

# Study of rheological behaviour of wines\*\*

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Received November 25, 2015; accepted October 18, 2016

A b s t r a c t. This study deals with rheological properties of various wine varieties. Samples of the following wines were used for this experiment: André, Cabernet Moravia, Laurot, Saint Laurent, Gruner Veltliner, Pinot Blanc, Müller Thurgau, and Riesling Italico. These samples were obtained from wine produced from the grapes collected in the Czech Republic (Morava region, subregion Velke Pavlovice). In the first phase, the chemical composition of the samples was determined. The following chemical parameters were determined: total acidity, pH, content of the alcohol, reduced sugars, free SO<sub>2</sub>, total SO<sub>2</sub>, and volatile acids. In the second phase of the study, the physical properties of the samples were determined and the samples of the wines were subjected to rheological tests. These tests consisted in determination of apparent viscosity in relation to temperature, hysteresis loop tests, and apparent viscosity related to time. The dependence of the shear rate on the shear stress was described with the Herschel-Bulkley mathematical model. The experiment vielded the following findings: seven out of the eight samples behaved as non-Newtonian fluids at low temperature (5°C); non-Newtonian behaviour was changed into Newtonian at the temperature higher than 10 °C; non-Newtonian behaviour was characterised as thixotropic behaviour; the degree of thixotropy is relatively small and reaches 1.85 Pa s-1 ml-1.

K e y w o r d s: thixotropy, rheology, chemical properties, wine

#### INTRODUCTION

Grapevine is the most commonly grown kind of fruit worldwide. Currently, the area of vineyards is about 8 million hectares. In Europe, it occupies approximately 57% of the hectareage *ie* about 4.5 million hectares. According to the information from the Organisation Internetionale de la Vignet et du Vin (OIV, 2009), 66.5 million t of grapevine is processed every year. Out of this amount, 38 million t of grapevine is processed in Europe. This indicates that wine is a very important food commodity and detailed description of its chemical and physical properties is highly desirable. For example, the chemical and physical properties of grapes were described in works by González-Fernández et al. (2012), and the basic physical properties of wine (specifically Sauvignon Blanc wines) were described in the work by Baiano et al. (2012). Although problematic, the rheological behaviour of wines has not been extensively discussed in scientific works. Generally, the rheological properties of beverages have been described in many works. These are mainly orange and tomato juices (Ibarz, 1999; Giner et al., 1996, Tiziani et al., 2005); many works deal with grape juices (Zuritz et al., 2005; Arslan et al., 2005; Bayindirli, 1993) or milk (Kumbár and Nedomová, 2015). Still, the basic rheological properties of wine have been evaluated in only a few works. An example can be the work by Košmerl et al. (2000). Košmerl states that knowledge of the thermophysical and chemical properties of wine, especially the density and viscosity data, are essential for the design and evaluation of industrial processing equipment. This information is needed for a variety of research and engineering applications over a wide range of concentrations and temperatures (Košmerl et al., 2000). That is the reason why mapping of rheological properties of wines is very important.

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<sup>\*\*</sup>This work was supported by project CZ.1.02/5.1.00/10.06433 Acquisition of Instrumentation for BAT Centre at MUAF in Brno for Categories of Food Processing Activities and Categories of Facilities for Disposal or Destruction of Animal Bodies and Animal Waste, 2007-2013.

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The aim of this work is to provide detailed description of the rheological properties of selected Czech wines and their mathematical evaluation.

## MATERIAL AND METHODS

Four samples of white and four samples of red wine varieties were used in the laboratory analysis. These wines were produced from grapes collected in 2014 in the Czech Republic (Morava region, subregion Velke Pavlovice).

There are several methods designed for measurement of the rheological behaviour of substances with different types of measuring geometry such as concentric cylinders, cone and plate, or parallel plates (Vítěz and Severa, 2010). An extensive overview of measurement techniques for rheological testing is given in the paper by Boger *et al.* (2009). Rheological measurement of substances for this paper was performed using an Anton Paar MCR 102 rheometer (Austria) with measuring cone-plate geometry with an angle of 1°. The diameter of the plate was 50 mm. The gap was set at the value of 0.213 mm. The constant shear test was performed with a 50 s<sup>-1</sup> shear rate. The hysteresis loop test was performed at an interval of the shear rate from 0 to 100 s<sup>-1</sup> at temperatures 5, 12, 30, and 40°C. The flow curves were modelled using the following model:

Herschel-Bulkley model:

$$\tau = \tau_0 + K \dot{\gamma}^n,$$

where:  $\tau$  – shear stress (Pa),  $\tau_0$  – yield stress (Pa), K – consistency coefficient, n – flow behaviour index,  $\dot{\gamma}$  – shear rate (s<sup>-1</sup>).

