INFLUENCE OF HIGH VOLTAGE ELECTRICAL DISCHARGE PLASMA TREATMENT ON THE PHYSICOCHEMICAL CHARACTERISTICS OF WINE*

UTJECAJ VISOKONAPONSKOG ELEKTRIČNOG PRAŽNJENJA-HLADNE PLAZME NA FIZIKALNO-KEMIJSKE KARAKTERISITKE VINA

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Original scientific paper

Rezime

Cilj ovoga istraživanja bio je ispitati utjecaj visokonaponskog električnog pražnjenja-hladne plazme na fizikalno-kemijske karakteristike vina, zbog potencijalne primjene ove tehnologije u proizvodnji vina. Istražen je utjecaj procesnih parametara hladne plazme, frekvencije (60, 90, 120 Hz) i trajanja tretmana (3, 5, 10 min) pri pozitivnom polaritetu na koncentraciju otopljenog kisika, koncentracije slobodnog i ukupnog sumporovog dioksida (SO_2), te električnu provodljivost u bijelom i crnom vinu. Neposredno nakon tretmana provedene su analize, gdje je koncentracija otopljenog kisika određena pomoću uređaja za mjerenje kisika, koncentracija slobodnog i ukupnog SO_2 potenciometrijskom titracijom, dok je konduktometrom izmjerena električna provodljivost. Dobiveni rezultati pokazali su da primjenom tretmana hladnom plazmom dolazi do smanjenja koncentracije otopljenog kisika i ukupnog SO_2 u usporedbi sa kontrolnim vinima. S druge strane, električna provodljivost se povećala nakon primijenjenog tretmana, dok se koncentracija slobodnog SO_2 ili smanjila ili povećala. Također, rezultati su pokazali da frekvencija i trajanje tretmana značajno utječu na fizikalno-kemijske karakteristike vina.

Ključne riječi: *hladna plazma, vino, fizikalno-kemijski parametri*

Summary

The aim of proposed research was to study the influence of high voltage electrical plasma discharges on the physicochemical characteristics of wines, due to the potential use of this technique in winemaking. The effects of plasma discharge frequency (60, 90, 120 Hz) and treatment duration (3, 5, 10 min) with positive electrode polarity on the changes in concentrations of dissolved oxygen, free and total

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sulfur dioxide (SO_2) and electrical conductivity in white and red wines were investigated. The analyses were done immediately after treatment, where the dissolved oxygen was measured by oxygen-meter, free and total SO_2 by potentiometric titration while conductometer was used for electrical conductivity measurements. The results showed that applied treatments influenced the decrease in concentration of dissolved oxygen and total SO_2 in comparison to control wines. On the other hand, electrical conductivity increased after applied treatment, while concentration of free SO_2 was either decreased or increased. The results also showed that physicochemical characteristics of wines were significantly affected by frequency as well as processing time.

Key words: *high voltage electrical discharge plasma, wine, physicochemical characteristics*

INTRODUCTION

The new innovative technologies, such as high hydrostatic pressure, pulsed electric fields, high voltage arc discharge and non-thermal plasma, are today of great interest in food industry. Among these novel technologies, the application of plasma technology to wine has not been investigated so far. Most of the studies have been carried out on inactivation effect of various plasma treatments on microorganisms (Ziuzina *et al.*, 2013; Shi *et al.*, 2011; Vukušić *et al.*, 2016; Misra and Jo, 2017). Recently, the focus has begun to shift towards impact of plasma on food constituents (Grzegorzewski *et al.*, 2011; Misra *et al.*, 2015; Bursać Kovačević *et al.*, 2016; Elez Garofulić *et al.*, 2015; Ramazzina *et al.*, 2016), which is still insufficiently explained. Because of the lack of knowledge on the primary modes of action and on the effects on sensory and nutritional properties of the products, the use of plasma technology for food processing has not been yet allowed (Niemira, 2012). The plasma is a non-thermal technology, which is described as partially or completely ionized gas with electrical, chemical and physical properties (Petitpas *et al.*, 2007). The plasma can be produced by many methods such as electric discharges (corona, spark, glow, arc, microwave discharge, plasma jets and radio frequency plasma) and shocks (electrically, magnetically and chemically driven) (Petitpas *et al.*, 2007). The primary effects of electrical discharges are the UV radiation and the generation of reactive chemical species by the plasma ionization process (Niemira, 2012).The inactivation efficiency of plasma is associated with large number of variables, primarily with employed plasma sources and process parameters as well as with the characteristics of treated product (Misra and Jo, 2017). Apart from the nutritional and sensory quality, the physicochemical parameters are often employed for judging the quality of products. Basic physicochemical parameters such as pH, sulfur dioxide (SO_2) and others are generally used to define and to express wine quality (García Martín and Sun, 2013). In wine, oxygen can influence the composition and quality of wine drastically due to its involvement in various reactions (Du Toit *et al.*, 2006).

