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Combination Effect of Ozone and Heat Treatment for the Color Reduction in Sugarcane Juice

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Abstract
We have been studied the mechanism of color reduction of sugarcane juice as a new innovative technology to crystal sugar production as a substitute for sulfur use, which was related to health problems. This work evaluated the effect of ozonation on sugarcane juice in two different conditions, heated and non-heated juice. The samples in both conditions were ozonized for 120 min in a stainless-steel batch reactor, connected to an ozonation system with constant flow (17.3 mg O_3/min). Ozonation did not change the values of reducing sugars (RS) and the apparent sucrose content (POL); however, the color rate ICUMSA showed significant decrease for the heated juice, but there was no response to ozonation in the non-heated juice. These responses represent a key point to the industry, which during the clarification process, heats the juice before the sulfitation. The settling should become more efficient after ozonation (results not shown), showing great potential to use this technology in production systems because of the optimization of reaction parameters for color reduction ICUMSA in sugarcane juice.
Keywords*:* Ozone, Clarification, Sugarcane, ICUMSA, UFLC/ELSD.

1. Introduction

Sugar is essential for Brazilian exportation. In 2010, the country accounted for 48 percent all global sugar exportation (McConnel et al., 2010). According to the Union of Bioenergy Producers (2014), Brazil produced circa 590 million tons of sugarcane in the 2012/2013 harvest. From which, roughly 38 million tons of sugar were produced with almost 19 million tons exported. This places Brazil as the world's largest producer and exporter of crystal sugar (2014). Given the competitive sugar market in the world and the role that Brazil plays in this sector, investments in new technologies are required to obtain a product of better quality and at lower cost.

The clarification process of sugarcane juice has been the subject of several studies because sulpho-defecation or sulphitation is the current process used to obtain white crystal sugar. In 1953, Honig (1953) reported that sulphitation was the main process to clarify sugarcane juice used in Brazil to produce white crystal sugar, and currently it is still the traditional way of clarification (Hamerski, 2009). Sulphitation consists of the addition of gaseous sulfur dioxide (SO_2) to pre-heated (60°C) mixed juice until the pH value reaches between 3.8 and 4.2 (approximately 150 to 300g of sulfur per ton of sugarcane) and subsequent alkalization with lime to obtain pH 7.0-7.2. The clarification method used is considered harmful to the environment and to humans because of the toxicity of sulfur and its derivatives. Favero et al. (2011) reported that enzyme deficiency sulfite oxidase, naturally present in humans, may be related to adverse reactions caused by sulphiting agents. Asthma sufferers can be induced to have episodes or bronchospasm following ingestion of food with sulfite. The Canadian Government released a booklet answering questions about sulfite, considered one of the ten priority food allergens (Health Canada, 2012). Therefore, due to problems caused by the use of sulphiting agents as food additives to human health, alternative methods need to be used to preserve the food and beverage industry in order to minimize these effects (Machado et al., 2006).

Clarification aims to remove impurities, namely soluble, insoluble, and colloids in suspension, from the juice to preserve sucrose, main product of interest, preventing the decomposition of reducing sugars (Copersucar, 1987). Sulphitation is the current method used for sugar clarification. Sulphitation is well known in the white sugar production sector, and even though it is less costly and provides expected results, it has problems related to irregularity, operational obstacles, sucrose losses, among others (Hamerski, 2009). Recently, alternative methods for clarification such as the Fenton reaction, ozonation and the use of hydrogen peroxide are considered promising (Almeida et al., 2004). The industrial interest for ozone (O_3) has grown considerably in recent decades with the development of ozone generators on a large scale, which inflicts lower costs with installation and operation. Ozone has been widely used in treatment of drinking water, disinfection, odor and algae removal, as well as degradation of organic pollutants (Britto and Rangel, 2008).

Ozonation of compounds dissolved in water constitutes AOP (advanced oxidation process) due to the generation of hydroxyl radicals (°OH) from ozone decomposition and the reaction may be catalyzed by the presence of traces of transition metals, for example, Fe^{+2} (Chen and Chou, 1993). Hydroxyl radicals are noted for

having the ability to degrade various organic compounds and having high reaction rate (Huang et al., 1993). Ozone has long been recognized as water disinfectant, with its first use in 1940 in the United States. Since 1982, the Food and Drug Administration (FDA) certified ozone as a GRAS product ("Generally Recognized as Safe") (USDA, 1998). According to Leusink (2012), in the United States, more than 280 major water treatment plants incorporate ozone in their processes, and this number is increasing. Cities like Los Angeles, Dallas, Seattle, and Orlando use this technology to treat their drinking water.

Ozone has been tested, particularly in the pulp and paper industry, as a reference to facilitate the transfer of this technology to the sugar-energy industry (Bourzutschky, 2005). In Brazil, the use of ozone in sugarcane juice clarification is already a reality and improvement of this technology implies modifying part of the structure currently used for sulphitation to ozone. This modification requires the implementation of an ozone source connected to the same type of pipes used for sulphitation with an additional opening in the tower for the juice to have contact with the ozone gas (Silton, 2005). Vercellotti and Clarke (1997) reported that the use of ozone has an additional benefit as it reduces considerably not only the color of the crystallized product, but also the color of molasses.

