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pH Modification of Cynthiana Wine Using Cationic Exchange

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Membrane and resin ion-exchange technology was used for pH reduction and production of Cynthiana (*Vitis aestivalis*) wine, which can have high pH and high titratable acidity. Wine attributes were monitored during storage for 6 months at 21 and 38 °C. Nonadjusted Cynthiana wine (pH 4.1) was compared to ion-exchange-adjusted wine (pH 3.5). Ion exchange lowered the pH and potassium content and increased the titratable acidity of wine without having detrimental effects on color and phenolics. No trends were found to indicate differences between manufacturers of membranes and resins on pH-adjusted Cynthiana wine. Wine treated with membrane ion exchange was higher in color density and phenolics than resin-treated wine. During storage at both temperatures, the quality of the wine decreased, with greater degradation at 38 °C. Ion exchange decreased the pH of Cynthiana wine without negatively affecting wine quality attributes. A panel familiar with characteristics of Cynthiana wine found that the color and flavor of the pH-adjusted wine was improved.

KEYWORDS: Cynthiana wine; ion exchange; resins; membranes

INTRODUCTION

Cynthiana (*Vitis aestivalis*) is a vigorous, disease-resistant grape variety that is native to North America and produces a deep-colored and full-bodied red wine. Production of Cynthiana is better in regions where the growing season is extended. Cynthiana wine is commercially produced in Arkansas, Illinois, Indiana, Kansas, Louisiana, Maryland, Missouri, Oklahoma, New Jersey, Pennsylvania, Tennessee, Texas, West Virginia, and Virginia (*1*).

A grape must that is to be made into a wine should have an optimum pH less than 3.5 and a titratable acidity of 5.5−7.5 g/L of tartaric acid (*2*). Cynthiana grapes from most regions commonly have both high pH (3.5−3.9) and high titratable acidity (8.5−14 g/L tartaric acid). The concurrence of high titratable acidity with a high pH is due to the presence of weak acids, tartaric and malic, in Cynthiana musts. Tartaric and malic acids are present predominately in the undissociated form; therefore there are few free hydrogen ions (H^+) in solution, and the pH is relatively high for wine. However, while measuring titratable acidity, both the dissociated and undissociated H^+ ions are measured (*3*).

The pH of Cynthiana wines can be affected by other factors, such as soil type, rootstock, vine vigor, leaf shading, cultivar, crop level, and seasonal variations (*2*). A high concentration of potassium ions (K^+) in juice and wine is associated with high pH (*4*). Potassium from the soil is transported to the berry, where K^+ increases the net positive charge in solution, thereby forcing H^+ to reassociate with tartaric and malic acids. This net loss of H^+ ions results in a pH increase during berry ripening (*3*). Increased pH of Cynthiana wines is also attributed to the high malic acid content that can result in spontaneous malolactic fermentations (*2*). The conversion of each malic acid to lactic acid causes the loss of one titratable hydrogen (*5*). Malolactic fermentation in *Vitis vinifera* wine results in an increase of up to 0.3 pH unit, but since Cynthiana wine has more malic acid, the pH can increase by up to 0.6 pH unit.

Control of pH and acidity in winemaking is imperative for maintaining quality during storage. Enhanced red color, brightness, and fresh, fruity flavors are associated with low-pH wines. High pH negatively affects red wine color and flavor and decreases microbial and chemical stability and storage life (*2*, *5*−*10*). The pH of some wines can be reduced by addition of tartaric acid; however, tartaric acid addition is not a viable option for Cynthiana wine, since the titratable acidity is already high. Wines with high pH and high acid content cannot be adjusted by acid addition because the wines become too tart to be palatable. The addition of tartaric acid to reduce the pH is also chemically impractical. For the pH range of Cynthiana wines (3.5−3.9), the added acid will ionize to give a proton yield of only 32−46% (*5*). The reduction of pH can also be achieved without the increasing tartness associated with acid addition by using resin and membrane ion exchange.

