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Effect of concentration on the physicochemical, particle size and rheological properties of grapefruit juice (*Citrus paradise* var. Macfadyen)

Ali Motamedzadeghan, Abdolkhalegh Golkar*, Mehdi Porshayegan, Sara Maghsodi

Sari Agriculture Sciences and Natural Resources University, Department of Food Science and Technology, Sari, Mazandaran Po Box 578

Corresponding author: Abdolkhalegh Golkar

ABSTRACT: In this research, the effect of concentration on the physicochemical, particle size and rheological properties of grapefruit juice at different °Brix was investigated. The pH of initial grapefruit juice was 2.77±0.07 and continuously decreased ($P<0.05$); but density and turbidity parameters increased ($P<0.05$) during concentration. Mean particle size (D_{32}) of grapefruit concentrates with 9.5, 22, 34.5, 47, and 59.5 °Brix were as follows: 238.12±46.78, 271.95±22.70, 239.41±12.06, 217.44±9.24, and 231.18±1.93 µm. Also, other particle size characteristics showed significantly decreased. Lightness (L*) of samples decreased; but Redness (a*) and Yellowness (b*) significantly ($P<0.05$) increased during concentration. All samples showed shear-thinning behavior and well fitted with Herschel-Bulkley model. Flow behavior index of samples varied in the range of 0.5092-0.6514 and correlation coefficient was in the range of 0.9246-0.9848. Moreover, consistency index increased during concentration. In all samples (even in samples with low °Brix 9.5), the elastic modulus (G') values were higher than viscose modulus (G'') values (G'>G''). Complex modulus (G*) and loss factor (tan δ) increased with increasing °Brix. The relation between particle size and consistency coefficients of Herschel-Bulkley model was not detected. In general, concentration process had significant effect on the physicochemical, particle size distribution and rheological properties of grapefruit concentrates. Above results can be used for the controlling of quality parameters of fruit juices during concentration.

***Keywords*:** Grapefruit, Concentration, Physicochemical, Rheological, Color

Highlights:
- pH, density, turbidity, and colorimetric measurement of grapefruit juice concentrates were measured.
- All samples showed shear-thinning trend and well fitted with Herschel-Bulkley model.
- The network structure of all samples showed as a weak gel (G'>G'').
- The relation between particle and rheological properties was monitored.
- Results can be recommended to controlling of quality parameters of fruit juices during concentration.

Practical applications

Many fruits are available in fresh form during in the part of the year. In order to have fruit juice with good quality during year, it must be processed. Since most citrus juice containing about 80-90 % water, the most economical way is the concentrate form. In general, physicochemical, particle size and rheological properties of fruit juices will be changed during concentration process, which seems to corresponding to the microstructural properties of fruit concentrates. This study can be used to controlling of quality parameters of fruit juices during concentration.

1.INTRODUCTION

In recent years, fruit juice consumption has been increased attention in many countries due to the natural source of nutrients. Citrus juice is the most popular juice and has more than 50 % of international commerce in juice. The quality of citrus juice depends on the quality of fruit, processing and storage conditions that influencing enzymatic reactions and organoleptic, nutritional and functional properties. Flavor, color, suspension stability, and cloudiness are quality parameters which are approved by consumers. Moreover, rheological properties of juice are indicator of consumer experience in relation to viscosity, particle size distribution, and mouth-feel (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014). Fruit juice have a short shelf-life and are liable to microbial spoilage and enzymatic activities, so treatments such as thermal treatment is used to inactivation of the micro-organisms and enzymes. Viscosity of fruit juice influences the choice of evaporator selection. Film evaporators are usually used for juice concentration. The knowledge of the flow behavior of fruit juice is required for the development of reliable and safe processes. The knowledge of the rheological properties of juice is useful in quality, process control, calculating energy consumption and selection of suitable equipment. The flow behavior of fluids depends on their molecular structures. Depending on the nature of the juice, the rheological properties of fruit juice can be described by different rheological models (Belibağli, & Dalgic, 2007). Rheological properties have been considered as an analytical tool to provide fundamental insights on the structural organization of food and play an important role in heat transfer of fluid. The rheological properties of food products were strongly influenced by temperature, concentration and physical properties of dispersion (Ahmed, Ramaswamy, & Sashidhar, 2007). There are many studies that were carried out on the rheological properties of strawberry (Juszczak, & Fortuna, 2003), pomegranate (Altan, & Maskan, 2005), melon (Mohamadi Sani, Hedayati, & Arianfar, 2014), sour cherry (Belibağli, & Dalgic, 2007) and aloe vera juice (Swami Hulle, Patruni, & Rao, 2014).

Grapefruit like most citrus fruits and vegetables have been grown in specific seasons. They grow only under specific climatic conditions, i.e., tropical and subtropical regions such as of Florida, Arizona, California, Texas, Brazil, Spain, Spain, Italy, Israel and Egypt. Grapefruit are available in fresh form during in the part of the year. In order to have grapefruit juice with good quality during year, it must be processed. Since most citrus juice containing about 80 to 90 % water, the most economical way to storage is the concentrate form (Strobel, 1986). Color changes of frozen grapefruit juice concentrate have been studied during storage (-23 °C for 12 months) (Lee, & Coates, 2002). In addition, recently physical properties (particle size distribution, flow behavior, density, turbidity, and color) and sensory evaluation of pasteurized grapefruit juice with two methods (microwave and conventional heating) were measured. Finally, microwave treatment recommended as a method for the pasteurization of grapefruit juice (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014). Based on literatures, rheological properties of grapefruit juice have not been studied to date. Therefore, in current research, the effect of concentration on physicochemical (pH, density, turbidity, particle size distribution, and colorimetric measurement) and rheological properties of grapefruit juice at different °Brix (9.5, 22, 34.5, 47, and 59.5) were investigated.

2. Materials and Methods

2.1. Preparation of grapefruit juice and their concentration

Grapefruits (*Citrus paradise* var. Macfadyen) were provided from a local supermarket, Gorgan, Iran. Juice extraction was carried out using a kitchen juicer (Tiger model, Parskhazar, Iran), followed by sieving (>0.5 mm diameter) to remove pulp and other external particles. Grapefruit juice was pasteurized in water bath (Memmert, Germany) at 90 °C for 15 seconds. Grapefruit juice concentration was performed using a vacuum rotary evaporator (TAT-94-1046, Tyf-Azma-Teb, Iran) at 60 °C and 60 rpm rotating speed. Therefore, grapefruit concentrates prepared with °Brix of 9.5 (total soluble solid of fresh juice), 22, 34.5, 47, and 59.5.

