COMPARISON OF RHEOLOGICAL PROPERTIES OF VARIETAL GRAPE SEED OILS

Patrik Burg, Petr Trávníček, Vladimír Mašán, Kazimierz Rutkowski, Vladimír Višacki

ABSTRACT
The aim of this work was to determine the rheological properties of grape seed oils from different varieties selected at different temperatures. Measurement of the rheological properties of grape seed oils was performed on the instrument Anton Paar MCR 102. The rheological properties of the liquid have been performed at temperatures of 0 °C, 15 °C, 30 °C, 45 °C and 60 °C. The density of measured samples ranged from 0.905 ±0.002 to 0.948 ±0.002 g.mL⁻¹. Subsequently, there were determined viscosity values at a shear rate of 5 s⁻¹. As expected, the viscosity decreased with increasing temperature. Highest viscosity values reached grape seed oil of variety Pinot gris where at 0 °C the viscosity reached 0.206 ±0.037 Pa s. Samples measured at 0 °C showed non-Newtonian behavior, while at higher temperatures liquids behave as Newtonian substances. All grape seed oils samples exhibit non-Newtonian behavior at lower temperatures. In experiments carried out at 0 °C, it was observed that the tested samples tends to behave as shear-thinning system with thixotropic properties. At higher temperatures was, in line with other scientific works, observed that samples behave as Newtonian fluids. Knowledge of the rheological properties of oils are very important for their processing, storage, and may affect their quality.

Keywords: grape seeds; grape seed oil; rheology; viscosity

INTRODUCTION
Globally, there are produced more than 120 million tons of edible oils and fats while approximately 80% of them are derived from plant sources and thus they are referred to as vegetable oils. The development of natural oils is one of the alternatives how to protect the environment from hazardous materials (Fasina and Colley, 2008). Oils and fats are the essential materials for margarine, shortening, salad oil and other specialty or tailored products, which have become significant ingredients in food preparation or processing in homes, restaurants, food manufactures and they are one of the main ingredients used to manufacture soaps, cosmetics and pharmaceutical products (Rodenburg et al., 1999). The majority of edible oils and fats produced worldwide annually is derived from plant sources and these are referred as vegetable oils. Common commercially-available vegetable oils are colza, olive, sunflower and others (Frančáková et al., 2015). New possibilities in terms of application are in larger scale offered by grape seed oil (Hamm and Hamilton, 2000).

According to chemical composition, grape seed oil belongs to oils with a high proportion of unsaturated fatty acids (90%), 75% of which is represented by linoleic acid (Baydar and Akkurt, 2001). Thus, it can be considered as very valuable in terms of nutrition. A high proportion of tocotrienols in wine oil, i.e. substances, which are together with tocopherols included in the group of vitamins E, makes this oil significantly different from the other described vegetable oils (Hassanein and Abedel-Razek, 2009). Tocotrienols may have a much higher antioxidant capacity in comparison to tocopherols, which are often a single component representing vitamin E in other vegetable oils (Choi and Lee, 2009; Hassanein and Abedel-Razek, 2009).

From the perspective of contained substances, grape seed oil has been studied rather in detail, however, information about its physical properties are insufficient (Fasina and Colley, 2008). Oil viscosity has the greatest importance from the perspective of rheological properties. Oil viscosity is typically measured and defined in two ways, either based on its absolute (dynamic) viscosity or its kinematic viscosity. The absolute viscosity of oil is its resistance to flow and shear due to internal friction and it is measured with SI units of Pa·s. In contrast, the kinematic viscosity of oil is its resistance to flow and shear due to gravity and it is measured with SI units of m².s⁻¹. The kinematic viscosity of oil can be obtained by dividing the absolute (dynamic) viscosity of oil with its corresponding density (Diamante and Lan, 2014). In case of non-Newtonian fluids, we talk about the so-called apparent viscosity. This value is a variable depending especially on the shear rate value. Therefore, it is reasonable to state this value only when we know measuring conditions (Singh and Heldman, 2001).
It has been well established that temperature has a strong influence on the viscosity of fluids with viscosity generally decreasing with increase in temperature (Rao, 1999). The Power Law (Ostwald) is commonly used to describe the relationship of the temperature dependence on vegetable oil viscosity (Fasina and Colley, 2008). Several researchers have reported the viscosity of vegetable oils at room temperature (Lang et al., 1999; Diamante and Lan, 2014). The studies about temperature effect on viscosity of vegetable oils have been mostly carried out at temperatures above 30 °C. The absolute viscosity of fluids is an important property needed in fluid flow and heat transfer unit operations. This includes pumping, flow measurement, heat exchange, sterilization, freezing and many other operations. The aim of this study was to evaluate the rheological behavior of varietal grape seed oils at different temperatures.