In the 1090s, Moodley et al. (1999) reported the possible use of ozone to clarify refined sugar on industrial scale. The authors tested ozone use on large scale in a sugar refinery in South Africa, and showed that its use is possible in the bleaching process of refined sugar. According to Paninka (2010), at least three sugar refineries in northeastern Brazil and another in the southeast are already using this technology, and this change of technology is viewed with caution and enthusiasm. However, questions arise regarding implementation cots of this new technology. Does the equipment currently used need to be replaced? What is the best way to apply ozone? Which conditions should the sugarcane juice have before ozonation? What changes may occur to the quality of the sugar produced? Major studies are required to investigate the use, efficiency and negative effects of applying ozone in sugarcane juice clarification.

Therefore, this study assessed the use of ozone as a color reduction agent of sugarcane juice as an alternative to the sulphitation method, analyzing its effects on oxidation of colored compounds, and levels of sucrose and reducing sugars in sugarcane juice.

2. Material and Methods

2.1. Sugarcane Juice Preparation

The sugarcane juice was obtained from the Experimental Station at Piracicaba, São Paulo State, Brazil (22°42'S lat, 47°38'W long and 596 m a.s.l.). The juice was made with a grinding machine and sieved through a 200 mesh. After that, the juice was stored in polypropylene bottles at -18ºC, and naturally defrosted until room temperature (27ºC) for the experiment. The sugarcane juice used in the experiment was divided in two parts, heated and non-heated. The heating process is a common practice in power plants to remove soluble impurities from the juice. Both parts received the same ozone treatment, each physicochemical analysis had three repetitions, and the juice did not have the pH controlled before or during ozonation.

2.2. Sugarcane Juice Ozone Treatment

For the clarification trials, we prepared a kit (Figure 1) containing a stainless-steel batch reactor (V_{total} = 6 L), an ozone generation unit (HTU Azcozon Model 500AC), 250 mg O_3/h of synthetic air that produces ozone through pulse, corona discharge with constant flow, and two bottles to wash the wasted gas containing 400 mL each of potassium iodide (2%, v/v). The test used 5 L of the sieved sugarcane juice, heated or non-heated, in the batch reactor, and ozone was added (constant flow = 17.30 mg O_3/min) under constant shaking (=100 rpm). The juice was sampled in aliquots of 200 mL following a specific sequence, where 0 (control sample) corresponded to juice extracted from the reactor before the ozone treatment. After that, the sampling followed the sequence according to time of exposure to ozone in minutes at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 40, 60, 90 and 120 min for non-heated juice. For the heated juice, the sampling time was 5, 10, 15, 20, 30, 40, 50, 60, 80, 100, 120 min. The temperature in the reactor was controlled at around 27ºC using a warm/cold water mechanism. The pH was analyzed, but not controlled during ozonation.

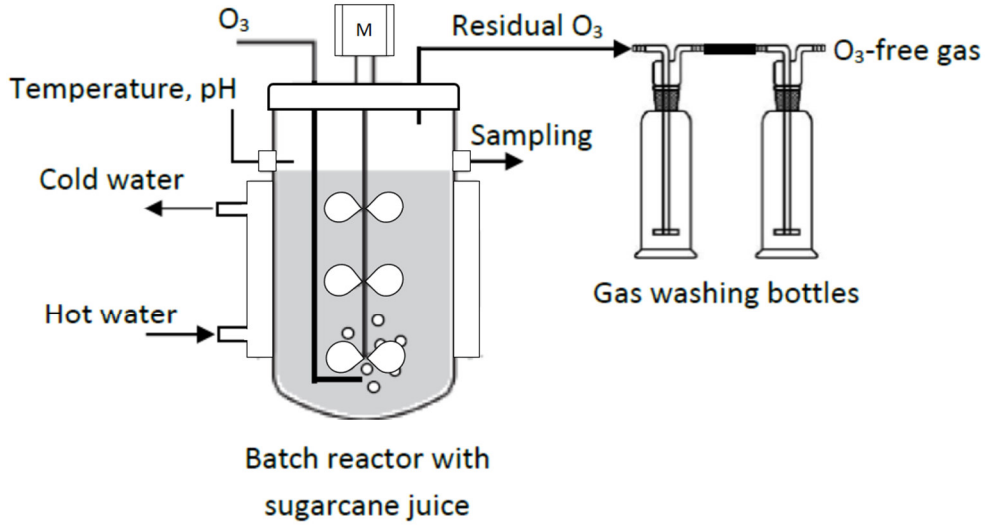

Figure 1. Laboratory scale batch reactor (6 L) with bottles for gas washing.

2.3. Total Soluble Solids (TSS) and Polarization of Sugarcane Juice

TSS were determined by direct reading on a digital refractometer (RFM model 712 from Bellingham Stanley, UK) and the means were expressed as TSS rate in weight/volume of sugarcane juice. To assess polarization, the sugarcane juice was previously clarified by adding lead subacetate P.A. Then, it was filtered to allow the reading on a digital saccharimeter (Bellingham Stanley, Model ADS420), and the means were expressed by ºZ (Zucker scale).

2.4. Reducing Sugars (RS)

RS were quantified using 500-µL of samples and 1000-µL of 3.5-dinitrosalicylic acid (Sumner et al. (1921) report by Miller (1959)), completing to 25 mL with deionized water (Milli-Q grade). The reagent tubes were conditioned for 5 min in boiling water and left to cool at room temperature. Afterward, absorbance at 540 nm was carried out in a spectrophotometer (UVmini 1240, Shimadzu Co.).

