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Aldehydes, Acids and Esters Analysis of Brandy Aged in Oak Barrels Treated by Electric Field

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Abstract: In natural brandy aging, it normally takes many years, resulting in low production efficiency and high cost. For shortening the aging time, electric field (EF) treatment was used to test and verify the effectiveness of accelerating the brandy aging process. In this paper, the effects of using an EF treatment on brandy stored in 5-L and 2-L oak barrels to simulate the natural aging process were investigated. The compounds of aldehydes, acids and esters were analyzed by gas chromatography-mass spectrometry (GC-MS). Results showed that after being treated by EF the content of most beneficial materials on brandy quality such as esters and β-phenethyl alcohol were increased while the increment of acids was reduced. The application of an EF treatment of 1 kV/cm to the oak barrels could probably enhance the chemical reaction and accelerate the aging process. The current study indicated that application of EF treatment directly on oak barrel maybe a promising and feasible technology for accelerating brandy maturation in the brandy industry.

Keywords: Electric Field, Brandy, Oak Barrel, Maturation

1. Introduction

Oak barrels are commonly used to store brandy for improving its quality in the brandy industry. For obtaining complex aroma, attractive colour and harmonious mouth feel, fresh distilled spirit are usually aged in oak barrels for many years to ease their harsh taste and pungent smell [1, 2]. During maturation, much more oak wood compounds are extracted by brandy that can significantly modify brandy's aroma [3, 4]. Moreover, the quantity of extraction compounds is affected by geographical origin and species of oak tree, and toasting and seasoning of the barrel [5, 6].

Several processes take place during brandy maturation in oak barrels, including extraction of phenol compounds from wood; depolymerizing of structural molecules to brandy; and occurrence of physical and chemical reactions between oak wood components and brandy, and the final product quality is significantly affected by these processes [1, 5].

More than 200 substances can be extracted from oak by brandy, which directly participate in the formation of the brandy's aroma. For example, the degradation of lignin can form the volatile phenols and phenolic aldehydes, and the thermolysis of cellulose and hemicelluloses can form furfural compounds [7-10].

In natural aging, it normally takes many years, resulting in low production efficiency and high cost. Therefore, research should be conducted to accelerate the aging process for shortening the aging time, speeding up the turnover ratio, and improving economic benefit.

Several physical methods to artificially accelerate wine aging process have been used, such as ultrasonic wave [11], gamma irradiation [12], ultraviolet visible light [13] and electric fields (EF) including pulsed electric field (PEF) [14, 15]. It was reported that these methods were efficient and non-thermal. Chang reported that treatments with ultrasonic wave, and γ-irradiation significantly accelerated the maturation of maize wine[11], as compared with standard maturation, and treatment with gamma irradiation appeared to be a suitable method for producing high quality rice wine [12]. In addition, it was also reported that treatment with 20 kHz ultrasonic waves aged rice wine much more quickly than standard aging [16]. Furthermore, Falguera et al. reported that it was possible to ferment without SO_2 by irradiating ultraviolet visible light before wine fermentation, which resulted in the final product being more stable [13].

Electric fields including pulsed electric field are also important physical methods for accelerating the aging processes of wines. Studies [17] indicated that when freshly fermented model wines were treated by PEF, colour intensity and total phenols in the wines could be enhanced. Also Liu et al. showed decrease in relative contents of fusel oil and increase in relative contents of total ester, total acid and phenyl ethyl alcohol in red wine after PEF treatment [18]. Zeng et al. reported that the total content of ester was increased after treated by EF in dry red wine [19], and the quality of a young wine was improved and the wine maturing time was shortened by using high voltage EF [20]. Other study also illustrated that the risk of alteration by microorganisms of genera *Brettanomyces* and *Lactobacillus* could be reduced by EF treatment. For PEF treatments [21], Zeng et al. reported that it was a promising technique to enhance chemical reaction in non-catalytic condition [22]. It was also possible to produce and store wines without SO_2 by sterilizing musts with PEF treatment [23], and the concentration of most phenolic compounds in young red wine could be increased after treatment with PEF [14]. In addition, Puértolas et al. demonstrated that PEF treated wine had higher contents in flavan-3-ols, flavonols and hydroxycinnamic acids, and derivatives comparing with the control one [24]. Finally, Puértolas et al. showed that wines obtained from PEF-treated grapes produced higher anthocyanin content than control wines after storage for 2 months in bottles as the extraction of anthocyanins was accelerated by PEF treatment [15].

Despite the above studies, little research is focused on the effects of electric field directly on oak barrel to enhance brandy maturation. Until recently, Zhang et al. reported that applying an EF treatment could increase the content of aroma compounds during brandy maturation in 5-L oak barrels for 180 days [25]. Even so, the brandy aging time was too short so that the evolution trend of aroma compounds contents was not obvious; moreover, the real effect of EF cannot be identified with the amount of aroma compounds without compared with industrially used oak barrels. Therefore, in the current study, brandy aging in 5-L and 2-L oak barrels was prolonged to 15 months with EF directly acting on these barrels, effects of the EF application on the evolution of phenols, aldehydes, acids and esters in brandy were investigated, and the results were compared with those from industrial oak barrels (225-L). It should be noted that the purpose of using smaller barrels of 5-L and 2-L was to test and verify the concept and effectiveness of EF to accelerate the brandy aging process. The effects of EF on phenol compounds have been reported by Zhang et al. [26], and the compounds of aldehydes, acids and esters will be showed in this paper. The purpose of the study was to shorten the aging time, speed up the turnover ratio, and improve economic benefit, accelerating the brandy aging process in the brandy industry.

The compounds of aldehydes, acids and esters play an important role in the quality of brandy as their pronounced sensory effects, which are complicated mixture of a huge number of volatile compounds such as different alcohols, esters, aldehydes, acids, and ketones [6]. For example, Ethyl esters are important aroma compounds with pleasant fruity aromas, which are mainly synthesised during fermentation by yeasts, and during maturation, ethyl esters could be synthesised through esterification by corresponding acid and ethanol, and furfural could be degraded into furfural alcohol by means of biological mechanisms, resulting in an aroma quality shift. In addition, acetaldehyde is also an important sensory carbonyl compound, which constitutes over 90% of total aldehydes in wine [8]. The right amount of acetaldehyde is in favour of the aroma, but high levels of acetaldehyde are generally undesirable. Excessive acetaldehyde can also fortify the colour and flavour of brandy.

