



Experimental study of physical and rheological properties of grape juice using different temperatures and concentrations. Part II: Merlot



Maurício Bonatto Machado de Castilhos*, Lilian Fachin Leonardo Betiol, Gisandro Reis de Carvalho, Javier Telis-Romero

São Paulo State University – UNESP, Institute of Biosciences, Humanities and Exact Sciences – IBILCE, Campus São José do Rio Preto, Food Engineering and Technology Department – DETA, Cristóvão Colombo St. 2265, 15054-000 São José do Rio Preto, Brazil

ARTICLE INFO

Keywords:

Rheology
Physical properties
Merlot
Grape juice
Activation energy

ABSTRACT

The effect of the temperature and concentration on rheological behavior of Merlot juice concentrates was assessed using a rheometer over a wide range of temperature (1–66 °C) and concentrations (13.6–45.0 Brix) at shear rates of 0.84–212.1 1/s. The Ostwald-De Waele was the best rheological model fitted the data ($R^2 = 0.99967$ and relative error = 7.99%). The consistency levels were significantly reduced with the increase of temperature and increased with the increase of the concentrations, ranging from 0.1766 (13.6 Brix at 66 °C) to 19.1140 Pa·sⁿ (45.0 Brix at 1 °C). The flow behavior index presented no up or downward pattern when the temperatures were compared. The flow activation energy ranged from 13.95 (45.0 Brix) to 24.88 KJ/mol (21.0 Brix) with a $R^2 = 0.9822$ and 0.9812, respectively. Density and specific heat were influenced by both temperature and concentration; however, thermal conductivity was only influenced by concentration and temperature in two cases (13.6 and 29.0 Brix). The data showed the potential use of Merlot juice concentrates as wine chaptalization agent in winemaking.

1. Introduction

Merlot grape cultivar is a classic grape responsible for the most known high quality wines from Saint-Émilion and Pomerol regions and it is considered one of the most grape cultivars cultivated in the Bordeaux region, France. In Brazil, Merlot was introduced as a result of a study from Porto Alegre Agronomic Station and then was spread for other states (Rizzon & Miele, 2009). Merlot grape, as the major *Vitis vinifera* species, presents in its composition a great concentration of phenolic and bioactive compounds which are responsible for the high antioxidant properties and nutritional benefits (Đorđević et al., 2017). It is normal to notice fruit nuances of cooked plums and dried figs in Merlot juices and young red wines, mainly due to several factors such as climate changes, higher temperatures, variation in the soil composition and grapevine management (Pons, Allamy, Lavigne, Dubourdiou, & Darriet, 2017).

The rheological behavior of the Merlot juice is an important subject of research since the Merlot grape presents a relevant use for winemaking due to its sensory features that are very appreciated by the Brazilian consumers. In addition, the production of the grape juice and the winemaking itself are considered as complex procedures which

involve several steps since the temperature control until the control of the concentration of reducing sugars and acidity (Jackson, 2008). Due to the complexity of the production of grape juices and wines, the study of the rheological behavior of grape juices becomes crucial in order to design unit operations, process optimization and evaporation processes resulting in the production of juice concentrates. Since grape juices present a relevant amount of chemical compounds which directly responds for the sensory features, the study of the physical properties such as density, specific heat and thermal conductivity can be considered very important in this context (Augusto, Ibarz, & Cristianini, 2012).

There are several studies that show relevant results about the rheology of juices from several raw materials such as soy-ogi, a fermented food product made from maize (Ojo & Akanbi, 2006); blueberry and raspberry (Nindo, Tang, Powers, & Singh, 2005); blood orange juice (Mondal, Cassano, Conidi, & De, 2016); white carrot juice (Kobus et al., 2015); passion fruit juice (Jiraratananon & Chanachai, 1996); “Totapuri” mangoes (Dak, Verma, & Sharma, 2006) and beverage emulsions (Buffo & Reineccius, 2002); however, there is a lack of studies regarding the rheological behavior of grape juices mainly from *Vitis vinifera* grapes, since these grapes are commonly used for winemaking.

* Corresponding author at: São Paulo State University – UNESP, Institute of Biosciences, Humanities and Exact Sciences – IBILCE, Campus São José do Rio Preto, Food Engineering and Technology Department – DETA, Cristóvão Colombo Street, 2265, São José do Rio Preto, São Paulo, Brazil.

E-mail address: mbonattosp@yahoo.com.br (M.B.M. de Castilhos).

<https://doi.org/10.1016/j.foodres.2017.12.026>

Received 7 October 2017; Received in revised form 10 December 2017; Accepted 12 December 2017

Available online 13 December 2017

0963-9969/ © 2017 Elsevier Ltd. All rights reserved.

As a possible alternative for winemaking procedure, Brazilian law allows the direct introduction of sucrose in the must in order to correct the alcoholic content of the wines. This procedure is known as chaptalization and it is commonly applied in Brazilian wineries since the grapes did not achieve the necessary sugar content in the grapevine, which is crucial for achieving the alcoholic content fixed by legislation (8.6 to 14.0% v/v of ethanol) (Brasil, 2005). Based on that, a possible alternative for the substitution of the sucrose as chaptalization agent is the insertion of grape juice concentrate allowing the maintenance of the wine features; which is an uncommon practice in Brazil.

The chaptalization process is a subject that assembles for a strong discussion by the winemakers and the oenological experts since the direct insertion of the sucrose in the fermentative must may result in the loss of varietal features for some wines such as volatile compounds of Riesling wine (Jackson, 2008). In some countries, the practice of the insertion of juice concentrate is common, using a partially fermented or an unfermented grape juice or juice concentrate known as sweet reserve (Jackson, 2008); however, in Brazil this practice is still uncommon. Since this procedure is not applied in winemaking yet, the study of the rheological behavior of this type of raw material become suitable.

Based on the above considerations, the present study aimed at evaluating the rheological behavior of Merlot juice concentrates at different concentrations and temperatures and, additionally, predict a possible influence of these aforementioned parameters on density, specific heat and thermal conductivity.

2. Material and methods

2.1. Juice samples

Merlot grape juice (*Vitis vinifera*) was produced from grapes grown in Santa Catarina State, Brazil and the grape juices were obtained directly from the producers and being classified as “ready-to-drink”. A previous visual assessment of the wines, consisted in observe the glass of wines against white/bright light in order to see if the samples presented particulate matter, showed that they presented no particulate matter. The juice (initial 13.0 Brix) was concentrated to 13.6, 21.0, 29.0, 37.0 and 45 Brix in a rotary low pressure evaporator (Marconi MA 130) at 44 °C. The soluble solid content of the juice and concentrates was assessed by a refractometer (PAL-BX/RI-Atago). All samples remained at rest for at least 24 h before being submitted to rheological measurements.

2.2. Rheological characterization

Steady shear rheological tests were carried out in a controlled stress rheometer, model ARG2 (TA Instruments, New Castle, USA) using a concentric cylinder geometry (inner cylinder – 42 mm × 28 mm; outer cylinder – 78.5 mm × 30.15 mm) with 5920 μm gap under controlled stress and temperature, the latter controlled by a Peltier system. The system was operated by the Rheology Advantage software, in which steady flow was reached ranging shear rate from 0.84 to 212.1 s⁻¹ at different temperatures (1, 10, 19, 28, 37, 46, 56 and 66 °C). These temperatures were chosen based on the pasteurization process, since the grape juice is pasteurized before its application in wineries and before consumption.

