INFLUENCE OF THE GLUCOSE SYRUP COMPOSITION ON THE QUALITY OF HIGH BOILED SYRUPS

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Abstract*:* The presence of fructose in high boiled syrups can determine unwanted phenomenon such as hygroscopicity and the modification of structure by crystallisation. The study of the factors influencing hydrolysis of saccharose in boiled syrups is important in assuring the quality of candies. In this study we present the influence exerted by protein hydrolysed and salt on the hydrolysis of saccharose in the high boiled syrups obtained with demineralised glucose syrups. The action of these compounds is obvious but not big enough to determine a meaningful modification of the syrups quality. As a result of the NaCl action, the concentration of fructose in the high boiled syrup increases four times. A consequence of the protein hydrolysate adding, the fructose content increases two times. The quantity of fructose remains at very low values (below 1%), in this concentration having not influence on the quality of high boiled syrups.

Keywords*:* high boiled syrup, demineralised glucose syrup, hydrolysis, saccharose, fructose.

INTRODUCTION

The hydrolysis of saccharose during the thermal treatment of high boiled syrups (called also caramel syrups) can be a cause of the occurrence and the growth of the fructose content in high boiled candies, with unwanted consequences on quality. Among other factors, the hydrolysis of saccharose in forming the high boiled syrups (HBS) is influenced by the composition of glucose syrup. Also, the action of sodium chloride in accelerating the saccharose degradation is known (Schiweck et al., 2000). The effect of sodium chloride from the glucose syrups seems to be enhanced by other compounds obtained through acid hydrolysis; at the same pH value, the acidity of syrups obtained through acid hydrolysis is different from the syrups resulted through enzymatic hydrolysis (Howling, 1992).

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The literature refers to the complexation of large amounts of salts (NaCl, $CaCl_2$, KI) in glucose syrups with small Dextrose Equivalent DE (Gallali et al., 2006). It is the case of glucose syrups obtained through acid method used in obtaining HBS, which must have a small DE value and which contain large amounts of salt. At these syrups there is a strong need of demineralisation (Trifan and Mironescu, 2006).
Taking into account these observations, we assumed that some buffer substances are obtained during the acid hydrolysis. Such substances are the protein hydrolysates resulted from the proteins remained in starch (Mironescu, 2005). This paper is a continuation of some research referring to the influence of different compounds from glucose syrup on the degree of hydrolysis of saccharose in high boiled syrups (Trifan and Mironescu, 2006). The purpose of this research is to determine the influence of protein hydrolysates and of NaCl on the saccharose hydrolysis in HBS. For this investigation, demineralisated glucose syrup was used, in order to eliminate the other compounds different from sugars.

MATERIALS AND METHODS

Materials

The raw materials at the obtaining of HBS are sugar and glucose syrup. Sugar used has superior quality (very high purity).
The composition in sugars of the two products was determined by a chromatographic methods using normal phase HPLC (Table 1).

Table 1. The composition in sugars of raw materials

	DP1	DP2	DP3	DP4
Saccharose	0	99.953	0	0
Glucose syrup	13.190	12.247	12.933	61.485

For testing the different influences on the degree of hydrolysis in HBS, salt of alimentary purity and protein hydrolysates were used. Salt was used in the following ratios: 0.1%, 0.2% and 0.3%. The protein hydrolysate was obtained from gluten resulted at the production of corn starch and has 91.67% dry substance, 61.25% total protein and 1.42% ash.

Methods

The gluten was hydrolysed with hydrochloric acid in the conditions of starch hydrolysis: pressure 0.3 MPa, temperature 140°C. The gluten was added as solution 1% in the ratios 0.1%, 0.2% and 0.3 % of dry substance.
The ratio of the two compounds expressed as dry substance is 60/40.
A blind sample was also obtained (HBS without any adding).
The high boiled syrup was obtained through boiling at normal pressure. In this case, the final temperature of HBS was 152°C, for a 98% dry substance content.
The degree of saccharose hydrolysis was determined through cromatography, using normal phase HPLC (Trifan and Mironescu, 2006). For the HPLC analysis, solutions with 5% HBS were used. The injection volume was 80 µl. The column was loaded with calcium ions for a better separation of sugars; the working temperature in the column was 96°C, and the temperature in the RI detector was 60°C. The Degree of Polymerisation DP was measured. In the chromatograms, the products are:

- DP1 is glucose;
- DP2 represents maltose + saccharose;
- DP higher as two are maltotrioses (DP3), maltotetroses (DP4);
- F is fructose.

RESULTS AND DISCUSSIONS

The results obtained with the adding of protein hydrolysates are shown in Table 2.

