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Changes in Rheological Properties of Koruk (Unripe Grape) Juice Concentrates During Vacuum Evaporation

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ABSTRACT

The time-dependent and time-independent rheological properties of koruk juice (unripe grape juice) concentrates were determined over a wide range of temperatures (10-80°C) and concentrations (4.6-25.0% soluble solids contents, SSC). Power-Law model was the best model describing the time-independent rheological behavior of unripe grape juice. Apparent viscosity of concentrates decreased with an increase in temperature for all concentrations. The flow activation energy for the consistency coefficients and the apparent viscosity of unripe grape juice concentrates were 40.70 and 13.54 kJ/mol, respectively. The time-dependent thixotropic energy of unripe grape juices decreased as the temperature increased.

Keywords: Unripe grape juice, Rheology, Concentration, Temperature, Thixotropic

Vakum Evaporasyon İşlemi Sırasında Koruk Suyu Konsantrelerinin Reolojik Özelliklerindeki Değişimler

ÖZ

Koruk suyu konsantrelerinin zamana bağlı ve zamana bağlı olmayan reolojik özellikleri farklı sıcaklık (10-80°C) ve konsantrasyonlarda (%4.6-25.0 suda çözünür kuru madde, SÇKM) belirlenmiştir. Üssel model, koruk suyunun zamana bağlı olmayan reolojik özelliğini tanımlayan en iyi model olarak bulunmuştur. Konsantrelerin görünür viskozitesi tüm konsantrasyonlar için sıcaklık arttıkça azalmıştır. Koruk suyunun kıvam katsayısı ve görünür viskozite değeri için aktivasyon enerjisi değerleri sırasıyla 40.70 ve 13.54 kJ/mol olarak belirlenmiştir. Koruk suyunun zamana bağlı tiksotropik enerjisi sıcaklık arttıkça azalmıştır.

Anahtar Kelimeler: Koruk suyu, Reoloji, Konsantrasyon, Sıcaklık, Tiksotropik

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INTRODUCTION

Koruk juice (unripe grape juice) is an unfermented green grape juice made by pressing unripe grapes. It is used as an acidifying and flavoring agent with salad vegetables like vinegar and lemon juice in the Mediterranean countries and also consumed as a drink after being sweetened. The active compounds in unripe grape juice have attracted the interest of nutrition, health, and medicine based researches [1]. Unripe grape juice is used to reduce blood pressure and cholesterol as well as maintaining the body weight in traditional medicine [2-4]. Unripe grape juice is produced without any technological application at homesteads for their own consumption, especially in the Mediterranean and Southeastern regions of Turkey. It has a limited shelf life because it is easily fermented by molds present naturally in grape, which limits the endurance of unripe grape juice. However, it is difficult to market the fresh unripe grape juice at a commercial scale since it has a very short shelf life [3]. It is thought that several preservation techniques should be used to increase the shelf life, and hence the commercial availability of this valuable juice or consumers. For this purpose, the thermal preservation methods such as the concentration, pasteurization and sterilization etc. are generally preferred.

Fruit juices are subjected to different temperatures and concentrations during processing, storage, transportation, marketing etc. [5]. Before shipping, fruit juice is usually concentrated to reduce transportation, packaging, and storage costs [6, 7]. The concentration process is a major unit operation which has a critical importance since it determines the quality characteristics of the final product such as flavor, color, aroma, appearance and mouth feel [8, 9]. Nowadays, the concentrated fruit juices have become one of the trends to preserve the nutrients and flavors of the fresh fruit [10]. On the other hand, the concentration process ensures longer storage life (because of its low water activity) and easier transportation. During the thermal concentration process, the water is partially removed in the form of vapor from a boiling solution, while all solid compositions such as vitamins, minerals, and sugars remain in more concentrated solution [6, 7, 11]. The evaporation rate and the changes on quality depend on the type of evaporation method. For example, the concentration of fruit juices by conventional evaporation methods (at atmospheric pressure) causes color degradation and loss of most volatile compounds due to thermal effects [6, 9, 12]. On the other hand, the vacuum evaporation occurs at low temperatures so causes less quality losses. The low temperature processes with fast mass transfer are achieved in a vacuum system [7, 13].

