COMPARISON OF SELECTED VEGETABLE OILS RHEOLOGIC PROPERTIES

POREĐENJE REOLOŠKIH OSOBINA ODABRANIH BILJNIH ULJA

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ABSTRACT

The article is focused on measuring and comparison of rheologic parameters of selected vegetable oils. Determined were these properties: density, dynamic, kinematic viscosity and fluidity. Measurements were performed in approximate temperature range (5 - 32) °C on two samples of vegetable oils: sunflower oil and olive oil. Density of vegetable oils was determined by oscillation method using digital densimeter Anton Paar DMA 4500 M at different temperatures. For dynamic viscosity measurement was used rotational viscometer Anton Paar DV-3P, which principle is based on dependency of sample resistance against the probe rotation. Other rheologic parameters as kinematic viscosity and fluidity were determined according to the definitions. Results of measurements are shown as graphical dependencies of rheologic parameters to the temperature. Temperature dependencies of vegetable oils dynamic and kinematic viscosity had decreasing exponential shape which is in accordance with Arrhenius equation and temperature dependencies of fluidity had an increasing exponential shape for both samples. Dependencies of samples density on temperature were characterized by decreasing linear function in measured temperature range. Similar results were obtained by other authors. From measured values can be seen that dynamic viscosity of olive oil is higher than viscosity of sunflower oil. This proportion is caused by different composition of oils.

Key words: vegetable oil, rheologic parameters, temperature, density, comparison.

REZIME

Rad je usmeren na merenje i upoređivanje reoloških parametara odabranih biljnih ulja. Odabrane su sledeće osobine: gustina, dinamička i kinematska viskoznost i tečljivost (fluidnost). Merenja su obavljena u približnom temperaturnom opsegu ulja od 5°C do 32°C na dva uzorka biljnih ulja: suncokretovo ulje i maslinovo ulje. Gustina biljnih ulja određena je metodom oscilovanja koristeći digitalni denzimetar Anton Paar DMA 4500 M pri različitim temperaturama ulja. Za dinamičko merenje viskoznosti korišćen je rotacioni viskozimetar Anton Paar DV-3P, koji se zasniva na zavisnosti otporu obratanja sonde u uzorku. Drugi reološki parametri, kao kinematička viskoznost i fluidnost, određeni su prema definicijama. Rezultati merenja su prikazani kao grafičke zavisnosti reoloških parametara od temperature ulja. Zavisnosti dinamičke i kinematske viskoznosti od njihove temperature imale su eksponencijalni oblik, koji je u skladu sa Arrheniusovom jednačinom, a zavisnosti tečljivosti (fluidnosti) od temperature imale rastući eksponencijalni oblik za oba uzorka. Zavisnost gustine uzoraka od temperaturi ulja karakterisala se opadajućom linearnom funkcijom u izmerenom temperaturnom opsegu. Slične rezultate dobili su i drugi autori. Iz rezultata se vidi da je dinamička viskoznost maslinovog ulja veća od viskoznosti suncokretovog ulja. Ovakva zakonitost uzrokovana je različitim sastavom ulja.

Ključne reči: biljno ulje, reološki parametri, temperatura ulja, gustina, poređenje osobina

INTRODUCTION

At controlled processes in manufacturing, handling, and holding is required precise knowledge of physical quantities of materials. It is important to know their physical properties particularly, mechanical, rheologic and, thermophysical for the quality evaluation of food materials (Božiková and Hlaváč, 2010).