2.2. Measurement of total soluble solid (°Brix)

The total soluble solid of samples were measured using refractometer (A-Kruess, DR 301-95 model, Germany) at 22±1°C and expressed in °Brix (Belibağli, & Dalgic, 2007).

2.3. pH determination

The pH was measured using a digital pH meter (Sana pH.MV.TEMP/METER, Iran) at 22±1°C (Belibağli, & Dalgic, 2007).

2.4. Density

Density of grapefruit samples were measured using a pycnometer (25 ml) at 22±1°C and distilled water as the reference (Altan, & Maskan, 2005).

2.5. Turbidity measurements

Firstly, all grapefruit concentrates diluted to the total soluble solid of fresh juice (9.5 °Brix). Then, samples was centrifuged (Universal Centrifuge, PECO, Iran) at 3000 rpm for 10 min. The absorbance of upper phase was determined using a UV-VIS spectrophotometer (UV-2100 SPECTROPHOTOMETER, Unico, UK) at 660 nm (Nicolau, Andrey, Vitoriano, & Cecilia, 2008). Turbidity was calculated using Eq. (1):

(1)

$$T=100-(100\times10^{-A})$$

2.6. Particle size distribution of samples

Particle size distribution was performed by laser light scattering (Horiba, LA-930, Japan). Before any analysis, all samples were diluted (1:100) with distilled water. The samples were shacked to ensure the homogeneity and injected to every unit cell until the transmittance reached to 60-80 % against distilled water as a blank. The particle size measurements are reported as D_{43}, D_{32}, $D_{0.1}$, $D_{0.5}$, $D_{0.9}$, and Span. $D_{0.1}$, $D_{0.5}$, and $D_{0.9}$ indicating that 10, 50, and 90% of the droplets are below this value. D_{43} and D_{32} are defined as the volume and surface mean diameter, respectively. Span or polydispersity index is determined using Eq. (2) below:

(2)

$$\text{Span} = \frac{(D_{0.9} - D_{0.1})}{D_{0.5}}$$

The particle size properties were automatically calculated using the LA-920 software. All measurements are at least a mean of two replications (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014).

2.7. Color measurement

The color of samples was performed using a colorimeter (Color & Appearance Measurment System, Shomal Fanpouyaye Abzarkaran Co., Iran). The L* coordinate denotes lightness on a 0-100 scale from black to white. a* (+: Red, -: Green) and b* (+: Yellow, -: Blue) are the Redness and Yellowness parameters, respectively in the range of -120 to +120 (Lee, & Coates, 2002).

2.8. Rheological measurements

Rheological properties of samples were performed using a rheometer (Anton-Paar, Physica MCR 301, Austria) at 25 °C. The temperature was controlled with a Peltier plate circulator system at 20°C with 0.01°C sensitivity (Ahmed, Ramaswamy, & Sashidhar, 2007).

A) Flow Behavior

Flow behavior was performed with concentric cylinder equipment (diameter= 50 mm, plate space= 1 mm). Flow behavior curves of samples were programmed to increase shear rate in the range of 0.0001-300 s^{-1}. The Newtonian, power law and Herschel-Bulkley model were applied by fitting experimental data of flow behavior tests using Eqs. (3, 4, and 5).

(3)

$$\tau = \eta\gamma$$

(4)

$$\tau = \kappa\gamma^{n}$$

(5)

$$\tau = \tau_0 + \kappa'\gamma^{n'}$$

Where τ is the shear stress (Pa); η is viscosity (Pa s); γ is the shear rate (s^{-1}); κ and κ' are the consistency coefficients (Pa s^n); n and n' are the flow behavior indices (without dimension); and τ_0 is the yield point (Pa s).

B) Frequency Sweep

Frequency sweep tests were evaluated using a previous geometry system at 25 °C. Linear viscoelastic range were determined in a range of 0.01-100 % strain at constant frequency of 1 Hertz, followed by mechanical spectra measured in the linear viscoelastic range at constant strain 0.01 % and in a range of frequency of 0.01-100 Hertz. Values of storage (G') and loss (G'') moduli were determined and mechanical spectra were described by power law Eqs. (6 and 7):

(6)

$$G' = K'.\omega^{n'}$$

(7)

$$G" = K'' . \omega^{n''}$$

Where G' is storage modulus (Pa), G'' is loss modulus (Pa), ω is angular frequency (rad/s), K', K'', n' and n'' are experimentally determined constants. All rheological parameters were obtained using Rheoplus software (3.0x version, Anton Paar, Austria).

2.9. Statistical analysis

All experiments were carried out in a completely randomized block design with at least two replications. In order to analyze the data, the method of ANOVA with SAS 9.0 software was used. All mean comparisons were conducted by the test of LSD (least significant difference) at the level of 5 %.

3. Results and discussion

3.1. Physicochemical properties

pH: pH variation during concentration process 9.5 to 59.5 °Brix was shown in Table 1. pH of fresh grapefruit juice was 2.77±0.07 and significantly ($P<0.05$) decreased after concentration that related to the organic acid concentration of juice. In the previous researches, pH of grapefruit juice (*Ruby Red variety*) was reported 3.3 (Lee, & Kim, 2003).

Density: Results (Table 1) showed that density continuously increased by increasing total soluble solid in significant order ($P<0.05$). However, the results demonstrated that density of grapefruit juice concentrates influenced by total soluble solid of samples. Similar trends for densities of peach (Ramos, & Ibarz, 1998), grape (Zuritz et al., 2005) and melon (Mohamadi Sani, Hedayati, & Arianfar, 2014) juices have been reported

Turbidity: Opacity is considered as a desirable characteristic of many kinds of fruit juices. During juice extraction, the cells are broken and colloidal materials compound of proteins, hesperidin, cellulose, hemicellulose, and pectin appear suspended in the juice. Those materials are what provide the citrus juice with their opacity, which is directly associated with the parameter "turbidity" (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014). Based on Table 1, fruit juice turbidity increased by increasing concentration process that resulting to the total soluble solid content. In addition, a significant difference ($P<0.05$) was existed between fresh grapefruit juice and other concentrates with higher °Brix. In fact, turbidity increased after submitting the grapefruit juice to heat treatment related to the combination of pectin and proteins. It should be noted that turbidity value of 59.5 °Brix grapefruit juice concentrate was lower value than concentrate with lower °Brix (89.07±0.10). This phenomenon may be related to the development of Maillard reactions and formation of color compounds with higher molecular weight that are precipitated after centrifugation (before turbidity measurement). Similar trend was reported in orange juice concentration (Klavons, Bennett, & Vannier, 1994). In addition, previous research reported that turbidity of grapefruit juice significantly increased after pasteurization (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014).