Temperature changes have important effects on the flow characteristics of juices so it is important to investigate the rheological behavior of thermal processed juices. Since thermal processed unripe grape juice has a potential as a commercially available product in markets in future, the knowledge on its rheological properties is necessary for designing transport systems and equipment, choosing the pump capacity and determining the power requirements in industrial production scale. The rheological behavior of fluids depends on their molecular structures [5, 10]. Numerous rheological models have been used to describe the flow behavior of fruit juices such as Newtonian (one parameter), Bingham and Power law (two parameters), Herschel-Bulkley models (three parameters) depending on the nature of the juices [10, 13-18]. In general, several fluid foods do not exhibit Newtonian behavior because their apparent viscosities are dependent of shear rate or shear stress and time. For this reason, it is necessary to develop more complex models to describe their behavior [18, 19]. The Power law model has been used most extensively to describe the time independent rheological behavior of most fruit juices especially on handling, heating and cooling operations because it is convenient, simple and straightforward to be used [5, 10, 20, 21]. Several studies on rheological modeling of fruit juices have been conducted in published literature [5, 10, 16, 20, 22-24, 30]. However, there is no information about the changes on the rheological properties of unripe grape juice during its concentration process, according to the knowledge of authors.

Rheological properties could be time-dependent. Time-dependency of materials is defined to be inelastic with a viscosity function which depends on time. Fluids have been described with their time-dependent characteristics which are thixotropic and rheopectic. Thixotropy refers to the time-dependent decrease in viscosity. In contrast, rheopectic is defined as the fluid having increasing shear stress with time. Time dependency of liquid foods is especially important in design of pumping lines on its production, and in shelf life estimations [14].

In this study, the effect of concentrations and temperatures on the consistency and the flow behaviors of unripe grape juice was determined. The suitability of different rheological models was assessed statistically to determine the best model describing the rheological characteristics of unripe grape juice. The time dependency of rheological properties of concentrated juices during vacuum concentration process was investigated.

MATERIALS and METHODS

Material

Unripe grapes (*Vitis vinifera* L.) were obtained from a local agricultural company in Izmir, Turkey. They were separated from their stalks, and sorted before they were washed with tap water and dried. The unripe grape juice was squeezed by using a juice extractor (Arzum Mela Plus, Istanbul, Turkey). The insoluble pulp content in the unripe grape juice was removed by filtration using Büchner funnel from coarse filter paper. The pH and the titratable acidity of unripe grape juice obtained were 2.8±0.01 and 11±0.163%, respectively.

Vacuum Evaporation

The unripe grape juice having 4.6%±0.1 initial soluble solid contents was concentrated by using rotary evaporator (BuchriR-3, Switzerland) at 400 rpm and 60°C. The concentrates having SSC of 10, 15, 20, and 25% were produced as different batches.

Total Soluble Solids Content Determination

The soluble solids content of the juice concentrates was measured by a refractometer (Hanna Instruments 96801, Romania) at 20°C and expressed as %SSC.

Rheological Measurements

Rheological properties were measured using a concentric cylinder type viscometer (Brookfield LVDV-II, Brookfield Engineering Laboratories, USA). Rheological measurements of unripe grape juice were carried out at five different SSC (4.6, 10, 15, 20, and 25% SSC) for four different temperatures (10, 25, 40, and 80°C). The cooled water bath (Selecta Precisdig, Spain) and circulating pumping system (Cole Palmer Masterflex L/S, USA) was used to keep the temperature constant during rheological measurements. The measurement range of viscometer between 0 and 100% full scale torques was adjusted by selecting both the specific spindle (S-18) and its rotational speed (0.0–200 rpm). During the rheological measurement, shear stress (SS), shear rate (SR), viscosity (cP) and % torque (T) values were recorded for each rotational speed (rpm). Experimental shear stress-shear rate measurements were fitted to selected rheological models to obtain viscous properties of unripe grape juice. Four different rheological models were applied to find the suitable rheological model best fitting the experimental data; Newton model (Eq. 1), Power Law model (Eq. 2), Bingham model (Eq. 3) and Herschel-Bulkley model (Eq. 4) [25]:

$$\sigma = \eta \cdot \dot{\gamma} \tag{1}$$

where η is Newtonian viscosity (Pa·s), σ is shear stress (Pa) and $\dot{\gamma}$ is shear rate (s^{-1});

$$\sigma = K \cdot (\dot{\gamma})^n \tag{2}$$

$$\sigma - \sigma_0 = K \cdot \dot{\gamma} \tag{3}$$

$$\sigma - \sigma_0 = K \cdot (\dot{\gamma})^n \tag{4}$$

where K is the consistency coefficient ($Pa \cdot s^n$), σ_0 is the yield stress (Pa) and n is the flow behavior index (dimensionless). The apparent viscosity values were calculated by using power law model constants and shear rate of 50 s^{-1} (Eq. 5). The shear rate of 50 s^{-1} was reported as the shear rate characterizing the textural sense in mouth best [26].