A brief study was conducted in order to evaluate the necessary time to reach steady state conditions and the steady state was obtained for each shear rate assessed. The accuracy of the rheometer was previously done using a rheological study of chlorobenzene and acetic acid (50:50 v/v) as standard substances according to Neto, De Castilhos, Telis, and Telis-Romero (2014).

The rheological models were fitted to the experimental shear stress and shear rate data using the nonlinear estimation procedure of Statistica software (StatSoft Inc., 2014). In order to represent the experimental data, four rheological models were used as follows: Newton

law of viscosity (Eq. (1)), Ostwald-de Waele (Eq. (2)), Bingham (Eq. (3)) and Herschel-Bulkley (Eq. (4)). This approach allowed the determination of the rheological parameters, which could be correlated with the aforementioned temperatures. The best rheological model that fitted the experimental data was selected according to the coefficient of determination (R²) as well as by the minimization of the relative error (Eq. (5)) between observed and predicted values.

$$\tau = \mu \dot{\gamma} \quad (1)$$

$$\tau = k \dot{\gamma}^n \quad (2)$$

$$\tau = \tau_0 + \eta \dot{\gamma} \quad (3)$$

$$\tau = \tau_0 + k \dot{\gamma}^n \quad (4)$$

$$\text{Error (\%)} = \frac{|\text{observed} - \text{predicted}|}{\text{observed}} \times 100 \quad (5)$$

The different values of n indicate the fluid behavior, i.e., n = 1 for Newtonian or Bingham plastic fluid, n < 1 for pseudoplastic fluid and n > 1 for dilatant fluid.

The rheological parameters as consistency level (k) and viscosity (μ) are influenced by temperature and the effect of this aforementioned variable was studied by fitting the rheological data to the Arrhenius equation (Eq. (6)) as follows:

$$k = k_0 \exp\left(\frac{E_a}{RT}\right) \quad (6)$$

As only the consistency level dependency was assessed, in this expression k₀ is an empirical constant, R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), T is the absolute temperature (K) and E_a (KJ·mol⁻¹) is the activation energy required for the flow (Telis-Romero, Thomaz, Bernardi, Telis, & Gabas, 2006).

2.3. Determination of physical properties

2.3.1. Density

Merlot juices density was determined in triplicate using a digital electronic densimeter (model DMA 4500-M, Anton Paar, Austria) at the same temperature range as done for rheological assays. These temperatures were established in the own equipment after inserting approximately 50 mL of each juice for density measurements. The equipment accuracy was evaluated using aqueous solution of acetic acid (50:50 v/v) by Neto et al. (2014) with well-known densities described by Perry and Chilton (1986).

2.3.2. Thermal conductivity

The effective thermal conductivity of the Merlot juices was measured at different moisture contents and temperature by a steady-state technique. The apparatus used consists of a jacketed cylindrical cell (106 cm long, 9.8 cm inner diameter, 12.2 cm outer diameter) of stainless steel divided in four modules. A thermal resistance of 200 W, located along the axis of the cell, provided a uniform heat flux during the experiments. Both ends of the apparatus were isolated with Teflon discs (1 cm thickness, 17 cm diameter) to prevent axial heat transfer. The power input to the heater resistance was regulated by a laboratory DC power supply (MPS-3006D, Minipa, São Paulo, Brazil), which allowed to adjust the current with a stability of 0.05%. Five type-J thermocouples were fixed between the surfaces of the resistance and the inner cylinder allowing the measurements of the temperature as can be seen in Fig. 1 (De Castilhos, Betioli, Carvalho, & Telis-Romero, 2017). Temperatures were monitored using a data logger (NI 9213, National Instruments, Austin, USA) and a program for data acquisition developed in LabVIEW (National Instruments, Austin, USA). During the experiments, cold water passed through the jacket from a thermostatic bath (MA-184, Marconi, São Paulo, Brazil) in order to control the temperature in the inner surface of the cell.

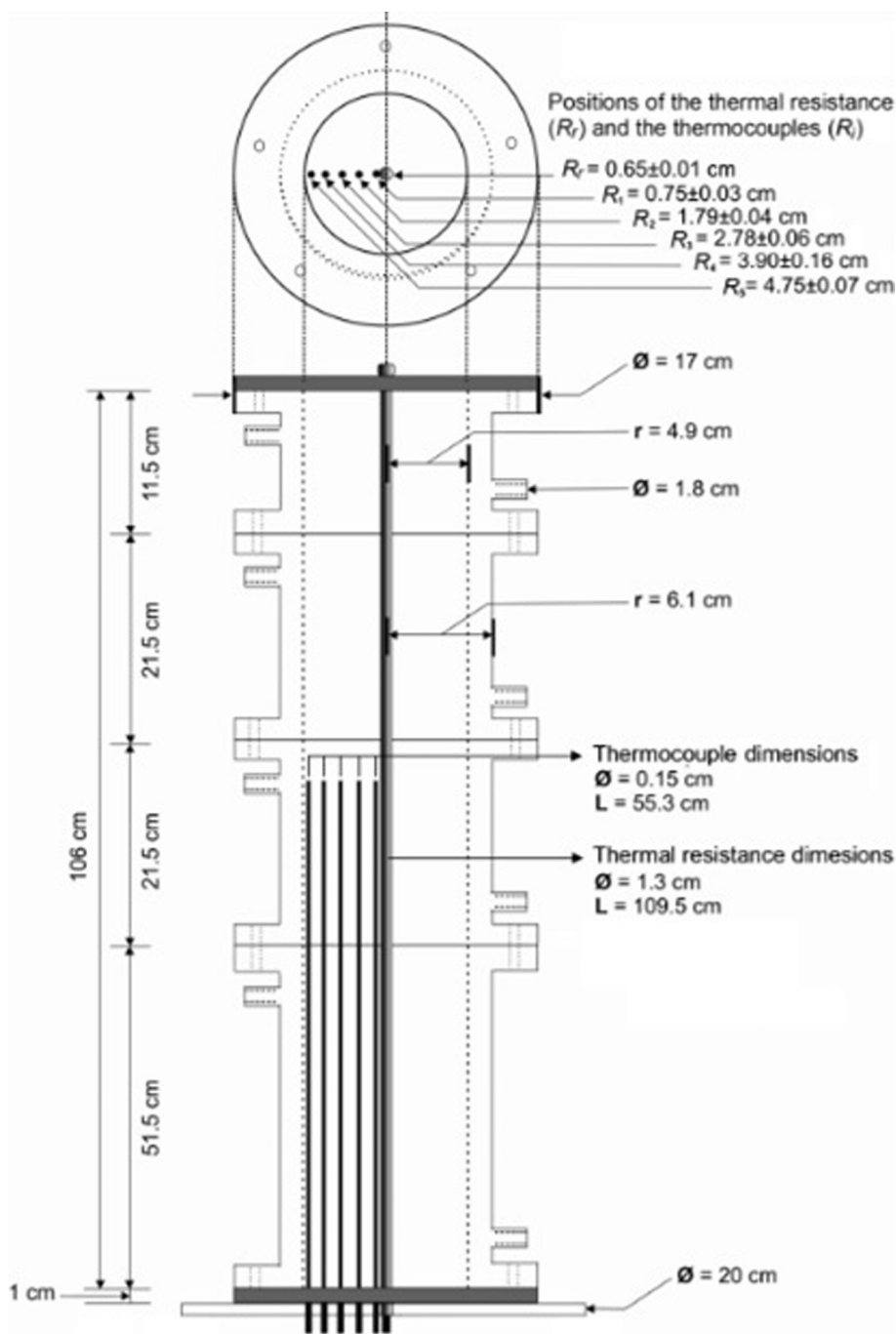


Fig. 1. Apparatus used to determine the thermal conductivity.

