Egypt. J. Chem. **Vol. 66**, No. 9. pp. 395 - 407 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Physical and Rheological Properties of Pomegranate Juices and Concentrates

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Abstract

The present work was designed to extract the pomegranate juices of Egyptian varieties Manfalouty and wonderful and to evaluate physical and thermal Properties of their concentrates obtained by rotary evaporator under vacuum. The results showed that Manfalouty juice contained higher °Brix, sugar/acid-ratio than those of Wonderful variety, while the later was characterized by higher content of total phenolics, flavonoids, tannins, anthocyanins and ascorbic acid as well as higher antioxidant activity. Rheological properties of the pomegranate concentrates showed Newtonian behaviour until a concentration of 52% and then shifted to non- Newtonian flow pattern with yield stress and thixotropic content at higher concentration (68% to 78%). Apparent viscosity values were reduced as temperature was increased from 5°C to 40°C. The reduction in viscosity was more remarkable for high °Brix-Concentrates (68% - 78%) rather than for low or medium °Brix-Concentrates. Values of activation energy of flow ranged between 13.72 to 79.84 kj/mol. °k, where the higher Ea-values were related to concentrates with high °Brix-values. Rate of viscosity increase was slowly until 68 °Brix, and then it changed almost vertically at higher concentration. Therefore, concentration of 68 °Brix could considered as the inflection point in viscous behaviour of pomegranate juice concentrates. Freezing curves of 72% pomegranate juice concentrates showed neither super-cooling temperature nor starting freezing temperature. The concentrates started to freeze as an eutectic mixture at temperature range of -22 to- 24°C. Specific heat values of pomegranate concentrate (72%) was measured to be 2.675 kj/kg. °C at 30°C and it was increased to 4.083 kj/ kg. °C as the temperature of the concentrates was increased to 60°C. The obtained data are important for designing Pumping, handling and thermal processing juices of Egyptian pomegranate fruits.

keywords: Pomegranate concentrates, bioactive components, rheological behavior, freezing curves, specific heat.

1. Introduction

The total production of pomegranate fruits (Punica granatum L.) in Egypt is estimated to be 405000 tons in 2018 representing 13.5% of the world production. The major varieties cultivated in Egypt are Manfalouty and Wonderful (1).

Pomegranates produce a reddish-purple, moderately acidic juice containing in average 15.6% dry substance, composed of sugars, organic acids, pectic substances, anthocyanins, polyphenols, vitamins and minerals. However, the juice composition, as well as organoleptic attributes, is strictly correlated to the pomegranate variety and juice production technology. Pomegranate juice exhibits high antioxidant capacity because of its rich content of polyphenols, mainly ellagic acid and its derivatives, anthocyanins and hydrolysable tannins, which represent the highest proportion of phytochemicals in pomegranate (2).

The health beneficials of pomegranate juice have recently received great attention. Pomegranate juices can be consumed fresh or processed. Anthocyanins are responsible for the color in pomegranate juice. Besides, organic acids, sugar and mineral content are significant for the sensory and nutritional quality and authenticity of pomegranate juice. The degradation of monomeric anthocyanins and their polymerization

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Received date 2022-12-21; revised date 2022-12-27; accepted date 2023-01-01
DOI: 10.21608/EJCHEM.2023.182371.7366

lead to formation of brownish color during processing and storage (3).

Among the extraction methods, use of hydraulic or screw press yield pomegranate juices with proper quality parameters such as color and functional phenolic components (4).

Evaporative concentration processes are one of the solutions that can safely address the challenge of fruit juice concentrates production (5).

Concentrates present higher resistance to microbial and chemical deterioration than the original juice as a result of water activity reduction. The concentration also reduces the volume with consequent reduction of transport, storage and packaging costs (6).

Evaluation of thermal properties of juice concentrates such as specific heat and freezing curves are essential for designing unit operation of concentrates production and preservation.

Specific heat (Cp), is highly dependent on the water content, temperature, and chemical composition of food products. Thus, detailed knowledge about the specific heat capacity (Cp) of food products over a broad range of temperatures is required for the heat transfer equipment (7). Specific heat values between 3. 815 and 3.88 kj/kg. °C have been reported by (5). for some fruit juices.

Freezing is generally considered as the least destructive preservation technology for phenolic compounds. Quick freezing technology can provide a fast-freezing rate to decrease the size of the ice crystals and it is an effective method for retaining color, flavor, nutritive value and texture. (3) and (8).

Rheological properties, in addition to chemical and physical properties, have several applications in the field of food acceptability, food processing and food handling. Rheological data are also needed for computation in any unit operation involving flow (e.g., pump sizing, filtration, extrusion, pasteurization, concentration and dehydration. Several equations have been used to describe the flow behavior of foods, for example, linear (Newtonian or Bingham), power law (Ostwald-de-Waele) power law with yield stress (Herschel- Bulkey) and Casson models. The effect of temperature on the apparent viscosity, (calculated at specified shear rate), is generally expressed by an Arrhenius-type model. Rheological behavior of juices will be influenced by the concentration and chemical composition of the solids. Heating processes significantly change the thermo-physical properties of fruit juices. It is necessary to study viscous behaviour of fruit juices in order to understand and control the juice production processes. Since the fruit juices are subjected to different temperatures and concentrations during processing, storage, transport, marketing and consumption, the viscosity is studied as a function of temperature and concentration. Fruit Juices vary greatly in their rheological behavior and their viscosity as a function of temperature and concentration. Thus, there is a great practical interest to study the effect of temperature and concentration on viscosity of fruit juices at various conditions. Therefore, the modeling of viscosity based on concentration and temperature is very important in terms of its use in designing the production process. (9) and (10).

Typical values of flow behavior index, consistency coefficient and activation energy of flow are rather limited considering the varieties of pomegranate fruits. Power equation indicated that consistency coefficient increased non-linearly with concentration increase. The rheological behavior of pomegranate juice prepared from fresh pomegranates was studied as a function of solids concentration in the range 17.5–75 °Brix at 10–55 °C. The juices exhibited Newtonian behavior regardless of the concentration method. The effect of temperature was described by an Arrhenius-type equation with activation energy in the range 5.34–32.2 kj/mol depending on concentration (increased with increasing soluble solid concentration). An exponential model described better the effect of the soluble solids on the viscosity and Ea-values (11).

The aim of the present work was the evaluation of physical, functional, thermal and rheological properties of pomegranate juice concentrations prepared from Egyptian Manfalouty and Wonderful varieties.

2- MATERIALS AND METHODS

2.1. Materials Source

Pomegranate (Punica granatum L.) fruits namely: cv. (Wonderful and Manfalouty) were collected from Egypt during seasons of 2019, 2020 and 2021. About 150 kg of each fruit cultivar were collected during the tested three seasons and were immediately transported to the laboratory and kept at 7 °C until analysis.

