Effect of Chemical Descaling of Evaporator Back Pans During the Season on the Properties of Maple Syrup

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Maple sap is processed into syrup on an open traditional evaporator by a thermal treatment. Increasing the Brix during evaporation involves the concentration of elements existing naturally in the sap, such as sugars and mineral ions, to almost a saturation point. Many reactions can occur during the evaporation step between some of these ions and other compounds like organic acids (Allard and Belzile., 2004). This will result in the formation of suspended heavy complex in the syrup. Some of these complex will deposit on the surface of evaporator pans as scale which will form a persistent layer during heating (Isselhardt et al., 2002).

Many factors can affect the rate of scale formation, such as sap composition, sugar content of concentrate feeding the evaporator, intensity of heating, depth of liquid, and the roughness of the pan's surface. A rough surface will have a greater tendency to promote nucleation and scaling than a smooth surface (Arzate et al, 2013). Air injection for instance, does not have the potential to lower the thickness of scale formed on evaporator pans (Van den Berg et al, 2009).

The scale can take many forms depending on its chemical composition. Calcium, magnesium and manganese are the most common minerals found in scale (Isselhardt et al., 2002). The amount and characteristics of scale will also change throughout the season and from one season to another depending on the composition of the sap (Gallander, et al., 1967; Perkins and Van Den Berg, 2009). Unfortunately, very little data is available on the chemical composition of scale such as sugars, mineral salts and organic acids.

The presence of scale is known to cause many problems, such as the overheating of the evaporator, the reduction of heat transfer, and the efficiency of production, which will affect the color and flavor of maple syrup (Heiligmann et al., 2006). To overcome these problems, a periodic shutdown and cleaning of the evaporator is necessary to remove the scale from the surface of the evaporator. Many methods can be used like manual clean, descaling with a food grade acid solution with or without reversing the flue pans (Allard and Belzile., 2004; Perkin and Van den Berg, 2009). Many acid detergents are available for maple syrup producers. These detergents are composed of various acids like Phosphoric, Nitric, Chloric, and Sulfuric and their salt complex. Vinegar (acetic acid) is naturally present in maple sap (Lagacé et al, 2015). For this reason, acetic acid was chosen to be tested for cleaning the back pans during the season. The objective of this work was therefore to investigate the effects of using this acid on the chemical composition and the sensory quality of syrup produced after cleaning. The main goal is to ensure that no acid residues can be found in syrup and that its sensory properties are not affected.

Cleaning operation:

Maple syrup producers regularly experiencing a scale formation problem in their evaporator were solicited to participate in this project. Four producers from different regions of Quebec, Canada were chosen based on specific criteria (availability of equipment, number of taps, number of annual cleanings). The size of the sugarbushes studied ranged from 10,000 to 20,000 taps. Three producers had a traditional evaporator and one producer had an evaporator equipped with an automatic cleaner. Two of the traditional evaporators were wood-fired evaporators and the other two were oil-fired. All producers used sap concentrate from 11 to 15 °Brix to feed their evaporator. The brix of concentrate was maintained at the same level before and after cleaning.

Three tests (ER-1, ER-2 and ER-3) were carried out on the evaporator equipped with an automatic cleaner between the middle and end of the season while one test was made on each of the three traditional evaporators (ER-4, ER-5 and ER-6) at the middle of season. So the cleaning procedure was repeated three times for each type of evaporator. Thirty-one barrels of syrup (32 imperial gallons each) were produced between each cleaning test on evaporator equipped with automatic cleaner. However, 45 to 88 barrels of syrup were produced before cleaning on each traditional evaporator at the middle of season. Heat intensity and liquid depth in back and front pans was maintained at the same values before and after cleaning to avoid their effect on the quality of produced syrup. Before cleaning, processed sap was removed from back and front pans at the end of production. Then, physical state of scale on the pans was recorded. Pans were then rinsed with cold water by a pressure washer before acid solution was applied.