This article deals with rheologic properties which are very complicated characteristics of materials. Rheologic properties were measured for different food materials: strawberry mash (Bukurov et al., 2012), quince puree (Bikić et al., 2012), dark chocolate (Glicerina et al., 2013), mixture of apple pomace and wheat flour (Diósi et al., 2014), milk (Hlaváč and Božiková, 2011), honey (Hlaváč and Božiková, 2012), whisky (Hlaváč et al., 2013), etc. Viscosity is an important rheologic property of many liquid products. The viscosity is the physical property which more affects the engine operation, since a larger fuel viscosity may provoke failures in the feeding system, and deposit formation within the combustion chamber, the feeding channels, the filters, etc. (Corsini et al., 2015). Viscosity is defined as the resistance of a fluid to flow and its physical unit 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 Eyring theory molecules of liquids continuously move into the vacancies (Bird et al., 1960). This process permits flow but requires energy. Activation energy is more readily audible at higher temperatures and the fluid flows easily. The temperature effect on viscosity can be described by an Arrhenius type equation

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

where η_0 is reference value of dynamic viscosity, E_A is activation energy, R is gas constant and T 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 is defined as a ratio of dynamic viscosity η to density of fluid ρ at the same temperature

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

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

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

Oils extracted from plants have been used since ancient times and in many cultures. The production process of vegetable oil involves the removal of oil from plant components, typically seeds. This can be done by mechanical extraction using an oil mill or chemical extraction using a solvent. Then the extracted oil can be purified and, if required, refined or chemically altered. Many vegetable oils are consumed directly, or indirectly as ingredients in food and oils can be heated and used to cook other foods. Vegetable oils consist of triglycerides (Rafiq et al., 2015).

Properties of different vegetable oils were examined by many authors. Stedile et al. (2015) had made a comparison between physical properties and chemical composition of various bio-oils. Moser et al. (2009) had analysed composition and physical properties of selected vegetable oils (cress, field pennycress and soybean). Influence of composition on vegetable oils oxidation using differential scanning calorimetry was studied by Qi et al. (2016). Examined were eight vegetable oils: refined palm oil, olive oil, grapeseed oil, sunflower oil, corn oil, soybean oil, safflower oil and sesame oil. Activation energy of measured oils was also determined. Purification of vegetable oils by application of metal-organic frameworks was described by Vlasova et al. (2016). Authors found out that metal-organic frameworks improve the physicochemical properties of unrefined vegetable oils (more pleasant taste and odour) due to the binding of free fatty acids and peroxide compounds. Electrical properties of pumpkin seed oil were investigated by Prevc et al. (2015). They found out that typical roasted pumpkin seed oil had higher electrical conductivity than unrefined extra virgin olive oils and refined sunflower oils. It is due to the fact that electrical conductivity is highly correlated to the phospholipids and metals concentration in oil. Pillai et al. (2016) had described structure, chemical composition and physical properties of metathesized palm oil and novel polyol derivatives. Physical characteristics of spray-dried dairy powders containing different vegetable oils (sunflower oil, palm oil and its mixtures) were studied by Kelly et al. (2014). Thermal properties of oils extracted from raspberry and blackberry seed using differential scanning calorimetry were studied by Micić et al. (2014).

Vegetable oils are also used as an ingredient or component in many manufactured products. Vegetable oils as additives in biodegradable films and coatings for active food packaging were examined by Atarés and Chiralt (2016). The effect of waste edible vegetable oil on rejuvenation of aged asphalt binders in terms of physical, chemical and rheological properties was investigated by Chen et al. (2014). The results indicate that waste edible vegetable oil can effectively soften aged asphalt. Physical properties and rheological properties of aged asphalts can be improved to that of their corresponding virgin asphalts