The change in apparent viscosity in relation to the temperature was measured at the temperature range 5, 12, 30, and 40°C. The shear rate was constant with a value of 50 s<sup>-1</sup>.

All measurements were performed in three repetitions. For the determination of the density of individual samples, the pycnometric method was used. For this purpose, pycnometers with a volume of 50 ml and an analytical balance Radwag AS 220/X (Poland) with an accuracy of 0.0001 g were used. For each sample of liquid, the density value was performed in three repetitions.

For the determination of total acidity, a Schott TitroLine Easy titrator (SI Analytics, SRN) was used. All titrated acids (EEC No. 2676/90) in the wine are the sum of compounds titratable by standard alkaline solution to pH 7. Carbonic acid is not included in total acidity.

For the determination of pH, a pH meter WTW with a combined glass and an argentochloride gel electrode was used. The value of pH is determined on the basis of measurement of the potential of the glass electrode. The potential depends on the activity of hydrogen cations.

For the determination of the total alcohol content, the Dujradin-Salleron ebullioscope was used. This type of device facilitates measurement of the alcohol content on the basis of differences in the boiling point of the samples. This method is based on the boiling point of distilled water and the measured wine samples. Generally, alcohol has a low boiling temperature; when the content of alcohol is higher, the boiling point is lower.

The concentration of reduced sugars was determined with the shortened iodometrical method according to Rebelein, from the difference of consumption rates of sodium thiosulphate on the titration of the copper cation (which has a defined concentration), and the balance after reaction with reducing sugars in wine.

Free and total  $SO_2$  was determined by titration of the standard solution of iodine. For this purpose, an HI 84500 titrator was used. The standard solution of iodine oxidizes to free SO<sub>2</sub> contained in wine.

The amount of volatile acids was determined with the spectrometric method. A FTIR Nexus 670 spectrometer was used. It allows measurement of the MIR absorption spectra (from 7800 to 350 cm<sup>-1</sup>) and FIR absorption spectra (from 700 to 50 cm<sup>-1</sup>). Interaction of microparticles (molecules) with infrared radiation is the basis of the measurement.

Each measurement was repeated three times. Therefore, standard deviation (SD) was determined for every value characterizing the wine samples.

Principal component analysis of selected measured data was performed. For this purpose, statistical software package the 'Statistica 12.0' (StatSoft Inc., USA) was used.

## RESULTS AND DISCUSSION

The basic chemical properties of wines are given in Table 1. The limit values of substances contained in wine available on the market must comply with the European Union law and the national law of the Czech Republic.

These include Council Regulation (EC) No. 479/2008 (the basic Regulation) and Commission Regulation (EC) No. 606/2009, Regulation No. 607/2009 (oenological practices), and Act No. 321/2004 Coll. on viticulture and winemaking. It is evident from the results obtained that the content of total acids in the evaluated samples ranged from 5.12 to 6.68 g l<sup>-1</sup>. Iland *et al.* (2000) states that total acids represent the amount of all anions of organic acids in the must. The content of organic acids is measured, as well as their salts if they are present. Jackson (2008) states that the typical content of acids in wine produced in the area of temperate zone ranges from 5 to 9 g l<sup>-1</sup>. Similarly, other authors, *ie* Ribéreau a Traduction (2003), report that the content of acids in wine ranges between 5 and 7.5 g l<sup>-1</sup>.

The value of pH can be considered as the key parameter of wine quality. The value of pH depends on the content of the individual acids. The value of pH commonly ranges from 3.0 to 4.0 (Jacobson, 2006). There is a relation between the value of pH and acids contained in wine. When the content of acids is higher, the pH value is lower (Ribéreau-Gayon, Branco, 2006). Values ranging between 3.0 and 3.8 are considered as optimal pH for wine. The

