World Academy of Science, Engineering and Technology
International Journal of Nutrition and Food Engineering
Vol:7, No:5, 2013

Ripper and Sugar Effects on Hydroxymethylfurfural Formation in Gingerbread Biscuits

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Abstract**—**Hydroxymethylfurfural (HMF) is formed by thermally treating products rich in carbohydrates. HMF and other furan derivatives are toxic.

The aim of the research was to establish the content of HMF in gingerbread biscuits with honey and sugar syrup additives by using three leavening agents— ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$), baking powder, and baking soda ($NaHCO_3$).

The content of HMF is significantly affected by the leavening agent used. The content of HMF with honey where ammonium carbonate was used as additive range from 5.7 to 27.3mg $100g^{-1}$, but when sugar syrup is used the content varies from 2.3 to 7.4mg $100g^{-1}$. When baking powder and baking soda are used as leavening agents, the content of HMF exceeds 4mg $100g^{-1}$ in the event honey had been added and the baking time had been longer (10 minutes at 180°C or 9 minutes at 200°C).

Keywords**—**gingerbread biscuits, honey, hydroxymethylfurfural, rippers.

I. Introduction

IN this paper, flour confectionery products — gingerbread biscuits — have been examined. By thermally treating products rich in carbohydrates such hazardous compound as hydroxymethylfurfural (HMF) forms. Large content of HMF in food products is not acceptable. HMF and other furan derivatives are toxic, and already in small amounts they cause damage to the nervous system, but in large amounts they can cause spasms and paralysis. [4]

A. HMF and Maillard Reactions

HMF forms in Maillard reactions between amino acids and reducing sugar. Maillard reactions are series of complex reactions in which various compounds may form depending on the compounds involved in the reaction and conditions of the reaction (temperature, pH, etc.). [3]

In Maillard reactions, melanoidins — hundreds of different aromatic and colorful compounds — are formed. Large amount of such compounds is hazardous to human health.[8] Maillard reactions are affected by many various factors: color and aroma, pH (acidity), different kinds of amino acids and sugars, temperature, time, presence of oxygen, water, water activity, and other food ingredients. [7]

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Research Support: ESF Project "Support of the Master Studies LLU", Contract No. 211/0020/1DP/1.1.2.1.1./11/IPIA/VIAA/011

B. HMF and Honey

One of the sources of sugar in the production of biscuits is honey. Honey is pure natural product and, if it has not been specially filtered and heated, it contains not only sugar, but also little amount of pollen, as well as other substances important for the health. Little is known on the changes in the biological qualities of honey when adding it to food products that are treated thermally.

Honey is a product rich in sugar (70–75% of honey is D-fructose and D-glucose) and, when it is treated thermally or kept for a long time, the level of HMF increases. The content of HMF is an indicator of the purity of honey— the acceptable content in honey according to the EU standards is 4mg/100g. [1]

During heating the amount of this substance in honey grows, especially rapid increase takes place at high temperature. The formation of HMF in gingerbread biscuits depends on technological conditions— time and temperature of baking. It is known that it is easier for HMF to form from fructose, than from glucose and other reducing sugar. The higher temperature is used for heating fructose, the more HMF forms. [5]

C. HMF and Leavening Agents

An integral ingredient in the production of biscuits is leavening agents. Depending on the type of leavening agent in flour products, the content of HMF changes significantly. Leavening agents are substances or their mixtures that cause dough to rise by producing gas. As leavening agents, salts are used: phosphates, diphosphates, carbonates, and hydrogen carbonates. These additives to products perform also other functions.

Ammonium carbonate most often is used to leaven thin and dry products from shortcrust pastry— different biscuits, hard gingerbread biscuits, shortcrust pastry plates for cakes, etc. During the decomposition, ammonium carbonate leavens products by use of carbon dioxide and ammonium gas, which are produced when the temperature exceeds 60ºC. The products of reactions mainly are gasiform substances and they affect the leavening of pastry. Ammonia (NH_3) is partially soluble in the water-phase as ammonium ions and creates the taste of “salammoniac” (ammonium chloride). Ammonium carbonate fosters the formation of acrylamide (one of the products of Maillard reactions) in bread and pastry products.

[4] There is no such information regarding the formation of HMF.