2. Method

2.1. Material

2.1.1. Barrels

Six 5-L and six 2-L new oak barrels were all purchased from Gaomi Genmei Wood Product Co., LTD (Weifang, China) with the same French oak *Q. petraea* from the Allier forest in France. The wood was naturally seasoned for 3 years, meanwhile during cooperage the wood was submitted to a medium toasting. Six 5-L barrels and six 2-L barrels were divided into two groups, respectively, i.e., group A and C as control (natural aging), and group B and D under EF treatment. The cellar temperature ranged from 15°C to 20°C with the relative humidity being controlled between 65% and 82%.

2.1.2. Brandy

The original brandy selected from Sun Spirit Winery Company (Yunnan, China) was a 2006 distilled spirits from Cabernet sauvignon grape wine with alcoholic percentage of 55% (v/v). The same conditions of humidity and temperature in the cellar were kept for all barrels.

2.1.3. EF Equipment

The EF equipment shown in Figure 1 with maximum output voltage and current of 50 kV and 60 mA, respectively, was designed by the PEF Team from South China University of Technology (Guangzhou, China), which generated a continuous square-wave with a frequency of 50 Hz.

The treatment chamber was composed of two parallel plate electrodes with dimension of 35×40 cm, which was placed in the two side of the oak barrel that was filled with brandy. The distance between the two parallel plate electrodes was 28 cm and 23 cm for 5-L and 2-L barrels, respectively. Due to the length of the 5-L barrel (d_1) was 27 cm and that of 2-L barrel was 22 cm, the edge thickness ($2d_0$) of both oak barrels was about 0.4 cm and the air space ($2d_2$) was about 0.6 cm. According to the classic dielectric physics theory, the effective electric field strength can be calculated by the following equation [25-27]:

$$2E_0d_0 + E_1d_1 + 2E_2d_2 = U \quad (1)$$

$$E_0\varepsilon_0 = E_1\varepsilon_1 = E_2\varepsilon_2 \quad (2)$$

where U (V) is voltage between electrodes, E_0 (V/cm), E_1 (V/cm) and E_2 (V/cm) is the electric field strength of oak, brandy (55% v/v ethanol-water solution), and air, respectively. In Eq. (2), ε_0, ε_1 and ε_2 is the dielectric constant of oak, brandy and air, which is about 2, 33 and 1, respectively. Therefore, the effective electric field strength of the brandy in 5-L and 2-L barrels is both about 1 kV/cm when treated by a voltage (U) of 50 kV.

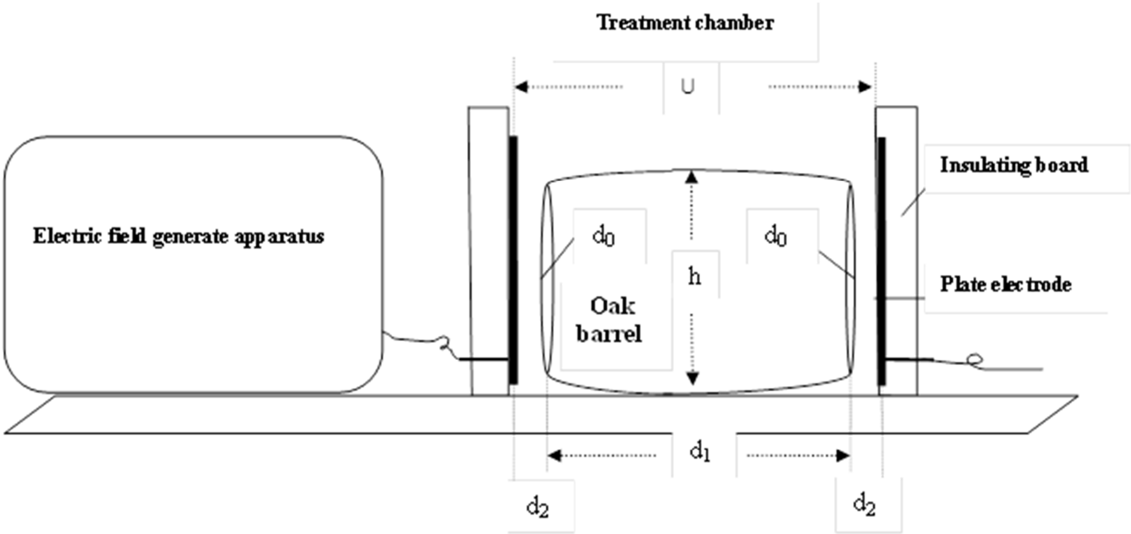

Figure 1. *EF equipment schematics used in this investigation.*

For chemical analysis, 100 mL brandy sample at about 5 cm in depth in the barrels was taken using a glass sucker every 1 month, of which 50 mL was used immediately for instrumental analysis, while the other 50 mL was retained for later observation. Moreover, the same original brandy was timely replenished to the constant volume in the barrels. A voltage of 50 kV was applied for the EF treatment barrels from 8 AM to 8 PM each day. The humidity was controlled by an automatic humidity control system MRF012 from Shenzhen Xinguangxin Company (Shenzhen, China), while the cellar temperature was maintained by an air conditioner.

The electrical conductivity, oxidation reduction potential and dissolved oxygen concentration at a distance of 5 cm deep from the surface in barrels were detected by Multi-parameter Analyzer DZS-707 (Shanghai Precision & Scientific Instrument Co., Shanghai, China).

