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**ORIGINAL RESEARCH PAPER**

# INFLUENCE OF DIFFERENT HYDROCOLLOIDS ON PHYSICO-CHEMICAL AND HEAT-STABLE PROPERTIES OF FRUIT FILLINGS

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High bakery-stability of fruit fillings during baking at elevated temperatures is a very significant and desirable quality attribute in the manufacturing of filled bakery products.

This research was performed with the aim of evaluating the basic physico-chemical changes that occur as well as the heat-stability of apple fillings during the baking process in the oven at a temperature of 200°C for 10 minutes.

Three different hydrocolloids (xanthan gum, carboxymethyl cellulose and low methoxyl pectin) were added at the levels established by $2^k$ Factorial Design to three different apple filling formulations which were processed from the same raw materials: aseptic apple puree, sugar, citric acid, and the effect of these hydrocolloids on the physico-chemical and heat-stable properties of the finished fruit fillings was investigated.

There were obtained the final equations in terms of actual factors in order to describe the influence of total soluble solids and hydrocolloids on fruit fillings' heat-stable and physico-chemical properties. The adequacy of the regression equations was evaluated by the F-test for analysis of variance using statistical package STATISTICA v.6 and has shown that the model was statistically significant. 3D surface plots were drawn by using MATCAD v.15 to investigate the effect of all the factors on the response variables. The experimental data values closely agreed with the predicted ones of the developed models with acceptable percentage errors.

**Keywords**: filling, heat-stable, hydrocolloid.

## Introduction

Apples (species *Malus domestica* in the Rosaceae family) are one of the most popular and nutritious fruit in human diet and widely grown in Eastern Europe. They are rich in food antioxidants necessary for the normal growth of human such as phenolic substances and ascorbic acid (vitamin C), and are also rich in dietary fiber. The predominant phenolic phytochemicals in apples are quercetin, epicatechin, and procyanidin $B_2$ (Lee, et al., 2003). The famous proverb "An apple a day keeps the doctor away", addressing the health benefits of the fruit, dates from 19th century Wales (Phillips, 1866).

To supply throughout the year, it is necessary to preserve apples for a longer period. Depending on variety, apples may be stored for short time in cold storage by chilling or using modified atmosphere storage method. However, these methods are costly and require the availability of special equipment.

For long term preservation, processing is considered to be one of the best methods for developing countries. Therefore, it is essential to develop suitable inexpensive methods for processing and preservation of apple products while saving their healthy properties for consumers.

There are numbers of processed products like apple filling, apple jam, apple juice, apple puree, powder and others. Among the various apple products, filling is the most important one as it requires limited equipment and the methods used are inexpensive.

The basic ingredients in modern filling making process are fruit-based raw material, sugar or sweeteners, acids (citric, ascorbic, etc.), water, while sometimes thickening agents are used in order to obtain thermostable product. Thickening agents are natural or chemically modified carbohydrates that absorb some of the water present in the food, thereby making the food thicker (Sahin and Feramuz, 2005). Commonly used carbohydrates are starch, carboxymethyl cellulose (CMC), pectin, guar gum, xanthan gum, gellan gum, etc. (Srivastava, 1982).

The fruit filling consistency is one of the main quality characteristics for consumer acceptance. This parameter is frequently considered as an essential physical property related to the quality of food products. Thus, precise and reliable rheological data are required for optimization or development of different food manufacturing machines and equipment such as heat exchangers, evaporators, pumps, piping, filters and mixers.

Apple and other fruit purees used for fillings manufacturing belong to non-Newtonian fluids that show a small thixotropy. These foodstuffs acquire their viscosity from naturally occurring pectic substances found in processed fruits, while the rheological behaviour of the fruit fillings prepared on their base depends on many technological aspects, including other added ingredients. The following factors often affect the consistency of the finished fruit fillings: interaction between raw materials, pectin and other filling's ingredients, pulp and soluble solids content, homogenization process and concentration. The proper structure of the final product may also be obtained by addition of different hydrocolloids with thickening and water-absorbing properties.

For consumers' acceptability, the bakery stability of fruit fillings is also very significant. Hydrocolloids with strong water-binding properties can be added to improve heat-stability and decrease the syneresis of the finished fruit filling during all steps of preparation. Fruit fillings are generally used in many food applications, including filled bakery products. Thus, they should possess strong bakery stability; otherwise high oven temperatures will affect their quality properties.

