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FERNANDA SVIECH

INFLUÊNCIA DA COMPOSIÇÃO NO PROCESSO DE CONGELAMENTO DE PITANGA (*Eugenia uniflora* L.) E ARAÇÁ (*Psidium cattleyanum*)

INFLUENCE OF COMPOSITION ON THE FREEZING BEHAVIOR OF FRUIT PITANGA (*Eugenia uniflora* L.) AND ARAZA (*Psidium cattleyanum*)

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Dissertação apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Mestra em Engenharia de Alimentos.

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Orientadora: Prof[a] Dr[a]. Ana Silvia Prata

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RESUMO

O Brasil possui uma enorme biodiversidade de frutas nativas e exóticas, mas uma grande parte dessas frutas são perecíveis e sazonais, portanto o mercado interno e indústria ainda não tem acesso a toda essa variedade de "frutas não convencionais". O processamento pode ser uma alternativa para o desenvolvimento de produtos a base dessas frutas. O processamento térmico é um exemplo pois é capaz de preservar o produto inativando enzimas e microrganismos ou reduzindo o teor de umidade e aumentando a vida de prateleira. As frutas são sistemas complexos, sendo constuídas principalmente por carboidratos e grande parte desses carboidratos são açucares simples como mono- e dissacarídeos. Como esse açucares são muito sensíveis a transformações sofridas durante a variação de temperatura e umidade, o processamento de frutas é muito desafiador. Por outro lado, o conhecimento das propriedades físicas dos frutos e do comportamento durante a mudança de fase, é necessário para melhorar seu processamento e armazenamento. Nesse trabalho polpa de pitanga *(Eugenia uniflora* L.) e araçá *(Psidium cattleyanum)* foram estudadas para entender o efeito da composição durante o congelamento para aplicação em produtos congelados. Essas frutas foram escolhidas pois são nativas brasileiras, da família das Myrtaceae, amplamente distribuídas no território nacional e possuem grande potencial para a aplicação em produtos. Esse estudo do comportamento de congelamento foi feito a partir das polpas inteiras (WP), da fração solúvel das polpas (SF) e de sistemas simulado (SS) contendo apenas açúcares (glicose, frutose e sacarose) e ácidos orgânicos (cítrico, málico e tartárico) que correspondem à composição da fração solúvel (SF) de (WP). As curvas de fusão de gelo (T_m) foram construídas usando calorimetria diferencial de varredura (DSC) para as três amostras ao longo de uma faixa de concentrações de sólidos solúveis (10 a 40% p/p). Observou-se que a equação de Chen se ajusta bem aos dados de fusão de gelo para as amostras de SS das frutas, porém com desvio no ponto mais concentrado (40%). A presença de ácidos orgânicos não alterou, significativamente, o comportamento da T_m das amostras. As curvas de fusão de gelo são fundamentais no processamento de frutas para adotar as condições de processamento e armazenamento adequados, portanto o desenvolvimento desses estudos pode contribuir para aumentar a gama de produtos à base de frutas.

Palavras-chave: Frutas não convencionais brasileiras; temperatura de derretimento de gelo; transições de fase; propriedades coligativas; fração de gelo.

ABSTRACT

Brazil has a huge biodiversity of native and exotic fruits. However, most of them are perishable and seasonal, then the Brazilian market and the Brazilian industry still do not have access to all this variety of "unconventional fruits". However, processing can be an alternative to develop a wide variety of products based on these fruits. The thermal process is an example because it can preserve the product by enzymatic and microorganisms inactivation or by reducing the moisture content and increasing the shelf life. Fruits are complex systems, mainly constituted by carbohydrates and most of these carbohydrates present in fruits are simple sugars, such as mono- and disaccharides. As these sugars are very sensitive to changes in temperature and humidity, processing fruits very tricky. Therefore, knowledge of the physical properties of fruits and the phase transition behavior is necessary to improve processing and storage. In this work, Pitanga (*Eugenia uniflora* L.) and Araza (*Psidium cattleyanum*) were studied to understand the effect of the composition on the freezing behavior for application in frozen products. These fruits were chosen because they are native to Brazil and belong to the Myrtaceae family, widely distributed in the national territory and even if still unexplored, which has great potential for application in products. This study of the freezing behavior was made from the composition of whole pulps (WP), simulated systems (SS) containing only sugars (glucose, fructose and sucrose) and organic acids (citric, malic and tartaric) that corresponded to the composition of the fruits originals, and the soluble fraction (SF) of WP. The melting ice curves were constructed using differential scanning calorimetry (DSC) for the three samples over a concentration range (10 to 40% wt.). It was observed that the Chen equation fits well with the melting data for fruit concentrates and model systems with some deviation at the most concentrated point (40% wt.). The presence of organic acids did not significantly change the melting behavior of fruits. The ice melting curves are fundamental in fruit processing to define the appropriate processing and storage conditions. Therefore, the development of these studies can contribute to increasing the range of fruit-based products.

Key-words: Nonconventional Brazillian fruits; ice melting temperature; phase transitions; colligative properties; ice fraction

SUMÁRIO

CAPÍTULO 1: INTRODUÇÃO E OBJETIVOS

1.1. INTRODUÇÃO

O Brasil possui uma extraordinária biodiversidade que se reflete na variedade de frutas nativas e das que se adaptaram bem ao nosso clima. Segundo o Ministério da Agricultura, Pecuária e Abastecimento (MAPA), o pais é o terceiro maior produtor de frutas atrás da China e da Índia (Brasil, 2019). A comercialização de frutas, tanto no mercado interno quanto em exportação, desempenha um papel importante na economia do país (Kist et al., 2018). Em 2019, as exportações superaram um milhão de toneladas, tendo como principais frutas exportadas as “frutas convencionais” como manga, melão, limão, melancia, banana e abacate (Brasil, 2019).

Porém, o país possui uma variedade muito grande de "frutas não convencionais" que infelizmente, o mercado externo e uma grande parte do interno brasileiro não tem acesso (Teixeira et al., 2019). Isso se deve a fatores como alta perecbilidade devido à casca e parede celular finas, alto teor de água e abundância de mono e dissacarídeos (Clerici & Carvalho-Silva, 2011) aliado com a sazonalidade e regionalidade de muitas dessas frutas (Teixeira et al., 2019). Neste contexto, o processamento surge como uma forma de aumentar a vida de prateleira, reduzir o desperdício e agregar valor à produção, possibilitando o fortalecimento deste mercado e da indústria nacional, promovendo ampla distribuição e desenvolvimento desse setor.

O processamento deve ter condições operacionais adequadas para cada tipo de produto, a fim de evitar perda de nutrientes e qualidade e desenvolver características de textura, cor, odor e sabor adequadas (Alabi et al., 2020). Assim a avaliação do estado físico e do comportamento das fases de produtos alimentícios pode ser empregada para estabelecer condições de armazenamento adequadas e condições mais assertivas de processamento (Biglia et al., 2016; Mahato et al., 2019; Qu et al., 2017; Welsh et al., 2021).

O diagrama de estado é usado para identificar o estado físico de um alimento em determinada temperatura e concentração, interpretando o comportamento na mudança de estado líquido-sólido, como por exemplo em processos de congelamento (curva de fusão do gelo), na formação de fases saturadas em processos de concentração (curva de saturação) ou na mudança sutil de fase, quando o produto está no estado sólido (curva de transição vítrea) (Levine & Slade, 1986; Rahman, 2006, 2010). Entender a relação destas transformações de fase com a composição do produto pode auxiliar a definir condições apropriadas para processamentos de forma mais racional.

Muitos produtos à base de frutas são processados no estado congelado como polpas, frutas inteiras congeladas (Fernandes et al., 2011) e misturas congeladas como sorvete (Celli et al., 2016). Além de diminuir reações indesejáveis e prolongar a vida de prateleira dos produtos (Verma & Singh, 2015), a imobilização da água por formação de gelo auxilia no desenvolvimento de atributos sensoriais e modula a textura do produto.

O entendimento da formação de gelo permite um controle tanto do processo de congelamento, quanto para definições de condições durante o armazenamento no estado congelado (Celli et al., 2016). Para produtos como sucos concentrados congelados, o ponto de congelamento deve permitir a produção e armazenamento com maior percentual de água congelada, o que reduz os efeitos do choque térmico no varejo e em freezers domésticos convencionais (Smith & Bradley, 1983). Para produtos que são consumidos no estado congelado como sorvete e granitas, o ponto de fusão deve ser adequado para que a fração de gelo permaneça limitada, caso contrário, a textura do produto ficará muito dura e granulada. Durante a transformação da água líquida em gelo ocorre o aumento da concentração da solução, o que altera as propriedades coligativas da água residual na fase crio-concentrada (Kerr, 2006, 2019).

Pesquisas foram realizadas para determinar as curvas de fusão de várias frutas (Bazardeh & Esmaiili, 2014; Moraga et al., 2004, 2006; Ruiz-Cabrera et al., 2016; Ruiz-Cabrera & Schmidt, 2015; Sá et al., 1999). Porém, a comparação entre dados de diferentes autores é difícil, pois a composição dos frutos depende da sazonalidade, condições do solo, clima e variedade. Além disso, construir uma curva de fusão para cada colheita ou lote de processamento de frutas é demorado e caro.

A solução para esse problema torna-se possível percebendo que o ponto de congelamento é influenciado principalmente pelo conteúdo de compostos de baixa massa molecular e que apenas um número limitado desses compostos estão presentes na maioria das frutas em concentrações significativas (Roos, 1993). Assim, identificando os principais compostos responsáveis pelo comportamento da transição de fase líquido-sólido, um comportamento geral de fusão pode ser escrito para representar uma grande variedade de produtos. Além disso, a possibilidade de encontrar uma representação geral para curvas de T_m amplia a oportunidade para novas formulações com frutas não convencionais brasileiras.

Na revisão bibliográfica (Capítulo 2) é abordado o potencial do Brasil no mercado de frutas, bem como a diversidade de frutas que poderiam ser utilizadas para o processamento e que ainda são desconhecidos por grande parte do mercado e da indústria. Foram abordados os conceitos diagrama de estado e aspectos envolvidos nas transições de fases em alimentos. A importância do estudo da transição de fases para o processamento de frutas e a escassez de estudos com frutas "não convencionais" brasileiras também são ressaltados neste capítulo.

No capítulo 3 está descrito a caracterização da matéria-prima, o processo de obtenção e preparação das amostras das frutas e as análises térmicas por calorimetria diferencial de varredura (DSC). A curva T_m foi determinada e ajustada pela equação de Chen que é comumente utilizada na literatura para descrever o efeito da composição de sólidos na depressão do ponto de congelamento. Além disso, a fração de gelo em diferentes concentrações e temperaturas para as amostras de sistema simulados de pitnga e de araçá (SS-P e SS-A) é apresentada neste capítulo. Finalizando, no capítulo 4 estão listadas as discussões e conclusões obtidas.

1.2. OBJETIVOS

O objetivo geral desta pesquisa foi avaliar a influência da composição de frutas no comportamento de fusão do gelo das mesmas.

Os objetivos específicos deste estudo foram:

- Compilar dados sobre a biodiversidade brasileira em frutas não convencionais com potencial de comercialização e industrialização discutindo o estado da arte da transição de fase de frutas.

- Caracterizar as frutas (araçá e pitanga) em termos de açúcares simples, ácidos orgânicos e fração insolúvel.

- Compreender a influência dos açúcares simples e dos ácidos orgânicos na T_m bem como a influência das propriedades coligativas no comportamento de fusão de gelo de duas frutas brasileiras: araçá e pitanga, através da construção das curvas T_m para as amostras polpa de fruta inteira de pitanga WP-P (baixo teor em fibras) e araçá WP-A (alto teor de fibras), bem como, suas frações solúveis (SF-P e SF-A, respectivamente para pitanga e araçá).

- Averiguar a compatibilidade de uma formulação sintética que representa a composição da fruta em seus monossacarideos e ácidos orgânicos com o comportamento térmico da fruta em si. Um modelo matemático foi ajustado aos dados experimentais possibilitando encontrar uma representação geral para curvas de fusão e ampliar a oportunidade formulações com frutas não convencionais brasileiras.

- Determinar a fração de gelo em diferentes concentrações, pois essa determinação é uma previsão das propriedades térmicas para o congelamento e descongelamento de alimentos.

1.3. REFERÊNCIAS

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CAPÍTULO 2: POTENTIAL FOR THE PROCESSING OF BRAZILIAN FRUITS - A REVIEW OF APPROACHES BASED ON THE STATE DIAGRAM

POTENTIAL FOR THE PROCESSING OF BRAZILIAN FRUITS - A REVIEW OF APPROACHES BASED ON THE STATE DIAGRAM

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Abstract

Despite the huge Brazilian biodiversity, the "nonconventional fruits" access a limited local market, and they are unavailable to the industry. The reason for that scenario is the high perishability of such fruits in fresh state, which renders them unsuitable for long distribution chain. Thermal-processing is an alternative to preserve the product by reducing moisture content and to manufacturing fruit-based food products, but the relation structure-composition of fruits is very challenging due to the presence of mono- and disaccharides as main compounds. The knowledge of the phase behavior of fruits may be useful to assertively estimate the thermal conditions for several thermal processing, as well as, for properly store the final food product. This review compiles information available in the literature, and suggests that, in general, the knowledge of sugar composition of fruits should be enough to estimate their melting behaviour but, contrarily, the glass transition is a more complex phenomenon. By providing the state-of-the-art of phase behavior for fruits, it is aimed to highlight the potential use of Brazilian fruits..

Key-words: Nonconventional Brazillian fruits; glass transition temperature; ice melting line, phase transitions.

2.1. INTRODUCTION

Brazil has an extraordinary biodiversity that is reflected both in the enormousvariety of native fruits and in the significant number of introduced exotic ones, that are well adapted to the tropical climate (Valli et al., 2018). A substantial portion of vitamins and minerals in the diet comes from fruit and vegetable consumption (Bailão et al., 2015; Rico et al., 2007; Zappi et al., 2015) contributing to a good dietary status and the prevention of diet-related chronic diseases (Neri-Numa et al., 2018). However, fresh fruits have a high to very high water content and furthermore contain numerous easily fermentable low-molecular weight comoiunds, in particular sugars, lead to rapid deterioration. Together with the often thin skins and the soft texture, which easily leads to bruising, such fruits are difficult to distribute to locations far from centers of production (Clerici & Carvalho-Silva, 2011; Gorayeb et al., 2019; Teixeira et al., 2019).

