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INFLUENCE OF TEMPERATURE AND STORING TIME ON SELECTED RED WINE PHYSICAL PROPERTIES

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Abstract

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Presented article is focused on red wine rheological and thermal properties. Effects of temperature and short term storage on density, rheological parameters and thermal parameters were investigated. First measurement was done at the beginning of storage and then the same sample was measured again after one week of storing. Density was measured by densimeter Mettler Toledo DM 40 at different temperatures. For dynamic viscosity measurement was used rotational viscometer Anton Paar DV-3P. The kinematic viscosity and fluidity were determined according to the definitions. Thermal parameters were measured by instrument Isomet 2104. Temperature dependencies of wine dynamic and kinematic viscosity had decreasing exponential shape and temperature dependencies of fluidity had an increasing exponential shape. Temperature dependencies of red wine thermal conductivity and diffusivity had increasing linear character. Decreasing polynomial functions were obtained for temperature dependencies of red wine density. The values of dynamic and kinematic viscosity, thermal conductivity and diffusivity, and density of red wine were a little bit higher after short term storing, which can be expressed by changed amount of water caused by evaporation. Due to the same reasons were values of fluidity little bit lower after storage.

Keywords: red wine, rheologic parameters, thermal parameters, density, temperature, storing time

INTRODUCTION

Precise knowledge of materials physical quantities is required at controlled processes in manufacturing, handling, and holding. For the quality evaluation of food materials is important to know their physical properties, particularly mechanical, rheological and thermophysical (Božiková and Hlaváč, 2010).

This article deals with rheological and thermal properties which are very complicated characteristics of materials. The object of the observation was red wine. Wine is an alcoholic beverage made from fermented grapes or other fruits. The natural chemical balance of grapes lets them ferment without the addition of sugars, acids, enzymes, water, or other nutrients. Yeast consumes the sugars in the grapes and converts them into alcohol and carbon dioxide. Different varieties of grapes and strains of yeasts produce different styles of wine. The well-known variations result from the very complex interactions between the biochemical development of the fruit, reactions involved in fermentation, along with human intervention in the overall process (Johnson, 1989). Composition of wine depends on various factors. Mostly it consists from water (70–90%), alcohol (8–20%), acids (0.3–1%), sugars (0.1–20%), pigments, phenols, minerals, vitamins, etc. (Johnson, 2010). There are many different types of wine, but grape wine is the most favourite and popular fruit wine all over the world (Zeng *et al.*, 2008). Some physical and chemical properties of wine and similar drinks are mentioned in the literature. Physical parameters of liquids especially drinks were examined by many authors. The model of heat transfer in wine tank was described by Colombié *et al.* (2007), thermal properties of drinks were detected by Ikegwu and Ekwa (2009), density, viscosity and selected thermal parameters were measured by Zuritz *et al.* (2005).

Viscosity is an important rheologic property of liquid food products, which affects pumping, filtration, clarification as well as other processes (Yanniotis *et al.*, 2007). Viscosity is defined as the resistance of a fluid to flow. Physical unit of dynamic viscosity in SI units is Pa·s. Viscosity changes with temperature. The difference in the effect of temperature on viscosity of fluids and gases is related to the difference in their molecular structure. Viscosity of most of the liquids decreases with increasing temperature. Theories have been proposed regarding the effect of temperature on viscosity of liquids. According to Eyering theory molecules of liquids continuously move into the vacancies (Bird *et al.*, 2002). This process permits flow but requires energy. Activation energy is more readily overcome at higher temperatures and the fluid flows easily. The temperature effect on viscosity can be described by an Arrhenius type equation

$$\eta = \eta_0 e^{\frac{E_A}{RT}}, \qquad (1)$$

where η_0 (Pa·s) is reference value of dynamic viscosity, E_A (J·mol^{-1}) is activation energy, R (J·mol^{-1}·K^{-1}) is gas constant and T (K) is absolute temperature (Figura and Teixeira, 2007).