Ion Exchange. Resin-based ion exchange has been used to adjust acidity and pH and to tartrate-stabilize wines since the 1950s (*8*, *11*−*13*). In-winery and mobile membrane system units are available to tartrate-stabilize wines in the United States and Europe (*14*). Bureau of Alcohol, Tobacco, and Firearms regulations permit cation exchange and anion exchange, provided that inorganic anions are not added to the wine (*15*). Ion-exchange treatments cannot lower the pH below 2.8 or raise

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the pH above 4.5 (*15*). The most common use of ion exchange involves cation-exchange resins in the H^+ form, for increasing acidity and removing K^+ from juice or wine. Ion exchange is effective because juice or wine pH is more sensitive to changes in concentrations of K^+ than similar molar changes in the principal organic acids, tartaric and malic (*2*).

Resins. Cation-exchange resins have been used to impart tartrate stability in nonpremium wines. In this process, sodium or hydrogen ions replace potassium ions in wine. If H^+ is used to replace K^+ in Cynthiana wines, the pH of the wine will be reduced without the addition of acid. An additional benefit arises from the reduction in the concentration of K^+, which decreases the solubility coefficient and the likelihood of potassium bitartrate precipitation at cool temperatures (*2*, *5*, *13*, *16*, *17*).

Unfortunately, resins can deplete nutrients from juice and subsequently affect fermentation (*5*). Flavor compounds and color may also be removed, which reduces the flavor and bouquet of wines, making resin-based ion exchange less suitable for premium wines (*2*, *5*, *11*, *16*). Ion-exchange resins require regeneration mainly with sulfuric acid and extensive rinsing of resin beds as well as monitoring equipment (*11*, *13*, *16*). There is also concern about disposal of the waste stream from the regeneration process.

Membranes—Electrochemical Cells. Ameridia, Division of Eurodia Industrie, Wissous, France, has in-winery and mobile units in Europe and the United States that use ion-exchange membranes in a proprietary technology to tartrate-stabilize wines (*2*, *14*). The process removes tartrate, potassium, and calcium ions in wine and guarantees tartrate stability without having a significant impact on wine quality. Since the electrochemical cell uses ion-selective membranes rather than a resin bed, there is no resin bed to adsorb desirable components or to regenerate. Several patents have been issued for the use of ion-exchange membranes with wine in the United States and Europe (*12*, *18*−*21*).

Due to the lack of information both on ion-exchange technology for use in Cynthiana wine and on the storage stability of Cynthiana wine, the benefit of pH reduction of Cynthiana wine using two ion-exchange systems (membrane versus resin) was evaluated, and wine attributes resulting from the use of three ion-exchange membranes and two resins from different manufacturers were compared.

MATERIALS AND METHODS

Wine Production. Cynthiana grapes were obtained from the research vineyard at the Arkansas Agricultural Experiment Station, Fayetteville, AR, for wine production. Grapes were hand-harvested and placed into storage at 2 °C for approximately 36 h. Grapes were allowed to warm to 21 °C before processing. Cynthiana grapes were crushed, destemmed, and placed in 120-L plastic containers with food-grade polyethylene liners for fermentation. The liners were partially sealed with tape. The must cap was punched down twice daily through the bag. Initial juice composition was analyzed. After crushing of the grapes, 0.26 g/L of dehydrated commercial D254 yeast and 0.26 g/L of Fermaid were added (Lallemand, Inc., Montreal, Canada). The musts were batch fermented at 21 °C on the skins until dryness (0 °Balling). The must was pressed in a 70-L Enrossi bladder press at 4 bar (Enoagricol Rossi s.r.l., Calzolaro, Italy), and the wine was collected into glass carboys with fermentation locks. All wine was inoculated with malolactic bacteria EQ 54 MBR (Lallemand S.A., St. Simon, France) after primary fermentation to induce malolactic fermentation. The wine was racked three times to clarify and remove spent yeast cells. After completion of the malolactic fermentation, sulfur dioxide (100 mg/L) was added as potassium metabisulfite. The finished wine was further divided into ion-exchange treatments, filtered using a Microfine 10-in. depth-type filter (Presque Isle Wine Cellars, North East, PA), bottled into 375-mL bottles, and stored at 21 or 38 °C until analyzed.