Table 1
Coefficient of determinations and relative errors (mean ± standard deviation) of Merlot concentrates obtained by fitting the experimental data to the rheological models.

Model name	Model equation	R ²	Relative error (%)
Newtonian	$\tau = \mu\dot{\gamma}$	0.99942 ± 0.0002	14.97 ± 5.4
Ostwald-de Waele	$\tau = k\dot{\gamma}^n$	0.99967 ± 0.0003	7.99 ± 3.5
Bingham	$\tau = \tau_0 + \eta\dot{\gamma}$	0.99941 ± 0.0021	11.86 ± 4.6
Herschel-Bulkley	$\tau = \tau_0 + k\dot{\gamma}^n$	0.99967 ± 0.0003	8.11 ± 3.6

Experiments were performed in triplicate by loading the cell with juice at the different moisture contents and monitoring the temperature profile during heating at constant heat flux. When the deviation among the temperatures within the cell was almost constant, steady state conditions could be assumed and thermal conductivity (*k*)

(W·m⁻¹·°C⁻¹) was calculated from the unidirectional radial heat transfer equation (Eq. (7)), as described by Fourier equation in cylindrical coordinates with the boundary conditions corresponding to the transfer between the two concentric cylindrical surfaces kept at constant temperatures (Carvalho, Chenlo, Moreira, & Telis-Romero, 2015; Telis-Romero, Gabas, Polizelli, & Telis, 2000) and considering heat supplied by the thermal resistance (*q*) (W) was equal to the heat that passed through the juice:

$$k = q \frac{\ln\left(\frac{R_1}{R_5}\right)}{2\pi l(T_5 - T_1)} \tag{7}$$

where *l* is the cell length (m), *R*₁ and *R*₅ are the radial positions (m) of the thermocouple closest to the thermal resistance and the thermocouple closest to the inner surface of the cell, respectively, and *T*₁ and

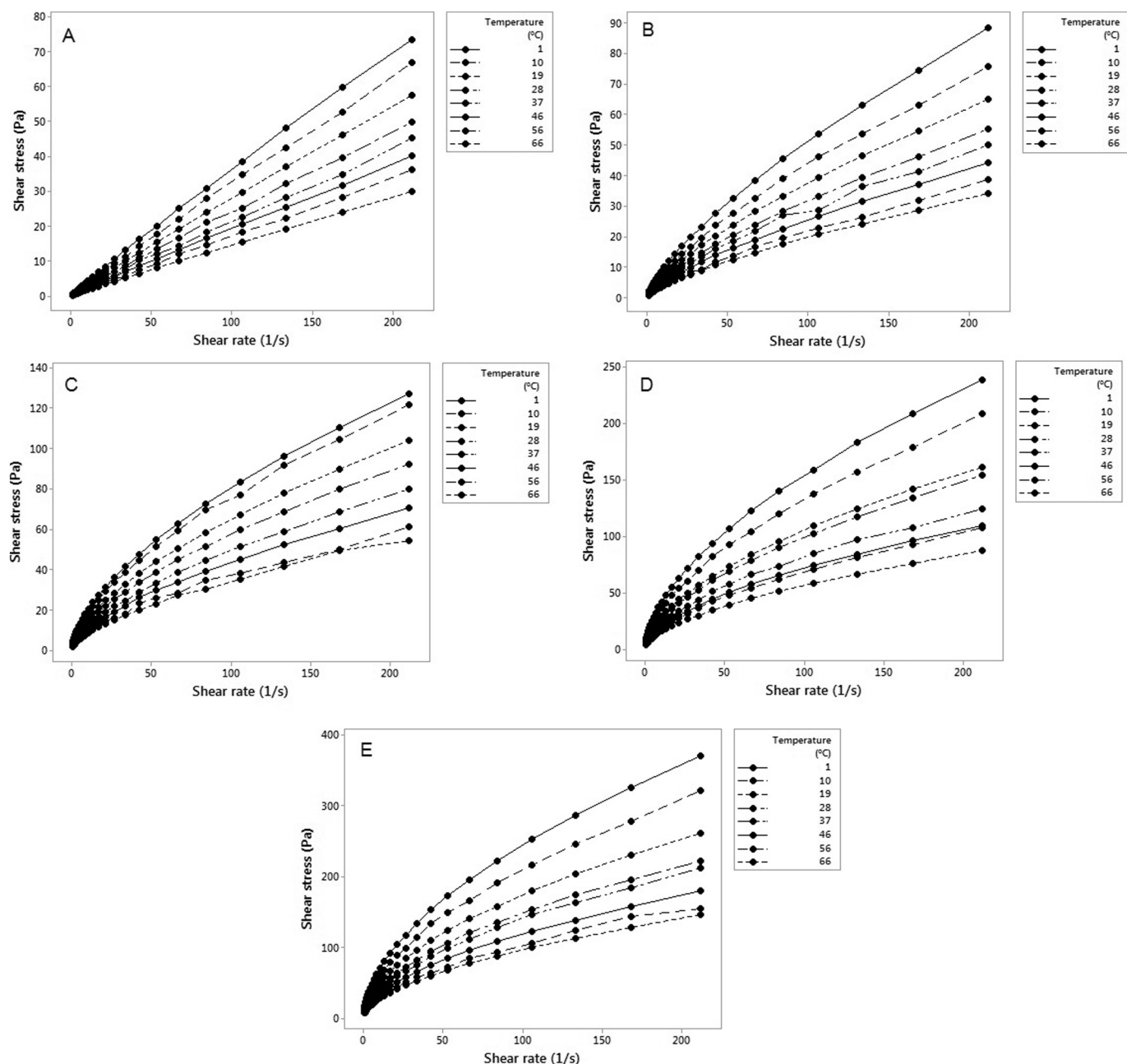


Fig. 2. Rheological behavior of the Merlot concentrates according to the different temperatures and soluble solid contents. (A) 13.6 Brix, (B) 21.0 Brix, (C) 29.0 Brix, (D) 37.0 Brix and (E) 45.0 Brix.

T_5 are the steady state temperatures ($^{\circ}\text{C}$) at R_1 and R_5 , respectively.