Baking powder is a mixture of chemical substances which is added to pastry to leaven it. The baking powder used in the research is composed of starch, baking soda, acidity regulator. Baking powder is one of the most often used leavening agents. [6]

Baking soda can be used as leavening agent for pastries that are stored for long time only if the necessary amount of acid is ensured. In pastries that are formed and baked right after making it the decomposition of baking soda and emission of carbon dioxide take place only at elevated temperature. It must be taken into account that part of the baking soda remains as undivided sodium chloride. Since soda is alkaline, it loosens the pastry and it flows out, but the products made of it have alkaline taste. [6]

D. The Aim of Research

The aim of the research was to establish the content of HMF in gingerbread biscuits with honey and sugar syrup additives by using three leavening agents — ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$), baking powder, and baking soda ($NaHCO_3$). The biscuits were baked at two different temperatures for two different periods of time: at 180ºC for 7 and 10 minutes, and at 200ºC for 6 and 9 minutes. There is no scientific research if presence of ammonium ions fosters the formation of HMF.

II. Materials and Methods

For the research, 24 samples of gingerbread biscuits were prepared; the biscuits contained 45% flour, 9% egg and butter, and 1% leavening agent — ammonium carbonate (E503), baking powder, or baking soda (E500). The biscuits also contained sweetener (36%), which was honey made from different flowers or sugar syrup. All these products were purchased in Latvian food product stores. The clear sugar syrup "Dansukker" is made in Denmark and the honey "Vinnis" made from different flowers — in Cēsis, Latvia.

The samples were thermally treated at 180° and 200°C for 7, 10 and 6, 9 minutes, respectively. The optimum baking time at 180°C is 7 minutes, but 10 minutes is the time when approximately 30% of biscuits are over-baked. When baking at 200°C, the optimum baking time is 6 minutes, but 9 minutes is the time when 30% of biscuits are over-baked (but not burned).

The samples of gingerbread biscuits were grinded and extracted in distilled water. The extract liquid was then centrifuged (10minutes, 6000rpm) and filtered by using 0.45µm nylon filter.

The content of HMF in honey and sugar syrup was estimated by using high-performance liquid chromatography (CHIMADZU, Japan).

A. Chromatographic Conditions for Establishing HMF

The content of HMF in samples was determined by the calibration curve method. The filtrate of the sample (10µL) was injected into the HPLC, and analyzed by using (10/90) acetonitrile (CH_3CN/H_2O) by flow rate of 1.3ml/min as mobile phase, and Alltech C18 column (4.6 x 250mm) connected to a UV/VIS detector (SPD-20A) set at 280nm. Data were acquired and processed using Shimadzu LabSolutions software (Lesolution Version 1.21 SP1).

The content of sugars in samples was determined by the calibration curve method. The filtrate of sample (10µl) was injected into the HPLC, and analyzed by using (80/20) acetonitrile (CH_3CN/H_2O) by flow rate of 1.3ml/min as mobile phase, and Altima Amino column (4.6 x 250mm) connected to a refractive index detector (RID-10A).The pH level of samples was determined by potentiometry.

B. pH Level and Water Content

pH level of honey and sugar syrup was determined by the potentiometer.

The water content in honey was determined by refractometry. Honey was determined by refraction coefficient (20°C). Using the refractive index was calculated water content in honey. The refractive index was determined using a digital refractometer.

III. Results and Discussion

A. Glucose, Fructose and Sucrose in Honey and Sugar Syrup

The content of the main mono and disaccharides (glucose, fructose, and sucrose) of honey and sugar syrup was estimated.