2.1.4. Chemicals

Acetaldehyde, ethyl acetate, acetal, acetic acid, ethyl lactate, ethyl octanoate, furfural, ethyl caprate, ethyl laurate, β-phenethyl alcohol, octanoic acid and capric acid were obtained from Sigma-Aldrich Chemical Reagent Co., Ltd. (Shanghai, China). Absolute ethanol (purity > 99.8%) and methanol were purchased from Merck (Darmstadt, Germany) and all chemicals were of analytical grade.

2.2. Gas chromatography-Mass Spectrometry (GC-MS) Analysis

All samples were detected by SPME along with GC-MS. A Carbowax^{TM} -Divinylbenzene 65 μm fiber (Supelco, Bellefonte, PA, USA) was used for the absorption of volatiles. A thermoly/magnetic hotplate agitator SP131010-33Q from Barnstead Company (Dubuque, Iowa, USA) with a stirrer (3.0 mm × 10.0 mm) was employed for heating and stirring by assuming that the agitator was installed on the right side and the injection unit in the fiber exposition position on the right edge just touching the left rear edge of the agitator. 4-methyl-1-pentanol was prepared into 5 mg/L solution with 10% ethanol as internal standard, and 50 μL internal standard as well as 2 mL brandy sample were injected into a 4 mL screw-capped glass vial with a Teflon-rubber septum (12 mm, Red TFE/SIL, Agilent, Avondale, PA, USA), and then the mixed-liquid was stirred at 35°C for 10 min. Then a constant length of the fiber was exposed to the headspace of air for 5 min [28]. A 0.75 mm ID liner from Agilent (Avondale, PA, USA) was used for absorbing volatiles at 250°C for 10 min, and the splitter (at 1:20) was opened after 2 min.

A 6890 gas chromatograph associated with a 5975 quadrupole mass spectrometer from Agilent (Avondale, PA, USA) was used for GC-MS analysis. Electron impact mode was performed with 70 eV electron energy, and mass range of 25-400 m/z (2.35 scan/s) was used. The quadrupole temperatures were set at 150 °C, and the source was set at 230°C while keeping the transfer line at 220°C. The column (30 m × 0.32 mm) with 0.25 μm film thickness was a *DB-WAX* from Agilent (Avondale, PA, USA). Helium was used for carrier gas with a flow rate (0.7 mL/min, 30 cm/s). The oven temperature was firstly held at 35°C for 5 min, and then raised to 60 °C (2°C /min), 220 °C (5°C /min), and finally to 250°C (15°C /min) and holding for 5.5 min.

Calibration graphs were arranged for all the compounds by analyzing synthetic samples, which contained known amounts of odorants. Then the compounds were detected according to the relative time of retention to the internal standard as well as on the mass spectra (SCAN) of the reference patterns. The aromatic compounds (acetaldehyde, ethyl acetate, acetal, acetic acid, ethyl lactate, ethyl octanoate, furfural, ethyl caprate, ethyl laurate, β-phenethyl alcohol, octanoic acid and capric acid) were identified by the SPME-GC-MS.

2.3. Sensory Evaluation and Statistical Analysis

There are 12 experienced tasters were chosen to evaluate the brandy samples that centesimal score system of Clarity 10 scores, color 10 scores, aroma 30 scores, taste 40 scores and typicality 10 scores were used [29].

Variance analysis (ANOVA) was performed at p＜0.05 by Student's t-test with SPSS 13.0 software (SPSS Inc., Chicago, IL, USA) to study the effects of EF during brandy maturation.

3. Result

Aldehydes, acids and esters of naturally aged brandy

The 225-L oak barrels were used widely in the brandy industry. The values of aldehydes, acids and esters in brandy that were naturally aged for 36 months in 225-L oak barrels are shown in Table 1. For comparison, brandy from the same batch was also used in 5-L and 2-L new oak barrels treated by EF.

Table 1. *Amounts of aldehydes, acids and esters aged in 225-L industrially used oak barrels [a] (mg/L).*

Compounds	12 months	24 months	36 months
acetaldehyde	38.54±0.73	43.51±1.98	45.69±1.13
acetal	28.95±1.49	39.53±0.64	48.41±1.58
furfural	6.89±0.25	8.45±0.17	9.36±0.16
acetic acid	358.76±5.53	395.21±7.18	416.42±8.97
octanoic acid	24.38±0.38	33.62±0.41	38.41±0.47
capric acid	38.70±0.51	55.61±0.64	59.42±0.55
ethyl acetate	78.33±1.17	87.14±1.73	94.20±1.89
ethyl lactate	129.75±4.05	150.36±3.62	165.79±2.54
ethyl octanoate	105.69±2.87	131.70±2.19	143.05±3.08
ethyl caprate	41.28±1.24	48.94±0.96	51.37±1.31
ethyl laurate	36.08±0.62	42.55±1.03	51.17±0.98
β-phenethyl alcohol	118.57±3.05	123.05±2.26	138.19±2.24

[a] Values are the means ± standard deviation (n = 3). Different letters in the same row and section are significantly different ($p < 0.05$).