Table 1. Some of physicochemical properties of grapefruit juice and concentrates

Parameters		Grapefruit juice and concentrates				
		°Brix 9.5	°Brix 22	°Brix 34.5	°Brix 47	°Brix 59.5
pH		2.77±0.07^{a}	2.59±0.02^{b}	2.54±0.01^{b}	2.42±0.07^{c}	2.26±0.05^{d}
Density		1.042±0.007^{a}	1.125±0.022^{d}	1.167±0.011^{c}	1.238±0.015^{b}	1.312±0.007^{a}
Turbidity		76.81±4.67^{b}	89.28±0.10^{a}	88.60±0.08^{a}	89.07±0.10^{a}	86.13±0.08^{a}
Droplet size distribution parameters	D_{32}	238.12±46.78^{b}	271.95±22.70^{a}	239.41±12.06^{bc}	217.44±9.24^{c}	231.18±1.93^{bc}
	D_{43}	573.19±62.30^{a}	480.13±30.40^{b}	454.32±22.42^{b}	412.95±5.55^{c}	419.40±5.19^{c}
	$D_{0.1}$	155.99±20.28^{a}	130.87±11.54^{ab}	116.77±7.39^{b}	104.69±4.32^{b}	111.05±0.82^{b}
	$D_{0.5}$	580.23±98.04^{a}	425.14±39.31^{b}	357.64±18.66^{bc}	328.32±21.22^{c}	356.86±8.40^{bc}
	$D_{0.9}$	978.27±66.71^{a}	906.34±58.07^{ab}	925.57±63.42^{ab}	850.83±15.96^{b}	824.91±9.30^{b}
	Span	1.42±0.36^{b}	1.82±0.25^{ab}	2.26±0.22^{a}	2.28±0.18^{a}	2.00±0.02^{ab}
Color measurement	L*	51.16±1.83^{a}	47.58±1.40^{b}	30.78±1.16^{c}	13.93±1.23^{d}	8.97±1.16^{e}
	a*	-6.96±1.19^{e}	2.07±1.26^{d}	11.63±1.51^{a}	9.32±0.95^{b}	5.99±1.33^{c}
	b*	24.37±1.72^{b}	26.65±0.79^{a}	18.54±0.73^{c}	8.66±0.63^{d}	5.46±0.56^{e}

- All results were carried out in triplicate and results are reported as the mean±SD.
- For each row, similar small superscript letters are not significantly different at $P<0.05$.

Particle Size Distribution: Generally, food processing can affect the properties of plant-tissue-based particles, such as particle size and morphology of food suspensions. By the use of mechanical unit operations, plant tissue can be ruptured into particles with specific particle properties. Finally, variations in particle characteristics lead to different functional properties of food materials (Moelants et al., 2014). The physical properties of the dispersed particles such as the average particle size, the size distribution, and the shape of the particles, will influence the juice flow behavior. It is expected that an easy flow will be obtained with smaller particle sizes (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014). Table 1 shows the effect of concentration on the particle size of grapefruit juice samples using static laser scattering technique. It should be noted that particle size analyzer evaluated the particle size of materials considering the sphere; although usually particles in plant tissue are not sphere and is in fibrous formation.

Mean particle size is demonstrated based on surface (D_{32}) and volume bases (D_{43}). Volume based particle size distribution can be seriously influenced by particle size distribution. Based on Table 1, surface based particle size (D_{32}) significantly ($P<0.05$) decreased by concentration, and then increased to 59.5 °Brix concentrate. In fact, breaking aggregates in the original juice may play an important role in determining the viscosity of fruit juice concentrate. Damage of the pectin molecules due to the elevated temperature of evaporator resulted to decreasing particle size with concentration advancement. Continuous decreasing of particle size (391.1 µm to 360.8 µm) during tomato concentration from 4.9 to 30.5 was reported (Ouden, & Vliet, 2002). In the case of increasing the particle size of the 59.5 °Brix sample, it can be concluded that some of particles in system aggregated during severe concentration and increased significantly mean particle size.

Based on Table 1, the mean volume particle size (D_{43}) also showed a similar trend to D_{32}, and this parameter decreased significantly ($P<0.05$) during the concentration process. The droplet size distribution was shown in Figure 1.