$$\mu_{app} = K \gamma_{50}^{n-1} \tag{5}$$

The effect of temperature both on K and μ_{app} was described by the Arrhenius relationship;

$$K = A_0 \exp^{E_{a1}/RT} \tag{6}$$

$$\mu_{app} = A_{0\mu} \exp^{E_{a1}/RT} \tag{7}$$

where A_0 (or $A_{0\mu}$) was the frequency factor ($Pa \cdot s^n$), E_a (or E_{a1}) was the activation energy (kJ/mol), T was the temperature (Kelvin, K) and R was universal gas constant (kJ/kg·K). When Eqs (6) and (7) were linearized, A_0 was the exponential of the y-intercept and E_a was the product of slope.

The time dependency of rheological properties of unripe grape juice was investigated. Thixotropic and/or rheopectic character of unripe grape juice was determined by analyzing hysteresis loop between forward and backward shear stress-shear rate relations. If viscosity decreases with time and then returns to the initial level on rest after shearing, such a phenomenon is called thixotropy. The reverse phenomenon is called rheopexy [27].

To investigate the time dependency, the area below the forward shear stress-shear rate curve was defined as A_1 while the area below the backward shear stress-shear rate curve was defined as A_2. The polynomial fitting of the experimental shear stress-shear rate curves was considered. The area between the upward (A_1) and downward flow curves (A_2) of the hysteresis loop was calculated by the Simpson's rule (Eq. 8) [28]. This area had the dimensions of power per unit volume (Pa s^{-1} or $ML^2T^{-3}/L^3 = ML^{-1}T^{-3}$, where M represented the dimension of a mass, L, length, and T, time) and corresponded to the power necessary to break down the thixotropic structure of a given volume of solution [29].

$$\int_a^b f(x)dx = \frac{h}{3}[(y_0 + y_n) + 4(y_1 + y_3 + .. + y_{n-1}) + 2(y_2 + y_4 + .. + y_{n-2})] \tag{8}$$

Statistical Analysis

All experiments and measurements were carried out in triplicate. The ANOVA and Duncan test were applied to determine the effects of temperature and concentration on rheological properties by using statistical software package (SPSS v20, 2012). T test was applied to compare viscosity (from Newton model) and apparent viscosity values (from Power law model). The confidence level was 95%. The compatibility of the model with experimental data was determined by using a non-linear regression analysis. Regression coefficient (R^2), root mean square error (RMSE) (Eq. 9) and chi-square (χ^2) (Eq. 10) values were calculated. The statistical criteria of having highest R^2, lowest RMSE and lowest χ^2 were chosen for selection of best model for fitting [28].

$$\text{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(KG_{predicted,i} - KG_{experimental,i})^2\right]^{0.5} \tag{9}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(KG_{predicted,i} - KG_{experimental,i})^2}{N-n} \tag{10}$$

where KG is rheological data (experimental and predicted), i is observation values at the i^{th} experiment, N is observation number, and n is number of parameters in model.

RESULTS and DISCUSSIONS

Figure1 shows the rheograms of experimental shear stress and shear rates of unripe grape juice concentrates for three different concentrations (4.6, 15, and 25 %SSC) in the temperature range of 10-80°C. For the same temperature value, shear stress values increased as the concentration values increased ($p<0.05$). On the other hand, it was determined that as the temperature values increased the shear stress values decreased, for the same concentration values ($p<0.05$). Similar results were obtained in the rheological studies for different fruit juice samples [10, 20, 21, 31, 32].

For different temperatures (10, 25, 40, and 80°C) and different SSC of unripe grape juice (4.6, 10, 15, 20, and 25%SSC), the experimental data were fitted to several rheological models statistically (Table 1). RMSE and χ^2 values were used to compare the compatibility of the rheological models to experimental shear stress-shear rate data statistically. It was determined that the Herschel-Bulkley and the Bingham models could not have been compatible for whole range of concentrations and temperatures studied. In addition, it was determined that Power law model had higher R^2 and lower error values (RMSE and χ^2) than Newtonian model ($p<0.05$) (Table 1).