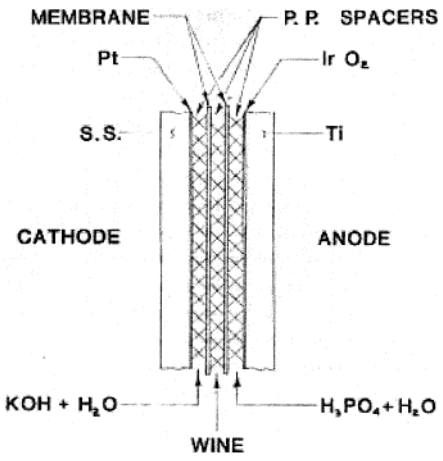

Figure 1. Diagram of three-cell electrochemical unit for ion exchange using membranes.

Ion-Exchange Column System. A 60- × 4.8-cm Chromaflex glass column (Kimble/Kontes, Vineland, NJ) with two end fittings and 20-μm-porosity HDPE bed supports was packed with 500 g of resin beads. The column was flushed with nitrogen, and wine was pumped into the column at a flow rate of 700 mL/min using a peristaltic pump with food-grade tubing. Resins were regenerated using a 1.0 N sulfuric acid solution. Two resin types, Amberlite IR120 H (Rohn and Haas Co., Philadelphia, PA) and Lewatit S 112 MB/H (Bayer Corp., Pittsburgh, PA), were evaluated in this study.

Ion-Exchange Membrane System. An electrochemical three-cell ion-exchange unit was constructed using 26-mm Plexiglas, a platinum cathode, an iridium oxide anode, and two cation membranes. This unit is based on U.S. patent 4,374,714 (*20*). The ion-exchange membranes separate the middle cell from adjacent cells. As direct current is passed across the cell, H^+ is exchanged for K^+ in the juice or wine, and K^+ moves to the catholyte. Flow rate is balanced in each cell by using a peristaltic pump with three pump heads. Each membrane in the unit has a surface area of 250 cm^2. Flow rate through the system is variable up to about 700 mL/min. The anolyte solution is H_3PO_4, the catholyte is KOH, and the middle cell is wine (**Figure 1**). Three cationic membranes, Nafion 424 (Dupont−Ion Power, Inc., Bear, DE), Ionics CR 61-CMP-447 (Ionics Inc., Watertown, MA), and Ultrex CMI-7000 (Membranes International Inc., Glen Rock, NJ), were evaluated in this study.

pH, Titratable Acidity, and Soluble Solids. Wine pH was measured with a Beckman model 250 pH meter (Beckman Coulter, Inc., Fullerton, CA). Titratable acidity (tartaric acid in grams per liter) was measured by placing 5 mL of wine sample into 125 mL of deionized water and titrating with 0.1 N sodium hydroxide to an endpoint of pH 8.2. Soluble solids (°Brix) were measured using a Bausch & Lomb Abbe Mark II refractometer (Scientific Instrument, Keene, NH).

Color Analyses. Color measurements were made using a Unicam Helios Beta UV−vis spectrophotometer (Unicam, Cambridge, United Kingdom). Absorbance measurements were made at 420 and 520 nm for browning and red color, respectively. The absorbance measure at 520 nm estimated the concentration of red-colored anthocyanins, whereas the absorbance measure at 420 nm estimated the concentration of yellow-brown pigments present in the wine (*22*). Total red pigment color (OD_{520}^{HCl}), color density ($OD_{520} + OD_{420}$), and total phenolics ($OD_{280} - 4$) were measured.

Conductivity. Conductivity (expressed as siemens per centimeter) was measured using an Orion model 550A conductivity meter (Orion Research, Inc., Boston, MA). The standard measure of conductivity is defined by the reciprocal of the resistance in ohms, measured between opposing faces of 1 cm^3 of liquid at a specific temperature. Wine conductivity is pH dependent and relies on K^+ concentration. Potassium bitartrate is monitored by changes in wine conductivity primarily due to loss of K^+ from solution as tartrate crystallization occurs.

Table 1. Main Effects of Ion-Exchange pH Adjustment and Storage on Cynthiana Wine Attributes