Cleaning was made with a diluted solution of acetic acid at a concentration varying from 3.5% to 3.9%. Cleaning and rinsing procedures were adapted depending on the type of evaporator. For the traditional evaporators, cleaning was carried out according to the following steps:

1. Cleaning procedure:

   a. Cleaning solution was prepared in the feeding tank of the evaporator by adding acetic acid concentrated at 56% to a predetermined filtrate volume. This method was employed to avoid many potential risks (fall, splash) of adding the concentrated acid directly into the back pans and to ensure the homogeneity of the solution. The required volume of water was set in order to be slightly greater than the volume of back pans.

   b. The cleaning solution was then transferred to back pans.

   c. The solution was heated to 80-85°C (176-185°F) by running the evaporator to reach the required temperature and then turned off.

   d. The pans were left filled with the hot cleaning solution overnight.

2. Rinsing procedure:

   a. The next morning, the cleaning solution was removed and the pans were rinsed many times with water. First, a primary rinse was made with a pressure washer to remove soft, wet pasta-like scale and to detach some remaining small pieces of scale.

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b. Then, a second rinse was done by immersing back pans into cold filtrate for at least five minutes.

c. The last rinse was made by filling the pans with new filtrate, then heating it to boiling by running the evaporator and keeping the pans immersed for at least five minutes.

d. Three samples of the last rinsing solution (hot filtrate) were taken from three different places in the pans for pH measurement. If the average pH was higher than 5, rinsing was satisfactory and finally completed with a last rinse by pressure washer with a cold water or filtrate. However, if pH was less than 5, second rinse was made with another hot filtrate.

For the evaporator equipped with an automatic cleaner, cleaning was made according to the following steps:

1. Cleaning procedure;

a. Cleaning solution was prepared in a separated tank by adding concentrated acetic acid at 56% to a predetermined volume of hot filtrate at 80-85°C (176-185°F).

b. Then, hot cleaning solution was recirculated in the back pans with an automatic cleaner during many hours until the pans became clean. The number of cleaning hours depended upon the thickness of the scale and the percent of the pan surface covered.

2. Rinsing procedure;

a. After cleaning, the solution was discarded and the same steps to rinse the pans from the cleaning agent were followed. First, a primary rinse was made with cold water using a pressure washer.

b. Then, cold filtrate was recirculated in the pans by the automatic cleaner for 15 minutes followed by a recirculation of new hot filtrate during an additional 15 minutes.

c. The pH of the final filtrate was measures as it was for the traditional evaporators, following the same procedure to determine if rinsing was completed. A final rinse with cold water was made with the automatic cleaner for 10 to 15 min.

Sampling:

Two samples of sap concentrate feeding the traditional evaporator were taken during the last hour before cleaning and during the three hours after cleaning. Likewise, samples of corresponding syrups were taken before and after cleaning. Two samples of sap concentrates and produced syrup were taken during the last hour before cleaning. Likewise, samples were taken during three hours of syrup production after cleaning.

Samples were taken also from the last hot filtrate used to rinse the pans. Total soluble solids (Brix), pH, conductivity, and acetic acid content were measured for those samples. Content of mineral ions were measured in all produced syrups.

Properties analyzed:

The pH of samples was measured by using a PHM82 Radiometer pH-meter supplied by VWR (Toronto, ON, Canada). Total soluble solids were measured by an AR200 Digital Hand-Held refractometer of Reichert Scientific Instruments (Buffalo, NY, USA). The electrical conductivity was measured by an electric conductivity meter (WTW; COND 3400i). Minerals analysis was

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analyzed by ICP/OES, optima 430 from PerkinElmer (Woodbridge, ON, Canada) by the IRDA laboratory. Acetic acid was analyzed using a Shimadzu Prominence liquid chromatographic system purchased from Mandel Scientific (Guelph, ON, Canada). The sensory evaluation of produced syrups was assessed by three experts of Maple Syrup Inspection Division of Centre ACER. Statistical analysis of data was performed using XLSTAT (Addinsoft, Paris, France). Mean values for concentrated sap were compared using analysis of variance (ANOVA) with the Tukey multiple comparison test to evaluate the significant difference between the means ($p < 0.05$). Standard deviation (SD) is presented alongside the means in tables of results.