Scientific hypothesis
Grape seed oils obtained through pressing at different temperatures behave as Newtonian fluids.

MATERIAL AND METHODOLOGY
Sample
For the purpose of this paper, grape seed oil of six grape species was used. The oil was pressed on the UNO FM 3F press. This press model is designed for pressing of all oil seeds. The drive is configured for the three-phase voltage with the possibility to change main drive speed by a frequency changer, which enables better optimization of press parameters. The press consists of an electric motor (power 1.5 kW), transmission, stamping system and motor starter including a frequency changer. The stamping system consists of a matrix, scroll, head, holder, nozzles, nozzles with diameter of 10 mm and heating cup.

Rheological measurement
The rheological evaluation of grape seed oil for this paper was performed on an Anton Paar MCR 102 Rheometer (Austria) with the measuring geometry cone-plate. The gap between the cone and the plate is set at the stable value of 0.103 mm. The diameter of the cone equaled to 50 mm with the angle of 1°. Rheological tests were performed at the temperatures 0 °C, 15 °C, 30 °C, 45 °C and 60 °C. Values of shear rates at individual rheological tests were following: Hysteresis loop test – the range of shear rate was set from 2 to 100 s⁻¹, Time dependent test – the constant value 50 s⁻¹ of shear rate was set. The apparent viscosity was measured at the shear rate 5 s⁻¹.

The Power Law (Ostwald) model was used to evaluate dependence of the shear rate on the shear stress. This model is applied to fluids without initial yield stress and it was utilized for rheological description of foods. For example, authors Al-Mahasneh et al. (2014) state that the Power Law model is appropriate for description of rheological behavior of honey. This model is given by equation:

\[ \tau = K \times \gamma^n \]  

where: \( \tau \) – shear stress (Pa), \( K \) – consistency coefficient, \( \gamma \) – shear rate (s⁻¹), \( n \) – flow behavior index.

The linear regression analysis of measured values was also carried out for the comparison.

Statistical analysis
Each measurement was repeated three times. Therefore, a standard deviation was determined for every value characterizing the sample of grape seed oil. The data were treated with a one-factor analysis of variance. Tukey HSD (honest significant difference) at the significance level of 0.05 was utilized for multiple comparisons of data. A statistical analysis was carried out using the software package 'Statistica 12.0' (StatSoft Inc., USA).

RESULTS AND DISCUSSION
Sampling of wine marc from 6 species (Dornfelder–Dr, Blaufränkisch–BF, Pálava–Pa, Riesling–RR, Pinot gris–PG, Zweigelt–ZW) was carried out in order to separate seeds immediately after pressing on pneumatic presses in the processing season 2015. The compression pressure in the pneumatic presses was in the range of 1.8 bar. In order to separate seeds from wine marc, there was used a vibratory separator prototype, which applies the principle of mechanic vibrations transmitted to three plane sieves with different hole shape and size. In order to achieve successful pressing of seeds and for their potential storage, their initial humidity was decreased from 40 – 45% to 8 – 10%, because at higher humidity around 20% there occurs fast mould infection and subsequent spoilage. The temperature during drying in a chamber dryer did not exceed 40 °C. The varietal grape seed oil was pressed on the UNO FM 3F press. All oils were stored at room temperature (around 20 °C) and in a dark place before the analysis. Table 1 shows the species of tested oils according to varieties, place of their origin and volume weight.

