



## Starch and ICUMSA color removal in sugarcane juice clarified by carbonatation

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**ABSTRACT.** The manufacture of sugar with sulfur dioxide during the clarification process faces market difficulties and rejection by consumers who are more and more concerned on food safety. The alternative may be sugar clarification with carbon dioxide which consists in adding carbon dioxide and calcium hydroxide to sugar juice at constant pH. Under these conditions, a calcium carbonate complex is formed which adsorbs and precipitates impurities. Current assay analyzes the clarification of sugarcane juice in a laboratory carbonatation process. Assays were performed randomly with a two-level factorial design with three replications at the center point to evaluate the effect of pH and carbon dioxide flow in clarification. Process efficiency was assessed according to rates of starch removal, ICUMSA color and calcium left in the juice. Rates of starch removal at 89.19 and 85.75% and of ICUMSA color at 92.93 and 91.66% were obtained, respectively, in assays with carbon dioxide flow at 200 NL h<sup>-1</sup> and pH at 8.0 and 9.0. Results show that total added calcium was almost removed as calcium carbonate.

**Keywords:** sugar, carbon dioxide, calcium carbonate, clarification.

## Remoção de amido e cor ICUMSA em caldo de cana clarificado pelo processo de carbonatação

**RESUMO.** A produção de açúcar, utilizando o dióxido de enxofre no processo de clarificação, encontra barreiras de mercado e de consumidores cada vez mais preocupados com a segurança alimentar. Uma alternativa é a clarificação por carbonatação, esta consiste em adicionar dióxido de carbono (CO<sub>2</sub>), ao caldo de cana juntamente com hidróxido de cálcio (Ca(OH)<sub>2</sub>), mantendo o pH constante, e formando o complexo carbonato de cálcio, que adsorve impurezas e as precipitam. O objetivo deste trabalho é clarificar o caldo de cana-de-açúcar pelo processo de carbonatação, em escala de laboratório. Os experimentos foram realizados aleatoriamente seguindo o delineamento fatorial 2<sup>2</sup> com três repetições no ponto central a fim de avaliar o efeito do pH e da vazão de CO<sub>2</sub> na clarificação. A eficiência do processo foi avaliada, segundo a remoção de amido e cor ICUMSA e quanto ao teor de cálcio remanescente no caldo clarificado. Remoções de amido de 89,19 e 85,75% e cor ICUMSA 92,93 e 91,66% foram obtidas nos experimentos com vazão de CO<sub>2</sub> de 200 NL h<sup>-1</sup>, em valores de pH igual a 8,0 e 9,0 respectivamente. Os experimentos mostraram que a quase totalidade do cálcio adicionado ao processo foi removido na forma de carbonato de cálcio.

**Palavras-chave:** açúcar, dióxido de carbono, carbonato de cálcio, clarificação.

### Introduction

Brazil plays a relevant role in sugar manufacturing and is one of the greatest world producers and exporters. According to MAPA (2012), almost thirty-five million tons of sugar were produced in the country during the 2010-2011 harvest and data for previous harvests showed that the demand for sugar has been increasing owing to rising demands in sugar-added foods.

The clarification process is one of the most important steps in the manufacturing of white sugar. The clarification of sugar cane juice aims at

eliminating as much impurities as possible by colloids coagulation and formation of precipitates which adsorb and drag the colloidal impurities. However, the process must not cause sucrose inversion, destruction of reducing sugars or decrease in purity (CHEN; CHOU, 1993). When clarification is inefficient, the juice retains impurities which accumulate as the juice is concentrated and which are finally incorporated to the sugar impairing its quality (BEZERRA, 2005).

Starch is one of the components which must be removed during the clarification process, since its presence inside the sucrose crystals hinders

subsequent crystallization and refining steps (CHEN; CHOU, 1993; RONALDSON; SCHOONEES, 2004).

The color of manufactured sugar is another highly important feature since there is currently an increasing demand for whiter and purer types of sugar. Colored substances from different sources are present in raw sugar, including those derived from plants (pigments) and others formed during sugar manufacturing (BOURZUTSCHKY, 2005; HONIG, 1953).