Thermal food-processing operations can be an alternative to preserve the product by the combined effect of time and temperature, focused on the inactivation of some microorganisms or enzymes and reduction of the moisture content (Joardder et al., 2017; Ibarz & Barbosa-Cánovas, 2003). Currently, such processes must have operating conditions adapted to each product class, to minimize, the loss of nutrients and consequently their nutritional quality, to develop an adequate texture, and to avoid fouling or caking (Bhandari & Howes, 1999; Claude & Ubbink, 2006). These adaptations are currently carried out in a very empirical way, which requires significant experimentation based on trial and error when the ingredient source is modified or in case a new product is developed. Furthermore, on basis of trial and error, it is difficult to optimize energy use in the processing (Bhandari & Howes, 1999; Claude & Ubbink, 2006; Raju & Bawa, 2006).

Since the 1970s the understanding of the relation between water activity and various biological, chemical and physical phenomena in foods has significantly advanced (Troller & Christian, 1978). The understanding of the amorphous nature of most foods and the realization that the physics state of the amorphous material are governed by the glass transition (Levine & Slade, 1986; Rahman & Labuza, 1999; Roos, 1995a 1995b) were employed to develop fundamental relations between water activity, water content and temperature to predict the behavior of amorphous food systems (Rahman, 2006; Slade et al., 1991). This approach is having major impact in particular in the systematic definition of storage conditions and the rational development and optimization of food processes (Bazardeh & Esmaiili, 2014; Bhandari & Howes, 1999; Celli, Ghanem, & Su-Ling, 2016; Rahman, 2009). Over the past decades, this approach was applied to many different dehydrated and frozen food systems, including those produced by freezing, freeze-drying, spray-drying, and extrusion (Biglia et al., 2016; Mahato et al., 2019; Qu et al., 2017; Welsh et al., 2021; Zhu et al., 2019)

The glass transition temperature of an amorphous material is dependent on its composition of compounds of high and low molecular weight, as well as the intermolecular interactions acting between the species. In foods, compositions that are high in high molecular weight compounds, such as starches and other polysaccharides, may have glass transition temperatures that may be above 200 ºC. However, the glass transition temperature is strongly depressed by the presence of low molecular weight compounds. In particular, small hydrophilic compounds, in particular water, but also mono- and disaccharides, lead to a significant decrease of the glass transition temperature by a mechanism that is known as plasticization (Roos & Drusch, 2015; Ubbink, 2016).

As fundamental physical property, glass transition impacts the behavior of the materialk during processing, including drying processes and the viscosous structuring of concentrates (Asp, 1996; Roos, 1995a). Owing to their high amount of low molecular weight compounds, fruits (see Table 2) represent a challenge for such operations in order to lead to stable products as they generally have a very low glass transition temperature, and optimal yield. Additionally, their storage regimes for the preservation of nutritional and sensorial attributes are very narrow (El Bulk et al., 1997; Jaya & Das, 2009; Roos, 1995b). However, specifically for exotic fruits that are very little known but that have potential for food product applications, very few such thermal behavior characterizations have been published. This paper aims to compile data of phase transitions of fruits from the literature, with focus on tropical fruits, and to discuss the of the phase behavior of fruits in terms of their state diagrams.

2.2. DIVERSITY OF BRAZILIAN FRUITS

Brazil has a huge diversity of underexploited fruit varieties with attractive market potential (Valli et al., 2018) beyond being one of the world's largest producers of "conventional" fruits such as banana, orange and melon (Kist et al., 2018). Every year, about 44 million tons of fruit are harvested. The total value of the export of these fruits was over US$

1 billion in 2019 (Brasil, 2019). However, just 26.5% of this total represents the export of fresh fruit, another 74.5% represents exports of fruit-based products, mainly orange juice. Whereas, this makes the country the largest exporter of orange juice in the World (Brasil, 2019).

Brazil extends 4.394 km from South to North, crossing climates from temperate in the Southern to equatorial and tropical in the North and Northeast, with semi-arid and subtropical regions at intermediate latitudes. This diversity in regional climates results in multiple biomes (Figure 1) that gives rise to significant variations in vegetation that is also reflected in a large regional diversity of "non-conventional fruits" such as cambuci, grumixama, uvaia, cambucá, pitanga, pitangatuba, pitomba, araçá, camu-camu, umbu, cajá, guabiju, bacuri, cupuaçu, pupunha, pitomba, and others (Albuquerque, 2016). Unfortunately, the external market and even the internal Brazilian market do not have access to this major variety of non-conventional fruits (Valli et al., 2018).

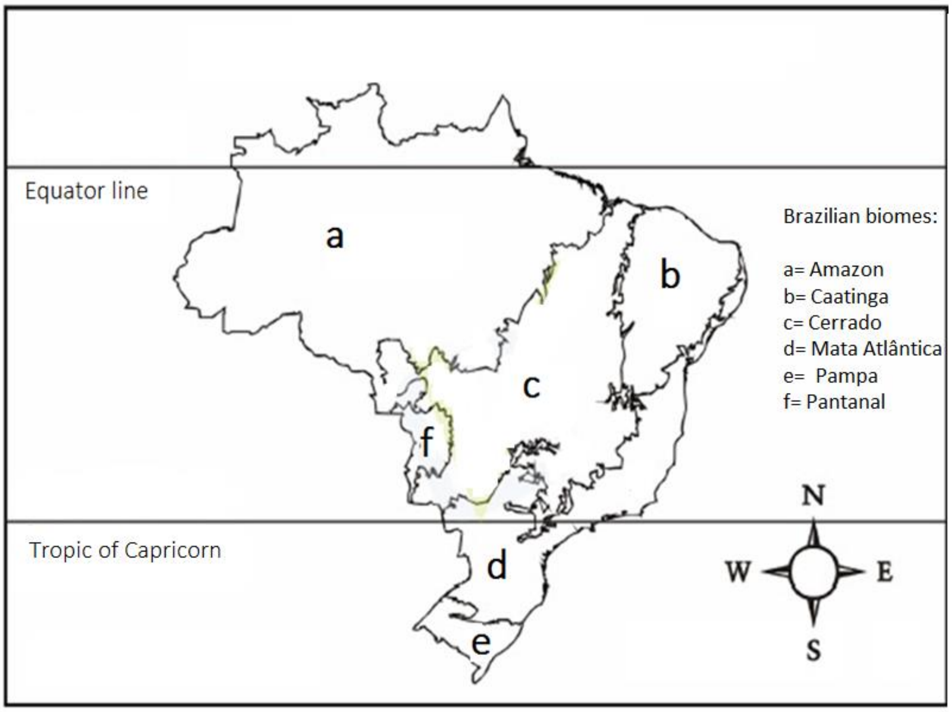

Figure 1. Brazilian biomes: a=Amazônia (hot and humid), b=Caatinga (dry shrubland), c= Cerrado (savanna), d= Mata Atlântica (hot and humid), e= Pampa, f=Pantanal(wetlands) (adapted from IBGE,2013).

The monumental handbook "Dictionary of Useful and Cultivated Exotic Plants of Brazil" written by Manoel Pio Corrêa (1926) has catalogued 504 species of fruits. According to Teixeira et al. (2019), only a tiny fraction of this diversity of exotic fruits has its potential explored and used on a significant scale (Teixeira et al., 2019). A compilation of some types of fruits produced in Brazil with huge potential for commercialization and industrialization is showning in Table 1.

Table 1: Edible fruits in Brazil produced on a commercial scale, as function of Brazilian biome, origin and family. Types of biomes: "a=Amazon, b=Caatinga, c=Cerrado, d=Mata Atlântica, e=Pampa, f =Pantanal" (Reflora, 2020).

Family	Name/ popular name	Native or exotic to Brazil	Brazilians bioma	Some research reported in the literature
Anarcadiaceae	*Spondias dulcis/* Cajá-manga	Exotic	b,c	(Benkeblia & Lopez, 2015)
	Anacardium occidentale/ Cashew	Native	a,b,c,d,e	(Mog et al., 2019; Rodríguez et al., 2017)
	Mangifera indica/ Mango	Exotic	a,b,c,d,e,f	(Liu et al., 2013; Rosas-Mendoza et al., 2011; Tejada-Ortigoza et al., 2017)
	Spondias purpurea/ Seriguela	Native	b,c,d	(Vargas-Simón, 2018)
	Spondias tuberosa/ Umbu	Native	b,c	(Albuquerque et al., 2015; de Lima et al., 2018)
Anxnaceae	*Anxna montana*/ Araticum	Exotic	b,c,d,f	(Cardoso et al., 2013; Roesler et al., 2007)
	Anxna muricata/ Graviola	Exotic	a,b,c,d,e,f	(Sacramento et al., 2003; Smith & Shejwalkar, 2020)
Apocynaceae	*Hancornia speciosa/* Mangaba	Native	a,b,c,d	(Clerici & Carvalho-Silva, 2011; Lima et al., 2015; Oliveira Yamashita et al., 2020)
Arecaceae	*Astrocaryum aculeatum*/ Tucumã	Native	a,b,c,d,e,f	(Silva et al., 2018)

	Euterpe oleracea/ Açai	Native	a	(Pacheco-Palencia et al., 2009)
	Mauritia flexuosa/ Buriti	Native	a,b,c	(Moser et al., 2019)
	Copernicia prunifera/ Carnaúba	Native	b,c,	(Freitas et al., 2019)
	Cocos nucifera/ Coconut	Exotic	a,b,c,d,e,f	(Srivaro et al., 2020)
Bromelaceae	*Ananas comosus/* Pineapple	Native	d	(Bamidele & Fasogbon, 2017; Vieira et al., 2012)
Caricaeae	*Carica papaya*/ Papaya	Exotic	a,b,c,d,e,f	(Fatombi et al., 2019; Gomes et al., 2018; Telis et al., 2007)
Caryocaceae	*Caryocar brasiliense*/ Pequi	Native	a,b,c,d,	(Mendonça et al., 2017)
Cucurbitaceae	*Citrullus lanatus*/ Watermelon	Exotic	a,b,c,d	(Mendoza-Enano et al., 2019; Yang et al., 2020)
	Cucumis melo/Melon	Exotic	b,c,d,e,f	(Madrid, 2020)
Laureaceae	*Persea americana*/ Avocado	Exotic	d	(Permal et al., 2020; Rodríguez et al., 2019)
Malpighiaceae	*Malpighia emarginata*/ Acerola	Native	c,d	(Bicas et al., 2011; Silva et al., 2020)
Moraceae	*Morus/*BlackBerry	Exotic	b,c,d	(Clerici & Carvalho-Silva, 2011; Syamaladevi et al., 2009)
	Byrsonima crassifolia/ Murici	Native	c,d	(Sousa & Souza Buarque, 2020)
	Artocarpus heterophyllus/ Jaca	Exotic	a,b,d	(Bicas et al., 2011)

Musaceae	*Musa paradisíaca L*/Banana	Native	a,b,c,d,e,f	(Rahman & Al-Saidi, 2017; Zotarelli et al., 2012)
Myrtaceae	*Psidium cattleianum*/ Araçá	Native	a,b,c,d,e,f	(Damiani et al., 2011, 2013; Galho et al., 2007; Lopes & Silva, 2018)
	Eugenia dysenterica/Cagaita	Native	b,c,d	(Silva et al., 2017)
	*Myrciaria dubia/*Camu-camu	Native	a,c	(Silva et al., 2006; Carmo et al., 2020)
	Campomanesia xanthocarpa Berg/ Gabiroba	Native	a,b,c,d,e,f	(Barbieri et al., 2019)
	Psidium guajava/ Guava	Exotic	a,b,c,d	(Clerici & Carvalho-Silva, 2011; El Bulk et al., 1997)
	Eugenia brasiliensis/ Grumixama	Native	d	(Teixeira et al., 2019)
	Plinia cauliflora/ Jabuticaba	Native	d	(Resende et al., 2020)
	Syzygium cumini/ Jambolão	Native	a,b,c,d,e,f	(Faria et al., 2011; Lago et al., 2006)
	Eugenia uniflora L/ Pitanga	Native	b,c,d,e	(Franzon et al., 2018; Lopes et al., 2005;Lopes & Silva, 2018; Sviech et al., 2019; Vizzotto et al., 2011)
	Eugenia pyriformis/ Uvaia	Native	a,b,c,d,e,f	(Jacomino et al., 2018)
Passifloraceae	*Passiflora edulis/* PassionFruit	Native	a,b,c,d,e,f	(Motojima et al., 2018; Zappi et al., 2015)

Rubiaceae	*Genipa americana/* Jenipapo	Native	a,b,c,d,e	(Náthia-Neves et al., 2017)
Sapindaceae	*Paullinia cupana/* Guaraná	Native	a	(Roncon et al., 2011)
	Talisia esculenta/ Pitomba	Native	a,b,c,d,e,f	(Rodrigues et al., 2018)
Sapotaceae	*Pouteria caimito*/ Abiú	Native	a,c,d	(Falcão & Clement, 1999)
Sterculiacea (Malvaceae)	*Theobroma grandiflorum*/ Cupuaçu	Native	a	(Pereira et al., 2018)
Oxalidaceae	*Averrhoa carambola*/ Carambola	Native	a,b,c,d,e,f	(Benkeblia & Lopez, 2015; Warren & Sargent, 2011)

We uinfer that the fruits listed in Table 1, are very attractive for the development of food products , as they are known for their sensory appeal, and most of these fruits have health benefits. The economic impacts that can be generated from a more extensive production and marketing of these fruits can also contribute to the preservation of biodiversity by providing a stable income for local population that is based on the sustainable management of these natural resources (Teixeira et al., 2019; Valli et al., 2018).

Brazilian fruits are classified into 69 botanical families. Fruits of the species of Myrtaceae represent 13% of total Brazilian fruits (Teixeira et al, 2019). In this review, we will list two representative fruits from this family that, to highlight the possibilities for industrialization.

Pitanga (*Eugenia uniflora* L.) and Araza (*Psidium cattleianum)* have both a high yield of pulp for the manufacturing juices, ice creams others products (Teixeira et al., 2019). Pitanga is popularly known as the "Brazilian cherry" (Vizzotto et al., 2011; Bezerra et al., 2000), and its pulp is rich in calcium, anthocyanin and flavonoids, carotenoids, and vitamin C, indicating its high antioxidant and property (Franzon et al., 2018). These fruit has been used to produce fresh juices, frozen pulp, jellies and liqueurs by small manufacturers located close to the production place. This is mainly due to lack of improvement in technological knowledge on the processing and preservation of these fruits, resulting in spoilage, loss of nutrients, in particular vitamins and loss of flavor during storage (Freitas et al., 2014; Lopes et al., 2005; Silva, 2006).