The apparent viscosity was determined as the first rheological parameter of the analyzed samples. The values for apparent viscosities of the individual samples at various temperatures and at the shear rate of 5 s⁻¹ are shown in Table 2. For comparison, the dynamic viscosity of wine ranged from 0.001479 to 0.001945 mPas in the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>Variety</th>
<th>Density at 20 °C (g.mL⁻¹ ±SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr</td>
<td>Velké Bílovice</td>
<td>Dornfelder</td>
<td>0.948 ±0.002</td>
</tr>
<tr>
<td>BF</td>
<td>Rakvice</td>
<td>Blaufränkisch</td>
<td>0.911 ±0.004</td>
</tr>
<tr>
<td>Pa</td>
<td>Rakvice</td>
<td>Pálava</td>
<td>0.943 ±0.001</td>
</tr>
<tr>
<td>RR</td>
<td>Velké Pavlovice</td>
<td>Riesling</td>
<td>0.941 ±0.003</td>
</tr>
<tr>
<td>PG</td>
<td>Velké Bílovice</td>
<td>Pinot gris</td>
<td>0.905 ±0.002</td>
</tr>
<tr>
<td>ZW</td>
<td>Rakvice</td>
<td>Zweigelt</td>
<td>0.933 ±0.001</td>
</tr>
</tbody>
</table>
The value of apparent viscosity in rendered fat at the temperature 10 °C and the shear rate 50 s\(^{-1}\) reached the approximate value 0.16 Pa s (Trávníček et al., 2013). Diamante and Lan (2014) conducted determination of values of viscosity in vegetable oils of different origin. In case of grape seed oils, they determined the value 0.0227 Pa s at the temperature 50 °C, at the temperature 26 °C then viscosity reached the value 0.0466 Pa s. Authors of the publication state that in this range of temperatures grape seed oil behaved like Newtonian fluid. Also Fasina and Colley (2008) carried out determination of viscosity of vegetable oil at different temperatures. Results of their measuring in grape seed oil range from 0.0415 to 0.0169 Pa s (temperature 35 – 65 °C). As in the previous case, authors Fasina and Colley (2008) state that in the tested range of temperatures (35 – 180 °C) grape seed oil behaved like Newtonian fluid. It is then apparent from Table 2 that viscosity values are in correspondence with values measured by other authors (Diamante and Lan, 2014; Fasina and Colley, 2008). It is also evident that according to expectations viscosity decreases with increasing temperature. The same effect of temperature on the absolute viscosities of vegetable oils was also observed by Steffe (1992), Abramovič and Klofutar (1998) and Santos et al. (2005) for various vegetable oils at different temperatures.

In statistical evaluation of measured data by ANOVA, there was the hypothesis H0 accepted in all cases stating that there is no statistically significant difference in apparent viscosity among samples at individual temperatures at the level of importance \(\alpha = 0.05\).

Afterwards, the so-called hysteresis loop test was performed. It consisted of gradual increasing of the shear rate to the set value. The sample was stressed at the constant shear rate value and then the shear rate was gradually decreased. If a loop was created, it was possible to describe the given sample as showing either thixotropic or anti-thixotropic (rheopetic) behavior. Thixotropic behavior is obtained from shear-thinning fluids in which no equilibrium is established between the structural breakdown and reformation process (Pyle et al., 1997) and can be described as a time dependent shear–thinning system. On the other hand, anti-thixotropy can be considered as a time dependent shear–thickening system.

Hysteresis loops of individual samples were observed at 0 °C. However, it was evident that hysteresis loops are not significant. This test was conducted also for further temperatures (15 °C, 30 °C, 45 °C and 60 °C). Significant hysteresis loops were not recorded at these temperatures.

It is possible to determine the so-called degree of thixotropy (in case of positive values) or antithixotropy (in case of negative values) when calculating the area of created loop. The software provided together with the equipment Anton Paar MCR 102 was used for the calculation. Calculation results are visible in Tab. 3. It is obvious from the table that values of the hysteresis area are very low and they decrease with increasing temperature. By the influence of high variability of measured data there were calculated high values of standard deviations (SD). Also according to the assumption (probably again by the influence of high variability of data) there were not recorded any statistically significant differences between individual samples and individual temperatures. For comparison, the value of the hysteresis area of heather honey at the temperature 10 °C is 25000 Pa s\(^{-1}\) (Witczak et al., 2011), in case of wine lees this value moved around 1.25 Pa s\(^{-1}\) (Lachman et al., 2015). However, Baudez (2006) states that hysteresis area is simply a consequence of the shear localization rather than thixotropic behavior and its area is closely linked to the apparatus and the data sampling. This means that the loop test is only an approximate test for rheology evaluating of samples. Due to this reason, there is necessity of another types of rheological tests.

Thus, based on this type of test, it is not possible to decide if it is Newtonian or non-Newtonian fluid, especially due to high variability of data (Table 2). In case it was Newtonian fluid, dependence of the viscosity value on the shear rate value would be constant. If it was non-Newtonian fluid, viscosity would change with the increasing shear rate value. In Figure 1 there are shown