Results and Discussion:

Descaling and rinsing efficiencies

Scale formed on back pans of tested evaporators varied from a brown and white-beige crust to a simple orange-brown film (Figure 1). The average thickness of measured scale was 0.22 mm. Cleaning with acetic acid solution removed the scale in both evaporator types. The removal rate reached 100% for the traditional evaporators and varied between 75% to 95% for the automatic cleaner evaporator, depending on the time of the cleaning cycle and the volume of syrup produced before cleaning.

Figure 1: Sample of dried scale recovered from back pans of traditional evaporator.

As cited above, producers with traditional evaporators produced more barrels of syrup before cleaning than those equipped with an automatic cleaner. Consequently, time of cleaning varied from 2.5 hours to 15 hours for the evaporator with automatic cleaner and from 12 to 18 hours for the traditional evaporators.

Average physicochemical characteristics of hot filtrates used for rinsing the pans of both types of evaporator are shown in Table 1. After rinsing, the last hot filtrates had a pH higher than 5.0 for both systems with very low concentration of acetic acid. However, the pH of the last filtrate used for rinsing the automatic cleaner evaporator was higher than pH of filtrate obtained with the traditional evaporator. A lower residual concentration of acetic acid in this filtrate was also observed (less than the quantification limit). This indicates that a complete removal of residual acetic acid from the surface of the pans was accomplished. Results shown in Table 1 show that no traces of acetic acid remained in the pans of the evaporator, especially when the pH of the final rinsing filtrate was higher than 6. The electrical conductivity of filtrates was also found to be low after rinsing both type of evaporators. It increased very slightly after rinsing from 14 to 17 (μS/cm) indicating a removal of similar amount of mineral ions remained on back pans.

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Parameters	Automatic cleaner		Traditional	
	Before rinsing	After rinsing	Before rinsing	After rinsing
pH	6.4 ± 0.2^a	6.3 ± 0.1^a	6.2 ± 0.5^a	5.3 ± 0.4^b
Electrical Conductivity (µS/cm)	24.4 ± 25.3^a	38.9 ± 27.3^b	7.7 ± 1.7^a	25.5 ± 7.3^b
Acetic acid (mg/kg)	0.07* ± 0.0^a	0.8* ± 0.6^a	0.25* ± 0.0^a	9.6 ± 7.9^b

*: concentration is less than quantification limit=1 (mg/kg).

Table 1: Physicochemical properties of last hot filtrate before and after rinsing of back pans for the two types of tested evaporators.

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Syrups composition and properties:

Syrups produced before and after cleaning had similar chemical characteristics. No significant changes in the Brix, pH and electrical conductivities were observed on tested syrups (Table 2).

Likewise, syrups had similar content of main mineral ions as shown in Table 3. Potassium (K+) and calcium (Ca++) remained the two main mineral ions in all produced syrups. The concentration of calcium and phosphor was increased slightly in syrup produced after cleaning the evaporator with the automatic cleaner. This is probably related to the higher heat transfer of cleaned pans, which led to a reduction of syrup's cooking time

Type of evaporator	Automatic cleaner		Traditionnal	
Parameters	Before cleaning	After cleaning	Before cleaning	After cleaning
Brix (%)	67.5 ± 0.3[a]	67.6 ± 0.5[a]	66.1 ± 0 9[b]	66.5 ± 0.4[b]
pH	6.8 ± 0.2[a]	6.7 ± 0.2[a]	7.0 ± 0.3[b]	7.0 ± 0.04[b]
Electrical Conductivity (µS/cm)	198 ± 38[a]	208 ± 49[a]	230 ± 50[b]	208 ± 35[b]

Values with the same letter are not different significantly ($p > 0.05$).

Table 2: Physicochemical properties of maple syrups produced before and after cleaning with solution of acetic acid.

and the precipitation of these ions on the pan's walls.