treatment	pH	titratable acidity (g/L)	conductivity (μS/cm)	potassium (mg/L)	color density	total red pigment color	total phenolics
			21 °C				
pH adjustment							
control	4.11 a[a]	6.00 b	3937	2267	60.18 b	31.78 a	27.68
ion exchange	3.49 b	8.00 a	2525	1294	68.04 a	30.96 a	26.33
storage (months)							
0	3.75 c	7.30 a	3343	1560	77.35 a	41.77 a	49.49
2	3.83 a	7.30 a	3239	1771	62.22 b	36.29 b	43.39
4	3.81 b	6.80 b	3252	1846	57.97 c	26.70 c	11.26
6	3.80 b	6.60 c	3090	1944	58.98 c	20.73 d	3.87
			38 °C				
pH adjustment							
control	4.09	5.80	3910 a	2265	55.58	27.93 a	16.10 a
ion exchange	3.48	7.80	2569 b	1263	59.04	27.29 a	15.57 b
storage (months)							
0	3.79	7.20	3372 a	1530	54.68	41.04 b	44.68 a
2	3.79	7.10	3274 a	1743	57.21	44.24 a	7.97 b
4	3.80	6.60	3248 a	1814	58.02	13.97 c	6.48 c
6	3.77	6.30	3064 b	1969	59.34	11.19 d	4.20 d

[a] Means with the same letter within a column are not significantly different ($p \leq 0.05$).

Storage. Wines were stored at 21 and 38 °C for 6 months. Storage at elevated temperature was used to simulate accelerated shelf life. Storage for 6 months at elevated temperatures was equivalent to a shelf life of 20−24 months (*23*, *24*).

Mineral Analysis. The University of Arkansas Agricultural Diagnostics Laboratory analyzed potassium content using an inductively coupled plasma spectrometer. Samples were diluted five times with water and run using standards of similar matrix background. Standards were verified using commercial external standards.

High-Performance Liquid Chromatography (HPLC). Organic acids, sugars, and ethanol content were determined using HPLC. Two columns were used in series: a Bio-Rad Organic Acid Analysis Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) followed by a Bio-Rad HPLC column for fermentation monitoring (150 mm × 7.8 mm) (Bio-Rad Laboratories, Hercules, CA). A Bio-Rad Micro-Guard Cation-H cartridge (30 mm × 4.5 mm) was used as a guard column. The columns were maintained at 65 °C by a temperature control unit. The mobile phase consisted of sulfuric acid and HPLC grade water with a resistivity of 18 MΩ obtained from a Millipore Milli-Q reagent water system. A sulfuric acid solution at pH 2.28 was used as solvent at a flow rate of 0.65 mL/min. The solvent delivery system was a Waters 515 HPLC pump equipped with a Waters 717plus autosampler (Waters, Milford, MA). The injection volumes were 10 μL for all wines, and time for completion was 32 min.

A Waters 410 differential refractometer connected in series with a Waters 996 photodiode array detector monitored the eluting compounds. Citric and tartaric acids were detected by photodiode array at 210 nm; malic, lactic, succinic, and acetic acids, glucose, fructose, glycerol, and ethanol were detected by a differential refractometer. The peaks were quantified using external standard calibration based on peak height estimation with baseline integration. Waters Millennium[32] Chromatography Manager software was used for processing, recording, and storage of chromatograms and injection data.

Treatment Design and Data Analysis. The treatment design was a 6 × 4 × 2 factorial in a completely randomized design with two replications. HPLC samples were injected three times and averaged for each replication. The factorial treatment design contained three factors: ion-exchange treatment (control, Amberlite resin, Lewatit resin, Nafion membrane, Ionics membrane, and Ultrex membrane), storage time (0, 2, 4, and 6 months), and storage temperature (21 and 38 °C). Data were analyzed by analysis of variance using the Statistical Analysis System PROC GLM procedure (*25*). Treatment means were separated by least significant difference at the 5% significance level.

RESULTS AND DISCUSSION

Cynthiana wine was produced to examine the benefits of pH reduction using ion-exchange systems. The initial must chemistry after crushing and destemming of Cynthiana grapes was 9.10 g/L tartaric acid, pH 3.60, and 19 °Brix. No adjustments were made to the must prior to fermentation. Prior to pH adjustments through ion exchange, Cynthiana wine had 5.99 g/L tartaric acid, pH 4.10, and an ethanol content of 10.6%. The ethanol content was not affected by ion exchange.

A three-way analysis of ion-exchange treatment, storage time, storage temperature, and their interactions was considered. Of the 54 possible interactions of a three-way analysis, only seven of the interactions were not significant (data not shown). Due to the extreme difference in deterioration of wine attributes at the storage temperatures, data were analyzed by storage temperature (21 and 38 °C) as a two-way interaction of ion-exchange treatments over storage time.