Pigments are naturally occurring compounds present in sugarcane and other plants. During sugarcane crushing, the extracted pigments constitute the juice's non-sugar portion which ultimately impairs the white sugar production process. Flavonoids are a critical group for sugar processing since they cause up to 30% of the raw sugar color when the sugar is produced at pH 7.0. Anthocyanins, which belong to the flavonoids group, produce a red and blue color respectively in an acid and alkaline medium (BOURZUTSCHKY, 2005). Other authors report that the removal of anthocyanins from sugar juice occurs by precipitation, which results from the excess calcium used during the carbonation process (ARAÚJO, 2007; CASTRO; ANDRADE, 2007).

In Brazil the clarification of sugarcane comprises two types of process: whereas the addition of lime is commonly used in manufacturing raw sugar for export, the addition of sulfur dioxide is mostly used for the manufacturing of crystal sugar (PRATI et al., 2005). According to Bezerra (2005), the ban of sulfides in sugar exported to Europe and the United States seems to have changed this state of affairs. Alternative technologies for clarifying sugar include the employment of ozone and carbon dioxide.

The carbonation of sugar cane juice consists in adding carbon dioxide concomitantly with calcium hydroxide, stabilizing its pH and forming the calcium carbonate complex, which acts as an agglutinating agent for the removal of substances diluted in the juice (HAMERSKI et al., 2011).

Nowadays the main concern on the presence of sulfur in sugar is that it may be harmful to most people (FAVERO et al., 2011). Mathison et al. (1985) reported that asthmatic patients suffered from acute asthmatic asphyxia immediately after the ingestion of low doses of sulfides.

Therefore, as a contribution to studies dealing with the clarification of sugar cane juice by carbonation, current investigation studied the influence of the addition of carbon dioxide and pH control on starch and ICUMSA color removal in the clarification of sugar cane juice.

## Material and methods

### Raw material

The in natura juice was obtained from conventional crushing of the sugar cane harvested during the 2010 harvest in the Vale do Ribeira region lying between the south of the state of São Paulo and the eastern area of the state of Paraná, Brazil.

Purified calcium oxide was used to prepare calcium hydroxide aqueous solution at a concentration of 75 g L<sup>-1</sup> concentration. Anionic polyelectrolyte was CIBA®MAGNAFLOC®LT27AG.

### Experimental design

A 2<sup>2</sup> full factorial design with three replications at center point was employed to investigate the effect of pH and CO<sub>2</sub> flow on the carbonation process. One single lot of sugar cane was used. Levels of independent variables were selected, foregrounded on results of previous studies (AOKI; TAVARES, 1986; HAMERSKI et al., 2011; MOODLEY et al., 2003). Several studies showed that the highest removal rates of undesirable constituents and the lowest sucrose degradation rates were observed at pH between 8.0 and 9.0. Other studies employed a CO<sub>2</sub> flow of 120 NL h<sup>-1</sup>, which was both increased and decreased in current analysis. Table 1 shows the experimental design employed.

**Table 1.** Experimental design.

Trial	pH	CO <sub>2</sub> flow (NL h <sup>-1</sup> )	Variables in codified units	
1	8.0	40	-1	-1
2	8.0	200	-1	+1
3	9.0	40	+1	-1
4	9.0	200	+1	+1
5 <sup>CP</sup>	8.5	120	0	0
6 <sup>CP</sup>	8.5	120	0	0
7 <sup>CP</sup>	8.5	120	0	0

CP: center point.

### Carbonation apparatus

Figure 1 shows the apparatus used for collecting the experimental data which were retrieved during the sugar cane juice clarification in current assay.

In natura sugar cane juice was previously weighed (500 g), heated and kept at 80°C in a thermostatic bath throughout the reaction. A 75 g L<sup>-1</sup> calcium hydroxide solution was then added to the juice until the desired pH levels were reached, i.e., pH 8.0 (Trials 1 and 2), pH 8.5 (Trials 5, 6, and 7) and pH 9.0 (Trials 3 and 4). The desired pH levels remained constant due to the addition of calcium hydroxide during the reaction. Carbon dioxide flows were adjusted according to levels planned in the experimental design, or rather, 40 NL h<sup>-1</sup> (Trials 1

and 3), 120 NL h<sup>-1</sup> (Trials 5, 6, and 7) or 200 NL h<sup>-1</sup> (Trials 2 and 4). After releasing the flow of carbon dioxide, the reaction took place during 50 minutes.