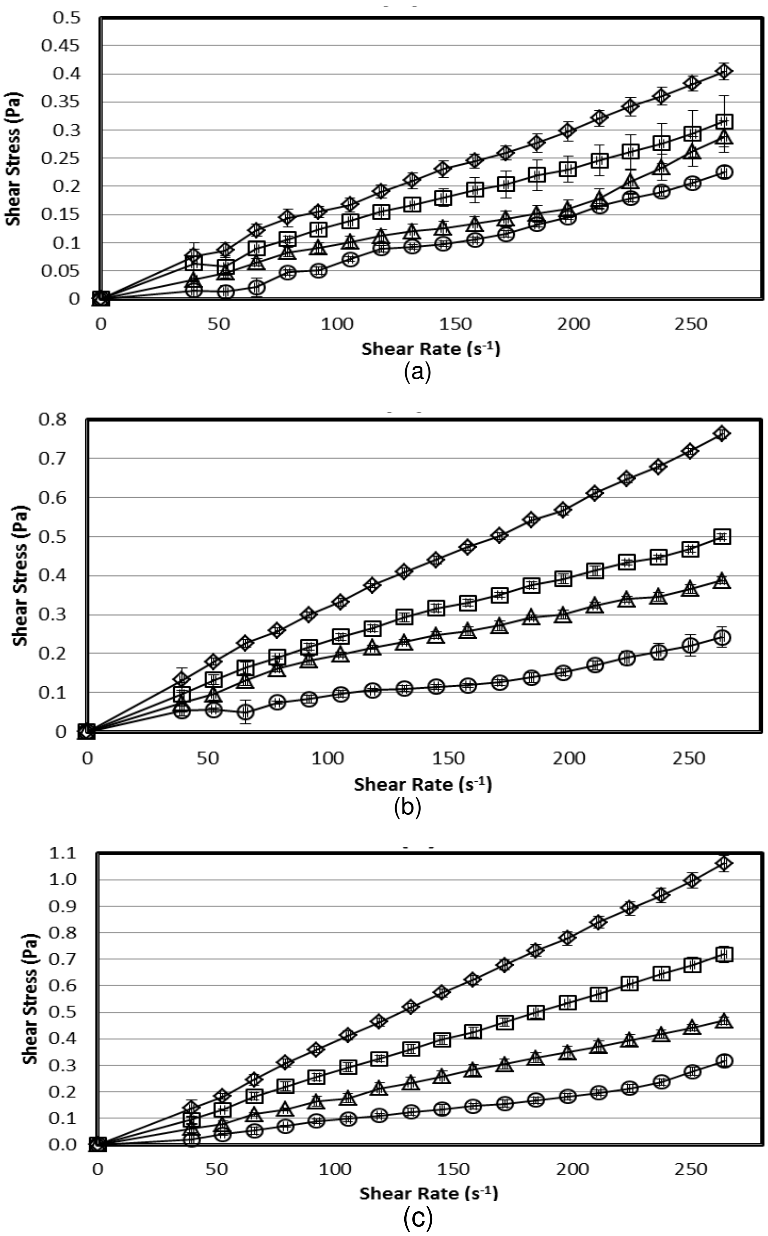

Figure 1. Rheograms for shear stress versus shear rates plots of unripe grape juice concentrates at various temperatures 10°C (◊), 25°C (□), 40°C (Δ), 80°C (O) for concentrations of (a) 4.6 % SSC, (b) 15 %SSC, and (c) 25 % SSC.

Since Newton and Power law models had sufficiently higher R^2 values, both models could have characterized the rheological changes during evaporation of unripe grape juice. Power law model showed and lowest error values at all conditions, statistically ($p<0.05$) (Table 1). R^2, RMSE and χ^2 values of Power law model were in the range of 0.933-0.999, 0.0073-0.0215 and 0.00007-0.00055, respectively. Since unripe grape juice was prepared without using filtration as traditionally, it was not clear and had some suspended solids crystalized during evaporation. It was thought that these contents diverted the rheological behavior of unripe grape juice concentrates from Newton character to Non-Newtonian character. Several juices had been reported as pseudo-plastic fluid in literature; mango juice [5], soursop juice [10], pummelo juice [20], and date syrup [21].