2.2. Extraction of juice

The fruits were washed with tape water and dried, manually peeled, and the arils were manually separated. juice was extracted using a stainless-steel hand screw press containing a screw with variable pitch distances and equipped with a metal sieve along the axis of the screw to get the strained juice, while pulp solids were separately with drawn at the end of the screw (Germany). Analysis was done and the concentrates were made immediately after pressing. Manufacture of concentrates was done under vacuum by a rotary evaporator attached to a water jet pump at a temperature of < 60° C, up to the 72% concentration.

2.3. Chemical Composition

Chemical Composition include pH, titrable acidity, and total soluble solid were determined in triplicate according to (12). The pH of pomegranate juice was determined by using digital pH meter (Jenway 3510) at 21° C, and the titrable acidity was determined by titration to pH =8.1 with 0.1 M NaOH solution and expressed as g of citric acid per 100ml of juice (13). the TSS were determined with Abbe refractometer (Zeiss, Germany) and the results were reported as °Brix at 21°C The density of the juice was measured using the density bottle.

2.4. Determination of total phenolics (TPs)

Total phenolics were determined by using Folin-Ciocalteu method. The results were expressed as mg gallic acid equivalent in 100 ml of fruit juice (mg GAE/100ml of juice). (14).

2.5. Total flavonoids (TF)

The total flavonoid content in juices was determined spectrophotometrically based on the formation of a complex flavonoid-aluminum. Rutin was used to establish the calibration curve as follows: 1 ml of diluted sample was separately mixed with 1 ml of 2% aluminum chloride methanolic solution. After incubation at room temperature for 15 min, the absorbance of the reaction mixture was measured at 430 nm with a Spekol 11–Visible spectrophotometer and the flavonoid content was expressed as mg of rutin equivalent per 100 ml of juice. (14).

2.6. Total anthocyanins (TA)

The TA was estimated by pH differential method using two buffer systems: potassium chloride buffer pH 1.0 (25 mM) and sodium acetate buffer pH 4.5 (0.4 M). according to (14). with some modifications. Briefly, 0.4 mL of pomegranate juice sample was mixed with 3.6 mL of corresponding buffers and 0.5 ml of pomegranate concentrates was mixed with 27 ml of corresponding buffers and read against water as a blank at 510 and 700 nm. Absorbance (A) was calculated as:

A = (A510nm - A700nm) pH1 - (A510nm - A700nm) pH4.5 ……. (1)

The TA of samples (mg cyanidin-3-glucoside/L of PJ) was calculated by the following equation =

TA = (A x MW x DF x 100) x 1/MA…..(2)

where A: absorbance; MW: molecular weight (449.2 g/mole); DF: dilution factor (10); MA: molar absorptivity coefficient of cyanidin-3-glucoside (26,900).

2.7. Determination of antioxidant activity by DPPH assay

A free radical test was carried out according to the method described by (15). Briefly, 200 µL of sample were added to 3.8 mL of DPPH• methanolic solution (25 mg/L). The absorbance of the reaction mixture (MR) was determined at 517 nm after 20 min at room temperature in the dark.

The antioxidant activity was determined according the equation mentioned below:

Antioxidant activity% = (1 – (Abs sample 517 nm / Abs control 517 nm)) X 100 ……. (3)

2.8. Ascorbic Acid

The ascorbic acid content determined by direct colorimetric method is based on measurement of the extent to which 2,6-dichlorophenol-indophenol solutions. The concentration of ascorbic acid from the standard curve and calculate the ascorbic acid content in the sample as mg of ascorbic acid per 100g or ml of sample. (16).

2.9. Total Tannins content

Total Tannins content were determined according to (12). for pomegranate juice and concentrate by Folin- Denis method. The absorbance of formed color was measured at 760 nm.

The results were presented as mg tannic acid equivalent (TAE) per 100ml of juice.

Physical properties

2.10. Rheological measurements

Rheological measurements of different pomegranate juice concentrates (16 – 27 – 52 – 68 – 72 – 78 %) at different temperatures (5, 15, 25, and 40°C) were measured by using the rotational viscometer (Rheotest, type RV2, Pruefgreat, Medingen, Germany). Samples were introduced into the (N – S2 – H) cylinders of viscometer. The developed shear stress at different shear rates ranging from 0.3 to 1312 sec-1 was obtained as torque deformation (α) and converted to shear stress (τ) according to the following equation:

τ = Torque value (α) . Cylinder constant ….. (4)

obtained flow curves were analyzed as described by (17). according to the Newtonian and power low models:

Newtonian model: $\tau = \mu \cdot \gamma$ …. (5)

Non- Newtonian model: $\tau = K \cdot \gamma^{n}$…. (6)

Where: γ is the shear rate (s^{-1}), K is the consistency coefficient Dynes/cm2.s and n is the flow behaviour index.

For comparison between different treatments, apparent viscosity values (µa) were calculated at selected shear rate (729 s^{-1}) according to the followingequation :

Apparent viscosity $(\mu a) = k * \gamma^{n-1}$ ..... (7)

2.11. Freezing Curves

Freezing curves were recorded using a temperature and atmosphere test cabinet type WK (Weiss Technik, Germany). Concentrate samples were placed in a stainless-steel tube of 15 cm length and 1.3 cm diameter. Two thermocouples were inserted in the center of the concentrate and at the wall of the tube. Temperature signals were recorded at 5 seconds intervals using a personal computer (PC). Temperature of the cabinet was set at -35°C.

2.12. Specific Heat

The specific heat was determined by a laboratory calorimeter consists of isolated cup and cover heated resistance, small fan and thermocouple connected to a PC. Measurements were carried out at temperature range between 25 °C to 65 °C. (3B scientific GmbH, Hamburg, Germany).

Electrical energy (q_1) consumed to heat the resistance was used to heat the concentrate. The rate of temperature increase over heating time $\Delta t / \Delta \tau$ was used to calculate the specific heat according to the following equation:

$(q1) = m.cp.(\Delta t / \Delta \tau)$ .... (8)

2.13. Statistical analysis

All experiments were performed in triplicate and mean values and standard deviations reported. t-test was performed and the mean separations were performed by a statistical package test ($P < 0.05$) using SAS 9 Inc.

3. RESULTS AND DISCUSSION

3.1. Some Physical and Chemical Characteristic

Table (1) Shows Some Physical and Chemical Characteristic of Pomegranate juice obtained by screw Pressing. Juice of Manfalouty variety is Characterized by higher Brix value (16.5°), lower acidity (1.015%) and higher Sugar acid ratio (16.256) compared with those of Wonderful juice. The Sugar acid ratio present that the Manfalouty Juice is more Palatable then did Juice of Wonderful variety.

