Impact of sugar cane juice chemical composition on clarification and VHP sugar quality†

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abstract

It is well known that sugar cane composition affects clarification, sugar recovery, and quality. However, not so well known are the levels of such variables in clarification and VHP sugar that affect quality. This research was performed in a sugar and ethanol plant in Brazil which crushes 4 million tons of cane per season (25,000 tons per day). Fifty four samples were collected in first extraction juice, limed juice and clarified juice during several weeks and also samples of the VHP sugar, were analyzed. The samples were analyzed for the concentration of sucrose, glucose, fructose, lactose acid, acetic acid, dextran, minerals, insoluble impurities, turbidity and color. Positive correlations were found between phosphorus and clarification efficiency and VHP sugar quality. Lactic and acetic acids, as well as glucose and fructose in juice, correlated negatively with sugar quality (increased color). Iron concentration correlated with color of the clarified juice as it may contribute to the oxidation of polyphenolic compounds and catalyzes the alkaline destruction of glucose and fructose. Dextran interfered in clarification and in sugar quality, due to positive correlation with clarified juice and VHP sugar color. Finally, it was observed that the interpretation Honig-Bogstra ratio can be affected by microbial contamination. Having better knowledge about the variables that affect clarification and sugar quality makes it possible to improve the process.

Keywords: cane juice clarification, dextran, Honig-Bogstra ratio, organic acids, phosphate influence on sugar color, VHP sugar process

Efecto de la composición química del jugo de caña de azúcar sobre la clarificación y la calidad del azúcar VHP

Se sabe que la composición de la caña de azúcar afecta la clarificación, la recuperación de azúcar y la calidad. No obstante no se conocen bien los niveles de esas variables en la clarificación y en el azúcar VHP que afectan a la calidad. Esta investigación se llevó a cabo en una planta de azúcar y etanol en Brasil que mueve 4 millones de toneladas de caña por temporada y 25000 toneladas por día. Se recogieron y analizaron cincuenta y cuatro muestras del jugo de primera extracción, jugo alcalinizado y jugo clarificado durante varias semanas y también muestras del azúcar VHP. En las muestras se determinó la concentración de sacarosa, glucosa, fructosa, ácido láctico, ácido acético, dextrano, minerales, impurezas insolubles, turbiedad y color. Se encontraron correlaciones positivas entre fósforo y eficiencia de clarificación y color del azúcar VHP. Los ácidos láctico y acético así como la glucosa y la fructosa en el jugo estuvieron correlacionados negativamente con la calidad del azúcar (aumento de color). El dextrano interfiere en la clarificación y afecta el índice de Honig-Bogstra. Un mejor conocimiento sobre las variables que afectan la clarificación y la calidad del azúcar hacen posible la mejora del proceso.

Impacto dos componentes químicos do caldo de cana na clarificação e na qualidade do açúcar VHP

Sabe-se que a composição química do caldo de cana-de-açúcar afeta o processo de clarificação, a recuperação e a qualidade do açúcar. Porém, os níveis que as diferentes substâncias químicas presentes no caldo influenciam no processo de clarificação e na qualidade do açúcar VHP ainda não são bem conhecidos. Desta forma, foi realizada uma pesquisa em uma usina de açúcar e álcool no Brasil que processa 4 milhões de toneladas de cana por safra (25.000 toneladas por dia). Foram analisadas cinquenta e quatro amostras de caldo (caldo primário, caldo caldeado e caldo clarificado) e amostras do açúcar VHP coletados durante várias semanas. As amostras foram analisadas para a determinação da concentração de sacarose, glicose, frutose, ácido láctico, ácido acético, dextrano, minerais, impurezas insolubles, turbidez e cor. Foram encontradas correlações positivas entre o fósforo e eficiência do processo de clarificação e qualidade do açúcar VHP. A concentração de ácido láctico e ácido acético, bem como de glicose e frutose no caldo, correlacionaram negativamente com a qualidade do açúcar (aumento da cor). Foi observada uma correlação positiva entre a concentração de ferro e a cor do caldo clarificado, visto que este metal pode contribuir para a oxidação dos compostos polifénólicos e catalisar a destruição alcalina de glicose e frutose. A Dextrana interferiu na clarificação e na qualidade do açúcar devido a correlação positiva com a cor do caldo clarificado e cor do açúcar VHP. Por fim, foi observado que a interpretação do índice de Honig-Bogstra pode ser afetado pela contaminação microbiana. Conhecendo-se as variáveis que afetam a clarificação e qualidade do açúcar torna-se possível melhorar o processo.
Introduction

The cane juice clarification process is one of the most important steps in sugar manufacture. It consists of the removal of the non-sugar impurities (organic and inorganic) while preserving sucrose, glucose and fructose.