Aldehydes

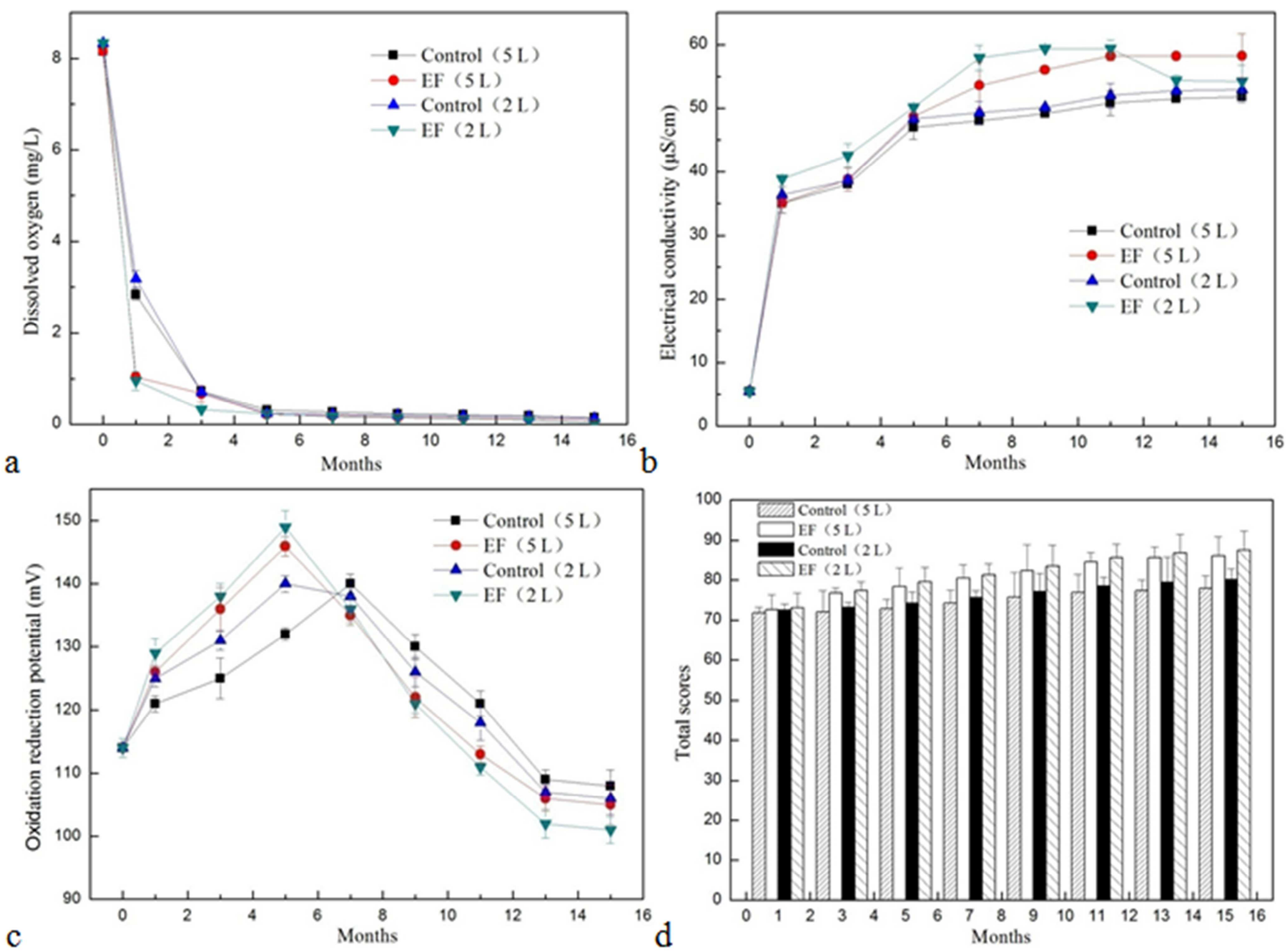

Figure 2. *Effect of EF on aldehydes and acids during maturation in oak barrels.*

Aldehydes including acetaldehyde, acetal and furfural in control (group A and C) brandy and EF treated (group B and D) samples during 15 months maturation in 5-L and 2-L oak barrels are shown in Figure 2. It can be seen that the general trend of acetaldehyde, acetal and furfural in both barrels decreased first, and then increased gradually with aging time.

Acetaldehyde is an important aroma component in brandy, which mainly comes from the oxidation of alcohol [30].

Acetaldehyde could form acetal by reaction with ethanol, which could also form acetic acid by its own oxidation. However the content of acetaldehyde should be controlled for its strong irritating smell in brandy [32].

Figure 2 shows that the content of the acetaldehyde in brandy decreased gradually, and reached the lowest value in 7 months. It was also explored that the EF treatment enhanced the decreasing of acetaldehyde. For example, acetaldehyde content of the brandy treated by EF was 2.20 mg/L, which was 0.53 mg/L lower than those of the control brandy after 7 months of maturation in 5-L and 2-L barrels, respectively.

The results in Figure 2 also show that the smaller size of barrel was in favour of the decreasing of acetaldehyde, which was due to the fact that acetaldehyde could be easily infiltrated to the barrel outside for the good permeability of new barrel in the first 7 months, thus the amount of infiltration, with the addition of formation of acetal and acetic acid was higher than the generation of acetaldehyde.

In the later 8 months, the microporous structure of oak barrel was blocked with the accumulation of infiltration, so the infiltration rate was reduced. Moreover, the amount of acetaldehyde generated by oxidation of ethanol was higher than that by volatilization, leading to an increasing trend in the acetaldehyde content. The water and organic compound molecules were ionized and excited in brandy when treated by EF, and then free radicals were generated. Therefore, the transformation from acetaldehyde to acetic acid and acetal was promoted.

Acetal was constituted by additional reaction of acetaldehyde and ethanol, which has a delicate fragrance, and in favour of balance and coordination of wine with acetaldehyde [30]. Figure 2 shows that the general trend of acetal exhibited a decrease in the first 6 months, and then increased all the time. For example, acetal contents of the brandy treated by EF were 9.8% and 20.9% higher than those of the control after 11 and 15 months of maturation in 5-L barrels, respectively, while they were 27.0% and 34.7% higher than those of the control after 11 and 15 months of maturation in 2-L barrels, respectively. This was due to greater inside specific surface area for smaller barrels.

Furfural is the most important derivative of the furan ring system with bitter taste and is one of the important brandy aroma substances [30]. Furfural mainly comes from the pyrolysis of cellulose and hemicellulose during oak barrel baking as well as degradation of residual sugar in distillation process. Figure 2 shows that furfural decreased in the first 7 months, and then increased all the time. The reasons for these changes were that furfural could be easily infiltrated to the outside of barrel as the good permeability of new barrel in the first 7 months, with the blocking of micropores in the later stage of aging, the formation reaction of furfural was promoted by EF, leading to the increase in the content of furfural.