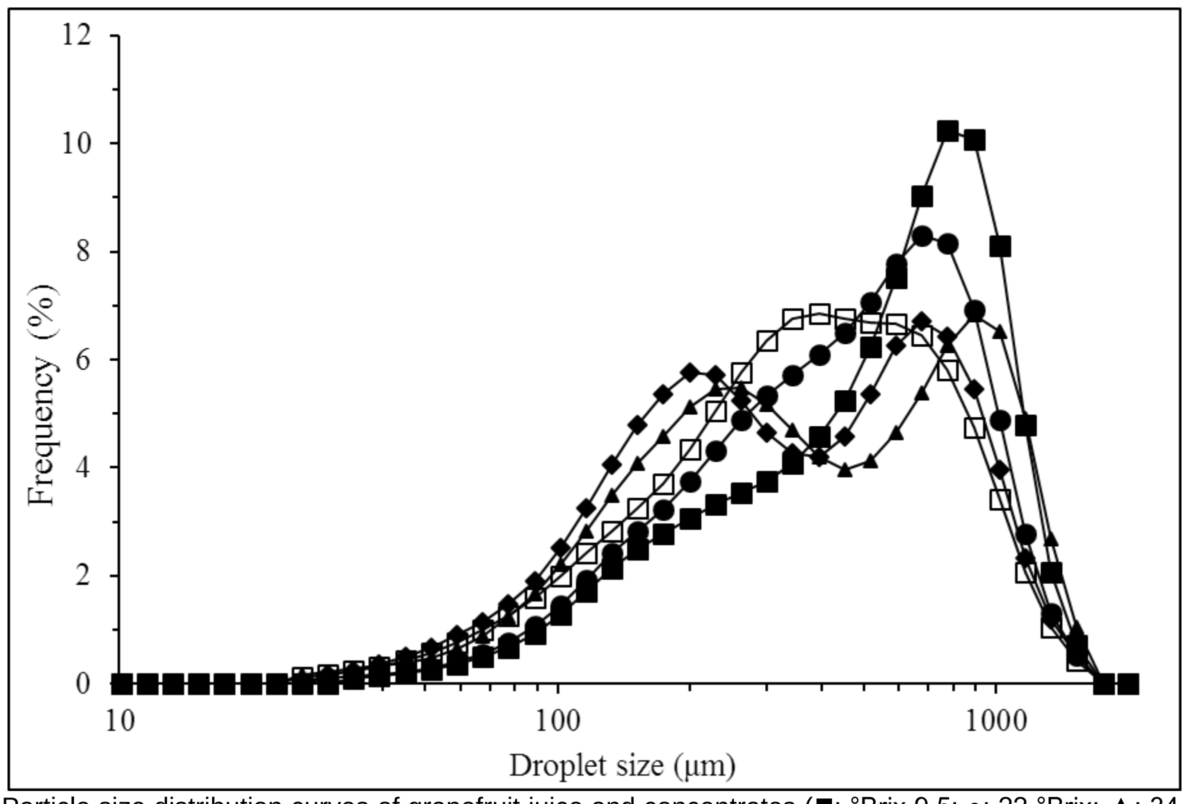


Fig. 1: Particle size distribution curves of grapefruit juice and concentrates (■: °Brix 9.5; ●: 22 °Brix; ▲: 34.5 °Brix; ♦: 47 °Brix; □: 59.5).

Based on Figure 1, it can be reported that some large particles with a high diameter of 1 mm, and some small particles with a diameter of 100 µm occurred in grapefruit juice concentrate. In addition, the droplet size distribution of 34.5 and 47 °Brix samples were bimodal curves, while in other samples it was monomodal. Bimodal curves of

the sample indicated that two groups of particles with different sizes occurred. Decreasing and increasing trends of particle size can be demonstrated with the shift of curves to the left and the right side of the X axis, and this phenomenon was clearly observed for the increasing particle size of the 59.5 °Brix sample in comparison of 47 °Brix sample. Moreover, $D_{0.1}$ and $D_{0.5}$ had a significantly ($P<0.05$) decreasing trend at first, afterward showed an increasing trend. For $D_{0.1}$, it was shown that approximately 10 % of the particles had a size lower than 104.69-155.99 μm. Based on $D_{0.5}$ and D_{43} values, it can be demonstrated that the particle size distribution of 9.5 °Brix sample was normal, while the shoulder of the other curves were shifted toward left and right sides, which indicating the non-uniformity of the particle size distribution of samples. The $D_{0.9}$ value of the samples decreased with the advancement of the concentration process, and approximately 90 % of particles had a size lower than 1000 μm. According to these findings, it may be supposed that only some of the particles were higher than the value.
The Polydispersity index (Span) was observed to exhibit a trend contrary to the previous parameters, and this parameter increased with total soluble solid to 47 °Brix sample, and then decreasing trend for the 59.5 °Brix sample.

Color measurement: Color is an important factor in the acceptance of various products by consumers. According to the colorimetric measurements data in Table 1, the effect of concentration on the lightness of grapefruit concentrates showed that L* value significantly ($P<0.05$) decreased during concentration and the samples were darker. Redness (a*) of samples was increased significantly ($P<0.05$) during the concentration process. Moreover, yellowness (b*) of samples was increased significantly ($P<0.05$). To better understanding of the color changes, the appearances of the samples are shown in Figure 2. A similar trend was reported by Igual *et al*. (2014), and reported that the pasteurization process of grapefruit juice significantly ($P<0.05$) decreased the lightness, but b* value was increased (Igual, Contreras, Camacho, & Martínez-Navarrete, 2014).

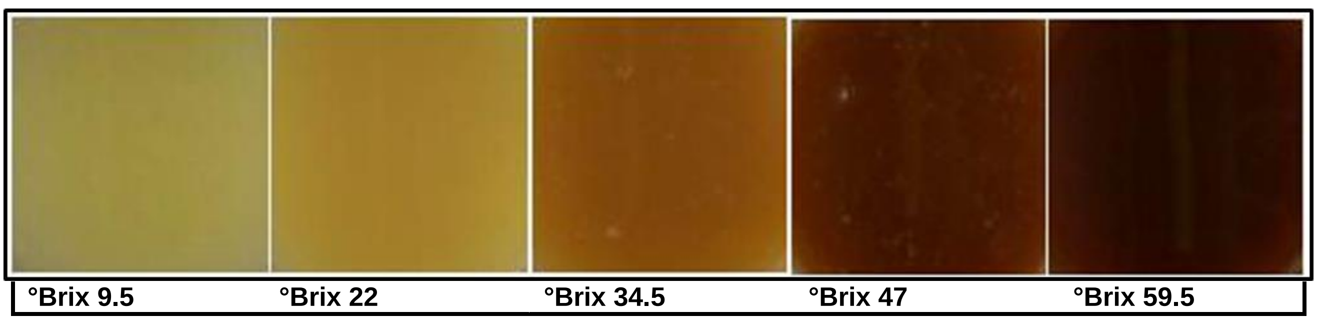


Fig. 2: The appearance of grapefruit juice and concentrates

3.2. Rheological properties

Flow behavior of grapefruit concentrates

The rheological behaviors of systems depend on their molecular structure. Thus, the rheological behavior of fruit juice may have expressed different rheological models (such as Newtonian, Herschel-Bulkley, etc.). Figure 3-1 shows the viscosity curves of grapefruit juice and concentrates at different shear rates. As can be shown, viscosity of all samples was decreased when the shear rate increased, indicating the shear-thinning behavior of the samples. As the fruit juice concentrate has a suspension structure, the shear-thinning phenomena resulting from the orientation of solid particles along the flow lines. Viscosity of all samples increased by increasing total soluble solid. Samples with 9.5 °Brix and 59.5 °Brix had lower and higher viscosity, respectively. Previously, shear-thinning behavior at different shear rates have been reported for other fruit juice-based products (Ahmed, Ramaswamy, & Sashidhar, 2007; Mohamadi Sani, Hedayati, & Arianfar, 2014; Swami Hulle, Patruni, Rao, 2014).