when the dosage of waste edible vegetable oil is optimum. Bounding of masonry units with waste vegetable oil was analysed by Heaton et al. (2014). Chemical analysis and evaluation of engineering properties was done. Physical quality and surface hydration properties of wood based pellets blended with waste vegetable oil were analysed by Mišljenović et al. (2015). The results showed that oil addition significantly increased energy content of wood pellets. But on the other hand strength of pellets was reduced with oil addition, due to the lower friction on the pellet-die wall contact area. The performance of vegetable oil based nanofluids as potential cutting fluids on machining performance during turning of AISI 1040 steel was investigated by Padmini et al. (2016). In many cases are vegetable oils used as alternate fuels or lubricants. Emberger et al. (2015) had studied chemical composition and physical properties of ten vegetable oils (coconut, palm, high oleic sunflower, rapeseed, sunflower, camelina, linseed, soybean, corn, jatropha). They also investigated its ignition and combustion behaviour after injection in a constant volume combustion chamber. Ashraful et al. (2014) had compared fuel properties, engine performance, and emission characteristics of biodiesel from various non-edible vegetable oils (karanja, polanga, mahua, rubber seed, cotton seed, jojoba, tobacco neem, linseed and jatropha). Various biodiesel types with different vegetable oils (soybean, rapeseed, mustard, canola, palm, sunflower, rice bran, jatropha, karanja and used cooking oil) were analysed by Issariyakul and Dalai (2014). Biodiesel fuels prepared from different vegetable oil sources (canola, soybean, sunflower, and corn) were studied through electrochemical impedance spectroscopy by M'Peko et al. (2013). Authors had made correlations between electric properties (resistivity and dielectric constant) and dynamic viscosity. The use of vegetable oils as a fuel in burners was studied by San José et al. (2015). During the investigation authors used four vegetable oils from: rapeseed, soya, sunflower and refined seed. For the optimal combustion process, it is important to know the physical characteristics (density, viscosity, etc.) and composition of the fatty acids of the oils. Cermak et al. (2013) had compared properties of new crop oils (lesquerella, field pennycress, meadowfoam and cuphea) with common commodity vegetable oils. They found out that all the oils had unique properties or characteristics that make them suitable for lubricant application.

MATERIALS AND METHODS

Measurements were performed in laboratory settings (temperature 20 °C, atmospheric pressure 1013 hPa and relative air humidity 45 %) on two samples of vegetable oil, purchased in local market. First sample was sunflower oil and next sample was olive oil. The samples of vegetable oils were cooled to temperature 3 °C and dynamic viscosity was measured at particular temperatures. During the experiments were analysed rheologic parameters as: dynamic viscosity, kinematic viscosity, fluidity and density. Selected parameters were measured during the temperature stabilisation in approximate temperature range (5 – 32) °C. Measuring of dynamic viscosity was performed by digital rotational viscometer Anton Paar (DV-3P) and measuring principle is based on dependency of sample resistance against the probe rotation. Density of vegetable oils was determined by densimeter Anton Paar DMA 4500 M. Density was measured at same temperatures as measurement of dynamic viscosity. Density value along with dynamic viscosity value was used at calculation of kinematic viscosity (Eq. 2). Reciprocal value of dynamic viscosity (fluidity) was also determined (Eq. 3). Relations of rheologic parameters to the temperature and comparison of vegetable oils were made.

Temperature dependencies of dynamic and kinematic viscosity can be described by decreasing exponential functions (4, 5), in the case of temperature dependencies of fluidity can be used increasing exponential functions (6), and temperature dependencies of density were described by decreasing linear function (7).

$$\eta = A e^{-B\left(\frac{t}{t_0}\right)} \quad (4)$$

$$\nu = C e^{-D\left(\frac{t}{t_0}\right)} \quad (5)$$

$$\varphi = E e^{F\left(\frac{t}{t_0}\right)} \quad (6)$$

$$\rho = -G\left(\frac{t}{t_0}\right) + H \quad (7)$$

where t is temperature, t_0 is 1 °C, A, B, C, D, E, F, G, H are constants dependent on kind of material, and on ways of processing and storing.

RESULTS AND DISCUSSION

Temperature dependencies of vegetable oils dynamic viscosity are shown on Fig. 1.