Liquid molecules are closely spaced with strong cohesive forces between them. The temperature dependence of viscosity can also be explained by cohesive forces between the molecules (Munson *et al.*, 1994). As temperature increases, these cohesive forces between the molecules decrease and flow became freer. As a result viscosities of liquids decrease as temperature increases. In liquids, the intermolecular (cohesive) forces play an important role. Viscosities of liquids show little dependence on density, molecular velocity or mean free path. In most liquids, viscosity is constant up to a pressure 10.134 MPa, but at higher pressures viscosity increases as pressure increases (Sahin and Sumnu, 2006).

Kinematic viscosity ν (m^2·s^{-1}) is defined as a ratio of dynamic viscosity η to density of fluid ρ (kg·m^{-3}) at the same temperature

$$\nu = \frac{\eta}{\rho}. \qquad (2)$$

Its physical unit is m^2·s^{-1}. Reciprocal value of dynamic viscosity η is called fluidity φ and unit of fluidity is Pa^{-1}·s^{-1}

$$\varphi = \frac{1}{\eta}. \qquad (3)$$

Thermal conductivity and thermal diffusivity are basic thermal parameters of materials. Thermal conductivity is defined as the quantity of heat transmitted through a unit surface to a unit temperature gradient in unit time. This thermophysical parameter depends on many factors as: material's structure, pressure, temperature etc. Thermal conductivity is mathematically defined by Furrier's law

$$\vec{q} = -\lambda \, grad\, T, \qquad (4)$$

where q is density of thermal flow (W·m^{-2}), λ is thermal conductivity (W·m^{-1}·K^{-1}).

Thermal diffusivity characterizes the velocity of the temperature equalization in material during non stationary processes. In numeric view it is equal to temperature change of unit volume caused by heat, which is transferred in unit time, by unit surface of coat with unit thickness, in unit temperature difference on her facing side. This thermal parameter is defined by thermal conductivity λ, specific heat c (J·kg^{-1}·K^{-1}) and density ρ

$$a = \frac{\lambda}{c\rho}. \qquad (5)$$

The main aim of paper was the comparison of red wine rheological, thermal parameters and density on the beginning and after one week of storing.

MATERIALS AND METHODS

Measured sample of red wine (Frankovka modrá, produced in year 2013) had 12% of alcohol. All measurements were performed in laboratory settings (laboratory temperature 20 °C, atmospheric pressure 1013 hPa and relative air humidity 45%) in temperature range (0–30 °C) for rheologic parameters and density, in the temperature range (6–25 °C) for thermal parameters. Temperatures higher than 20 °C were obtained by heating in the water bath and lower temperatures were obtained by cooling in the refrigerator. The measurements were not performed at higher temperatures because of the degradation possibility.

Measuring of dynamic viscosity was performed by Anton Paar (DV-3P), which principle is based on dependency of sample resistance against the probe rotation. Probe with signification R2 was used in our measurements. The frequency of probe rotation was 200 min^{-1}. Two series of dynamic viscosity measurements were done. First measurement was done at the beginning of storage and then the same sample was measured after a short storing (1 week) in refrigerator. Other rheologic parameters were calculated according to definitions Eqs. (2) and (3).

Both thermal parameters were measured by instrument Isomet 2104. It is thermal parameters analyzer which can use transient methods – hot wire and plane source method according to the used probe. In our case, measurements of thermophysical parameters were performed by needle probe. This needle probe contains hot wire with heating function and during the measurement is immersed into the measured material. The mathematical description of measurement method can be described as follows: Measuring of thermal parameters was performed by simplified transient Hot Wire (HW) technique. The simplified HW method is technique based on the measurement of the temperature rise of a linear heat source (hot wire) embedded in the tested material (Assael *et al.*, 2008a; Parsons and Mulligan, 1978; Kadjo *et al.*, 2008). For an infinitely long metallic wire (length/radius ratio >> 200) heated at time $\tau > 0$ with a constant heat flux per length unit q and immersed in an infinite homogeneous medium, thermal conductivity and diffusivity: λ and a with uniform initial temperature, the temperature rise $\Delta T(\tau)$ of the wire is given (Carslaw and Jaeger, 1959)

$$\Delta T(\tau) = \frac{q}{4\pi\lambda} \ln \frac{4F_0}{C} \quad (6)$$

with $C = e^{\gamma} = 1.781$, where γ is Euler's constant ($\gamma = 0.5772$) and F_0 is the Fourier number defined as

