Keep it natural !
Adjusting the pH of food products without chemical additives thanks to Bipolar Membrane Electrodialysis

by

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In the processing of food products, it is often necessary to adjust the pH for different reasons, such as improving taste, texture, shelf life, functionality, ease of processing, etc. Traditionally, this is accomplished by the addition of chemicals such as hydrochloric, sulfuric, or organic (acetic, ascorbic, citric, tartaric) acids to lower the pH and sodium or potassium hydroxide to increase the pH. These can be the source of additional salinity in the final products and mean that such added chemicals must be listed as an ingredient, something that many processors wish to avoid. Alternatively, ion exchange resins are also used: cation-exchange resins to acidify products or anion-exchange resins to increase the pH (in this case, to get an accurate pH, blending is necessary). These generate large volumes of salt effluents due to acid and base solutions that are consumed to regenerate the resins. For both options, there is a consumption of chemicals to achieve the required pH adjustment.

Bipolar Membrane Electrodialysis (EDBM) can be used to increase or decrease the pH of aqueous streams and can be an attractive alternative to the traditional methods to change the pH of aqueous food products. Electrodialysis is a membrane process used extensively to demineralize process streams by removing the salts (but also acids and bases). Eurodia Industrie and its American division Ameridia, have successfully installed hundreds of electrodialysis systems worldwide for food-related applications such as the demineralization of cheese whey, the stabilization of wine and grape juice (reduction of tartrates), the deashing of sweeteners, desalting of brackish water, etc. The heart of the process is the electrodialysis stack: a large number of anion- and cation-exchange membranes separated by spacers, and installed in a clamping system between electrodes. Contrary to the pressure-driven membrane processes, the separation driving force is a DC current that makes the anions and cations migrate across the membranes toward the electrodes, generating a diluate (desalted) stream and a concentrate stream.

A bipolar membrane (see Figure 1) is made of an anion-exchange layer (AEL) and a cation-exchange (CEL) chemically bonded at the interface. When a bipolar membrane is placed in an electric field with the anion-exchange layer facing the anode, the only way for the current to be carried across the membrane is by the splitting of the water that diffuses inside the membrane at the interface between the two layers. A good bipolar membrane efficiently generates and concentrates hydrogen (H^+) cations and hydroxyl (OH^-) anions from the splitting of the water around it: this is why it is often called a "water splitting" membrane. These can be the source of acidity or basicity to change the pH of products that are in contact with the membrane: the pH is changed thanks to the splitting of its own water under the action of the DC current, without the addition of chemicals. When bipolar membranes are installed in an electrodialysis stack, an acidified (or basified) product is generated, along with a dilute base or acid that can be reused in the plant operations.

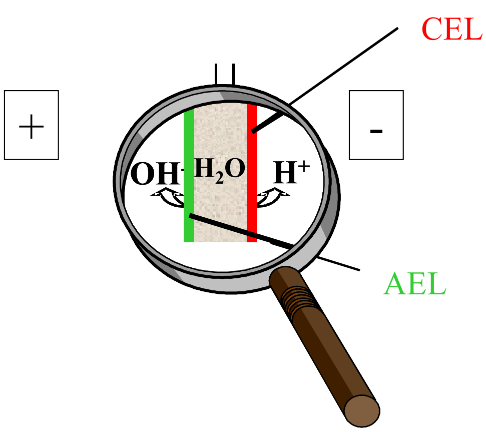

Figure 1: Bipolar Membrane

Bipolar membrane electrodialysis has been successfully applied worldwide for the production of specialty chemicals such as the production of organic acids (e.g. lactic acid) from fermentation broths and the production of organic acids or bases from their salts (e.g. sodium acetate or formate). However, since the membranes meet the requirements of the FDA and are food-compatible, they can be installed in the Eurodia/Ameridia electrodialysis stacks for food applications. As discussed above, an EDBM stack can be used to change the pH of aqueous solutions. This feature has been evaluated for various specialty chemical and pharmaceutical applications, and for aqueous food streams, the focus of this article. We will review how EDBM can be applied to adjust the pH of beverages, such as wines, grape juice or must, apple juice and orange juice.

The adjacent picture shows the two EUR40 stacks for an EDBM unit in Europe to convert a sodium acetate by-product of specialty chemical production into acetic acid and sodium hydroxide

In addition, the “conventional” three-compartment EDBM stacks (with bipolar, anion-, and cation-exchange membranes) can be used for the production of food grade HCl and NaOH from good quality, food grade salt. The main benefit in the food industry is the total control of the source for these chemicals, leading to higher product value.