On the other hand, the Araza is a climacteric fruit, which makes it highly perishable (Galho et al., 2007; Hernández et al., 2007; Lopes & Silva, 2018) and it is less accessible than Pitanga due to the presence of enzymes responsible for browning. The popular names rasing for this type of araza include araza-rosa, araza-de-comer, araza-da-praia and araza-coroa (Teixeira et al., 2019). Araza is sweet, aromatic, and juicy, with a characteristic flavor and spicy touch (Biegelmeyer et al., 2011). Besides, it is rich in phytochemicals, phenolics, and vitamin C, and is known for its high content of bioactive compounds, in particular antioxidants. These characteristics make the fruit attractive and with the potential for the development products (Damiani et al., 2011; Galho et al., 2007; Lopes & Silva, 2018; Reyes-Álvarez & Lanari, 2020).

These fruits can not be shipped to regions far from the production locality and the post-harvest losses reach very high levels of between 35% to 55% of the total production (Henz, 2017). The analysis of post-harvest losses of fruits classifies storage (43.2%) as the majority contributor to the losses in Brazil, followed by problems in packaging and handling (23%), and transportation (17.6%) (Henz, 2017).

It is recognized that fruit processing may play an important role in the reduction of food waste (Freitas et al., 2014). Methods based on the reduction of water content, such as solute additions or thermal treatments such as dehydration, concentration, refrigeration, freezing, chilling, and frozen storage (Celli, Ghanem, & Su-Ling Brooks, 2016; Fernandes et al., 2011; Verma & Singh, 2015), are commonly used to produce juices, purees, jams, dried fruits, powders, frozen pulp among other products (Fernandes et al., 2011; Celli et al., 2016).

Knowledge of the physical properties of fruits and fruit pulps, in particular their phase behavior, is required to improve their processing and storage (Rahman, 2010). However, information about the phase behavior of such fruits is hardly available in the literature. There is consequently a pressing need to determine such physical properties of exotic fruits to optimize their processing and products and establish appropriate storage conditions.

2.3. STATE DIAGRAMS IN FOOD

The state diagrams are widely used in food science are maps of the phase and state transitions as a function of temperature and water content. State diagrams can be used to predict and optimize processing and/or storage procedures of food products and usually include the ice melting line (T_m), the glass transition line (T_g), and the solubility lines (T_s) (Roos, 1995a).

The ice melting line (T_m) describes the depression of the freezing point as a function of solids content and is directly related to the concentration of a non-volatile solute. As a colligative property, it depends on the number of particles (molecules) rather than the molecular weight of the dissolved solute (Chen, 1986; Schwartzberg, 1976). Low molecular compounds affect the freezing point much more effectively than compounds of higher molecular weight, in particular for the prediction and optimization of processing strategies or storage procedures of sugar-rich products such as fruits and fruit-based products (Jaya & Das, 2009; Mahato et al., 2019).

The glass transition temperature (T_g) is defined as the temperature at which an amorphous material passes from the rubbery state to the glassy state (Karel et al., 1994; Levine & Slade, 1986; Roos, 1995a). This transition from one amorphous state to another is accompanied by a major decrease in molecular mobility. As a glass transition is a continuous phase transition there is no latent heat involved in this state change (Roos, 1995a). However it exhibits the characteristics of a second-order thermodynamic transition, such as discontinuity in the heat capacity (Roos, 1995b; Sablani et al., 2010). The glass transition temperature is dependent on the moisture content (Roos, 1995b). In structural materials such as fruits that moreover are characterized by composition, the glass transition behavior is very complex as compared to the pure components. The glass transition in fruits is dominated by the most abundant low-molecular-weight compounds, in particular the mono- and disaccharides that are present in fruits. An issue with the stability of fruit-based products is that such mono- and disaccharides have very low glass transition temperatures (Roos, 1995a; Slade & Levine, 1991; You & Ludescher, 2010).

The solubility line (T_s) is another physical attribute that is integrated into the state diagram. The solubility of mono- and disaccharides generally increases with increasing temperature (Cowie & McEwen, 1974; Levine & Slade, 1986). Crystallization of carbohydrates occurs when the solution is supersaturated, i.e. when the concentration in the solution is higher than the solubility of the dissolved compound (Roos, 1995a; Slade & Levine, 1991). The solubility line and the degree of supersaturation are critical parameters that represent the behavior of a solution during the concentration process in evaporators and during the crystallization process in crystallizers (Giulietti et al., 2001). A representative state diagram shown in figure 2 with four different macro-regions.

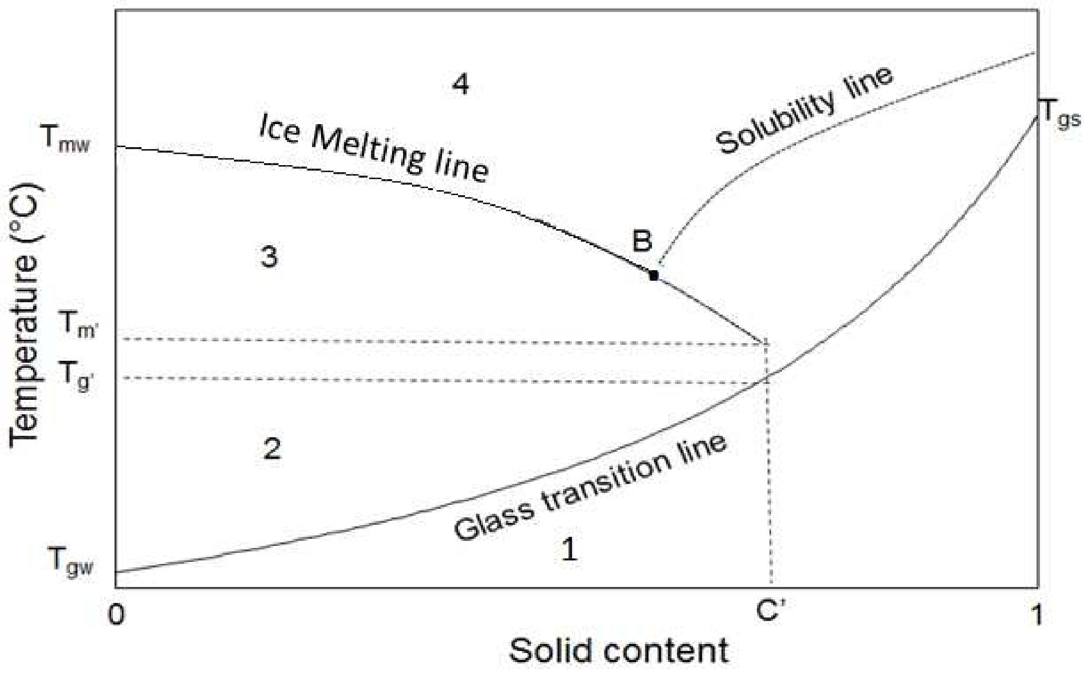

Figure 2: A typical state diagram with the macro-regions separated by phase and state transitions. The regions indicate the various phase regimes in the state diagram (Levine & Slade, 1986; Rahman, 2010). T_{mw} is the melting temperature of ice (0 ºC), T_{gs} and T_{gw} are the glass transition temperatures of the anhydrous sample and water, and T_m' is the temperature of the onset of the melting of ice in the maximally cryo-concentrated system. Point B is the eutectic point, and T_g' and *C*' are the glass transition temperature and concentration of the maximally cryo-concentrated state. Regions 1 to 4 are described in the text.

The properties of pure water are represented by the melting point (T_{mw}) and glass transition temperature (T_{gw}= −135 °C). T_{gs} is the glass transition temperature of the anhydrous material. T_g' is the glass transition temperature of the maximally freeze-concentrated solution and T_m' is the onset temperature of ice melting in the maximally freeze-concentrated solution. In this temperature can find the maximum concentration for which freezing can still occur. That is, at higher concentrations, it is no longer possible to form ice crystals when reducing the temperature (Rahman, 2010; Roos, 1995a).

Region 1 defined in Figure 2 is regime below the T_g line, where the amorphous solid is in the glassy state. In this regime, the molecular mobility is frozen out, with the exception of small molecular vibrations and the slow migration of compounds of very low molecular weight, in particular water (Karel et al., 1994; Roos, 1995a, 2010). Because of the very low molecular mobility (Roos, 1993), region 1 is the regime with the greatest stability. Above the T_g line, where the system is in the rubbery state the molecular dynamics suddenly increases, allowing for macroscopic flow and a viscosity that decreases with increasing temperature (Rahman, 2010). While the greater molecular mobility in the rubbery state is essential for processing, it also leaves the system susceptible to caking and collapse and to degradation reactions (Claude & Ubbink, 2006).

Region 2 is demarcated by the T_g line and T_g'. This is a biphasic regime, with a pure ice phase and a so-called cryo-concentrated phase, that is in the glassy state. Water is removed from the solids containing phase, forming a separate ice phase, and increasing the solid content of the solid-containing phase (Rahman, 2006). This process of cryo-concentration continues up to point *C'* (Figure 2), which is the concentration of the maximally cryo-concentrated phase. As the water content of the solids-containing phase is thus effectively decreasing, the glass transition temperature of the solids-containing phase is continuously increasing, until at point *C'*, it arrives at T_g' that is characteristic of the maximally cryo-concentrated phase.

In region 3, the temperature is below the T_m line but above T_g'. In this region, the cryo-concentrated phase is in the rubbery state. In region 3, two sub-regions need to be distinguished. Below T_m', the ice content is independent of the temperature, and the viscosity of the cryo-concentrated phase is solely determined by the temperature (Rahman, 2006, 2012; Roos, 1993). For temperatures above T_m', the ice fraction in the system is determined by the temperature, and will continuously decrease with increasing temperature until at T_m all ice will have disappeared.

Region 4, above the T_m line, represents the material in the monophasic liquid state (Slade & Levine, 1991). The regime between T_g' and T_m' can be considered as the temperature region for maximum ice formation and *B* is the eutectic point (Bessa et al., 2019;Rahman, 2009;

Suresh et al., 2017). For samples with solid content above point, C' the thermogram is relatively simple. In this case, the samples do not form ice during cooling (Bai et al., 2001)

These transitions are usually identified in thermograms by differential scanning calorimetry (DSC). DSC as a technique that determines the heat flow with high accuracy and is used to identify the solid or liquid phase transitions that produce or absorb heat (Stark & Bohmeyer, 2013). A schematic DSC thermogram showing the different phase changes that occur in a frozen food sample is shown in Figure 3.

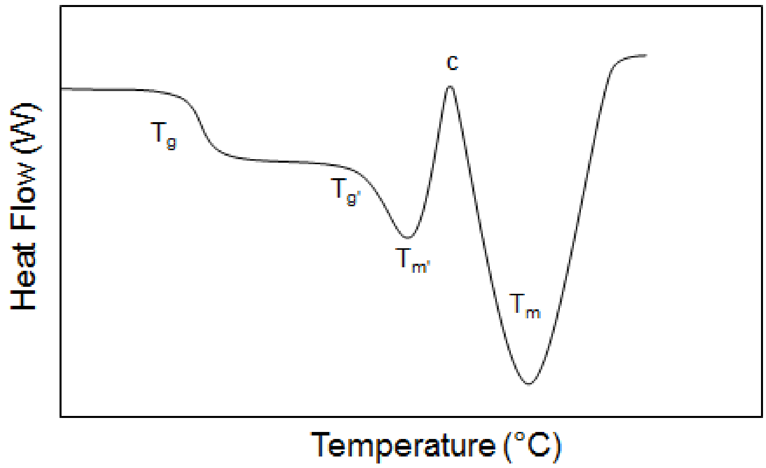

Figure 3. Example of DSC thermogram for ice-containing samples. $T_{g:}$ glass transition temperature, $T_{m'}$: end point of freezing, $T_{g'}$: glass transition for maximal freeze concentration temperature, c: overshoot, T_m melting of ice. (Bai et al., 2001; Charoenrein & Reid, 1989).

The exothermic in point *c* of the diagram is due to devitrification on rewarming and results from the crystallization of freezable water trapped in the solid matrix during the fast cooling process. This phenomenon can be avoided by isothermal holding (annealing). Studies of frozen sugar solutions have reported two low-temperature endothermic transitions previously the melting endotherm during the rewarming of samples (Bai et al., 2001; Charoenrein & Reid, 1989; Figueiredo et al., 1999; Roos & Karel, 1991; J. H. Zhao et al., 2016)

The glass transition temperature of fruits decreases with increasing water content. This sensitivity to water affects the stability during processing and storage. Models may predict the glass transition temperature. The Gordon–Taylor equation is most commonly used to model the water content-dependence of the glass transition temperature (Gordon & Taylor, 1952):

$$T_g = \frac{X_s T_{gs} + K X_w T_{gw}}{X_s + K X_w} \qquad \text{Eq. (1)}$$

Equation 1 is known as the Gordon-Taylor equation. T_{gs} and T_{gw} are the glass transition temperatures of the anhydrous solids and water, respectively. X_w and X_s are the mass fractions of water and solids and K is the Gordon–Taylor parameter that is specific to a system. Values of K = 4.52 and 5.42 are for instance reported for glucose and sucrose (Roos, 1995a)

For predicting T_m, Chen (1985) presented two general models for predicting the freezing point of solutions. The first model is for ideal solutions (Chen, 1985; Schwartzberg, 1976). The second model is a modification of the first model and includes the variable b that corrects for the non-ideal behavior of solutions at higher concentrations. Many researchers, including Grajales-Lagunes et al. (2018) and Auleda et al. (2011), have selected these models for the modeling of experimental data on various systems. Overall, the Chen models have proven to be useful in the fitting of experimental freezing data for a variety of food systems (Auleda et al., 2011; Grajales-Lagunes et al., 2018).

The Chen equation that includes the correction for non-ideality is given by (Chen, 1985):

$$T_m = T_w + \frac{K}{L_m} \ln \left[\frac{1 - X_s - b \cdot X_s}{1 - X_s - b\ X_s - E\ X_s} \right] \qquad \text{Eq. (2)}$$

T_m and T_w are the freezing temperatures of, respectively, the sample and the pure water in °C; xs is the mass fraction of solute in kg/kg solution, $K = 1000 \cdot K_f$ and K_f is the molal freezing point depression of water (K_f = 1.86 °C kg/mol). L_m is the molecular weight of pure water (L_m = 18.0 kg/kmol), E is the molecular mass ratio of water to solids and b is a parameter used to quantify the deviation from the ideality of the system (b = 0 for ideal solutions), and defines the amount of water which is ‘bound’ to the solid components.ie, water unavailable for freezing/total solids (Grajales-Lagunes et al., 2018).