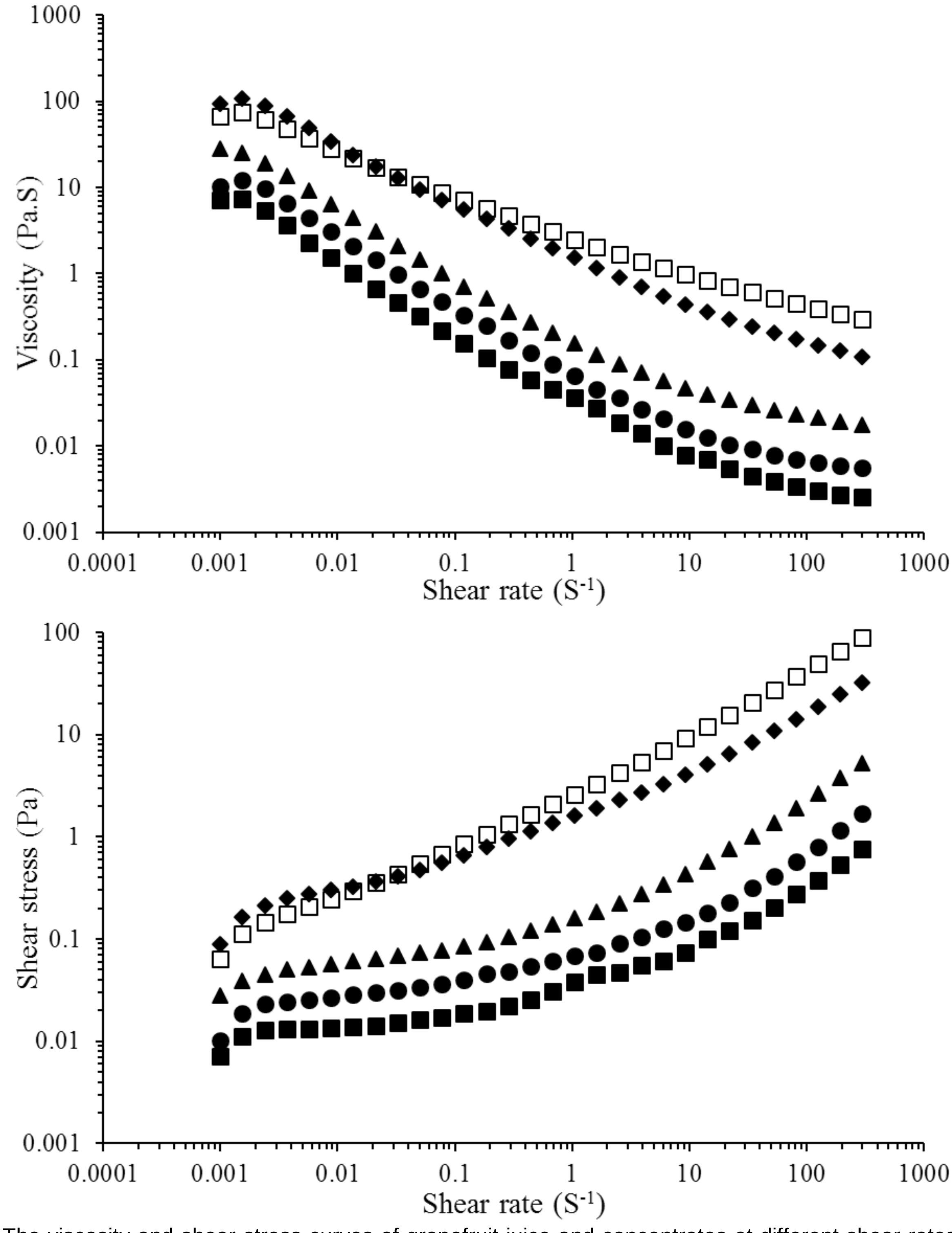


Fig. 3: The viscosity and shear stress curves of grapefruit juice and concentrates at different shear rates at 25°C (■: °Brix 9.5; ●: 22 °Brix; ▲: 34.5 °Brix; ♦: 47 °Brix; □: 59.5).

Figure 3 demonstrates the shear stress curves of samples as function of different shear rates. Shear stress changed non-linear trend with increasing shear rate. Thus, it can be easily noted that the samples were not showing Newtonian behaviors. A similar trend was reported for aloe vera concentrates (Swami Hulle, Patruni, Rao, 2014). Presence of pectin and other dispersed solid particles in liquid phase lead to the non-Newtonian behavior of grapefruit concentrates. The Hysteresis area for the 9.5, 22, 34.5, 47, and 59.5 °Brix samples were 6.50, 9.00, 26.84, 297.52, and 880.08 Pa/Sec respectively. The results showed that the Hysteresis area increased by increasing the total soluble solid of the samples.

The rheological parameters of grapefruit concentrate were obtained by the fitting of the experimental using Newtonian, power law, and Herschel-Bulkley models, which are shown in Tables 2 and 3 respectively. The correlation coefficients (R^2) of the three models showed that the Herschel-Bulkley model of grapefruit concentrate was better fitted, in comparison of the Newtonian and power law models. Although, the power law for 24.5, 47, and 59.5 °Brix samples had higher correlation coefficients than Herschel-Bulkley.