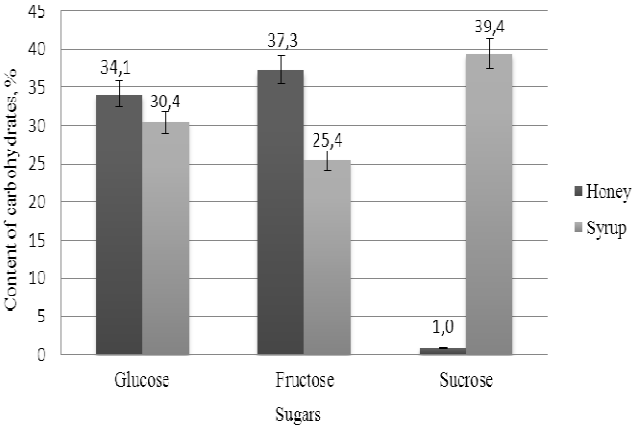

Fig. 1 Content of sugar (sucrose, fructose, glucose) in honey

The content of glucose and fructose of reducing sugar in honey is larger, if compared to sugar syrup (Fig. 1). But the non-reducing disaccharide sucrose dominates in sugar syrup. The formation of HMF is significantly more affected by fructose. Since the honey has larger proportion of fructose and glucose, it could be expected that gingerbread biscuits with honey would have more HMF than in biscuits with syrup additive. [1]

B. pH Level and Water Content in Honey and Sugar Syrup

The pH of honey and sugar syrup was also evaluated.

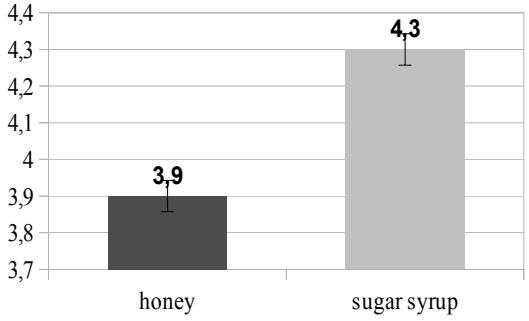

Fig. 2 pH level in honey and sugar syrup

For honey the average pH was 3.9, but for sugar syrup — 4.3 (Fig. 2). pH in honey is lower than pH in sugar syrup. Also lower level of pH can foster the formation of HMF. That means – in gingerbread biscuits with honey additive may be higher level than in gingerbread biscuits with sugar syrup additive.

In flower honey moisture content was 16.2g/100g (1.496 refraction coefficient), which means that the honey is of high quality and relevant criteria adopted.

It also means that the honey which was used in gingerbread biscuits are high quality and has not been heated or stored for long periods at elevated temperatures.

C. HMF in Heated Honey and Sugar Syrup

The HMF content was evaluated for not heated honey and syrup; for honey it was 2.1mg $100g^{-1}$ on average, but for sugar syrup — 1.9mg $100g^{-1}$ on average. As it is shown, there are no significant differences among the content of HMF in raw materials. The ratio for honey is nearly two times less than stipulated in the European standards for quality, i.e., less than 4mg $100g^{-1}$. [2]

Also the increase of the content of HMF in honey and sugar syrup was analyzed based on the results of heating them at 180°C for 5, 10, and 15 minutes.

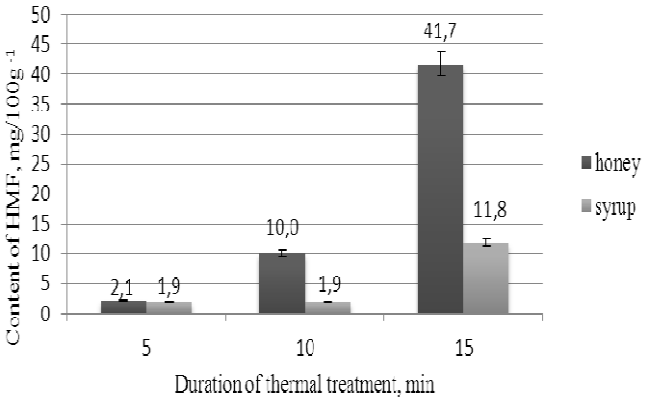

Fig. 3 Content of HMF in heated honey and sugar syrup in 180°C

As shown by the Fig. 3, five-fold increase of HMF in honey can be observed already after 10 minutes (in comparison to non-heated honey), and it exceeds the norm set in the European standards for quality for 2.5 times.

After thermal treatment for 15 minutes, this norm was exceeded 10 times. However, the content of HMF in sugar syrup does not change in the first 10 minutes, but after 15 minutes it has increased for almost 6 times.

D. HMF in Gingerbread Biscuits

Gingerbread biscuits were baked at 180°C un 200°C by using either honey, or sugar syrup as raw material, as well as three different leavening agents: ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$), baking powder, or baking soda ($NaHCO_3$).

The results on the content of HMF in biscuits have been summarized in Figs. 4-7.