Initial analysis was conducted to compare the control (nonadjusted wine) to the average of all the wines adjusted using ion exchange (**Table 1**). Ion-exchange systems lowered the pH of wine from 4.11 to 3.49, corresponding to lowered conductivity and K^+ content as compared to the nonadjusted control. The decrease in pH and K^+ content indicated that ion exchange was successful in exchanging K^+ for H^+. Titratable acidity increased after ion exchange as compared to the control due to the increased H^+ content of the pH-adjusted wines. Modest trends in color and phenolics content were exhibited at both temperatures when comparing the control and ion-exchange treatments. Ion exchange increased color density, did not affect total red pigment color, and showed a slight decrease in total phenolics. Degradation of color and phenolics occurred during storage at both temperatures. Overall, ion exchange had a positive effect on wine quality.

The nonadjusted control wine was removed from the remaining analysis to determine the effect of pH adjustment using resins and membranes from different manufacturers (**Tables 2−4**). Some wine attributes over storage time for the ion-exchange treatments are presented graphically (**Figures 2−4**) at both storage temperatures. As expected, there was more rapid degradation of wine quality during storage at 38 °C as compared to 21 °C. Membrane and resin systems effectively lowered the pH of wine from 4.11 to approximately 3.50 and 3.45, respectively (**Tables 2** and **3**). The resin system allowed faster rates of ion exchange than the membrane system due to increased resin surface area and gravity flow through the column. However, achieving the pH goal was less difficult when

Table 2. Main Effects of Ion-Exchange Type and Storage (21 °C) on Cynthiana Wine Attributes

treatment	pH	titratable acidity (g/L)	conductivity (μS/cm)	potassium (mg/L)	color density	total red pigment color	total phenolics
ion-exchange type							
Nafion membrane	3.50 a[a]	8.20	2648 a	1356 a	72.70	25.88	27.13
Ionics membrane	3.50 a	8.10	2487 bc	1242 b	70.51	29.23	26.86
CMI-7000 membrane	3.52 a	7.80	2552 b	1287 b	68.80	35.20	27.79
Amberlite resin	3.45 b	7.90	2451 c	1288 b	63.41	32.08	25.01
Lewatit resin	3.46 b	7.80	2484 bc	1297 b	64.79	32.38	24.85
storage (months)							
0	3.43 c	8.30	2606 a	1094 b	81.52	41.65	47.77
2	3.53 a	8.30	2526 b	1364 a	66.81	36.58	42.51
4	3.51 ab	7.70	2536 b	1340 a	61.33	25.76	11.12
6	3.48 b	7.60	2432 c	1377 a	62.51	19.83	3.91
interaction							
type × storage	ns[b]	0.0001	ns	ns	0.0019	0.0001	0.0001

[a] Means with the same letter within a column are not significantly different ($p \leq 0.05$). [b] Not significant ($p \leq 0.05$).

Table 3. Main Effects of Ion-Exchange Type and Storage (38 °C) on Cynthiana Wine Attributes

treatment	pH	titratable acidity (g/L)	conductivity (μS/cm)	potassium (mg/L)	color density	total red pigment color	total phenolics
ion-exchange type							
Nafion membrane	3.49 ab[a]	7.80 ab	2874	1322 a	61.36 a	24.66	16.20 a
Ionics membrane	3.49 ab	7.90 a	2478	1228 bc	60.55 a	28.39	16.38 a
CMI-7000 membrane	3.50 a	7.70 ab	2529	1207 c	61.17 a	28.91	15.87 a
Amberlite resin	3.45 c	7.90 a	2467	1283 a	56.51 b	27.91	14.71 b
Lewatit resin	3.46 bc	7.60 b	2498	1278 ab	55.61 b	26.55	14.67 b
storage (months)							
0	3.48 b	8.30 a	2754	1075 c	59.55 a	42.00	44.15 a
2	3.47 b	8.10 a	2562	1331 ab	59.51 a	43.49	7.93 b
4	3.51 a	7.50 b	2551	1291 b	57.94 a	13.16	6.27 c
6	3.46 b	7.10 c	2409	1357 a	59.17 a	10.49	3.92 d
interaction							
type × storage	ns[b]	ns	0.0001	ns	ns	0.0001	ns

[a] Means with the same letter within a column are not significantly different ($p \leq 0.05$). [b] Not significant ($p \leq 0.05$).