### Table 2 Apparent viscosity of samples at the shear rate 5 s\(^{-1}\) (n = 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 °C</th>
<th>15 °C</th>
<th>30 °C</th>
<th>45 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr</td>
<td>0.195 ±0.005</td>
<td>0.075 ±0.002</td>
<td>0.042 ±0.000</td>
<td>0.027 ±0.000</td>
<td>0.019 ±0.001</td>
</tr>
<tr>
<td>BF</td>
<td>0.172 ±0.015</td>
<td>0.078 ±0.001</td>
<td>0.041 ±0.000</td>
<td>0.024 ±0.001</td>
<td>0.017 ±0.002</td>
</tr>
<tr>
<td>Pa</td>
<td>0.180 ±0.001</td>
<td>0.078 ±0.000</td>
<td>0.043 ±0.001</td>
<td>0.025 ±0.001</td>
<td>0.021 ±0.002</td>
</tr>
<tr>
<td>RR</td>
<td>0.163 ±0.020</td>
<td>0.079 ±0.000</td>
<td>0.044 ±0.001</td>
<td>0.028 ±0.001</td>
<td>0.018 ±0.001</td>
</tr>
<tr>
<td>PG</td>
<td>0.206 ±0.037</td>
<td>0.075 ±0.003</td>
<td>0.040 ±0.001</td>
<td>0.024 ±0.001</td>
<td>0.017 ±0.001</td>
</tr>
<tr>
<td>ZW</td>
<td>0.165 ±0.002</td>
<td>0.076 ±0.002</td>
<td>0.042 ±0.000</td>
<td>0.027 ±0.000</td>
<td>0.017 ±0.001</td>
</tr>
</tbody>
</table>

### Table 3 Hysteresis areas of samples at various temperatures (n = 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 °C</th>
<th>15 °C</th>
<th>30 °C</th>
<th>45 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr</td>
<td>2.01 ±1.28</td>
<td>1.57 ±2.23</td>
<td>1.25 ±0.56</td>
<td>0.97 ±0.37</td>
<td>0.01 ±0.25</td>
</tr>
<tr>
<td>BF</td>
<td>2.91 ±1.07</td>
<td>2.46 ±1.40</td>
<td>1.17 ±0.73</td>
<td>0.34 ±0.28</td>
<td>0.13 ±0.47</td>
</tr>
<tr>
<td>Pa</td>
<td>5.20 ±3.42</td>
<td>4.40 ±1.37</td>
<td>1.29 ±0.11</td>
<td>0.20 ±0.20</td>
<td>0.12 ±1.13</td>
</tr>
<tr>
<td>RR</td>
<td>7.97 ±27.54</td>
<td>0.65 ±0.84</td>
<td>0.59 ±0.13</td>
<td>0.66 ±0.51</td>
<td>0.09 ±0.46</td>
</tr>
<tr>
<td>PG</td>
<td>3.04 ±15.80</td>
<td>1.95 ±1.00</td>
<td>0.46 ±0.04</td>
<td>0.23 ±0.35</td>
<td>0.11 ±0.20</td>
</tr>
<tr>
<td>ZW</td>
<td>4.61 ±0.42</td>
<td>1.74 ±0.75</td>
<td>0.53 ±0.44</td>
<td>0.16 ±0.05</td>
<td>0.06 ±0.05</td>
</tr>
</tbody>
</table>
dependences of the shear rate on the apparent viscosity in individual samples at the temperature 0 °C.

It is obvious from the picture, that there occurs decrease of viscosity with the increasing shear rate. This would indicate that it is the shear-thinning system, alternatively the shear-thinning system with thixotropic behavior.

Nevertheless, it is necessary to mention that in some cases there are small changes of viscosity with the increasing shear rate. In case of increasing temperature, changes of viscosity are not almost noticeable in individual samples.

The next step utilized the Ostwald mathematical model to evaluate dependence of the shear rate on shear stress.

Figure 1 Dependence of the apparent viscosity on the shear rate at the temperature of 0 °C for samples.
This model is mostly used to describe flow curve material(s) with shear-thinning (pseudo plastic) or shear-thickening (dilatant) behavior without initial yield stress.

The results of calculation showed that determination coefficient of all temperatures and varieties is very high, ranging from $R^2 = 0.9974$ to $R^2 = 0.9999$. Authors
Diamante and Lan (2014) described dependence of the shear rate on shear stress by linear regression. The coefficient of determination in case of description of dependence of the shear rate on shear stress in grape seed oil ranged from $R^2 = 0.9995$ to $R^2 = 1.000$. In case of description of dependence of the shear rate on shear stress by linear regression, the coefficient of determination in individual samples ranged in the interval from $R^2 = 0.9996$ to $R^2 = 0.9999$.