2.3.3. Specific heat measurements

The specific heat capacity was measured by a DSC 8000 (Perkin Elmer, Shelton, CT). The DSC instrument was calibrated with indium (m.p. = 156.6 $^{\circ}\text{C}$, h_f = 28.45 J/g) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The purge gas was nitrogen (purity, 99.5%) with a flow rate of approximately 20 mL/min. Sample liquid aluminum pans weighing 24.01 ± 0.04 mg (ref. 0219-0062, Perkin Elmer, USA) were used as the baseline, and also as recipients for the reference material (Arched, 1993). Samples were sealed and weighed before and after the experimental procedures. The baseline material, reference material, and samples were subjected to the following temperature program: isothermal 0 $^{\circ}\text{C}$ for 4 min, heat flow of 10 $^{\circ}\text{C}/\text{min}$ to 60 $^{\circ}\text{C}$, and isothermal for 4 min, according to the ASTM-E1269 method (ASTM, 2005). The PYRIS 10.1 software (Perkin Elmer, Shelton, CT) was used to analyze

the thermal data. The specific heat capacity (c_p , J/kg $^{\circ}\text{C}$) of the concentrates was calculated using Eq. (8), where D_s is the net thermal power with respect to a reference material at a given temperature (mW), W_s is the sample mass (mg) and θ is the heating rate ($^{\circ}\text{C}/\text{s}$).

$$c_p = \frac{D_s}{W_s \theta} \quad (8)$$

2.4. Data analysis

The experiment was repeated three times and each sample was collected in triplicate. The data were analyzed using a completely randomized design in order to avoid carryover effects. The statistical significance of the rheological parameters and physical properties was evaluated by Analysis of Variance (ANOVA) followed by Tukey's multiple comparison *post-hoc* test with $P < 0.05$. Statistical approach was

Table 2Rheological parameters (mean \pm standard deviation) of Ostwald-de Waele equation of Merlot juice concentrates at various concentrations and temperatures.

Temperature (°C)	Consistency level, k (Pa·s ⁿ)				
	Concentration (Brix)				
	13.6	21.0	29.0	37.0	45.0
1	0.4712 \pm 0.0077 ^a	1.8183 \pm 0.0179 ^a	4.8651 \pm 0.0306 ^a	10.5710 \pm 0.1030 ^a	19.1140 \pm 0.1410 ^a
10	0.3921 \pm 0.0042 ^b	1.5141 \pm 0.0228 ^b	4.2690 \pm 0.0638 ^b	8.8337 \pm 0.0563 ^b	16.1340 \pm 0.1390 ^b
19	0.3447 \pm 0.0023 ^c	1.3305 \pm 0.0147 ^c	3.6405 \pm 0.0214 ^c	7.6946 \pm 0.0793 ^c	14.3560 \pm 0.1150 ^c
28	0.3048 \pm 0.0042 ^d	1.1493 \pm 0.0036 ^d	3.1537 \pm 0.0089 ^d	6.7083 \pm 0.0293 ^d	12.4540 \pm 0.0089 ^d
37	0.2528 \pm 0.0017 ^e	1.0457 \pm 0.0109 ^e	2.7561 \pm 0.0056 ^e	5.9335 \pm 0.0546 ^e	10.7660 \pm 0.0375 ^e
46	0.2302 \pm 0.0009 ^f	0.8938 \pm 0.0097 ^f	2.4084 \pm 0.0193 ^f	5.1927 \pm 0.0192 ^f	9.5573 \pm 0.0325 ^f
56	0.1997 \pm 0.0049 ^g	0.7696 \pm 0.0112 ^g	2.2160 \pm 0.0475 ^g	4.4882 \pm 0.0057 ^g	8.5575 \pm 0.06190 ^g
66	0.1766 \pm 0.0017 ^h	0.6850 \pm 0.0106 ^h	1.9306 \pm 0.0184 ^h	4.0203 \pm 0.0228 ^h	7.4995 \pm 0.0279 ^h
P value ¹	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Temperature (°C)	Flow behavior index, n				
	Concentration (Brix)				
	13.6	21.0	29.0	37.0	45.0
1	0.9435 \pm 0.0031 ^d	0.7246 \pm 0.0011 ^{ab}	0.6089 \pm 0.0009 ^c	0.5814 \pm 0.0013 ^b	0.5530 \pm 0.0008 ^b
10	0.9589 \pm 0.0033 ^{abc}	0.7293 \pm 0.0023 ^a	0.6254 \pm 0.0028 ^{ab}	0.5877 \pm 0.0013 ^a	0.5565 \pm 0.0009 ^a
19	0.9553 \pm 0.0012 ^{bc}	0.7253 \pm 0.0017 ^{ab}	0.6251 \pm 0.0005 ^{ab}	0.5673 \pm 0.0015 ^d	0.5419 \pm 0.0015 ^d
28	0.9514 \pm 0.0026 ^{cd}	0.7212 \pm 0.0002 ^b	0.6299 \pm 0.0006 ^a	0.5837 \pm 0.0006 ^b	0.5379 \pm 0.0001 ^e
37	0.9631 \pm 0.0014 ^{ab}	0.7225 \pm 0.0036 ^{ab}	0.6275 \pm 0.0004 ^{ab}	0.5677 \pm 0.0014 ^d	0.5557 \pm 0.0009 ^{ab}
46	0.9615 \pm 0.0002 ^{ab}	0.7265 \pm 0.0009 ^{ab}	0.6284 \pm 0.0011 ^{ab}	0.5684 \pm 0.0008 ^d	0.5474 \pm 0.0013 ^c
56	0.9668 \pm 0.0065 ^a	0.7277 \pm 0.0045 ^{ab}	0.6088 \pm 0.0053 ^c	0.5900 \pm 0.0004 ^a	0.5410 \pm 0.0014 ^d
66	0.9576 \pm 0.0012 ^{bc}	0.7288 \pm 0.0026 ^a	0.6229 \pm 0.0018 ^b	0.5725 \pm 0.0001 ^c	0.5544 \pm 0.0007 ^{ab}
P value ¹	< 0.001	0.011	< 0.001	< 0.001	< 0.001

¹ Different letters in the same column indicate significant differences according to Analysis of Variance and post-hoc Tukey's test ($\alpha = 0.05$).**Table 3**Parameters of Arrhenius equation, activation energy and coefficient of determination (R²) (mean \pm standard deviation) of Merlot juice concentrates at various concentrations.

Concentration (Brix)	k ₀ (Pa·s ⁿ) ²	E _a (KJ/mol) ³	R ²
13.6	0.2551 \pm 0.001 ^e	22.54 \pm 0.4 ^b	0.9780 \pm 0.0035
21.0	1.0559 \pm 0.011 ^d	24.88 \pm 0.8 ^a	0.9812 \pm 0.0026
29.0	2.7809 \pm 0.005 ^c	22.84 \pm 0.4 ^b	0.9796 \pm 0.0029
37.0	5.9870 \pm 0.056 ^b	22.87 \pm 0.8 ^b	0.9795 \pm 0.0024
45.0	10.825 \pm 0.038 ^a	13.95 \pm 0.2 ^c	0.9822 \pm 0.0012
P value ¹	< 0.001	< 0.001	

¹ Different letters in the same column indicate significant differences according to Analysis of Variance and post-hoc Tukey's test ($\alpha = 0.05$).² k₀: empirical constant.³ E_a: activation energy.

performed using the software Minitab 15 (Lead Technologies, State College, PA, USA).