Therefore, the state diagram is an important tool, widely used to correlate the composition and storage conditions of food with the changes that occurred in the food, to improve the conditions of processing and shelf life of the products (Rahman, 2009).

2.4. PHASE TRANSITIONS IN FRUITS

The main constituents of fruits are water, sugars, and fibers. Fruits, also, contain numerous minor compounds, including micronutrients that are beneficial to human health, such as phytochemicals, vitamins and folic acid that are important for the human diet (Joardder et al., 2017; ; Tejada-Ortigoza et al., 2017; Valente et al., 2011). After water, carbohydrates (mainly mono- and disaccharides) are the most abundant constituents in fruits, accounting for 50–80% of dry weight (Vincente et al., 2014). Owing to their high abundance in fruits and their low molecular weight, many important aspects of the behavior of fruits and fruit pulps can be understood based on the properties of sugar solutions. This includes the behavior during storage and the design of food structuring processes involving phase transitions (Rahman, 2006).

Mono- and disaccharides act as plasticizers for compounds of higher molecular weight owing to their low molecular weight and the great affinity to make hydrogen bonds (Mahato et al., 2019).

The glass transition is important for the stability of amorphous . Phase transitions of sugar is important in the freezing process and to frozen food to stability (Roos, 1995a). If the food is processed and stored at a temperature higher than T_g the food is in the unstable state, the rubber state. The rubber state is prone to collapse, shrinkage, and viscosity change (Joardder et al., 2017; Rahman, 2012; Roos & Karel, 1991).

In fruit-based products, such as freeze-concentrated juices, dried fruits, and fruit juice powders, the proportion of low weight molecules such as sugars (fructose, glucose, and sucrose) and organic acids are typically high (Clerici & Carvalho-Silva, 2011) and they can control the physical properties of the products (Al-Farsi et al., 2018). However, the content of both sugars and organic acids may vary significantly, depending on the variety of a fruit and it is ripening stage (Vincente et al., 2014).

The properties of high-solids products based on fruits, often powders are largely determined by the glass transition. Such products turn out to be very sensitive to changes in moisture content and temperature, owing to their high hydrophilicity and low glass transition temperatures. This gives rise to difficulties in processing and storage (Bhandari & Howes, 1999). Therefore, there is a need to understand the transition states of low molecular sugars, their mixtures at low moisture content and the products rich in sugars, to predict and optimize processing strategies or storage procedures of sugar-rich products (Jaya & Das, 2009; Rahman, 2012; Roos, 1993; Ruiz-Cabrera et al., 2016). In the sections below, we discuss the various phase and state transitions, as they are included in the state diagram for various fruits.

2.4.1. Ice Melting line of fruits

The fruit juice concentration by freezing, for example, is a process that has been widely studied, due to this technique maintaining the thermosensitive molecules and other properties of the juice. The process underlying the process consists of the first-order transition phase of ice formation, by cooling the fluid to be concentrated at temperatures below the freezing point, followed by the removal of the ice crystals (Auleda et al., 2011; Hernández et al., 2007). The freezing point is an important variable in the process for the freeze juice concentration process (Al-Farsi et al., 2018; Roos, 1987; Roos & Karel, 1991). As the freezing point is dependent on the concentration, the ice melting line needs to be constructed.

Auleda (2011) studied the freezing point of concentrated peach, apple, and pear juices for application in freeze concentration. As expected, the freezing point of the juices decreases with increasing concentration. The differences in the freezing point between the juices are due to differences in relative concentrations of the three main sugars (fructose, glucose, and sucrose). That way the authors compared the juice curves with the theory's curve for pure sugars, forming the "juice zone" the theoretical upper limit (sucrose) and lower limit (glucose). When we compare the juice zone presented by Auleda (2011) with melting ice temperature of other authors, we observe that this relationship is valid and the behavior of the phase change in solutions rich in sugars, as is the case of fruits, is predominantly determined by the concentration of simple sugars (fructose, glucose, and sucrose), such as shown in figure 4.

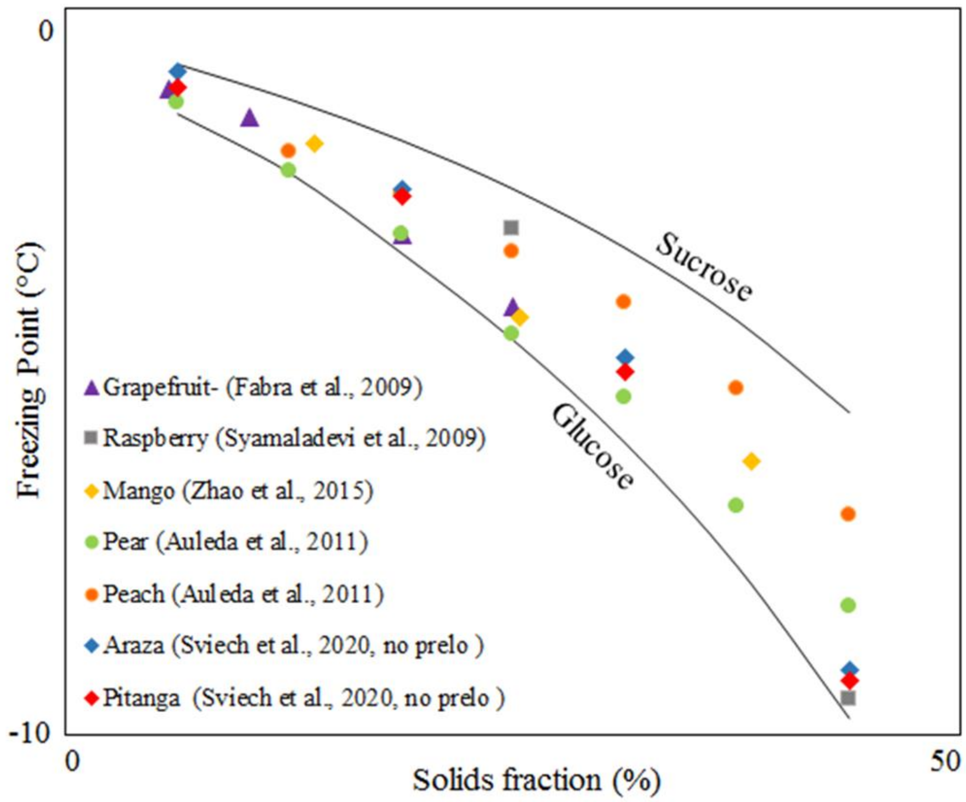

Figure 4: Juice zone and freezing point of the juice fruits from different authors compared to the upper limit (sucrose) and lower limit (glucose) determined by Auleda, et.al, 2011.

2.4.2. The Glass Transitions in Fruits

In general, the dominant carbohydrates in fruits are of low molecular weight. In particular, sucrose, fructose, and glucose are prevalent in fruits. Consequently, the glass transition temperature is low to very low, as shown in Table 2. In dry products, this therefore easily causes various undesirable physical changes such as stickiness, collapse, and sugar crystallization (Jaya & Das, 2009; Matveev et al., 2000). To avoid these physical changes, maltodextrin is widely used to increase the T_g of dry fruits, as they display a glass transition that is typically significantly higher than the pure fruit systems (Edris et al., 2016; Fongin et al., 2017). The glass transition temperature of maltodextrin varies with the dextrose equivalent (DE) value, and decreases with DE value from around 243 °C in the dry state for maltodextrin DE 6 to below 100 ºC for DE values above 50 (Goula & Adamopoulos, 2008). The T_g enhancing properties of maltodextrin were used to obtain stable preparations of freeze-dried camu-camu

(Silva et al., 2006), spray-dried tomato pulp (Goula & Adamopoulos, 2008), grapefruit juice poder (Fabra et al., 2009), spray-dried orange juice concentrate (Goula & Adamopoulos, 2008), freeze-dried strawberry (Mosquera et al., 2012), and spray-dried mango powder (Zotarelli et al., 2017).

Various researchers have studied the glass transition temperature and ice melting temperature of various pure carbohydrates (glucose, fructose, and sucrose) and various fruits. The T_m', T_g', and C' values are shown in Table 2. In the analysis of the published state diagram of the above-mentioned pure carbohydrates and fruits rich in sugar showed the T_m', T_g', C' values.

Table 2: Glass transition temperature, melting temperature, maximum solid concentration of various freeze-dried carbohydrates, fruit.

Material	T_{gs} (°C)	T_m' (°C)	T_g' (°C)	C'	References
Glucose	36	-30	-53	0.8	
Fructose	10	-48	-53	0.82	(Roos, 1993b, 1995)
Sucrose	67	-34	-41	0.82	
Maltodextrin (DE = 4–21)	100 to 243	-	-	-	(Goula & Adamopoulos, 2008)
Apple	-	-50.3	-57.8	0.74	(Bai et al., 2001)
Banana	-	-34.5	-40.8	0.74	(Rahman & Al-Saidi, 2017)
Cactus pear	18	-41,8	-55,1	0.75	(Grajales-Lagunes et al., 2018)
Date syrup	-	-	-42.8	0.73	(Al-Farsi et al., 2018)

	-	-33	-54.6	0.84	(Zhao et al., 2015)
Mango	48.9	-	-	-	(Fongin et al., 2017)
	40.8	-35.9	-50.5	0.77	(Grajales-Lagunes et al., 2018)
Orange	23.5	-35.3	-52.4	0,77	(Grajales-Lagunes et al., 2018)
Plum	-	-	−57.5	0.87	(Telis et al., 2006)
Pineapple	-	-	-51.6	-	(Telis & Sobral, 2001)
	17.5	-39.9	-54.2	0.75	(Grajales-Lagunes, et al 2018)
Raspberry	-	-38	-47	0.82	(Syamaladevi et al., 2009)
Strawberry	-	-	−51.3	0.75	(Moraga et al., 2004)
	22	-32.5	-53.2	0.76	(Grajales-Lagunes et al., 2018)
Kiwi	-	−40.4	−52	0.81	(Moraga et al., 2006)

Studies reported in Table 2, showed differences between T_g, T_g', T_m' and C' values for the same or very similar composition for fruits and sugars. These differences are probably due to residual water, differences in sample handling techniques and differences in techniques used to measure the parameters.

To maintain the stability of products that are kept under freezing, cryopreservation is used, that is, the food is kept at temperatures below its T_g’. Fruits and products rich in sugars and organic acids have a very low T_g', so it is possible to modify the formulation of food to increase T_g' to a safe and more suitable temperature (Torreggiani et al., 1999). To increase T_g', stabilizers can be used are hydrophilic polymers that disperse in the solution like colloids and this stabilizing function of these "cryostabilizers" is derived from their high molecular weight and their potential to raise the T_g' of a complex frozen system. Besides that elevating T_g', the addition of cryostabilizers causes a narrows temperature range between the glassy (stable) frozen product and a hard texture to a rubbery and smooth texture (with the desired quality to be consumed) (Levine and Slade, 1990; Miyawaki, 2018).

In ice cream processing, for example, dextran is added to the formulation to increase T_g' and cause a cryoprotective effect. Cryoprotectants have the effect of inhibiting the growth of ice crystals during the freezing step and inhibiting the recrystallization of ice and lactose during storage. (Camacho et al., 2001). Nowadays there are a lot of studies, with news cryostabilizers such as Enoki mushroom extract, for reduced the quality changes of whipped cream during frozen storage (Arai et al., 2021) or with Potential Cryoprotectant of Marine Antifreeze Proteins (Kim et al., 2017).

2.4.3. Model studies

Sugars and other components in fruits are present and the number of possible compositions is huge, but the physical properties may often be due to the principal sugar (Roos, 1995a). Authors have tried to understand the behavior of whole fruits through model systems (Grajales-Lagunes et al., 2018; Ruiz-Cabrera et al., 2016).

State diagram of model food systems prepared with glucose, fructose and sucrose mass fractions were developed for Ruiz-Cabrera, et al. (2016). For this study, 16-sugar mixtures including pure sugars, binary and ternary mixtures were prepared. On another hand, Grajales-Lagunes et al., (2018) determined the state phase transition of model food systems using different mass fractions of glucose, fructose, sucrose, pectin and citric acid and compared with five fruit juices. Both studies demonstrated that sugar composition should be considered. The parameters drawn from state diagrams of fruits T_g, T_m, T_g', and T_m' were found to be affected by the sugar composition, but in Ruiz-Cabrera, et al (2016) observed no the significant effect of the sugar composition maximum freeze-concentration (C′) values. Thus, future experimental studies to determine accurately the C' are required (Grajales-Lagunes et al., 2018; Ruiz-Cabrera et al., 2016; Ruiz-Cabrera & Schmidt, 2015). However, the study by Grajales-Lagunes et al.

(2018) reveals that both citric acid and pectin also play an important role in the thermal transitions and state diagrams of systems rich in sugars, such as fruit juices.

2.5. CONCLUSION

Studies on the optimization of processing, preservation and storage using state diagrams were previously published for conventional fruits, including strawberry, pineapple, mango and orange. However, for exotic fruits, including those that belong to the Myrtaceae family, such studies are scarcely available in the literature, notwithstanding the huge potential for the development of innovative products with important nutritional and sensory characteristics. Studies comprising preservation preserves and the process of exotics fruits can also contribute to biodiversity conservation and improve the income of local populations.

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CAPÍTULO 3: INFLUENCE OF COMPOSITION ON THE FREEZING BEHAVIOR OF FRUIT PULP OF ARAZA AND PITANGA USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

INFLUENCE OF COMPOSITION ON THE FREEZING BEHAVIOR OF FRUIT PULP OF ARAZA AND PITANGA USING DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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HIGHLIGHTS

- Tropical fruits araza and pitanga were separated in soluble and insoluble fractions
- Influence of sugars and organic acids on the ice melting line was determined
- Impact of colligative versus nonideal effects on melting behavior was determined
- Temperature-dependent ice fraction was determined from the ice melting curves
- Results enable process and product development of underutilized tropical fruits

ABSTRACT

Most Brazilian fruits are perishable but in frozen state have the potential to be developed into a variety of commercially-viable products. Pitanga and araza were investigated to determine the effect of composition on the freezing behavior using differential scanning calorimetry (DSC). Based on the composition of fruit pulp sample (WP), simulated systems (SS) were prepared containg only the principal low-molecular weight sugars (glucose, fructose and sucrose) and organic acids (citric, malic, and tartaric acids). In addition, soluble fractions (SF) were isolated from WP. Melting curves were constructed for both fruits for the three samples (WP, SS and SF) over the range of concentrations between 10 and 40 wt. %. The ice melting data is fitted well using the Chen equation for both fruits, concentrates and model systems. Deviations between the predictions of the Chen equation and the experimental data are observed mainly for the highest concentration studied (40 wt. %); these deviations can be minimized by fitting the parameters of the Chen equation to the experimental data rather than calculating them based on the molecular properties and composition of the system. We observe that the sugars have the highest impact on the melting behavior, with a limited effect of the organic acids. The melting curves are used to calculate the ice fraction as a function of temperature. Our results are useful for fruit processing to elaborate a formulation that has the desired freezing behavior.