Table (1): Some chemical and physical characteristics of fresh pomegranate juice obtained by screw pressing.

Parameters Cultivars	Brix°	pH	Acidity (%)	Density (gm/cm^3)	Sugar/acid ratio
Manfalouty juice	16.5±0.5774	3.76**±0.0033	1.015**±0.0029	1.035±0.0006	16.256
Wonderful juice	15.41±0.5774	3.62**±0.0058	1.191**±0.0009	1.033±0.0006	12.938

On other Side, Table (2) includes the bioactive and functional components of pomegranate Juices and their 72% concentrate. Juices of Wonderful showed higher total phenolics (431.36 mg /100ml), higher Flavonoids (2.081 mg /100ml), Anthocyanin (28.64 mg/ l00ml) and Ascorbic acid (11.88 mg/100ml) than those of Manfalouty variety. Correspondingly, the antioxidant activity of Wonderful juices Was (61.57%), being slightly higher than that of Manfalouty juice (58.56%). However, Wonderful Juice showed significantly higher content of total tannins (256.09 mg l00ml) compared with Manfalouty Juice (134.57 mg/100ml). Concentration of pomegranate juice under vacuum to the level of 72 °Brix did increased total phenolics, total tannins and total flavonoids by 5- to 11-folds compared with those of fresh juice. A slight change has been observed in total Anthocyanins, ascorbic acid and antioxidant activity in the concentrates. In general, Manfalouty juice concentrates showed higher functional components than the those of Wonderful juice concentrates. The obtained results agree with those reported by (18) and (19).

Table (2): Bioactive and functional components of pomegranate juice and concentrates

Parameters Cultivars	Total Phenolics mg / 100ml	Total Tannins	Total Flavonoids	Total Anthocyanin	Ascorbic acid	Antioxidant activity %
Manfalouty juice	286.949**±7.63	134.57**±2.09	1.628**±0.04	22.781*±0.64	9.762**±0.006	58.56**±0.18
Manfalouty concentrate 72%	1440.508±11.56	1601.814±4.56	11.649±0.39	26.114**±0.57	14.518**±0.005	71.16**±0.19
Wonderful juice	431.356**±7.22	256.087**±8.53	2.081**±0.07	28.644*±0.006	11.883**±0.006	61.57**±0.55
Wonderful concentrate 72%	1418.475±11.56	1563.727±14.85	10.614±0.23	15.461**±0.81	16.773**±0.053	77.75**±0.29

* Significant at the 0.05 level ** Significant at the 0.01 level

3.2. Rheological Properties:

Fig (1) and (2) Shows the rehograms of the tested concentrates of Manfalouty and Wonderful juices, respectively. The rehograms were obtained for concentration ranging between 27% and 78%. as well as at temperature range 5 to 40°C for both concentrates. It could be seen that the obtained shear stress response values of Wonderful concentrates were relatively higher than those of Manfalouty concentrate at all tested shear rate and temperatures may be because of the higher content of suspended solids in the Wonderful juices and concentrates. The flow data were subjected to analysis according to the Newtonian and Power low models as described before (Material &Methods) and the results are given in Tables (3) and (4), respectively for Manfalouty and Wonderful Juice concentrates. Concentrates of 27%, 52% and 68% showed higher R^2-values when analyzed according to the Newtonian law rather than Power low model (as non-Newtonian fluid). However, data of analysis according to both lows are given in Tables (3) and (4). That means that Pomegranate juice concentrates up to 68%. Concentration could be considered as Newtonian fluid rather than non-Newtonian fluid. For concentrations of 72% and 78%. the R2 - values were shifted in favor of the non-Newtonian flow model which could be considered as non-Newtonian fluid. For comparison between the two different flow models, the apparent viscosity (μa) was calculated at shear rate 729s-1 to compare it with the dynamic viscosity obtained from the Newtonian low of viscosity and the result are also given in Tables (3) and (4). As seen, the apparent viscosity values from the non- Newtonian low were very close to the dynamic viscosity values obtained from Newtonian flow models.

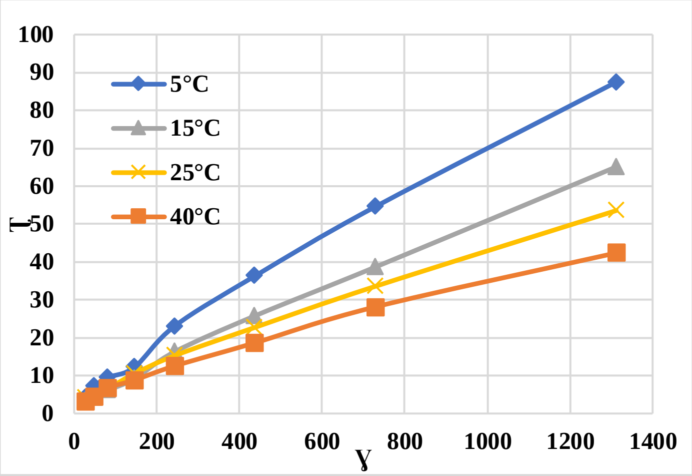
As seen from Table (3) and (4), the apparent and dynamic viscosity values were increased by increasing the concentration of the pomegranate juice from 27% to 78% soluble solids. For example, the (μa) of 27% concentrate (Manfalouty juice) measured at 5°C was 7.50 Cp and it was increased by 5.88- fold and reached 44.1 Cp as concentration was raised to the level of 52%. This value was further increased by l0.9-Folds to reach 482 Cp at concentration of 68%. At 72% and 78% concentrations the viscosity was increased to the level of 3101 and 13933 Cp, respectively making 4.49 to 6.43-folds increase. Viscosity Values obtained from Newtonian flow behavior were close to those obtained from non- Newtonian fluid analysis, since the viscosity values were increased from 6.46 Cp at 5°C for 27% concentrate to 14841 Cp at same temperature for 78% concentrate. Similar behavior was also observed for the viscosity data of wonderful Juice concertantes (Table 4), expect that the viscosity values were slightly higher than those obtained for Manfalouty concentrates due to the higher solid content in the suspended materials of Wonderful pomegranate juice. As seen in Tables (3) and (4) some concentration showed a yield stress values (τ0), specially those with concentration higher than 52%. Also, concentration of 72% and 78% showed thixotropic values, where the descending flow curves were much lower than their corresponding ascending curves. Viscosity values of both concentrates were decreased as the measurement temperature was raised from 5°C to 40°C as seen in Tables (3) and (4). The effect of temperature on pomegranate juice concentrate could be analyzed according to the following equation (20).

