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RHEOLOGICAL PROPERTIES OF WATERMELON JUICE AS AFFECTED BY CONCENTRATION

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ABSTRACT Rheological properties are presented based on the flow behavior and the deformation of a substance by the action of stress. Among the juices, watermelon is very popular and also very nutritious. In this research, the flow behavior of watermelon juice was determined at concentrations of 40, 50 and 60 ^{0}Brix and temperatures of 15, 20 and 30 °C.Shear stress data obtained from juices were fitted with rheological models including Newtonian, power law. Also, concentration relation and temperature was determined by Arnius model and exponential law models. Based on the results obtained, both temperature and concentration decreased n values but increased K values. The power law model was also able to predict the dependence on apparent viscosity with concentration with high precision. The combined Arnius-power law model showed a high compliance for the effect of concentration-temperature on the apparent viscosity. It can be concluded that the temperature and concentration completely affect the rheological properties of Iranian watermelon juices
Keywords: Concentration, Juice, Rheological properties, Watermelon

INTRODUCTION

In recent years, extensive studies have been carried out on identifying healthy foods and tried to make them as the product of processing, which increases the utility and acceptance of the consumer. Meanwhile, watermelon juice, which has many properties, including antimicrobial, anticonvulsant and anti-inflammatory. (Kim *et al.,* 2010).

Although exports of various types of watermelon showed 21% growth compared to the same period of the previous year, the share of exports in this sector decreased to 0.4%. Watermelon juice has the highest global market in terms of production, having different vitamins and also rich in potassium ion. (chuah *et al*., 2008) . Watermelon juice is rich in minerals and vitamins such as vitamins A, B, C, potassium, iron, calcium, manganese, zinc, antioxidants, and other nutrients. (Keshani *et al*., 2012).

Among the export items, over the past decade, Iran with the annual production of more than 2 million and 200 thousand tons of watermelon was in fourth place in the world. . The product has been planted in four seasons, and more than 100,000 tons of watermelon has been exported to Iraq, the United Arab Emirates and Kuwait annually. (Mohammadi sani *et al.*, 2013).

Juices are condensed with evaporative condensation, freezing and osmotic methods. (Maskon, 2006). The evaporation method is superior to many other methods because of the possibility of achieving higher concentrations, higher production capacity and being economical to rheological knowledge, (Guno *et al*., 2006). Examining the rheological properties of food can provide a great deal of information about how to change their structure when they are subjected to the properties of different processes. (Quek *et al*., 2007).

The juice production industry is one of the industries that plays an important role in the food industry, and it is important to provide product with high quality in order to achieve effective competition. (Dak *et al*., 2007).

The rheological properties of fruit juices and their concentrates are of great importance for devising design, the transfer of materials and also flavor. (Hanil *et al.,* 2014).

According to published data, nearly 564 million kilograms, equivalent to 126 million and 578 thousand dollars of watermelon has exported to countries such as Georgia, Azerbaijan, Albania, Germany, Russia, Hungary, Netherlands, Nevada, Poland, Kuwait, in 2014, global. China accounted for 67% of the total production in the world. They had the next rank with less than 4% of the world's production of Turkey, Iran, Brazil and Egypt. (Grato *et al*., 2002; Guala *et al*., 2011).

Watermelon has an amino acid called citrulline and substances called carotene, lycopene, and mannitol. (Azoubel *et al*., 2005).

Watermelon like tomatoes containing large amounts of lycopene, organic pigments from carotene materials (Alami *et al*., 2012). These materials, which are considered to be antioxidants, neutralize active molecules called free radicals that produce chemical reactions in the body for developing of diseases such as cancer. (Cabral *et al*., 2007).

Depending on the different factors such as concentration, temperature, or lack of a clear process, fruit extracts can have different rheological behavior such as Newtonian, Psodo plastic, plastic and Thixotropic. On the other hand, finding an appropriate model for describing their rheological behavior can lead to a reduction in experimental experiments and the design of processes and devices. (Ahmed, 2004).

Considering the importance of rheological behavior of fruit juices, the purpose of this study is to model shear flow behavior of Iranian watermelon juices which concentrate (40-60ºBrix) at 15, 20 and 30ºC.

MATERIAL AND METHODS

Material

In this research, Persian watermelon was prepared from Mashhad market.
They were washed with water to remove waste materials. Surface water was dried with a clean cloth and then cut into lengthwise sections with a knife. Dewatering was done through Electric Juicer (Toshiba -Model JC-17E) made in Japan. Then by using a vacuum system, juice was clarified.

Protein: Protein content was done with using the Kjeldahl method (AOAC, 2000).

Fat: was determined by the method described in AOAC(2000)0

Carbohydrate: was determined by the method described in AOAC(2000.)

Sample Preparation

100 g of sample was poured into the balloon and was heated at 70°C. The sample was placed inside the evaporator chamber. The water

of watermelon was taken and in 3 stages the product was concentrated from 40 to 60°Brix. Then, stored at 4°C until analysis (Mohammadi Sani et al).