Keywords: Tropical fruits; Ice melting temperature; Colligative properties; Un-freezable water; Ice fraction.

3.1. INTRODUCTION

Brazil has an extraordinary biodiversity of native fruits that have adapted well to the local climate. According to the Ministry of Agriculture, Livestock and Supply (MAPA), Brazil occupies the 3rd position in the world as fruit producer (Brasil, 2019). This position is due to the vast territorial extension of the country and the climatic conditions that regionally allow extensive fruit production. While many "conventional" fruits are sufficiently robust to be exported in natura, exotic fruits are, with few exceptions, highly perishable due to their thinner skins and their high water content. Therefore, fruit processing is pivotal to allow a wider distribution of these exotic fruits.

Many products based on or containing perishable fruits are processed in the frozen state, such as concentrated juices, fruit pulp and frozen whole fruits, such as berries (Fernandes et al., 2011), and frozen concoctions such as sorbet and ice cream (Celli et al., 2016). As well as decreasing undesirable reactions and to extend the shelf-life of products (Verma & Singh, 2015), the immobilization of water by ice formation helps to develop sensory attributes and modulates the product texture.

The fundamental understanding of ice formation in solutions and concentrates allows for a precise control of the freezing process and during storage in the frozen state, thereby avoiding the formation of large and inhomogeneous ice crystals (Celli et al., 2016). For products, such as juice by freezing concentrates, the freezing point of formulations must be high enough to allow adequate ice crystal production, with a greater percentage of frozen water, which reduces the effects of heat shock in retail and conventional home freezers (Smith & Bradley, 1983). For products that are directly consumed in the frozen state, such as ice cream and sorbet, the melting point should conversely be sufficiently low so that the ice crystal fraction remains limited, as otherwise the product texture will get too hard and grainy (Kerr, 2006). The melting curves of solutions and concentrates are employed to determine the proper temperatures for processing and storage (Kerr, 2019; Sá & Sereno, 1994). The increased concentration of such solids changes the colligative properties of the residual water in the cryo-concentrated phase (Glover, 1975; Van der Sman, 2016).

Differential scanning calorimetry (DSC) is one of the most useful experimental techniques to identify phase transitions in food systems, as it is a sensitive probe for heat effects that are associated with these transitions (Biliaderis, 1983). While several techniques can be employed to determine the ice melting curves of solutions and concentrates, DSC is a preferred technique as it 1. Provides results that can be consistently interpretated; 2. Provides quantitative results about the multifarious processes that accompany the melting transition; 3. Allow for the unambiguous identification of such processes, including the melting enthalpy and the glass transition temperature of the cryo-concentrated state and 4. Can be implemented using only minimal amounts of samples (Layer, 2002; Šesták, 1979; Shalaev & Franks, 1995; Svoboda & Málek, 2011). In the light of the usefulness of DSC to determine the melting transition, various authors have developed protocols to determine the melting temperature and the glass transition temperature of the maximally cryo-concentrated state (Champion et al., 2000; Goff et al., 2003; Vásquez et al., 2013).

Thermal properties were previously determined for several fruits, including blackberries, pineapple, apples, strawberries, blueberries, grapes and mangoes (Aggarwal, 2001; Bazardeh & Esmaiili, 2014; Figueiredo et al., 1999; Moraga et al., 2006; Ruiz-Cabrera & Schmidt, 2015; Tamm et al., 2016; Vásquez et al., 2013). These thermal properties were used to construct state diagrams of fruits (Vásquez et al., 2013). The state diagram includes the melting and glass transition temperature curves as a function of the solid concentration or water content of the samples. In addition, the maximally cryoconcentrated state can be plotted in the state diagram (Rahman, 2004). For fruits, comparing data between different data sets on the same fruit is difficult since the fruit composition is rather significantlty dependent on the specific variety, seasonality, soil conditions and climatatic conditions, impacting the phase and state transitions. In principle, this would require constructing a melting curve for each harvest or processing batch; this is, however, is impracticable as it is very time-consuming and costly.

A structured approach to this issue of variability between different batches of fruits is by realizing that the freezing point depression is principally influenced by the solids non-volatile, and that furthermore only a limited number of such low molecular weight compounds are present in most fruits at appreciable concentrations. Thus, knowledge of the composition of such low molecular weight compounds, for fruits specifically sugars and organic acids of low molecular weight (Roos, 1993), is expected to allow a prediction of in the colligative properties, including the freezing behavior, of individual batches, provided that a predictive model is available.

In the present study, the composition of two fruits (pitanga and araza) that are commercially available but not yet used on wide scale was employed to explore the influence of sugar and organic acids on the thermal transitions in the sub-zero domain. Therefore, the objectives of this investigation were the following: to determine the ice-melting curve of dry whole pulp fruit (WP), soluble fraction (SF) and simulated systems (SS) using DSC. The pre-selection of fruits was based on a literature review carried out in a previous study by our research group that demonstrated the lack of available information on state diagrams of these fruits. These simulated systems consist of the prevalent mono and disaccharides and the organic acids in the fruits, in the molecular ratios as we determined for the WP samples. Then, we evaluated whether the Chen equation and the assumptions underlying this equation are compatible with the experimental results obtained on WP, SF and SS, as this allows us to determine the influence of colligative properties on the melting behavior of araza and pitanga.

3.2. MATERIALS AND METHODS

3.2.1. Materials

Sucrose, fructose, glucose and citric, malic and tartaric acid were obtained from Sigma-Aldrich (purity 99%). Enzymatic kits to determine the content of sucrose, glucose and fructose were obtained from K-SUFRG, Megazyme International (Bray, Ireland). Solvents were purchased from Fisher Scientific and were of the highest available purity.

3.2.2. Preparation of samples: pulp, soluble solid fraction and simulated system from fruits

Pitanga (Eugenia uniflora) and araza (Psidium cattleianum) belong to the Myrtaceae family and could have important economic perspectives (Teixeira et al., 2019). Samples 1, 2 and 3 (WP, SF and SS) for pitanga and araza (described below), were prepared 10, 20, 30 and 40 wt.% solids soluble and stored in Eppendorf at -18°C, to be submitted later to DSC analyses for determination of freezing temperatures.

3.2.2.1. Sample 1: Whole freeze-dried pulp fruit

Araza and pitanga pulps were obtained from the Sitio do Bello Industry (São Paulo, Brazil) and immediately frozen at -18 °C. Samples to be freeze dried were first frozen at -60 °C for 24h and then transferred a Terrroni lyophilizer (LH 2000TT, Brazil). Freeze drying was carried out for 48 h at -48 °C and a pressure of 1.33 Pa. These samples are designated as whole pulp pitanga (WP-P) and whole pulp araza (WP-A).

3.2.2.2. Sample 2: Freeze-dried water-soluble fraction of pitanga (SF-P) and araza (SF-A)

The unfrozen pulp samples were centrifuged in a Thermo Scientific Sorvall ST 8R centrifuge at 9500 gx for 30 min. The fractions (after separation) were weighted to determine the separation yield. The soluble fraction was submitted to the freeze-drying process as outlined above. These samples are designated as soluble fraction of pitanga (SF-P) and soluble fraction of araza (SF-A). After the separation of the soluble part (SF-P and SP-A).

3.2.2.3. Sample 3: Simulated systems based on pitanga (SS-P) and araza (SS-A) composition

Following the determination of the amount of sugars and organic acids in the fruit pulp samples, simulated systems were prepared following the schematic representation shown by Equation 1:

$$\text{Simulated System} = \left(X_g + X_f + X_s + X_c + X_m + X_t\right).\%\,T_s + \text{water} \quad \text{Eq. (1)}$$

These simulated systems consist of the mass fractions of glucose (X_g), fructose (X_f), and sucrose (X_s), and the organic acids citric acid (X_c), malic acid (X_m) and tartaric acid (X_t) as determined for the pulp of pitanga and araza. Crystalline sugars were ground using a mortar and pestle before dissolving them in deionized water. Final concentrations ($\%T_s$) of 10, 20, 30 and 40 wt. % were prepared for determining the ice melting temperature T_m.

The equivalent molecular weight of each simulated matrix was calculated:

$$M_{w\_fruit} = \sum M_{wi} X_i \quad \text{Eq. (2)}$$

Where the subscript "i" represents a the compounds of the simulated system (sugar or organic acid), X_i, is the corresponding mass fraction of the compound and $M_{W,i}$ is its molecular weight. The following compounds were used: glucose ($M_{W,g}$ = 180.16 g/mol, fructose ($M_{W,f}$ = 180.16 g/mol), and sucrose ($M_{W,g}$ = 342.3 g/mol), as low molecular-weight carbohydrates, and citric acid ($M_{W,c}$ = 192.12 g/mol), malic acid ($M_{W,m}$ = 134.08 g/mol) and tartaric acid ($M_{W,t}$ = 150.08 g/mol) as organic acids.

3.2.3. Methods

3.2.3.1. Macrocomponent composition

The weight of the fruits was determined using an analytical balance with an accuracy of 0.001 g. Whole integral pulp was characterized by moisture using AOAC method 934.06 (AOAC, 1996) by drying 5 g of the samples in a vacuum oven (FANEM, model 099EV) at 70 °C for 48 hours, Total soluble solids were determined using a portable digital refractometer (model K52-032, Kasvi, China) and the results are expressed in ºBrix. The total sugar content was obtained using the 3,5-dinitrosalicylic acid (DNS) method (Maldonade et al., 2013). All analyses were performed in triplicate and the results are expressed in g sugar/100 g of wet pulp. and titratable acidity was determined by titration with a 0.1 N sodium hydroxide solution (NaOH), according to AOAC method 942.15A (AOAC, 1996). The results were expressed as g of acid per 100 g of wet pulp.

After the lyophilized, the water content of the samples: Whole freeze-dried for pitanga (WP-P) and araza (WP-A) were determined using AOAC method 934.06 (AOAC, 1996) by drying 5 g of the samples in a vacuum oven (FANEM, model 099EV) at 70 °C for 48 hours. The protein content was determined by the Dumas method (NDA 701, VELP Scientifica, Italy). The lipid content was determined according to the method of Bligh and Dyer (Bligh & Dyer, 1959) Fibers were determineted by AOAC method, 978.10 method (AOAC, 1996). The mineral residue (ashes) was determined according to AOAC method 900.02 by submitting the samples to 550 °C. The results were expressed in g/100 g of sample (AOAC, 1996). The carbohydrate content was determined by difference.

3.2.3.2. Characterization of the composition of low molecular weight compounds

The content of sugars and organic acids were determined for Freeze-dried water-soluble fraction of pitanga (SF-P) and araza (SF-A). The contents of sucrose, D-fructose and D-glucose were determined using commercial enzymatic assays (K-SUFRG, Megazyme International, Bray, Ireland). In short, this involved converting each sugar to glucose-6-phosphate (G6P) and quantifying NADPH after oxidation in the presence of NADP + and G6P-dehydrogenase. All experiments were performed in triplicate. The results were expressed in mg/g of dry sample.

The content of organic acids was determined according to the HPLC-method proposed by Scherer et al. (2012) with a Waters 600 HPLC System (Milford MA. USA) equipped with degasser, quaternary pump (Waters 600), autosampler (Waters 717), diode array detector (Waters 996) and an interface Waters 600 Controller, running under the Empower Pro Software (Scherer et al., 2012). The compounds were quantified by external standard calibration. All samples were performed in triplicate the results expressed in mg acids/g de dry sample.

3.2.3.3. Melting temperature analysis by Differential Scanning Calorimetry (DSC)

Melting temperatures were firstly determined at one concentration (30 wt. %), to optimize the DSC protocol. Then, all samples (WP, SF and SS) of pitanga and araza at 10, 20, 30 and 40% wt. solids soluble were submitted to DSC analyses for determination of freezing temperatures.

The thernograms of samples at different water contents at 25 °C were obtained using a DSC (TA2010, TA Instruments, Delaware, USA) equipped with a thermal control system (TA5000, TA Instruments, Delaware, USA). Samples of approximately 15–60 mg were hermetically sealed in DSC pans. The DSC was calibrated using indium (T_m = 156.6 °C, dHm = 28.6 kJ/kg) and gallium (T_m = 29.8 °C, dHm = 79.9 kJ/kg). The energy calibration was also performed simultaneously with the known enthalpy of fusion of each of these melting transitions. Estimated errors in temperatures and in energies are, respectively, below 0.5 ºC and ~5% of the measured energies. Nitrogen was employed as the purging gas at a flow rate of 50 ml/min, and an empty DSC pan was used as a reference for each experimental test. Analyses were performed in duplicate. The DSC protocols are listed in Table 1.

Table 1. DSC protocol for determining the glass transition temperature of the maximally cryo-concentrated phase (T_g') and melting temperature of ice (T_m).

Ramp	T_g'	T_m
1	20 °C → -60 °C (-5 °C/min) Isothermal -60 °C (3 min)	20 °C → -60 °C (-5 °C/min) Isothermal -60 °C (3 min)

2	-60 °C→ -10 °C (10 °C/min) Isothermal -10 °C (3 min)	-60 °C → -10 °C (1 °C/min) Isothermal -10 °C (3 min)
3	-10 °C → - 60 °C (.1 °C/min) Isothermal -60 °C (3 min)	-10 °C → -40 °C (1 °C/min)
4	-60 °C → -30 °C (-5 °C/min) Isothermal -30 °C (3 min)	-40 °C → -60 °C (-5 °C/min) Isothermal -60 °C (3 min)
5	-30 °C → -60°C (5 °C/min) Isothermal -60 °C (3 min)	-60 °C → 5 °C (1 °C/min)
6	-60 °C → 5 °C (1 °C/min)	-
Analysis	Intersection of tangent of low-temperature baseline and tangent at the inflection point (ramp 5)	Peak (ramp 5) estimated at -5 °C.
Samples	WP, SF and SS at 30 wt. %	WP, SF and SS at 10, 20, 30, 40 wt. %

We fit the T_m data using the Chen equation (Chen, 1985):

$$T_m = T_w + \frac{K}{L_m} \ln \left[\frac{1 - X_S - bX_S}{1 - X_S - b\, X_S - E\, X_S} \right] \quad \text{Eq. (3)}$$

In Eq. (3) T_m and Tw are the freezing temperatures of, respectively, the concentrate and pure water in °C; xs is the mass fraction of solute in kg/kg solution, $K = 1000 \cdot K_f$ and K_f is the molal freezing point depression of water (K_f = 1.86 °C kg/mol); *Lm* is the molecular weight of pure water (18.0 kg/kmol). E is the molecular mass ratio of water to solids (Lm / M_w) and b is a parameter used to quantify the deviation from the ideality of the system (b = 0 for ideal solutions), and defines the amount of water which is 'bound' to the solid componentes or kinetically hindered from freezing, i.e., the water unavailable for freezing/total solids (Grajales-Lagunes et al., 2018). We estimate b from the solids concentration of the maximally freeze-concentrated phase (*C'*) for state diagrams of sugar-rich foods. This concentration *C'* is determined from the intersection of melting curves with glass transition temperature curves of the samples (manuscript in preparation) (Cardoso et al., 2020 no prelo) and defines the corresponding value of $T_{g'}$.