At the end of the clarification process, the juice was removed from the thermostatic bath and 1 mL of a solution containing the anionic polyelectrolyte was added. Final juice electrolyte concentration was 2 mg L<sup>-1</sup>. The system was then stored for 1 hour under room temperature so that the electrolyte adsorbed the impurities in the juice. Samples were then collected for further analyses.

### Experimental analyses

Juice acidity, starch content, ICUMSA color, total soluble solids and pH were evaluated according to methods described by the International Commission for Uniform Methods of Sugar Analysis (ICUMSA).

Calcium contents in raw and clarified juices were evaluated by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), following guidelines of the Center for Food Research and Processing (CEPPA, 2010).

All analyses were performed in triplicate to estimate any experimental error.

### Statistical

Data underwent analysis of variance (ANOVA) at 5% confidence level and Tukey's mean test was employed when there were differences between means. Factor's influence on responses was expressed by using response surface plots whilst pareto chart of effect was used to show the kind of effect observed.

## Results and discussion

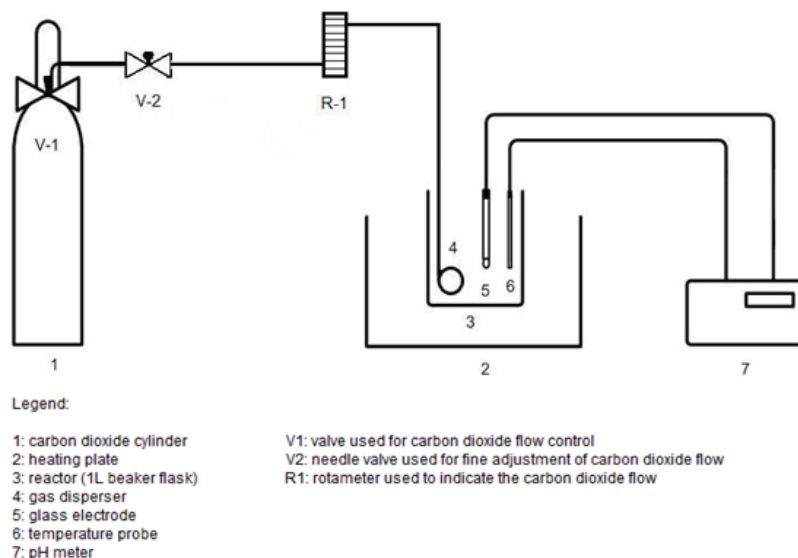
### Characterization of in natura sugar cane juice

In natura sugar cane juice was previously evaluated to compare and quantify the effect of the carbonatation process on its composition (Table 2).

The in natura sugar cane juice's pH was approximately 5.27. Chen and Chou (1993) reported that pH of juice obtained from healthy, fully mature sugar canes ranged between 5.2 and 5.4, which varied according to cane variety and harvest area. Current results show that the sugar cane juice samples were proper for consumption and could be used to study the carbonatation process.

### Starch and ICUMSA color removal in the clarified juice

Table 3 shows the influence of carbonatation conditions on the removal of starch and ICUMSA color in the clarified juice.



**Figure 1.** Carbonatation apparatus.

**Table 2.** In natura sugar cane juice composition.

Analysis	Lot
pH	5.27 ± 0.00
Titrate acidity (mg of CH <sub>3</sub> COOH 100 mL <sup>-1</sup> of sample)	48.16 ± 7.25
Total soluble solids (°Brix)	21.10 ± 0.01
Starch (%mg TSS <sup>-1</sup> )	238.60 ± 2.11
ICUMSA color (UI)	32633 ± 1203.24
calcium (mg kg <sup>-1</sup> )	80.29 ± 0.36

**Table 3.** Mean rates of starch concentration and ICUMSA color and their percentage removal after the clarification process.