| Sample           | Total acidity        | pH        | Alcohol   | Reduced sugars | Free SO <sub>2</sub>  | Total SO <sub>2</sub> | Volatile acid |
|------------------|----------------------|-----------|-----------|----------------|-----------------------|-----------------------|---------------|
| r                | (g l <sup>-1</sup> ) | (-)       | (%)       | (g l-1)        | (mg l <sup>-1</sup> ) | (mg l <sup>-1</sup> ) | (%)           |
| André            | 5.61±0.01            | 3.51±0.01 | 13.4±0.01 | 3.3±0.02       | 56.1±0.07             | 149.7±0.07            | 0.49±0.01     |
| Cabernet Moravia | 5.12±0.02            | 3.48±0.01 | 14.5±0.02 | 2.8±0.01       | 54.8±0.14             | 154.6±0.42            | 0.45±0.01     |
| Laurot           | 6.16±0.01            | 3.27±0.01 | 13.9±0.00 | 3.5±0.02       | 79.8±0.00             | 159.9±0.07            | 0.55±0.02     |
| Saint Laurent    | 5.66±0.04            | 3.32±0.01 | 13.4±0.01 | 4.3±0.01       | 59.8±0.14             | 159.6±0.07            | 0.38±0.01     |
| Gruner Veltliner | 6.27±0.01            | 3.53±0.01 | 13.3±0.07 | 1.6±0.01       | 38.4±0.21             | 170.5±0.21            | 0.02±0.03     |
| Pinot Blanc      | 5.59±0.02            | 3.12±0.01 | 13.0±0.01 | 1.9±0.02       | 19.9±0.00             | 156.3±0.21            | 0.15±0.04     |
| Müller Thurgau   | 5.54±0.02            | 3.01±0.01 | 13.4±0.00 | 2.1±0.03       | 20.7±0.07             | 148.5±0.21            | 0.20±0.01     |
| Riesling Italico | 6.68±0.01            | 3.36±0.01 | 13.5±0.02 | 8.5±0.01       | 25.9±0.00             | 160.5±0.28            | 0.09±0.01     |

T a b l e 1. Basic chemical properties of wines

pH value can increase fractionally during maturation. The results of our analysis demonstrate that the pH value was in this range and reached values from 3.01 to 3.53. Schneider (2004) carried out long-term monitoring of pH in wine and found that very high or very low pH values caused many problems. Wine with higher pH can deteriorate, is less stable, lose complexity and the wine tones often have a murine odour. On the contrary, low pH has a negative impact on the colour of red wine and fullness of the flavour.

Breier (2012) reports that the content of alcohol in the white wine ranges between 10.5 and 12% vol and in the red wine between 12 and 14% vol in the northern areas of grapevine cultivation. Kaltzin (2012) states that the content of alcohol in wine is affected by many factors, such as ripeness of the grapes at the time of harvest, grape processing technology, and fermentation technology. Burg et al. (2013) also evaluated the influence of agrotechnical measurements of the sugar content of grapes in the vineyards and the quality of wines. In terms of sensory evaluation, wines with alcohol content from 12 to 14% vol are marked as strong. The analysed samples had higher alcohol content ie over 13% vol. This was related to the fact that the harvested grapes had high quality and they were fermented without temperature regulation, since most carbohydrates contained in the compress must be fermented.

Breier (2012) states that silent wine (fermented wine with low content of residual sugar) can contain maximum 4 g of residual sugar per litre. This value was exceeded by the variety Saint Laurent (4.3 g  $l^{-1}$ ) and Riesling Italico (8.5 g  $l^{-1}$ ). Both samples can be classified into the category of semi-dry wines, where the highest value of residual sugar is restricted by the upper limit of 12 g  $l^{-1}$  of wine.

Sulphur dioxide in wine is represented by two forms: free and bound; the sum of both of these forms creates the total amount of sulphur dioxide in wine. Only the free form of sulphur dioxide has an impact on conservation and

T a b l e 2. Basic physical properties of wines

| Sample           | Density<br>(20°C)<br>(kg m <sup>-3</sup> ) | Activation<br>energy<br>(kJ mol <sup>-1</sup> ) | R <sup>2</sup> |
|------------------|--|---|----------------|
| André            | 1021.2±1.2                                 | 22.2  | 0.936          |
| Cabernet Moravia | 1019.3±0.8                                 | 22.5  | 0.937          |
| Laurot           | 1017.7±1.8                                 | 28.6  | 0.972          |
| Saint Laurent    | 1006.0±1.1                                 | 21.8  | 0.948          |
| Gruner Veltliner | 1007.0±0.9                                 | 23.5  | 0.934          |
| Pinot Blanc      | 983.2±1.3                                  | 16.7  | 0.792          |
| Müller Thurgau   | 1022.5±2.1                                 | 30.2  | 0.949          |
| Riesling Italico | 975.4±0.9                                  | 21.0  | 0.884          |

reduction of wine (Ribéreau-Gayon, Traduction, 2003). Sulphur dioxide in wine is harmless to health, but the maximum allowed limit must not be exceeded. Dry red wines have maximum allowed limit 160 mg l<sup>-1</sup>, white and rosé wine 210 mg l<sup>-1</sup>. None of the evaluated samples exceeded the maximum allowable limit.

