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THERMOLYSIS OF STARCH IN THE ATMOSPHERE OF AMMONIA

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The thermolysis of all potato, maize and triticale starch in the atmosphere of ammonia gives solid products with either residual content of nitrogen or entirely nitrogenless substances. They are accompanied by a small fraction of volatile compounds of the aroma of roasted peanuts. The affinity of starch to the reaction with ammonia depends on its origin. However, in every case ammonia prevents a deep dextrinization of starch.

Reaction of mono-, di- and oligo-saccharides with ammonia and nitrogen containing compounds pays an attention. Ammonia is excellent although dangerous catalyst of caramelization of sugars. The reaction of sugars with nitrogen compounds, mainly amino acid, peptides and proteins, generates in nature as well as in industry well known secondary food aromas (see [1] and [2] and references therein).

Surprisingly, enough similar reactions on starch have not provoced any systematic sudies yet. Recently, hardly few reports have been available on the reaction of urea with starch. Hebeish et al. [3] have obtained a product of low nitrogen content containing low content of nitrogen, probably a starch carbamate. They observed that starch suffered only small changes in this reaction although it required 165°C. Sroczyński et al. [4] added. acid catalyst in reacted starch with urea at 125°C. They observed that crossliking of starch took place. Unfortunately, the authors did not report the nitrogen content of their products.

Recently heating of starch with urea have been used as a kind of pretreatment of starch grains in order to loosen their structure before a reaction with poorly penetrating reagent [5].

Our group develops more extensive studies on the reaction of starch and cereals with ammonia and amino acid. Thus it was observed that potato starch [6] and cereals [7] thermolyzed in the atmosphere of ammonia developed the aroma of roasted peanuts. There is lack of systematic studies on the nature of the products. More attention has been paid to the reaction of amino acids with starch [8]. This reaction generates secondary food aromas depending on the use of amino acid. These aroma differ from aromas generated in the reaction of given amino acid and monosaccharide.

In this report, some details are given on the character of solid products from the thermolysis of starch under ammonia as well as on the affinity of starch of various origin to this reaction.

MATERIALS AND METHODS

Potato starch (Głowno, 1988), maize and triticale starch (both laboratory made) were subjected to thermolysis. Thus starch was predried in the oven for 3 h at 105°C. Then starch was heated for 2, 4 and 6 h at 140, 160, 180, 200 and 220°C in various combinations specified in subsequent tables. The heating was carried out in the rotatory evaporator providing continous of the sample. A stream of ammonia was delivered from the tank to the bottom of the rotating reaction flask. After the reaction was over the product of it was left to stand for 48 h in the air, passed through the sieve (0.22 mm) and extracted with ethanol in the Soxhlet apparatus (10 g starch, 100 mL ethanol for 3 h). Finally so prepared samples were analyzed for nitrogen content (the Lassaigne test followed by the quantitative estimation of nitrogen by the Dumas method if the first test was positive).

Dry mass content (after drying in the oven for 1 h at 13°C), temperature of gelation (microscope with the polarized light), IR absorption spectra (KBr pellets) and characteristics of gelation of 7.2% aqueous suspensions of the reaction products (Rheotest II, GDR), reducibility according to Somogy-Nelson and solubility [9] were also run.

RESULTS

The results of the thermolysis of starch are given in consecutive tables: potato starch in Tables 1–4 maize starch in Tables 5 and 6 triticale starch in Table 7.

The thermolysis of starch under experimental conditions changes the original appearence of the material. Starch turns gradually from white through yellow to dark brown. Potato starch is most sensitive to these changes. The intensity of the aroma of roasted peanuts increases with the time and temperature of roasting. Again potato starch develops the most intensive aroma, whereas maize starch gives the most subtle aroma.

Table 1. The solubility of dextrins after thermolysis of potato starch in the atmosphere of ammonia

Duration of heating [h]	Temperature of modification and aqueous solubility at room temp. [%]			
	160°C	190°C	200°C	210°C
1	0	0.51	0.59	2.28
2	0	0.31	1.35	4.46
3	0	0.60	1.95	9.20
4	0	0.84	3.18	15.60
5	0	1.64	4.31	24.44
6	0.3	1.82	6.43	31.42

Table 2. The range of temperature of gelation and dry mass content for potato starch modified thermally in the atmosphere of ammonia

Conditions of modification under ammonia	Range of temperature of gelation [°C]	Dry mass content [%]
Original starch	62-71	80.44
180°, 6 h	62-73	87.37
6 h[a]	58-68	89.36
4 h	59-72	88.04
2 h	60-73	88.08
160° 6 h	60-72	88.63
4 h	61-71	88.61
2 h	59-73	87.86
140° 6 h	60-73	87.66
4 h	60-72	87.78
2 h	61-72	85.76

[a] The experiment in the air i.e. without ammonia.

