

## STUDY OF RHEOLOGICAL PROPERTIES OF RED WINES UNDER THE HEATING EFFECT

Hasime Manaj<sup>1\*</sup>, Anisa Dhroso<sup>1</sup>, Rozana Troja<sup>1</sup>, Ilirjan Malollari<sup>1</sup>

<sup>1</sup>Department of Industrial Chemistry, Faculty of Natural Sciences,  
University of Tirana, Boulevard "Zogu I", 1001 Tirana, Albania

\*e-mail: hasime.manaj@fshn.edu.al

### Abstract

Red wine is made from dark-colored grape varieties; production process involves extraction of color and flavor components from the grape skin. The red wine quality can be influenced by the plant's environment, varieties, viticulture and enological practices. Red wine available in Albanian market was characterized for physicochemical and rheological properties.

The study was focused on wines produced from grapes of vineyards of different geographical areas of Albania, Merlot variety produced in Tirana and Korcha was selected. Several physicochemical properties were examined: density, total and volatile acidity, content of the alcohol, reduced sugars,  $\text{SO}_2$ , pH, and electric conductivity. The dynamic viscosity of wine was experimentally determined as a function of temperature from 5 to 40 °C. The electric model L-81 was used to increase the temperature of the wine samples to a specific temperature. Kinematic viscosity and fluidity were determined according to the definitions. For the determination of the density, the pycnometric method was used. The content of alcohol in wine was determined by SSH 1446-1:1987 method. The concentration of reduced sugars was determined with Fehling method (SSH 1446-2:1987). For the determination of total acidity, an analytical method was used (SSH 1446-3:1987). The free acidity was determined according to SSH 1446-4:1987. Free and total  $\text{SO}_2$  was determined by titration of the standard solution of iodine (SSH 1446-7:1987 and SSH 1446-6:1987). The pH and electric measurements of red wine was obtained with a PHS-3CW Microprocessor pH-meter and DDS-120W microprocessor conductivity meter, respectively. Viscosity and temperature of red wine samples were measured using the Digital Viscometer Model at 60 rpm, with accuracy  $\pm 1\%$ .

The limit values of physicochemical and rheological parameters in wine available on the market must comply with the national law of the Albanian Food Law and EU Food legislation. Typical pH levels in wine normally range from 3 to 4, and our results demonstrate that pH values for merlot wines from Tirana and Korca were in this range, 3.49 and 3.74. Density of merlot variety from Korca at different temperatures ranges of 1.004 to 0.9945 g/cm<sup>3</sup>, while from Tirana 1.002 to 0.9925g/cm<sup>3</sup>. The merlot variety from Korca, had the highest value of dynamic viscosity at 5 °C (7.4 mPa.s). Meanwhile, Merlot variety from Tirana had the lowest value of dynamic viscosity at 5 °C (6.2 mPa.s). The dynamic viscosity of all samples was approximately equal at the temperature 40 °C. The temperature dependencies of dynamic and kinematic viscosity have a decreasing character, whereas the fluidity increased with the temperature. The variation of the dynamic viscosity of red wine with the temperature is analyzed applying different mathematical models (Arrhenius, Andrade and Clements models). In all cases the determination coefficient ( $R^2$ ) exceeded values >0.99.

The physicochemical parameters results depend on red wine nature and can be used as a way of characterizing the wine quality. The value of correlation coefficient and mean absolute percentage error indicates that the models fit satisfactorily to experimental data. However, comparisons of the results obtained indicate that the temperature dependence of viscosity for the red wine samples from Tirana and Korca, were best described by the Clements model.

**Key words:** Red wine, Heating effect, Rheological properties.

## 1. Introduction

Red wine is made from dark-colored grape varieties; production process involves extraction of color and flavor components from the grape skin. The red wine quality can be influenced by the plant's environment, varieties, viticulture and enological practices. Albania has one of the oldest wine making traditions, dating back to the ice and Bronze Age whereas Ancient Illyrians and Greeks inhabited the country's territory some 3,000 years ago. It belongs chronologically to the old world of wine producing countries [9]. Albania is a mountains Mediterranean country and extends within the Mediterranean Basin with the Mediterranean Sea in the west. Albania can be separated into four wine regions, which are mainly defined by their altitude [8]. Favorable climate and fertile soil of the mountainous areas of the country are well suited to viticulture. The wine production is associated mainly with countries of moderate climate with long, hot summers. However, the vineyards are located also in countries of cooler climate [14]. Albania produced an estimated 17,500 tons of wine in 2014. Red wine available in Albanian market was characterized for physicochemical and rheological properties.