The Chen equation was first derived by Schwartzberg (1976) and later applied by Chen (1985) to analyze the freezing behavior of meat and fish (Chen, 1985; Schwartzberg, 1976). The Chen equation arises from the definition of the chemical potential and activity of water in solutions.

Furthermore, the colligative nature of the freezing point depression is accounted for by one lumped parameter, *E,* that accounts for the molar mass ratio of water to solutes. For predicting the freezing point, Chen (1985) presented two general models for predicting the freezing point of solutions. The first model was for ideal solutions based on the model proposed for (Chen, 1985; Schwartzberg, 1976). The second model to introduce the variable *b* for correct for the non-ideal behavior of solutions at higher concentrations. The first model can not be used to predict the freezing point depression of fruit juices because fruit juices do not show ideal behavior. Nevertheless, researchers, such as Grajales-Lagunes (2018) and Auleda (2011), have depicted from these models for further studies and they have proven to be useful albeit highly approximate in the fitting of experimental freezing data for a variety of food systems (Auleda et al., 2011; Grajales-Lagunes et al., 2018).

3.2.3.4. Equilibrium ice fraction

The fractions of ice and unfrozen water in a food are strongly depend on temperature. The Eq. 3 was inverted (Eq. 4) to determine the solids fraction of the cryo-concentrated phase in weight fraction ($x_{s,\ cryo\ (T)}$) in temperature below ice melting curve (T_m):

$$X_{s,cryo(T)} = \frac{\exp\left[\frac{L}{K}(T_m - T_w\right] - 1}{(1+b+E).\exp\left[\frac{L}{K}(T_m - T_w)\right] - (1+b)} \qquad \text{Eq. (4)}$$

The weight fraction of ice (Q_{ice}) was determined according to the lever rule from thermodynamics to Equation 5 (Kirkwood & Oppenheim, 1961):

$$Q_{ice} = \frac{x_{s,cryo\,(T)} - x_s}{x_{s,cryo(T)}} \qquad \text{Eq. (5)}$$

3.2.3.5. Statistical analysis

Statistically significant differences between mean values were evaluated by statistical analysis for comparison of the estimated and predicted parameters using a Student's t-test for means of two paired samples ($\alpha = 0.05$). All statistical analysis was performed using R software (R Development Core Team. 2017, Vienna, Austria). For the fit of the Chen equation (Eq. 3) to the experimental data, a non-linear fitting procedure was used employing the Solver utility in Excel (Microscoft Excel 2013). In the fitting, the residue $(T_{m,exp} - T_{m,fit})^2$ was minimized for all combinations (x_s, T_m) under simultaneous variation of the parameters E and b for fixed values of T_w, K_f and L_m. As initial values for the fit, the parameter values as calculated based on the composition of the system were used.

3.3. RESULTS AND DISCUSSION

3.3.1. Composition

Fresh fruits pulps are multicomponent systems containing solids that are dispersed and solubilized in water. The macrocomponents of araza and pitanga pulps were characterized using the methods outlined in Section 3.2.3.1 and the results are shown in Table 2.

Table 2 Characterization of pulp fruit and mass balance of the pulp fractions.

	Pitanga	**Araza**
Water content (wt. % wet basis)	89.6 ± 0.05 [a]	86.3 ± 0.1 [b]
Soluble Solids (°Brix)	8.9 ± 0.1 [a]	9.0±0.06 [a]
Total sugar (g glucose/100g on wet basis)	5.62 ± 0.12 [a]	5.14 ± 0.14 [b]
Acidity (g acid/100g on wet basis). % wet basis)	1.88 ± 0.01 [a]	1.91 ± 0.02 [a]
Soluble fraction (wt. % dry basis)	83.8 ±1 .3[a]	64.6 ± 1.0[b]
Insoluble fraction (wt. % dry basis)	13.8 ± 0.5[a]	33.6 ± 0.5[b]

Results reported as mean ± standard deviation. Entries in the same row that are indicated by different letters are statistically different ($p < 0.05$).

The soluble and insoluble fractions from the WP were determined as percentage of the freeze-dried pulps, as shown in Table 2. Araza and pitanga show similar amounts of soluble solids (~ 9 °Brix) and acidity (~ 1.9%), differing from the quantity of insoluble solids present in the whole pulp: 33.6% for araza and 13.8% for pitanga. The quantity of soluble solids determined by °Brix, resulted in solids contents of 85.8% and 65.7 wt. % for pitanga and araza, respectively. These values are slightly different from those found in Table 2. This is likely related to experimental differences among determinations.

The largest components in fruit pulps consist carbohydrates, with 81.7% and 61.5% for pitanga and araza, respectively. This fraction includes the total soluble sugars and soluble fibers such as pectins. The total fiber determined for pitanga (4 g/100 g) corresponded to just 29% from the insoluble material found by centrifugation (insoluble Table 2). For araza, the fiber content represented 83.3% of insoluble fraction. A main part of the insoluble material of araza consists of celulose (Damiani et al., 2011). However, high molecular weight compounds should not have an influence on the colligative properties (Glover, 1975).

Araza is characterized by similar amounts of insoluble and soluble solids, but had a total acidity that was higher by a factor 3.5 than reported in a previous study (Damiani et al., 2011). Frozen pitanga pulp with 12.3% of total solids, represented 17% more total sugar content and 60% from the total acidity content that those determined in this work (Santos et al, 2002). One should keep in mind, however, that the molecular composition of fruit varies according to climatic and soil conditions, harvesting time, as well as plant species.

Table 3. Centesimal characterization of freeze-dried pulp.

	Pitanga (WP-P)	**Araza(WP-A)**
Water content (wt. % wet basis)	2.3 ± 0.01[a]	1.8 ± 0.05 [b]
Soluble carbohydrates* (wt. % wet basis)	81.7	61.49
Protein (wt. % wet basis)	4.88 ± 0.03[a]	2.46 ± 0.03[b]
Fat (wt. % wet basis)	3.6 ± 0.38[a]	2.2 ± 0.3[b]
Fiber (wt. % wet basis)	4.0 ± 0.3[a]	28.0 ± 0 .5[b]
Ashes (wt. % wet basis)	3.4 ± 0.07[a]	4.14 ±0 .06[a]

Results reported as mean ± standard deviation. All values are in wt. %
*calculated by difference.

The total sugar and acidity determined in the samples is lower than the difference of soluble solids (15.7 wt. % for pitanga; 21.7 wt. % for araza). Vitamins, pigments, pectin and other carbohydrates that are not determined likely account for the observed differences. For instance, for araza, Damiani (2011) reported 0.5 g/100 g of soluble pectin, and Franco (1999) reported 0.32 g of vitamins, including ascorbic acid, per 100 g of fruit pulp.

By separating the fruit pulp in soluble and insoluble fractions, essentially all of the mono- and disaccharides and the organic acids should be concentrated in the soluble fraction, whereas the fibers should remain in the insoluble fraction. The pulp of both pitanga and araza contained a large soluble fraction, corresponding on average to 83.8 wt. % from pitanga pulp and 64.6 wt. % from araza pulp, on dry basis. The content of the sugars and organic acids of the dried pulps is shown in Table 4. Table 4 also shows the relative concentrations in terms of the mass fraction (Xi) for the sugars (glucose, fructose, and sucrose) and organic acids (citric acid, malic acid, and tartaric acid) content, measured in solids fraction samples for pitanga and araza (SF-P and SFA, respectively) measured in araza pulp and in pitanga pulp of the in this work. These values were used in preparing the simulated solutions.

Table 4: Composition of low molecular weight compounds of the soluble fraction of pitanga and araza pulp and mass fractions of the sugars and organic acids of the simulated systems.

Compound	**Concentration in soluble fruit pulp fractions (mg/g)**		**Mass fraction Xi in simulated systems (-)**	
	Pitanga (SF-P)	**Araza (SF-A)**	**Pitanga**	**Araza**
Sucrose	55.3 ± 0.7	38.6 ± 0.7	0.64	0.60
Fructose	66.2 ± 0.3	54.9 ± 0.5	0.11	0.13
Glucose	371.2 ± 0.7	215.6 ± 0.4	0.10	0.09
Citric acid	59.0 ± 0.6	67.5 ± 0.7	0.10	0.16
Malic acid	24.8 ± 0.3	6.7 ± 0.1	0.04	0.018
Tartaric acid	3.95 ± 0.05	0.78 ± 0.04	0.01	0.002

Results reported as mean ± standard deviation

The concentration of all sugars was significantly higher for pitanga than for araza, but the relative presence of the sugars in both samples followed the same order: glucose > fructose > sucrose. For pitanga, the concentration for glucose was 5.6 times higher than the concentrations of fructose (66.20) and 6.7 times higher than sucrose. In the case of araza, the levels were 3.9 and 5.6 higher when glucose was compared to concentrations of fructose and sucrose, respectively.

Regarding to the organic acid composition, araza was found to be the richest in citric acid, while the malic and tartaric acid contents were about four times higher for pitanga than for araza. The total acidity is directly linked to the content of organic acids. Damiani et al. (2011) have also quantified the ascorbic acid in addition to the above three organic acids, and ascorbic acid represented about 7 % from the total acid determined.

According to the concentrations of the sugars and acids organics in the samples (Table 4) and their molecular weights, the equivalent molecular weight of each pulp fruit was be calculated following Equation 2. The equivalent molecular weight of the simulated systems is 193.8 g/mol for pitanga and 197.6 g/mol for araza.

3.3.2. Melting temperature by Differential Scanning Calorimetry (DSC)

Thermograms were obtained in duplicate for fruit pulp (WP), the soluble fraction extracted from the fruit pulp (SF) and for the simulated system (SS) for both araza and pitanga. Examples of the thermograms for SS-P and SS-A are shown in Fig. 1. The sigmoidal transition that is observed at the lower temperatures was associated with the glass transition temperature of the maximally freeze-concentrated sample (T_g'). The endothermic peak at somewhat higher temperatures was associated with the melting trajectory of ice in the freeze-concentrated matrix (T_m) (Ruiz-Cabrera et al., 2016). T_m, which is the highest temperature at which ice crystals occur, is indicated in the thermogram. For example, for the sample shown in (a) value of T_m = -3.8°C; (b) T_m = -3.75°C; (c) T_m = -3.85°C; (d) T_m = -3.81°C ; (e) values of T_g' = −57.46 °C and T_m = -3.9 °C and (f) values T_g' = −54.11°C and T_m = −3.8 °C were obtained at a solids content of 30% (wet basis). All the results from the DSC analysis are collected for various concentrations of both the pitanga and araza samples in Table 6.

The T_m values are very similar when comparing the fruit pulp samples (WP), soluble fraction based on fruits (SF) and the simulated systems (SS), but for Araza, the deviation is greater at highest solid content. Statistical analysis for comparison of the estimated and predicted parameters using a Student's t-test for means of two paired samples ($\alpha = 0.05$) are given in Table 6.

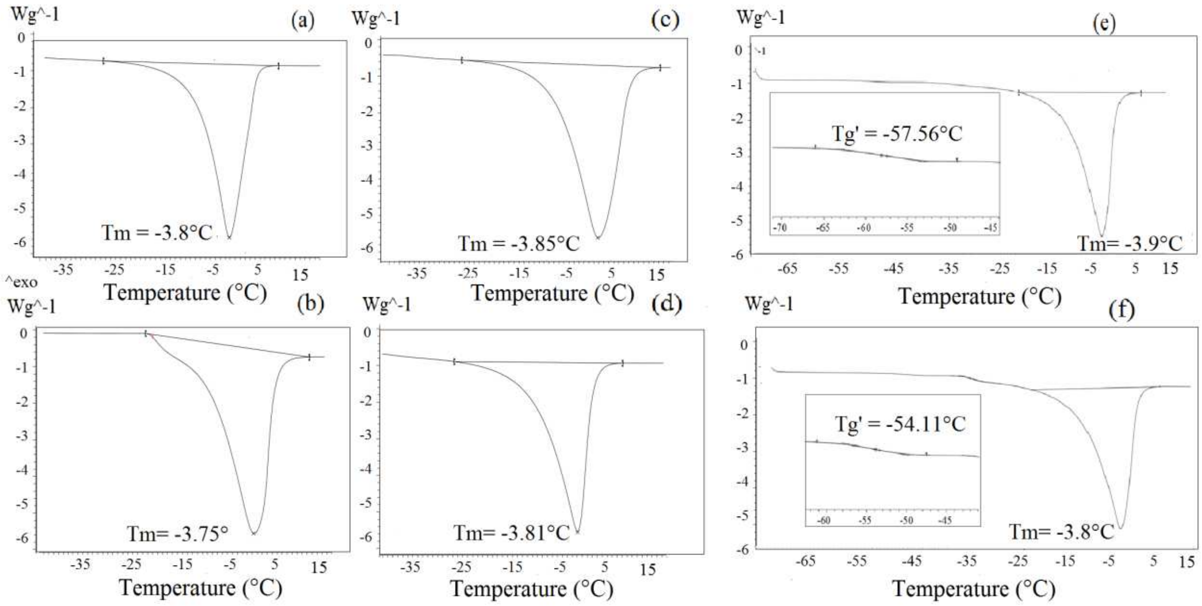

Figure 1. Thermograms at a solids content of 30% (wet basis) for (a) WP-P; (b) WP-A; (c) SF-P; (d) SF-A; (e) SS-P and for (f) SS-A content of 30 %. T_g' and T_m for sample of SS are indicated on the thermograms.