2.5. ICUMSA Color

The color index was determined by ICUMSA (1935) method, with modifications, for liquid samples, and consisted of prior dilution of the juice to obtain an approximate value of TSS equivalent to 1.25 °Brix. Then, the samples were vacuum-filtered through 0.45 µm PTFE filter (Millipore) and the pH was adjusted to 5.5 with HCl P.A. or NaOH 0.05 M. Afterward, absorbance at 420 nm was performed in a spectrophotometer (UVmini 1240, Shimadzu Co.). The color index was determined by the equation:

$$\textbf{ICUMSA Color} = \frac{(Abs^{420\ nm} * 1000)}{[\rho * (Brix_c/100)]} \qquad \rho = \frac{1 + [\ Brix_o * (200 + Brix_o)\ ]}{54000} * \frac{Brix_c}{Brix_o}$$

Where: $Brix_o$ = Concentration of TSS in the original sample, $Brix_c$ = Concentration of TSS in the diluted sample, and ρ = density of sample.

2.6. Turbidity of Sugarcane Juice

To determine juice turbidity, samples were placed in specific cuvettes to allow the reading on the digital turbidimeter (Tecpon, Model TB1000), and the means were expressed by NTU (Nephelometric Turbidity Units).

2.7. UFLC-Evaporative Light Scattering Detector for Analysis of Sugars

The UFLC this analysis used an ultra-fast liquid chromatograph (Shimadzu Co., Japan) model Prominence UFLC equipped with ELSD detector LT II (Sartori et al., 2014). The volume injected to determine glucose and fructose was 20 µL/min at a pressure of 350 kPa and a gain of seven. The retention time was 12 min. To determine sucrose, the flow rate was 5 µL/min used under the same pressure (350 kPa) at a gain of three. The retention time was 9 min. The Shim-pack VP-ODS C_{18} column (250 mm × 4.6 mm) was used and 100% acetonitrile with HPLC grade (Tedia Company Inc.) was used as mobile phase. As nebulizer gas, the Shim-pack VP-ODS C_{18} column (250 mm × 4.6 mm; 5 µm) was used and 100% acetonitrile (HPLC grade; Tedia Co.) was used as mobile phase eluted by an Asahipak NH_2P-50 4E (250 mm×4.6 mm) column at constant flow rate of 1 mL/min N. The sugar contents were determined by diluting juice samples in ultrapure water respecting the linear

range of the detector and the quantification limi. The standard curves for each sugar were determined and each analysis was made in triplicate (sucrose: ≥99.0%; glucose: ≥99.0%; and fructose: ≥99.0%) purchased by Sigma-Aldrich Co.

2.8. Titrimetric ozone dosage for ozone flow measurement

The ozone concentration (mg/min) was carried out according to Eaton et al. (2005) adapted from APHA (1980) and consisted of washing the ozone-rich gas in a solution of potassium iodide (KI 2%, w/v) and determining the ozone reacted by titration using sodium thiosulfate ($Na_2S_2O_3$ 0.005 mol/L). The gas stream that left the generator and the reactor was washed in a solution of KI 20 mg/L for 10 min. As gas scrubbers, we used two bottles containing 400 mL of KI 2% (w/v). Subsequently, 10 mL of H_2SO_4 (2 mol/L) were added to the KI solution bubbled with ozone and titrated with $Na_2S_2O_3$ 0.005 mol/L until the yellow iodine color almost disappeared. Next, we added 2 mL of starch solution (1%, w/v) and titrated the solution until the complete disappearance of blue-grayish color. The ozone flow was expressed in mg/min, according to the equation: O_3 (mg/min) = (A*N*24)/t, where A is the volume (mL) titrated of contents in flask A, N is the normality of $Na_2S_2O_3$ that was corrected by the primary standard, and t is the time of bubbling gas (min).

3. Results and Discussion

The samples were evaluated in two groups of treatments. The first treatment ozonized sugarcane juice, but without applying a heating process (non-heated) and the second ozonized sugarcane juice using a heating process before ozonation (heated). Table 1 shows the initial physiochemical characteristics of both sugarcane juices presented as average values of three repetitions with each parameter compared between both juices. The results in Table 1 show that the heating process affects the initial characteristics of the juice. The heating was able to concentrate sugars and decrease turbidity, but parameters such as RS and pH were maintained. Table 2 shows the behavior of the juices and focuses on parameters such as TSS, RS, and polarization. The results show that no significant variation occurred during ozonation. This data is fundamental to confirm that ozonation did not change the quality of the sugar juice, as observed by analyzing the levels of RS, which did not have significant changes during 120 min of ozonation, indicating that there was no hydrolysis of RS contents.

Table 1. Initial physochemical composition of sugarcane juice used for ozone treatment*.

1 *Parameters*	2 *Sugarcane juice non-heated*	3 *Sugarcane juice heated*
4 TSS (%. w/v)	5 20.9±0.01 b	6 22.0±0.01 a
7 pH	8 4.07±0.5 a	9 4.95±0.3 a
10 ICUMSA color (IU)	11 32307.5±1096.4 a	12 3196.95±103.2 b
13 Polarization (ºZ)	14 79.8±0.1 b	15 82.27±0.2 a
16 Reducing sugar (g/L)	17 13.2±0.1 a	18 12.73±0.05 a
19 Turbidity (NTU)	20 1240.2±2.68 a	21 290.6±0.55 b
22 Sucrose (g/L)	23 182.14±0.05 b	24 210.62±0.03 a
25 Glucose (g/L)	26 1.34±0.002 b	27 1.65±0.001 a
28 Fructose (g/L)	29 1.88±0.001 b	30 2.10±0.003 a

*Means±standard deviations followed by the same letters in line do not differ significantly by the Tukey test ($p < 0.05$).