Acids

Acetic acid is a brandy aroma component that can obviously improve the flavour of brandy with a moderate amount [30, 31]. However, its content should be controlled because of its irritating smell. Acetic acid mainly comes from oxidation reaction in brandy with some from the distillation process of original brandy. As shown in Figure 2, it can be seen that the content of acetic acid in both barrels increased gradually with aging time. Meanwhile, EF treatment significantly reduced the increment. In addition, evolution of acetic acid concentration was different between 5-L and 2-L oak barrels, because the esterification reaction of acetic acid with alcohols was promoted by EF, and at the same time the diffusion of acetic acid was also accelerated so that acetic acid content was reduced. Furthermore, it can also be seen that the content of octanoic acid and capric acid increased gradually with aging time. Meanwhile, EF treatment significantly reduced the increment. The reason was that the esterification reaction of octanoic acid and capric acid with alcohols was promoted by the application of EF.

Esters and β-phenethyl alcohol

Esters are important aroma compounds in brandy, which mainly include ethyl acetate, ethyl lactate, ethyl caprylate, ethyl caprate and ethyl laurate. It was reported that the amount of three domain esters in grape wine were increased by at least 4.1% after EF treatment with 600 V/cm for 3 min, and then esterification in wine was apparently enhanced by the application of EF [20]. As esterification is a kind of reversible reaction, it should reach the reaction equilibrium within several hours and the conversion rate of alcohols can reach over 85%, if suitable catalyst exists and reaction takes place under extreme conditions [33]. However, it always takes a long time to reach the esterification equilibrium during maturation.

In order to study the connection among the esters during maturation, in the current, clustering analysis [34] was conducted on the evolution trend of the concentration of esters, in which 5 kinds of esters were divided into two categories by clustering. The first category included ethyl lactate, ethyl caprylate, ethyl caprate, and ethyl laurate; and the second included ethyl acetate. The general trend of the first category exhibited an increase all the time and EF treatment significantly increased their concentration. On the other hand, the second category increased first and then remained unchanged with EF treatments exhibiting an apparent positive effect. That was because the esterification reaction of ethyl lactate, ethyl caprylate, ethyl caprate, and ethyl laurate did not reach the reaction equilibrium all the time, but the esterification reaction of ethyl acetate reached the reaction equilibrium when treated by EF. In addition, the concentration of esters in both barrels showed significant difference between EF treated samples and control ones ($p < 0.05$). Results showed that after being treated by EF the content of esters were increased.

By comparing results from Table 1 and Figure 3, it can be seen that the content of ethyl acetate in 225-L natural aging oak barrels used in the brandy industry for 12 months was exceeded by the control brandy in 5-L and 2-L barrels for 10 months of natural aging, while the EF treated sample in 5-L and 2-L barrels aged for 9 months reached the same level of ethyl acetate contents in 225-L oak barrels naturally aged for 12 months, and the contents in both small barrel aging for 12 months exceeded that of 225-L barrel natural aging for 24 months. Moreover, the content of ethyl acetate in 5-L and 2-L barrels showed significant difference between EF treated groups and control ones ($p < 0.05$).These implied that the esterification reaction was promoted by EF application.