$$\ln \mu_a = \ln \mu_0 + E_a/R \cdot (1/T) \quad ..... \quad (9)$$

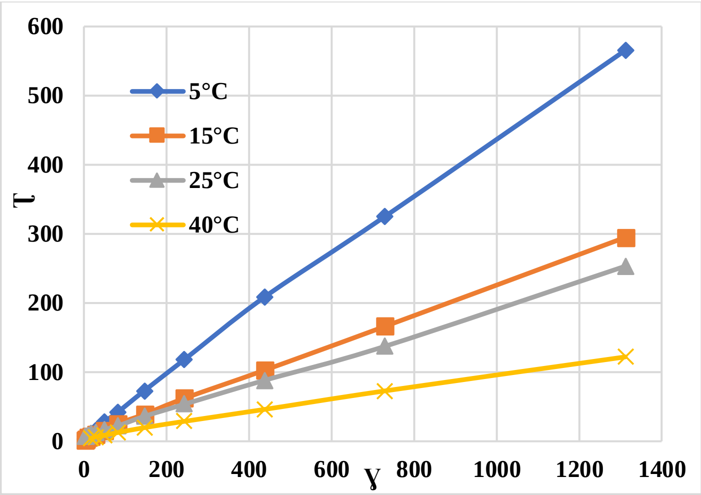
Where Ea is the activation energy for viscosity Change.

Figure (1): Flow Curves of pomegranate juice concentrates

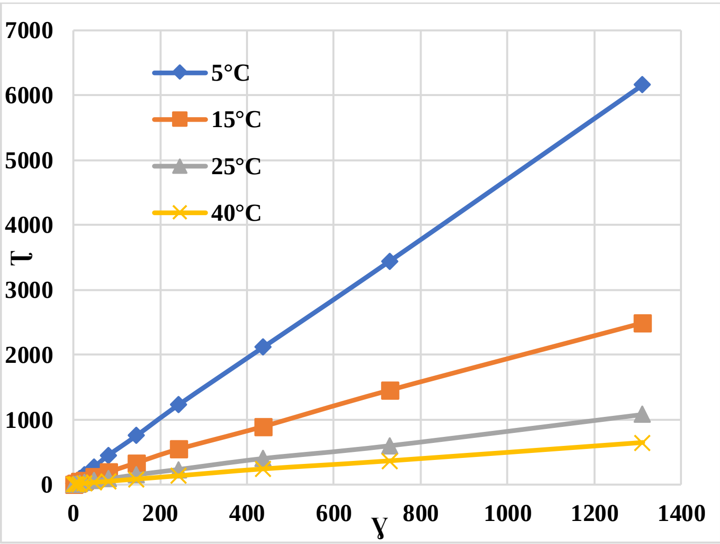
Fig (1-a): Manfalouty juice Concentrates