There are different juice clarification methods but, in Brazil, the most employed is the method using milk of lime. Regarding the temperature, the most used is the addition of milk of lime at intermediate temperature (70-80°C). However, hot lime clarification (100°C) is also being used in client mills of Fermentec with good results.

Although clarification is considered a simple process, many factors can affect the quality of the clarified juice, such as pH and concentrations of inorganic ions, especially phosphate, organic acids, colloidal materials, etc.

In view of the large number of factors that can affect clarification, this research was designed to evaluate the influence on the clarification process of various chemical components present in sugarcane juice. For this, various juices from the process were sampled from the sugar mill and the analyzed parameter concentrations were correlated with the quality of clarified juice and the produced sugar.

Experimental

Samples

The samples were collected from September to December of 2008 in the RAIZEN - Costa Pinto Mill, which has the capacity to crush 4 million tons of cane per crop season (25,000 t/day) and produces 1,400 tons of VHP sugar per day.

There were a total of 17 sampling cycles being that each cycle consisted of the sampling of first extraction juice; limed juice (after the addition of milk of lime and polymer, but right before the clarifier); clarified juice. Samples were collected manually, but to obtain a representative sample, each type of sample was collected during a time window from 2 to 6 hours and at a frequency of 15 minutes (for a 2-hour window) or 30 min (for a 6-hour time window), according to Eggleston et al. [2002]. Each sample was first collected in a 500-mL container of and then 100 mL transferred to a bottle kept inside a cooler with dry ice. At the end of the collection period, the bottles were transferred to a freezer until the analysis. It should be noted that the retention times were reported for the sample collection. Altogether 54 juice samples were collected.

Determination methods

The analytical determinations were carried out as described below:

1. Brix or refratometric dissolved solids (RDS) by the measurement of refractive index.
2. Mannitol, glucose, fructose and sucrose by HPAEC-PAD.
3. Lactate, acetate, formate, pyruvate, chloride, sulfate, oxalate, soluble P₂O₅, citrate, cis-aconitate and trans-aconitate by HPIC with suppressed conductive detection.
4. Total P₂O₅, SiO₂, Fe₂O₃, Al₂O₃, Ca, Mg, S, Mn, Cu and Zn by ICP-AES after sample digestion.
5. K by flame emission photometry after sample digestion.
6. ICUMSA turbidity at 900 nm according to ICUMSA method GS7-21(1994).
7. ICUMSA color at pH 7, according to ICUMSA method GS1/2(2000).
8. Solid impurities, carried out as: 50 mL of juice sample was centrifuged for 30 min at 3500 rpm. The supernatant was discarded and the insoluble material was washed with water and centrifuged again. The supernatant was also discarded and the solid material was transferred quantitatively to a beaker previously dried and weighed. The beaker was placed in an oven at 110°C for approximately 16 hours (overnight) to remove water and with the mass difference was calculated the solid impurity.

Besides the analyses described above, dextran in sugar cane [Clarke et al., 1987] and ICUMSA color of VHP sugar (at pH 7) were determined in the mill and were also correlated to clarified juice and sugar quality.

Results

As described in the Experimental section, samples of cane juice for sugar manufacture were collected in the clarification process. It is noted that before sampling the operation of a clarifiers was

Figure 1. Correlation (5% significance) between ICUMSA color of clarified juice and P₂O₅ concentration in first extraction juice

![Graph showing correlation between ICUMSA color and P₂O₅ concentration](chart.png)

**Equation:**

\[ Y = 14688.57992 - 18.56657X \ (r = -0.60422) \]
Figure 2. Correlation (1% significance) between VHP sugar ICUMSA color and $P_2O_5$ concentration in first extraction juice

\[ Y = 1198.65906 - 3.24741X \quad (r = -0.78714) \]

Figure 3. Correlation (5% significance) between ICUMSA turbidity of the clarified juice and Bogstra Ratio of first extraction juice

\[ Y = 48.10476 - 63.04482X \quad (r = -0.79470) \]

Figure 4. Correlation (1% significance) between $Fe_2O_3$ concentration in limed juice and ICUMSA color of the clarified juice

\[ Y = 10198.48644 + 5.58135X \quad (r = 0.72126) \]

checked to verify if the clarification process was running appropriately for its specifications. Although many different analyses were carried out in this study, below are described the influences only of the key parameters that correlated to the quality of the clarification process of sugarcane juice:

1. Influence of phosphorus ($P_2O_5$) concentration

Phosphorus is the main substance that, together with calcium, promotes the removal of impurities in the clarification by the formation of calcium phosphate salts, which during precipitation improve the settling of impurities from the juice [Honig, 1963].