$$F_0 = \frac{a\tau}{r_0^2}, \quad (7)$$

where r_0 is the distance from the hot wire (needle probe) and τ is time. Eq. (6) is the analytical solution of an ideal thermal conductive model valid for $F_0 >> 1$ and without convective transfers (Wakeham *et al.*, 1991; Tavman, 1996). From this ideal model and with known q values, the thermal conductivity can be calculated

$$\lambda = \frac{q}{4\pi}\left(\frac{dT}{d(\ln\tau)}\right)^{-1}, \quad (8)$$

where $dT/d(\ln\tau)$ is a numerical constant deduced from experimental data for τ values which satisfy the condition $F_0 >> 1$. For practical applications of the HW method, wire and material sample dimensions, among other ideal model hypothesis, are finite and the deviations from the ideal model have then to be evaluated. In fact, the $e(\tau)$ answer to the wire heating $\Delta T(\tau)$ resultant of the Joule effect due to an electrical current

$$R = R_0(1 + \beta_0(T(\tau) - T_0)), \quad (9)$$

where R (Ω) is the instantaneous electrical resistance of the wire, R_0 (Ω) is the resistance of the wire at the reference temperature T_0, and β_0 (K^{-1}) is the temperature coefficient of the wire at 22 °C. Taking into account Eqs. (8) and (9), the thermal conductivity λ can be calculated as follows

$$\lambda = \frac{qR_0\beta_0 i}{4\pi}\left(\frac{de(\tau)}{d(\ln\tau)}\right)^{-1}, \quad (10)$$

where $de(\tau)/d(\ln\tau)$ is a numerical constant deduced from the experimental data and from the linear part of the $e(t) = f(\ln(\tau))$ curve (Assael *et al.*, 2008a; Assael *et al.*, 2008b).

Last observed parameter was density. The density of homogeneous material is defined

$$\rho = \frac{m}{V}, \quad (11)$$

where ρ is density of material ($kg \cdot m^{-3}$), m is total mass of material (kg), V is total volume of material (m^3). It is one of most important parameter of wines which strongly depends on temperature and chemical composition of the sample. For detection of wine samples density was used densimeter Mettler Toledo DM 40 with measurement accuracy 10^{-3} $g \cdot cm^{-3}$. Densimeter DM 40 measures density, concentrations and other related values. It has an internal Peltier thermostat for automatic temperature control and therefore does not require external thermostatic bath circulator. Results are automatically converted into user-defined units ($kg \cdot m^{-3}$). It contains also error detection, single-point adjustment of the entire temperature range and viscosity correction.

RESULTS AND DISCUSSION

Temperature dependencies of dynamic and kinematic viscosity can be described by decreasing exponential functions Eqs. (12), (13) and in the case of temperature dependencies of fluidity can be used increasing exponential functions Eq. (14)

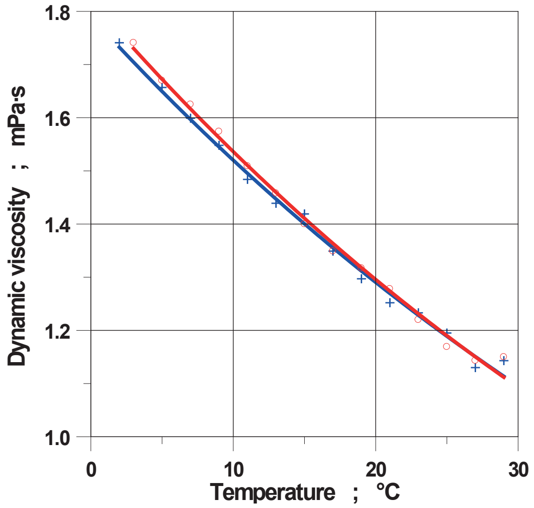
$$\eta = A e^{-B\left(\frac{t}{t_0}\right)}, \quad (12)$$