Table 4. Main Effects of Ion-Exchange Type and Storage (21 and 38 °C) on Cynthiana Wine Organic Acids

	citric acid (g/L)		tartaric acid (g/L)		malic acid (g/L)		lactic acid (g/L)	
treatment	21 °C	38 °C	21 °C	38 °C	21 °C	38 °C	21 °C	38 °C
ion-exchange type								
Nafion membrane	1.09 a[a]	1.09 a	2.63	2.57 a	2.30	2.22 b	3.34	0.77
Ionics membrane	0.86 b	0.86 b	2.64	2.58 a	2.32	2.25 a	3.36	0.77
CMI-7000 membrane	0.84 b	0.85 b	2.62	2.59 a	2.33	2.25 a	3.37	0.77
Amberlite resin	0.77 c	0.78 c	2.59	2.54 b	2.28	2.23 b	3.32	0.76
Lewatit resin	0.77 c	0.77 c	2.58	2.53 b	2.28	2.23 b	3.30	0.76
storage (months)								
0	0.81 b	0.80 b	2.61	2.58 a	2.31	2.30 a	3.36	3.35
2	0.80 b	0.80 b	2.54	2.51 c	2.30	2.17 c	3.33	3.24
4	0.84 a	0.85 a	2.59	2.55 b	2.38	2.26 b	3.48	3.36
6	0.80 b	0.83 ab	2.59	2.71 a	2.37	2.25 b	3.42	3.31
interaction								
type × storage	ns[b]	ns	0.001	ns	0.001	ns	0.001	0.0008

[a] Means with the same letter within a column are not significantly different ($p \leq 0.05$). [b] Not significant ($p \leq 0.05$).

using the membrane system because the flow of current controlled the electrochemical ion exchange in the wine. Storage time or temperature did not drastically affect pH.

Titratable acidity showed no trend in terms of specific ion-exchange method (**Figure 2**). The titratable acidity of wine decreased when the wine was stored at both temperatures over the 6-month storage period. Titratable acidity reduction could be due to removal of bitartrate ions as insoluble potassium salt, which precipitated during storage (*6*, *9*, *11*). The membrane-treated samples analyzed by HPLC revealed slightly higher values for citric, tartaric, malic, and lactic acids than resin-treated samples stored at both 21 and 38 °C (**Table 4**). No trend was evident in the HPLC data to indicate that organic acids were negatively affected by ion-exchange techniques.

Conductivity was lower for resin-treated wine than for Nafion- and CMI-7000-treated wines at both storage temperatures. Conductivity decreased for most wine treatments during the 6-month storage at 21 and 38 °C. Conductivity decreased as a result of crystallization of potassium bitartrate over time.

Wine adjusted with the Nafion membrane had the highest K^+ content as compared to the other ion-exchange types (**Tables 2** and **3**). There was no significant difference in potassium content of the wines that received the other treatments and were stored at 21 °C. The K^+ levels of the wines were lower initially

