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ADVENTAGES AND LIMITS ON USAGE OF THERMAL METHODS IN COMPLEX SYSTEMS
Bread and bread additives analyses

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In order to increase the nutrition value of bread, one of the most commonly used foodstuff all over the world, different additives are used in bread processing. In this paper we describe the thermal changes in bread and that of with 0.5% crude soybean lecithin additive. Their thermal stability has been investigated by TG, DSC and EGD methods. The thermal changes were also followed of soy products, lecithin and lysine, ingredients used as bread additives in order to check if they may suffer any thermal degradation during the baking process. The data obtained can be of use only for qualitative conclusions. According to the obtained data at the usual bread baking temperature only the additives in crust may partly decompose while in the crumb, at lower temperatures the additives, due to baking, are not damaged. The thermal methods give a possibility for rapid estimation of processes induced by heat effects in additives during the baking, and they are suitable to detect the changes during the bread-making procedure. However, they are neither suitable to provide any quantitative data on these changes nor facts affecting the nutrition value and of the bread.

Keywords: *bread analysis, crude soybean lecithin, soy flour, TA*

Introduction

Soybean products like soy flour, lecithin and mixtures containing soybean products are widely used in food processing.

Soy flour is made by grinding whole dry soybeans into flour, which means that it contains all the components present in soybeans, including about 35% of proteins, 20% of oils, vitamins and mineral components. There is controversial information about indications that soybean proteins may elicit allergic reactions in sensitive individuals [1–3]. However, the risk assessment is rather low, compared to its similar biological value to animal proteins, necessary to regular human growth and development.

Lecithin is one of the most valuable components of the soybean. It is a complex mixture of acetone-insoluble phosphatides: phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl inositol combined with variety amounts of fatty acids and carbohydrates [4]. Choline is a cofactor to produce acethylcholine hormone, source of essential ω-3 fatty acids, undersupplied in most people's diet. One of the functions of lecithin is its emulsifying ability. It is due to contribution of its non-polar groups (the two fatty-acid ester groups), insoluble in water and of polar, water soluble (phosphatidyl choline) portion. Due to this kind of structural characteristics, lecithin influences the baking performance of wheat dough. Lecithin improves the fermentation behaviour of yeasted dough, the loaf volume of the bread and the structure of bread crust [5]. At different baking temperatures different processes are taking places [6] as transformation of the dough to readily digestible product [7], the Maillard reaction causing the colour, flavour, functional and nutritional value changes. Caramelization occurs at temperatures above 120°C, together with water evaporation [8]. As the surface temperature during the baking is higher than that of in the middle of the bread, the composition of the crust is different from that of the crumb [9]. All these processes during the baking of the bread determine its taste and nutrition value.

Lysine belongs to essential amino acids. It is found in wheat, but during the baking of the bread the blocking and destruction of lysine [10] may occur. In order to improve the nutrition value of bakery products it is also a useful additive.

The quantitative (but even the qualitative) determination of the above listed components in such complex systems as bread and other similar products is a complex, time consuming procedure. Separation of the com-

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ponents usually includes high-performance liquid chromatography (HPLC) or enzymatic methods, with also time consuming sample preparation methods [11, 12] which is followed by qualitative or quantitative determination of the specific components.

On the other hand, studies on oxidative stability of food and food components are necessary due, among others, to commercial, nutritional and health reasons. The accelerated oxidation tests give indirect results. Conclusions drawn on the basis of volatile product detection also may be misleading due to different extents of autoxidation [13, 14]. The usage of DSC is a direct analytical method for continual monitoring of total thermal effect of autoxidation [15], but also for oxidation processes which may be involved during baking of the bread. DSC is a suitable and quick method *e.g.*, to make difference between a natural and recombined butter [16], containing lecithin. Microemulsions, with lecithin content operate as vehicles for solubilisation of active molecules. DSC technique is an effective tool to investigate the temperature induced phase transitions in these microemulsion systems, too [17].

The aim of our study was to find a rapid method in order to follow the changes of the ingredients added to improve the quality of bread with rising temperature and to check if the components suffer any thermal degradation up to baking temperature. Thus, we have chosen thermal analysis including TG, DTG, DSC and EGD in order to follow the thermal degradation of additives and the final product, *i.e.*, bread.