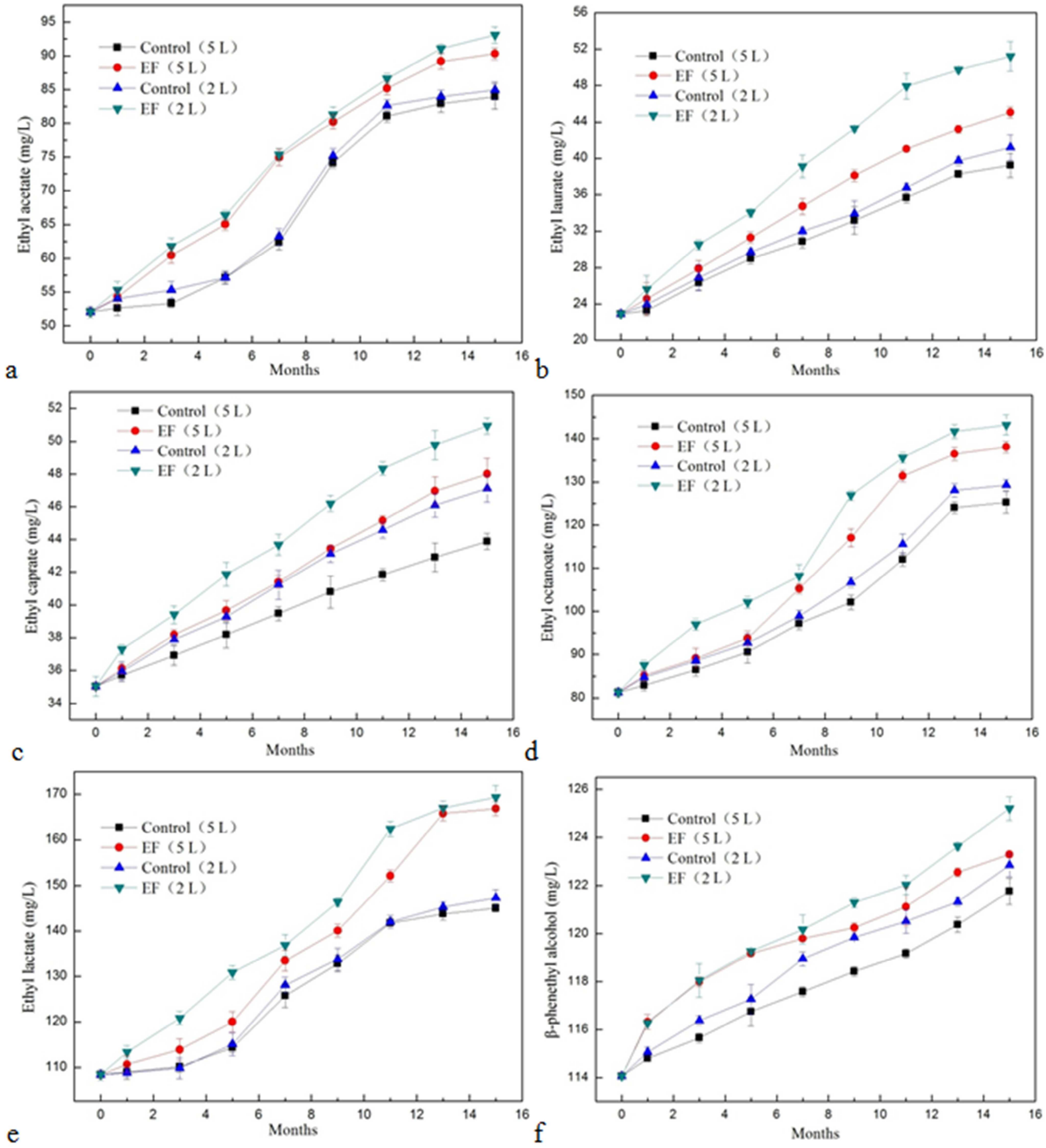

Figure 3. *Effect of EF on esters and β-phenethyl alcohol during maturation in oak barrels.*

β-phenethyl alcohol plays an important role in brandy aroma formation [31]. It can be seen from Figure 3 that the content of β-phenethyl alcohol in both barrels increased gradually, and EF treatment appreciably enhanced the increment. By comparing results from Table 1 and Figure 3, it can be seen that the content of β-phenethyl alcohol in 225-L natural aging oak barrels for 12 months was exceeded by the control brandy in 5-L barrels for 10 months of natural aging and 2-L barrels for 7 months of natural aging. Moreover, it was observed that the EF treated sample in 5-L and 2-L barrels aged for 4 months exceed the level of β-phenethyl alcohol compared with that naturally aged for 12 months in 225-L barrels. Moreover, the content of β-phenethyl alcohol in both barrels showed significant difference between EF treated groups and control ones ($p < 0.05$).

Kinetic model of aromatic compounds

For studying the mechanism and effects of EF treatments on the compounds of aldehydes, acids and esters, kinetic model of aroma compounds are needed. For describing the evolution of aldehydes, acids and esters concentration in brandy aging process, logistic model was used in the current study.

Table 2 shows the logistic model describing the internal relations among various compounds, of which model parameters were obtained by statistical analysis using Student's *t*-test with SPSS 13.0 software (SPSS Inc., Chicago, IL, USA). By using linear regression analysis, the regressed model parameters as a function of electric field intensity (E) and barrel volume (V) are listed in Table 2. As shown in Table 2, the electric field intensity coefficient is larger than that of oak barrel volume, indicating EF treatment played a much more effects than the size of barrel for formation of aldehydes, acids and esters. Moreover, the electric field intensity coefficients are all positive when the brandy was treated by EF, indicating that EF played a positive role in promoting the increase of the content of aroma compounds.

Table 2. *Logistic model of aldehydes, acids and esters as function of E and V in brandy.*

Aroma compounds	Regression equation
acetaldehyde	$\frac{dc_1}{dt}=(0.0665V+0.9989E)c_1+(0.2573V+4.5366E)c_2+(0.0240V+0.1517E)c_4$
acetal	$\frac{dc_2}{dt}=(0.4234V+5.0360E)c_1+(1.3683V+17.0952E)[1+(0.0018V+0.0140E)c_2]c_2$
furfural	$\frac{dc_3}{dt}=(1.2308V+3.1371E)c_3$
acetic acid	$\frac{dc_4}{dt}=(0.1036V+0.9153E)[1+(0.1036V+0.9153E)c_4]c_4+(0.2376V+5.5221E)c_4c_1c_7c_0$
octanoic acid	$\frac{dc_5}{dt}=(0.0037V+0.4624E)[1+(0.0418V+1.0917E)c_5]c_5+(0.1639V+3.2213E)c_5c_9$
capric acid	$\frac{dc_6}{dt}=(0.1072V+2.5594E)c_6[1+(0.00619V+0.0668E)c_6]+(0.3682V+5.1981E)c_6c_{10}$
ethyl acetate	$\frac{dc_7}{dt}=(0.1497V+1.0046E)[1+(0.0015V+0.0561E)c_7]c_7+0.0011Ec_4c_0$
ethyl lactate	$\frac{dc_8}{dt}=(0.0948V+0.4271E)[1+(0.0017V+0.2649E)c_8]c_8+(0.6182V+3.9061E)c_0$
ethyl octanoate	$\frac{dc_9}{dt}=(3.4852V+12.5884E)[1+(0.0021V+0.0948E)c_9]c_9+(0.1518V+7.6049E)c_5c_0$
ethyl caprate	$\frac{dc_{10}}{dt}=(0.3088V+1.3022E)[1+(0.0060V+0.7153E)c_{10}]c_{10}+(0.0013V+0.0076E)c_6c_0$
ethyl laurate	$\frac{dc_{11}}{dt}=(0.0588V+0.2598E)[1+(0.0050V+0.4713E)c_{11}]c_{11}+(0.2644V+7.8417E)c_0$
β-phenethyl alcohol	$\frac{dc_{12}}{dt}=(0.0699V+0.3417E)[1+(0.0019V+0.0531E)c_{12}]c_{12}$

Dissolved oxygen, electrical conductivity and oxidation reduction potential

Dissolved oxygen refers to the molecules oxygen in wine, which has important effects on chemical reaction in wine aging process [35-39]. Electrical conductivity is characterization of the wine conductivity, and proportional to the number of free ions in wine [39, 40].

Oxidation reduction potential indicate the of redox state, the value of oxidation reduction potential in new wine is higher than aged wine. Moreover, the larger of the value, the easier of chemical reaction, meanwhile, the low value relate to weak taste stimulation [40, 41].

Figure 4a shows the evolution of dissolved oxygen in brandy during maturation. It can be seen that the content of dissolved oxygen in 5-L and 2-L barrels decreased gradually, and the EF treatment significantly enhanced the decrement of dissolved oxygen. For example, when treated by EF, the content of dissolved oxygen was 8.9%、35.6% and 42.9% lower than the control brandy in 3, 9 and 15 months aging, respectively. Moreover, it was 54.8%、28.5% and 75.0% lower than the control in 2-L barrels, respectively. The possible reason is that the oxidation reaction was promoted, thus consumption of dissolved oxygen was accelerated.