Pectin, xanthan gum and carboxymethyl cellulose are high molecular weight hydrophylic biopolymers that fulfill a variety of functions in food systems, like all hydrocolloids. These functions include: improving texture, control of crystallization, inhibition of syneresis, encapsulation of flavours and increasing the physical stability and storage time (Dziezak, 1991; Garti and Reichman, 1993).

The aim of this research was to study the effects of thickening agents such as carboxymethyl cellulose, xanthan gum and low-methoxyl pectin on physico-chemical and heat-stable properties of apple fillings.

## Materials and methods

### *Raw materials*

Aseptic apple puree, with a total soluble solids (TSS) content of 12%, was manufactured at the canning plant "Conserv-E" (Chisinau, Republic of Moldova). Sugar typically used in fruit filling preparation was purchased from a local supermarket in Chisinau (Republic of Moldova). Citric acid solution (50%) was prepared locally in the Laboratory of Functional Foods of the Practical Scientific Institute of Horticulture and Food Industry (Republic of Moldova). Three different hydrocolloids (xanthan gum, carboxymethyl cellulose and low-methoxyl pectin) used in this study were acquired at the Moscow International Exhibition for Food Ingredients, Additives and Flavorings – “Ingredients Russia-2013” (Moscow, Russian Federation).

### *Apple filling preparation*

The apple fillings’ samples were produced locally according to the procedure for jam manufacturing presented by Basu et al., i.e. mixing the ingredients, evaporation to reach the desired ºBrix level, etc. (Basu, et al., 2011). Apple filling was hot filled and further sterilized in glass jars.

The apple fillings were prepared and developed within a wide range of soluble solids – from 30 to 70 °Brix in accordance with elaborated formulations, using the ingredients shown in Table 1.

Three different hydrocolloids (xanthan gum, carboxymethyl cellulose and low methoxyl pectin) were added at the levels established by $2^k$ Factorial Design to three different apple filling formulations which were processed from the same raw materials: aseptic apple puree, sugar, citric acid, and the effect of these hydrocolloids on the physico-chemical and heat-stable properties of the finished fruit fillings was investigated.

### *Physico-chemical analysis*

The physico-chemical analysis of the apple fillings was conducted at the Laboratory of Functional Foods of the Practical Scientific Institute of Horticulture and Food Industry of the Republic of Moldova.

The soluble solids of the prepared fruit fillings were measured using benchtop refractometer ABBE and expressed in °Brix. The pH was determined by the potentiometric method, introducing the electrode directly into the fruit fillings.

**Table 1.** Recipe used for the preparation of formulated apple fillings

| Ingredients | Formulation, g |
|---|---|
| Apple puree | 45 |
| Sugar[a] | 30÷60 |
| Citric acid (50% solution) | 0.6 |
| Hydrocolloids[b] | 0.2÷1.2 |

[a]Sugar content strictly depends on the final soluble solids of the apple fillings.

[b]Hydrocolloids were added into apple fillings at the following concentrations: from 0.2% up to 0.6% for xanthan gum, from 0.2% up to 1.0% for carboxymethyl cellulose and from 0.5% up to 1.2% for low methoxyl pectin.

The total polyphenols content was determined by spectrophotometric method (Sahin and Feramuz, 2005) using Folin-Ciocalteau reagent. The total content of polyphenols was measured in apple puree before preparing apple fillings, and after that in filling samples prepared with stabilizing agents. The difference between initial content of polyphenols in apple puree and the remained content of these compounds in apple fillings has revealed the total polyphenol losses in each sample.

The prepared apple fillings were also put through standard bakery test to evaluate their thermal stability by determining bakery index (BI) through measuring the diameter of a fruit filling's sample before and after the baking process performed under the exactly fixed conditions: at a temperature of 200°C for 10 minutes (Herbstreith and Fox KG).

A specific amount of each fruit filling's sample was given into a base of special filter paper named "Blue ribbon" with a diameter of 120 mm by a metal ring with defined geometry (50 mm diameter and 10 mm height) and then was baked under the exactly fixed conditions: at a temperature of and 200°C for 10 minutes (Herbstreith and Fox KG).