27%

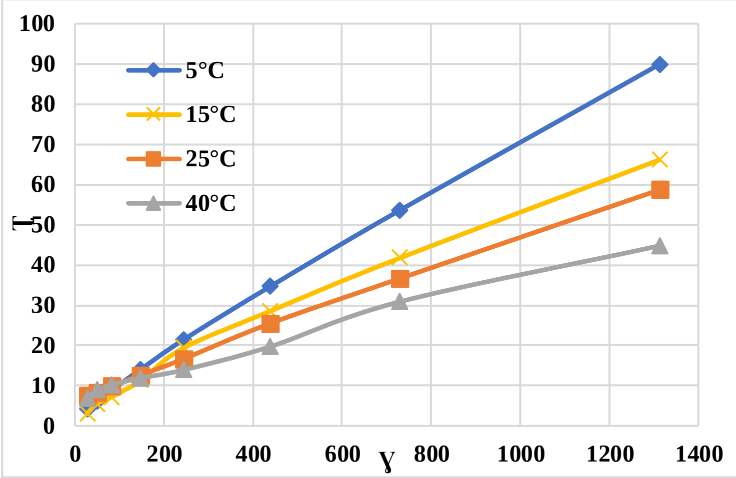


52%

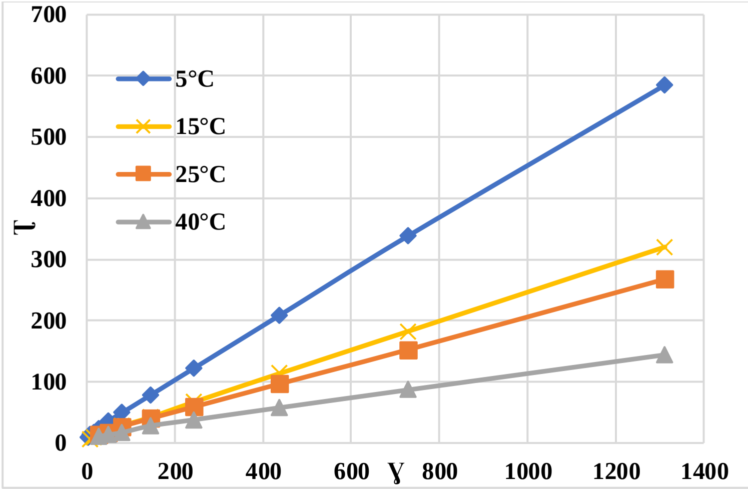


68%

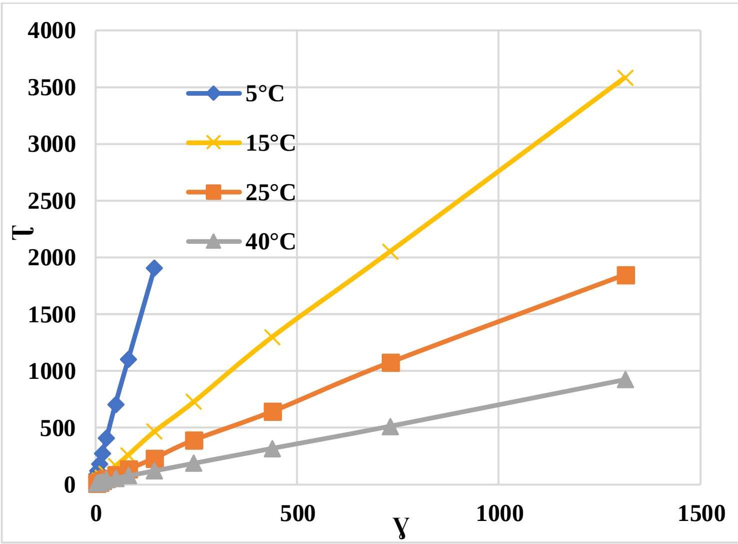
Fig (1-b): Wonderful juice Concentrates



27%



52%

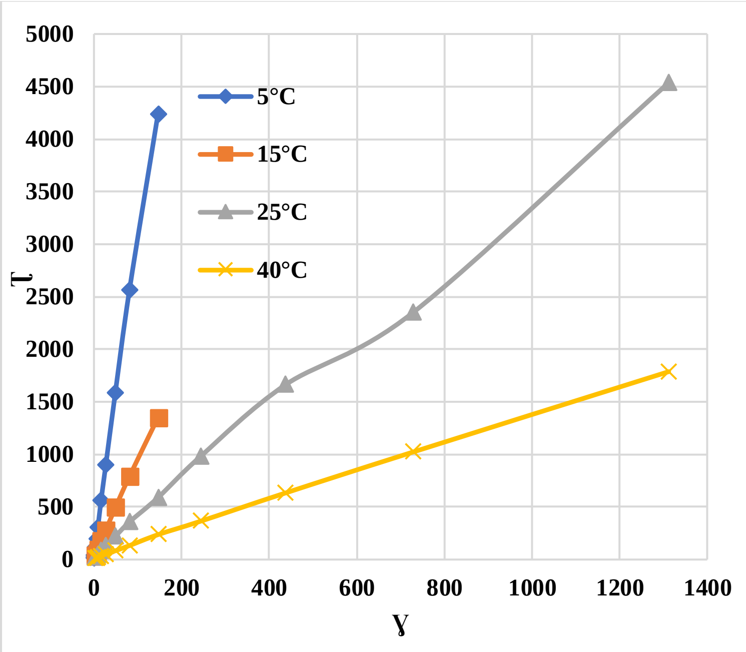


68%

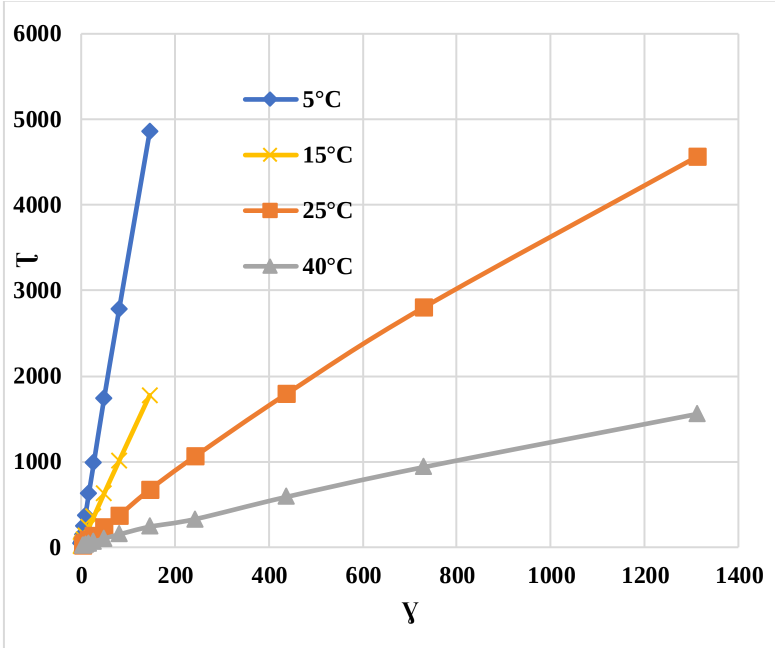
Continue Figure (1): Flow Curves of pomegranate juice concentrates

Continue Figure (1-a): Manfalouty juice Concentrates

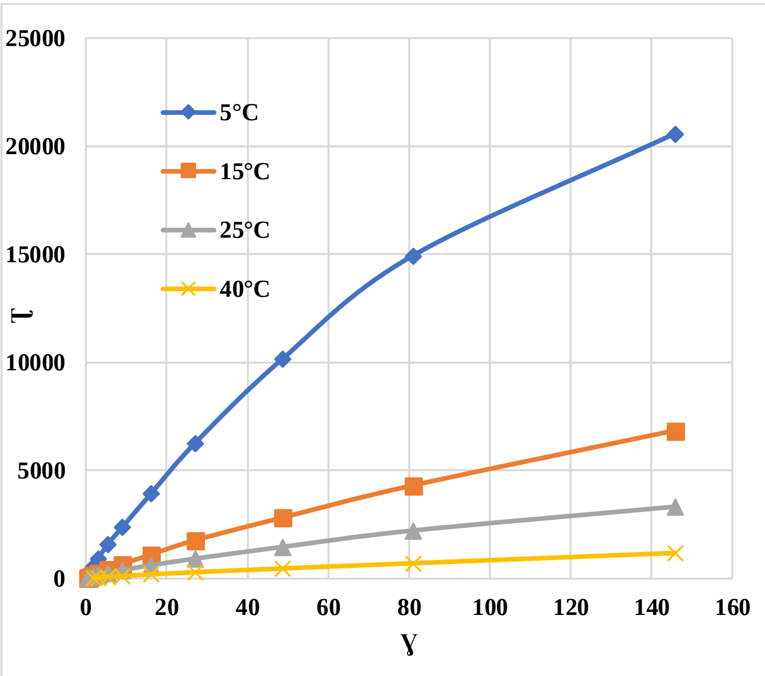
Continue Figure (1-b): Wonderful juice Concentrates



