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WET-MILLING HIGH-AMYLOSE CORN IN THE INDUSTRIAL SCALE

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Abstract
Due to its properties, high-amylose corn containing about 70% amylose can be better wet milled by including some modifications in the process conditions. The most important changes can be made in the steps of steeping and protein separation. In this paper we compared the results obtained during three procedures of high-amylose corn processing performed in a starch factory located in the south-eastern part of Romania. The aim is to establish the optimal processing procedure for high-amylose corn in an industrial scale. To obtain a reliable process evaluation, the amylose content of the starch produced was analysed by using two different conventional colorimetric methods, a potentiometric method and a spectrofotometric one. As compared to the laboratory and pilot scale the industrial scale wet-milling has some advantages materialized in higher starch yields and protein content of starch.

Key words*: high-amylose corn, industrial scale, wet-milling*

INTRODUCTION

High-amylose corn is grown to be used exclusively to wet-milling processes, the starch obtained having applications in the textiles, candies and adhesives industries (Thomison, 2013). High-amylose starch is composed by round and filamentous granules with length of approx. 15 µm (Liu, 2005). It can be consumed without any problems also by diabetics and others who try to control insulin levels in blood, because it has a glycemic index lower than conventional corn. Another advantage is that the high-amylose starch is an excellent resistant starch source, considered to be functioning as prebiotic and reducing the colorectal cancer incidence. In addition, this starch type can be used to manufacture the biodegradable packaging materials and adhesive materials (Polaske *et al.*, 2005). High-amylose corn is processed through the wet-milling process, too being necessary some small changes due to its properties. The most important changes were observed in steeping and protein separation steps. A comparative study of three starch types with different amylose content (63%, 23% and 2%), performed in 2010 by Kibar *et al.,* showed several specific characteristics for the high amylose corn, such as higher water absorption, lower degree of swelling due to its internal structure and the presence of endogenous lipid granules.

The steeping of high-amylose corn kernels is made more rapidly than for conventional corn, while it is observed that supplementary steeping water of 6 to 9% is consumed. For example, Anderson *et al.*, in 1959 observed that for corn with amylose content of approx. 49%, the steeping water consumed was 6% higher and in 1960 for corn with amylose content of 68% was 9% higher than for the conventional corn. The steeping time and temperature seem to be the same, but the steeped corn total volume achieves 128%, while for conventional corn is only 68% (Anderson *et al*., 1959). In the protein separation step appear some difficulties due to the small dimensions of granules, which are of 11 µm in the high-amylose starch instead 14 µm in the conventional starch

(Wittenberger, 2003). Also, this fact is easily observed in the gluten protein content, 35-44% (Anderson *et al*., 1959, Anderson *et al*., 1960) and in the starch protein content 0.5-0.7% (Anderson *et al*., 1959, Anderson *et al*., 1960). As the amylose content is high, the starch gelatinization is more difficult and increases susceptibility to retrogradation, the main mechanism of resistant starch formation in processed food (Hódsági and Salgó, 2011).

The most high-amylose studies found in the literature were performed in laboratory scale and only some in pilot scale; therefore in this study we present the wet-milling high-amylose corn process in the industrial scale, considering this approach to be more useful for the starch producers.

MATERIALS AND METHODS

In the literature there can be found some studies made in the period 1959-1961 by several researchers in order to observe the processing behaviour of high-amylose starch containing 57, 66, 68 and 75% amylose. The tests were performed in the laboratory and confirmed in pilot stations. In the starch factory from Tandarei, where our study took place, there were performed until now three high-amylose corn processing cycles, the first one in the beginning of 2011 (batch 2011) and the others two, in the beginning and the end of 2012, batch 2012-1 and 2012-2, respectively. For the first high-amylose processing we took as reference the test made in 2003 by the pilot station of innovation centre Zuckerforschung Tulln from Austria and for the others, in addition we used the experience acquired. The high-amylose corn used was cultivated in Hungary for the first processing cycle and in Romania for the other two processing cycles.