Merlot is a dark blue-colored wine grape variety that is used as both a blending grape and for varietal wines. The name Merlot is thought to be a diminutive of merle, the French name for the blackbird, probably a reference to the color of the grape [13]. Merlot grapes are identified by their loose bunches of large berries. Merlot grapes with a thinner skin and fewer types of tannin per unit volume tend to have a higher sugar content and lower malic acid. Merlot is one of the world's most widely planted grape varieties. France is home to nearly two thirds of the world's total plantings of Merlot [12]. Albania wine is often excellent. The best wine-producing are around Korca and Berat; some of the vineyards further north, around Tirana and between Lezha and Shkodra are also reliable. The distinctive long-necked bottles of Merlot produced by different vineyards in Korca are easy to recognize [4].

The aim of this study is to determine the best mathematical model of the dependence of viscosity on the temperature of red wine from different geographical areas of Albania. Furthermore it aims to specify the physicochemical properties of these wines and to compare the results with the Albanian standard.

## 2. Materials and Methods

This study was focused on wines produced from grapes of vineyards in different Albania geographical areas, or more precisely, Merlot variety produced in Tirana and Korca was selected. Two samples of red wine were used in the laboratory analyses.

In the first phase, following physicochemical parameters were determined: density, total acidity, volatile acids, content of the alcohol, reduced sugars, free  $\text{SO}_2$ , total  $\text{SO}_2$ , pH and electric conductivity following the analytical methods described in Albanian Standard [3]. In the second phase of the study, density and dynamic viscosity were experimentally determined as a function of temperature from 5 to 40 °C. The Electric model L-81 was used to increase the temperature of the wine samples to a specific temperature. All measurements were performed in three repetitions. For the determination of the density, the pycnometric method was used. Content of alcohol in wine was determined by SSH 1446-1:1987 method. Concentration of reduced sugars was determined with Fehling method (SSH 1446-2:1987). For the determination of total acidity, an analytical method was used (SSH 1446-3:1987). Free acidity was determined according to SSH 1446-4:1987, and free and total  $\text{SO}_2$  were determined by titration of the standard solution of iodine (SSH 1446-7:1987 and SSH 1446-6:1987). The pH and electric measurements of red wine was obtained with a PHS-3CW microprocessor pH Meter and DDS-120W microprocessor conductivity meter, respectively. Viscosity and temperature of red wine samples were measured using the digital viscometer model at 60 rpm, with accuracy  $\pm 1\%$ . Kinematic viscosity and fluidity were determined according to the definitions.

Office Excel 2016 software was used to carry out the effect of temperature on dynamic viscosity of red wine by different mathematical models, were, the dynamic viscosity of wine was represented as a function of temperature by using proposed mathematical models. Arrhenius model is presented in the following equation:

$$\mu = \mu_{\infty, T} \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

Where:  $\mu$  is the dynamic viscosity in mPa.s,  $\mu_{\infty, T}$  is the viscosity at infinite-temperature in mPa.s,  $E_a$  is the exponential constant that is known as activation energy (J/mol),  $R$  is the gas constant (J/mol.K) and  $T$  is the absolute temperature Kelvin.

Andrade (three constant) and Clements (four constant) models are represented in the following equations [1, 2]:

$$\ln \mu = A + \frac{B}{T} + \frac{C}{T^2} \quad \text{and} \quad \ln \mu = A + \frac{B}{T} + \frac{C}{T^2} + \frac{C}{T^3} \quad (2)$$

Where:  $\mu$  is the dynamic viscosity in mPa x s,  $T$  is the temperature in Kelvin,  $A$ ,  $B$  and  $C$  are constants.