$$\nu = C e^{-D\left(\frac{t}{t_0}\right)}, \quad (13)$$

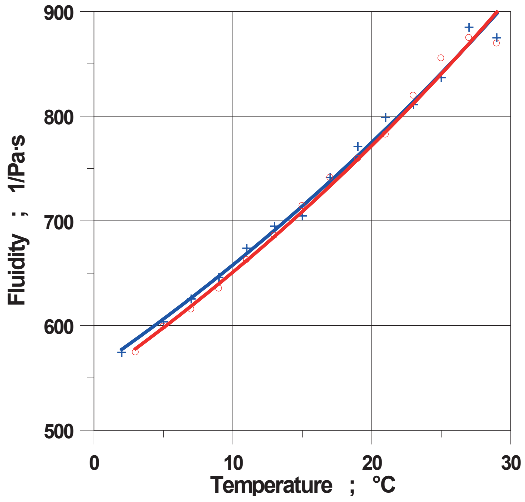
$$\varphi = E e^{F\left(\frac{t}{t_0}\right)}, \quad (14)$$

where t is temperature, t_0 is 1 °C, A, B, C, D, E, F are constants dependent on kind of material, and on ways of processing and storing. Temperature dependencies of red wine dynamic viscosity for both measurements are shown on Fig. 1. All values were measured once, because in case of repeated measurements the properties of sample could be changed.

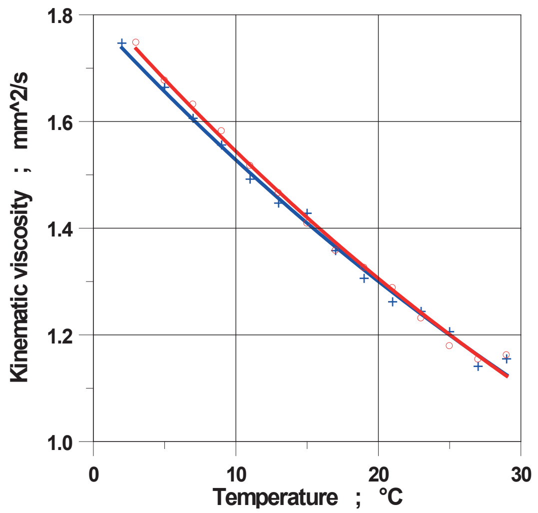
It is possible to observe from Fig. 1 that dynamic viscosity of red wine is decreasing with increasing of temperature. The progress can be described by decreasing nonlinear (complex) function, which is in accordance with Arrhenius type equation (1). Especially in our case for temperature range (0–30 °C), the temperature dependence can be fitted by exponential function. Regression coefficients and coefficients of determination are shown in Tab. I. From Fig. 1 can be seen that values of dynamic viscosity of red wine were a little bit higher after short term storing, which can be expressed by changed amount of water caused by evaporation. These differences are small during one week of storing but they could be higher in case of longer period of storing. The effect of longer storage was



1: *Temperature dependencies of dynamic viscosity for red wine sample, first measurement + and second measurement ○*



3: *Temperature dependencies of fluidity for red wine sample, first measurement + and second measurement ○*



2: *Temperature dependencies of kinematic viscosity for red wine sample, first measurement + and second measurement ○*

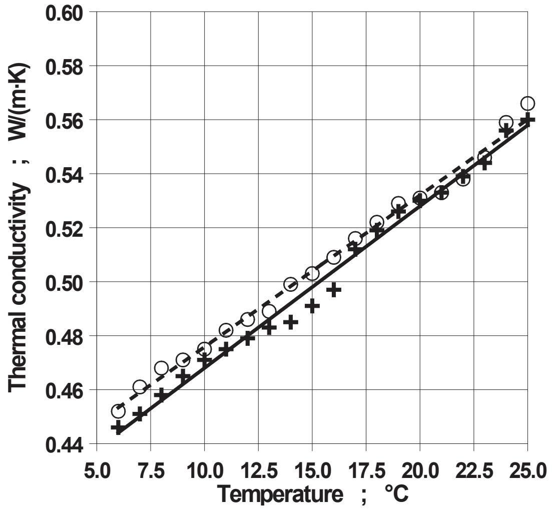
investigated by Kumbár and Votava (2015) for partially fermented wine must.

On Fig. 2 are presented temperature dependencies of kinematic viscosity for measured sample of red wine. Dependencies of kinematic viscosity on temperature can be described also by decreasing function in both measurements. Similar results were obtained e.g. by Havlíček *et al.* (2007). Regression coefficients and coefficients of determination are shown in Tab. I. Values of kinematic viscosity were also little higher after storing (Fig. 2). This proportion is caused by same reason as for dynamic viscosity.