Experimental

Materials

Samples were commercial products of SOJAPROTEIN, Bečej, Serbia.

- Crude soybean lecithin (CL) with tell quell data: acetone insolubles (phospholipids) 70%, moisture and volatile matter 0.5%;
  Soy flour and Functional Mixture samples with phospholipids content (PL, %): SF0 (SOPRO UTB; 0.02), SF1 (SOPROMIX He; 1.4), SF2 (SOPROMIX 1; 1.8), SF3 (SOPROMIX 2; 2.4), SF4 (SOPROLEC 8 TB; 2.4).
- SF5 (PL 19.3) and SF6 (PL 36.2) were mixed using SOPROLEC 8 TB and crude lecithin in a mass ratio of 3 :1 (75% soy flour, 25% CL) and 1:1 (50% soy flour, 50% CL). The phospholipid (PL) content of the samples, which is proportional to the lecithin percentage, was determined according to the official specification [18].

Lysine (99%) was obtained from PT. CHEIL JEDANG, Jakarta.

The bread was prepared by mixing of wheat flour (T-500), yeast and table salt with water: 300 g wheat flour, 180 cm^3 water (30°C), 10 g yeast and 5 g salt were mixed using a farinograph mixer for 5 min at 30°C. The dough was left for fermentation for 45 min, after which it was mixed again for 1 min. The second fermentation was carried out in a thermostat at t=32°C for 15 min. After the second fermentation the dough was divided into two equal parts and gathered into balls. The final proof was accomplished at t=30°C and relative humidity of 80% until the effect of a finger dip in dough remained unchanged. The dough was placed in a baking dish with Teflon covering and placed at the bottom of a Chopin Laboratory Furnace. The backing temperature was 230°C. The baking was completed at mass loss of about 10% and the bread was cooled down to room temperature on wooden shelf without the dish.

The same bread making procedure was repeated with 0.5% crude lecithin additive.

Thermal measurements

The thermogravimetric measurements have been carried out using TA Instruments, type 2050 TGA V5.3C with module TG 1000°C, in platinum crucible and sample masses of about 10 mg. The DSC runs were recorded employing 2920 MSDC Instrument with DSC standard cell in an open aluminum sample pan (6–8 mg) and an empty pan as reference. The measurements were conducted in flowing air with a 120 cm^3 min^{-1} gas flow and a 10°C min^{-1} heating rate up to 250°C. Thermal tests of some of the samples were carried out under similar conditions also in flowing argon atmosphere. The presented data are the average of three parallel measurements. Evolved gas detection (EGD) was accomplished using DuPont 916 TEA (Thermal Evolution Analyzer) instrument in flowing nitrogen and 8°C min^{-1} heating rate.

Results and discussion

The measurements were conducted in flowing air, except of some probes, which were repeated also in argon under the same conditions as in air gas carrier. The thermal curves did not depend on the atmosphere, so the following discussion refers to measurements carried out in air, *i.e.*, under real bread processing conditions.

The soy product samples were commercial products for nutritional purposes (SF0, SF1, SF2, SF3 and SF4), except SF5 and SF6. In the last two samples the crude lecithin content was increased significantly in order to examine how it affects the thermal behavior of the flour samples. Figure 1 demonstrates the TG curves of soy flour products with different PL con-

tent, given in Experimental. It shows very similar decomposition pattern for the samples with low and close PL content. The differences are insignificant between the curves. Thus, they are not suitable to give any indirect quantitative information about the composition of the samples. In the case of the samples with significantly higher PL content, the course of the decomposition differs significantly, but the TG data offer no possibility for the quantification of the mixture composition. The first mass loss belongs to adsorption water evaporation. The flour samples (SF0–SF4) with low PL content have a more pronounced capability to absorb water. It is due to high surface of the flour particles and to the polar part of PL. The dehydration of the flour samples is accomplished around 96±1°C. The mass losses are also similar, Δm=5.5±0.3%, referring that thermogravimetry is not sensitive enough even for indirect determination of PL (lecithin) content of the samples. Up to about 180°C there is an additional mass loss which may belong to structural water or/and soy oil components evaporation that extends not more than 0.7%. The total mass loss up to this onset temperature amounts Δm=6.2±0.5%. Above 180°C the decomposition of all these samples speeds up, probably due to autoxidation/oxidation reactions.