Table 2. Parameters of the Newtonian model for describing the flow behavior of grapefruit juice and concentrates

Treatment	Newtonian model	
	Viscosity (Pa.s)	**R^2**
°Brix 9.5	0.0039	**0.7269**
°Brix 22	0.0083	**0.7643**
°Brix 34.5	0.0276	**0.7147**
°Brix 47	0.1841	**0.6149**
°Brix 59.5	0.5119	**0.5630**

Table 3. Parameters of power law and Herschel-Bulkley models for describing the flow behavior of grapefruit juice and concentrates

Treatment	Powel law			Herschel-Bulkley			
	κ (Pa s^n)	n	R^2	τ_0 (Pa)	κ' (Pa s^n)	n'	R^2
°Brix 9.5	2.0793	0.0656	0.6789	0.0125	0.0190	0.6000	0.9595
°Brix 22	1.6441	0.09224	0.7317	0.0240	0.0386	0.5975	0.9246
°Brix 34.5	7.0849	0.1148	0.9896	0.0494	0.1029	0.6514	0.9674
°Brix 47	14.7830	0.1995	0.9962	0.1494	1.4249	0.5092	0.9668
°Brix 59.5	10.6270	0.2849	0.9939	0.0749	2.5952	0.5924	0.9848

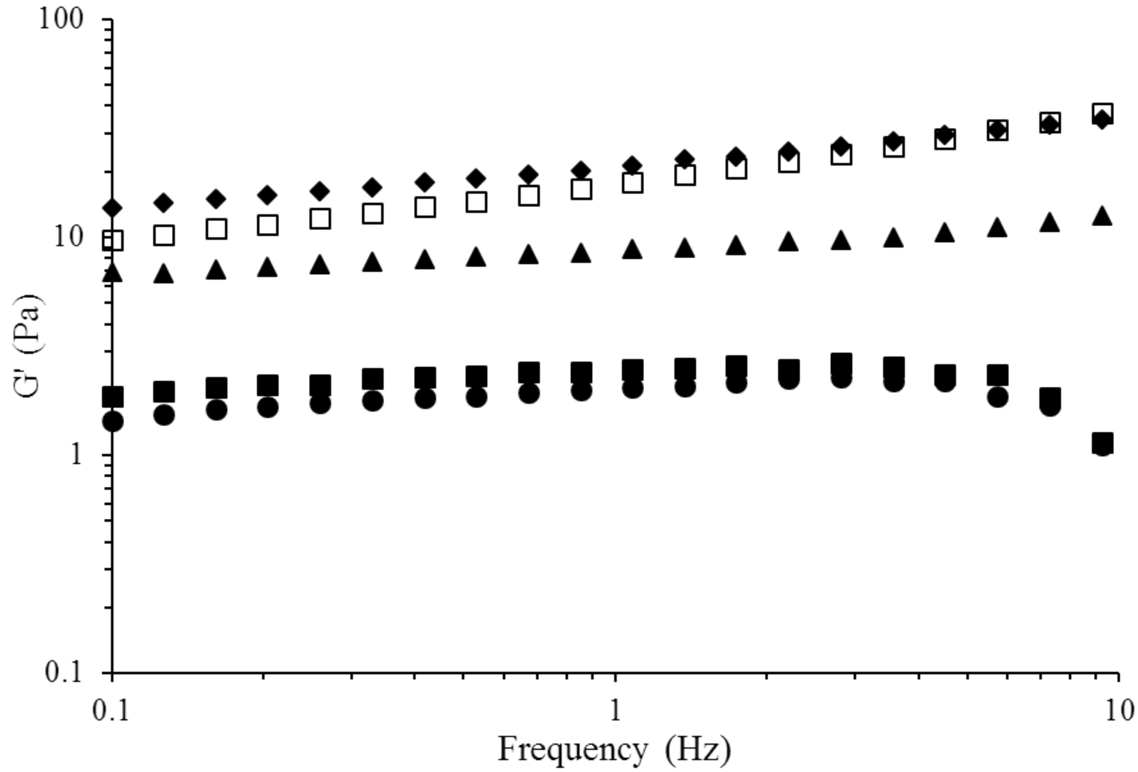
* κ and κ' (consistency coefficient, Pa s^n), n and n' (flow behavior index, without dimension) and τ_0 (yield point, Pa) were obtained by fitting the power law and Herschel-Bulkley models, respectively.

Table 2 shows the rheological parameters of Newtonian models. As can be seen, the viscosity of the samples continuously increased by increasing the total soluble solid, but R^2 decreased, which is indicating the Newtonian behavior of the samples. Moreover, Figure 3-2 showed the incompatibility behavior of the samples from the Newtonian model. The correlation coefficient (R^2) varied in the range of 0.7643-0.5630.

Parameters of the power law and Herschel-Bulkley models are reported in Table 3. The power law model showed that the flow behavior index of the samples increased with the advancement of concentration process. The flow behavior index increased during concentration process that related to the shear thinning behavior (pseudoplastic) of the samples. Based on the Herschel-Bulkley model, the flow behavior index of the samples varied in the range of 0.5092-0.6514. Flow behavior index values were n<1, indicating the pseudoplastic behavior of the concentrates. Based on Table 3, the correlation coefficients varied in the range of 0.6789-0.9939 and 0.9246-0.9848 for the power law and the Herschel-Bulkey models respectively. The correlation coefficient of the Herschel-Bulkey model confirmed the good fitting of this model with the rheological behavior of grapefruit juice concentrates. The consistency coefficient of Herschel-Bulkey models increased continuously with increasing concentration. In fact, when the food systems concentrate, the particles are in contact with each other, but still have their maximum volume. In highly concentrated suspensions, the particles are deformed and fill the space available, and the suspension is thus packed fully. In concentrated systems, the interactions and contact between particles clearly dominate over the Brownian forces (Bayod, 2008). Finally, these changes resulted to the increasing viscosity and consistency coefficient of the final products. A similar trend was observed for yield stress, but it was decreased only for the 59.5 °Brix sample. Decreasing yield stress during concentration may be related to the reduction of the mean particle size. In addition, the hydrolysis of hydrocolloid materials can be influenced this phenomenon (Moelants et al., 2014) [15]. The pectin in the acidic area and the thermal treatment condition was degraded and hydrolyzed. Anthon *et al.* (2008) reported the variations in soluble pectin and the decreasing of consistency with the concentration process of tomato paste (Anthon, Diaz, & Barrett, 2008).