Further important parameters of the Ostwald model are parameters $n$ and $k$. The consistency index $k$ indicates the extrapolated shear stress at the unit shear rate. The flow index is the rate of deviation from Newtonian behavior; when $n < 1$, the apparent viscosity of the sample decreases (shear-thinning behavior), although the apparent viscosity of the sample increases when $n > 1$ (shear-thickening behavior). If $n = 1$, it is Newtonian fluid. Values of coefficients $n$ is always close to 1. Generally, it can be said, that coefficient $n$ is the lowest at the temperature 0 °C. While the lowest value $n$ was shown in case of the sample Dr at the temperature 0 °C ($n = 0.91 ± 0.011$). The highest value of parameter $k$ was calculated also for the sample Dr at the same temperature ($k = 0.246 ± 0.013$).

After completion of the analysis of variance there were found statistically significant differences in the coefficient $n$ in samples Dr and Pa, RR, Zw at the temperature 0 °C and in samples PG and Pa, RR, Zw at the same temperature.

On the basis of past findings, it can be assumed that oil samples at low temperatures (0 °C) behave as shear-thinning fluids or as shear-thinning fluids with thixotropic behavior. Thixotropic fluids are time-dependent, or viscosity value changes over time at the constant press. It is necessary to conduct another type of test in order to confirm or rebut the presumption about thixotropic behavior of samples. The subsequent set of tests consisted of measuring of change of apparent viscosity depending on time at a constant value of shear rate.

Results of the experiment at the temperature 0 °C for individual samples of species are stated in Figure 2. It is apparent in pictures, that there occurs decrease of apparent viscosity over time in all samples. Nevertheless, it is necessary to remark that decrease is very small. In the Dr sample decrease of the apparent viscosity makes approximately 5% from the original value, in the BF sample approximately 2.5%, in the sample Pa 4.5%, in the sample RR 3%, PG 2%, and in the sample Zw also approximately 2%. After circa 10 minutes, apparent viscosity values stabilize and there does not occur further decrease.

From the perspective of previously stated information it is possible to consider that a system becomes a shear-thinning system with thixotropic properties at lower temperatures. At higher temperatures a system becomes Newtonian fluid. This phenomenon can be explained by the fact, that oil pressed from grape seeds contains micro particles, which are diffused within the fluid. In case of lower temperatures, intermolecular powers increase and probably help diffused particles to create aggregates in a stressed sample, which afterwards result in decrease of viscosity and so-called shear-thinning behavior with thixotropic properties. In case of longer pressure these aggregates disorganize and values of apparent viscosity stabilize. Another aspect, which can contribute to this behavior of fluid, is formation of ice crystals from water, which is in a small amount represented in oil. We also cannot forget the fact, that at lower temperatures may occur crystallization of fats (Bell et al., 2007). Generally, the crystal size, shape and alignment, degree of formation of mixed crystals and ability of crystals to flocculate into a network which increases firmness are important (Opfer, 1978).

CONCLUSION

The professional publications cited in the text, which dealt with rheological properties of oils (including grape seed oils), imply that all monitored samples showed Newtonian behavior. Temperature 26 °C was the lowest temperature at which these fluids were tested (Diamante and Lan, 2014). In the work, there were tested grape seed oil samples also at lower temperatures. Followings conclusions can be draw from this work:

1. Samples of grape seed oil behave like Newtonian fluid at higher temperature.
2. It was observed during the experiments that tested oils have the tendency to behave like the shear-thinning system with thixotropic properties at the temperature 0 °C.
3. This phenomenon may be caused for example by micro particles, which are due to higher values of intermolecular forces at lower temperatures attracted and create aggregates. Non-Newtonian behavior may be also caused by formation of crystals from water contained in oil or also by formation of crystals caused by fat crystallization at lower temperatures.

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Contact address:

Patrik Burg, Mendel University in Brno, Faculty of Horticulture, Department of Horticultural Machinery, Valtícká 337, 691 44 Lednice, Czech Republic, E-mail: patrik.burg@mendelu.cz

Petr Trávníček, Mendel University in Brno, Faculty of Agronomy, Department of Agricultural, Food and Environmental Engineering, Zemědělská 1, 61300 Brno, Czech Republic, E-mail: petr.travnicek@mendelu.cz

Vladimir Masan, Mendel University in Brno, Faculty of Horticulture, Department of Horticultural Machinery, Valtícká 337, 691 44 Lednice, Czech Republic, E-mail: vladimir.masan@mendelu.cz

Kazimierz Rutkowski, University of Agriculture, Faculty of Production and Power Engineering, Institute of Agricultural Engineering and Informatics, ul. Balicka 116 B, 30-149 Krakow, Poland, E-mail: kazimierz.rutkowski@ur.krakow.pl

Vladimir Višacki, University of Novi Sad, Department of Agricultural Engineering, Trg Dositjea Obradovića 8, 21000 Novi Sad, Serbia, E-mail: vladimir.visacki@polj.uns.ac.rs