Trial (**)	Starch concentration (% mg TSS <sup>-1</sup> )	Removal (%)	ICUMSA color	Removal (%)
1 (8.0 - 40)	44.32 ± 1.46	81.95cd ± 0.59	5100 ± 360.56	84.37f ± 1.10
2 (8.0 - 200)	25.78 ± 0.08	89.19a ± 0.03	2308 ± 76.92	92.93a ± 0.24
3 (9.0 - 40)	46.44 ± 0.89	80.54d ± 0.37	4567 ± 152.75	86.01e ± 0.47
4 (9.0 - 200)	34.00 ± 0.81	85.75b ± 0.34	2722 ± 96.23	91.66ab ± 0.29
5 (8.5 - 120)	41.40 ± 0.08	82.65c ± 0.03	4000 ± 100.00	87.74d ± 0.31
6 (8.5 - 120)	40.51 ± 0.65	83.02c ± 0.27	2872 ± 44.41	91.20b ± 0.14
7 (8.5 - 120)	42.94 ± 4.21	82.00cd ± 1.7	3485 ± 138.87	89.32c ± 0.43

Note: Different letters in the same column denote statistically significant difference at 5% confidence level. \*\*Experimental conditions: pH and carbon dioxide flow (NL h<sup>-1</sup>).

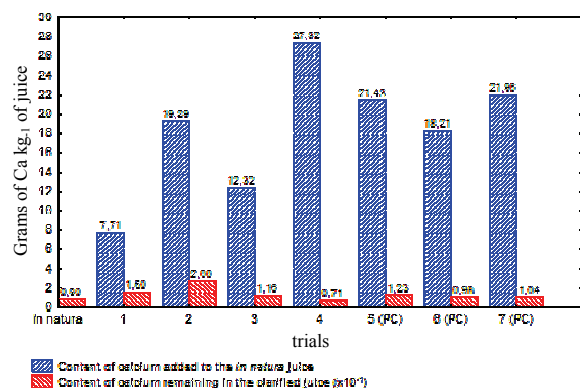
Maximum percentage removal of starch occurred in Trial 2 (89.19%), followed by Trial 4 (85.75%) although removals were statistically different. Moodley et al. (2003) studied the clarification of raw sugar by carbonatation and observed a removal of 93% of the starch, whereas Hamerski et al. (2011) obtained 87.07% starch removal.

In the case of ICUMSA color removal, treatments 2 and 4, statistically similar to one another (92.93% and 91.66%, respectively), were the most effective. Hamerski et al. (2011) obtained a higher color removal (66.57%) with the following process conditions: pH 8.0; 40 min. reaction time; 80°C.

#### Analysis of calcium content

Different amounts of calcium were added in each experiment. The difference may be attributed to the several acidities obtained by using various carbon dioxide flows and several pH rates to be reached according to the planned experimental design. Once the amounts of calcium hydroxide added in each experiment were acknowledged, the amount of added calcium could be calculated.

After the clarification process, the clarified juice calcium concentration was evaluated (Figure 2) and the removal of most calcium added was reported.

**Figure 2.** Comparison between the calcium added during the clarification process and the calcium remaining in the clarified juice.

Since Moodley et al. (2003) obtained similar results, the above demonstrated that calcium removal from the clarified juice took place with the

formation of the calcium carbonate complex, as shown below.

Initially, when Ca(OH)<sub>2</sub> was added, the dissociated Ca<sup>++</sup> and OH<sup>-</sup> ions were introduced in the juice, according to reaction (1):



The carbon dioxide bubbled into the alkaline medium was absorbed to form the bicarbonate ion, according to reaction (2).



The bicarbonate ion in alkaline medium decomposed into carbonate ion and neutralized the medium, according to reaction (3).



Further, the carbonate precipitate was formed, according to reaction (4).



The calcium carbonate complex formed during the reaction between the added carbon dioxide and the added (Ca(OH)<sub>2</sub>) demonstrated the capacity of adsorbing substances and precipitating them because of an increase in the complex's molecular weight. Therefore, high CO<sub>2</sub> flows reduced pH more rapidly and required higher amounts of Ca(OH)<sub>2</sub> to stabilize the pH. Higher quantities of calcium carbonate were thus formed which, in turn, removed higher amounts of undesirable constituents.