Table 2. The composition in sugars of different products

Product type	**Fructose**	**DP1**	**DP2 +DP3**	**DP4**
HBS without hydrolysate	0.299	5.898	73.469	20.333
HBS with 0.1% hydrolysate	0.339	6.185	71.045	22.430
HBS with 0.2% hydrolysate	0.500	6.377	71.017	22.066
HBS with 0.3% hydrolysate	0.622	7.226	68.507	23.645

In the blind sample a very small amount of fructose is formed and the fructose content becomes higher at the addition of protein hydrolysate (Table

2). This is correlated with the increase of the glucose content, but the relation is not proportional.
A certain difference in the content in DP2 to D4 products is registered, being considered as a transfer between the compounds in DP2 and DP4 groups.
Some results of the analysis are partially presented as chromatograms (for viewing). A chromatogram for the blind sample is presented in Figure 1. Chromatograms for a sample with 0.3% protein hydrolysate is presented in Figure 2.

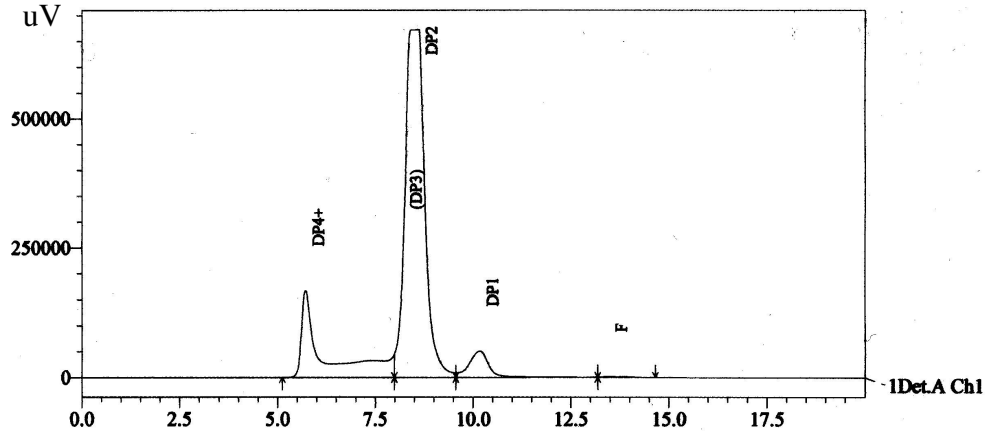

Figure 1. Chromatogram of a blind sample (high boiled syrup without protein hydrolysate)

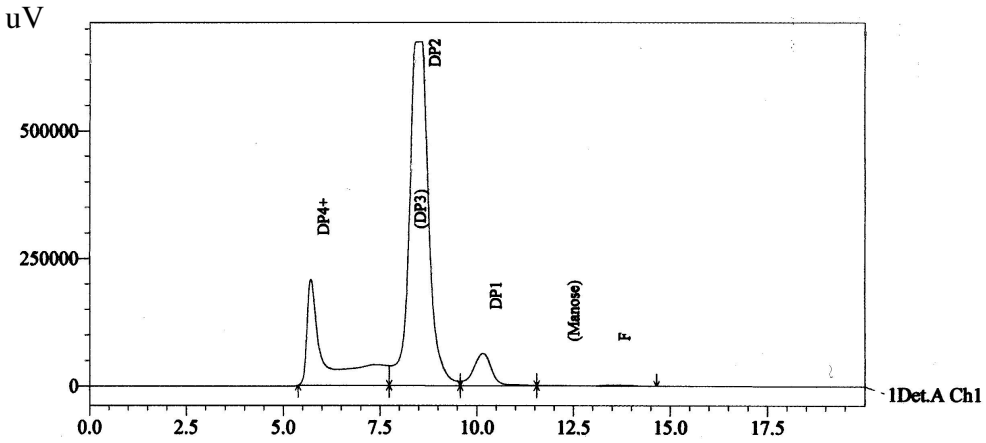

Figure 2. Chromatogram of a high boiled syrup with 0.3% protein hydrolysate

The results of the experiments realised with the addition of NaCl in the initial sugars mixture for high boiled syrup production are presented in Table

3. The influence of the salt content on the saccharose hydrolysis is confirmed for this case; the degree of inversion is much smaller that the one obtained in non-demineralisated syrups (Trifan and Mironescu, 2006).