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Acidification of Wine, Grape Juice, and Grape Must:

For wine, grape juice or grape must it is possible to achieve a reduction of the pH using an EDBM stack combining bipolar and cation-exchange membranes in a two compartment configuration as shown in Figure 2. Only cations (mainly potassium) are removed from the wine and none of the other components are affected. Flavors and colors are preserved. It is possible to achieve a very accurate pH reduction with this treatment. A typical range of pH reduction for wine and grape must is 0.1 to 0.3 and 0.7 to 0.9 for grape juice. Another benefit of wine acidification without chemical addition is that it minimizes the need for SO_2. The dilute base (KOH) by-product can be used in the winery as a cleaning solution for tanks and other equipment.

The two figures below show how a pefect titration curve can be obtained for pH reduction by EDBM. Figure 3 shows the voltage/current curves over a run of ~3½ hours: the current is allowed to drop when the maximum voltage is reached. Table 1 shows some analytical data for grape must treatment before malo-lactic fermentation, comparing EDBM with the addition of tartaric acid. One can see that the level of organic acids, sugars, and alcohol remain constant, while only the potassium content is reduced. For this must, the capacity is approx. 100 L/h.m2 of membrane for a pH reduction of 0.3.

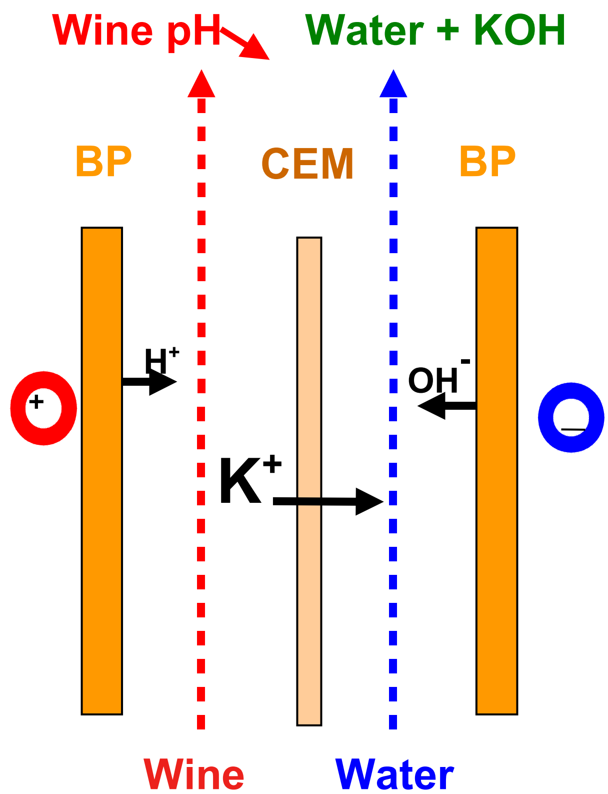


Figure 2

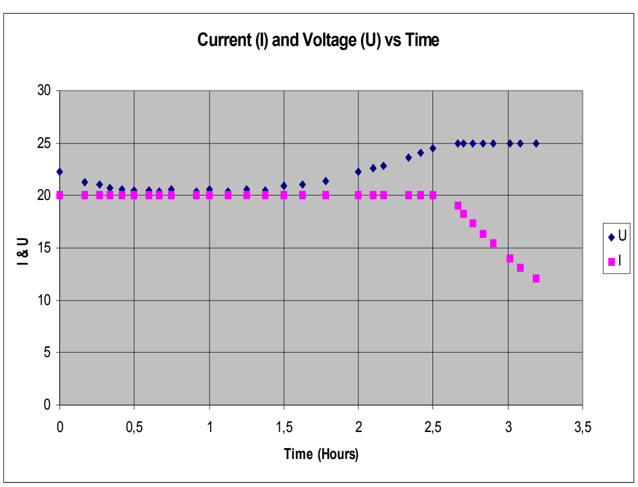
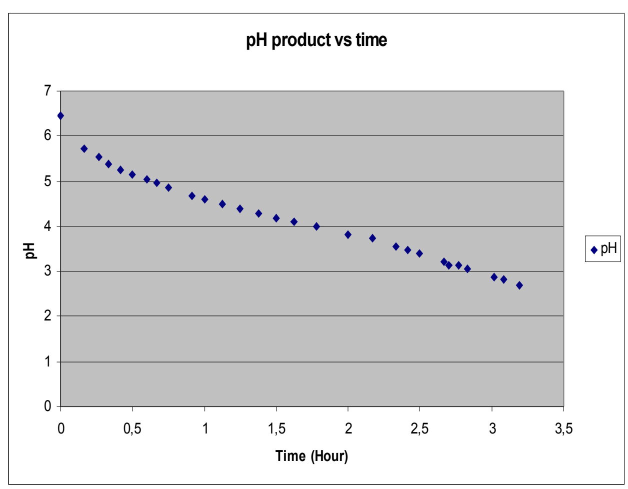