The analysis methods performed for the corn and for the final products and by-products were the same as those used for the conventional corn, as following:

- The starch content in corn, germs, fiber and gluten was analyzed using the polarimetric method of Ewers.
- The protein content in corn, starch, corn gluten meal and corn gluten feed was analyzed using Kjeldahl method.
- The fat content in germs was analyzed according to Soxhlet method.
- The moisture of steeped corn was monitored at each 5 h until achieving 35 h of steeping, then every hour, using the rapid drying method halogen lamp moisture analyzer.
- The sulphur dioxide content from steeping water was performed through iodometric method.
- The soluble substances from steeping water were analyzed using a refractometer capable to measure 0 – 95 brix degrees.

The analysis of starch amylose content and starch viscosity were specific, as follows:

- The amylose content for the samples obtained in the first two processing cycles was analyzed using only the potentiometric method, but for the samples obtained in the third processing cycle we used both potentiometric and spectrofotometric method.
- Beginning with the third processing high-amylose corn, in addition we analyzed also the starch viscosity using a Brookfield viscometer, type RV DV-E equipped with small volume sample adapter (measure chamber SC4-13R and spindle SC4-27.

RESULTS AND DISCUSSIONS

Studies made in the factory from Tandarei upon the high-amylose corn wet-milling process and high amylose starch characteristics had as the main goal to establish the optimal high-amylose wet-milling procedure. This study shows some advantages as compared to other studies found in literature, because the results were obtained in a production plant which processed between 75 and 350 to of high-amylose corn for these three processing cycles.

As we mentioned above, the production steps in which appear differences over the conventional corn wet-milling process are corn steeping and protein separation from starch suspension. In the following two tables (1 and 2) we centralized the average results obtained during the three wet-milling processes for corn characterisation, steeping and protein separation processes. The values presented in

Table 1 show a decreasing of starch content in high-amylose corn from the first to the third processing, apparently unexplainable. After a literature review we can conclude that it is possible that these results are not reliable due to the fact that amylose hydrolysis with hydrochloric acid is quite difficult and the method SR EN ISO 10520:2002 (polarimetric method of Ewers) excludes the high-amylose starch from its field of application. The steeping time varies from 46 to 61 hours, but this fact did not have any impact on the corn moisture content after steeping, this being maintained at around 50%. The soluble substances and SO_2 content in steeping water increased with steeping time, most probably because in the industrial scale production the recirculation in counter-flow process is used. This steeping industrial way brings in the steeping vessel (which is filled with dry high-amylose corn) the steeping water circulated through all steeping vessels in different steeping phases, leading to a higher content of soluble substances and the lowest SO_2 content. In the same time the SO_2 solution, with the lowest content of soluble substances and the higher SO_2 content is introduced in the steeping vessel filled with a corn having the highest moisture content.

Table 1: Corn and steeping process characteristics

	Batch 2003 Austria	Batch 2011	Batch 2012-1	Batch 2012-2
Starch content (%/DS)	59	53.1	41.5	35.8
Corn moisture after steeping step (%)	53	52.2	51.1	49.3
Steeping time (h)	48	46.0	61.0	57.0
Soluble substances in steeping water (%)	-	4.2	8.7	6.7
SO_2 in steeping water (%)	-	0.047	0.069	0.048

Table 2: Protein separation process and starch characteristics

	Batch 2003 Austria	Batch 2011	Batch 2012-1	Batch 2012-2
Starch slurry concentration (^{0}Be)	15	22.1	18.5	20.0
Ratio washing water / starch slurry	-	1.2	1.5	1.3
Protein in starch (%)	0.72	0.48	0.43	0.45
Starch content in gluten (%/DS)	-	10.8	19.8	17.5
Protein in gluten (%/DS)	-	41,3	47,2	47,6
Amylose (%/DS)	55.3	65.6	71.0	75.3

We have observed (Table 2) that the concentration of the starch slurry does not negatively influences the protein content in the starch, for the highest concentration of the starch slurry obtained during the three processing, 22.1 ^{0}Be in the batch 2011, the highest protein content in the starch being obtained (0.48 %/DS). Conversely, if we take into consideration the values recorded for the ratio washing water / starch slurry and the protein content in the starch, we can easily observe that the value of the ratio is influencing in a favourable way the protein separation from the starch slurry. The lowest protein content from starch, 0.43 %/DS, was obtained in the batch 2012-1 for which the ratio was the biggest, 1.5. If we compare the protein content of high-amylose starch reported in the literature, either obtained in laboratory (average 0.59 %/DS) or in pilot scale (average 0.72 %/DS) we can say that the industrial scale processing is more advantageous for the protein separation step, the average value being 0.46 %/DS.