Table 3. The composition in sugars of high boiled syrup with different NaCl additions

Product type	**Fructose**	**DP1**	**DP2+DP3**	**DP4**
HBS without salt	0.299	5.898	73.469	20.333
HBS with 0.1% salt	0.428	6.984	69.701	23.192
HBS with 0.2% salt	0.583	7.352	68.734	23.331
HBS with 0.3 % salt	0.825	7.467	67.791	23.917

Figure 3 shows a chromatogram of a HBS sample prepared with 0.2% salt. The presence of fructose in small amounts is also observed. As at the addition of protein hydrolysate, the increase of salt content increases the fructose concentration. It is ascertained here, too, the occurrence of the peak between DP2 and DP4, which becomes more and more obvious with the increase of the salt content.

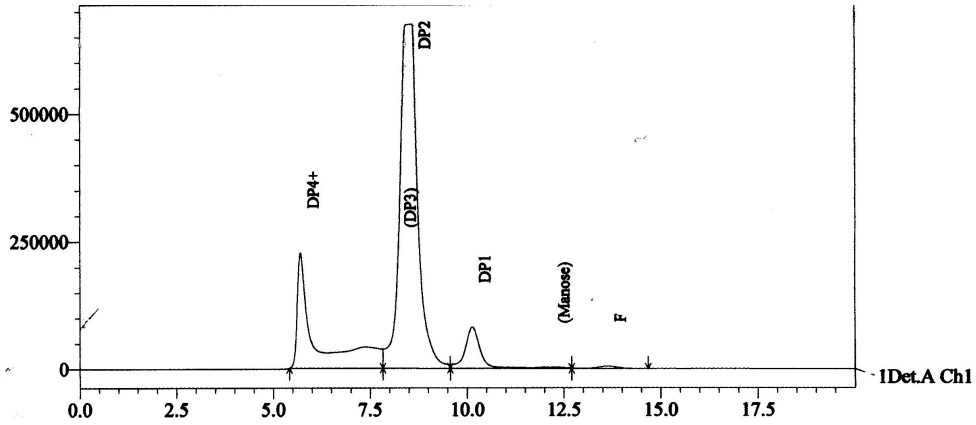

Figure 3. Chromatogram of high boiled syrup with 0.2% NaCl

The relation between the quantity of the two added compound and the degree of fructose formation in the HBS obtained with demineralised glucose syrup is presented in Figure 4.

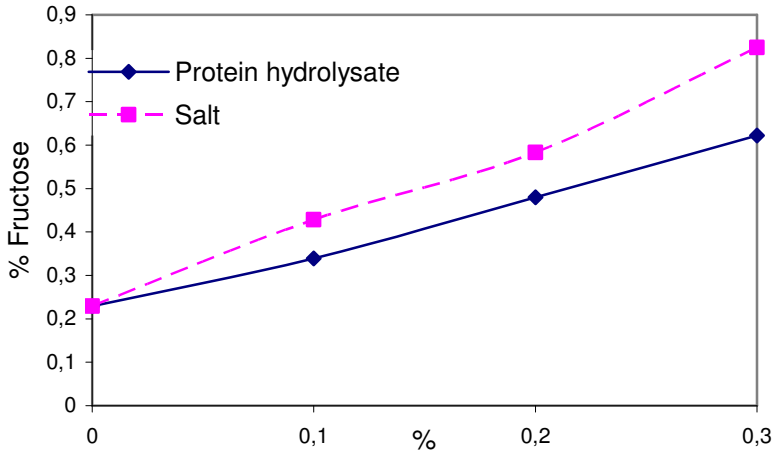

Figure 4 The influence of the protein hydrolysates and the salt on the forming of fructose in HBS

On ascertain that the hydrolytic action of the added compounds increases with the increase of the added quantity. The relation isn't linear, but the action is more intense at higher concentrations. At the same concentrations, however, the added salt has a higher hydrolytic action.
Comparing with the previous results obtained with non-demineralisated glucose syrups, it can observed that the complex composition of the syrups has a synergic action on the process of saccharose hydrolysis, which would justify the approximate 20 times increase of the hydrolysis degree of saccharose.

CONCLUSIONS

The action of protein hydrolisates and of the salt on the hydrolysis of saccharose in HBS is obvious and the increase of the concentration of added substances determines an increase of the hydrolysis degree.
The action of salt is higher at the same ratio of adding.
The action of salt in demineralisated solutions of glucose syrup is 20-30 times smaller as in non-demineralisated solutions.
The presence of NaCl in the glucose syrups obtained through acid hydrolysis is inevitable. For this reason, it is recommended to use demineralisated syrups for the obtaining of HBS.
The presence of salt and protein hydrolysates in the glucose syrups can be a cause of the saccharose hydrolysis in high boiled syrups, but not the only

one. The complex structure of these requires more detailed studies of composition.
The concentration of fructose has very low values (below 1%), fact that doesn't' influences the quality of high boiled syrups.

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