When the PL content of the samples is significantly different, the shape of TG curves is also different. The dehydration temperatures are somewhat lower, but inside the experimental error. However, the wettability of the samples with high PL percentage is significantly lower. So, the first mass loss of SF6, sample with the highest PL content, is only 0.9%, while that of the SF5 is 2.2%. The second mass loss of SF6 to 177°C is additional 3.9%, which is due to higher oil content of the sample. The additional mass loss of SF5 to the same temperature is only 0.5% which is somewhat less than expected. The mass losses of the last two samples suggest that for a sample series with PL differences of about 5%, some kind of calibration curve might be constructed for a rapid determination of PL content, measuring the mass losses of the dehydration (the first decomposition step) in function of PL content. However, to prove this supposition additional measurements are needed.

The DSC curves of SF0–SF4 flour samples are presented in Fig. 2. The endothermic evaporation processes take place up to about 180°C. On the basis of the DSC-curves the separation of the processes is even more difficult than on the basis of the corresponding TG-curves. At higher temperatures the thermal decomposition is highly exothermic, supporting the proposition of oxidation processes. The shape of the curves is very similar. However, they are not suitable to obtain any quantitative data as heat flows cannot be compared on the basis of *W*/*g*.

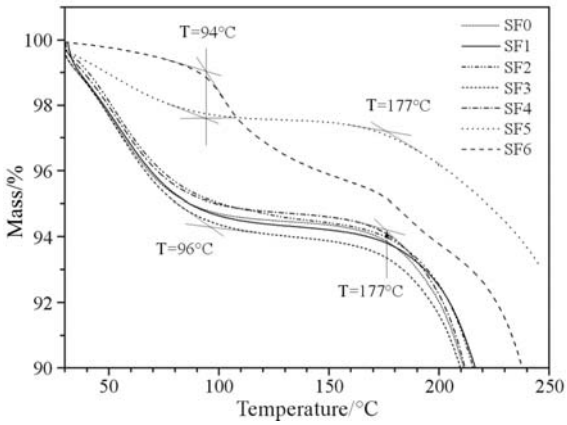

Fig. 1 TG curves of soy products with differnt lecithin content

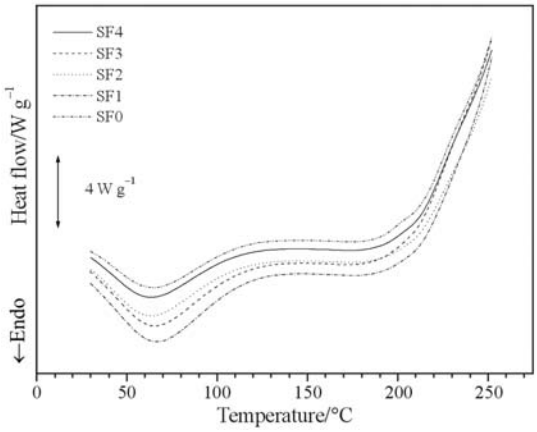

Fig. 2 DSC curves of soy products with different lecithin content

The TG–DTG and DSC curves of crude lecithin are presented in Figs 3 and 4. From room temperature up to about 150°C the mass loss amounts 0.5% that belongs mostly to water evaporation (this value is in accordance with the data given in Food Chemical Codex [4]), accompanied at higher temperatures with departure of oil components. The stepwise thermal decomposition of the lecithin according to the TG curve in air and argon begins to be explicit at 175°C, followed by the next one at about 210°C. The steps are overlapping. The mass loss in this ca. 35°C temperature range is about 6%. With rising temperature the decomposition speeds up.

The DSC curve (Fig. 7) is not suitable to detect unambiguously the water evaporation in spite of the existence of a prolonged endothermic process in the temperature range from room temperature up to 180°C, containing also a sharp endothermic peak at 66°C onset temperature. This peak belongs to the melting of crude lecithin. The complete melting of the lecithin crystals, according to literature data [19] is achieved above 50°C.