3. Results and discussion

3.1. Rheological behavior of merlot juice concentrates

The aforementioned rheological models were fitted to the data from Merlot juice concentrates and the goodness of fitting was analyzed by the coefficient of determinations (R²) and the relative errors (%) (Table 1).

All models showed high values of goodness of fitting with R² > 0.999; however, both Ostwald-de Waele and Herschel-Bulkley models were more perfectly fitted to the experimental data with R² = 0.99967. In addition, the lower relative error was observed for Ostwald-de Waele model (7.99 \pm 3.5%) indicating that the juice concentrates were better adjusted to the referred rheological model. In all Brix assessed, the Herschel-Bulkley fitting resulted in negative stress

values which are meaningless in a physical point of view (Gratão, Silveira, & Telis-Romero, 2007) and resulted in a null τ_0 , meaning that the Ostwald-de Waele rheological model was the best to describe the rheological behavior of the Merlot concentrates. This result is similar to the previous results obtained by De Castilhos et al. (2017) who reported the same rheological behavior for the Cabernet Sauvignon juice concentrates.

The rheograms of the experimental data collected in the different soluble solid contents of the Merlot juice concentrates ranging from 1 °C to 66 °C using the Ostwald-de Waele rheological model were also performed (Fig. 2). As stated in the previous study, the relationship between the shear rate and shear stress showed a non-Newtonian behavior of the concentrates assessed with a concave curve downward pattern, assuming a pseudoplastic behavior (De Castilhos et al., 2017).

3.2. Effect of concentration on rheological behavior of Merlot concentrates

The effect of the concentration on the consistency level (k) and flow behavior index (n) for eight different temperatures was also assessed (Table 2). The results showed a significant reduction of the consistency level (k) as the temperature increase (P < 0.001) and this result corroborate the reported by some studies (Dak et al., 2006; Dak, Verma, & Jaaffrey, 2007; De Castilhos et al., 2017; Kobus et al., 2015).

The rheological behavior of a fluid is influenced by several factors, mainly the intermolecular forces and the water-solute interaction which limit the movement of the particles at a molecular level. Changes in the temperature and concentration can lead to significant changes in the intermolecular forces (Shamsudin, Ling, Adzahan, & Daud, 2013). Based on this, the significant increase of the consistency level (k) indicates that it will be necessary a longer heating and holding time during juice pasteurization before its use for direct consumption or chaptalization agent in wineries, since the flow rate in the pipe will decrease due to the high flow resistance caused by the fluid (Quek, Chin, & Yusof, 2013).

Table 4
Density, specific heat and thermal conductivity (mean \pm standard deviation) from Merlot juice concentrates.

Temperature (°C)	Density (kg·m ⁻³)					P value
	Concentration (Brix)					
	13.6	21.0	29.0	37.0	45.0	
1	1052.9 \pm 0 ^{aE}	1093.3 \pm 2 ^{aD}	1126.2 \pm 0 ^{aC}	1168.0 \pm 2 ^{aB}	1208.9 \pm 4 ^{aA}	< 0.001
10	1050.6 \pm 0 ^{aE}	1086.1 \pm 1 ^{bD}	1123.0 \pm 0 ^{abC}	1164.5 \pm 2 ^{abB}	1207.2 \pm 4 ^{abA}	< 0.001
19	1047.4 \pm 0 ^{abE}	1083.5 \pm 1 ^{bD}	1120.4 \pm 1 ^{abcC}	1161.4 \pm 2 ^{abB}	1204.6 \pm 5 ^{abA}	< 0.001
28	1044.2 \pm 0 ^{bcE}	1080.4 \pm 1 ^{bcD}	1119.1 \pm 1 ^{bcC}	1158.5 \pm 2 ^{abcB}	1202.8 \pm 5 ^{abA}	< 0.001
37	1042.7 \pm 1 ^{bcE}	1079.6 \pm 2 ^{bcD}	1117.1 \pm 2 ^{bcC}	1155.3 \pm 2 ^{bcB}	1199.6 \pm 5 ^{abcA}	< 0.001
46	1041.8 \pm 2 ^{bcE}	1076.1 \pm 2 ^{cdD}	1114.0 \pm 2 ^{cdC}	1155.6 \pm 4 ^{abcB}	1196.4 \pm 5 ^{abcA}	< 0.001
56	1038.9 \pm 2 ^{cdE}	1072.6 \pm 2 ^{cdD}	1110.4 \pm 2 ^{decC}	1148.7 \pm 2 ^{cb}	1186.5 \pm 2 ^{bcA}	< 0.001
66	1035.4 \pm 2 ^{deE}	1065.6 \pm 0 ^{edD}	1107.3 \pm 2 ^{ecC}	1147.7 \pm 3 ^{cb}	1180.7 \pm 2 ^{ca}	< 0.001
P value	< 0.001	< 0.001	< 0.001	< 0.001	0.003	

Temperature (°C)	Specific heat (J·kg ⁻¹ ·°C ⁻¹)					P value
	Concentration (Brix)					
	13.6	21.0	29.0	37.0	45.0	
1	3737.5 \pm 0 ^{dA}	3544.9 \pm 40 ^{eB}	3330.4 \pm 3 ^{fC}	3120.2 \pm 23 ^{ed}	2907.3 \pm 13 ^{fE}	< 0.001
10	3756.1 \pm 7 ^{dA}	3560.6 \pm 10 ^{deb}	3348.4 \pm 3 ^{efC}	3137.9 \pm 19 ^{ded}	2925.6 \pm 17 ^{efe}	< 0.001
19	3774.0 \pm 7 ^{cdA}	3578.6 \pm 11 ^{cdeB}	3367.0 \pm 10 ^{defC}	3156.0 \pm 20 ^{cdeD}	2943.5 \pm 18 ^{defE}	< 0.001
28	3792.0 \pm 7 ^{bcdA}	3596.6 \pm 11 ^{bcdB}	3385.6 \pm 19 ^{decC}	3174.2 \pm 23 ^{bcdD}	2961.5 \pm 19 ^{cdeE}	< 0.001
37	3810.7 \pm 16 ^{abcdA}	3615.7 \pm 26 ^{abcdB}	3403.6 \pm 21 ^{bcdC}	3192.2 \pm 23 ^{abcdD}	2979.5 \pm 19 ^{bcdE}	< 0.001
46	3830.1 \pm 34 ^{abcA}	3633.3 \pm 22 ^{abcB}	3421.6 \pm 21 ^{abcC}	3210.5 \pm 30 ^{abcd}	2997.5 \pm 20 ^{abcE}	< 0.001
56	3850.9 \pm 43 ^{abA}	3653.3 \pm 22 ^{abB}	3441.6 \pm 21 ^{abC}	3230.2 \pm 24 ^{abd}	3018.5 \pm 22 ^{abE}	< 0.001
66	3870.9 \pm 44 ^{aA}	3672.0 \pm 4 ^{aB}	3462.0 \pm 25 ^{aC}	3248.6 \pm 11 ^{ad}	3036.8 \pm 7 ^{aE}	< 0.001
P value	< 0.001	< 0.001	< 0.001	< 0.001	0.036	