Total soluble solid evaluation (TSS) (Brix)

Brix was determined with refractometer (Atago Rx-7000a, Tokyo, Japan)

Moisture content (dry basis); was determined by drying the samples in an oven (MX-50 model (A&D Co., Limited, Tokyo, Japan) at 105 °C for 24 h (AACC, 2000).

PH: pH was determined by pH meter (HORIBA, F12, and Japan) (AOAC, 2000).

Determination of density

The empty and dry pycnometer was weighed down to a specified volume (25 cc). Then, filled with the desired liquid and weighed while the outer wall was dry. The difference between the weight of the empty pycnometer and the pycnometer was filled with desired liquid weight. By dividing it with the volume of the pycnometer container, the density of the liquid at a given temperature was achieved (Mohammadi Sani et al).

Rheological parameters

The behavior of shear flow of Iranian watermelon juice was determined at the concentrations mentioned at a temperature of 15, 20 and 30 ° C through a US rotating instrument Brockfield viscometer. Results were analyzed using rheological models. All rheological tests were performed in two replications and the average results were reported (Mohammadi Sani et al).

Effect of temperature on the consistency coefficient (Arrhenius equation)

The Arrhenius equation is a formula for the temperature dependence of reaction rates:

$$k = A_{*}\exp^{(-E_a/RT)} \qquad (1)$$

$$\text{Ln } k = \text{Ln. } A - \frac{Ea}{RT}$$

$$\text{Ln } \mu = \text{Ln. } \mu_{\infty} + \frac{Ea}{RT}$$

The consistency coefficient changes were indicated as a function of temperature with the Arrhenius equation.

After taking the natural logarithm of both sides, a linear equation is taken as the following form: where the rate constant is *k* , *T* is the absolute temperature (in kelvins), A is the pre-exponential factor (or simply the pre factor), E_a is the activation energy, and R is the universal gas constant: R has the value of 8.314 .10^{-3} kJ $mol^{-}K^{-1}$ .By plotting linear variations Ln K against the temperature and obtaining slope and width from the source, E_a and A were calculated respectively(Steff, 1996).

The flow behavior associated with the shear rate of Iranian fruit samples can be defined using the following rheological models (e.g. Newtonian (2), Power-Law (3), Herschel-Bulkley (4) equations depending on the nature of the juices (Altan *et al*., 2005; Belibagli *et al*., 2007).

$$\tau = \mu\gamma \qquad (2)$$

$$\tau = k.\gamma^{n} \qquad (3)$$

$$\tau = t. + k.\gamma^{n} \qquad (4)$$

Statistical Analysis

SPSS software (Version 18) was used to analyze the data .Microsoft Excel 2007was used for rheograms.

RESULT AND DISCUSSION

Table 1 shows the experimental values for physical properties of watermelon juice.

In Newtonian fluids, the relationship between shear stress and shear rates variations applied linearly, and the constant coefficient of converting this linear fit to the equation is the same as viscosity, but in non-Newtonian fluids, there is no longer any effect of the linear relationship between shear stress variations and the shear rate. In this fluids, the duration of the stress action plays an important role in the shear stress achieved. Consequently, in non-Newtonian fluids, a constant coefficient of viscosity is not meaningful way for describing the shear stress state. Non-Newtonian fluids are divided into three groups' independent of time, time dependent and viscoelastic (Gratao *et al*., 2002).

Table 1. Experimental values for physical properties of watermelon juice

T (º C)	C (ºBrix)	Moisture content (%, w.b)	pH	Density(kg/m^3)
15	40	77.5±0.01	4.1	1.189
	50	66.5±0.01	4.3	1.268
	60	55.0±0.02	5	1.345
20	40	64.80±0.01	4.9	1.179
	50	53.60±0.02	4.8	1.240
	60	42.30±0.01	5.6	1.331
30	40	41.0±0.02	4.2	1.165
	50	41.1±0.01	5.5	1.210
	60	30.9±0.01	4.6	1.320

The slope of the stress- strain curve at high shear intensities is referred to as the viscosity at infinite cutting and at low shear intensities to zero viscosity. In these materials, the rate of increase in stress versus the severity of the cutting is somewhat negative (viscosity is a descending function of the severity of the cutting). In other words, if the power law model is used as the base law for pseudo plastic materials, then n will be smaller than one. (Steffe, 1996).Table 2 shows the rheological properties of watermelon juice by the Power-

Law. As the flow tables show, with increasing shear velocity, the tangent tangency of graph decreases at each point of the strain, which demonstrates the presence of pseudo plastic for the fruit juices tested. This issue is further elucidated by the results of rheological modeling of the behavior of the Iranian water shear flow. As it can be seen, the Newtonian flow behavior index decreases with increasing temperature in a particular brix. For example, the consistency decreased by increasing the temperature from 15 to 30^{0}c. On the other hand, the results showed that increasing the brix at a specific temperature increased consistency. These results were fully expected because the temperature increase due to the increase in the molecular movement reduced the viscosity, and on the other hand, with increasing solids content of the bubble solution, the viscosity was also high. In a particular brix, the index of current behavior increases with increasing temperature, in other words, the amount of pseudo plastic of flow behavior decreases.