Table 1. Statistical evaluation for Newton and Power law models applied to fit the experimental shear stress-shear rate data for unripe grape juice concentrates at different temperatures

SSC* (%)	Temperature (°C)	Statistical Criteria	Model	
			Newton	Power Law
4.6	10	R^2	0.984±0.005	0.991±0.002
		RMSE	0.0123±0.0019	0.0089±0.0012
		χ^2	0.00016±0.00005	0.00009±0.00003
	25	R^2	0.971±0.022	0.983±0.006
		RMSE	0.0122±0.0031	0.0097±0.0012
		χ^2	0.00017±0.00009	0.00011±0.00003
	40	R^2	0.935±0.009	0.945±0.001
		RMSE	0.0177±0.0019	0.0163±0.0018
		χ^2	0.00034±0.00007	0.0003±0.00007
	80	R^2	0.923±0.008	0.979±0.007
		RMSE	0.0168±0.0012	0.0092±0.0014
		χ^2	0.0003±0.00004	0.0001±0.00003
10	10	R^2	0.960±0.009	0.993±0.003
		RMSE	0.0448±0.0075	0.0201±0.0083
		χ^2	0.00247±0.00075	0.00055±0.00043
	25	R^2	0.928±0.044	0.979±0.012
		RMSE	0.027±0.0034	0.013±0.0046
		χ^2	0.00078±0.00019	0.00021±0.00014
	40	R^2	0.861±0.057	0.960±0.016
		RMSE	0.0253±0.0027	0.0141±0.0038
		χ^2	0.00068±0.00015	0.00024±0.00012
	80	R^2	0.955±0.009	0.972±0.014
		RMSE	0.0154±0.0018	0.0148±0.0017
		χ^2	0.00026±0.00006	0.00024±0.00005
15	10	R^2	0.987±0.005	0.997±0.002
		RMSE	0.0208±0.0039	0.0099±0.0035
		χ^2	0.00047±0.00015	0.00012±0.00009
	25	R^2	0.950±0.008	0.992±0.006
		RMSE	0.0262±0.0022	0.0103±0.0038
		χ^2	0.00073±0.00012	0.00013±0.0001
	40	R^2	0.924±0.011	0.983±0.010
		RMSE	0.0247±0.0013	0.0117±0.0043
		χ^2	0.00065±0.00007	0.00017±0.00012
	80	R^2	0.944±0.006	0.954±0.011
		RMSE	0.0202±0.0027	0.0184±0.0041
		χ^2	0.00044±0.00012	0.00039±0.00015
20	10	R^2	0.993±0.007	0.997±0.001
		RMSE	0.0169±0.0061	0.0116±0.0014
		χ^2	0.00033±0.000026	0.00015±0.00004
	25	R^2	0.973±0.015	0.989±0.009
		RMSE	0.023±0.0064	0.0144±0.007
		χ^2	0.00059±0.00031	0.00027±0.00025
	40	R^2	0.937±0.018	0.987±0.014
		RMSE	0.0253±0.0031	0.0107±0.0057
		χ^2	0.00069±0.00015	0.00016±0.00017
	80	R^2	0.917±0.022	0.933±0.009
		RMSE	0.0234±0.0015	0.0215±0.0019
		χ^2	0.00058±0.00007	0.00053±0.00009
		RMSE	0.0091±0.002	0.0073±0.0029
		χ^2	0.00009±0.00004	0.00007±0.00005

*: Soluble solids contents

Power law model predictions were used in order to investigate the time independent changes of rheological properties. The consistency coefficient (K), flow behavior index (n) and the regression coefficient (R^2) values obtained from Power law model were given in Table 3. For the same concentration, the consistency coefficient decreased as the temperature increased ($p<0.05$). On the other hand, for the same temperature, K values increased as the soluble solids content increased. As expected, molecules move away from each other and cause the reduction of consistency coefficient as the temperature increased. Likewise, molecules are closer together due to the increase in soluble solids content at constant temperatures, and hence the consistency coefficient values increases [13]. Similar results were obtained by the different researchers in the literature [10, 20, 25, 33]. For the concentrations range of 10 and 20% SSC, the unripe grape juice exhibited non-Newtonian pseudo-plastic fluid character since the flow behavior index (n) values were lower than unity. On the other hand, n value approached to unity or reached the values of higher than unity depending on the temperature for the non-concentrated juice and the highest concentration (25% SSC). Hence, it was concluded that the unripe grape juice could have shown non-Newtonian dilatant character depending on concentration and temperature. The reason of this character could have been due to the natural structure of unripe grape juice because of the tartrate crystals occurred and changing the molecular structure at high temperatures.

