Foresight of physical-chemical characteristics of apple juice blends appointed to sparkling drink elaboration

Previsão das propriedades físico-químicas de misturas de sucos de maçãs destinadas à elaboração de espumantes

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1 Introduction

In Brazil, there is no apple production intended only for industrial use. In Brazilian cider production, only table fruits are used, i.e., apples that have desirable features for in natura consumption but, due to some deformities, were discarded of the trade (WOSIACKI, 2002).

For the sparkling drink elaboration, it is desirable that the must hold a combination of high acidity with high content of phenolic compounds and sugar, besides fruity aroma. This combination of parameters is not achieved in a single apple cultivar, being necessary the use of individual characteristics of each cultivar in blends (JORGE; TREPTOW; ANTUNES, 1998). According to Wosiacki and Nogueira (2005), some cultivars currently used as pollinating have more significant levels of organic acids and phenolic compounds and can be used in processed juice blends to give “body” to the beverages produced.

The most indicated statistical method to a blend elaboration is the component blend design, which adjusts models to represent the response on a surface. The goal of the method is to find a model that describes the physical-chemical characteristics of blends with the smallest error margin possible, when compared to the real results of the experiments. The simplest model of this design is the linear, which tries to explain the behavior of a property only with the results obtained with the utilization of each component individually. Besides this model, the design can be raised to quadratic and special cubic levels. In the former, one must employ the results of the interaction effects between two components, whereas in the latter, the effects of...
interaction of three compounds must be used (BARROS NETO; SCARMINIO; BRUNS, 2007).

This research had as objective to foresee the physical-chemical characteristics of ternary blends of apple juices using the component blend design with the response surface methodology, where the selection of the cultivars was based on the physical-chemical characteristics that better adapt to the requirements of a must intended to sparkling drink elaboration.

2 Materials and methods

2.1 Raw materials

Three apple cultivars were selected to the elaboration of the ternary blend design, namely, Catarina, Granny Smith and Pink Lady. The Catarina cultivar was selected because it has a high content of phenolic compounds (377.97 mg.L⁻¹) and total reducing sugars (142.86 g.L⁻¹). The Granny Smith and Pink Lady cultivars were selected for having high acidity (5.52 and 4.70 g.L⁻¹, respectively). The Pink Lady has fruity aroma as well. All of the cultivars were from the 2007/2008 harvests of the State of Santa Catarina and were provided by the company ‘Agrícola Fraiburgo Ltda’ (Videira - SC, Brazil).

The selected apples were washed in running water and crushed in a manual processor. The juice obtained was kept frozen (−20 °C) until the time of the analysis

2.2 Physical-chemical analysis

The total reducing sugars analysis was performed by the Somogyi-Nelson colorimetric method, and the result was expressed in g.L⁻¹ (TANNER; BRUNNER, 1985). For the determination of total titratable acidity, the technique of the ‘Instituto Adolfo Lutz’ was used, and the result was expressed in g.L⁻¹ (INSTITUTO..., 2008). The phenolic compounds were analyzed colorimetrically with the reagent Folin-Ciocalteau and expressed in mg.L⁻¹ of catechin (SINGLETON; ORTHOFER; LAMUELA-RAVENTOS, 1999).

2.3 Components blend design

Initially, the linear models for all properties considered were tested and these models were adjusted to more complex ones (quadratic and especial cubic) as a need to make them more meaningful.

For the determination of the equation coefficients, 12 experimental essays were used, where the blends proportions were defined by use of the components blend design, as Table 1. The blends were made with the juices of Catarina, Granny Smith and Pink Lady cultivars, represented by x1, x2 and x3, respectively. The sum of the percentages of these samples met the restriction mentioned by Bruns, Scarminio and Barros Neto (2001) where the sum should be equal to 1.

The response variables used in the design were: total reducing sugars (TRS), total titratable acidity (TTA) and phenolic compounds (PC). The results were organized in charts and analyzed by the response surface methodology.

3 Results and discussion

Figure 1 shows the values of total reducing sugars, total acidity and phenolic compounds for the 12 assays made, besides the representative point of the viable region (Intersection Point – IP).

Analyzing the chart (Figure 1), one can observe that the cultivar Catarina (assay 1) shows up more clearly, with higher content of total reducing sugars, than the other cultivars: Granny Smith and Pink Lady (assays 2 and 3, respectively), which have high acidity, in agreement with the reasons given for their selections.

According to Jorge, Treptow and Antunes (1998), cultivars with high degree of aroma generally have low acidity, so it must be mixed with higher acidity cultivars. The Pink Lady cultivar was selected for having more fruity aroma, in addition to its relatively high acidity (4.70 g.L⁻¹).

From the results obtained for the different compositions, it was possible to generate regression models at different levels, correlating the proportions of the apples juices to the results of the parameters studied. The models for each parameter were chosen from the validation of these models in a significance level of 95%. For each property, different regression models were generate and evaluated by variance analysis (ANOVA). Table 2 shows the statistic parameters used to analyze the linear, quadratic and special cubic models for all variables.

To evaluate whether the models had a significant regression in the confidence level of 95%, the F values obtained (related to regression and to the models fit) were compared to the respective F tabulated values. The R² value, which represents the variation explained by the model, had to be as close as possible to the maximum explainable value.