The measurements of dissolved oxygen in wine are significant because the contact between wine and oxygen is a critical point during the wine production (Castellari *et al*., 2004). Another important physicochemical parameter of wine is the electrical conductivity because of its good correlation with pH and assimilable nitrogen during fermentation (Colombié *et al*., 2008). Electrical conductivity is defined as the ability of a solution to conduct electric current (Colombié *et al*., 2008). Thus, the aim of this research was to study the influence of the plasma treatment, as possible alternative technique to reduce the addition of SO_2 in wine, on the changes of previously mentioned physicochemical parameters (dissolved oxygen, electrical conductivity and total/free SO_2 concentrations).

MATERIAL AND METHODS

Material

The white wine Graševina (*Vitis Vinifera L.)* and red wine Cabernet Sauvignon (*Vitis Vinifera L.)* used in this study were acquired from the winery Erdutski vinogradi d.o.o., harvest 2016, in Erdut, Croatia. Physicochemical properties of Graševina were: 11.4 vol %, total acidity (as tartaric acid) 5.1 g/L, volatile acidity (as acetic acid) 0.31 g/L, reducing sugars 2.8 g/L, pH 3.37, malic acid 1.2 g/L, lactic acid 0.3 g/L, while those of Cabernet Sauvignon were: 13.1 vol %, total acidity (as tartaric acid) 5.3 g/L, volatile acidity 0.61 g/L, reducing sugars 4.1 g/L, pH 3.46, malic acid 0.1 g/L, lactic acid 1.3 g/L.

Chemicals

Sulfuric acid 1/3 (941), sodium hydroxide 2N (908), sulfuric acid 1/10 (932) and iodide/iodate N/64 (921) were purchased from LDS Laboratoires Dujardin-Salleron (Noizay, France).

Methods

The plasma treatments of wine

The plasma treatments were conducted in a 1000 mL glass vessel with a point to point electrode configuration in a so-called hybrid reactor with discharges in and above the liquid. The plasma was generated by high-voltage (HV) pulsed power supply (Spellman, UK) by charging a load capacitor of 1.13 nF to up to 30 kV and then discharging the stored charge into the plasma reactor via a rotating spark gap. The voltage in the plasma reactor was measured and recorded using a Tektronix P6015A high voltage probe connected to a Hantek DS05202BM oscilloscope (data not shown). The experiments were performed at positive polarity and argon (purity 99.99%; Messer Croatia, Zagreb, Croatia) was bubbled trough stainless steel needle (Micrlolance TM 3.81 cm) at the gas flow of 4 L/min. 300 mL of wine was treated with plasma running at the combination of following processing parameters: frequency at 60, 90 and 120 Hz and treatment duration of 3, 5 and 10 min. The temperature and pH value of samples before and after the plasma treatment were monitored (data not shown). Before treatment, all samples were at the room temperatures of 21 ± 1 °C, while after the plasma exposure temperature raised up to 6 °C, depending on the treatment duration and applied frequency. The pH value of wines maintained relatively constant ranging from 3.1 to 3.4. After treatments, wine samples were subjected to physicochemical analysis.

Physicochemical analysis

In control and treated wines, immediately after plasma treatments, the concentrations of dissolved oxygen, free and total SO_2 and electrical conductivity were measured. The measurement of dissolved O_2 concentration was carried out using the oxygen measurement device (Nomasense O2 P6000, Nomacorc, Belgium), which is based on luminance principle. The device corrects the concentration of oxygen in terms of sugar and alcohol content and the temperature of the wine. Determination of dissolved oxygen was carried out immediately after treatment with plasma using an immersion probe with a detection limit of 15 μg/L of oxygen. The measurement of the free and total SO_2 concentration was performed on a SO_2 measurement device (LDS Sulfilyser, Laboratoires Dujardin-Salleron, Noizay, France) by titration with iodide/iodate solution whereby the iodine was reduced and SO_2 oxidized, with the potentiometric determination of the titration point via the LED indicator. Electrical conductivity was measured using a digital pH-meter HANNA edge (HANNA instruments, Croatia, Zagreb, Croatia). The measurement was performed by immersing the electrode for measuring electrical conductivity in the sample and after the stabilization the measured values were recorded.