Table 2. Physicochemical characteristics of sugarcane juice heated or non-heated*.

Time	*Sugarcane juice non-heated*			*Sugarcane juice heated*		
	TSS**	Pol**	RS**	TSS	Pol	RS
min	%. w/v	ºZ	g/L	%. w/v	ºZ	g/L
0	20.9±0.01 Aa	79.8±0.1 Aa	13.2±0.1 Aa	22.0±0.02 Bb	82.3±0.6 Cc	12.7±0.7 Aa
5	21.1±0.02 Aa	79.6±3.4 Aa	13.3±0.1 Aa	21.7±0.01 Cc	82.6±0.5 Cc	14.0±3.0 Aa
10	21.0±0.02 Aa	80.7±0.02 Aa	12.8±0.6 Aa	21.7±0.02 Cc	82.9±0.02 Bb	15.03±1.1 Aa
20	21.0±0.01 Aa	80.3±0.02 Aa	11.9±0.8 Aa	21.9±0.02 Cc	82.9±0.04 Bb	13.4±0.7 Aa
30	20.9±0.01 Aa	80.3±0.02 Aa	13.9±0.4 Aa	21.1±0.03 Cc	80.2±0.5 Dd	14.3±0.2 Aa
40	21.0±0.01 Aa	80.4±0.05 Aa	13.2±0.4 Aa	21.8±0.02 Cc	82.6±0.04 Cc	14.8±1.03 Aa
50	20.9±0.02 Aa	80.4±0.02 Aa	13.0±0.3 Aa	21.9±0.01 Cc	82.8±0.02 Cc	13.1±0.7 Aa
60	21.0±0.02 Aa	80.3±0.04 Aa	12.8±0.2 Aa	21.9±0.01 Cc	83.04±0.04 Bb	13.3±1.2 Aa
80	20.9±0.01 Aa	80.4±0.04 Aa	13.4±0.3 Aa	23.0±0.04 Aa	87.03±0.06 Aa	11.8±1.7 Aa
100	21.0±0.01 Aa	80.3±0.02 Aa	13.3±0.2 Aa	21.8±0.02 Cc	82.7±0.02 Cc	13.0±1.4 Aa
120	20.9±0.01 Aa	80.6±0.02 Aa	13.3±0.2 Aa	21.9±0.02 Cc	83.1±0.03 Bb	14.0±0.7 Aa

*Means±standard deviations followed by the same lower case letters and capital letters on a column do not differ significantly by the Tukey test ($p < 0.01$ and $p < 0.05$, respectively). ** TSS: total soluble solids in percetage of

solids in sugarcane juice; Pol: polarization at ºZ; RS: reducing sugars in g/L.

3.1. Evaluation of Sugarcane Juice Treated with Ozone

During the ozonation process, the gas was kept bubbling in the washing bottles, however, the color in KI solution change very little, which did not allow titration of these samples. This condition was observed in both treatments (heated and non-heated), then we assumed that there was no significant ozone output from the reactor. It also represents good reaction of ozone with the organic components of sugarcane juice. According to Mahmoud and Freire (2007), ozone may react as an electrophilic or nucleophilic agent. Generally, in degradation reactions of organic compounds, ozone reacts preferentially with unsaturated compounds such as alkynes or aromatic rings.

Hamerski (2009) stated that one of the most important parameters for the sugarcane industry is the final color of sugar because determines its quality and value. The reduction of color indexes in the first moment in the experiment was very prominent. It means a significant reduction of ICUMSA color in the sugarcane juice when compared with the initial color without treatment. There was significant reduction in the ICUMSA color indexes, however, the comparison of indexes (Table 3) showed a very significant difference in how these treatments behaved. This difference was attributed to the heating process.

Table 3. ICUMSA color values of sugarcane juice heated or non-heated*.

Time (min)	*Non-heated*				*Heated*			
	Color (IU)	*SD*	*p < 0.01*	*p < 0.05*	*Color (IU)*	*SD*	*p < 0.01*	*p < 0.05*
0	32307.5	±1096.4	A	a	3197.0	±103.2	A	a
5	13053.1	±300.7	BC	bc	2620.9	±79.4	B	b
10	12497.4	±242.7	BCD	bcd	2093.4	±84.3	CDE	cde
20	13414.5	±168.7	B	b	2174.4	±150.7	CD	cd
30	13147.0	±73.04	BC	b	1947.6	±210.8	CDE	def
40	10079.1	±73.04	F	fg	2319.5	±50.2	BC	bc
50	12051.4	±146.08	CD	cd	1801.2	±84.3	DE	ef
60	10249.6	±210.8	EF	fg	1747.2	±137.6	E	f
80	11418.4	±111.6	DE	def	1905.6	±79.4	DE	def
100	9251.4	±183.8	F	g	2161.4	±117.0	CD	cd
120	10468.9	±42.2	EF	ef	1981.6	±39.0	CDE	def

*Means (IU) ± standard deviations (SD) followed by the same lower case letters and capital letters on a column do not differ significantly by the Tukey test ($p < 0.01$ and $p < 0.05$, respectively).

