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# Contribution to the development of a method of maple sap soft drink stabilization by electro-activation technology

Kouassi Koffi [a,b], Steve Labrie [b,c], Alexandre Genois [a,b], Amara Aït Aissa [a,b], Mohammed Aïder [a,b,*]

[a] Department of Soil Sciences and Agri-Food Engineering, Université Laval, Quebec, Qc G1V 0A6, Canada
[b] Institute of Nutrition and Functional Foods (INAF), Université Laval, Quebec, Qc G1V 0A6, Canada
[c] Department of Food Science and Nutrition, Université Laval, Quebec, Qc G1V 0A6, Canada

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ABSTRACT

Electro-activation (EA) of a maple sap/syrup beverage was studied. The purpose of the study was to assess the product parameters, such as pH, ORP, transmittance and degree Brix, while minimizing energy consumption. The experiments were conducted using three different configurations of the reactor that differed by the position of the anion (AEM) and cation (CEM) exchange membrane relative to the electrodes as well as the nature of the electrolyte (NaCl vs. $Na_2CO_3$) in the central cell of the reactor. The results showed that the type of configuration, the electric current and the temperature influenced the parameters of the electro-activated beverage. At 23 °C, the beverage was acidified to pH 3.89 with a Redox potential (ORP) of 417.33 mV. At 55 °C and 150 mA, the minimum pH of 3.78 and an ORP of 329.67 mV were obtained. The electric resistance of the electro-activation reactor (EAR) decreased during electro-activation, indicating a gain of energy efficiency corresponding to an electric resistance of 266.76 Ω. Moreover, the reactor configuration and electric current affected the presence or absence of a fouling of the ion exchange membrane at the anodic side. The beverages' transmittance increased slightly during EA without any effect on the degree Brix.



## 1. Introduction

Maple sap is a clear, slightly sweet liquid, composed mainly of water (97 g/100 g sap) and approximately 2–3 g sugars/100 g fresh sap, which are represented mainly by 95 g sucrose/100 g sugar, 4 g glucose/100 g sugar and ≈1 g fructose/100 g sugar. The main monosaccharides of maple sap, glucose and fructose, are obtained from the inversion of sucrose by the action of microbial enzymes (invertase). Maple sap contains a very small percentage (1 g/100 mL) of minerals, such as potassium, calcium, silica oxides and manganese (Allard, 1974). Maple sap also contains amino acids (0.24–125 nmol/mg of dry matter of maple sap), organic acids, and vitamins in variable amounts, depending on the harvesting period and growing region (Morselli & Whalen, 1986). Among the non-volatile organic acids contained in the maple sap, malic acid was found at a concentration ten-fold higher than other types of identified organic acids, such as succinic, fumaric and dihydroxybutyric acid (Allard, 1974). Maple sap also contains significant amounts of terpenes and abscisic acid, which is a phytohormone recognized for its benefits to health. Maple sap contains nitrogenous macromolecules (proteins) corresponding to 0.025 g/100 mL of maple sap solids (Dumont, 1994). Organic nitrogen compounds, such as cytokinins, were also detected in maple sap, and their concentration was on the order of that of abscisic acid (Bertrand, Robitaille, Nadeau, & Boutin, 1994). Recently, it has been shown that maple sap and the subsequent syrup are rich in antioxidants.

Several studies have confirmed that maple sap is sterile just after harvesting (Chapeskie, 2005). Once a maple tree is notched, microorganisms can contaminate the maple sap. Moreover, unless the collection is conducted in a completely sterile fashion (which is impossible), immediately after the maple sap is collected from the tree, there is an inevitable fermentation due to microbiological contamination. During this fermentation, sucrose undergoes enzymatic hydrolysis and generates two reducing sugars, glucose

*Abbreviations:* EA, electro-activation; EAR, electro-activation reactor; AEM, anion exchange membrane; CEM, cation exchange membrane; ORP, oxidoreduction (redox) potential.

* Corresponding author. Department of Soil Sciences and Agri-Food Engineering, Université Laval, Quebec, Qc G1V 0A6, Canada.
*E-mail addresses:* Mohammed.aider@fsaa.ulaval.ca, mohammed.aider.1@ulaval.ca (M. Aïder).

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and fructose (Allard, 1974; Stuckel & Low, 1996). The microbiological contaminants of maple sap are bacteria, yeasts and molds (Filteau, Lagacé, LaPointe, & Roy, 2010). However, the main microbial contamination of maple sap is *Pseudomonas* (Chapeskie, 2005; Filteau, Lagacé, LaPointe, & Roy, 2011; Filteau, Lagacé, LaPointe, & Roy, 2012) because of the presence of sugars, minerals and amino acids as well as the very high water activity, which promotes their proliferation. Microbial contamination has two consequences in maple sap. The enzymes secreted by microorganisms break saccharose into glucose and fructose, and in this way, they confer a bad syrup taste and increase the viscosity of the syrup (Chapeskie, 2005). Maple sap and its derived products, such as beverages, must meet quality and safety standards. Treatments such as ultraviolet radiation (UV) and membrane techniques are able to remove contaminants from maple sap with different efficiencies. However, these methods often fail to completely eliminate all microorganisms and toxins (Rautenbach & Albrecht, 1989). Furthermore, these techniques result in the demineralization of the maple sap, leading to the loss of minerals and nutrients.