Temperature (°C)	Thermal conductivity (W·(m °C ⁻¹))					P value
	Concentration (Brix)					
	13.6	21.0	29.0	37.0	45.0	
1	0.498 \pm 0.000 ^{eA}	0.470 \pm 0.002 ^B	0.437 \pm 0.001 ^{bC}	0.407 \pm 0.005 ^D	0.377 \pm 0.006 ^E	< 0.001
10	0.499 \pm 0.000 ^{deA}	0.470 \pm 0.002 ^B	0.438 \pm 0.001 ^{abC}	0.408 \pm 0.005 ^D	0.379 \pm 0.007 ^E	< 0.001
19	0.501 \pm 0.000 ^{deA}	0.472 \pm 0.003 ^B	0.440 \pm 0.002 ^{abC}	0.410 \pm 0.004 ^D	0.381 \pm 0.007 ^E	< 0.001
28	0.502 \pm 0.002 ^{cdeA}	0.473 \pm 0.003 ^B	0.442 \pm 0.004 ^{abC}	0.411 \pm 0.005 ^D	0.383 \pm 0.008 ^E	< 0.001
37	0.504 \pm 0.003 ^{bcdA}	0.476 \pm 0.006 ^B	0.444 \pm 0.005 ^{abC}	0.412 \pm 0.005 ^D	0.385 \pm 0.008 ^E	< 0.001
46	0.507 \pm 0.003 ^{abcA}	0.477 \pm 0.005 ^B	0.445 \pm 0.005 ^{abC}	0.416 \pm 0.008 ^D	0.386 \pm 0.008 ^E	< 0.001
56	0.508 \pm 0.003 ^{abA}	0.479 \pm 0.005 ^B	0.447 \pm 0.005 ^{abC}	0.415 \pm 0.005 ^D	0.383 \pm 0.005 ^E	< 0.001
66	0.510 \pm 0.003 ^{aA}	0.478 \pm 0.001 ^B	0.448 \pm 0.005 ^{aC}	0.419 \pm 0.006 ^D	0.389 \pm 0.004 ^E	< 0.001
P value	< 0.001	0.057	0.017	0.137	0.541	

Different upper-case letters in the same row and different lower-case letters in the same column indicate significant differences according to Analysis of Variance and post-hoc Tukey's test ($\alpha = 0.05$).

Analyzing the same concentration (Brix), it was not possible to observe an increase or a decrease for the flow behavior index according to the variation of the temperature, since the data showed high and low values regardless the temperatures assessed. In all concentrations the results indicated significant differences ($P < 0.05$) when the different temperatures were statistically compared among them. In 13.6 Brix, the flow index was higher at higher temperatures; in 21.0, 37.0 and 45.0 Brix, the flow index was higher in low (around 10 °C) and high temperatures (around 56 up to 66 °C) and in 29.0 Brix, the flow index was higher in intermediate temperatures (around 28 °C). These aforementioned results showed that the flow index behavior presented no singular upward or downward pattern according to the temperature variation, corroborating the results obtained by De Castilhos et al. (2017).

This aforementioned result was also confirmed by other important studies such as Shamsudin et al. (2013) who reported the rheological behavior of ultraviolet-irradiated and thermally pasteurized Yankee pineapple juice; Kobus et al. (2015) who reported the effect of the pasteurization on the rheological properties of white carrot juice; Nindo

et al. (2005) who assessed the viscosity of blueberry and raspberry juices for processing applications and De Castilhos et al. (2017) who reported the rheological behavior of Cabernet Sauvignon juice concentrates at different concentrations and temperatures; however, disagree with other studies such as Quek et al. (2013) who reported the rheological behavior of soursop juice concentrates and the increase of the flow behavior index with the increase of the temperature at same concentration; and Dak et al. (2006) who reported the flow characteristics of juice of "Totapuri" mangoes and observed a decrease in the flow behavior index with the increase of the temperature at same concentration. These contrasting results were explained by these authors according to the intrinsic features of the raw material that has been analyzed, since each source present a punctual flow behavior even presenting the same rheological behavior.

3.3. Effect of temperature on rheological parameters

The consistency coefficient of the Ostwald-De Waele rheological model and the influence of the temperature were described by the