Table 2. Statistical evaluation for Newton and Power law models applied to fit the experimental shear stress-shear rate data for unripe grape juice concentrates at different temperatures *(continue)*

SSC (%)	Temperature (°C)	Statistical Criteria	Newton model	Power Law model
25	10	R^2	0.998±0.002	0.999±0.001
		RMSE	0.0124±0.005	0.093±0.0033
		χ^2	0.00018±0.00016	0.00011±0.00008
	25	R^2	0.998±0.001	0.998±0.001
		RMSE	0.0084±0.0023	0.0076±0.0025
		χ^2	0.00008±0.00004	0.00007±0.00004
	40	R^2	0.995±0.002	0.996±0.003
		RMSE	0.0091±0.002	0.0073±0.0029
		χ^2	0.00009±0.00004	0.00007±0.00005
	80	R^2	0.942±0.013	0.967±0.008
		RMSE	0.0191±0.0029	0.0143±0.0021
		χ^2	0.00039±0.00012	0.00023±0.00006

In grape juice, tartaric and malic acids are the predominant organic acids [34]. The level of tartaric acid is used as a critical parameter to determine stabilization of grape juice, wine etc. [35]. Tartrate crystals develop naturally, and they are the major cause of deposit in wines and grape juices. In addition, the deposition is accelerated by different temperature application. These tartrate crystals are undesirable compounds and must be removed. There are several methods (cold stabilization, electrodialysis or cation exchangers) to remove them from the juice [36]. In this study, any methods were not preferred to remove tartrates occurred in the juice since the main purpose was to determine the rheological properties of unripe grape juice produced traditionally. The large particles in the unripe grape juice concentrates were removed only with the help of coarse filter paper to assure the measurement precision of the rheological properties. The effect of suspended solids on the viscous character of unripe grape juice was investigated in detail. The viscosity values from Newton model and apparent viscosity values from Power law model were compared statistically. The prediction of the viscosity values from both models were statistically different ($p<0.05$) (Table 4). Power law model was selected as the model characterizing the rheological behavior of unripe grape juice concentrates for the conditions studied since it had lowest statistical errors in predictions as mentioned above. These results supported that suspended solids affected the rheological character of unripe grape juice and diverted it to non-Newtonian fluid type.

The Arrhenius relationship was used to describe the effect of temperature on the consistency coefficient for unripe grape juice concentrates (Table 3). The activation energy (E_a) and Arrhenius constant (A_0) values for five different %SSC of unripe grape juices were given in Table 3. The activation energy showed a decreasing trend up to 20% SSC, but tended to increase at the 25% SSC. Raw material and unripe grape juice having 25% SSC had statistically different temperature dependency from other concentrates ($p<0.05$). The activation energy for temperature dependency of consistency coefficient showed some perturbations throughout the concentration process. Irregular changes in the activation energy with increasing degree of concentration were previously reported in the literature [10, 15, 16, 20, 37-40]. This change may have encountered from the results of inconsistent changes of the E_a during the concentration process ($p<0.05$).

Since both the consistency coefficient (K) and flow behavior index (n) changed depending on concentration and temperature, the temperature dependency of apparent viscosity were investigated in order to reveal the change of activation energy for different concentrations in detail. E_{a1} and $A_{0,\mu}$ (Eq 7; Arrhenius equation with μ_{app}) values were given (Table 5). The R^2 values for the Arrhenius relations were in the range 0.856-0.97. Similar to the change of E_a for consistency coefficient (Table 3), E_{a1} for apparent viscosity tended to decrease as the SSC increased up to the 20%, then increased at 25% SSC (Table 5). In addition, the increase in the frequency factor ($A_{0,\mu}$) had similar trend compared to A_0. It was concluded that temperature dependency of the rheological behavior of unripe grape juice could be described with the Arrhenius relation conducted by using either the consistency coefficient or the apparent viscosity.

Table 3 . Parameters obtained from Power law equation for unripe grape juice concentrates at different temperatures, and temperature dependency of consistency coefficient at different concentrations (Eqs.2 and 6)