The heating in boiling (approximately 98°C, in Piracicaba/SP-Brazil) for 20 min has been a common practice to purify sugarcane juice, because after boiling, the juice cools down to room temperature, leading to the precipitation of waxes and proteins (Table 1). The increased polarization in heated juice (79.8±0.1 to 82.27±0.2 ºZ; non-heated to heated, respectively) indicates an opposite behavior against vegetable impurities (Turbidity: 1240.2±2.68 to 290.6±0.55 NTU). Thus, ozone may have served only as an adjuvant in color reduction (Table 3), a key point for the sugarcane industry, since in the traditional process of juice clarifying by heating, juice passes through heat before the chemical treatment as described by Rein (2007), which the author exemplifies in the typical methods used by sugar plants for clarification with liming. During the reaction time, juice ozonation promoted a decrease in the ICUMSA color index and was more significant in the first minutes of ozonation. About 34% of ICUMSA color reduction was observed in heated juice treatment, and around 60% in the non-heated (Table 3).

For polarization (Zº, apparent sucrose content by polarimetry), the starting behavior differs in both treatment, however, they followed the same trend at the end of the experiment, with a decrease the initial Pol values followed by some changes in the Pol values, leading to a slight increase in these levels when compared to the juice before ozonization (Tables 1 and 2).

RS showed no significant changes during treatments when comparing to start and end values of the treatment, but the samples suffered minor changes throughout the treatment, and heated juice was the most inconstant. There is a reduction in RS levels probably due to the consumption of sugars during the ozonation process, which promoted oxidation of glucose and/or fructose (Table 2 and Figures 2 and 4). Similarly, Soja et al. (2004) described that trials with O_3 in grape juice had no significant effects on RS. During ozonation, RS contents in non-heated sugarcane juice stopped varying and remained steady until the end of the experiment recording a small decrease (Figure 4). The variation was about 10.0% of that reported by Polívka et al. (2002), who stated that ozone does not influence RS amounts, pH and organic acids, or even the sensory properties of samples of fruit jams.

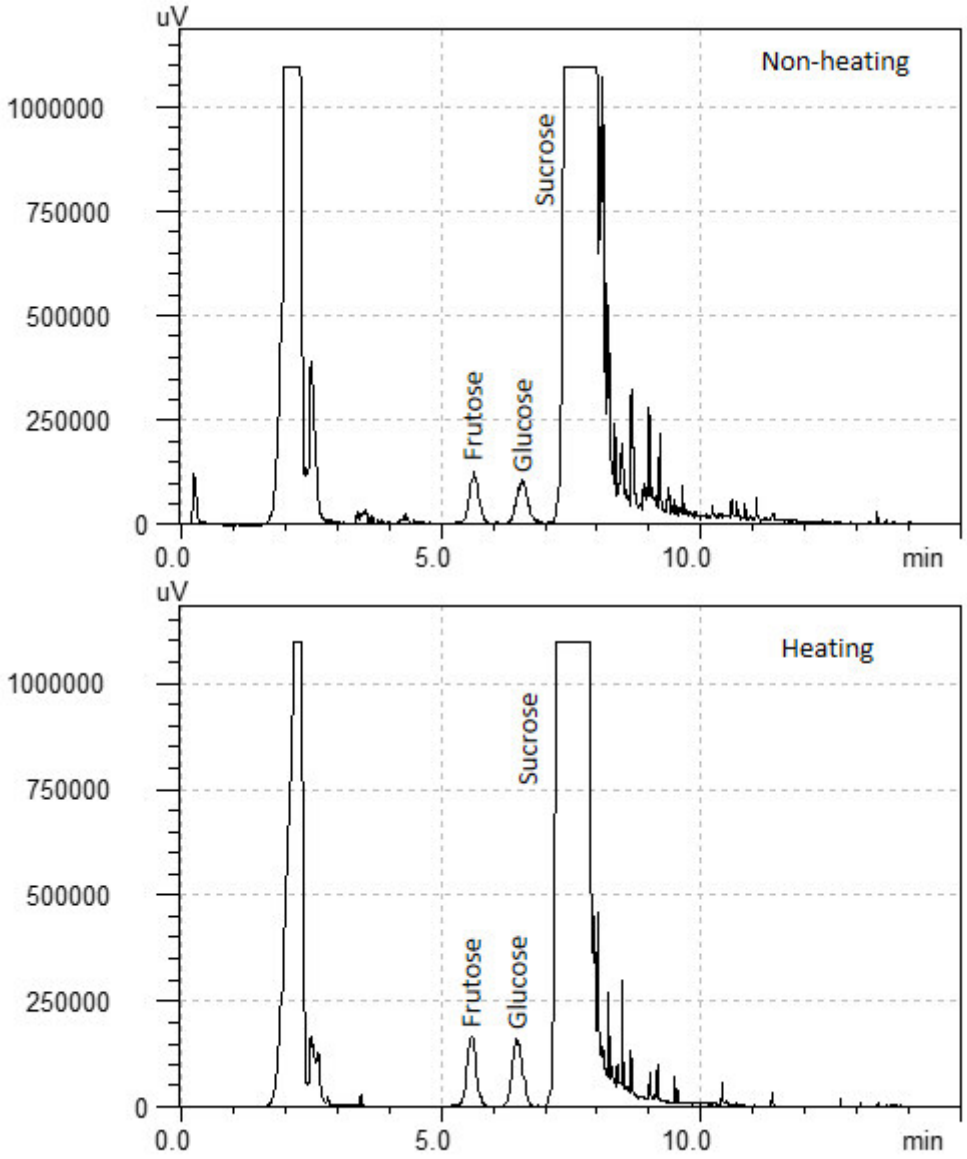

Figure 2. Chromatogram of fructose (Rt = 5.5 min) and glucose (Rt = 6.5 min) isolated from sugarcane juice by UFLC–ELSD at time zero without ozone treatment.