Light transmittance of most of the syrups produced after cleaning was increased, especially for syrup produced on evaporator (ER-6) which increased by 13.9%. Slight decreases from 1% to 5.7% occurred with syrups produced on the evaporators (ER-4) and (ER-2).

This later increase is possibly due to a greater heat transfer in back pans after removing the thick scale formed during the production of 88 barrels of maple syrup. Even with this noticeable increase in transmittance, syrups remained in the same color class as before cleaning. In general, chemical cleaning with a solution of acetic acid allowed the production of a syrup with a similar or higher transmittance in comparison to those produced before cleaning.

Sensory evaluation showed that, after cleaning, syrups retained the same taste as before cleaning. Two syrups of each evaporator type had good taste before and after cleaning. One syrup with a good taste but a light off-flavor was also detected for both types of evaporator before and after cleaning. Therefore, this specific light off-flavor seems to be persistent even after a cleaning operation (Table 4).

According to these results, cleaning of back pans with acetic acid solution as

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Content (mg/L)	Automatic cleaner		Traditional	
	Before cleaning	After cleaning	Before cleaning	After cleaning
Potassium (K^+)	2476 ± 253[a]	2508 ± 217[a]	2466 ± 654[a]	2405 ± 644[a]
Calcium (Ca^{++})	818 ± 525[a]	1090 ± 844[b]	715 ± 367[a]	808 ± 318[a]
Magnesium (Mg^{++})	189 ± 55[a]	210 ± 78[a]	248 ± 89[a]	253 ± 69[a]
Manganese (Mn^{++})	3.3 ± 2.3[a]	7.4 ± 9.2[a]	50 ± 80[a]	38 ± 58[a]
Phosphor (P^{+++})	4.7 ± 3.9[a]	8.2 ± 9.6[b]	6.2 ± 4.6[a]	5.0 ± 3.1[b]

Values with the same letter are not different significantly ($p > 0.05$).

Table 3: Contents of mineral ions in maple syrup produced before and after cleaning with acetic acid (mean ± SE).

Type of evaporator	Automatic cleaner		Traditional	
Syrup taste	Before cleaning	After cleaning	Before cleaning	After cleaning
Good flavor	2	2	2	2
Good with light off-flavor (√-VR4)*	1	1	0	0
Good with light off-flavor (√-VR1)*	0	0	1	1

√: Slight trace of undesirable taste and odor.
VR1: Unpleasant taste and odor of natural origin.
VR4: Unpleasant taste and odor of unidentified origin.
*: According to table of syrup taste classification by inspection division of Centre ACER

Table 4: Taste of maple syrups produced before and after cleaning of both tested evaporator types.

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it was performed in this study would not significantly affect the composition and the commercial properties of maple syrup.

Contents of acetic acid

The average concentration of acetic acid in syrups produced before and after cleaning are presented in table 5. In general, it showed no significant increase in the concentration of acetic acid in syrup produced after cleaning of evaporators. No significant increase was recorded in syrup produced after cleaning of three evaporators tested (Er-1, ER-3, and ER-4). Also, a significant decrease in acetic acid in syrups produced after cleaning was observed for two evaporators (Er-5 and Er-6).

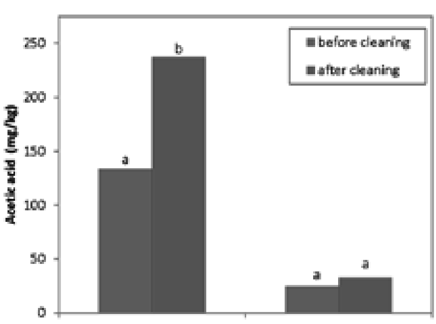

Figure 2: Average concentration of acetic acid in maple sap concentrates before and after cleaning of tested evaporators.