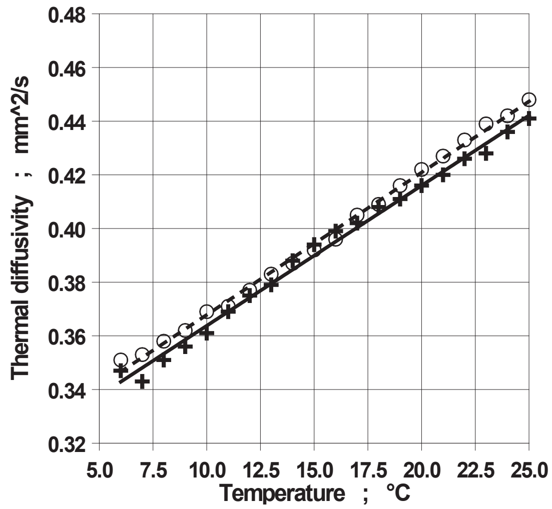
The temperature dependencies of red wine fluidity can be seen on Fig. 3. It is evident that fluidity is increasing with increasing of the temperature. Regression coefficients and coefficients of determination are shown in Tab. I. Proportion of curves in Fig. 3 can be explained in same way like for previous Fig. 1 and Fig. 2. It can be seen in Tab. I that in all cases were coefficients of determinations very high, in the range 0.9924–0.9933.

I: *Coefficients A, B, C, D, E, F of regression equations (12), (13), 14) and coefficients of determinations R^2*

	Regression equations (12, 13, 14)		
	Coefficients		
Sample of red wine	**A [mPa·s]**	**B [1]**	**R^2**
First measurement	1.790 28	0.016 372 6	0.993 287
Second measurement	1.820 94	0.017 013 8	0.992 854
Sample of red wine	**C [$mm^2 \cdot s^{-1}$]**	**D [1]**	**R^2**
First measurement	1.794 98	0.016 115 3	0.992 887
Second measurement	1.825 92	0.016 767 3	0.992 452
Sample of red wine	**E [$Pa^{-1} \cdot s^{-1}$]**	**F [1]**	**R^2**
First measurement	558.573	0.016 372 6	0.993 287
Second measurement	549.168	0.017 013 7	0.992 854



4: *Relations of thermal conductivity to the temperature for red wine samples, first measurement + and second measurement ○*



5: *Relations of thermal diffusivity to the temperature for red wine samples, first measurement + and second measurement ○*

The values of thermal conductivity and thermal diffusivity which are presented on Fig. 4 and Fig. 5 were obtained by thermophysical parameter measurements during the temperature stabilization in the temperature range 6–25 °C. Each point in the graphs for thermal parameters were obtained as arithmetic averages from ten measurements (provided by instrument Isomet 2104). Temperature changes simulated the process during the temperature stabilization from minimal storage temperature to maximal storage temperature. There were analyzed influences of temperature changes on basic thermophysical parameters.

Thermal conductivity range for first measurement of red wine was 0.446–0.560 $W \cdot m^{-1} \cdot K^{-1}$; the average value of thermal conductivity was 0.501 $W \cdot m^{-1} \cdot K^{-1}$. After storage was detected thermal conductivity in the range 0.452–0.566 $W \cdot m^{-1} \cdot K^{-1}$ and average value was 0.506 $W \cdot m^{-1} \cdot K^{-1}$. The second examined thermal parameter was thermal diffusivity. For 1st measurement was thermal diffusivity from range 0.347–0.441 $mm^2 \cdot s^{-1}$, the arithmetic average was 0.393 $mm^2 \cdot s^{-1}$ and after storing it was 0.397 $mm^2 \cdot s^{-1}$. All obtained results were compared with parameters known from the literature (e.g. Figura and Teixiera, 2007) and they are in good agreement. The graphical dependencies on Fig. 4 and Fig. 5 can be described by linear increasing regression equations