For Muthukumar et al. (2004), the treatment of colored wastewater effluents in acidic pH and reduction of total organic carbon (TOC) with ozone treatment are influenced by different variables such as salt concentration, pH and exposure time. Davis et al. (1998) reported that the mechanisms through which ozone destroys pigmented compounds are direct and varied. Different functional groups are attacked by ozone, which is highly oxidant (E^o=2.42 v), breaking these functional groups of molecules. Ozone also attacks phenolic groups, breaking the aromatic structure and many amino groups (precursors of Maillard reactions) by oxidizing them to nitrate.

Walter and Sherman (2006) found that the treatment of sugar solutions with a small dose of ozone (10 mg O_3/g sugar) could oxidize the solute directly or indirectly to the corresponding aldonic acids (HOOC-n-CH_2OH). Thus, during ozonation at doses studied here, degradation may occur from sucrose or from its monomers (glucose and fructose) (Figures 3 and 4 – label ○) and carboxylic acids. No significant changes were observed in the initial and final values of TSS contents (Table 2). Similar to other samples, the values for heated juice behaved inconsistently, but after treatment, the values were equal to the initial value analyzed for both treatments. Juice turbidity is an important reference as it reflects in the final quality of sugar crystals. In both ozonation treatments, turbidity was reduced (Table 4), but only it continued to decrease only in the non-heated juice. The heated juice showed a more significant reduction in the opening minutes, however, after around 80 minutes, turbidity values started to increase again, reaching a final index slightly higher than the initial. This behavior can be explained because impurities flocculate with heating, increasing purity of sugars in the juice

(Table 1). The decrease of turbidity is a response to the separation form the soluble to the liquid phase.

Table 4. Turbidity values of sugarcane juice non-heated or heated*.

Time (min)	*Non-heated*				*Heated*			
	Turbidity (NTU)	*SD*	*p < 0.01*	*p < 0.05*	*Turbidity (NTU)*	*SD*	*p < 0.01*	*p < 0.05*
0	1240.2	±2.7	A	a	290.6	±0.55	D	d
5	1228.8	±5.93	AB	ab	300.8	±1.30	B	b
10	1233.4	±5.41	AB	ab	295.6	±0.55	C	c
20	1227.0	±9.87	AB	ab	287.8	±0.45	E	e
30	1218.8	±7.3	B	b	246.2	±0.84	F	f
40	1200.8	±10.2	C	c	167.4	±0.55	H	h
50	1196.8	±4.43	C	c	133.8	±0.84	J	j
60	1205.6	±4.22	C	c	131.2	±0.45	K	k
80	1194.6	±12.34	C	c	137.0	±0.71	I	i
100	1169.6	±6.54	D	d	233.8	±0.84	G	g
120	1190.8	±19.33	C	c	321.6	±0.89	A	a

*Means (NTU) ± standard deviations (SD) followed by the same lower case letters and capital letters on a column do not differ significantly by the Tukey test ($p < 0.01$ and $p < 0.05$, respectively).