Concentration (% SSC)	Temperature (°C)	Consistency coefficient, K (Pa.s^n)	Flow behavior index, n	Coefficient of determination, R^2	Frequency constant in Arrhenius equation for consistency coefficient, A_0 (Pa.s^n)	Activation energy for consistency coefficient, E_a (kJ/ mol)
4.6	10	0.0025±0.0006	0.910±0.042	0.991±0.002	$1.9\text{x}10^{-10}\pm2.36\text{x}10^{-10a}$	40.70 ± 3.65^{b}
	25	0.0021±0.0007	0.920±0.070	0.983±0.006		
	40	0.0004±0.0001	1.144±0.048	0.945±0.001		
	80	0.0001±0.00002	1.381±0.038	0.979±0.007		
10	10	0.0060±0.0007	0.810±0.019	0.993±0.003	$9.6\text{x}10^{-7}\pm1.6\text{x}10^{-6a}$	24.02 ± 3.93^{ab}
	25	0.0061±0.0013	0.760±0.035	0.979±0.012		
	40	0.0049±0.0012	0.743±0.047	0.960±0.016		
	80	0.0010±0.0004	1.021±0.080	0.972±0.014		
15	10	0.0053±0.0006	0.881±0.015	0.997±0.002	$1.2\text{x}10^{-6}\pm1.3\text{x}10^{-6a}$	23.06 ± 5.7^{ab}
	25	0.006±0.0004	0.791±0.014	0.992±0.006		
	40	0.0055±0.0008	0.763±0.030	0.983±0.010		
	80	0.0015±0.0012	1.069±0.001	0.954±0.011		
20	10	0.0046±0.0013	0.897±0.048	0.997±0.001	$2.1\text{x}10^{-5}\pm4.4\text{x}10^{-6b}$	13.54 ± 0.45^{a}
	25	0.0041±0.0004	0.892±0.019	0.989±0.009		
	40	0.0040±0.0006	0.814±0.032	0.987±0.014		
	80	0.0021±0.0009	0.936±0.080	0.933±0.009		
25	10	0.0032±0.0004	1.039±0.020	0.999±0.001	$1.1\text{x}10^{-8}\pm8.03\text{x}10^{-9a}$	31.68 ± 3.73^{b}
	25	0.0027±0.0004	1.000±0.027	0.998±0.001		
	40	0.0016±0.0006	1.028±0.057	0.996±0.003		
	80	0.0003±0.0001	1.263±0.054	0.967±0.008		

^{a,b,c}: Different superscripts showed the statistically significant difference for the same column ($p<0.05$)

Table 4. Comparison between viscosity values from Newton model and apparent viscosity values from Power law model for unripe grape juice concentrates

Concentration (SSC, %)	Temperature (°C)	Viscosity (μ), from Newton Model x10^3	Apparent Viscosity (μ_{app}),	Probability (significance, 2. tailed)*
4.6	10	1.5±0.1	1.7±0.2	0.028
	25	1.2±0.1	1.4±0.1	0.043
	40	0.9±0.03	0.8±0.1	0.0002
	80	0.8±0.01	0.4±0.01	0.00001
10	10	2.2±0.1	2.9±0.1	0.00001
	25	1.6±0.02	2.2±0.1	0.00001
	40	1.3±0.1	1.8±0.2	0.0004
	80	1.1±0.1	1.1±0.1	0.498
15	10	2.9±0.01	3.4±0.1	0.00003
	25	1.9±0.03	2.6±0.04	0.00001
	40	1.6±0.03	2.2±0.1	0.00001
	80	1.3±0.05	1.3±0.2	0.993
20	10	3.3±0.2	3.5±0.3	0.124
	25	2.3±0.1	2.8±0.2	0.017
	40	1.8±0.1	2.4±0.3	0.001
	80	1.3±0.03	1.5±0.2	0.075
25	10	4.0±0.1	3.8±0.2	0.089
	25	2.7±0.1	2.7±0.1	0.987
	40	1.8±0.1	1.7±0.2	0.640
	80	1.0±0.1	0.7±0.1	0.0004

*Confidence level was 95%.

Table 5. Frequency factor and activation energy (Eq.7) for apparent viscosity of unripe grape juice concentrates

Concentration (% SSC)	$A_{0,\mu}$ (Pa.s^n)	E_{a1} (kJ/mol)	R^2
4.6	$3.4\text{x}10^{-11}\pm4.3\text{x}10^{-11}$	44.79±3.58	0.856±0.09
10	$3.3\text{x}10^{-5}\pm3.9\text{x}10^{-5}$	12.12±3.23	0.951±0.05
15	$5.3\text{x}10^{-5}\pm5.5\text{x}10^{-5}$	10.88±2.79	0.970±0.02
20	$6.3\text{x}10^{-5}\pm1.6\text{x}10^{-5}$	9.57±0.62	0.860±0.09
25	$3.3\text{x}10^{-9}\pm4.1\text{x}10^{-10}$	31.75±3.60	0.962±0.03

The time dependency of the rheological properties of unripe grape juice concentrates for different temperatures were examined. The consistency of the unripe grape juice was time-dependent during the concentration process (Table 6). Since upward shear rate applications responded higher shear stress values then downward shear rate applications, it was concluded that the unripe grape juice concentrates showed thixotropic character (Fig. 2). Thixotropic character of non-concentrated unripe grape juice decreased as the temperature increased. However, the effect of temperature on the thixotropic energy was not significant for the concentration of 15%SSC. For 20%SSC, the thixotropic energy for the temperatures above 40°C was higher compared to other temperatures. Furthermore, for 25%SSC, the temperature caused some fluctuations on the thixotropic energy. This might have been due to the crystallization of water-insoluble portions or the precipitation of some compounds such as tartrates in the unripe grape juice concentrates especially at high temperatures. Although the supernatant portion obtained by filtration after concentration process was used in rheological measurements, some crystallites remained in the solution could have affected the determination of the rheological characteristics possibly. Therefore, it caused irregularities on both the rheological constants and thixotropic character.