The bakery index was determined by measuring the sample diameter before and after baking established by placing a line across the sample and calculated by using the following formula:

$$BI = 100 - \frac{D_2 - D_1}{D_2} \cdot 100 \quad (1)$$

where

BI – bakery index, %;

$D_1$ – average sample diameter before baking, mm;

$D_2$ – average sample diameter after baking, mm.

The diameter of each filling sample before baking is 50 mm, because it is the diameter of the metal ring used in bakery test. For determining the sample diameter we measured all diameters of each irregular sample shape, and after that we calculated the average diameter.

***Statistical analysis***

Response surface methodology (RSM) was applied for predicting the optimal quantity of stabilizers (xanthan gum, carboxymethyl cellulose and low methoxyl pectin) added to apple filling's composition for attributing high quality and thermo-stable characteristics to the final product.

The critical and non-critical factors affecting the heat-stability of apple fillings were identified in preliminary experiments. It was established that mainly soluble solids and percentages of stabilizers affect apple fillings' thermal stability (at the same high temperature and for the same baking duration). Therefore, only a quantity of xanthan gum, carboxymethyl cellulose and low methoxyl pectin, and also soluble solids as independent variables were used in a two-level factorial design. Briefly, the two-level factorial design consists of k variables or factors, set at two different levels, indicated as "-1" (the minimum) and "+1" (the maximum). The levels of these variables were set at: 0.2 (-1) and 0.6 (+1) for percentage of xanthan gum, 0.2 (-1) and 1.0 (+1) for percentage of carboxymethyl cellulose, 0.5 (-1) and 1.2 (+1) for percentage of low methoxyl pectin, and 30 (-1) and 70 (+1) for soluble solids, °Brix. The heat-stability of fruit fillings as a response variable was expressed through the bakery index (BI, units). All experiments adjusted by the design planned in coded and encoded form of process variables, were conducted randomly.

There were obtained the final equations in terms of actual factors in order to describe the influence of soluble solids and stabilizing agents (xanthan gum, carboxymethyl cellulose and low methoxyl pectin) on apple filling's heat-stable properties. The adequacy of the regression equations was evaluated by the F-test for analysis of variance (ANOVA) using statistical package STATISTICA v.6.

## Results and discussion

Nowadays, the use of various thickening agents has become a common practice in the confectionary industry. Carbohydrates are commonly added to commercial bakery fillings products to improve the quality of filled bakery products. They help to minimize the negative effects of thermal treatment during preparation and baking.

The ultimate goal of the research was to reveal the bakery stability of fruit fillings prepared with three different carbohydrates: carboxymethyl cellulose, pectin and xanthan gum within a wide range of soluble solids – from 30 to 70 °Brix.

Xanthan gum is an excellent thickening agent. But, unlike many other thickening agents, it is stable at a range of temperatures. The viscosity will not change significantly between ambient temperature and a definitely "melting temperature" (Srivastava, 1982). In addition, xanthan gum is stable over the pH range 2 to 12 (Dziezak, 1991; Srivastava, 1982) and can provide good thermal stability for fruit fillings in a wide range of pH.

Pectin was also selected in this study for the testing heat-stable properties of fruit fillings, because has been used primarily in food industry as a gelling agent and is widely used for the production of jams, jellies, confectionary products and bakery fillings (May, 1997).

Carboxymethyl cellulose can also provide significant viscosity, excellent aroma release and clarity to fruit-based products; therefore it was tested for heat-stability of fruit fillings. It can also have a gummy texture at excessive levels (Sahin and Feramuz, 2005).

The main physico-chemical characteristics of the apple fillings prepared with xanthan gum, carboxymethyl cellulose and low methoxyl pectin are presented in Table 2.