The residue charts of each model were seen as random, and, for better representation of data, the chart should display randomly. These parameters were observed in all models of each variable and the model that was significant for all parameters

| Table 1. Proportions of each cultivar in the elaboration of 12 experimental assays, by use of the components blend design. |
|---|---|---|
| Essays Description | Proportions of each cultivar in the assays |
| | Catarina (x1) | Granny Smith (x2) | Pink Lady (x3) |
| 1 | Individual samples | 1 | 0 | 0 |
| 2 | 0 | 1 | 0 |
| 3 | 0 | 0 | 1 |
| 4 | Binary mixes | 1/2 | 1/2 | 0 |
| 5 | 1/2 | 0 | 1/2 |
| 6 | 0 | 1/2 | 1/2 |
| 7 | Ternary mixes | 1/3 | 1/3 | 1/3 |
| 8 | 1/3 | 1/3 | 1/3 |
| 9 | 1/3 | 1/3 | 1/3 |
| 10 | 2/3 | 1/6 | 1/6 |
| 11 | 1/6 | 2/3 | 1/6 |
| 12 | 1/6 | 1/6 | 2/3 |
The residual graphics of these models showed a linear trend, demonstrating that the model is not significant.

To the phenolic compounds variable, all models had a significant regression, but all of them had lack of fit, too. Nevertheless, the special cubic model had the lowest error (24.816) among the three models (97.90% of 99.95% possible).

After discarding the not significant coefficients, a simplified equation for each property considered was obtained, resulting in a linear model for the total reducing sugars variable (Equation 1), quadratic model for the total titratable acidity (Equation 2) and special cubic model for the phenolic compounds (Equation 3).

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TRS = 142.857 \times x_1 + 116.891 \times x_2 + 122.185 \times x_1^2
\]
From the regression models, ternary diagrams of response surfaces were made for each studied variable. Figure 2a shows the total reducing sugar, Figure 2b the total titratable acidity and Figure 2c the phenolic compounds variable.

The highest concentration of total reducing sugar was found in the compositions with the highest levels of the Catarina cultivar, in other words, near the vertex that represents this juice (Figure 2a). This fact that can also be observed in Equation 1, where the highest parameter is the one that represents the proportion of the cultivar Catarina (x1).

To the total titratable acidity variable, the Granny Smith and Pink Lady cultivars contributed to the increase of juice acidity (Figure 2b). In Equation 2, the greatest parameters were those that represented the individual proportions of the cultivars Granny Smith (x2) and Pink Lady (x3), as observed in Figure 2b. Besides, in these models, it is observed that, as all interaction binary coefficients are positive, the binary species interacted synergistically, i.e., the interaction between the juices contributed to increase acidity.

Figure 2c shows that the higher the Catarina and Granny Smith cultivars proportions, the higher the phenolic compounds content of the blend. In Equation 3, the parameter of interaction between Catarina and Pink Lady cultivars (x1 × x3) showed a negative value, demonstrating that the binary interaction contributes to decrease the phenolic compounds content of the blend (antagonistic interaction). Nevertheless, the significant value of the ternary interaction variable (x1 × x2 × x3) showed the substantial contribution of the blend to the increase of the phenolic compounds content.

The ideal blend under study must provide the highest possible values in all studied parameters, in conformity with what is necessary for a good sparkling drink. According to Rizzon, Meneguzzo and Gasparin (2005), the must has to show high acidity, high content of phenolic compounds and sugars, plus a highly fruity aroma.

To delimit the minimum values for the studied parameters, the following values were used: minimum of 123.0 g.L⁻¹ of total reducing sugar, once this is the quantity of sugar necessary to obtain a 7.0 %v/v alcohol wine (considering a conversion of 17.5 g.L⁻¹ for each alcoholic degree); minimum of 5.0 g.L⁻¹ of acidity in malic acid, since Brazilians high quality sparkling drinks have around 75.0 meq.L⁻¹ of total acidity (RIZZON; MENEGUZZO; GASPARIN, 2005); and minimum of 340.0 mg.L⁻¹ of phenolic compounds, where the value was defined by the conditions established at the charts intersection.

With the boundaries, a viable region was demarcated (gray region in Figure 3) representing an intersection area between all variables, where it is possible to find minimum and maximum proportions for each used juice, so that all variables have values within the pre-established standards. From this region, a central
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of 132.3 and 117.8 g.L\(^{-1}\) of total reducing sugar, 3.3 and 3.6 g.L\(^{-1}\) of total titratable acidity and 340.0 and 316.0 mg.L\(^{-1}\) of phenolic compounds, respectively.

Based on these results, one can verify that the total reducing sugar value of the must made with the blend is within the values presented by the authors. The blend acidity proved to be considerably above the indicated average, what is a positive point of the blend, since the intention was to obtain a must with high acidity. Regarding to the phenolic compounds content, it is believed that the use of a cultivar with more significant values of this variable in the formulation of the blend, would make the must more interesting; once, according to Rizzon, Meneguzzo and Gasparin (2005), for the elaboration of a quality sparkling drink, a must with high content of phenolic compounds is necessary, and the value obtained for this variable was very close to the values found by the authors.

4 Conclusions

The application of the components blend design, allied to the response surface methodology, allowed to define a range of apple juice compositions that make a must able to be employed in the sparkling apple drink preparation.

To the studied situation and according to the established models, the proportion of the blends that provides the physical-chemical characteristics more suited to the sparkling development, i.e., a must that holds high values for the properties total reducing sugars, total titratable acidity and phenolic compounds and has fruity aroma, should be composed, on average, by the following blend: 23.22% of the cultivar Catarina, 66.23% of the cultivar Granny Smith and 10.55% of the cultivar Pink Lady, being this the central point among the many combinations that satisfy the pre-set restrictions.

To obtain a must with more specific characteristics, like a high content of phenolic compounds, for example, it would be interesting to use another apple cultivar that has more expressive value of this characteristic. In this case, however, all the design must be performed again.

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