Similar to the present study, Ariaii et al. [41] reported that the rheological behavior of grape juice was time dependent and showed thixotropic character at different temperatures and different %SSC of the grape juice. Also, Ramos and Ibarz [42] stated that orange juice (55 and 60% SSC) showed thixotropic character when measurements taken at 0 and 20°C. In addition, it was reported that kiwi juice samples having different soluble solids (13.5-30% SSC) showed thixotropic character at low shear rate values while they showed rheopectic character at high shear rate values by Goula and Adamopoulos [43]. These results show that the time dependence of the rheological properties of fruit juices may change depending on the concentration, temperature and shear rate. Hence, the pumping power requirement and the flow characteristics may vary during the processing of fruit juices. It was suggested that researchers should be careful to remove the water insoluble portion of the unripe grape juice concentrates especially above 20% SSC. Further studies have been continuing for the determination of rheological properties of concentrated fruit juices at higher concentrations.

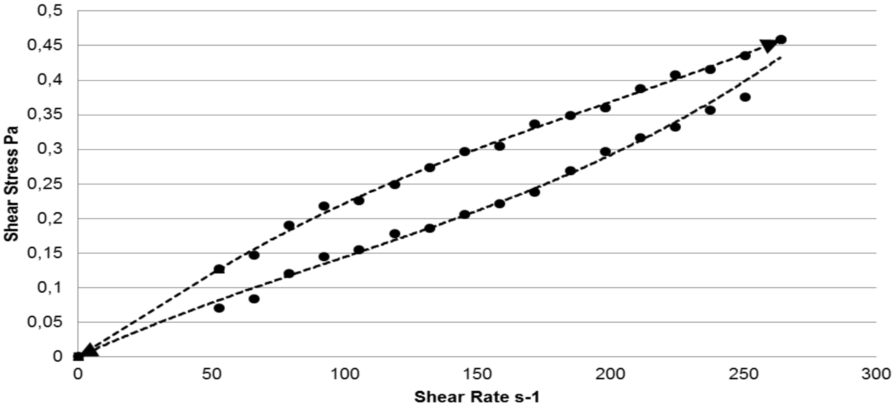

Figure 2. Example to thixotropic hysteresis curve for unripe grape juice; for 20% SSC, at 40°C

Table 6. Thixotropic characteristics of unripe grape juice at different temperatures and concentrations

Concentration (%SSC)	Temperature (°C)			
	10	25	40	80
4.6	8.47±1.59	6.18±1.16	1.63±0.52	1.98±0.94
10	8.14±1.23	9.88±1.19	4.03±1.48	3.93±1.88
15	8.10±1.99	8.56±0.86	9.94±0.23	8.85±1.90
20	8.31±1.56	7.52±0.95	12.02±0.83	12.35±0.91
25	9.76±0.29	14.64±1.80	12.88±1.41	6.02±0.78

CONCLUSION

In this study, rheological properties of unripe grape juice were investigated at various temperatures (10, 25, 40, and 80°C), concentrations (4.6, 10, 15, 20, and 25% SSC) and shear rates (0–264 1/s). The most appropriate model describing rheological behavior of unripe grape juice concentrates was the Power law model. The unripe grape juice generally exhibited non-Newtonian pseudoplastic ($n<1$) behavior; however, the flow behavior was changed to dilatant type ($n>1$) depending on the increase in the temperature and %SSC content. The effect of temperature both on the consistency coefficient and the apparent viscosity was satisfactorily described by Arrhenius equation, and the values of flow activation energy were obtained as the range of 13.54-40.7 kJ/mol. The thixotropic type time dependency of the rheological properties of unripe grape juice was determined. The characterization of rheological behavior of unripe grape juice could provide valuable data for designing of transportation, mixing and heating equipment to be used in commercial unripe grape juice processing. The tartaric acid precipitation or crystallization of the insoluble compounds occurred during the heating of the unripe grape juice should be investigated further in detail.

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