Kinematic viscosity ( $\text{m}^2 \times \text{s}^{-1}$ ) is defined as a ratio of dynamic viscosity to density of fluid  $\rho$  ( $\text{kg} \times \text{m}^{-3}$ ) at the same temperature. Reciprocal value of dynamic viscosity is called fluidity  $\phi$  and unit of fluidity is  $\text{mPa}^{-1} \times \text{s}^{-1}$  [5]. The mean absolute percentage error (MAPE), which indicates the deviance of the observed values from the calculated, was calculated.

### 3. Results and Discussion

The red wine quality and behavior can be influenced by the plant's environment, species and varieties, viticulture and enological practices [16]. The limit values of physicochemical and rheological parameters in wine available on the market must comply with the national law of the Albanian Food Law and EU Food legislation. By comparing our experimental data with standard value, we can see that they are roughly the same, with very little difference. This may come as a result of many factors that affect the quality of the wine and therefore the experimental results. Alcohol content in wine is affected by many factors, such as ripeness of the grapes at the time of harvest, grape processing technology, and fermentation technology [7].

Our results demonstrate that alcohol values for Merlot wines from Tirana and Korca were 11 and 11.4%. Typical pH levels in wine normally range from 3 to 4, and our results demonstrate that pH values for Merlot wines from Tirana and Korca were in this range, 3.49 and 3.74. The acids are important in maintaining pH low enough to inhibit the growth of many undesirable bacteria, thus giving advantage to wine yeasts [6]. Ribéreau and Traduction, [11], report that the content of acids in wine ranges between 5 and 7.5 g x L<sup>-1</sup>. 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 [10]. A total acidity of red wines were 4.43 (Tirana red wine) and 4.58 (Korca red wine), respectively. Flurry acidity of red wines were 0.62 (Tirana red wine) and 0.65 (Korca red wine).

According to the grams per liter residual sugar in a wine, we can determined the product type as: dry, medium dry, medium sweet and sweet. Wine with low content of residual sugar, in accordance with Europe wine regulations can contain maximum 4 g/L [15]. The analyzed samples had 2.5 and 2.9 residual sugar, for Tirana and Korca, so red wines can be classified into the category of dry wines. Electric conductivity of red wine samples was 2.19 and 2.64 mS, at 20 °C, for Tirana and Korca respectively. Sulfur dioxide (SO<sub>2</sub>) is widely used in wine production as a chemical antioxidant and inhibitor of microbial activity. There are a number of traditional methods for determining free and total SO<sub>2</sub> in wine involving distillation or iodometric titration. The total and free amount of sulphur dioxide in Merlot wine from Tirana, were 144 mg/L and 16 mg/L. Total and free amount of sulphur dioxide in Merlot wine from Korca, were 140 mg/L and 15.8 mg/L. Red wines have maximum allowed limit 160 mg x L<sup>-1</sup>. None of the evaluated samples exceeded the maximum allowable limit. Density of Merlot variety from Korca at different temperatures ranges of 1.004 to 0.9945 g/cm<sup>3</sup>, while from Tirana 1.002 to 0.9925 g/cm<sup>3</sup>. The experimental data of red wines versus temperature are presented in Figure 1.