The electrical conductivity was shown in Figure 4b with a trend of increased first and then stable in both barrels, while the trend of oxidation reduction potential is first increased and then decreased (Figure 4c). Meanwhile, the peak value was reached at 8 and 7 months in 5-L and 2-L barrels, but it was reached at 6 month in the brandy treated by EF in both barrels. It was probably explored that aging process of brandy was accelerated by the EF treatment, and the time of reaching balance of oxidation reduction potential was shortened.

Overall, the content of oxidation reduction potential and electrical conductivity was no significant difference in brandy treated by EF.

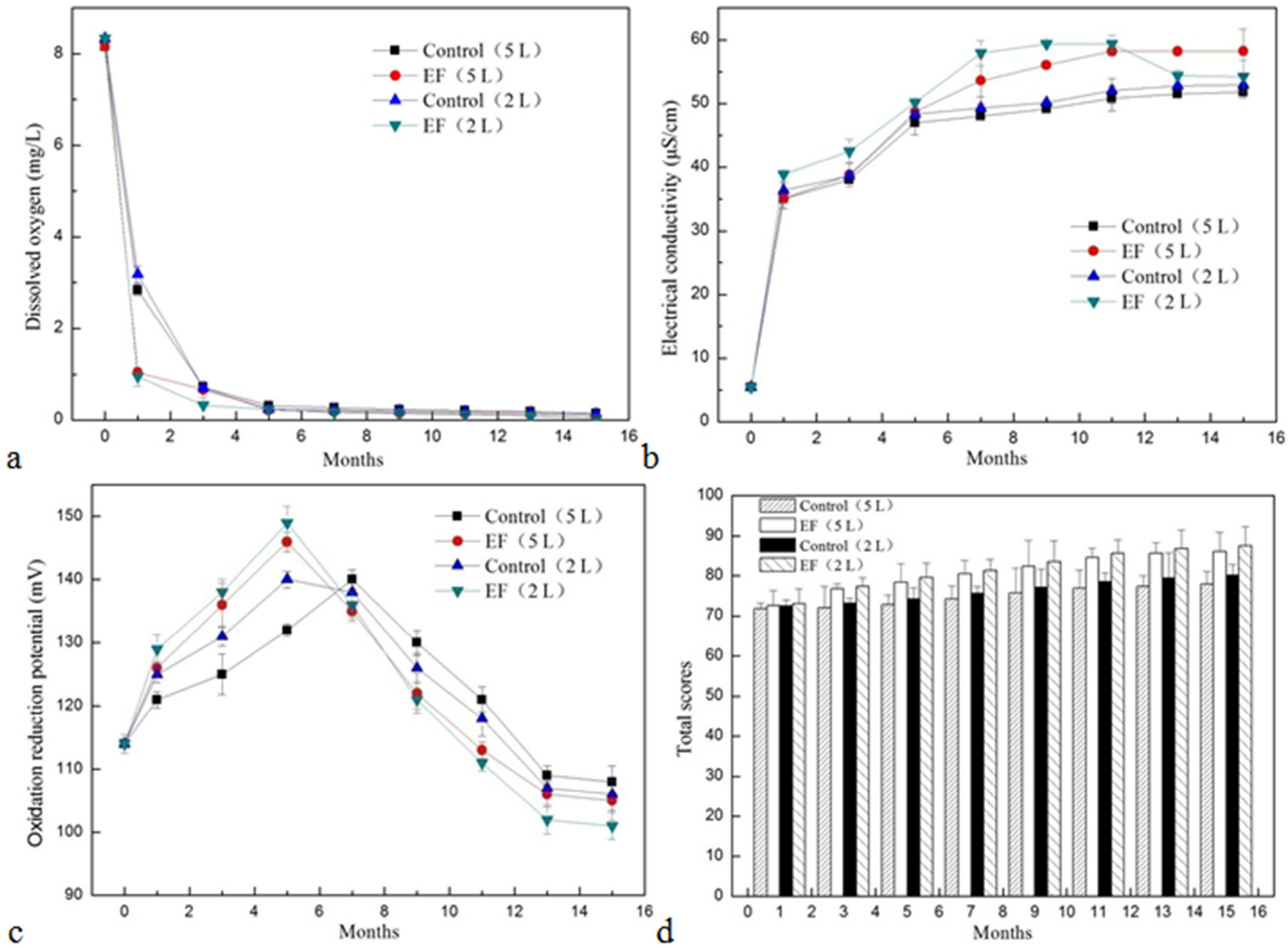

Figure 4. *Effect of EF on dissolved oxygen, electrical conductivity and oxidation reduction potential and total scores.*

Sensory analysis

The sensory evaluation of aged brandy samples showed that the brandy treated by EF was better valued than the controls. The scores of clarity, color, aroma, taste and typicality, in EF treated and control brandy samples during 3, 9 and 15 months aging in 5-L and 2-L oak barrels are shown in Table 3.

Table 3. *Sensory evaluation of aged brandy samples with and without EF treatments.*

		A	B	C	D
3 months	Clarity	9.02±0.11	8.91±0.22	9.03±0.11	8.81±0.12
	Color	7.40±0.31	7.92±0.21	7.62±0.16	7.72±0.19
	Aroma	21.53±1.09	23.72±1.13	21.91±2.11	23.93±2.08
	Taste	27.06±1.12	28.83±1.07	27.43±1.09	29.32±1.11
	Typicality	7.21±0.14	7.42±0.21	7.34±0.14	7.62±0.12
9 months	Clarity	9.07±0.09	8.93±0.12	8.91±0.21	8.62±0.12
	Color	7.60±0.13	8.11±0.18	7.92±0.13	8.12±0.21
	Aroma	22.63±0.86	25.50±0.95	23.64±1.12	26.80±1.05
	Taste	28.72±1.49	31.93±1.81	29.13±1.18	32.11±2.10
	Typicality	7.81±0.22	7.93±0.15	7.60±0.23	7.85±0.16
15 months	Clarity	9.12±0.24	9.14±0.11	9.17±0.33	9.11±0.17
	Color	7.82±0.22	8.21±0.31	8.24±0.26	8.42±0.12
	Aroma	23.40±1.05	27.93±2.03	24.90±1.32	28.32±1.08
	Taste	29.61±1.18	32.59±1.39	29.91±2.07	33.31±1.10
	Typicality	8.06±0.11	8.33±0.14	8.21±0.23	8.44±0.12

[a] Values are the means ± standard deviation (n = 3). Different letters in the same row and section are significantly different ($p < 0.05$).