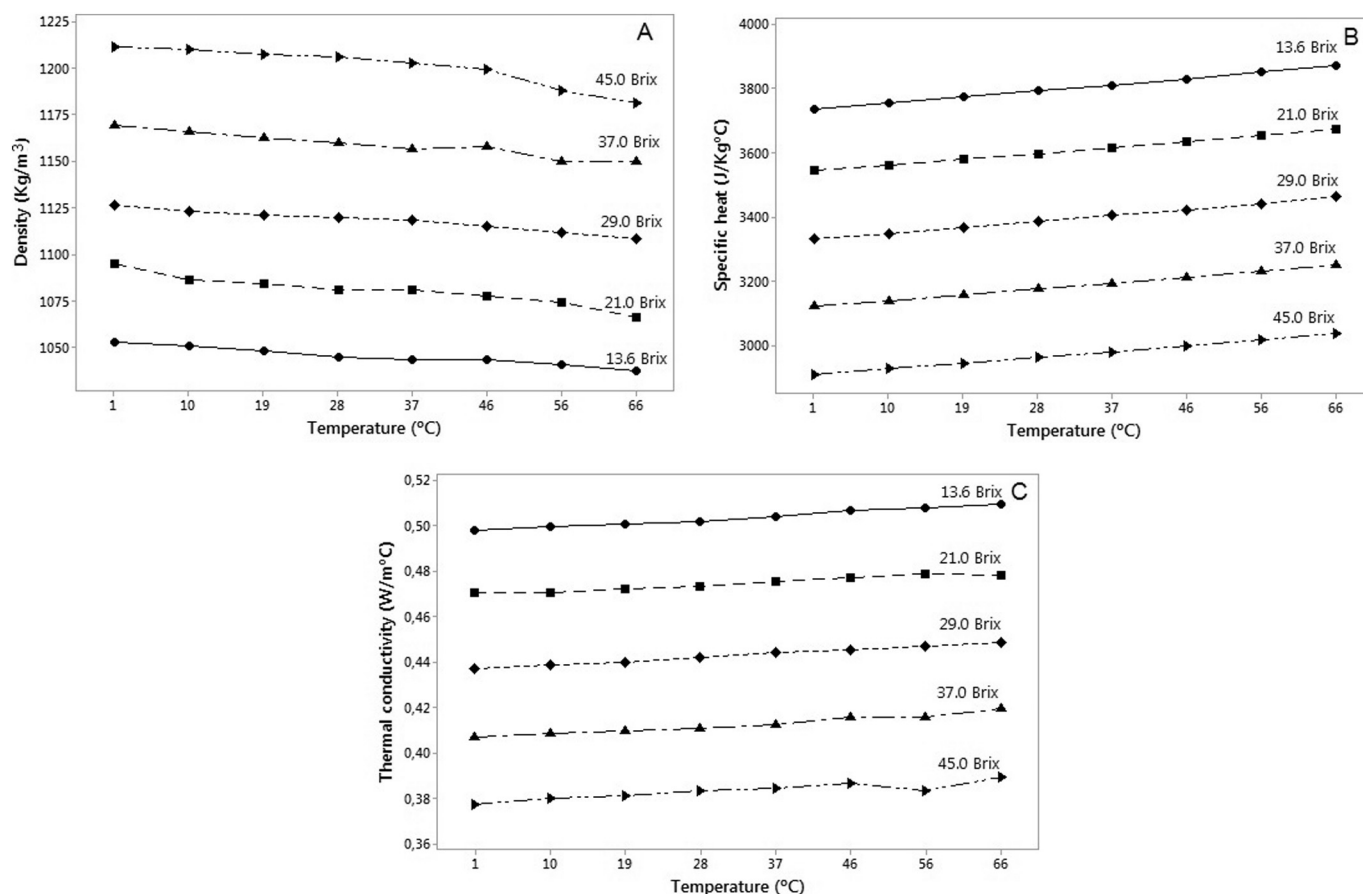


Fig. 3. Density (A), specific heat (B) and thermal conductivity (C) behavior of the Merlot concentrates according to the different temperatures and soluble solid contents.

Arrhenius relationship (Table 3). The values of activation energy from the Merlot juice concentrates presented significant differences ($P < 0.001$) when compared with the different assessed concentrations, showing that the activation energy of the juice concentrate at 21.0 Brix (24.88 KJ/mol) was significantly higher than the activation energy of the juice at 37.0 Brix (22.87 KJ/mol), 29.0 Brix (22.84 KJ/mol) and 13.6 Brix (22.54 KJ/mol), which, by the way, were significantly higher than the activation energy of the grape juice at 45.0 Brix (13.95 KJ/mol). The results showed that the higher the temperature the lower the activation energy, corroborating the results reported by De Castilhos et al. (2017); Chin, Chan, Yusof, Chuah, and Talib (2009) and Dak et al. (2006).

There is a slight tendency in consider that the lower activation energy results were observed in higher grape juice concentrations; however, this is not an assertive tendency. This aforementioned result corroborates the results from De Castilhos et al. (2017) and Dak et al. (2006) who reported the decrease of the activation energy due to the increase of the grape and mango juice concentration, respectively. However, Nindo et al. (2005) reported that the activation energy increased with the increase of raspberry and blueberry juice concentration; Arslan, Yener, and Esin (2005) reported the same behavior for tahin/pekmez juice concentrates, contrasting the aforementioned result.

Another study from Chin et al. (2009) who reported the rheological behavior of pummel juice concentrates showed that there is no up or downward tendency in the activation energy due to the variation of the concentration. These results from the aforementioned studies showed that there are inconsistent reports about the activation energy behavior due to the changes in juice concentration. The results for Merlot juice concentrate showed a significant increase in the activation energy from 13.6 to 21.0 Brix (Table 3), assuming that such behavior can be possibly

explained by the presence of micro particles suspended in the juice that influenced the activation energy at the time of the analysis (Chin et al., 2009). Despite this, the results obtained for the activation energy are fitted in a similar range for grape juice as reported by Zuritz et al. (2005) and De Castilhos et al. (2017). The higher activation energy responds for the higher effect of temperature on viscosity of the grape juice concentrate (Kobus et al., 2015) dealing with a higher sensitivity of the juice viscosity due to the temperature variation.

3.4. Effect of temperature and concentration on density, specific heat and thermal conductivity

The effect of the different temperatures and concentrations on the density, specific heat and thermal conductivity is shown in Table 4 (Fig. 3). The results showed that density and specific heat were influenced by the different temperatures and concentrations ($P < 0.05$); however, thermal conductivity presented significant differences when compared with the different assessed concentrations in all temperatures ($P < 0.001$ for all cases), but only 13.6 ($P < 0.001$) and 29.0 Brix ($P = 0.017$) presented significant differences when the different temperatures were compared. The concentrations 21.0 Brix ($P = 0.057$), 37.0 Brix ($P = 0.137$) and 45.0 Brix ($P = 0.541$) presented no significant differences when the thermal conductivity was compared with the different temperatures.

The increase of the temperature promoted the reduction of the Merlot juice densities considering the same concentration. As the concentration increase, the density also increase, which is an expected result, since the density is directly correlated with the increase of the soluble solid content of the concentrates. Specific heat increased with the higher temperatures; however, this parameter presented lower values for the higher concentration accounting for a negative correlation,

corroborating the results reported by Manohar, Ramakrishna, and Udayasankar (1991) who reported the specific heat of tamarind juice concentrates. Temperature was considered a significant factor for the increase of the thermal conductivity only for 13.6 and 29.0 Brix, showing that the increase of the temperature resulted in the increase of the thermal conductivity; however, for the other assessed concentrations, the temperature presented no significant influence on this physical property. In addition, the aforementioned parameter was strongly influenced by the different concentrations assessed, presenting a significant reduction as the concentration increased.

The density of the Merlot concentrates ranged from 1035.4 (at 13.6 Brix and 66 °C) to 1208.9 kg·m⁻³ (at 45.0 Brix and 1 °C) and these results are in accordance with the previous reports of De Castilhos et al. (2017), Zuritz et al. (2005) and Ramos and Ibarz (1998). The specific heat presented values ranging from 2907.3 (at 45.0 Brix and 1 °C) to 3870.9 J·kg⁻¹·°C⁻¹ (at 13.6 Brix and 66 °C) and these aforementioned results are in accordance with previous reports of Manohar et al. (1991). The thermal conductivity results ranged from 0.377 (at 45.0 Brix and 1 °C) to 0.510 W·m⁻¹·°C⁻¹ (at 13.6 Brix and 66 °C) which presented a concise proximity of the results obtained by De Castilhos et al. (2017) who reported the rheological behavior and the physical properties of Cabernet Sauvignon juice concentrates.

The range of the temperature assessed in this present study associated with the obtained results concerning the rheological behavior is relevant because the grape juices frequently are pasteurized and the knowledge of the physical properties behavior as well as the rheological profile becomes crucial in order to design equipment and heat changers. The differences regarding the behavior of the physical properties discussed in this study is natural since both the rheology and the physical properties change according to the different raw material and source. The obtained results have a great importance for food engineering because they can help to elucidate the behavior of the grape juice concentrates in order to enhance the process optimization and, additionally, help to predict the behavior of this fluid when used as chaptalization agent in winemaking as sucrose substitute.

4. Conclusions

Ostwald-De Waele model satisfactorily described the rheological behavior of the Merlot juice concentrates. The obtained results showed that the consistency level (k) reduces as the temperature increases and the flow index behavior presented particular results depending on the variation of the temperature. The activation energy of the assessed juices presented values that were in accordance with the range reported by some studies; however, this property presented relevant variation since it depends on the different sources and raw materials. Density and specific heat were significantly influenced by temperature as well as by the different concentrations; however, thermal conductivity was only significantly influenced by the different soluble solid contents. This physical property was also influenced by the different temperatures in two concentrations (13.6 and 29.0 Brix).