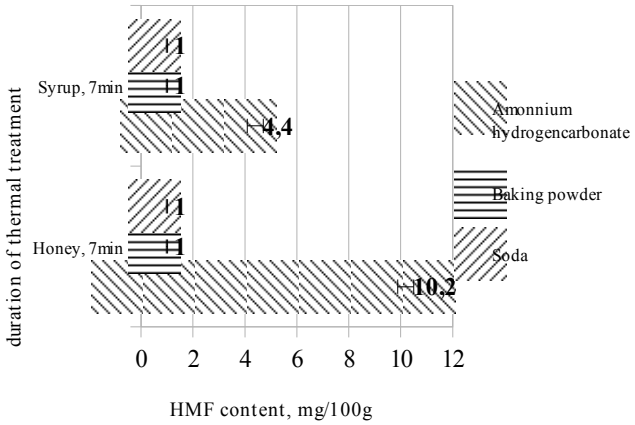

Fig. 4 Content of HMF in gingerbread biscuits baked at 180°C

As shown by Fig.4, HMF content in gingerbread biscuits at 180˚C with baking powder and soda additive is only 1mg/100g. HMF level is much higher in gingerbread biscuits with ammonium hydrogencarbonate additive - with syrup additive it is 4.4mg/100g and honey additive – 10.2mg/100g.

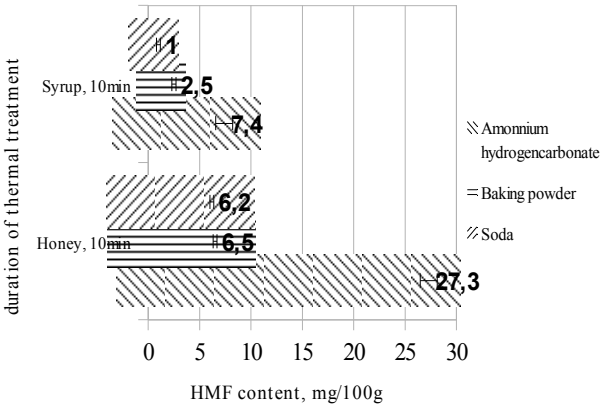

Fig. 5 Content of HMF in gingerbread biscuits baked at 180°C

Given the technological conditions studied together with other leavening agents, the content of HMF exceeds the

amount of 4mg $100g^{-1}$ only in gingerbread biscuits with honey baked for 10 minutes, with baking powder this amount is 6.5 mg $100g^{-1}$, and with baking soda — 6.2mg $100g^{-1}$.

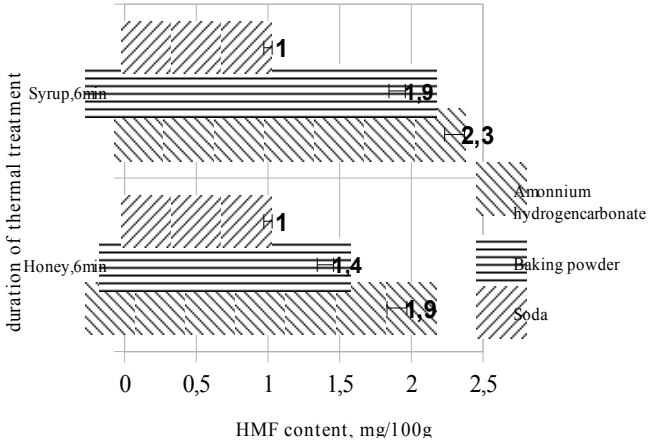

Fig. 6 Content of HMF in gingerbread biscuits baked at 200°C

If gingerbread biscuits are baked at 200°C for 6 minutes, the amount of concentration of HMF both in biscuits with honey, and syrup is less than if gingerbread biscuits are baked at 180°C for 7 minutes.