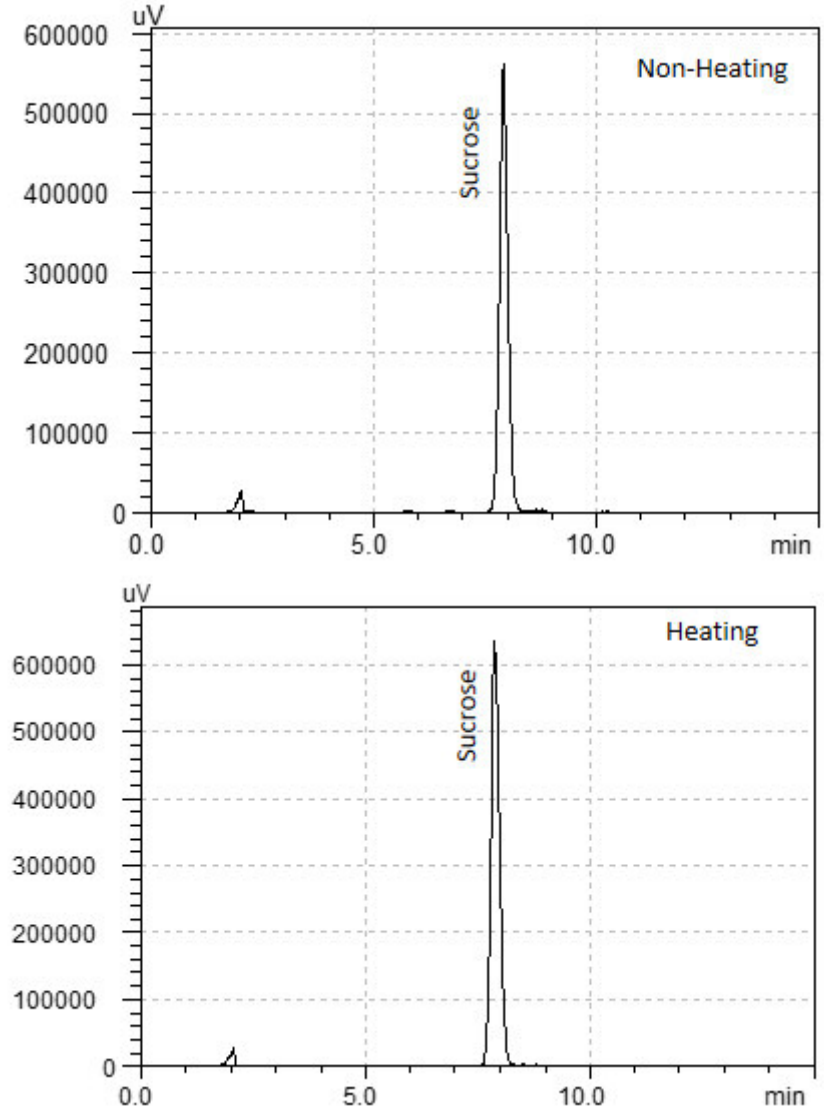

Figure 3. Chromatogram of sucrose (Rt = 7.9 min) isolated from sugarcane juice by UFLC–ELSD at time zero, without ozone treatment.

Glucose, fructose and sucrose contents were obtained by the comparative analysis (Figures 2, 3 and 4), performed in the heated and non-heated samples for glucose and fructose prior to treatment with O_3 (17.3 mg

O_3/min). The concentration of solutes in juice is high, therefore, analyses of the three different sugars should not be performed in only one way. Thus, sucrose was analyzed separately using a higher gain in chromatography to adjust the viewing scale. Peak areas were determined from these profiles, obtaining concentrations of glucose, fructose and sucrose (Figure 4) from both ozonized juices using the kinetic model of C/Co (Concentration kinetics).

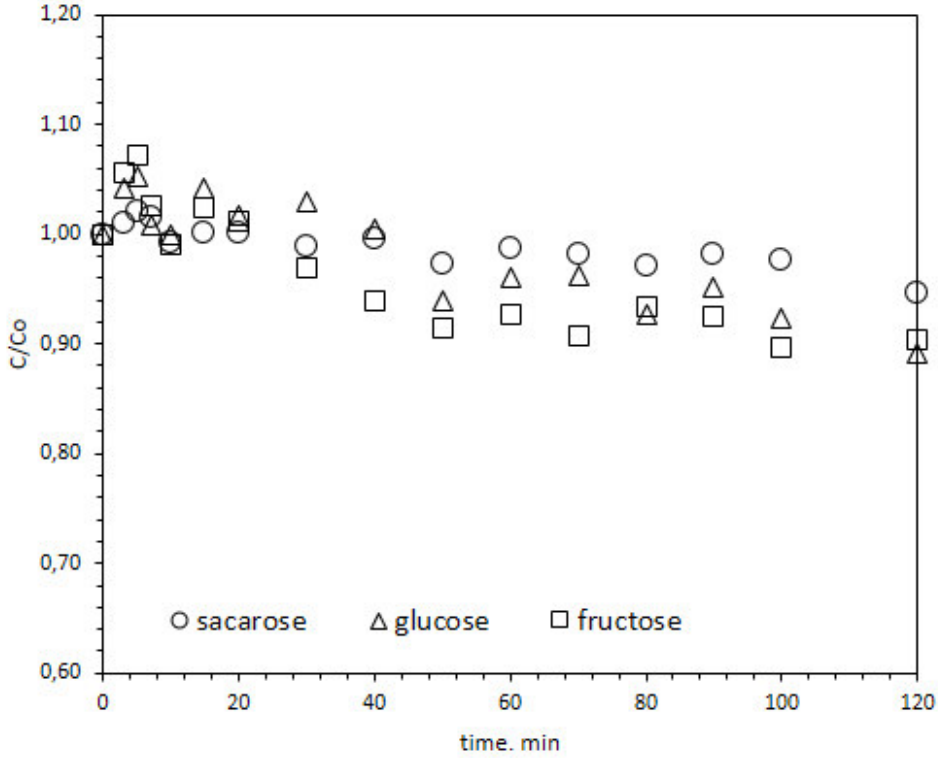

Figure 4. Degradation kinetics of sucrose (○), glucose (△) and fructose (□) forms during ozone treatment for 120 minutes. C/Co: concentration of each sugar at one time per initial concentration.

The heated juice showed higher quantity of sugars, which can be explained by the concentration of sugars after the heating process and before ozonation that evaporates water and concentrates the juice. We also carried out a concentration analysis of these sugars during the treatment with O_3 only for the non-heated juice, because the treatment was considered the most promising since the beginning of the experiment (data not shown).

4. Conclusions

The results allowed to conclude that the use of ozone in clarification of sugarcane juice is a viable alternative, since changes in reducing sugars and sucrose were not very significant, while the decrease of ICUMSA color was significant. However, it is necessary to determine the best way to obtain this technology in the clarification process because the heat treatment has great influence in juice color. This behavior can affect the correct use of O_3 as a clarifying agent as observed in treatments pre-heating sugarcane juice for the clarification process.

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References

Almeida E, Assalin MR, Rosa MA, Durán N (2004) Industrial wastewater treatment by oxidative processes in the presence of ozone. *Quimica Nova* 27, 818-824.