Figure 3 shows starch and ICUMSA color removal after treatments. Since Trials 2 and 4 were the most efficient ones, the above hypothesis was confirmed.

However, the mere addition of more calcium did not necessarily remove more constituents.

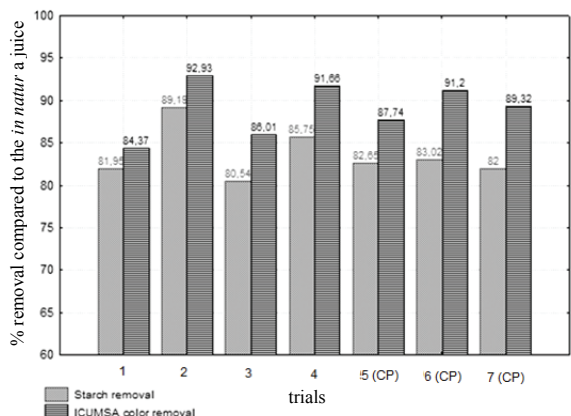


Figure 3. Removal of sugar cane juice constituents.

The above occurred because the addition of calcium affected the reaction's pH. For instance, higher pH rates (9.0) were correlated to lower starch removal when compared to those by lower pH rates (8.0).

Aoki and Tavares (1986) found similar results, or rather, an increase in the quantity of calcium added to the process improved the removal of color from the clarified juice up to a certain limit. ICUMSA color removals of 74.8% were observed for pH 8.5 and 70.2% for pH 8.0. Consequently, the same authors reported that high ICUMSA color removal was observed when the carbonatation process was conducted at pH 8.0 or 8.5.

Hamerski et al. (2011) reported that high pH values might be related to a higher reducing sugar degradation, yielding carboxylic acids that polymerized to form high molecular weight colorful compounds which provided the product with color. In current study, no statistically significant

differences for color removal were observed between Trials 2 and 4.

### Starch removal expressed in response surface plots

The analysis of variance for the linear model used to explain the effect of factors on starch removal yielded an adjusted coefficient of determination ( $R^2_{adj} = 0.77$ ). Further, ANOVA showed that the effects of pH and carbon dioxide flows on the starch removal were significant at 5% level. On the other hand, the interaction between factors was not significant.

Figure 4a shows the effect estimates. The rectangles that crossed the vertical line were significant factors at 5% level. The carbon dioxide flow was the most significant effect in starch removal. The pH also presented a significant effect, albeit negative, i.e., the higher the pH, the lower the starch removal.

Figure 4b shows response surface plot for the effect of the factors on starch removal. It has been observed that the use of higher carbon dioxide flow led to higher starch removal. In this case, optimal pH lay between 8.0 and 8.5.

### ICUMSA color removal expressed in response surface plots

The analysis of variance for the linear response surface models used for expressing the influence of factors on ICUMSA color removal yielded  $R^2_{adj} = 0.77$ . The effect estimates (Figure 5a) showed that either pH,  $CO_2$  flow or their interaction affected ICUMSA color removal.