It can be seen that the scores of clarity, color and typicality in both barrels increased with aging time, showed slight differences but the scores of aroma and taste. On the other hand, the treated brandy samples showed greater aromas and taste than the control samples, which indicated that more aromatic compounds were gained and retained in brandy when treated by EF. For example, the scores of aroma in the brandy treated by EF were 10.2%, 12.7%, and 19.4% higher than those of the control brandy after 3, 9 and 15 months of maturation in 5-L barrels, respectively, while for 2-L barrels, the scores were respectively 9.2%, 13.4% and 13.7% higher than the control. On the other hand, the scores of taste in the brandy treated by EF were 6.5%, 11.2% and 10.1% higher than those of the control brandy after 3, 9 and 15 months of maturation in 5-L barrels, respectively, while it was 6.9%, 10.2% and 11.4% higher than the control in 2-L barrels, respectively.

Figure 4d shows the total scores of brandy during maturation, it can be seen that the scores of brandy in both size barrels increased gradually, and EF treatment enhanced the increment of the scores. For example, the scores of the brandy in 5-L barrels was 8.8% and 10.7% higher than those in 5-L barrels after 9 and 15 months of natural aging, respectively, while in 2-L barrels it was respectively 8.3% and 9.2% higher than the controls.

The results obtained from sensory evaluation were highly agreement with the results that after being treated by EF the content of most beneficial materials on brandy quality such as tannins, total phenols, esters and β-phenethyl alcohol were increased while the increments of acids were reduced.

4. Discussion

Reaction enhancement

A series of complex chemical reactions take place during brandy maturation, such as oxidation reaction, esterification reaction, condensation reaction and polymerization reaction. Meanwhile, brandy becomes more pleasant and steady due to these reactions.

During natural aging, polymer hydrogen bonding can be formed between polar molecules and ethanol molecules, which are relatively stable, so the activity and the probability of collision between reactants are limited [39-42]. Colliding molecules should have enough energy before chemical reaction occurs. In order to collide with others, molecules must absorb enough energy to become active, which cannot be achieved under natural aging conditions, leading to the slowing of the natural aging process.

When treated by EF, the molecules in brandy would absorb the energy with electron transition to high energy level, which could result in the breakage of hydrogen bonding, causing molecules to escape from the molecular cage, therefore the chemical reaction rate was significantly enhanced [25].

Brandy in oak barrels could also infiltrate through the microporous structure of the oak wood during aging. There is oxygen infiltrating into the brandy, which could encourage the oxidation-reduction reactions. At the same time, some volatile substances including aldehyde and acetic acid would exhaust to outside.

EF energy

The influence of temperature change could be ignored when oak barrel was treated by EF directly as the input energy from the EF only resulted in a slight temperature increase of the brandy (about 0.3-0.5 °C/d). The input energy could accelerate the molecular motion and substance exchange in the oak barrels. According to the Gauss law, the energy can be described as follows [47, 48]:

$$W_e = w_e V \tag{3}$$

where W_e (J) is energy, V (L) is volume of oak barrel, and w_e (J/m^3) is energy density. Generally, the energy density can be expressed as:

$$w_e = \frac{1}{2} ED \tag{4}$$

where E (kV/m) is electric field strength，D (C/m^2) is electric displacement, and the electric displacement can be expressed as follows:

$$D = \varepsilon E \tag{5}$$

where ε is dielectric constant. By combining Eqs (3)-(5), W_e can be shown as:

$$W_e = \frac{1}{2} \varepsilon E^2 V \tag{6}$$

When oak barrel was treated by an electric voltage of 50 kV directly, the energy input was about 8250 J/d and daily electric energy per unit volume was 1650 J/L in 5-L barrels. Meanwhile, the energy input was about 3993 J/d and daily electric energy per unit volume was 1997 J/L in 2-L barrels.

The energy input from the electric field only resulted in a slight temperature increase of the treated brandy. The daily temperature increment was calculated to be about 0.4°C and 0.5°C in 5-L and 2-L oak barrels, respectively. However, the temperature would be restored to original state after 12 hours untreated by EF. Thus the influence of temperature change could be ignored.

As the energy needed by oxidation-reduction, esterification, condensation and polymerization reactions and substance exchange between inside and outside barrels was supplied by EF, the reactions could be promoted. Because the daily electric energy per unit volume in 2-L barrels was higher than that in 5-L barrels, the EF effects in promoting reactions was more obviously in 2-L barrels.

5. Conclusion

The application of an EF treatment of 1 kV/cm to the oak barrels enhanced the chemical reaction. The concentration of esters and β-phenethyl alcohol in the brandy were higher than untreated samples after being treated by EF for up to 15 months. Meanwhile, the increment of acids was significantly reduced by EF treatment. In addition, the EF treated samples in 5-L and 2-L barrels for 9 months exceeded the content of ethyl acetate in 225-L oak barrels naturally aged for 12 months. Thus, EF treatment possibly has a great effect to accelerate the aging process in the brandy industry.

The kinetic model of aldehydes, acids and esters followed the logistic model, and regression results demonstrated that

EF treatment played a possibly positive role in formation of aldehydes, acids and esters, which had a much more fortified impact than the size of barrel. It has been demonstrated that smaller size of barrels or large inside specific surface area could promote the generation of acetal, furfural, β-phenethyl alcohol and esters.

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