Fig. 1. Temperature dependencies of dynamic viscosity for vegetable oils Sunflower oil ○, Olive oil +

It is possible to observe from Fig. 1 that dynamic viscosity of oils is decreasing with increasing of temperature. The progress can be described by decreasing exponential function, which is in accordance with Arrhenius equation (1). Similar conclusions were made by authors *Diamante and Lan (2014)* and *Thomas et al. (2015)*. Regression coefficients and coefficients of determination are shown in Tab. 1. From Fig. 1 can be seen that values of dynamic viscosity of olive oil were higher than for sunflower oil, which could be caused by different composition of oils.

Fig. 2. Temperature dependencies of density for vegetable oils Sunflower oil ○, Olive oil +

Dependencies of oils density on temperature are presented on Fig. 2. It can be seen that values of density are decreasing with increasing temperature for both samples of oil. In this temperature range was used linear decreasing function. Same type of dependency was used also by *Thomas et al. (2015)*. Density of sunflower oil was higher than for olive oil. Similar results for sunflower oil were obtained by *Emberger et al. (2015)*, *San José et al. (2015)*, and for olive oil by *Tanilgan et al. (2007)*. On Fig. 3 are presented temperature dependencies of kinematic viscosity for measured samples. Dependencies of kinematic viscosity on temperature can be described also by decreasing function for both samples of oil. Regression coefficients and coefficients of determination are shown in Tab. 1. Values of olive oil kinematic viscosity were also higher than for sunflower oil (Fig. 3). This proportion is caused by same reason as for dynamic viscosity.

Fig. 3. Temperature dependencies of kinematic viscosity for vegetable oils Sunflower oil ○, Olive oil +

Fig. 4. Temperature dependencies of fluidity for vegetable oils Sunflower oil $\circ$, Olive oil $+$

The temperature dependencies of oils fluidity can be seen on Fig. 4. It is evident that fluidity is increasing with increasing of the temperature. Regression coefficients and coefficients of determination are shown in Tab. 1. Proportion of curves in Fig. 4 can be explained in same way like for previous Fig. 1 and Fig. 3.

It can be seen in Tab. 1 that in all cases were coefficients of determinations very high in the range (0.99993 – 1.0).

Table 1. Coefficients A, B, C, D, E, F, G, H of regression equations (4, 5, 6 and 7) and coefficients of determinations (R^2)

Regression equations (4, 5, 6, 7)			
Coefficients			
Sample	A [mPa·s]	B [1]	R^2
Sunflower oil	251.491	0.028 017 3	1
Olive oil	261.117	0.022 905 4	0.999 958
Sample	C [mm ² ·s ⁻¹]	D [1]	R^2
Sunflower oil	269.187	0.027 259 7	0.999 999
Olive oil	281.934	0.022 150 8	0.999 960
Sample	E [Pa ⁻¹ ·s ⁻¹]	F [1]	R^2
Sunflower oil	3.980 38	0.027 965 1	0.999 996
Olive oil	30828 43	0.022 919 6	0.999 937
Sample	G [kg·m ⁻³]	H [kg·m ⁻³]	R^2
Sunflower oil	0.682 059	933.866	0.999 997
Olive oil	0.684 142	926.042	0.999 996

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. Rheologic properties of selected vegetable oils were measured and analysed in this paper. Effect of temperature on measured samples of vegetable oils was searched and comparison of used vegetable oils was made.

Temperature dependencies of vegetable oils dynamic and kinematic viscosity had decreasing shape (Fig. 1 and Fig. 3) and

temperature dependencies of fluidity had increasing shape (Fig. 4). For temperature dependencies of rheologic properties were used exponential functions, which is in accordance with Arrhenius equation (1). Similar results were obtained also by other authors (Diamante and Lan, 2014; Thomas et al., 2015).

Linear decreasing functions were applied at temperature dependencies of oils density in this temperature range (Fig. 2). Similar results for vegetable oils density were obtained by other authors (Emberger et al., 2015; San José et al., 2015; Tanilgan et al., 2007).

We found out that values of dynamic and kinematic viscosity for olive oil were higher than for sunflower oil, which could be caused by different composition of oils. Due to the same reason were fluidity and density values lower for olive oil.

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