Up to 180°C, beside the dehydration, probably the evaporation of unsaturated soy oil components takes place which portion accounts for over 80% [20]. Above 200°C exothermic self-oxidation processes begin, as the decomposition curves of the crude lecithin are identical both in argon and air atmospheres.

As the literature data refer to a possible enzymatic inactivation and destruction of lysine during the baking process [10], the thermal stability of a lysine sample was tested, also. As Fig. 5 illustrate, the thermal decomposition of lysine as an additive is insignificant at bread baking temperature. The sample contains only a small amount of water (Δm=0.7%). Above 100°C the lysine anhydrate is stable up to 216°C. The literature data for *L*-lysine monohydrate gives a melting point at 225°C [21]. In the case of this lysine sample the melting is accompanied by the decomposition. However, the high decomposition temperature, compared to baking temperature offers a possibility to use it as an additive to replace a part of inactivated natural lysine in soy flour (SF0: Lys 3.10% and ε-Lys 2.32%) determined by standard methods at VMA (Vojna medicinska akademija) in Belgrade.

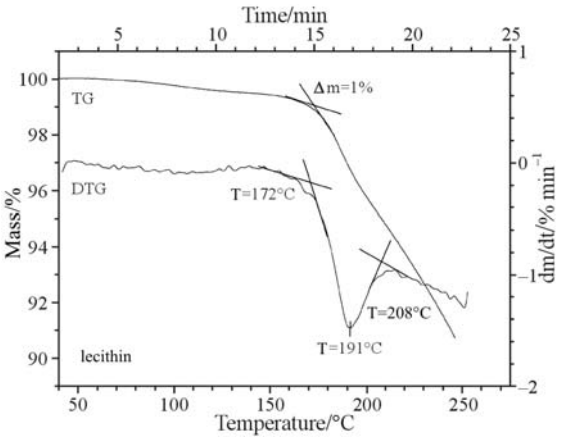

Fig. 3 TG–DTG curves of crude lecithin

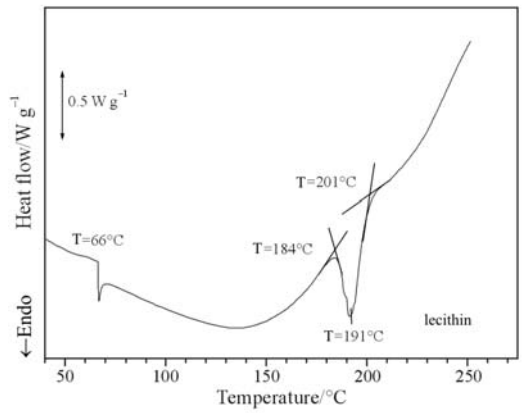

Fig. 4 DSC curve of crude lecithin

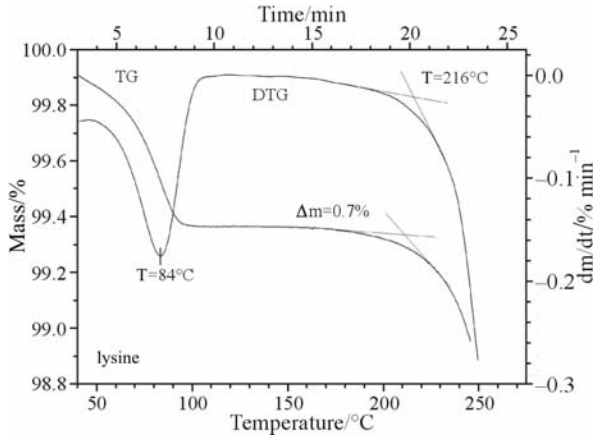

Fig. 5 TG–DTG curves of lysine

The thermal curves of bread samples are presented in Fig. 6 (TG–DTG) and 7 (DSC). The samples were dried at room temperature and ground before the measurements.