APHA. American Public Health Association (1980) *Standard methods for the examination of water and was and wastewater.* Washington: American Public Health Association.

Bourzutschky HCC (2005) Color formation and removal: options for the sugar and sugar refining industries: a review. *Zuckerindustrie* 130, 470-475.

Britto JM, Rangel MC (2008) Advanced oxidation processes of phenolic compounds in industrial effluents.*Química Nova* 31, 114-122.

Chen JCP, Chou C (1993) *Cane Sugar Handbook.* A manual for cane sugar manufacturers and their chemists.

12th ed. New York John Wiley & Sons.
Copersucar (1987) *Handout of course Engineering Sugar* - Sugar Manufacturing process - Part I. Centro de Tecnologia Copersucar – CTC. Copersucar, Piracicaba.
Davis SB, Moodley M, Singh I, Adendorff MW (1998) The use of ozone for colour removal at the Malelane refinery. *Proceedings of South African Sugar Technologists Association* 72, 255-260.
Eaton, A. D. *Standard methods for the examination of water and wastewater*. APHA, 21 st ed., 2005
Favero DM, Ribeiro CSG, Aquino AD (2011) Sulfites: importance in the food industry and its possible harm to the population. *Segurança Alimentar e Nutricional* 19, 1-120.
Hamerski F (2009) *Study of variables in the sugarcane juice carbonation process* 149 p. Thesis in Food Technology - Graduate Program in Food Technology, Technology Sector of Paraná Federal University , Curitiba.
Health Canada (2012) *Sulphites - One of the Ten Priority Food Allergens.* Health Products and Food Branch, ISBN 978-1-100-21160-2, Canada.
Honig P (1953) *Principles of sugar technology*. New York: Elsevier Publishing Company, v. 1.
Huang CP, Dong C, Tang Z (1993) Advanced chemical oxidation it's present role and potential future in hazardous waste treatment. *Waste Management* 13, 361-377.
ICUMSA (1935) International commission for uniform methods of sugar analysis. International Sugar Journal 37, 180-187.
Leusink J (2012) *Ozone use in drinking water.* [Online] Available: http://www.ozonesolutions.com/journal/2012/ozone-use-in-drinking-water (May 14, 2014)
Machado RMD, Toledo MCF, Vicente R (2006) Sulfites in foods. *Brazilian Journal of Food Technology* 9, 265-275.
Mahmoud A, Freire RS (2007) New methods for enhancing ozone efficiency on contaminated water treatment. *Química Nova*, 30, 198-205.
McConnel M, Dohlman E, Haley S (2010) World sugar price volatility intensified by market and policy factors. *Amber Waves*, 8, 28.
Miller GL (1959) Use of dinitrosalicylic acid reagent for determination of reducing sugars. *Analytical Chemistry* 31, 426-428.
Moodley M, Davis SB, Abendorff M (1999) Full Scale decolourisation trials with ozone. *International Sugar Journal* 101, 165-170.
Muthukumar RM, Sargunamani D, Selvakumar N, Venkata-Rao J (2004) Optimisation of ozone treatment for colour and COD removal of acid dye effluent using central composite design experiment. *Dyes Pigments*, 63, 127-134.
Paninka RM (2010) *Clarification of sugarcane juice with ozone gas: an alternative to conventional treatment.* Monograph. Specialization Master of Technology Administration (MTA). Federal University of São Carlos.Araras, Brasil.
Polívka L, Fendric E, Skarka B (2002) Influence of ozone on properties of jams. *Czech Journal of Food Sciences*20, 113-115.
Rein P (2007) *Cane Sugar Engineering*. Berlim: Verlag Dr. Albert Bartens KG, 768 p.
Sartori, J. A. d. S., Galaverna, R., Eberlin, M. N., Correa, N. T., Mandro, J. L. and de Aguiar, C. L. (2014), Elucidation of Color Reduction Involving Precipitation of Non-Sugars in Sugarcane (*Saccharum* sp.) Juice by Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry. *Journal of Food Processing and Preservation.* doi: 10.1111/jfpp.12417.
Silton RNC (2005) Process of clarifying the sugarcane juice by ozonation. Brazil patent PI 0505003-0 A. Date of Deposit 26/10/2005. Publication date 07/08/2007.
Soja G, Reichenauer TG, Eid M, Soja A-M, Schaber R, Gangl H (2004) Long-term ozone exposure and ozone uptake of grapevines inopen-op chambers. *Atmospheric Environmental* 38, 2313–232.
Sumner J. B., Graham V. A.. Dinitrosalicylic acid: a reagent for the estimation of sugar in normal and diabetic urine. *Journal of Biological Chemistry*, 47: 5-9, 1921.
UDOP. Union of Bioenergy Producers (2014) [Online] Available: http://www.udop.com.br/index.php?item=acucar (June 25, 2014)
UNICA. Industry Union Cane Sugar (2014) [Online] Available: http://www.unica.com.br/dadosCotacao/estatistica (June 25, 2014)
USDA. United States Department of Agriculture (1998) *Food safety technology*: a potential role for ozone? Washington: Economic Research Service/USDA, p. 13-15.
Vercellotti JR, Clarke MA (1997) Color removal – chemical treatment symposium: sugar colour in refineries. *Proceedings of Sugar Industry Technologists*, 56, 272-295.
Walter RH, Sherman RM (2006) Reduction in chemical oxygen demand of ozonated sugar solutions by charcoal. *Journal of Food Science* 43, 404-406.

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