$$\lambda = G\left(\frac{t}{t_0}\right) + H\,, \tag{15}$$

$$a = I\left(\frac{t}{t_0}\right) + J\,. \tag{16}$$

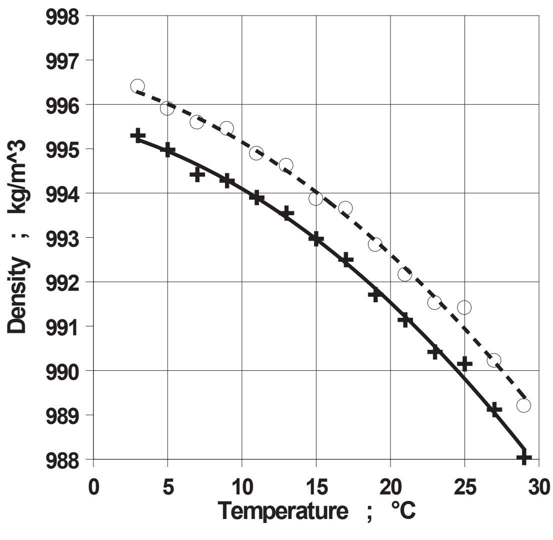
These relations showed influence on storage to the red wine thermal parameters. Higher values of thermophysical parameters for red wine were obtained after storage. From presented facts is clear that composition and one week of storage time had small influence on wine thermal conductivity and thermal diffusivity.

For temperature relations of density (Fig. 6) were obtained polynomial decreasing progress

$$\rho = K - L\left(\frac{t}{t_0}\right) - M\left(\frac{t}{t_0}\right)^2. \tag{17}$$

In Eqs. (15), (16) and (17) G, H, I, J, K, L and M are constants dependent on kind of material, and on the ways of processing and storing. These constants and coefficient of determination are in Tab. II.

All presented dependencies have very high coefficients of determination in approximate range 0.9899–0.9966.



6: *Temperature dependence of red wine density, first measurement + and second measurement ○*

II: *Coefficients G, H, I, J, K, L, M of regression equations (15), (16), (17) and coefficients of determinations R^2*

	Regression equations (15, 16, 17)			
	Coefficients			
Sample of red wine	**G [W·m⁻¹·K⁻¹]**		**H [W·m⁻¹·K⁻¹]**	**R^2**
First measurement	0.005997		0.408047	0.989901
Second measurement	0.005620		0.419635	0.992540
Sample of red wine	**I [mm²·s⁻¹]**		**J [mm²·s⁻¹]**	**R^2**
First measurement	0.005224		0.311527	0.992746
Second measurement	0.005302		0.314815	0.996575
Sample of red wine	**K [kg·m⁻³]**	**L [kg·m⁻³]**	**M [kg·m⁻³]**	**R^2 (2nd degree)**
First measurement	992.320	1.74343	0.246078	0.996047
Second measurement	993.408	1.71751	0.231128	0.993567

CONCLUSION

Food materials are very complex in their composition and in their physical properties. These properties depend on the manipulation, external conditions and other factors, which determine their behaviour. Rheological properties of wines were measured by some authors. Rheologic, thermal properties and density of selected Slovakian red wine Frankovka modrá were measured and analyzed in this paper. Effect of temperature and also one week of storing on used red wine was searched.
Temperature dependencies of red wine dynamic and kinematic viscosity had decreasing shape and temperature dependencies of fluidity had increasing shape (Figs. 1–3). For temperature dependencies of rheologic properties were used exponential functions. Thermal properties, such as thermal conductivity and thermal diffusivity characterize heat transfer ability of material, velocity of the temperature equalization and the intensity of the temperature changes in the material. These facts were examined by thermal parameters measurement. From obtained results is clear that thermal conductivity and thermal diffusivity of red wine increases linearly in observed temperature range (Figs. 4 and 5). The temperature dependence of examined wine density had polynomial shape (Fig. 6). All graphical dependencies had very high coefficients of determination. The results showed that influence of one week storing had only small effect on the red wine physical parameters.
We found out that values of dynamic viscosity, kinematic viscosity, thermal conductivity, thermal diffusivity and density of red wine were a little bit higher after short storing. That could be caused by changed amount of the water. Due to the same reason were fluidity values a little bit lower after storing.

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