HYDROXYMETHYL FURFURAL FORMATION IN GRAPE AND POMEGRANATE JUICES OVER HEATING TREATMENTS

Seda Ersus, Ayça Akyüz, İdil Tekin
Department of Food Engineering, Ege University, Bornova, İzmir

Abstract

Hydroxymethyl furfural (HMF) occurs as an intermediate product by breaking down sugars in acidic media or during the Maillard reaction. The formation of HMF is used as a chemical index to determine the storage time of food products and to determine if the heat treatment is performed properly to the food products such as fruit juices, milk, honey, cereal products and jams. In this study, it was investigated the formation of hydroxymethyl furfural due to heating process in white grape, red grape juice and pomegranate juices. The fruit juices were heated at 200 °C and HMF occurrence was analyzed over period for different raw materials. Temperature, pH value and Brix values of the samples were also measured. Heating was continued until 68 ˚Bx for white grape juice, 74 ˚Bx for red grape juice and 37.5 ˚Bx for pomegranate juice. The initial HMF content of white grapes, red grapes and pomegranate juices which are sold in the market were found as 21.44, 26.46 and 27.32 mg/kg, respectively. As a result of heating treatment at 200 °C, the Brix value was reached to 68 for white grape juice and 74 for red grape juice and the HMF content of white and red grape juices were increased to 3292.01 in 190 min and 2741.61 mg/kg in 220 minutes, respectively. For the same target Brix value of pomegranate juice was reached to 37.5 at 360 minutes and the HMF value were found 2867.79 mg/kg. Consequently, the HMF content of white grape, red grape and pomegranate juices was increased 153, 103 and 104 times higher than their initial content by long term heating process under atmospheric conditions.

Hydroxymethyl Furfural Formation in Grape and Pomegranate Juices Over Heating Treatments

1. Introduction

Food products are subjected to a number of processes to improve sensory or tissue properties to provide microbiological safety and to eliminate enzymatic activities. Physical, chemical and microbiological changes occur in foods during and after these processing steps. Reactions related to heat treatment are very important in producing sensory properties such as aroma, taste and color. Hydroxymethyl furfural (HMF) is a quality criterion due to storage of carbohydrate-rich foods at inappropriate temperatures and chemical reactions caused by heat treatment during production. Unfortunately, in addition to sugar matrices, there are also some other food components, including fats, mineral compounds and proteins. In this case, various mechanisms should be considered for the formation of HMF (Batu et al., 2014; Metin, 2014).

Maillard reaction, which plays an important role in HMF formation, is a series of reactions between aldehyde ketone and reducing sugar, amine, amino acid, peptide and protein. To begin the reaction, the carbonyl group and the amino group must be present in the system. The reaction is influenced by temperature, time, various sugar and protein, pH, acidity, phenolic substances, metal ions and water activity. Many by-products are formed as a result of Maillard reactions which are released as a result of heat treatments applied to fruit juices (Resnik and Chirife, 1979).

Demand for grape and pomegranate juices has increased rapidly due to its rich nutritive values and various benefits to human health. The composition of grape and pomegranate changes during the ripening of the fruit and varies from region to region according to soil, ground and climatic conditions. The quality of the fruit juice depends on the sugar, acid content and the number of flavoring agents such as methyl anthranilate and other volatile substances, organic acids and colored substances (Igual et al., 2010; Zuritz et al., 2005)

During the heating process of the fruit juices obtained from white grapes, red grapes and pomegranates selected within the scope of this study; temperature, Brix, pH, titration acidity, sugar and HMF values were measured. In addition, the effect of the heating process on HMF formation and the changes occurred during heating process was examined.

2. Materials and Methods

2.1. Materials

In this study, the raw materials that are white grapes, red grapes (*Vitis vinifera*) and pomegranates (*Punica granatum*) were purchased from a local market in Izmir. The stems of white and red grapes were first sorted out and washed, then dried and shredded with the help of blender. After this process, juices were filtered with the help of cheesecloth and prepared for analysis. On the other hand, pomegranates were cut into two pieces and squeezed and prepared in the same way.

The fruit juices were heated at constant temperature (200 ˚C) and HMF determination was made by taking samples at certain intervals. At the same time, temperature, pH value and Brix values of the samples taken at regular intervals were measured. Heating was continued until 68 ˚Bx for white grape juice, 74 ˚Bx for red grape juice and 37.5 ˚Bx for pomegranate juice.

2.2. Methods

HMF determination was performed in all sample groups of white grape, red grape and pomegranate juices obtained from raw materials. In addition to this; Brix, pH value, titratable acidity and sugar analyzes were also performed.

2.2.1. Determination of HMF

The HMF content of fruit juices was determined according to TS 6178/ISO 7466 Turkish Standard (Turkish Standards Institution (TSE), 2002). 2 ml of juice samples were transferred to each 3 glass test tubes and 5 ml of ρ-toluidine solution was added to all tubes. 1 ml of pure water was added to one (blank) tube and the same amount of barbituric acid solution was added to the other tubes. The absorbance values of the samples at 550 nm were determined on the spectrophotometer. The HMF content of the samples was calculated as mg/kg.

2.2.2. Determination of water soluble solids (Brix)

The amount of water soluble solids in grape and pomegranate juices was determined by refractometer. For this purpose, ATAGO brand RX-7000a model abbe refractometer was used. The measurements were made at 20 °C and the results were expressed as °Bx (Yılmaz, 2005).

2.2.3. Determination of pH value

The pH values (at 25 ˚C) of samples taken at certain intervals were measured with using WTW-Inolab branded pH-meter (Cemeroğlu, 2010).

