilie Korbel:** Visualization, Validation, Supervision, Methodology. **Francine Fayolle:** Visualization, Validation, Supervision, Methodology, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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