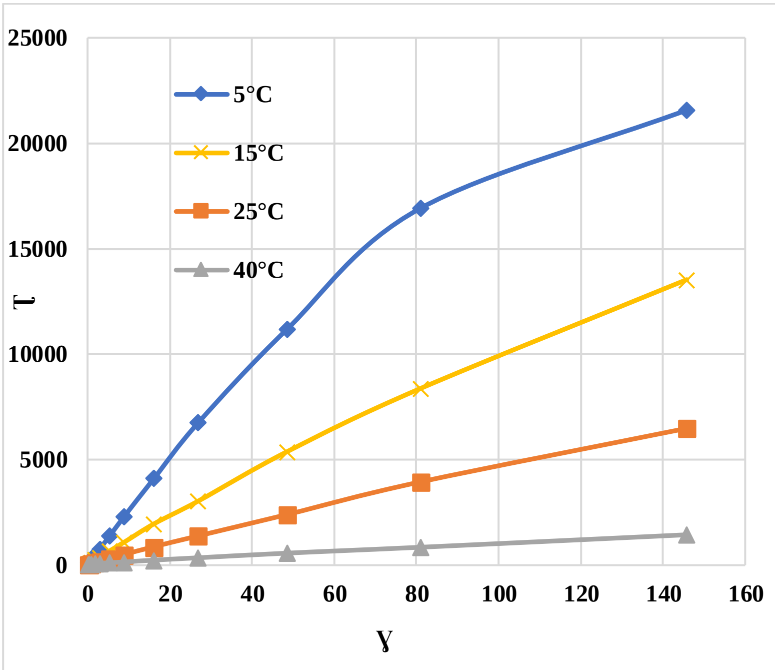
72%



72%



78%



78%

Table:(3) Rheological data of tested Manfalouty pomegranate juice concentrates

	As Newtonian Fluid			As non- Newtonian Fluid			
Manfalouty	**µ (Cp)**	**τ_0 (Dynes/cm2)**	**R^2**	**K (Dynes/cm2.sn)**	**n**	**R^2**	**µa (Cp)**
78% 5 °C	**14841**	**965.31**	**0.966**	**335.69**	**0.866**	**0.997**	**13933.35**
78% 15 °C	**4778**	**192.7**	**0.991**	**92.71**	**0.878**	**0.999**	**4159.38**
78% 25 °C	**2329**	**142.83**	**0.983**	**65.94**	**0.799**	**0.998**	**1753.91**
78% 40 °C	**796**	**51.19**	**0.996**	**20.25**	**0.815**	**0.998**	**598.07**
72% 5 °C	**2949**	**47.11**	**0.997**	**34.92**	**0.982**	**0.999**	**3101.43**
72% 15 °C	**926**	**18.79**	**0999**	**13.50**	**0.919**	**0.997**	**794.80**
72% 25 °C	**339**	**52.71**	**0.997**	**7.45**	**0.882**	**0.998**	**341.13**
72% 40 °C	**136**	**18.09**	**0.999**	**2.62**	**0.903**	**0.999**	**137.99**
68% 5 °C	**468**	**40.98**	**0.999**	**6.79**	**0.948**	**0.999**	**482.05**
68% 15 °C	**191**	**32.36**	**0.999**	**3.38**	**0.923**	**0.998**	**202.90**
68% 25 °C	**81.6**	**17.87**	**0.998**	**2.42**	**0.835**	**0.995**	**81.59**
68% 40 °C	**49**	**8.86**	**0.998**	**0.988**	**0.903**	**0.998**	**52.03**
52% 5 °C	**43**	**6.40**	**0.998**	**0.83**	**0.903**	**0.999**	**44.10**
52% 15 °C	**22.3**	**4.11**	**0.999**	**0.548**	**0.868**	**0.992**	**23.02**
52% 25 °C	**18.6**	**7.01**	**0.999**	**0.63**	**0.779**	**0.954**	**14.68**
52% 40 °C	**9.1**	**5.05**	**0.998**	**0.46**	**0.764**	**0.996**	**9.73**
27% 5 °C	**6.5**	**5.15**	**0.993**	**0.321**	**0.779**	**0.999**	**7.49**
27% 15 °C	**4.8**	**2.83**	**0.996**	**0.207**	**0.791**	**0.991**	**5.23**
27% 25 °C	**3.9**	**4.18**	**0.993**	**0.332**	**0.698**	**0.988**	**4.55**
27% 40 °C	**3**	**4.10**	**0.989**	**0.329**	**0.671**	**0.997**	**3.76**

Table:(4) Rheological data of tested Wonderful pomegranate juice concentrates

	As Newtonian Fluid			As non- Newtonian Fluid			
Wonderful	**μ (Cp)**	**τ_0 (Dynes/cm^2)**	**R^2**	**K (Dynes/cm^2.s^n)**	**n**	**R^2**	**μa (Cp)**
78% 5 °C	**16006**	**977.73**	**0.951**	**294.62**	**0.913**	**0.997**	**16603.93**
78% 15 °C	**9472**	**232.15**	**0.995**	**136.77**	**0.937**	**0.998**	**9028.98**
78% 25 °C	**4497**	**99.876**	**0.998**	**91.21**	**0.833**	**0.994**	**30.23.79**
78% 40 °C	**962.2**	**63.313**	**0.998**	**55.48**	**0.587**	**0.967**	**364.84**
72% 5 °C	**3318**	**60.012**	**0.999**	**73.19**	**0.800**	**0.987**	**1963.67**
72% 15 °C	**1214**	**19.501**	**0.999**	**21.04**	**0.876**	**0.993**	**927.44**
72% 25 °C	**353**	**86.601**	**0.995**	**8.299**	**0.877**	**0.999**	**369.86**
72% 40 °C	**118**	**38.71**	**0.998**	**6.07**	**0.749**	**0.994**	**116.32**
68% 5 °C	**1276**	**59.717**	**0.999**	**43.95**	**0.713**	**0.981**	**662.72**
68% 15 °C	**274**	**34.452**	**0.999**	**4.54**	**0.928**	**0.999**	**282.39**
68% 25 °C	**141**	**20.972**	**0.999**	**3.89**	**0.839**	**0.995**	**134.02**
68% 40 °C	**68.9**	**17.238**	**0.999**	**3.92**	**0.724**	**0.989**	**63.45**
52% 5 °C	**44.1**	**12.09**	**0.999**	**2.84**	**0.701**	**0.981**	**39.57**
52% 15 °C	**24.1**	**6.367**	**0.999**	**0.88**	**0.801**	**0.992**	**23.66**
52% 25 °C	**19.7**	**9.946**	**0.999**	**0.89**	**0.778**	**0.994**	**20.74**
52% 40 °C	**10.3**	**10.504**	**0.998**	**0.98**	**0.679**	**0.9892**	**11.79**
27% 5 °C	**6.6**	**3.867**	**0.998**	**0.27**	**0.800**	**0.998**	**7.28**
27% 15 °C	**4.9**	**4.350**	**0.989**	**0.24**	**0.787**	**0.997**	**5.79**
27% 25 °C	**3.8**	**4.953**	**0.997**	**0.58**	**0.608**	**0.977**	**4.40**
27% 40 °C	**2.9**	**7.247**	**0.993**	**1.31**	**0.467**	**0.955**	**3.89**

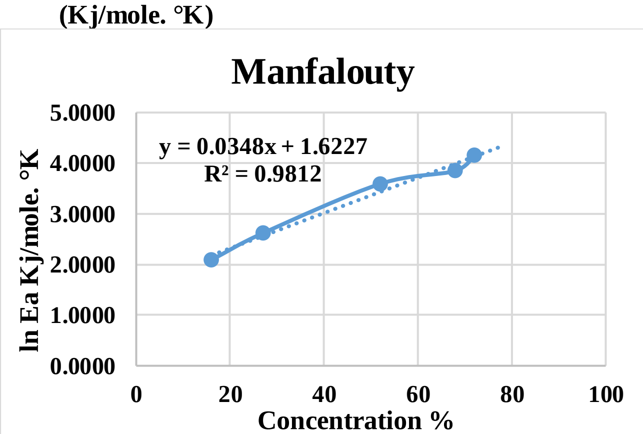
As seen in Table (5), the activation energy values were affected with the concentration of the tested pomegranate juice. For 27% concentrate of Manfalouty juice, the activation energy was 13.72 kj/mole. K°, while it Was increased to the level of 71.48 kj /mole. K° as the concentration was raised to the level of 78%. Higher values of activation energy mean more significant effect of temperature change on the viscosity values of the concentrate. For example, at 78% concentration, the viscosity at 5°C was 13933.35 Cp at it was reduced rapidly to the level of 4159.37 Cp as the temperature of measurement was increased to 15°C. The reduction in viscosity of 78% concentrate was 335%, while under the Same condition the reduction in viscosity of 27% concentrate was only 143%. which indicate the higher effect of temperature on the concentrates with higher Brix-values. Concentrates of Wonderful juices showed, in general, activation energy values similar to those of Manfalouty concentrates.