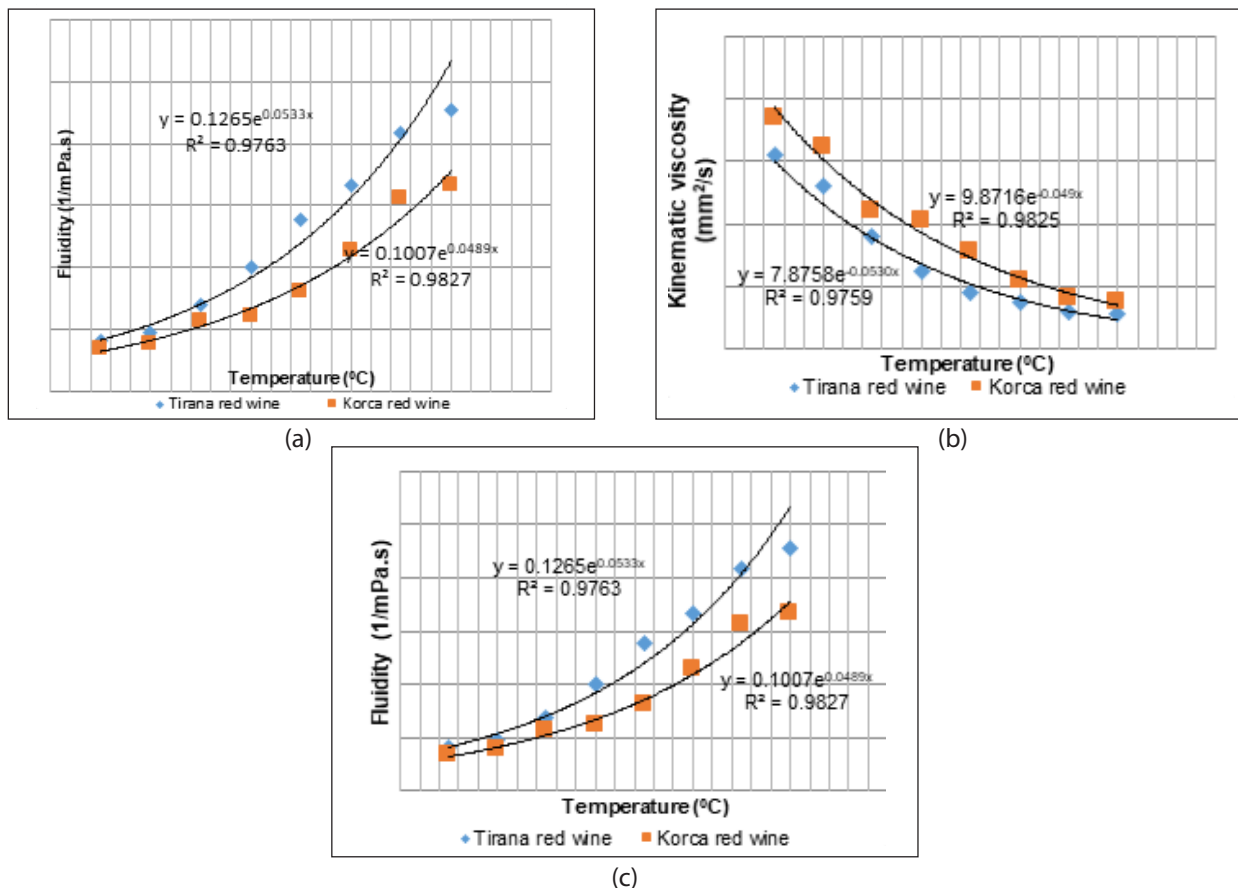
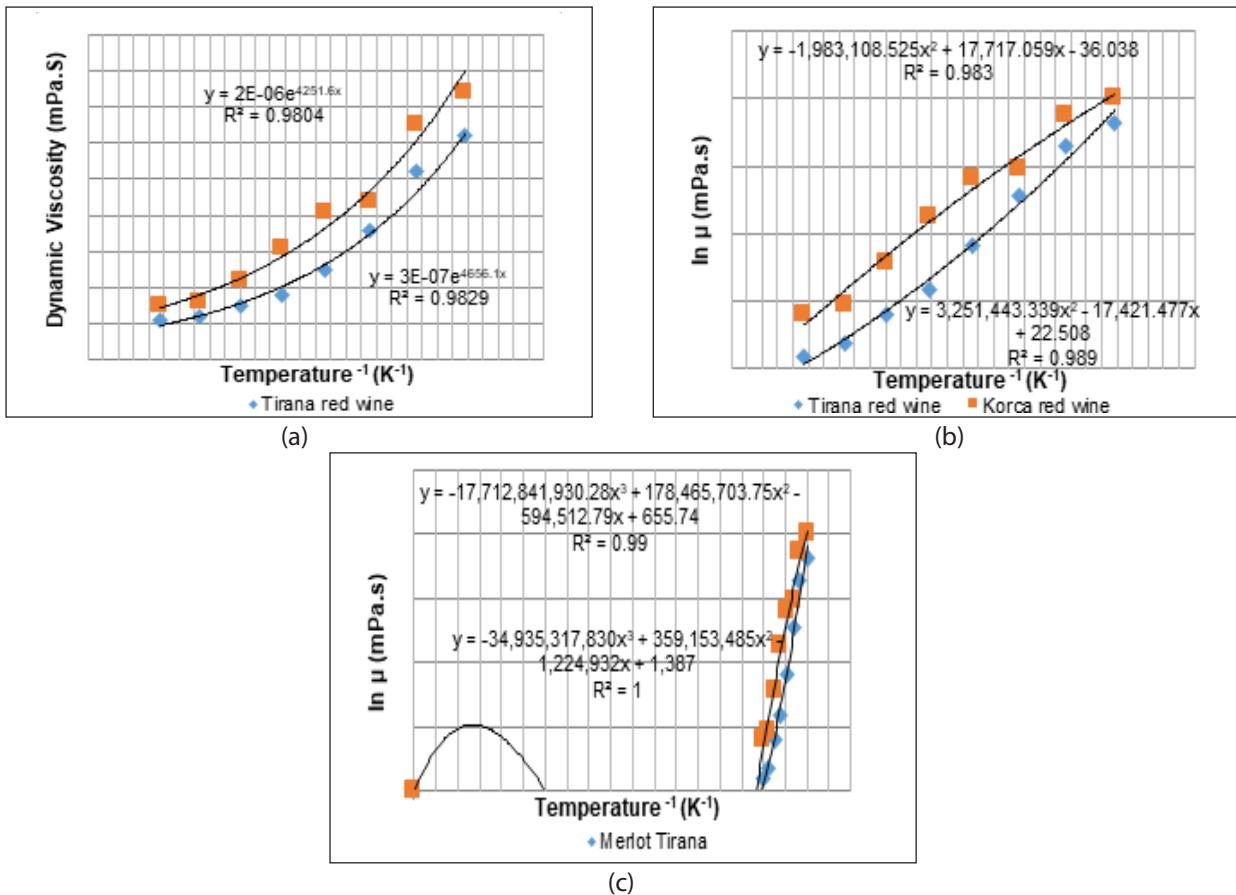