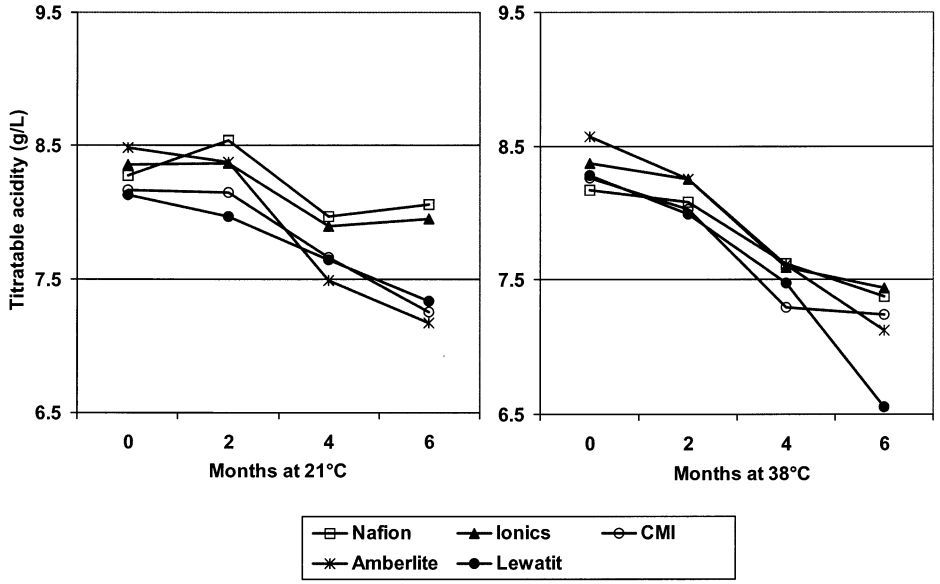

Figure 2. Effect of storage at 21 and 38 °C on titratable acidity of pH-adjusted Cynthiana wine using membranes (Nafion, Ionics, and CMI) and resins (Amberlite and Lewatit) from different manufacturers.

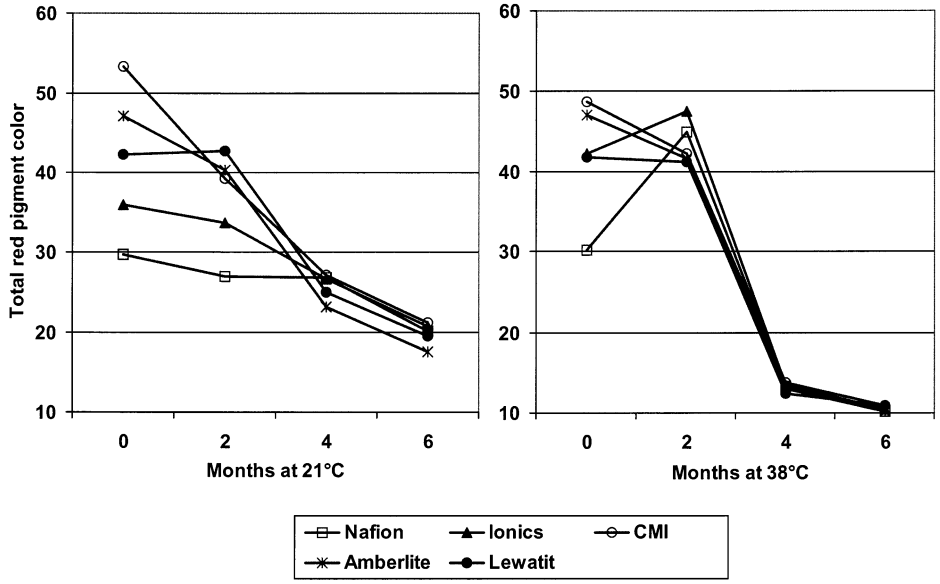

Figure 3. Effect of storage at 21 and 38 °C on total red pigment color of pH-adjusted Cynthiana wine using membranes (Nafion, Ionics, and CMI) and resins (Amberlite and Lewatit) from different manufacturers.

than after storage, showing an apparent trend of increasing potassium during storage (**Tables 1**−**3**). However, a new inductively coupled plasma spectrometer was installed between month 0 and month 2 of the storage study and affected the initial K^+ levels. Because potassium readings are sensitive to the torch settings of a spectrometer, the month 0 readings cannot be compared to the rest of the storage study. No trend in potassium levels is detected in months 2−6 of the storage study. The K^+ data analyzed after removal of the initial storage data indicated no trend in K^+ levels during storage (data not shown).

The comparison of membranes and resins from different manufacturers indicated that wine adjusted with membranes in the three-cell electrochemical unit was higher in color density than wine adjusted with resins at both storage temperatures (**Tables 2** and **3**). Wine color density described the intensity of color and related the concentration of red-colored pigments to yellow-brown pigments. Wine color density was higher initially (at storage month 0) when stored at 21 and 38 °C. Color density has been shown to diminish with time, possibly due to the destruction of free anthocyanins or due to gradual formation and precipitation of pigment polymers (*26*).

Total red pigment color measured the concentration of total pigments of both anthocyanins and tannins present in the wine. The CMI-7000 membrane-treated wine initially had the highest red pigment color at 21 and 38 °C (**Figure 3**). Initially, there was a wide range of variation for total red pigment color at both storage temperatures, but by the end of the 6-month storage, total red pigment color for all ion-exchange treatments was similar. There was a sharp decline between months 2 and 4 of storage among samples stored at 38 °C, whereas total red pigment color decreased less readily during storage at 21 °C.