Figure 6 illustrate that only the evaporation of the adsorptive water (Δm=8%, t=170°C) and probably of some oil components take place up to usual bread baking temperature (~230°C). However, the bread with lecithin additive releases the water at somewhat higher temperature (DTG curve), which is in the consistence with the experiences: the bread remains fresh for days with lecithin additive. Unfortunately, practically the thermogravimetry is not a suitable method to make difference between the bread without additive and of that one with 0.5% crude lecithin additive. The difference in water release process is somewhat more detectable with DSC showing a sharper peak of water evaporation in the case of bread without fat content, while with the lecithin additive the water release process begins at a somewhat higher temperature.

Neither of the EGD curve is suitable to make a difference between the breads without and with a

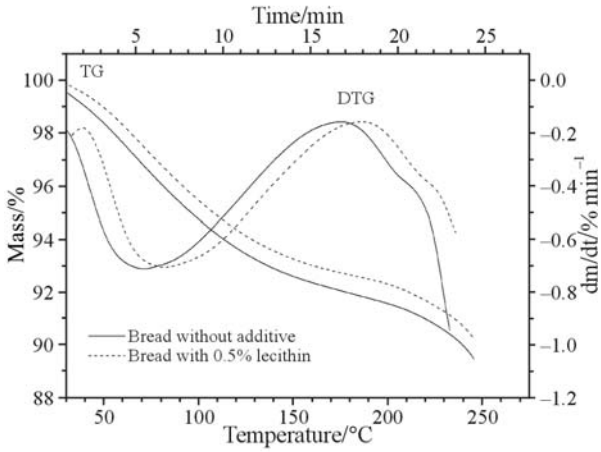

Fig. 6 TG–DTG curves of bread with 0.5% crude lecithin and without additves

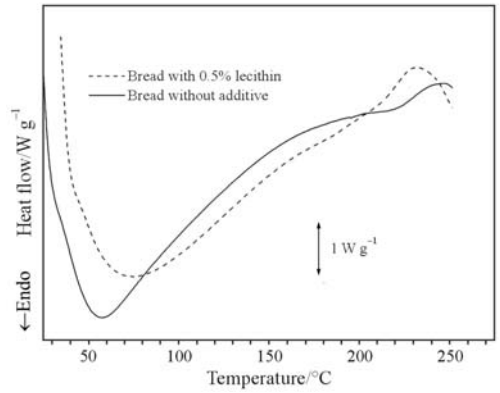

Fig. 7 DSC curves of bread samples

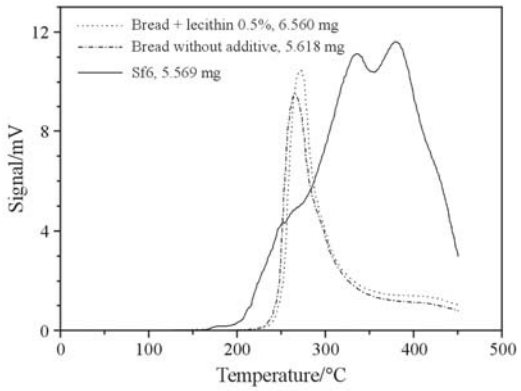

Fig. 8 EGD curves of SF0, bread without and with 0.5% crude lecithin additive

small amount of CL additive (Fig. 8), while in the case of the sample with considerable CL content (SF5) the curve shows that the oil components begin to depart from above 100°C, but only in minor quantities. The evaporation of the oil components of CL become more visible above 150°C and are expressed above 200°C. The different evaporation temperatures refer to a complex oil mixture of CL.

Conclusions

The usage of thermal methods is rather limited in complex materials like bread and its components. However, for the purpose of this work, namely, to determine if the additives suffer any change up to the baking temperature, the methods are suitable. The procedure is simple and can be completed in half an hour. As a consequence of the lower temperature in the inner part of the bread during the baking process the additives, due to the thermal treatment, does not change significantly in the crumb. However, their decomposition in the crust may take place, but this decomposition is not extensive, also.

Thermogravimetry provides a possibility for semi-quantitative estimates of phospholipids in flour samples if the difference in PL content is high enough (probably more than 5%), using of some kind of the calibration curve on the basis of the mass loss of emulsified water around 100°C. In order to elaborate such a method, further TA measurements are needed. In addition, methods for the quantitative PL determination are under development. These procedures are time consuming and expensive. However, the results of these measurements shall confirm the extent of the reliability of TA methods.

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