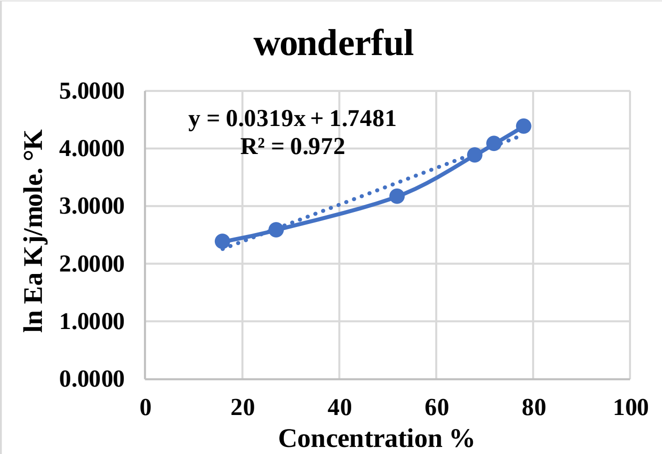
Table (5): Activation energy values of pomegranate juices and Concentrates (Kj/mole. °K)

Conc.	Manfalouty		Wonderful	
	Ea	R2	Ea	R2
27%	13.719		13.276	
52%	36.305	0.9812	23.771	0.972
68%	46.959		48.587	
72%	63.403		59.102	
78%	71.48		79.836	

Fig (2) Shows an increasing liner relationship between the concentration of the pomegranate juice concentrate and the obtained values of activation energy for both Manfalouty and Wonderful varieties.

Figure (2): Relationship between juice concentration (%) and values of activation energy (Kj/mole. °K)





The effect of concentration on the apparent viscosity of pomegranate juice concentrates was given in Fig (3) at different measuring temperature (5°C to 40°C) For concertantes of both of tested pomegranate varieties (Manfalouty and Wonderful), the increase in viscosity values the 16% to 68% concentrates was very slowly and then it showed a vertical inflection point and the viscosity was rapidly increased as the concentration was raised to the level of 72% and 78%. For both tested varieties. The angle of the inflection point was very sharp (near 90°) at 5°C and it was gradually decreased at the temperature was increased to 25°C, while it was almost flattened at temperature of 40°C. This behavior is very important and should be taken in consideration when designing and sizing transport devices (Pumps) during Cooling and freezing of the obtained concentrates. The obtained results agree with those reported by (21), (22), (23) and (24).

3.3. Effect of concentration on some thermal properties of pomegranate juices and concentrates.

3.3.1. Freezing curves

Figure (5) shows the freezing curves of Pomegranate juice concentrates for both Manfalouty and Wonderful varieties. As seen, the freezing curves consists of three phases without the occurrence of a clear super cooling temperature (ts) as it is common in the freezing of fruit juices, may be because the high concentration of soluble solids (72%) and the bound nature of the remaining water. The first part is characterized by a linear decrease of the concentrate temperature (in t°C) of 20°C until reaching the freezing (eutectic). point of the concentrates at -25°C and -21°C for 72% concentrates of Manfalouty and Wonderful concentrates, respectively. These values agree to great extent with the theoretical freezing point depression (Δtf) obtained from the Celuisios – Clapeyron equation (25) as follows:

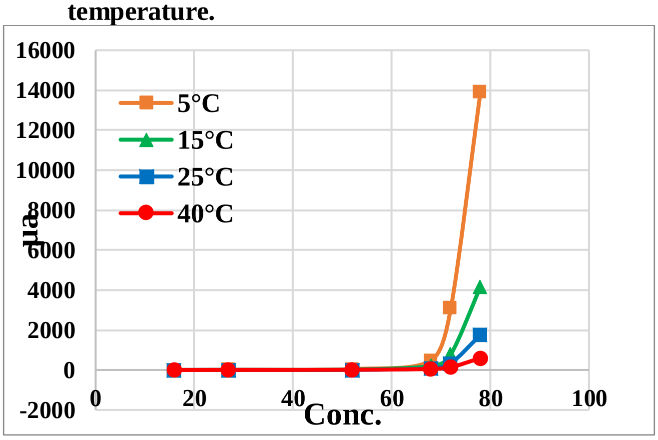
$\Delta t_f = 1.86\ (n)$ ….. (7) .

where (n) the number of solute moles (M=180) dissolved in 1000 g of solvent (water).

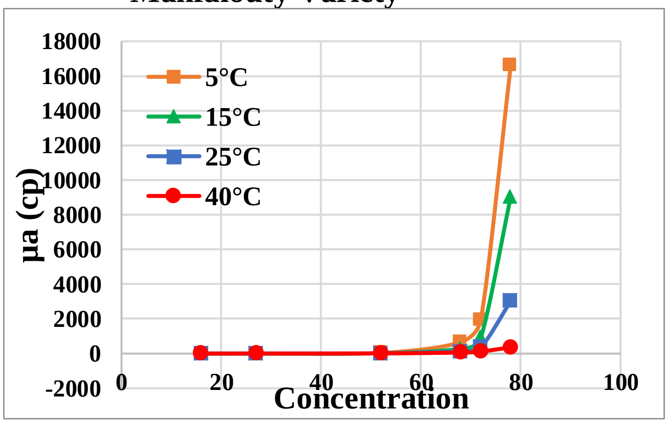
The obtained Δtf - values for pomegranate juice concentrates were found to be -24.1(degree Celesius), which agree with the aforementioned experimental results.

The second phase is in the range between -21°C and -31°C, which represent the completion of ice-solid crystals formation. The last phase (-31°C to -34°C) is the phase of cooling the formed ice-solid crystals to near the temperature of the cooling medium (-35°C). The obtained freezing curves agree with those reported by (26) for soursop fruit and by (8) for bayberry fruits and concentrates.