Acetic acid is the most important of all acids present in wine. The usual amounts ranging between 0.2 and 0.8 g l<sup>-1</sup> do not affect the taste and quality of wine (Iland, 2004). A concentration of 1.4 g l<sup>-1</sup> and higher is responsible for a disagreeable acetic aroma (Vilela-Moura *et al.*, 2008).

The basic physical properties of wine are shown in Table 2.

Here, we present density (measured at 20°C) and activation energy. The values of activation energy ranged from 16.728 to 30.205 kJ mol<sup>-1</sup>, and the mean of the measured values was approximately 22.7 kJ mol<sup>-1</sup>. In turn, the values of density were measured in the range from 975.4 to



**Fig. 1.** Evaluation of Arrhenius model for: a – red and b – white wines.

| Тa | b | l e | 3. | Dynamic | viscosity | of wines | at various | temperatures |
|----|---|-----|----|---------|-----------|----------|------------|--------------|
|    |   |     |    | ~       |           |          |            |              |

1022.5 kg m<sup>-3</sup>. Similar values of activation energy were reported in the work presented by Košmerl *et al.* (2000) and ranged from 18.631 to 20.136 kJ mol<sup>-1</sup>. For example, activation energy of clear grape juice ranged from 16.330 (at the density 1097.3 kg m<sup>-3</sup> at the temperature 20°C) to 52.015 kJ mol<sup>-1</sup> (at the density 1358.4 kg m<sup>-3</sup> at the temperature 20°C) in relation to the concentration of juice in the mixture (Zuritz *et al.*, 2005).

The evaluation of the Arrhenius model of individual samples is shown in Fig. 1.

The coefficient of determination had values from  $R^2 = 0.792$  (Pinot Blanc) to  $R^2 = 0.972$  (Laurot). However, the determination coefficient of most samples had a value over  $R^2 = 0.93$ , which is relatively high.

The apparent viscosity of wines was measured in the temperature range from 5 to  $40^{\circ}$ C (Table 3).

The Pinot Blanc variety had the highest value of apparent viscosity at 5°C (0.005 Pa s). In turn, the André variety had the lowest value of apparent viscosity at 5°C (0.004 Pa s). It is interesting that the apparent viscosity of all samples was approximately equal at the temperature of 40°C. For comparison, the apparent viscosity of wine ranged around 0.002 mPa s in the work presented by Košmerl *et al.* (2000). The viscosity of different beverages varied *ie* it was 0.006 mPa s in heat-processed watermelon juice (Aguiló-Aguayo *et al.*, 2010) and 0.002 mPa s in the case of blueberry juice (Nindo *et al.*, 2005).

The hysteresis loop test was the next experiment performed. This test consists in determination of the shear rate on the shear stress. When the shear rate was increased in the first step, it was decreased in the second step. This demonstrated a so-called hysteresis area. The size of the hysteresis area can be considered as a measure of the degree of thixotropy (Battistoni, 1997). However, the hysteresis area cannot be a sole measure for evaluation of thixotropy or