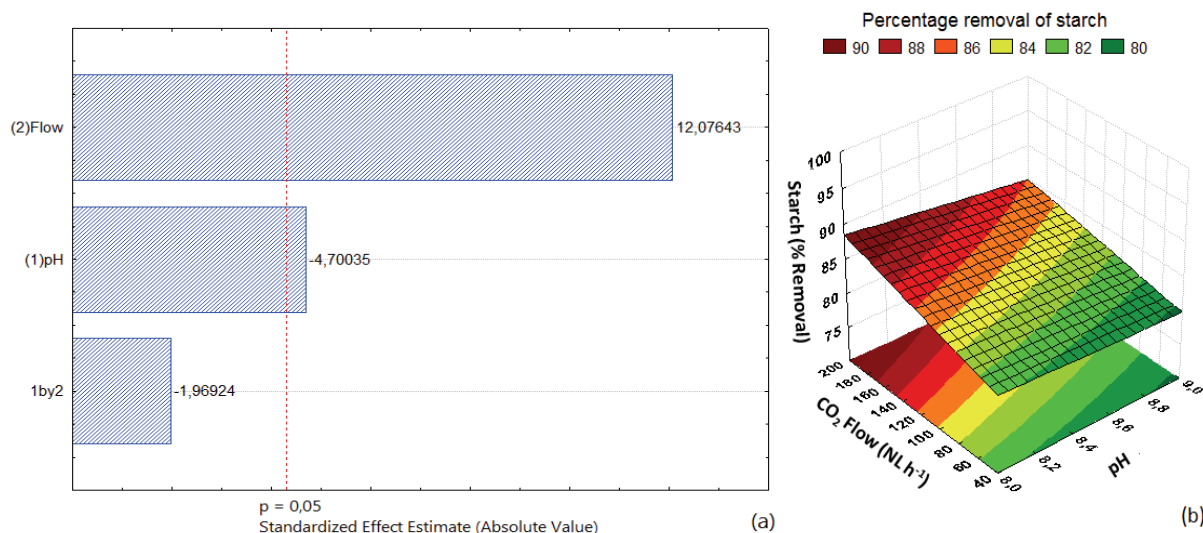
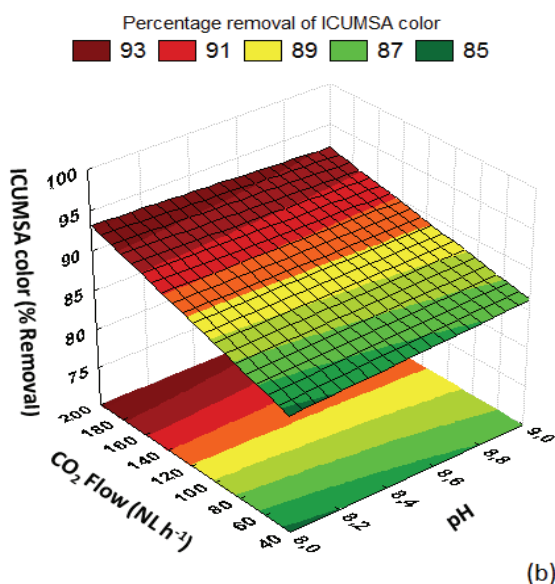
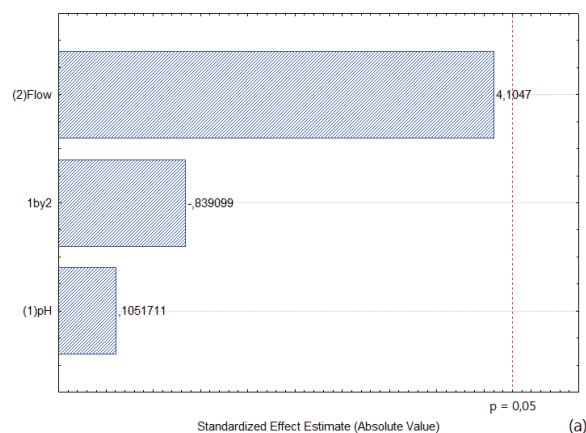


Figure 4. (a) Effect estimates; (b) Influence of factors on starch removal.



Figure 5b shows a slight slope toward CO<sub>2</sub> flow which must not be taken into account due to the insignificance of the effect of this factor on the studied response.



**Figure 5.** (a) Effect estimates; (b) Influence of the factors on the ICUMSA color removal.

## Conclusion

Results showed that carbon dioxide flow was the factor with the greatest effect on starch removal. When carbon dioxide flows at 200 NL h<sup>-1</sup> were combined with pH 8.0 or 9.0, starch removals at 89.19 and 85.75% were obtained.

The effect of carbon dioxide flow on ICUMSA color removal was roughly significant. When carbon dioxide flows at 200 NL h<sup>-1</sup> were combined with pH 8.0 or 9.0, ICUMSA color removals at 92.93 and 91.66% were obtained.

Total calcium added during the carbonatation process was almost removed as calcium carbonate. A positive correlation between added calcium content and starch and ICUMSA color removal was found when the pH was kept between 8.0 and 8.5, a range in which the removal of undesirable constituents was highest.

The process of carbonatation for clarifying sugar cane juice is an alternative for sulfur in the clarification process. In fact, carbonatation represents a process which preserves consumers' health and that of the people involved in sugar manufacturing while it increases the Brazilian sugar export market.

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