Figure 1. Effect of temperature on (a) dynamic viscosity, (b) kinematic viscosity, (c) fluidity of red wines



**Figure 2. Effect of temperature on (a) Arrhenius model, (b) Andrade model, and (c) Clements model of red wines**

Experimental data of red wine, for dynamic viscosity (mPa.s) versus temperature is shown in Figure 1 (a). The dynamic viscosity of red wine is decreasing with increasing of temperature. Kinematic viscosity can be calculated from the dynamic viscosity and the density. Merlot variety from Korca, had the highest value of dynamic viscosity at 5 °C (7.4 mPa x s). Meanwhile, Merlot variety from Tirana had the lowest value of dynamic viscosity at 5 °C (6.2 mPa x s). The dynamic viscosity of all samples was approximately equal at the temperature 40 °C. On Figure 1 (b) is presented kinematic viscosity decreasing versus temperature range from 5 to 40 °C, while fluidity is increasing with increasing of the temperature, which is presented in Figure 1 (c). Temperature dependencies of dynamic and kinematic viscosity have a decreasing character, whereas the fluidity increased with the temperature. The values of the estimated constants and correlation coefficients are shown in each equation, set in the graphs. In all cases the determination coefficient ( $R^2$ ) exceeded values > 0.95.

The variation of the dynamic viscosity of red wine with the temperature is analyzed applying different mathematical models (Arrhenius, Andrade and Clements models). The experimental data of red wines are presented in Figure 2 (a-c), by using equations 1 and 2 respectively.

According to the Arrhenius model results, the value of activation energy of the analyzed Merlot wine from Tirana was 38.7 kJ/mol and from Korca was 35.3 kJ/mol, which describe the sensitivity of viscosity to temperature changes. The values of the estimated constants are shown in each equation, set in the graphs. In all cases the determination coefficient ( $R^2$ ) exceeded values > 0.95. Comparisons of the calculated data indicate that the temperature-dependence of viscosity for both of red wine samples was best described by the Clements model:  $R^2 = 0.9$  Merlot wine from Tirana and  $R^2 = 1$  Merlot wine from Korca. An equation with lower mean absolute percentage errors values gives a better fit to experimental data compared to an equation with higher mean absolute percentage errors values. The mean absolute percentage errors were below 10%, or: Merlot wine from Tirana - 9.86% by Arrhenius model, 3.79% by Andrade model and 0.56% by Clements model, and Merlot wine from Korca - 9.76% by Arrhenius model, 0.386% by Andrade model and 0.056% by Clements model.