|                  | Dynamic viscosity (mPa s) |         |         |         |         |  |  |  |
|------------------|---------------------------|---------|---------|---------|---------|--|--|--|
| Sample           | Temperature (°C)          |         |         |         |         |  |  |  |
|                  | 5                         | 12      | 20      | 30      | 40      |  |  |  |
| André            | 2.9±0.1                   | 2.6±0.2 | 1.7±0.3 | 1.5±0.1 | 1.0±0.2 |  |  |  |
| Cabernet Moravia | 3.2±0.2                   | 2.5±0.1 | 1.7±0.2 | 1.4±0.2 | 1.3±0.1 |  |  |  |
| Laurot           | 3.9±0.3                   | 2.8±0.3 | 2.4±0.2 | 1.5±0.3 | 0.9±0.2 |  |  |  |
| Saint Laurent    | 3.0±0.2                   | 2.4±0.2 | 1.6±0.3 | 1.3±0.2 | 1.0±0.2 |  |  |  |
| Gruner Veltliner | 3.0±0.3                   | 2.2±0.2 | 1.9±0.2 | 1.1±0.2 | 1.0±0.2 |  |  |  |
| Pinot Blanc      | 4.5±0.4                   | 3.2±0.3 | 2.4±0.3 | 1.5±0.2 | 1.1±0.1 |  |  |  |
| Müller Thurgau   | 3.0±0.1                   | 2.4±0.2 | 1.7±0.2 | 1.5±0.1 | 1.4±0.1 |  |  |  |
| Riesling Italico | 2.9±0.2                   | 2.4±0.1 | 1.6±0.3 | 1.3±0.1 | 1.0±0.1 |  |  |  |

All values in the table as a mean from three repetitions  $\pm$  SD.



Fig. 2. Hysteresis loop of selected: a - red and b - white wines at 5°C

| T a b | le | 4. | Hysteresis | areas of | f samples | at various | temperatures |
|-------|----|----|------------|----------|-----------|------------|--------------|
|-------|----|----|------------|----------|-----------|------------|--------------|

antithixotropy. For example, Baudez (2006) argues that the hysteresis area is simply a consequence of the shear localization rather than thixotropic behaviour, and it is closely linked to the apparatus and data sampling. This means that the loop test is only an approximate test for rheological evaluation of samples. Therefore, there is a need of other types of rheological tests.

The dependency of the shear rate on the shear stress is shown in Fig. 2. The results of the measurements of the red wines are given in Fig. 2a. The results of the measurements of the white wines are presented in Fig. 2b. The figures show the results of the measurement performed at 5°C and for two varieties only. The reason is that the hysteresis loop was the biggest at this temperature and for the selected varieties. The values of the hysteresis area are shown in Table 4.

From Table 4, it is evident that all samples behaved as non-Newtonian fluids at the temperature of 5°C, which was caused by formation of the hysteresis loop. The only exception was the sample of André. When the temperature decreased, the measured samples started to behave as Newtonian fluids. Košmerl et al. (2000) argues that wine generally behaves as a Newtonian fluid. However, this is in contrast with the results of this work. It is important to note that the samples in the work of Košmerl were measured at the temperature from 20 to 50°C. The result that wine behaves as a non-Newtonian fluid at low temperature is a new finding. However, the values of the hysteresis areas are relatively small and the non-Newtonian behaviour is not sufficiently noticeable. For comparison, the value of the hysteresis area of heather honey is 25000 Pa s<sup>-1</sup> ml<sup>-1</sup> at the temperature of 10°C (Witczak et al., 2011).

The explanation of the non-Newtonian behaviour can be as follows. Wine is a microdispersive solution containing many particles in the form of mechanical impurities, lees forming substances, microorganisms (yeasts,

| _                | Hysteresis area (Pa s <sup>-1</sup> ml <sup>-1</sup> ) |           |    |    |    |  |  |  |
|------------------|--|-----------|----|----|----|--|--|--|
| Sample           | Temperature (°C)                                       |           |    |    |    |  |  |  |
|                  | 5  | 12        | 20 | 30 | 40 |  |  |  |
| André            | *  | *         | *  | *  | *  |  |  |  |
| Cabernet Moravia | 0.69±0.08  | *         | *  | *  | *  |  |  |  |
| Laurot           | 1.80±0.12  | *         | *  | *  | *  |  |  |  |
| Saint Laurent    | 0.59±0.05  | 0.25±0.15 | *  | *  | *  |  |  |  |
| Gruner Veltliner | 1.85±0.10  | 0.72±0.21 | *  | *  | *  |  |  |  |
| Pinot Blanc      | 1.09±0.15  | 0.46±0.12 | *  | *  | *  |  |  |  |
| Müller Thurgau   | 0.51±0.09  | 0.25±0.12 | *  | *  | *  |  |  |  |
| Riesling Italico | 0.79±0.11  | 0.43±0.09 | *  | *  | *  |  |  |  |

\*The sample behaves as Newtonian fluid. Other explanations as in Table 3.

bacteria), colloids, molecules of ions, and atoms with a size up to  $10^{-7}$  mm. The combined presence of these particles can influence the physical character of wines (Iland, 2004). The properties of these microdispersive solutions can be influenced by fundamental membrane processes occurring during filtration of wine (Monteiro *et al.*, 2001, Zimmer, 2006).