So, syrups produced with five tests did not show any significant increase in the concentration of acetic acid related to cleaning with acetic acid. Syrup produced after cleaning of evaporator Er-3 had a notable but not significant increase while syrup produced after cleaning of evaporator Er-2 had a light but significant increase. This increase stayed during the three hours of production of a large volume of syrup following cleaning which would not be realistically related to residual amount of acetic acid used for cleaning. This can be explained by the sharp increase of average concentration of acetic acid in sap concentrate used immediately after cleaning of the evaporator equipped with automatic cleaner (Figure 2). This increase would hardly come from a residual amount of acetic acid knowing that the concentration of acetic acid was stable and relatively high in sap concentrates during the three hours of production after cleaning for Er-2 and Er-3.

Further, the average concentration

Type of evaporator	Sugarbush	Concentration of acetic acid (mg/kg)		FC-(acid/°Brix) (after/before)
		Before cleaning	After cleaning	
Automatic cleaner	ER-1	303 ± 4.9^{a}	304 ± 5.7^{a}	0.9
	ER-2	356 ±10.4^{a}	418 ± 29^{b}	1.0
	ER-3	1093 ± 52^{a}	1780 ± 436^{a}	0.9
	Average	**584 ± 442^{a}**	**834 ± 821^{a}**	**0.93**
Traditional	ER-4	220 ± 8.2^{a}	171 ± 40^{a}	0.6
	ER-5	639 ± 6.7^{a}	357 ± 76^{b}	0.7
	ER-6	357 ± 70^{a}	298 ±20^{b}	0.6
	Average	**405 ± 214^{a}**	**275 ± 95^{b}**	**0.64**

Values with the same letter are not different significantly ($p > 0.05$).

FC: concentration factor

AF: after cleaning

BE: before cleaning

Table 5: Average concentration of acetic acid in maple syrup produced one hour before and three hours after cleaning with acetic acid (mean±SE)

of acetic acid in the last hot filtrate after rinsing of back pans of these evaporators was very low and around 0.6 (ppm). It is likely, however, that microbial activity in sap concentrate was stimulated after the cleaning. This is specially observed for the third test performed at the end of season (Er-3) when the atmospheric temperature was higher. The concentration of acetic acid in the syrup produced before cleaning of Er-3 was 3.6 times higher than concentration recorded in syrup produced in Er-1 (Table 5) showing a great variation in the natural concentration of this compound. Therefore, this apparent increase could be explained by the naturally higher concentration of acetic acid previously found in the corresponding sap concentrate used immediately after cleaning of this evaporator.

As explained above, acetic acid is an organic acid which is present naturally in maple sap. So, to follow the variation of its concentration between sap concentrates and corresponding syrups, concentration factor of this acid between these products were estimated. This permitted evaluation of the presence of residual amounts of cleaning acid in produced syrups. The ratio of concentration factors after cleaning and before cleaning was less than one for all tests (table 5). This shows that the concentration of acetic acid in syrup produced after cleaning of all evaporators including Er-2 and Er-3 is related to its natural concentration found in the corresponding collected concentrates.

Since no change was observed in the concentration of acetic acid in sap concentrate used for traditional evaporators (Figure 2), no increase was recorded in its concentration in the corresponding syrup produced after cleaning (Table

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5). This is also the case for syrup produced after cleaning of evaporator ER-1 at the middle of season. Therefore, we can assume that syrups produced after cleaning with both types of evaporator do not contain significant amounts of residual acetic acid used for cleaning.

Conclusion

Back pans of evaporators can be effectively cleaned with a 4% solution of acetic acid. This is a simple and low cost method for pan descaling during the season. The results showed, first, that cleaning with acetic acid solution allowed a good descaling of pans. Second, the composition and properties of syrups produced after cleaning were similar to those of syrup produced before cleaning. Third, syrups produced after cleaning were not affected by residues of acid when a good rinsing procedure was employed such as the one performed in the present work. It is recommended to ensure that the pH of the last hot rinsing filtrate is higher than 6.0 after cleaning. This way, descaling of back pans of evaporators with acetic acid during the sugar season can be a safe and suitable method for the production of regular and certified maple syrup.

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