Frequency sweep test

Frequency sweep test has several applications in measuring the viscoelastic properties of the food systems. The elastic (or storage) modulus value (G') expresses the magnitude of the energy that is stored in the material or is recoverable per cycle of deformation. The viscose (or loss) modulus value (G'') is a measure of the energy that is lost by viscose dissipation per cycle of deformation. The frequency sweeps of grapefruit juice and concentrates based on G', G'', G*, and tan δ in the function of the frequency is shown in Figure 4 and Figure 5. G' and G'' were increased by increasing the total soluble solid. In all samples (even in samples with low °Brix 9.5), the G' values were higher than G'' values in the range of 0.1-10 Hz frequency, indicating the dominant elastic nature of these samples compared to the viscose one, owing to weak gel-like behaviors. Both parameters were frequency dependent, so that their values (G' and G'') increased by increasing the frequency (except for the G' of 9.5 and 22 °Brix samples, which decreased at high frequency). This trend showed the viscoelastic properties of the samples. Pectin substances can be related to demonstrating this behavior in grapefruit concentrates. This trend is in agreement with the previous report of tomato suspensions, even at lower concentration (10 %) (Bayod, 2008).



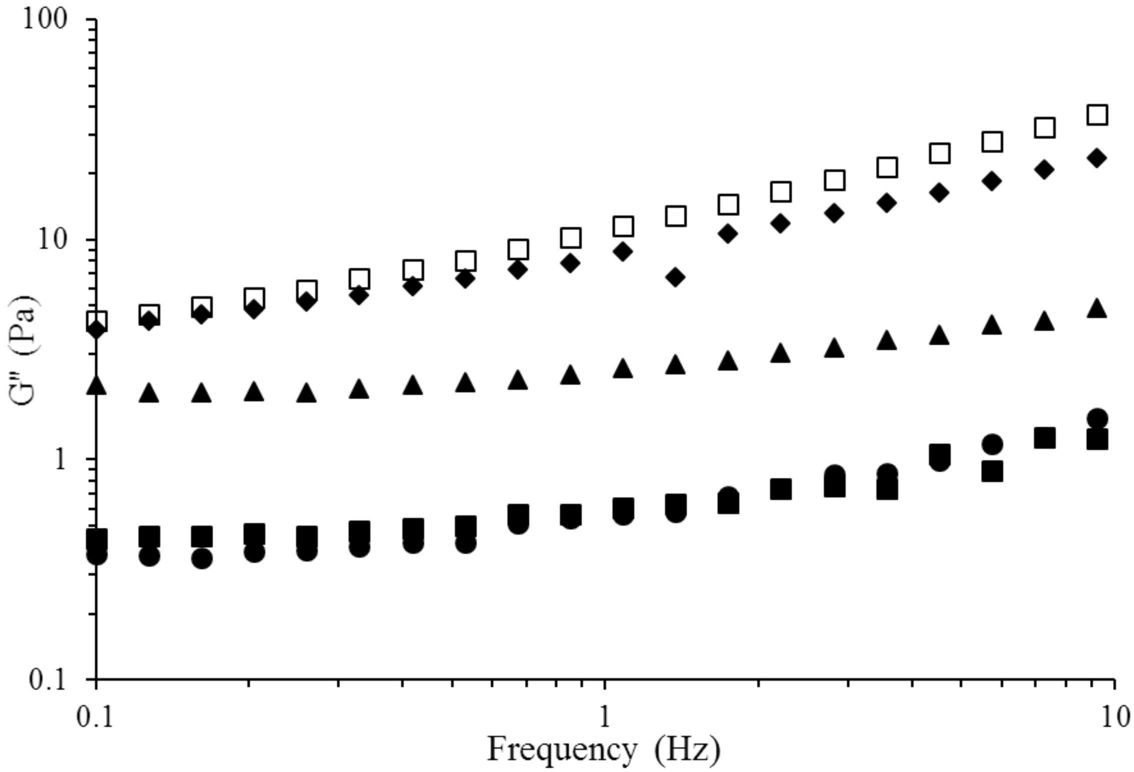
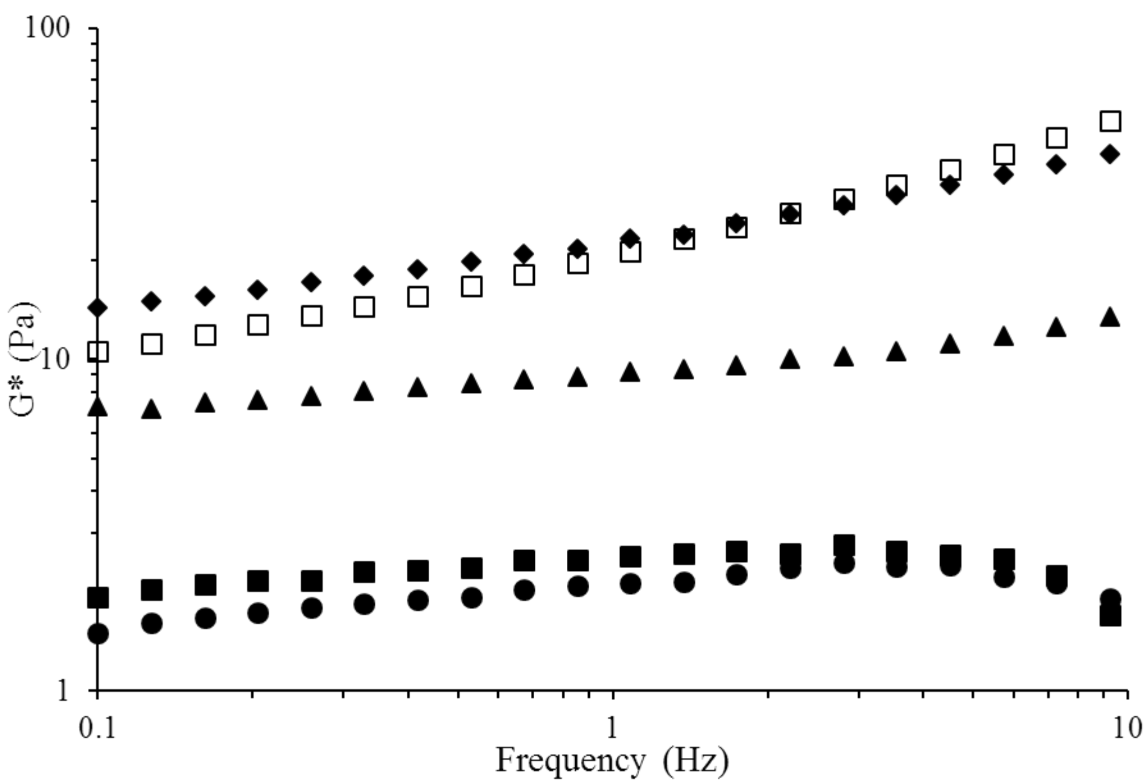


Fig. 4: The frequency sweeps of grapefruit juice and concentrates based on storage modulus (*G'*) and loss modulus (*G''*) in function of the frequency at 25°C. (■: °Brix 9.5; ●: 22 °Brix; ▲: 34.5 °Brix; ♦: 47 °Brix; □: 59.5).