The yields of high-amylose starch and by-products obtained for these three high-amylose corn processing are summarized in Table 3. We can observe that for the batch 2012-1 the yield was the lowest both for high-amylose starch and by-products, which is related to the lowest quantity of the raw material processed. If we try to correlate the high-amylose corn processed quantity with the total yield, we observe that the yield increases with quantity, but a reasonable correlation coefficient could not be obtained. The same remark is also valid for the starch and germs yields, but not for fiber and gluten yields, the latter two being influenced by the CSL dosed quantity used in order to adjust the protein content and increase the yield.

The diagram presented in figure 1 shows that during the three high-amylose corn processing cycles the starch content (SC) had a decreasing evolution, while the amylose content increased. This comparison between starch and amylose content confirms the above mentioned statements regarding the difficulty of quantifying the starch content in high-amylose corn and moreover, indicates a possible explanation of starch content decreasing from the first to the last high-amylose corn processing cycle. Figure 2 shows a comparison of the amylose content determined in the high-amylose starch obtained in the batch 2012-2 using either the potentiometric or the spectrofotometric method. As it is also known from the literature, the iodometric methods seem to overestimate the amylose content (Zhu *et al.* 2008; Vilaplana *et al.*, 2012), but remain the most reliable of all conventional methods (Duan *et al.*, 2012). With the exception of a single sample (no. 6) all the analysis results showed that the potentiometric method gives higher values than the spectrofotometric method.

In order to validate more correct analysis methods for high amylose starch this study should be continued.

Table 3: Yields after high amylose corn processing

Yield (%)	Batch 2011	Batch 2012-1	Batch 2012-2
High-amylose corn quantity (to)	**195**	**79**	**347**
High-amylose starch	53.0	51.8	57.4
Germs	8.5	7.1	9.0
Fiber *	22.1	19.0	19.8
Gluten *	7.8	6.5	6.9
TOTAL	**91.4**	**84.4**	**93.1**

* to which was added CSL (steeping water concentrated till DM of approx. 50%) to adjust the protein content.

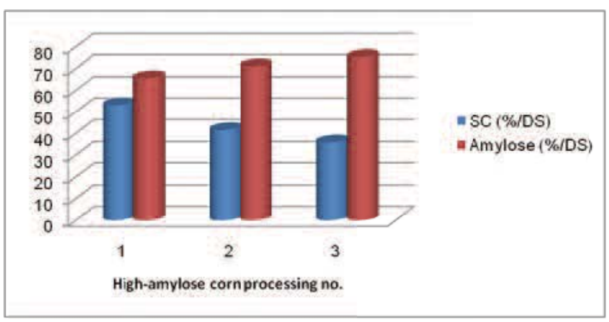

Fig. 1: Starch content vs. amylose content for the batch 2012-2

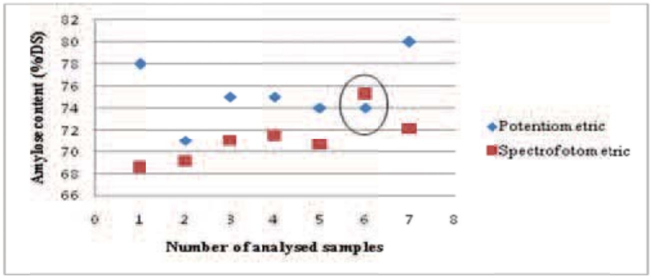

Fig. 2: Comparison of amylose content results obtained by two colorimetric methods for the third processing

CONCLUSIONS

The high-amylose corn can be processed following the classic wet-milling process for the normal corn, but making some small changes at corn steeping and protein separation steps, in order to accommodate the higher capacity of this type of corn to absorb water and also to cope with the smaller dimensions of its starch granules.

The stepping process in counter-flow used only in industrial scale is more advantageous than any stationary process used in laboratories or pilot stations, allowing a more rapid disaggregation of corn starch bonds and a much better separation of protein from starch slurry.

Even if the analysis methods for conventional corn were useful to a certain extent in the high-amylose corn processing control too, it is recommendable for future batches that the polarimetric method of Ewers for starch content to be replaced with another method, more specific for this type of corn. More studies are needed in order to find a more appropriate method for amylose determination in high-amylose corn products.

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