2.2.4. Determination of titratable acidity

The grape and pomegranate juice samples were titrated with 0.1 N NaOH solution to pH 8.1. The titration acidity of the samples was calculated as tartaric acid for grape juice and citric acid for pomegranate juice as g/100 mL (Cemeroğlu, 2010).

2.2.5. Determination of the sugar content

The amount of invert sugar and total sugar in white grape, red grape and pomegranate juices was determined according to Lane Eynon method (Cemeroğlu, 2010).

3. Results and Discussion

Before heating process, the ˚Bx, pH value, titratable acidity, total sugar and invert sugar content of juices were determined and was given in Table 1. As shown in Table 1, the ˚Bx of white grape juice was higher than both red grape and pomegranate juices. The pH value of pomegranate juice was the lowest with 3.09 while the pH value of white and red grape juice was similar. The titratable acidity of white and red grape juice was found as 8 g/100 mL and 4.4 g/100 mL in terms of tartaric acid, respectively. On the other hand, the titratable acidity of pomegranate juice was determined as 18.7 g/100 mL in terms of citric acid.

Table 1: The ˚Bx, pH value, titratable acidity, total sugar and invert sugar content of juices

	White grape juice	Red grape juice	Pomegranate juice
˚Bx	20.5	18	15.5
pH value	4.37	4.78	3.09
Titratable acidity (g/100 mL)	8.0	4.4	18.7
Total sugar (%)	14.58	14.92	14.22
Invent sugar (%)	18.11	18.04	16.15

The pH values, water soluble solids (˚Bx) and HMF content analysis results of white grape, red grape and pomegranate juices were given in Table 2, Table 3 and Table 4. It was indicated that HMF content increased with increasing temperature of the juices. In white grape juice, heating was continued until the ˚Bx reached at 68. When the temperature increased from 22 to 95 ˚C in 190 minutes, HMF content increased 21.44 mg/kg to 3292.01 mg/kg. In other words, HMF content of white grape juice increased by 153 times with increasing temperature.

Table 2: Effect of temperature on ˚Bx, pH value and HMF (mg/kg) in white grape juice

Time (min)	Temperature (˚C)	˚Bx	pH value	HMF (mg/kg)
0	22.0	20.5	4.37	21.44
20	61.0	21.0	4.27	36.29
60	90.5	23.5	4.20	55.97
80	94.5	25.8	4.22	119.85
120	94.5	33.0	4.32	320.55
160	95.0	49.5	4.18	1543.85
190	95.0	68.0	4.34	3292.01

As seen in Table 3, heating was continued until the ˚Bx reached at 74 in red grape juice. While the initial HMF content of red grape juice was 26.46 mg/kg, after 220 minutes (from 21.5 ˚C to 95 ˚C) the HMF content increased 103-fold to 2741.61 mg/kg.

Table 3: Effect of temperature on ˚Bx, pH value and HMF (mg/kg) in red grape juice

Time (min)	Temperature (˚C)	˚Bx	pH value	HMF (mg/kg)
0	21.5	18	4.78	26.46
60	93.0	21	4.61	31.28
100	93.0	24	4.59	80.66
140	93.5	28	4.47	334.10
180	94.5	35	4.54	417.22
200	95.0	50	4.54	854.33
210	95.0	67	4.48	1082.42
220	95.0	74	4.28	2741.61

The initial ˚Bx of pomegranate juice was expressed as 15.5 (Table 4). Heating was stopped at 360 minutes when the ˚Bx reached at 37.5. When the temperature increased from 22.5 to 93.5 ˚C in 360 minutes, HMF content increased 27.32 mg/kg to 2867.79 mg/kg. In other words, HMF content of pomegranate juice increased by 104 times with increasing temperature. Besides, it was generally seen that the pH value decreased at the end of the process although the pH values of all samples fluctuated.

Table 4: Effect of temperature on ˚Bx, pH value and HMF (mg/kg) in pomegranate juice

Time (min)	Temperature (˚C)	˚Bx	pH value	HMF (mg/kg)
0	22.5	15.5	3.09	27.32
30	47.0	15.5	3.00	49.95
90	86.0	17.0	2.80	51.44
120	90.5	17.0	2.83	66.67
150	91.0	18.5	2.82	202.62
180	86.5	20.0	2.89	472.20
210	86.0	21.5	2.91	751.90
270	86.5	25.5	2.83	837.94
300	87.0	29.5	2.79	1551.65
330	90.5	32.0	2.83	2338.94
360	93.5	37.5	2.81	2867.79

As a result, it was determined that the amount of HMF increased in all samples during the heating process. This increase in the amount of HMF could be explained by the increase in Maillard reaction rate with temperature. Studies show that every 10 °C temperature increase increases the Maillard reaction rate by 4 times (Eskin, 1990). Besides the temperature effect (Carabasa Giribet and Ibarz-Ribas 2000, Tsai et al., 2005; Yılmaz and Toledo, 2005), water activity (a_w) (Fellows, 2000), acidity and pH value (Telatar, 1985), sugar and amino acid composition of juices (Richardson, 2001; Şimşek et al., 2007) may cause the Maillard reaction to increase the HMF content. As a result, all these factors affected each other and increased the HMF content of the fruit juices.

4. Conclusion

In conclusion, food product goes through many stages from the farm to our table. Among these stages, especially the storage of sugary foods at inappropriate temperatures or the formation of HMF formed as a result of high heat treatment norm has been the subject of quality parameters in molasses, honey, milk and milk products, coffee, bread and many other products. The limited number of proven studies of adverse health effects does not undermine the amount of intake of HMF, but even the existence of doubts about this issue should be encouraged to increase the number of studies on the subject.

5. References

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