Table 6: Ice melting temperature T_m for the soluble fraction (SF), simulated systems (SS) and whole pulp (WP) for pitanga and araza for various weight fractions of solids.

Concentration of soluble solids (% wet basis)	T_m (WP-P) (°C)	T_m (SF-P) (°C)	T_m (SS-P) (°C)	T_m (WP-A) (°C)	T_m (SF-A) (°C)	T_m (SS-A) (°C)
10	-0.19 ± 0.01[a]	-0.2 ± 0.02[a]	-0.2 ± 0.01[a]	-0.19 ± 0.01[a]	-0.2 ± 0.01[a]	-0.19 ± 0.01[a]
20	-1.82 ± 0.02[a]	-1.84 ± 0.02[a]	-1.87 ± 0.01[a]	-1.64 ± 0.01[b]	-1.66 ± 0.02[b]	-1.68 ± 0.02[b]
30	-3.82 ± 0.01[a]	-3.86 ± 0.02[a]	-3.89 ± 0.01[a]	-3.76 ± 0.02[b]	-3.79 ± 0.02[b]	-3.80 ± 0.01[b]
40	-7.05 ± 0.01[a]	-7.14 ± 0.02[a]	-8.1 ± 0.01[b]	-5.0 ± 0.01[c]	-5.05 ± 0.01[c]	-7.28 ± 0.02[d]

Results reported as mean ± standard deviation. Entries in the same row that are indicated by different letters are statistically different ($p < 0.05$). Test of T student compere WP with SF and SF with SS.

The melting curves of SF-A and SF-P are shown in Figure 2. As expected, T_m decreases with increasing concentration for all samples. As a colligative property, the freezing point depression of water is principally determined by the presence of non-volatile small molecular weight-substances, due to the increased mixing entropy. The entropy change that occurs when non-volatile solutes are added to a solvent. Thus, when containing non-volatile small molecules in a solution, solvent energy is more dispersed and its entropy is increased as compared to the pure solvente (Lambert, 2002).

A freezing point depression (FPD) of almost 8 °C was observed for SF for pitanga (a) at the highest concentration tested (40 wt. %) The FPD for araza Figure 2 (b) was lower. The melting behavior of their respective simulated systems (SS) are also shown in Figure 2. The SS was prepared by mixing solutions representing all sugars and three of the organic acids that constitute about 50% of the total organic acid content in the sample fruit (Table 4).

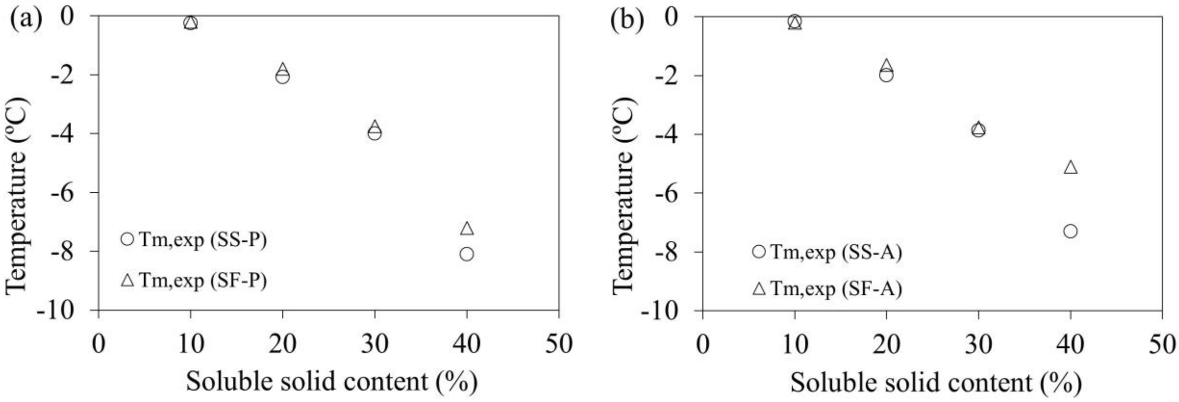

Figure 2. Melting ice for pitanga (a) and for araza (b), of soluble fraction (SF) were compared with their respective simulated systems (SS).

The T_m curves for the SF samples were similar to the T_m curves for the SS samples for both fruits. The superposition of these curves indicates that the simulated system samples (SS) adequately represent the behavior of the soluble solids samples. However, the SS-A samples at the highest concentration (upon 40%) do not adequately represent the behavior of the SF sample. Moreover, the influence of sugar content is dominant since they contribute to overall 80% of the soluble fraction in the fruit (Table 4). Moreover, it appears that the undetermined fraction of organic compounds does not influence the melting behavior to a significant degree.

Since the physical reasoning for the melting behavior of the whole solids and simulated solution is the same, the application of a model that takes into account the contribution of each component can be fitted to analyze the influence of components. Table 6 shows the fitted parameters found for the SS and the SF samples for pitanga and araza. As expected, these parameters are significantly influenced by the sugar and organic acids mass fractions. Consequently, mathematical models for constructing the state diagram, parameters based on the type and mass fraction of the main solutes of fruits are required.

Table 7: Parameters predicted and fitted from the Chen equation (Eq. (3).

Sample		**Predicted parameters**		**Fitted parameters**	
	M_w	E	b	E	b
SS-P	193.8	0.092	0.57	0.088	0.34

SS-A	197.6	0.091	0.37	0.062	0.60

Variable M_w was determined for equation 2, E and b predicted was determined according to section 2.3.3. Paramenters E and b fitted was determined using A non-linear regression procedure was used to adjust the experimental data for model Eq. (3)

A non-linear regression procedure was used to adjust the experimental data for the model Eq. (3) using Microsoft Excel (2013), and the model curve shown in Fig. 3 pitanga simulated system (a) and for the araza simulated system (b).

Figure. 3 shows the results of fitting Eq. (3) to the T_m data of the simulated systems of pitanga (SS-P) and araza (SS-A).

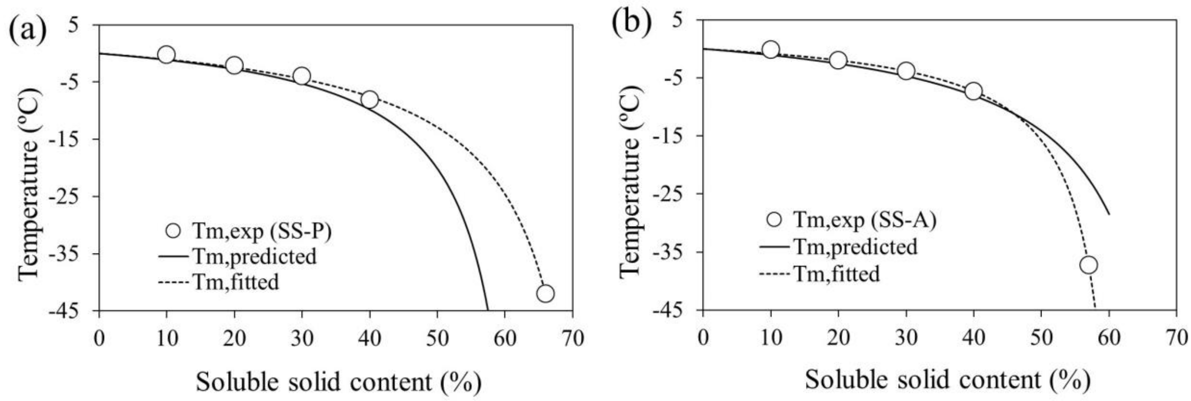

Figure 3. T_m data for pitanga and araza and T_m curves as predicted by and fitted to Eq. (3) for SS-P (a) and for SS-A (b).

From the curves in Figure 3, the deviation of the Chen equation (Eq. 3) with the predicted parameter values from the experimental data becomes more proncounced the higher the concentration. This is caused by non-ideality of the solutions resulting from the interactions of the solutes with the solvent. These non-idealities are taken into account in the Chen equation only via the fraction of unfreezeable water, which does not account for the true intermolecular interactions as they occur in concentrated solutions. Deviations between the Chen equation and experimental data was previouslyt observed for other fruit systems such as apples, peaches, pears, citric fruits (Auleda et al.,2011)

3.3.3. Influence of organic acids and sugar on T_m

Owing to their comparable molecular weight, changes in relative amounts of organic acids and monosaccharides do not contribute to a significant change in the effective molecular weight of the fruit solids. Their effect on T_m is consequently very similar. Figure.4

(a) and (b) show the curves obtained from Eq. 3 for the composition of organic acids and monosaccharides as specified in Table 5, and for the monosaccharides only. It is clear that, owing to their relative low abundance, the organic acids contribute only rather marginally to the freezing point depression. By far the largest effect is due to the monosaccharides.

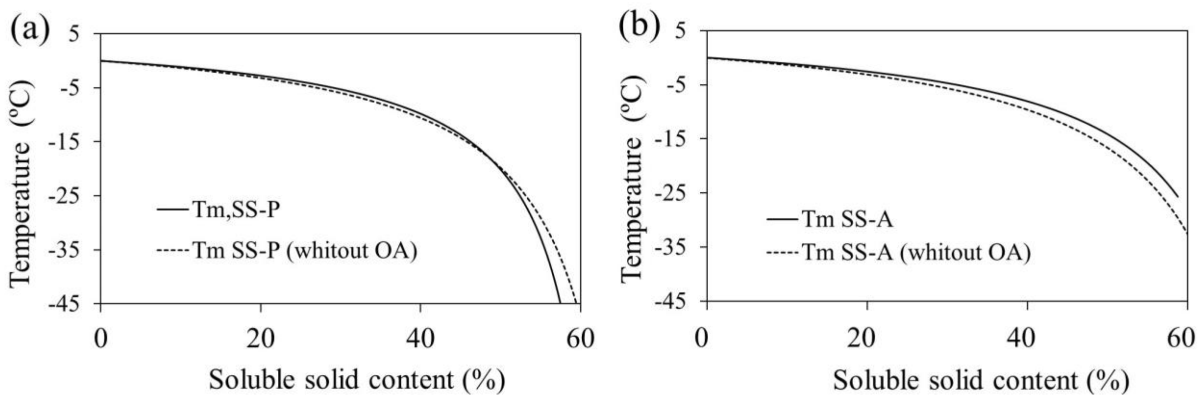

Figure. 4. T_m curve as predicted by the Chen equation (Eq. 3) for the simulated systems for pitanga (SS-P) (a) and for araza (SS-A) (b) compared to the T_m curve for the carbohydrates only (i.e. without organic acids).

As mentioned above, we did not account for all organic acids present in the system. However, in lower concentrations, below of 30 wt.% for araza and and 40 wt.% for pitanga, the presence of organic acids did not shift the curve. Thus, the mathematical model gives a fair prediction regardless the presence of organic acids.

As mentioned, we did not account for all organic acids present in the system. However, in lower concentrations, below of 30 wt. % for araza and below 40 wt. % for pitanga, the presence of organic acids in the amounts that we determined did not lead to appreciable shifts of the T_m curves. Thus, for case of pitanga and araza samples, with a relatively high amount of sugars and a fairly low amount of organic acids, the Chen equation gives a fair prediction of the T_m regardless if the organic acids are taken into account. This finding is in line with reports in the literature. Auleda et al. (2011), for example, report the T_m curves for apple juice, pear juice and peach juice and compare them to the T_m curves of only the sugars sucrose and glucose, and found the impact of the organic acids to be fairly limited.

Auleda et al (2011) furthermore evaluated clarified and depectinized juices, i.e. juices from which the insoluble fractions are removed. As for our soluble fractions of araza and pitanga, the juices turned out to be largely composed of sugars and other soluble compounds such as organic acids, vitamins and pigments (Auleda et al., 2011). As the compound with the highest molecular weight that contributes significantly to T_m in fruit juices is typically sucrose and as the compound with the lowest molecular weight that contributes significantly to T_m is glucose, the freezing point of any juice should be in the area between the T_m curves of sucrose and glucose. This area is commonly called the "juice zone" this behavior may also be verified from data for other juices, such as orange juice (Chen et al., 1990) and mango and papaya (Telis et al., 2007).

3.3.4. Equilibrium ice fraction

In the freezing region (below the ice melting curve), the ice fraction and the fraction of the cryo-concentrated phase are dependent on temperature. The dependence of the ice fraction on temperature is particularly important close to T_m, and changes in temperature cause important changes in thermal properties with temperature difference in such properties as specific heat and thermal conductivity between water and ice. In frozen food, some part of the water in the system is frozen and the other part left unfrozen because the physical state of water is heterogeneous (Pradipasena et al., 2007; Schwartzberg, 1976). Furthermore, the change in ice fraction with temperature leads to a coarsening of the ice crystal size distribution upon temperature cycling.

The determination of the ice fraction is thus very important both for the prediction of thermal properties for the simulation of freezing and thawing of food. Whereas we employ the le ver rule to determine the ice fraction, an alternative route was used e.g. by Chen (1985) who reported the ice fraction for meat, fish, and fruit juices based on the analysis of enthalpy (Chen, 1985).

Based on Eq. 4 and 5, ice fraction of SS-P and araza SS-A the four concentration levels from 10, 20, 30, and 40 wt. % , fraction frozen water results are shown in Fiure 5. For both samples, increased gradually with a decrease in temperature. The fraction of frozen water was dependent on the molecular weight of the solute. In Figure 5, SS-A has an increase in the ice fraction when compared, at the same temperature and concentration, with the SS-P. This is explained by the molecular weight (M_w shown in Table 6). Paradipasena (2007) reported the same behavior, analyzing the dependence of the ice fraction in solutions of glucose and other compounds with addition of higher weight molecular such as oligomers, dextrans, and potato starch (Pradipasena et al., 2007)..