In all first extraction juice samples that were analyzed, the $P_2O_5$ concentration was below 300 ppm, the recommended amount for obtaining a good clarification [Honig, 1963]. However, the importance of this mineral can be found in the correlations below, related to the color reduction in the clarified juice and also with the final product (Figures 1 and 2). The presence of phosphate can reduce the color formation by forming a complex with iron and reducing the availability of this metal for the reactions that produce colored compounds [Bento, 2008].

Analyzing the correlation graphs shown in Figures 1 and 2 it is possible to infer that each increase of 100 mg/L of $P_2O_5$ in the first extraction juice will reduce 1856 ICUMSA color units in clarified juice and 524 units in VHP sugar.

2. Influence of silicon and iron

Silicon exists primarily as a constituent of many silicate minerals, often linked to iron, magnesium and calcium that are relatively insoluble. In natural waters, silicon can be present as monosilicic acid - Si(OH)$_4$ - often called silica or dissolved reactive silicate, as well as short chains of polysilicic acid soluble fraction and bound to organic or inorganic material in suspension [Walford, 2003].

According to Honig [1963], silicic acid is considered the most harmful inorganic non-sugar in sugar manufacture, influencing the process of sedimentation and filtration. In fact, the ratio of the phosphate concentration and the sum of the concentrations of silicic acid, iron oxide and aluminum oxide is the Bogstra Ratio. It is highlighted by Honig as a way to predict the behavior of juice clarification.

As a rule, if this ratio is less than 0.15 in the cane juice, the clarified juice will have a poor quality, with more than 800 mg of suspended
Figure 5. Correlation (1% significance) between concentration of monosaccharides (% glucose + % fructose on Brix basis) and ICUMSA color of the clarified juice

\[ Y = 8777.61215 + 557.15609 \times X \quad (r = 0.75019) \]

Figure 6. Correlation (1% significance) between the concentration of monosaccharides (% glucose + % fructose on Brix basis) in first extraction juice and ICUMSA color of VHP sugar

\[ Y = 324.78179 + 68.02683 \times X \quad (r = 0.71857) \]

Figure 7. Correlation (1% significance) between concentration of glucose + fructose (%g/100mL) and lactate concentration (mg/L) in first extraction juice

\[ Y = 0.41564 + 0.00164 \times X \quad (r = 0.73112) \]

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Regarding iron, the higher the concentration of Fe \(_2\)O \(_3\) in the limed juice, the higher was the color of the clarified juice (Figure 4). The presence of iron can increase the color because it may contribute to the oxidation of polyphenolic compounds that result in colored compounds and also catalyzes the alkaline destruction of glucose and fructose (pH between 6 and 8) that form colored compounds with high molecular weight [Bento, 2008].

3. Influence of glucose and fructose

The concentration of monosaccharides, especially fructose, had a high negative correlation with the quality of clarified juice and the VHP sugar quality. This can be seen in Figure 5, where the ICUMSA color of Clarified Juice is shown as a function of the sum of concentrations of glucose and fructose. As will be shown later, the high concentration of glucose and fructose found in some samples of first extraction juice is directly related to the presence of high concentrations of organic acids from the bacterial metabolism.

During the evaporation process, glucose and fructose in the juice will accelerate the destruction of sucrose in the evaporators and also lead to the formation of organic acids, melassigenic substances and colored compounds [Eggleston and Amorim, 2006]. Figure 6 shows that the greater the sum of the concentration of glucose and fructose in the first extraction juice, the greater the color of VHP sugar.

The contribution of monosaccharides to increase of juice or sugar color is related to: 1) the alkaline degradation catalyzed by the presence of iron (pH between 6 and 8) that may occur in heaters and evaporators and 2) the Maillard
reaction between monosaccharides and amine compounds, which mainly occurs when the Brix is higher than 65° (as the case of vacuum pans) [Bento, 2008].

Analyzing the correlation graphs shown in Figures 5 and 6 it is possible to infer that each increase of 1% (on a Brix basis) of glucose and fructose in the first extraction juice will increase by 557 ICUMSA color units in clarified juice and 68 units in the VHP sugar.