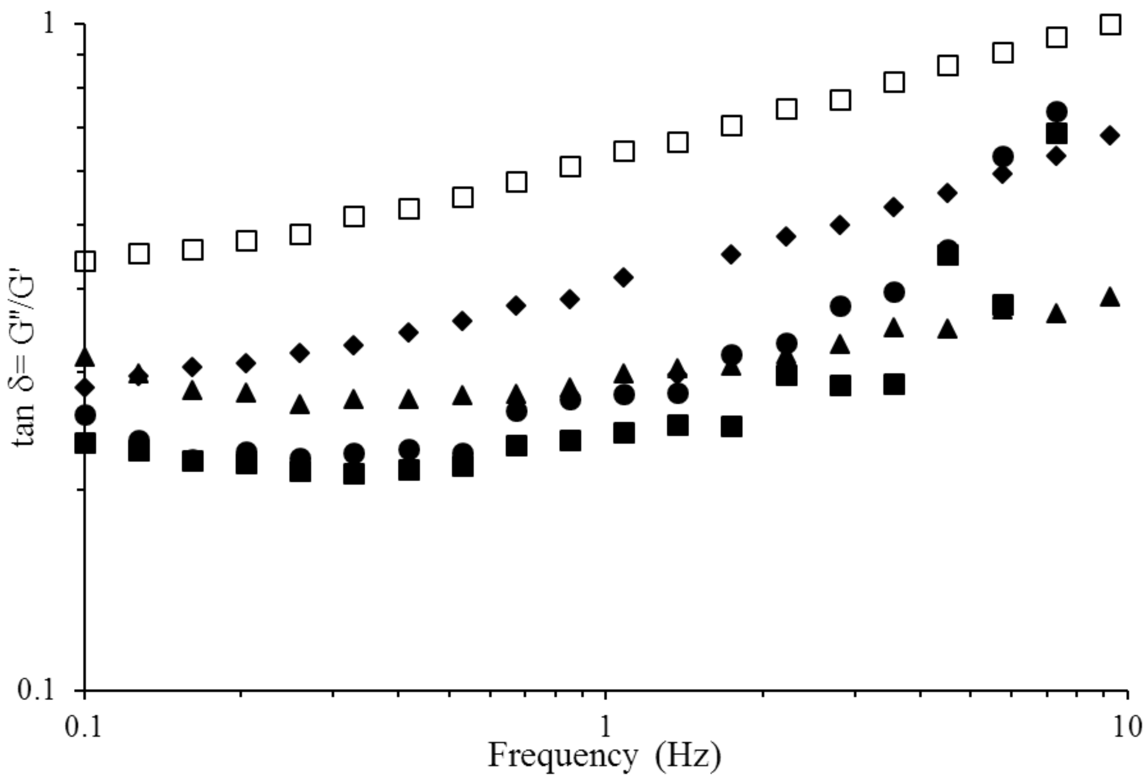


Fig. 5: The frequency sweeps of grapefruit juice and concentrates based on *G** and tan δ in function of the frequency at 25°C. (■: °Brix 9.5; ●: 22 °Brix; ▲: 34.5 °Brix; ♦: 47 °Brix; □: 59.5).

In Figure 5, the frequency sweeps of grapefruit juice and concentrates based on G* and tan δ in the function of the frequency is shown. Complex modulus (G*) shows a modulus of rigidity that included elastic modulus and viscose modulus. This parameter was calculated using Eq. 8 below:

Eq. 8:

$G^* = \sqrt{G'^2 + G''^2}$

G''/G' ratio is called loss modulus (Eq. 9):

Eq. 9:

$$\tan\delta = \frac{G''}{G'}$$

Figure 5 demonstrates that complex modulus or G* increased by increasing the total soluble solid. As can be shown, tan δ increased with increasing frequency in all samples due to the thinning behavior. In addition, loss modulus increased by increasing °Brix. In fact, if food systems have more semi-liquid behavior than semi-solid, loss modulus values will be higher than storage modulus. Loss modulus value is much higher for dilute liquids and amorphous solids varying in the range of 0.2-0.3, but this parameter is 0.01 in gels. Thus, sample behaviors were changed from semi-gel to liquid by increasing the °Brix of concentrates. As previously concluded, the important reason for this behavior is related to the thermal degradation of pectin during the concentration process.

4. Conclusion

Concentration had a significant (P<0.05) effect on the physicochemical and rheological properties of grapefruit juice concentrates. pH of grapefruit concentrates decreased significantly with the development of concentration process, but density and turbidity increased by increasing total soluble solid. The D_{43}, D_{32}, $D_{0.1}$, $D_{0.5}$, and $D_{0.9}$ samples showed a significantly decreasing trend to 47 °Brix, and then increased at 59.5 °Brix. Also, the polydispersity index (span) of the samples showed a similar trend. Lightness (L*), redness (a*), and yellowness (b*) of the samples decreased significantly (P<0.05) during the concentration process. All samples showed shear thinning behaviors and the Hershel-Bulky model of grapefruit concentrates had better fitting than the Newtonian and power law models. In all samples (even in samples with the low °Brix 9.5), the G' values was higher than G'' values (G'>G'') in the range of 0.1-10 Hz frequency, indicating the dominant elastic nature of samples rather than a viscose one, owing to weak gel-like behaviors. Complex modulus (G*) and loss factor (tan δ) increased by increasing the total soluble solid. The most important changes in the concentration process of grapefruit juice is related to the particle size distribution and its relation to the rheological properties of the final products. Structural changes have been monitored during the concentration process, which seems to corresponding to the grapefruit concentrates particles. In general, concentration process had significant effect on the physicochemical, particle size distribution and rheological properties of grapefruit concentrates. Results can be recommended to controlling of quality parameters of fruit juices during concentration.

5. Conflict of interest and ethical statements

The authors declare that they have no conflict of interest. This study was approved by the Sari Agriculture Sciences and Natural Resources University (SANRU).

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