The Herschel-Bulkley mathematical model was used for the evaluation of dependencies of the shear rate on the shear stress. This model is used for the description of flow curve of a material with shear-thinning or shear-thickening behaviour. The results are given in Table 5. From Table 5, it is evident that the determination coefficient for all the temperatures and varieties is very high and ranges from  $R^2 = 0.911$  to  $R^2 = 0.999$ .

Other important parameters, which are shown in Table 5, are the *n* and *k* parameters. The consistency index *k* indicates extrapolated shear stress at a unit shear rate. The flow index is a rate of deviations from Newtonian behaviour; when n < 1, the viscosity of the sample decreases, and when n > 1, the viscosity of the sample increases. As shown in Table 5, the values of parameter *n* are one or less than one in most cases.

| Sample           | Temperature (°C) | $\mathbb{R}^2$ | п         | k     |
|------------------|------------------|----------------|-----------|-------|
|                  | 5                | 1.000          | 1.00±0.00 | 0.003 |
|                  | 12               | 0.999          | 1.02±0.02 | 0.002 |
| André            | 20               | 0.999          | 1.00±0.00 | 0.002 |
|                  | 30               | 0.994          | 1.00±0.00 | 0.001 |
|                  | 40               | 0.995          | 1.07±0.03 | 0.001 |
|                  | 5                | 0.993          | 0.92±0.01 | 0.005 |
|                  | 12               | 0.996          | 0.69±0.08 | 0.013 |
| Cabernet Moravia | 20               | 0.946          | 0.86±0.09 | 0.003 |
|                  | 30               | 0.998          | 1.00±0.00 | 0.001 |
|                  | 40               | 0.998          | 0.95±0.02 | 0.001 |
|                  | 5                | 0.979          | 0.86±0.01 | 0.006 |
|                  | 12               | 0.999          | 1.07±0.02 | 0.002 |
| Laurot           | 20               | 0.999          | 1.00±0.00 | 0.002 |
|                  | 30               | 0.999          | 0.95±0.03 | 0.002 |
|                  | 40               | 0.993          | 0.89±0.04 | 0.002 |
|                  | 5                | 0.998          | 0.96±0.01 | 0.004 |
|                  | 12               | 0.999          | 0.99±0.01 | 0.002 |
| Saint Laurent    | 20               | 0.997          | 0.94±0.02 | 0.002 |
|                  | 30               | 0.998          | 0.93±0.02 | 0.002 |
|                  | 40               | 0.997          | 0.99±0.01 | 0.001 |
|                  | 5                | 0.978          | 0.85±0.02 | 0.006 |
|                  | 12               | 0.989          | 0.99±0.00 | 0.001 |
| Gruner Veltliner | 20               | 0.998          | 0.92±0.02 | 0.002 |
|                  | 30               | 0.996          | 0.89±0.03 | 0.002 |
|                  | 40               | 0.911          | 0.99±0.01 | 0.001 |

T a b l e 5. Rheological parameters of the Herschel-Bulkley mathematical model

| Sample           | Temperature (°C) | $\mathbb{R}^2$     | п               | k     |
|------------------|------------------|--------------------|-----------------|-------|
|                  | 5                | 0.990              | 0.92±0.00       | 0.004 |
|                  | 12               | 0.994              | 0.90±0.02       | 0.004 |
| Pinot Blanc      | 20               | 0.999              | 0.96±0.02       | 0.002 |
|                  | 30               | 0.996              | 0.88±0.01       | 0.002 |
|                  | 40               | 0.991              | 0.84±0.02       | 0.002 |
|                  | 5                | 1.000              | 0.99±0.00       | 0.003 |
|                  | 12               | 0.995              | 0.90±0.01       | 0.003 |
| Müller Thurgau   | 20               | 0.997              | 0.92±0.02       | 0.002 |
|                  | 30               | 0.998              | 0.98±0.02       | 0.001 |
|                  | 40               | 0.996              | 0.99±0.00       | 0.001 |
|                  | 5                | 1.000              | 0.99±0.01       | 0.003 |
|                  | 12               | 0.994              | 0.89±0.02       | 0.004 |
| Riesling Italico | 20               | 0.994              | 0.88±0.02       | 0.003 |
|                  | 30               | 0.998              | 0.96±0.01       | 0.001 |
|                  | 40               | 0.993              | 0.96±0.01       | 0.001 |
| a 0.08<br>0.07   |                  | b <sup>0.025</sup> | <sup>5</sup> ]* |       |
| 0.06             |                  | 0.0:<br>@          | 2 -             |       |