**Table 2.** Physico-chemical parameters of the apple fillings

| Product name | pH | Total polyphenol loses, mg/kg | Bakery index, units |
|---|---|---|---|
| Apple filling with 0.2% CMC and 30 ºBrix | 3.7 | 340.32 | 8.20 |
| Apple filling with 1% CMC and 30 ºBrix | 3.7 | 430.82 | 10.18 |
| Apple filling with 0.2% CMC and 70 ºBrix | 3.7 | 125.52 | 15.72 |
| Apple filling with 1% CMC and 70 ºBrix | 3.7 | 166.32 | 30.18 |
| Apple filling with 0.2% xanthan and 30 ºBrix | 3.6 | 381.42 | 58.82 |
| Apple filling with 0.6% xanthan and 30 ºBrix | 3.6 | 298.72 | 68.97 |
| Apple filling with 0.2% xanthan and 70 ºBrix | 3.6 | 251.54 | 38.46 |
| Apple filling with 0.6% xanthan and 70 ºBrix | 3.6 | 204.52 | 54.05 |
| Apple filling with 0.5% pectin and 30 ºBrix | 3.5 | 463.82 | 99.82 |
| Apple filling with 1.2% pectin and 30 ºBrix | 3.5 | 204.52 | 54.05 |
| Apple filling with 0.5% pectin and 70 ºBrix | 3.5 | 297.22 | 8.20 |
| Apple filling with 1.2% pectin and 70 ºBrix | 3.5 | 194.74 | 79.82 |

Quality characteristics of the apple fillings analyzed under laboratory conditions have demonstrated that they meet the international food standard CODEX STAN 296-2009 for jams, jellies and marmalades.

After processing the experimental data presented in Table 2, the following regression equations (2, 3 and 4) describing the heat-stability of the apple fillings prepared with various hydrocolloids in terms of actual values were derived:

$$BI_1 = 4.41 - 9.23 \cdot CMC + 0.11 \cdot SU + 0.39 \cdot CMC \cdot SU \quad (2)$$

$$BI_2 = 63.33 + 53.79 \cdot X - 0.18 \cdot SU - 1.86 \cdot X \cdot SU + 1.14 \cdot X^2 \cdot SU \quad (3)$$

$$BI_3 = 336.43 - 252.86 \cdot P - 5.43 \cdot SU + 5.08 \cdot P \cdot SU \quad (4)$$

where: BI – bakery index, units; CMC – carboxymethyl cellulose content, %;
X – xanthan gum content, %; P – pectin content, %; SS – soluble solids, ºBrix.

The results obtained through application of Response Surface Methodology were verified by conducting the validation experiments under the optimized conditions of all the factors. The experimental data values closely agreed with the predicted values of developed models with acceptable percentage errors.

In order to visualize the influence of all the factors on the response variables, 3D surface plots were drawn by using MATCAD v.15 (Figure 1).