Figure (3): Relation between concentration and apparent viscosity values of Manfalouty and wonderful concentrates at the four tested temperature.



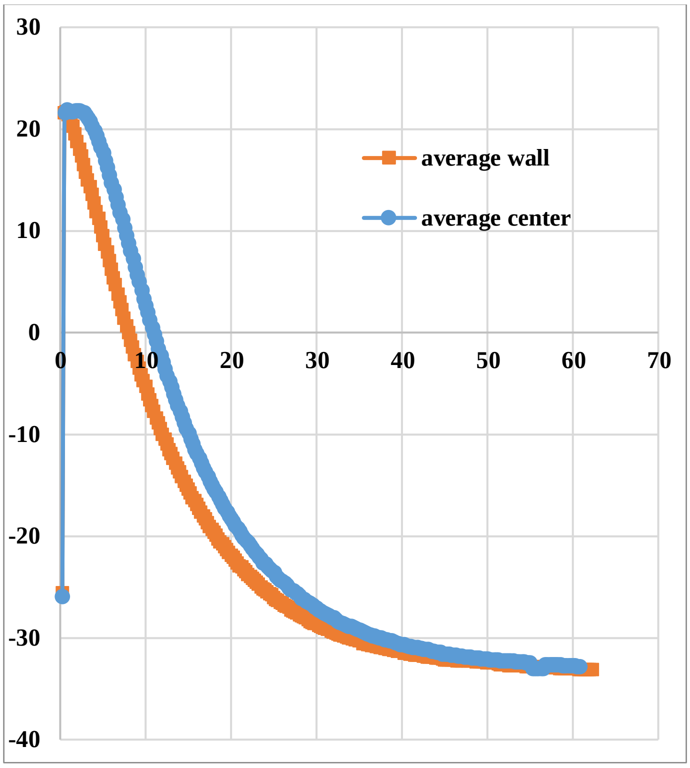
Manfalouty Variety



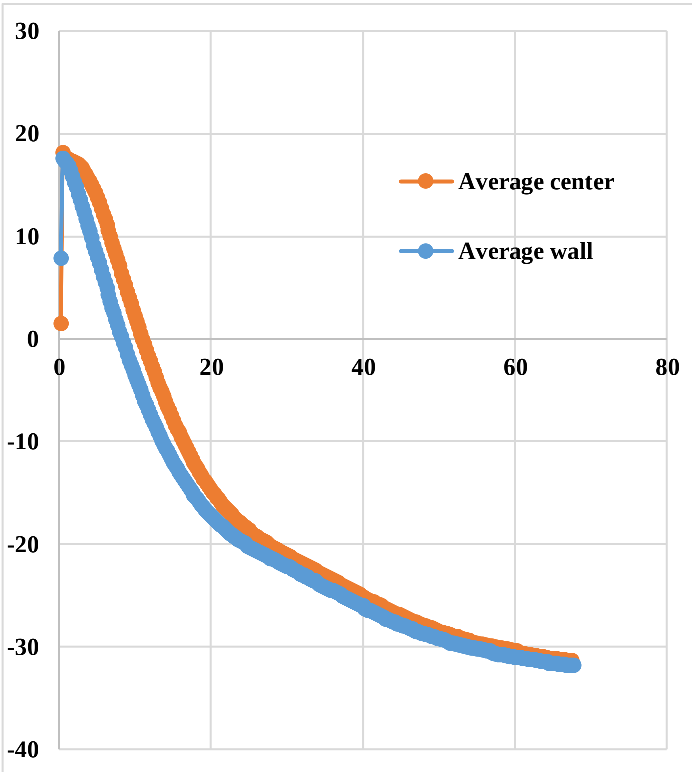
Wonderful Variety

Freezing curves

Figure (4): Freezing curves of 72% pomegranate juice concentrates



a-Manfalouty concentrate 72%



a-Wonderful concentrate 72%

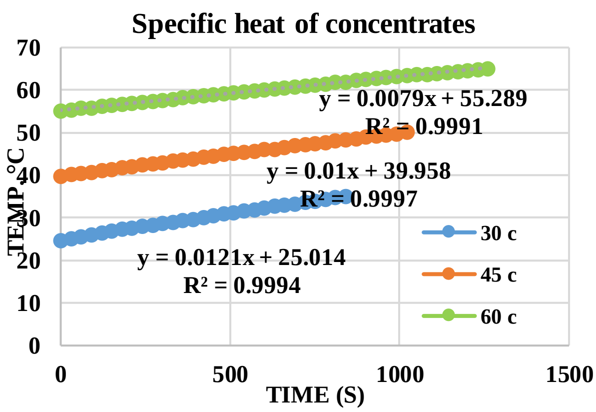
3.3.2. Specific heat

Specific heat of pomegranate juice concentrates was determined for a mixture of Manfalouty and Wonderful juice concentrates at different temperature ranges (25-35, 40-50, 55-65) and the results are given in Table (6) and Figure (5). As seen, the obtained heating curves (in t °C) of the concentrates showed a linear relationship with the heating time (in seconds) at all tested temperature ranges (Fig 5). The consumed current (A) was reduced from 1.0112 Ampere re to 1.0299 Ampere as the temperature range was increased (Table 6). The obtained specific heat values for the 72% pomegranate juice concentrates were 2.6746 kj/kg.°C at average temperature of 30°C and it was increased to the level of 3.223 and 4.083 kj/kg.°C as the temperatures of the concentrates were increased, respectively to 45°C and 60°C. It is clear, that the specific heat values of the concentrate increases with increase in heat temperature, which could be taken in consideration in designing their, thermal treatments. The obtained results agree with those of (27).

Table (6): Rate of temperature increase (Δt/ Δτ), the Consumed electrical Current (Ampere) and the Calculated specific heat of pomegranate juice concentrate (72%).

Concentration	Temperature Range (°C)	Δt/ Δτ Slope of heating curve °C/sec	Consumed Current (A)	Specific heat kj/kg. °C
72%	25-35	0.0121	1.0112	2.6746
	40-50	0.0100	1.004	3.22298
	55-65	0.007927	1.0299	4.08300

Figure (5) Heating curve of the Pomegranate concentrates (Mixture of Manfalouty and Wonderful)



Conclusion

Manfalouty juice showed higher sugar/acid ratio than Wonderful juice, but the later was superior in phenolic, anthocyanins and antioxidant activity. Pomegranate juice concentrates showed Newtonian behaviour until °Brix 52 and then shifted to non-Newtonian flow Pattern. Freezing Curves of 72% concentrates showed only Eutectic- formation and specific heat was increased by increasing temperature of the concentrate

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