#### Table 5. Continuation



Fig. 3. Dependence of apparent viscosity on the shear rate of selected: a - red and b - white wines at 5°C

The next experiment confirmed that the analysed samples were non-Newtonian fluids. The dependency of apparent viscosity on the shear rate was measured. The selected varieties of the red and white wines were again measured at 5°C. The results are given in Fig. 3.

It is evident that apparent viscosity decreases with the increasing shear rate. In the case of a Newtonian fluid, viscosity must be constant with an increasing shear rate.

The final step of the experiment was focused on the time-dependent behaviour of the samples. The determination of time dependency of measured samples is the key to the knowledge of the type and structure of the fluid. Figure 4a shows the dependency of the apparent viscosity of Cabernet Moravia and Laurot on the time.

The power function describes an analysis of measured data trends. The regression analysis indicates a negative trend – apparent viscosity decreases with increasing time.



Fig. 4. Dependence of apparent viscosity on the time of selected: a - red and b - white wines at 5°C and at 50 s<sup>-1</sup>.



Fig. 5. Statistical analysis of multivariate data: a - box and whisker plots, b - scree plot.

Unfortunately, the measured data are highly fluctuating. Hence, both determination coefficients were relatively small (variety Laurot  $R^2 = 0.659$  and variety Cabernet Moravia  $R^2$ = 0.209). Nevertheless, on the basis of results from the previous experiments, it can be concluded that these varieties exhibit shear-thinning behaviour with thixotropy.

A similar situation was observed in the case of the white wines. The results are shown in Fig. 4b.

The trend development was described by the power function mathematical model, and the tendency of the measured data for both samples was negative. This means that the apparent viscosity decreased with the increasing time and the measured substances are shear-thinning fluids with thixotropy. The results of principal component analysis are given by Figs 5 and 6.

All four plots are shown in the figure - box and whisker plots, scree plot, component weight plot, and scatterplot of component scores. The analysed datasets show normal distribution at a significance level  $\alpha = 0.05$ . Dependence of the rheological values (for example viscosity) is important to track from the viewpoint of rheology. The component weight plot shows dependences and similarities between the observed characters. From this plot, it is evident that viscosity does not exhibit any dependence or similarity to the other chemical values measured. This confirms the aforementioned hypothesis that rheological behaviour is determined by the contents of many particles of various origins. It should be noted that the two components compared explain approximately 68% of the total dispersion (Fig. 5). The scatterplot of the component scores represents relationships between the individual samples of wines (Fig. 6). It is possible to see that the white wines are located on the left side of the plot and the red wines are located on the right side of the plot. This suggests that the colour of wine is determined by chemical values.



**Fig. 6.** Statistical analysis of multivariate data: a – component weights plot, b – scatterplot of component scores.

## CONCLUSIONS

Detailed knowledge of the physical (rheological) and chemical properties of wine plays an important role in wine processing. The knowledge is essential for membrane processes, which are employed in microfiltration. The use of this technology increases the market value of wine. This implies an urgent need for information about rheological and chemical properties of wine. This article deals with current issues concerning the rheological properties of wine. Followings conclusions can be draw from this work:

1. All tests proved that the evaluated samples behaved as shear-thinning fluids, with thixotropy at low temperatures. The sample "André" was an exception.

2. Samples behave as Newtonian fluid at higher temperature. This result is in accordance with other works.

3. Non-Newtonian behaviour can be caused by physical properties of wine. Generally, wine is a microdispersive solution containing many particles in the form of mechanical impurities, lees forming substances, microorganisms, etc. There is an assumption that aggregates are created thanks to intermolecular forces at lower temperature. These aggregates can cause shear-thinning behaviour of fluid.

4. The component weight plot showed that measured rheological parameter – apparent viscosity – is not in relationship with other chemical parameters which were measured (at explanation of 68% of total dispersion).

5. Scatterplot of component scores showed that colour of wine depends on chemical parameters in accordance with assumption.

**Conflict of interest:** The Authors do not declare conflict of interest.

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