Figure 3

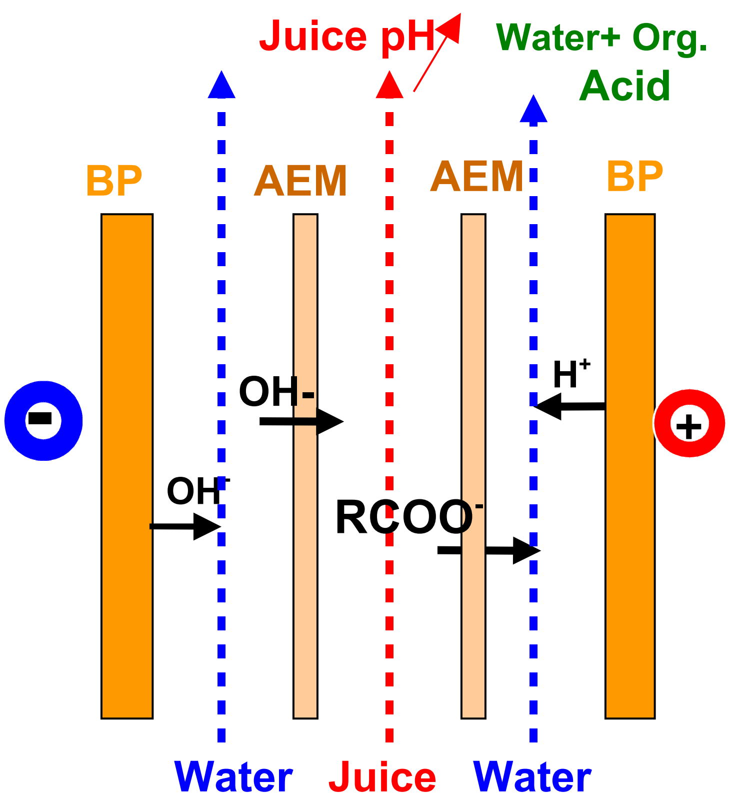


Figure

Analyses	Precision range	Units	Reference	EDBM -0.3 pH	EDBM -0.15 pH
Total Acidity	± 0.14	**g/L H_2SO_4**	**3.37**	**4.07**	**3.86**
Volatile Acidity	± 0.04	g/L H_2SO_4	0.24	0.30	0.27
pH	± 0.04		**3.88**	**3.62**	**3.70**
Tartaric Acid	± 0.5	g/L	3.1	3.6	3.5
Malic Acid	± 0.2	g/L	0.2	0.1	0.2
Lactic Acid		g/L	18	1.8	1.8
Total SO2	± 12	mg/L	87	75	79
Free SO2	± 6	mg/L	41	38	42
Sodium	± 3	mg/L	13	10	13
Potassium	± 50	mg/L	**1546**	**1268**	**1334**
Calcium	± 13	mg/L	70	83	75
Magnesium	± 17	mg/L	68	66	66
Phenolic Compounds	± 1.9	mg/L	58.3	58.9	58.8

Table 1: Typical analyses for pH reduction of grape must before Malo-lactic fermentation.

pH Increase for Apple or Orange Juice:



To increase the pH of juices, it is possible to consider the two-compartment configuration with bipolar and anion-exchange membranes. The treated product flows on the base (OH^-) side of the bipolar membrane and organic anions (tartrate, malate, lactate, …) are removed across the anion-exchange membranes, potentially allowing the recovery of valuable organic acids. Practically, a second anion-exchange membrane must usually be added in a three-compartment configuration (Figure 5) due to the precipitation of multivalent cations and/or organics from the juice because of the very high pH at the surface of the bipolar membrane.

Pilot tests for the treatment of apple juice show that it is possible to increase the pH by up to 1.5 pH units (from 3.58 to 5.1) for juice at 9.5 Bx with stable performance and a capacity of 39 L/h.m^2. The current density is 5 mA/cm2 at ~22ºC with a voltage <1 V/cell. For the treatment of orange juice, it is important to remove the pulp since solids can plug the channels in ED stacks. In a EUR40C stack with 43 m^2 of effective cell area, 908 l/h of orange juice at 13 Bx (starting from concentrate) were processed to increase the pH from 3.65 to 5.02.

In conclusion, pH adjustment by EDBM is a mild treatment that preserves the flavor and color of the product without the generation of effluents. Yet, it allows for a perfect "pH-tuning" within 0.05 units! All components, including ED membranes and stacks, meet the requirements of the FDA and systems can be designed in accordance with "3A" standards. This technology can help increase the value of products with a "natural ingredients" label.