4. Influence of organic acids

Organic acids represent a significant percentage of non-sugar in cane and are responsible for the acidity of sugarcane juice [Honig 1963]. The trans-aconitic acid is the main acid produced by sugar cane, but cis-aconitic, oxalic and citric acids are also found in cane sugar. Lactic, acetic and formic acids are also formed in some industrial processes, but are mainly the result of microbial activity and/or sugar degradation reactions [Zapata, 2007].

Among the analyzed parameters, lactic and acetic acids were the main substances related to the quality of clarified juice. In Figures 7 and 8 is possible to observe how the concentration of monosaccharides in the first extraction juice is related to the concentration of lactate and acetate and consequently with bacterial contamination. It is interesting to note that better correlations were observed with fructose concentration than for glucose concentration, probably because glucose is consumed by microorganisms and fructose is a by product of some enzymatic reactions, like dextranuclase, as example.

The organic acids hamper the clarification process by increasing the amount of lime required to adjust the pH and by competing with phosphate for the available calcium ions (thus increasing the amount of calcium needed for proper clarification). The calcium salts of organic acids do not precipitate during the clarification process and increase the insoluble impurities and ash of the final product [Honig, 1963]. This can be seen in Figures 9 and 10 that show a high correlation of lactic acid with insoluble impurities and ICUMSA color in clarified juice. That is, the higher the lactic acid concentration, the greater the amount of insoluble material and color compounds in the clarified juice that will probably follow on to other operations of sugar manufacture, contributing to a decrease in the sugar quality.

5. Influence of dextran concentration

In clarification, colloids may affect the coalescence of particulate matter, interfering
in their coagulation and precipitation [Simpson, 1996]. With the growth of microorganisms, there is more production of undesirable colloidal materials, which has a large effect in clarification, probably more than any other factor [Heinig 1963].

Deliquated cane juice never results in a clear clarified juice [Heinig, 1963] and this can be observed in Figures 11 to 13, where the concentration of dextran, a polysaccharide formed by bacterial activity, is correlated to turbidity and color of clarified juice and color of VHP sugar, respectively. Dextran (or some substance related to dextran production) inhibits the precipitation of juice impurities, mainly polysaccharides and other macromolecules (Indigenous Sugar Cane Polysaccharide) that may be associated with cane pigments (phenolic compounds). These pigments have a tendency to include in the sugar crystal, impacting on their quality [Moore et al., 2002]. As can be seen in Figures 12 and 13, each increase of 100 mg/L (on Brix basis) of dextran in cane will increase 800 color units in clarified juice and 65 color units in VHP sugar.

Conclusion

This study aimed to understand the main factors that influence the process of clarification of sugarcane juice in the production of VHP sugar. For this, samples from the clarification process were collected and analyzed for several parameters such as concentration of sugars, organic acids, dextran and minerals.

It was noted during the study that the parameters that most influenced negatively the clarification process and quality of VHP sugar were the concentration of monosaccharides (glucose and fructose), lactic acid, acetic acid and dextran. All of them are the result of bacterial contamination. These parameters were correlated with turbidity, solid impurities and color of the clarified juice and also the color of the VHP sugar. Undesirable effects of these substances can be cited:

1. increase the acidity of juice, hydrolysis of sucrose and sequestration of calcium by organic acids;

2. formation of colored and melanogenic compounds due to destruction of glucose and fructose in the heaters and vacuum pans; and

3. interference with the settling of impurities due to the high surface activity of particles of dextran. This protective colloid characteristic inherent to dextran should hinder the settling of other polysaccharides from sugarcane that may be associated with sugarcane pigments (polyphenols) and thus contribute to increasing the color of the juice and sugar. Also the dextran will interfere in settling other substances that contribute to turbidity, such as proteins, and colloidal silica in the form of calcium salts.

Regarding phosphorus, its concentration was below the ideal for obtaining a good clarification in the analyzed juice samples. Its importance was confirmed by its positive correlation with the quality of clarified juice and sugar.

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Figure 11. Correlation (5% significance) between ICUMSA Turbidity in Clarified Juice and Dextran concentration (mg/L on Brix basis) in cane

\[ Y = 22.2323X + 0.02009 \quad (r = 0.63993) \]

Figure 12. Correlation (1% significance) between ICUMSA color of clarified juice and dextran concentration (mg/L on Brix basis) in cane

\[ Y = 2031.2608X + 7.92521 \quad (r = 0.65342) \]

Figure 13. Correlation (1% significance) between ICUMSA color of VHP sugar and dextran concentration (mg/L on Brix basis) in cane

\[ Y = 217.9920X + 0.65222 \quad (r = 0.79305) \]

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References