Total phenolic measurements referred to all forms of phenolic compounds present in wine that absorb at 280 nm. Membrane-treated wine was higher in phenolics than resin-treated wine. Total phenolics decreased during storage for all ion-exchange treatments (**Figure 4**). There was a sharp decrease in total phenolics between months 0 and 2 of storage for all treatments stored at 38 °C, whereas wine stored at 21 °C showed only

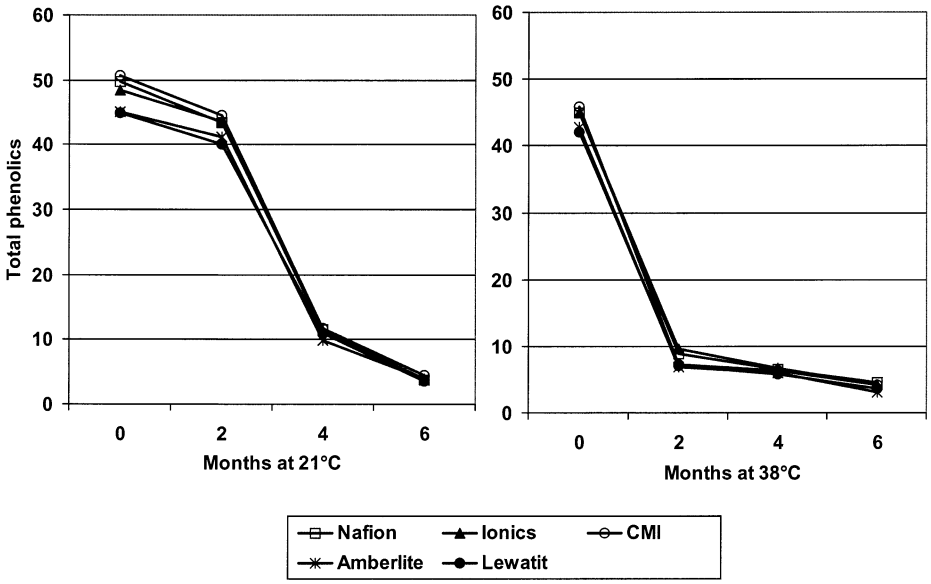

Figure 4. Effect of storage at 21 and 38 °C on total phenolics of pH-adjusted Cynthiana wine using membranes (Nafion, Ionics, and CMI) and resins (Amberlite and Lewatit) from different manufacturers.

slight decreases between months 0 and 2 of storage. Elevated storage temperature increased the rate of total phenolic loss in wine.

Because human perception is critical for the evaluation of wine, an informal panel familiar with Cynthiana wine characteristics was established. The wine produced had attributes (aroma and flavor) unique to Cynthiana wine. The panel found that the color and flavor of the wine was improved by adjusting the pH to 3.5. The wines that were not pH adjusted had more visual off colors and brown hues and a flat, flabby flavor, while the pH-adjusted wine had a sharper (acidic) flavor and better color. Resin-treated wine had less aroma and flavor than membrane-treated wines. The panel indicated that Amberlite resin stripped most of the characteristic flavor and aroma attributes of the Cynthiana wine. Wine adjusted with the CMI-7000 membrane had the most favorable Cynthiana characteristics.

CONCLUSIONS

Wine pH was lowered from 4.11 to 3.50 using ion-exchange techniques, resulting in increased titratable acidity, decreased K^+ content, and an improvement in visual color. Trends for color and phenolics changes were similar for control versus ion-exchange treatments. Therefore, ion exchange is a viable method to reduce the pH of Cynthiana wines.

Subtle differences were shown in wine produced using membrane versus resin systems. Wine treated with membrane ion exchange was higher in color density and phenolics. During storage at 21 and 38 °C, wine samples receiving both membrane and resin treatments showed decreases in phenolics, color density, and total red pigment color. Ion exchange decreased the pH of Cynthiana wine without negatively affecting the quality of the wine. Although a panel familiar with the characteristics of Cynthiana wine found that the color and flavor of the pH-adjusted wine were improved, further research is needed to investigate in depth the affect that ion exchange has on the sensory attributes of the wine.

ABBREVIATIONS USED

HPLC, high-performance liquid chromatography; H^+, hydrogen ion; K^+, potassium ion.

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