In recent years, the development of new techniques to ensure food safety using electrochemical techniques was explored (Efendiev & Chizhikov, 1977; Granovskii, Lavrov, & Smirnov, 1976). Among these techniques, direct electro-activation (EA) in solution is a promising new route for the treatment, stabilization and product quality improvement of aqueous food products. The peculiarity of water in food as a solvent is important for electro-activation applications. In fact, water is an important constituent of biological systems and plays a major role in the physicochemical properties of molecules in aqueous solutions (Stewart, 2009). Electrochemical activation of an aqueous solution is based on the principle of water electrolysis (Shaposhnik & Kesor, 1997). The passage of an electric current in the water creates a chemical decomposition of $H_2O$ into hydroxide ($HO^-$) and hydronium ions ($H_3O^+/H^+$). Moreover, under the effect of an electric field, the reducing oxidative couples involved in water electrolysis are $H^+/H_2$ ($E_0 = 0$ V by convention) and $O_2/H_2O$ ($E_0 = 1.23$ V) (Levie, 1999). EA is a process based on an electrochemical phenomenon that is able to significantly modify physico-chemical properties of aqueous solutions. The highest EA effect of solutions can be obtained at the electrodes/solution interfaces. Water activation is the process of water transfer into a non-equilibrium thermodynamic state, which is accompanied by a change in the water structure. Furthermore, water acquires a resonant microcluster structure. The anomalies in the pH and redox potential of electro-activated water have been reported to result from stable, high-energy resonant water microclusters that are based on co-vibrating dipoles of water molecules and charged species at near-electrode interfaces (Shironosov, Shironosova, Minakov, & Ivanov, 2003). Thus, EA allows the generation of optimal conditions for biological stabilization of aqueous solutions (Aider, Gnatko, Benali, Plutakhin, & Kastyuchik, 2012). The activated water is characterized by a high physico-chemical and biological activity (Kim, Hung, & Brackett, 2000). Water treated by EA at the anodic surface acquires a strong oxidant and antibacterial power. EA was successfully used in different fields of agricultural industries and the food industry to improve animal breeding performance, yeast inactivation and stabilization of mid-sweet white wines. EA has also been used as a substitute for the addition of $SO_2$ in wine stabilization (Drees, Abbaszadegan, & Maier, 2003; Godet, Poulard, Guillou, & El Murr, 1999; Guillou & El Murr, 2002; Guillouet et al., 2003; Petrushanko & Lobyshev, 2001; Suzuki et al., 2002).

In the present study, the hypothesis was based on the fact that hydronium ($H^+$) and oxidizers consisting of oxygenated species formed at the solution/anode interface are able to create acidic conditions that prevent maple beverage deterioration by the growth the of microorganisms. This is possible through (do to) the low pH and positive redox potential of the analyte. Thus, the aim of the present research work was to study the stabilization of a maple beverage by EA under different effects of the process conditions. The product physico-chemical characteristics and the reactor energy efficiency were also studied.

## 2. Materials and methods

### 2.1. Maple sap and syrup

Maple sap was collected in an experimental sugar-bush in the province of Québec. The sap was collected in 2 L opaque (to light) plastic bottles. The bottles of maple sap were immediately transferred to the laboratory where they were stored at 4 °C prior to use within 4 weeks. A 66 °Brix maple syrup was obtained at a food store in Quebec City, Canada.

### 2.2. Material

#### 2.2.1. Electro-activation reactor

The used EAR (Fig. 1) was a parallelepiped module composed of three compartments: an anode compartment, a central compartment and a cathode compartment. The anodic compartment was connected to the positive side of a direct electric current (DC) generator, whereas the cathodic compartment was connected to the negative side. The anodic and cathodic compartments were separated from each other by a central compartment that contained an electrolyte solution and communicated with the anodic and cathodic compartments by an anion and/or cation exchange membrane, respectively. The disposition of the ion exchange membranes in the central compartment depended of the targeted reactor configuration. The cell constant was set to $k = 1$ cm$^{-1}$. The anion exchange membrane MA-40 and the cation exchange membrane MC-40 were purchased from Shekina-azot (Shekina, Russian Federation). The membrane MK-40 was a composite membrane formed by the cation exchange resin KU-2 as a cross-linked polystyrene matrix with divinylbenzene and polyethylene and nylon as functional groups ($-SO_3^-$), whereas the membrane MC-40 had alkylammonium groups ($-NR_3^+$) as the functional group. Experiments were conducted by considering three different configurations of the electro-activation reactor. The configurations differed from each other according to the position of the membranes (anionic and cationic) relative to the electrodes (anode and cathode) and the nature of the electrolyte used in the central cell. Configuration # 1 was used to avoid the migration of the $H^+$ from the anodic compartment, which was filled with the maple beverage to maintain a sufficiently acidic pH. Configuration # 2 was used to justify the accuracy (rational) of Configuration # 1 because the conditions differ only by the nature of the membrane used to separate the anodic compartment from the central compartment. Configuration # 3 is similar to Configuration # 2, but the central cell was filled with a NaCl solution to avoid the effect of the carbonate ions at the interface. These configurations are as follows:

*Configuration 1:*
Anode | Maple beverage solution | AEM | $NaHCO_3$ 0.5 mol/L | MEC | 0.25 mol/L NaCl | Cathode

*Configuration 2:*
Anode | Maple beverage solution | CEM | $NaHCO_3$ 0.5 mol/L | MEA | 0.25 mol/L NaCl | Cathode

*Configuration 3:*
Anode | Maple beverage solution | CEM | 0.5 mol/L NaCl | MEA | 0.25 mol/L NaCl | Cathode