The obtained results were important for the grape and wine producers since the data regarding the rheological profile and the physical properties will elucidate the behavior of the grape juice concentrates as chaptalization agent. The use of grape juice concentrate instead of sucrose as chaptalization agent can produce wines with more quality since the sensory features might not be negatively changed due to the insertion of sucrose, being considered an alternative step to the classical chaptalization in winemaking.

Acknowledgments

The author M.B.M. de Castilhos thanks the PROPE - UNESP (Pró-Reitoria de Pesquisa) for the scholarship.

References

- Arched, D. G. (1993). Thermodynamic properties of synthetic sapphire (a-A1203) standard reference material 720 and the effect of temperature-scale differences on thermodynamic properties. *Journal of Physical and Chemical Reference Data*, 22, 1441–1453.
- Arslan, E., Yener, M. E., & Esin, A. (2005). Rheological characterization of tahin/pekmez (sesame paste/concentrated grape juice) blends. *Journal of Food Engineering*, 69, 167–172.
- ASTM E1269-11 (2005). *Standard test method for determining specific heat capacity by differential scanning calorimetry*. West Conshohocken: ASTM International.
- Augusto, P. E. D., Ibarz, A., & Cristianini, M. (2012). Effect of high pressure homogenization (HPH) on the rheological properties of a fruit juice serum model. *Journal of Food Engineering*, 111(2), 474–477.
- Brasil (2005). *Altera dispositivos da Lei n. 7678 de 8 de novembro de 1988*. Brasília: Diário Oficial da União.
- Buffo, R. A., & Reineccius, G. A. (2002). Modeling the rheology of concentrated beverage emulsions. *Journal of Food Engineering*, 51, 267–272.
- Carvalho, G. R., Chenlo, F., Moreira, R., & Telis-Romero, J. (2015). Physicochemical properties of aqueous sodium chloride solutions. *Journal of Food Process Engineering*, 38, 234–242.
- Chin, N. L., Chan, S. M., Yusof, Y. A., Chuah, T. G., & Talib, R. A. (2009). Modelling of rheological behaviour of pummelo juice concentrates using master-curve. *Journal of Food Engineering*, 93, 134–140.
- Dak, M., Verma, R. C., & Jaaffrey, S. N. A. (2007). Effect of temperature and concentration on rheological properties of “Kesar” mango juice. *Journal of Food Engineering*, 80, 1011–1015.
- Dak, M., Verma, R. C., & Sharma, G. P. (2006). Flow characteristics of juice of “Totapuri” mangoes. *Journal of Food Engineering*, 76, 557–561.
- De Castilhos, M. B. M., Betiol, L. F. L., Carvalho, G. R., & Telis-Romero, J. (2017). Experimental study of physical and rheological properties of grape juice using different temperatures and concentrations. Part I: Cabernet Sauvignon. *Food Research International*, 100, 724–730.
- Dorđević, N. O., Pejin, B., Novaković, M. M., Stanković, D. M., Mutić, J. J., Pajović, S. B., & Tešević, V. V. (2017). Some chemical characteristics and antioxidant capacity of novel Merlot wine clones developed in Montenegro. *Scientia Horticulturae*, 225, 505–511.
- Gratão, A. C. A., Silveira, V., Jr., & Telis-Romero, J. (2007). Laminar flow of soursop juice through concentric annuli: Friction factors and rheology. *Journal of Food Engineering*, 78, 1343–1354.
- Jackson, R. S. (2008). *Wine science: Principles and applications* (3rd ed.). San Diego: Academic Press.
- Jiraratananon, R., & Chanachai, A. (1996). A study of fouling in the ultrafiltration of passion fruit juice. *Journal of Membrane Science*, 111, 39–48.
- Kobus, Z., Nadulski, R., Guz, T., Mazur, J., Panasiewicz, M., & Zawislak, K. (2015). Effect of pasteurization on rheological properties of white carrot juice. *Agriculture and Agricultural Science Procedia*, 7, 99–102.
- Manohar, B., Ramakrishna, P., & Udayasankar, K. (1991). Some physical properties of Tamarind (*Tamarindus indica* L.) juice concentrates. *Journal of Food Engineering*, 13, 241–258.
- Mondal, S., Cassano, A., Conidi, C., & De, S. (2016). Modeling of gel layer transport during ultrafiltration of fruit juice with non-Newtonian fluid rheology. *Food and Bioprocess Processing*, 100, 72–84.
- Neto, F. S. P. P., De Castilhos, M. B. M., Telis, V. R. N., & Telis-Romero, J. (2014). Effect of ethanol, dry extract and reducing sugars on density and viscosity of Brazilian red wines. *Journal of the Science of Food and Agriculture*, 95, 1421–1427.
- Nindo, C. I., Tang, J., Powers, J. R., & Singh, P. (2005). Viscosity of blueberry and raspberry juices for processing applications. *Journal of Food Engineering*, 69, 343–350.
- Ojo, A., & Akanbi, C. T. (2006). Rheology of Soy-Ogi: Effect of concentration and temperature. *Journal of Food Engineering*, 72, 141–146.
- Perry, R. H., & Chilton, C. H. (1986). *Manual de engenharia química*. Rio de Janeiro: Guanabara Dois.
- Pons, A., Allamy, L., Lavigne, V., Dubourdieu, D., & Darriet, P. (2017). Study of the contribution of massoia lactone to the aroma of Merlot and Cabernet Sauvignon musts and wines. *Food Chemistry*, 232, 229–236.
- Quek, M. C., Chin, N. L., & Yusof, Y. A. (2013). Modelling of rheological behavior of soursop juice concentrates using shear rate-temperature-concentration superposition. *Journal of Food Engineering*, 118, 380–386.
- Ramos, A. M., & Ibarz, A. (1998). Density of juice and fruit puree as a function of soluble solids content and temperature. *Journal of Food Engineering*, 35, 57–63.
- Rizzon, L. A., & Miele, A. (2009). Analytical characteristics of Merlot wines from Serra Gaúcha region. *Ciência Rural*, 39, 1913–1916.
- Shamsudin, R., Ling, C. S., Adzahan, N. M., & Daud, W. R. W. (2013). Rheological properties of ultraviolet-irradiated and thermally pasteurized Yankee pineapple juice. *Journal of Food Engineering*, 116, 548–553.
- StatSoft Inc (2014). *Statistica 12*. (Tulsa, OK).
- Telis-Romero, J., Gabas, A. L., Polizelli, M. A., & Telis, V. R. N. (2000). Temperature and water content influence on thermophysical properties of coffee extract. *International Journal of Food Properties*, 3, 375–384.
- Telis-Romero, J., Thomaz, C. E. P., Bernardi, M., Telis, V. R. N., & Gabas, A. L. (2006). Rheological properties and fluid dynamics of egg yolk. *Journal of Food Engineering*, 74, 191–197.
- Zuritz, C. A., Muñoz Puentes, E., Mathey, H. H., Pérez, E. H., Gascón, A., Rubio, L. A., ... Cabeza, M. S. (2005). Density, viscosity and coefficient of thermal expansion of clear grape juice at different soluble solid concentrations and temperatures. *Journal of Food Engineering*, 71, 143–149.