Table 2. Parameters consistency (K), flow behavior i*ndex* (n) and Correlation Coefficient (R2) for power-law model

T (º C)	C (ºBrix)	K(pa.s^n)	*n*	R^2
15	40	0.195	0.955	0.899
	50	1.405	0.924	0.958
	60	3.460	0.913	0.880
20	40	0.180	0.933	0.939
	50	0.360	0.821	0.997
	60	2.030	0.982	0.968
30	40	0.150	0.924	0.896
	50	0.210	0.912	0.999
	60	1.290	0.876	0.975

The same results were also obtained by other scientists in various fruit juices, such as keshani *et al.,* 2010, which stated, power law and Herschel Balkil models described better Pomelo's behavior than Bingham and Casson models in high concentration. Also Goula *et al*., 2011, examined the rheological properties of kiwifruit juice. The rheological properties of pineapple juice were studied by Dak *et al.,* 2008 at different concentrations. As a result, the increase in temperature and concentration influenced the behavioral index of power law model. Dak *et al.*, 2006 studied the rheological properties of mango juice. The findings from the researchers were similar to those in blackberry juice” and mango juice (Cabral *et al.,* 2007; Dak *et al*., 2006). According to Sharma *et al s* (1996) findings, pectin plays a major role in the viscosity. Several reports have shown the influence of Brix and the coefficient of consistency at different juices like, orange juice, pineapple juice, pomegranate juice and cherry juice (Ibarz *et al.*, 1989; Shamsudin *et al*., 2007; Kaya *et al*., 2005; Juszczak *et al*., 2004).

The best fitting model have been reported by researchers (Ibarz *et al*., 2009; Ramos and Ibarz, 1998; Goula *et al*., 2011) in juices like pear, peach, orange and pineapple.

Evaluation of Temperature relevance with stability Coefficient

Temperature, according to literature, is known to have an inversely proportional relationship with the viscosity of liquids .reduction in the flow resistance lead to increase in flow ability (Hanil *et al.*, 2014) .Experimental results revealed that temperature affected the viscosity of juices. For the shear rate range considered, the viscosity of the juice decreased as temperature increased.

Arrhenius model was used to determine the stability coefficient, K_{0T} *and* $E_{a,}$ vales were achieved using linear regression. Table3 shows the stability coefficient, $E_{a,}$ and correlation coefficient with different temperatures for watermelon juice. As can be seen, the activation energy increases with increasing concentration. As it shown in table 3 at first in 40ºBrix E_a vales was 28.80. Experimental values of Stability coefficient k, varied from 0.01232–0.0018 Pa s^n and R^2 from 0.996 to 0.972.

The values of the parameters obtained from Arrhenius model were obtained by linear regression analysis and are tabulated in Table 3. These values of activation energy for the juices were significantly higher when the brix was increased.

Table 3. The Stability Coefficient (K_0T), Activation energy (Ea), Correlation Coefficient (R2), with different temperatures for watermelon juice

ºBrix	$K_{0T}(pa.s^n)$	$E_{a.}$ (kJ/mol)	R^2
40	0.012321	28.80	0.996
50	0.010031	30.070	0.954
60	0.001851	34.729	0.972

The Ea values corresponding to mentioned Brix numbers were 28.80, 30.07, 34.72 kJ/mol, respectively. The activation energy calculated by this method is consistent with Mohammadi sani et *al* (2013).

The Experimental values of concentrated watermelon juice in º Brix 40, 50, 60 at different temperature are shown in table 4. It indicates increasing stress can caused to viscosity reduction.

Table 4. Experimental values of concentrated watermelon juice in ºBrix 40, 50 and 60 at different temperature

T (º C)	ºBrix	Shear rate (s^{-1})	Apparent viscosity (pa.s)	Shear stress(pa)
15	40	9.1-370	0.020-0.225	1.56-760
	50	9.1-350	0.015-0.327	1.67-780
	60	9.3-360	0.014-0.357	2.51-810
20	40	9.1-350	0.028-0.217	1.67-750
	50	9.2-330	0.018-0.347	2.50-880
	60	9.3-330	0.014-0.387	3.33-890
30	40	9.1-350	0.035-0.237	1.67-780
	50	9.2-340	0.028-0.337	3.69-960
	60	9.4-340	0.015-0.397	4.10-980

The results showed that total soluble solids content and temperature had effect on the juice viscosity. It also shows the direct effect of concentration and temperature on the viscosity (Mohammadi sani *e*t a*l*., 2013).

CONCLUSION

Among the models used, power law model had the highest efficiency in predicting the shear flow behavior of Iranian watermelon and the parameters (n and k) which influenced by temperature and concentration. Study of these changes contributed to the design of fruit juice products with a suitable viscosity. Otherwise, the correct design of the water treatment process can be achieved. The Hybrid-Arnius Law for the expression of concentration-temperature effect on the apparent viscosity had a high correlation that could be used to predict viscosity under the influence of simultaneous concentration and temperature.Watermelon juice presented pseudo-plastic behavior for different concentration and temperature studied ($R^{2} >$ 0.899).

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