#### 4. Conclusions

- The study was focused on wines produced from grapes of vineyards of different geographical areas of Albania, Merlot variety produced in Tirana and Korca

was selected. The limit values of physicochemical and rheological parameters in wine available on the market comply with the national law of the Albanian Food Law and EU Food legislation.

- The dynamic viscosity versus temperature of wine was measured and described by different mathematical models. Comparisons of the calculated data indicate that the temperature-dependence of viscosity for both of red wine samples was best described by the Clements model:  $R^2 = 0.9$  Merlot wine from Tirana and  $R^2 = 1$  Merlot wine from Korca.

- An equation with lower mean absolute percentage errors values gives a better fit to experimental data compared to an equation with higher mean absolute percentage errors values. Merlot wine from Tirana: 0.56% Clements model. Merlot wine from Korca: 0.056% Clements model.

## 5. References

- [1] Abramovic H., Klofutar G. (1998). *The temperature dependence of dynamic viscosity for some vegetables oils*. Acta Chim. Slov., 45, (1), pp. 69-77.
- [2] Clements L. D., Nouredini H., and Teoh B. C. (1992). *Viscosity of vegetables oils and fatty acids*. J. Am. Oil Chem. Soc., 69, (12), pp. 1189-1191.
- [3] General Directorate of Standardization Albania. (2017). *SSH 1446:1987, on determination of content of alcohol in wine* (in Albanian). <URL: <http://www.dps.gov.al>. Accessed 6 April 2019.
- [4] Gloyer G. (2008). *Albania* (3rd Ed.). The Bradt Travel Guides, pp 41.
- [5] Hlaváč P., Božiková M., Hlavačova Z., Kubik L. (2016). *Influence of temperature and storing time on selected red wine physical properties*. Acta Universitatis Agriculturae et Silviculturae mendelianae brunensis, Vol. 64, 2, pp. 433-439.
- [6] Joshi V., Rao B. S., Reddy R. S. (2013). *Studies on the physico-chemical properties on wine in different varieties of grapes*. The Asian journal of horticulture, Vol. 8, 1, pp. 174-178.
- [7] Kaltzin W. (2012). *Natural wines as a trend* (in German). Der Winzer, 10, (4), pp. 85-87.
- [8] Ministry of Environment of Albania. (2009). *Albania's Second National Communication to the Conference of Parties under the United Nations Framework Convention on Climate Change*. <URL: <https://unfccc.int/resource/docs/natc/albnc2.pdf>. 6 April 2019
- [9] Patton W. (2010). *Bible Wines or the Laws of Fermentation and the Wines of the Ancients*. Kessinger Publishing, Whitefish, USA, pp. 41.
- [10] Ribéreau-Gayon P., and Branco J. M. (2006). *Handbook of enology*. John Wiley Sons, Chichester, UK.
- [11] Ribéreau-Gayon P., and Traduction A. (2003): *Handbook of enology: The chemistry of wine stabilization and treatments*. John Wiley Sons, Chichester, UK.
- [12] Robinson J. (2003). *Jancis Robinson's Wine Course* (3rd Ed.). Abbeville Press, New York, USA, pp. 142-143.
- [13] Robinson J., Harding J. J. (Eds.). (2015). *Oxford Companion to Wine*. Oxford University Press, Oxford, UK, pp. 10.
- [14] Tarko T., Duda-Chodak A., Sroka P., Satora P., Jurasz E. (2008). *Physicochemical and antioxidant properties of selected polish grape and fruit wines*. Acta Sci. Pol., Technol. Aliment., 7, (3), pp. 35-45.
- [15] Trávníček P., Burg P., Krakowiak-Bal A., Junga P., Vítěz T., Ziemiańczyk U. (2016). *Study of rheological behaviour of wines*. Int. Agrophys., 30, pp. 509-518.
- [16] Torres B. (2015). 4 factors that determine wine quality. <URL: <https://www.torres.es/en/blog/how-wine-made/4-factors-determine-wine-quality>. Accessed 6 April 2019.