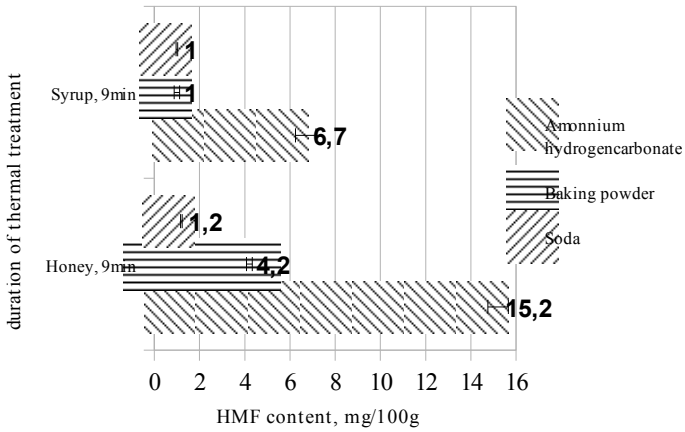

Fig. 7 Content of HMF in gingerbread biscuits baked at 200˚C

As could be expected, larger amount of HMF was found in gingerbread biscuits with honey if they were baked for longer period of time (9 or 10 minutes). Leavening agent significantly influencing the formation of HMF is ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$).

The largest content of HMF (27.3mg $100g^{-1}$) was established in gingerbread biscuits with honey and ammonium carbonate additive if they were baked at 180°C for 10 minutes. But if baked at 200°C for 9 minutes, the content of HMF was for 44% less (15.2mg $100g^{-1}$). HMF is formed significantly less if starch syrup is used for biscuits.

After baking such biscuits at 180°C for 10 minutes, the content of HMF is 3.6 times less than in biscuits containing honey, and 2.7 times less if biscuits are baked at 200°C for 9 minutes. In gingerbread biscuits with syrup, the concentration of HMF reached 4.4mg $100g^{-1}$ if baked for 7 minutes, and 7.4mg $100g^{-1}$ if baked for 10 minutes. If comparing the concentrations of HMF between biscuits baked at 180°C for 10 minutes and those baked at 200°C for 9 minutes, it can be concluded that these concentrations are less for biscuits baked at 200°C for 9 minutes than for biscuits baked at 180°C for 10 minutes, indicating that the determinative factor is not the baking temperature, but the baking time and the composition of gingerbread biscuits.

By comparing the effect of leavening agents, one can make sure that by baking gingerbread biscuits with ammonium carbonate additive for 7 minutes or more the content of HMF is larger than in biscuits with other leavening agents added.

One of the possible explanations is that ammonium ion, which is one of the components of ammonium carbonate, catalyses Maillard reactions, thus promoting the formation of HMF.

IV. Conclusion

In gingerbread biscuits where honey is used as raw material, the content of HMF increases more rapidly than in biscuits where sugar syrup is used as raw material. Honey contains more fructose (37.3%), but sugar syrup contains more sucrose (39.4%). Ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$) promotes the formation of HMF in gingerbread biscuits. When baking powder or baking soda is used as leavening agent, the content of HMF will be several times less than in the event ammonium carbonate is used as leavening agent, given the same conditions.

The formation of HMF is more affected by the baking time, not the baking temperature. It is better to bake at 200°C for 9 minutes than at 180°C for 10 minutes.

References

[1] M.L Almanni. *Enzymatic determination of glucose, fructose and saccharose and research on maize polysaccharides in honey.*1994, Vol.23, pp 81-86.
[2] Council Direktive 2001/110/EC of 20 December 2001 relating to honey. 2002. *Official Journal of the European Communities* 10, 47 – 52.
[3] Capuano E., Ferrigno A., Acampa I., Serpen A., Acar O.C., Gokmen V., and Fogliano V. (2011) Effect of flour type on Maillard reaction and acrylamide formation during to asting of bread crisp model systems and mitigation strategies. *Food Research International,* 42,p. 1295-1302.
[4] Napoli, Italy. Volume 44, Issue 4, p.793–810
[5] K. Skog and J.Alexander (2006)*Acrylamide and other hazardous compunds in heat treated foods*.. pp 331-342; 460, CRC Press, New York.
[6] H. Stadler Richard, David.R. Lineback(2009) *Process-induced food toxicants*, Wiley, Switzerland, pp 126.-165.
[7] P. Stanley Cauvain.(2012) Breadmaking. *Wood head Publishing Series in Food Science,* Technology and Nutrition Number 229. pp.3-5; 189-211.
[8] Y.Yuan Shu C., Zhou B., Qi X., Xiang J. (2011) Impact of selected additives on acrylamide formation in aspargine/sugar Maillard models systems. Food research International, pp 449-455.