Statistical analysis

Statistical analysis was carried out using analysis of variance (ANOVA) of Statistica V.10 software (Statsoft Inc., Tulsa, USA). Tukey's HSD test was used as comparison test when samples were significantly different after ANOVA ($p<0.05$).

RESULTS AND DISCUSSION

The results of the effects of various plasma treatments on the physicochemical parameters of wine are presented in Tables 1 (Graševina) and 2 (Cabernet Sauvignon). The results showed that physicochemical characteristics of wines were significantly influenced ($p \leq 0.05$) by the plasma treatment. As can be seen in Table 1, after different plasma treatments, the concentration of dissolved oxygen and total SO_2 values in white wine were reduced, while the concentration of free SO_2 was highly variable and independent of applied processing parameters. On the other hand, the value of electrical conductivity of the treated wine increased after the applied treatment compared to the untreated (control) wine. Regarding the SO_2 in wine, it is important to control its concentration after applied plasma treatments because SO_2 has antioxidant and antimicrobial effects on wine (Usseglio – Tomasset, 1992; Oliveira *et al*., 2011; Ugliano, 2013; Guerrero and Cantos – Villar, 2015). Except the SO_2, the concentration of dissolved oxygen also represents a crtical parameter for the control of various processing treatments (Castellari *et al*., 2004). Among these, the reaction of SO_2 with oxygen is slow and has a crucial role in SO_2 antioxidant activity (Ugliano, 2013). It is known that the amount of SO_2 that binds with other substances in wine, or that remains free, depends on the wine temperature and pH. These observations can be related to changes in temperature of samples after the plasma exposure and the fact that the plasma is oxidative method (Vukušić, 2016). From the processing parameters, the treatment duration had a greater impact on physicochemical parameters of wines, but also the influence of plasma discharge frequency should not be neglected. These data show that the largest decrease in the examined parameters (dissolved oxygen and total SO_2 concentrations) occurred at treatment at 120 Hz for 10 minutes. Furthermore, the highest reduction of free SO_2 concentration was observed at treatment at 90 Hz for 10 minutes, while the highest concentration of free SO_2 was determined in the sample treated at a frequency of 60 Hz for 3 minutes. It has been demonstrated that by increasing the plasma frequency a large number of discharges occur leading to the generation of numerous radicals. In addition, by creating a strong photoionization effect the part of energy transfers to the surrounding medium and warms it (Vukušić, 2016). Regarding the electrical conductivity of the treated wine, the values increased along with increasing the treatment duration, but also by increasing the plasma discharge frequency. By increasing the electrical conductivity, the voltage required for the initiation of the discharge reduces (Zhu *et al*., 2009). Also, the electron density in the liquid increases. That is why the electricity discharge is larger, resulting in plasma higher density and temperature and more intense UV radiation (Locke *et al*., 2006). When the conductivity values are above 5 mS/cm plasma bullets are shorter than 1 mm and strong acoustic waves are created (Šunka, 2001). Although the physical processes are more intense, shorter bullets also means that the smaller volume of the liquid will be in contact with the plasma (Vukušić, 2016). Furthermore, the similar effect of plasma treatments was also observed in red wine (Table 2), where the highest reduction of dissolved oxygen and total SO_2 concentrations, but also the highest concentration of free SO_2 occurred in the sample treated at 120 Hz for 10 minutes. Moreover, the highest reduction of free SO_2 concentration was observed at treatment at 90 Hz for 10 minutes. The values of electrical conductivity determined in red wine also increased by increasing plasma processing parameters. Overall, the characteristics of the obtained wines showed that the applied plasma treatments resulted in wines with different physicochemical parameters compared to the untreated wines.