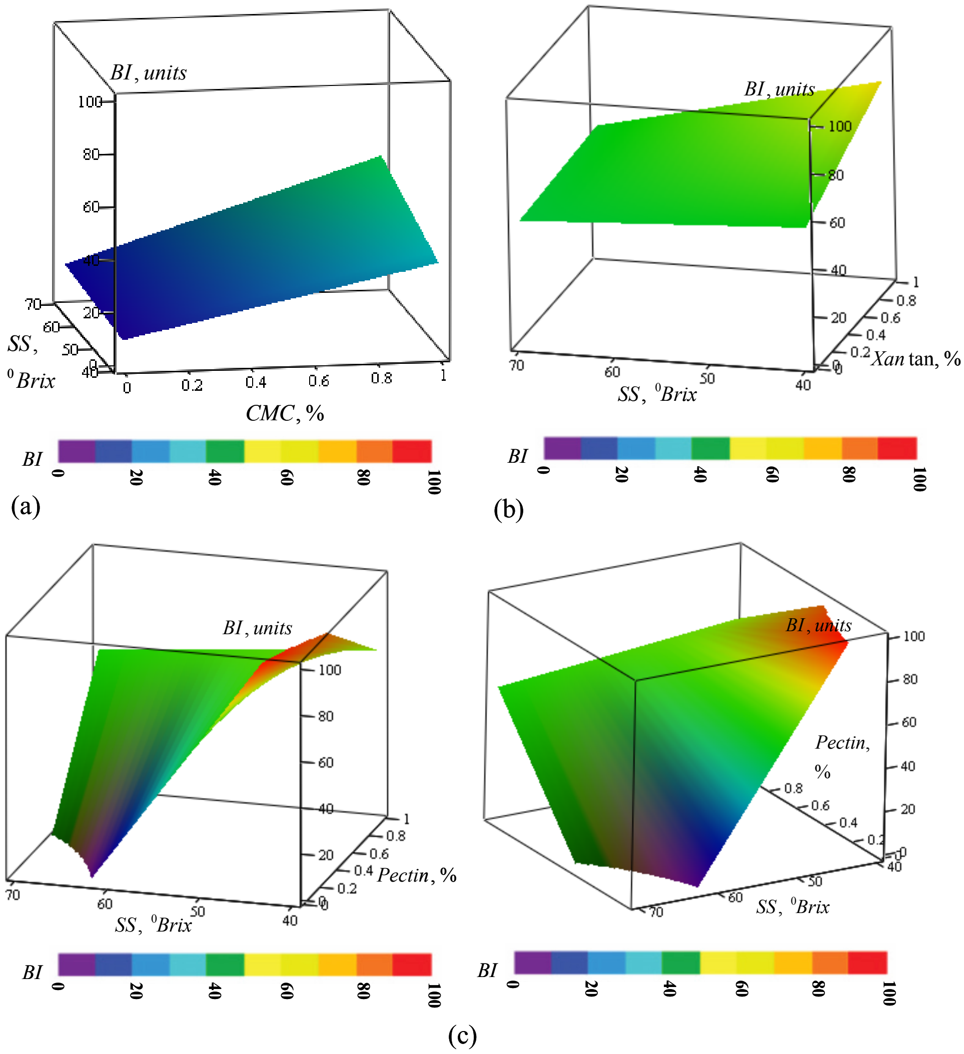


**Figure 1.** 3D plots: The simultaneous influence of soluble solids and percentage of CMC (a), xanthan gum (b) or pectin (c) on the bakery index of apple fillings

Judging from the figure, it is evident that apple fillings prepared with xanthan gum or carboxymethyl cellulose within a wide range of soluble solids – from 30 to 70 °Brix, are characterized by low thermal stability, while apple fillings prepared with low methoxyl pectin possess high and medium thermal stability and can maintain their initial shape and volume after baking under a temperature of 200 ºC for 10 minutes. But despite this, low methoxyl pectin requires the presence of one more thickening agent with strong water-binding properties, because fruit fillings made only with low methoxyl pectin exhibit a strong tendency to syneresis, which may negatively affect the quality of pastry after baking.

The use of low-methoxyl pectin can make possible to increase the heat-stability of fruit fillings up to the medium level and to ameliorate their physico-chemical properties.

Thus, the study reveals that xanthan gum can be added to bakery and fruit pie fillings before and after baking, in which it will improve texture and flavor release, but it cannot provide good heat stability to fruit fillings as it makes low-methyl pectin. Carboxymethyl cellulose also improves sensory characteristics of fruit fillings, but cannot provide good heat-stable properties to them.

Also the influence of thermal treatment on the total polyphenol losses in fruit fillings was investigated. The total polyphenols losses in fruit fillings prepared with pectin and xanthan gum were a little bit higher after thermal processing than in fruit fillings prepared with CMC, that demonstrates that the last carbohydrate is more effective in saving polyphenols from thermal damage than the first ones.

According to the present study, it is evident that low-methoxyl pectin would be more advantageous to use along with CMC in fruit fillings' compositions in order to improve their heat stability, while maintaining high textural characteristics and saving polyphenol compounds from thermal damage.

**Conclusion**

The major argument for introducing food hydrocolloids into fruit fillings is to improve their overall quality. This enhancement refers not only to its sensorial properties, but also heat-stable and textural characteristics, which are eventually judged by the consumer. If hydrocolloids are applied as stabilizing agents with the aim of stabilizing a food system under applied heat, the selection of the proper hydrocolloid is extremely important. Heat degradation of fruit fillings in the oven due to intensive boiling, syneresis and reduction in the viscosity of polymer compositions may deteriorate their physico-chemical properties and appearance sufficiently enough to reduce consumer acceptability of the finished products containing these fillings.

The quality criteria of bakery fruit fillings are especially determined by their heat-stable properties. The formulations of the fruit fillings as well as the heat-stabilizing agents used in manufacturing process play a crucial role in developing bakery fruit fillings with high-quality characteristics.

The present research investigated the influence of pectin, xanthan gum and carboxymethyl cellulose on the heat-stable and physico-chemical properties of apple fillings prepared within a large range of soluble solids – from 30 to 70 °Brix.

The study revealed that only low methoxyl pectin may lead to the required heat-stable properties of fruit fillings, but it also needs the presence of one more thickening agent with strong water-binding properties.

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