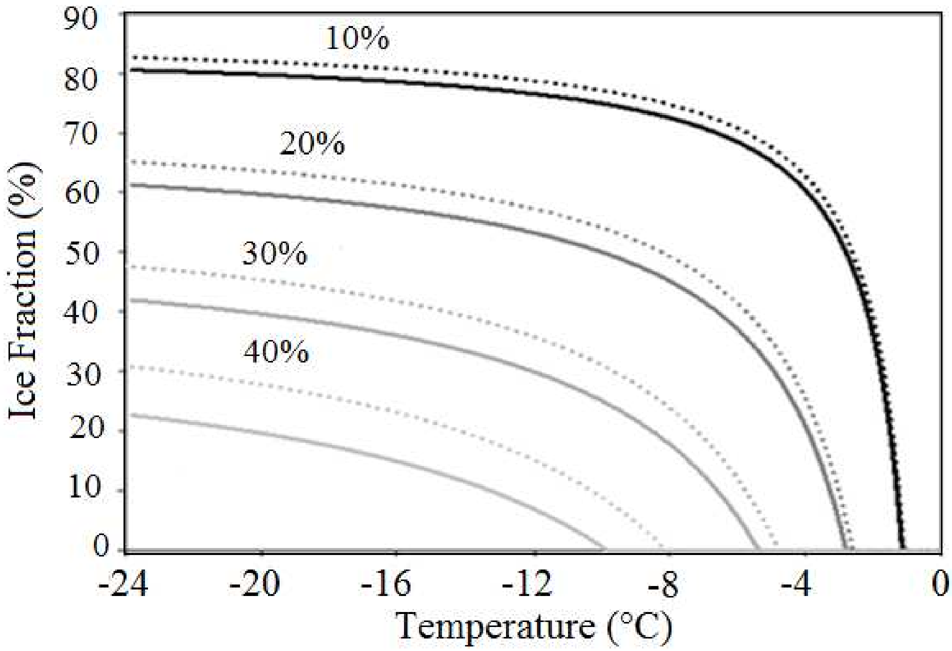

Figure 5. Ice fraction at four standard concentrations as a function of temperature. Solid lines: SS-P, dashe lines: SS-A. The concentrations in % (wt.) are indicated in the graph.

The fraction of frozen water was dependent on the molecular weight of the solute. In Figure 5, SS-A has an increase in the ice fraction when compared, at the same temperature and concentration, with the SS-P. This is explained by the molecular weight (M_w shown in Table 6). Paradipasena (2007) reported the same behavior, analyzed the dependence of the ice fraction in solutions of glucose and other compounds with in addition higher weight molecular such as oligomers, dextrans, and potato starch (Pradipasena et al., 2007). These data allow us to relate the temperature and the ice fraction, with thermal properties as specific heat and thermal conductivity.

3.4. CONCLUSION

We have investigated the ice melting curves for araza and pitanga as a function of concentration for both the pulp, the soluble fractions from the fruits and for model systems that consist of the monosaccharides glucose and fructose, the disaccharide sucrose and the organic acids malic acid, citric acid and tartaric acid in the proportions as they are found in the whole fruits. We find a very good agreement between the T_m curves for the soluble fractions and the model systems, indicating that indeed these six compounds contribute significantly to the observed ice melting behavior. Our results furthermore indicate that the melting behavior of fruits will be mostly determined by the melting behavior of the sugars in the fruits, with other constituents, in particular organic acids, playing secondary roles as they are less abundant. The ice melting data is fitted well using the Chen equation for both fruits, concentrates and model systems. Deviations between the predictions of the Chen equation and the experimental data are observed mainly for the highest concentration studied (40 wt. %); these deviations can be minimized by fitting the parameters of the Chen equation to the experimental data rather than calculating them based on the molecular properties and composition of the system. The estimates in this study have yielded correlations as a function of temperature and concentration that can be useful in the processing of frozen fruits, juices and concentrates, and in the development of frozen products containing fruits.

3.5. ACKNOWLEDGEMENTS

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CAPÍTULO 4: DISCUSSÃO E CONCLUSÕES

DISCUSSÃO E CONCLUSÃO

4.1. DISCUSSÃO

O Brasil possui um extenso terrritório com clima temperado no Sul, equatorial e tropical no Norte e Nordeste, passando por regiões semi-áridas e subtropicais. Essa diversidade nos climas regionais leva a uma enorme variedades de frutas nativas e exóticas produzidas no país (Albuquerque, 2016). Grande parte dessa frutas não são convencionais e possuem potencial atraente para a indústria de alimentos (Valli et al., 2018). Porém essas frutas não convencionais são subexploradas devido à alta perecibilidade aliada a sazonalidade e regionalidade de muitas dessas frutas. De acordo com Teixeira et al. (2019), apenas uma pequena fração tem seu potencial explorado e utilizado em escala significativa (Teixeira et al., 2019). O capítulo 2 compilou dados e aspectos sobre essa biodiversidade de frutas não convencionais com potencial de comercialização e industrialização.

O processamento é uma alternativa para preservar e ampliar a gama de produtos à base de frutas, desempenhando um papel importante na redução do desperdício de alimentos (Freitas et al., 2014). Métodos baseados na redução do teor de água e tratamento térmico, como: desidratação, concentração, refrigeração, congelamento e resfriamento (Celli, Ghanem, & SuLing Brooks, 2016; Fernandes et al., 2011; Verma & Singh, 2015), são comumente utilizados para a produção de sucos, purês, geléias, frutas secas, pós, polpas congeladas entre outros produtos (Fernandes et al., 2011; Celli et al., 2016). Entretanto o conhecimento do comportamento de fase dos frutos pode ser útil para estimar assertivamente as condições térmicas para diversos processos e armazenamento do produto final (Rahman, 2010). O capítulo 2 também reúne informações disponíveis na literatura, apresentando conceito e dados do uso de diagramas de estado na ciência de alimentos, esses mapas podem ser usados para prever e otimizar o processamento e / ou armazenamento de produtos de frutas e geralmente incluem a linha de fusão de gelo (T_m) e a linha de transição vítrea (T_g) (Roos, 1995a).

No capítulo 3, a composição das polpas de pitanga e araçá foi determinada para entender a influência da composição na T_m. Os principais componentes são os carboidratos, com 81,7% e 61,5% para a polpa liofilizada de pitanga e a araçá, respectivamente. Essa fração inclui os açúcares totais e carboidratos solúveis. Polpa integral de pitanga e araçá apresentaram quantidades semelhantes de sólidos solúveis (8,9 e 9,0 °Brix), acidez (1,88 e 1,91%) e açúcares totais (5.62 e 5.14 g/100g), diferindo a quantidade de sólidos insolúveis presentes na polpa: 33,6% para a araza e 13,8% para a pitanga. No entanto, os compostos de alta massa molecular e insolúveis não devem ter influência nas propriedades coligativas (Glover, 1975). Sabendo disso, investigou-se, a fração de sólidos solúveis de baixa massa molecular (açucares simples e ácidos orgânicos) presente nas polpas.

A concentração de todos os açúcares foi significativamente maior para pitanga do que para araçá, mas a presença relativa dos açúcares em ambas as amostras seguiu a mesma ordem: glicose> frutose> sacarose. Quanto à composição do ácido orgânico, a polpa do araçá foi considerada a mais rica em ácido cítrico, enquanto os teores de ácido málico e tartárico foram cerca de quatro vezes maiores para a pitanga do que para o araçá. A acidez total está diretamente ligada ao teor de ácidos orgânicos e a soma dos ácidos individuais escolhidos neste estudo representou 50% e 55% da acidez total determinada para pitanga e araçá, respectivamente.

Foram construídos soluções modelo (SS) mimetizando as concentrações de açucares simples (glicose, frutose e sacarose) e ácidos orgânicos (ácido cítrico, málico e tartárico) da fração solúvel baseada nas frutas (SF). Os valores obtidos de T_m (até 30% de sólidos solúveis) são muito semelhantes ao comparar as amostras de polpa de fruta integral (WP), fração solúvel baseada nas frutas (SF) e os sistemas simulados (SS), para o araçá o desvio é maior no maior teor de sólidos.

Como esperado, T_m diminui com o aumento da concentração para todas as amostras. Como uma propriedade coligativa, a depressão do ponto de congelamento da água é determinada principalmente pela presença de substâncias não voláteis de baixa massa molecular, devido ao aumento da entropia de mistura. A mudança de entropia que ocorre quando solutos não voláteis são adicionados a um solvente. Assim, ao conter pequenas moléculas não voláteis em uma solução, a energia do solvente é mais dispersa e sua entropia é aumentada quando comparada ao solvente puro (Lambert, 2002).

As curvas T_m para as amostras SF e WP foram semelhantes às curvas T_m para as amostras SS para ambas as frutas, indicando que as amostras do sistema simulado (SS) representam adequadamente o comportamento das amostras de sólidos solúveis. Além disso, a influência do teor de açúcar é dominante, uma vez que contribuem com 80% da fração solúvel na fruta. Além disso, a fração indeterminada de ácidos orgânicos não influencia o comportamento de fusão em um grau significativo. No entanto, as amostras do sistema simulado (SS) em concentração mais alta (40%) não representam adequadamente o comportamento da amostra SF.

A aplicação do modelo de Chen (1985) levou em conta a contribuição de cada componente e foi ajustado para analisar a influência desses componentes. Esses parâmetros são influenciados pelas frações de sólidos solúveis presentes na amostra (açúcares simples e ácidos orgânicos, para esse trabalho). Os desvio da equação de Chen com os valores dos parâmetros previstos dos dados experimentais torna-se mais pronunciado quanto maior a concentração. Isso é causado pela não idealidade das soluções resultante das interações dos solutos com o solvente. Essas não-idealidades são levadas em consideração na equação de Chen apenas por meio da fração de água não congelável, que não leva em consideração as verdadeiras interações intermoleculares conforme ocorrem em soluções concentradas. Desvios entre a equação de Chen e os dados experimentais foram observados anteriormente para outros sistemas de frutas, como maçã, pêssego e pera (Auleda et al., 2011)

Devido a sua massa molecular comparável, as mudanças nas quantidades relativas de ácidos orgânicos e monossacarídeos não contribuem para uma mudança significativa na massa molecular efetiva dos sólidos da fruta. Seu efeito sobre T_m é, consequentemente, muito semelhante. É claro que, devido à sua abundância relativamente baixa, os ácidos orgânicos contribuem apenas marginalmente para a depressão do ponto de congelamento. De longe, o maior efeito é devido aos monossacarídeos.

Conforme mencionado acima, não contabilizamos todos os ácidos orgânicos presentes no sistema. Porém, em concentrações mais baixas, abaixo de 30% em peso para araçá e 40% em peso para pitanga, a presença de ácidos orgânicos não alterou a curva. Assim, o modelo matemático fornece uma previsão justa, independentemente da presença de ácidos orgânicos. Essa relação está de acordo com relatos da literatura. Auleda et al. (2011), por exemplo, relatam as curvas de T_m para suco de maçã, suco de pêra e suco de pêssego e as comparam com as curvas de T_m apenas dos açúcares sacarose e glicose, e descobriram que o impacto dos ácidos orgânicos é bastante limitado.

Auleda et al (2011) avaliaram sucos clarificados e depectinizados, ou seja, sucos dos quais as frações insolúveis são removidas (Auleda et al., 2011). Quanto às nossas frações solúveis de pitanga e araçá, os sucos acabaram sendo compostos por açúcares e outros compostos solúveis, como ácidos orgânicos, vitaminas e pigmentos. Como o composto com maior massa molecular que contribui significativamente para a T_m em sucos de frutas é, tipicamente, a sacarose e o composto com menor massa molecular é a glicose, o ponto de congelamento de qualquer suco deve estar entre a curva da T_m da sacarose e da glicose. Essa área é comumente chamada de “zona do suco”. Esse comportamento também pode ser verificado a partir de dados de outros sucos, como suco de laranja (Chen et al., 1990) e manga e mamão (Telis et al., 2007).

Ainda no capítulo 3 a determinação da fração de gelo foi realizada. Na região de congelamento (abaixo da curva T_m), a fração de gelo e a fração da fase crio-concentrada dependem da temperatura. A dependência da fração de gelo é importante em temperaturas próximas a T_m, pois mudanças na temperatura causam mudanças importantes nas propriedades térmicas do alimento, como diferença entre calor específico e condutividade térmica entre água e gelo. Em alimentos congelados, parte da água do sistema é congelada e outra parte fica descongelada porque o estado físico da água é heterogêneo (Pradipasena et al., 2007; Schwartzberg, 1976).

Para ambas as amostras, a fração de gelo aumentou gradualmente com a diminuição da temperatura, além disso a fração de água congelada foi dependente da massa molecular do soluto. O SS-A apresenta um aumento na fração de gelo quando comparado, na mesma temperatura e concentração, com o SS-P. Isso é explicado pois a massa molecular da SS-P é ligeiramente menor (M_w=193,8), quando comparamos SS-A (M_w = 197,6). Paradipasena (2007) relatou o mesmo comportamento, analisou a dependência da fração de gelo em soluções de glicose e outros compostos de maior massa molecular, como oligômeros, dextranos e amido de batata (Pradipasena et al., 2007). Esses dados nos permitem relacionar a temperatura e a fração de gelo, com propriedades térmicas como calor específico e condutividade térmica.

4.2. CONCLUSÃO

Estudos de condições apropriadas para preservação e armazenamento por meio de diagramas de estado não são comuns na literatura para frutas não convencionais. O desenvolvimento desses estudos pode contribuir para aumentar a gama de produtos à base de frutas, oferecendo base tecnológica para o desenvolvimento da indústria nacional e contribuindo indiretamente para a conservação da biodiversidade.

Os sistemas simulados de pitanga e araçá (SS-P e SS-A) foram formulados com proporções pré-determinadas de açúcares (glicose, frutose, sacarose) e apenas os 3 ácidos orgânicos que foram quantificados na fruta in natura (ácido cítrico, ácido málico e ácido tartárico) e que representavam ~ 50% do total de ácidos das amostras. A compatibilidade do comportamento térmico das curvas de fusão do gelo de tais sistemas simulados com o apresentado pelas respectivas frações (SF-P e SF-A) evidencia a dependência do ponto de fusão com a quantidade de moléculas não voláteis de baixa massa molecular. Tais moléculas são responsáveis pelo aumento de entropia do sistema, já que a energia do solvente na presença do soluto é mais dispersa quando comparada ao solvente puro.

Além disso, como os açúcares possuem massa molecular próxima aos ácidos orgânicos, a fração mássica total determinou o comportamento de depressão do ponto de congelamento da água, não sendo necessário a caracterização dos ácidos orgânicos.

O modelo de Chen representou adequadamente os dados experimentais de fusão para concentraçõpes mássicas inferior a 30% para SS-P e inferior a 40% para SS-A. O desvio do modelo para as curvas experimentais em altas concentrações deve-se à não idealidade da solução, cujas interações soluto-solvente tornam-se mais pronunciada.

A fração de gelo foi dependente da massa molecular do soluto. Observou-se que o sistema simulado do araçá SS-A apresentou aumento na fração de gelo quando comparado, na mesma temperatura e concentração, com sistema simulado da pitanga SS-P. Isso é explicado pelo massa molecular M_w das amostras, comprovando assim a dependência da fração de gelo em soluções com as propriedades coligativas da solução. Esses dados permitem nos relacionar a temperatura e a fração de gelo, com propriedades térmicas como calor específico e condutividade térmica.

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