Table 1. Effects of plasma treatments on physicochemical parameters in white wine Graševina

Treatments	Dissolved oxygen (mg/L)	Free SO_2 (mg/L)	Total SO_2 (mg/L)	Conductivity (µS/cm)
Untreated (control)	3.03±0.04[f]	12.67±0.58[bc]	65.00±0.00[d]	1409.33±6.03[a]
60 Hz/3 min	2.80±0.02[e]	14.67±0.58[d]	65.00±0.00[d]	1528.00±15.10[b]
90 Hz/3 min	2.53±0.09[c]	12.67±0.58[d]	60.83±1.44[b]	1570.67±3.06[c]
120 Hz/3 min	2.17±0.04[c]	12.67±0.58[bc]	62.50±0.00[bcd]	1614.00±3.61[d]
60 Hz/5 min	2.96±0.06[f]	12.67±0.58[bc]	64.17±1.44[cd]	1576.33±12.50[c]

90 Hz/5 min	2.56±0.09^{d}	13.67±0.58^{cd}	60.00±0.00^{ab}	1556.33±13.32^{c}
120 Hz/5 min	2.14±0.03^{bc}	11.33±0.58^{ab}	60.83±1.44^{b}	1627.00±8.89^{d}
60 Hz/10 min	2.50±0.02^{d}	11.67±0.58^{ab}	61.67±1.44^{bc}	1583.00±7.94^{c}
90 Hz/10 min	2.01±0.02^{ab}	10.33±0.58^{a}	60.00±0.00^{ab}	1628.00±5.00^{d}
120 Hz/10 min	1.97±0.06^{a}	11.33±0.58^{ab}	57.50±0.00^{a}	1664.67±9.81^{e}

Data presented as average value of three analytical repetitions with stadard deviation. ANOVA to compare data; different letters indicate statistical differences between wines of all treatments at the same time (Tukey's test, $p < 0.05$).

Table 2. Effects of plasma treatments on physicochemical parameters in red wine Cabernet Sauvignon

Treatments	Dissolved oxygen (mg/L)	Free SO_2 (mg/L)	Total SO_2 (mg/L)	Conductivity (μS/cm)
Untreated (control)	1.64±0.01^{e}	16.67±0.58^{c}	40.00±0.00^{d}	1756.00±1.00^{a}
60 Hz/3 min	1.55±0.04^{d}	13.67±0.58^{ab}	39.67±0.58^{d}	1829.67±1.53^{de}
90 Hz/3 min	1.49±0.02^{cd}	14.67±0.58^{b}	42.00±0.87^{e}	1833.67±1.53^{e}
120 Hz/3 min	1.36±0.03^{ab}	13.67±0.58^{ab}	37.00±0.87^{c}	1820.33±1.53^{c}
60 Hz/5 min	1.40±0.02^{ab}	17.67±0.58^{cd}	30.33±0.58^{b}	1806.33±4.04^{b}
90 Hz/5 min	1.51±0.02^{d}	13.67±0.58^{ab}	30.00±0.00^{b}	1830.33±1.53^{de}
120 Hz/5 min	1.54±0.04^{d}	14.67±0.58^{b}	30.00±0.00^{b}	1811.33±3.21^{b}
60 Hz/10 min	1.33±0.03^{a}	18.33±0.58^{cd}	27.67±0.29^{a}	1823.00±3.61^{c}
90 Hz/10 min	1.41±0.02^{bc}	12.67±0.58^{a}	29.67±0.58^{b}	1830.33±2.52^{de}
120 Hz/10 min	1.33±0.03^{a}	18.67±0.58^{d}	27.00±0.87^{a}	1863.67±3.51^{f}

Data presented as average value of three analytical repetitions with stadard deviation. ANOVA to compare data; different letters indicate statistical differences between wines of all treatments at the same time (Tukey's test, $p < 0.05$).

CONCLUSION

In summary, this study showed that plasma treatments have influenced the physicochemical characteristics of wines. Compared to untreated wines, plasma treatments resulted in changes of all measured parameters, namely in reduction of dissolved oxygen and total SO_2. The concentration of free SO_2 was either decreased or increased, while electrical conductivity of wines increased after applied plasma treatments. Altogether, our results demonstrated the importance of determining the changes in wine physicochemical parameters after exposure to plasma treatments. Finally, these data are crucial precondition for possible application of plasma technology in wine industry. However, these parameters only provide overall quality of the wine. Future studies on the current topic are therefore required, particularly on sensory and chemical characteristics (phenolic and aroma compounds), in order to evaluate the plasma efficiency in winemaking.

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