Table 3. The characteristics of gelation of potato starch thermally modified under ammonia

Modification	η_{max} [mPs]	T_{max} [°C]	T_g [°C]	η_{96} [mPs]	η_{50} [mPs]
None	4182	73	64	119.6	4728
180°, 6 h	251.2	75	64	131.5	203.3
6 h[a]	no viscosity could be measured				
4 h	550.2	75	63	35.9	741.5
2 h	765.4	75	63	35.9	980.7

[a] The experiment run in the air i.e. without ammonia.

Table 4. Elemental analysis of potato starch thermally modified under ammonia

	Prior to extraction	Extracted
%C	43.69 43.68	42.61 43.27
%H	6.45 6.61	6.32 6.57
%N	0.20 0.19	0.22 0.20

Table 5. The range of temperature of gelation and dry mass content for maize starch thermally modified under ammonia

Modification	Dry mass content [%]	Temerature of gelation [°C]
None	90.02	64–76
180°, 6 h	91.37	62–74
6 h[a]	89.13	

[a] The experiment in the air i.e. without ammonia.

Table 6. The characteristics of gelation of maize starch thermally modified under ammonia

Modification	v_{max} [mPs]	T_{max} [°C]	T_g [°C]	η_{96} [mPs]	η_{50} [mPs]
None	645.9	92	72	131.6	1017
180°, 6 h	263.1	85	73	251,2	364.8
6 h[a]	no viscosity could be measured				

[a] The experiment in the air i.e. without amonia.

Table 7. The dry mass content, reducing sugars and range of temperatures of gelation for triticale starch thermally modified under ammonia

Modification	Dry mass content [%]	Reducing sugars [%]	Range of temp. gelation [°C]
None	89.90		54-60
180°, 6 h	92.55	0.19	51-54
4 h	92.07	0.18	50-56
2 h	92.09	0.19	48-56
160°, 6 h	92.16	0.16	52-57
4 h	91.84	0.17	52-57
2 h	92.16	0.18	53-58
140°, 6 h	92.82	0.18	52-57
4 h			54-56
2 h	92.43	0.20	52-58

DISCUSSION

It may be seen in Table 1 that the heating of potato starch in ammonia changes the structure of starch matrix on specific way. The temperature of gelation is practically unperturbed independently on the temperature and duration of the processing. The change of the index of dry mass before and after processing shows that the structure of starch undergoes some modification as it clearly looses its ability to adsorb and/or include some volatile compounds (mainly hunidity). However, this ability does not fully ceas even after most drastic conditions among applied ones. Up to temperature of 190°C applied for 6 h starch remains almost completely insoluble in water. It points that the damage of starch matrix is rather negligible. However, the chartacteristics of gelation are dramatically changed. Maxima of viscosity and affinity to retrogradation are particularly affected. The aroma of roasted peanuts comes probably from the reaction of ammonia with terminal α-glucose units of amylopectine and amylose to give azaheterocyclic compounds usually responsible for such aromas [10]. Our preliminary chromatographic separation of extracts of steam distillates of processed potato starch point that two azaheterocyclic compounds are present therein. Their structure will be presented in a separate report. The solubility of processed potato starch increases in more significant manner after rising temperature of the roasting up to 210°C with simultanous extention of duration of the process to 4 h, at least. However, even after roasting potato starch at 210°C for 6 h the solubility of the product reaches hardly 31.5% whereas the same sample roasted either in the air or under nitrogen is water soluble in over 90% [11]. It points to the possible crosslinking of starch which is catalyzed by ammonia or rather its lone electron pair. As it is shown by elemental analysis ammonia is rather not incorporated in this crosslinked material. The residual content of nitrogen in the solid matter after ethanolic extraction is on the level of uncertainity of the analytical method for such biopolymers. The results of analysis allow to calculate the overall molecular formula $C_{231}H_{380}O_{190}N$ for the solid product. It means that there is one nitrogen atom for each 38 α-glucose units of the solid product. Contrary to potato starch triticale and maize starch does not trap to the matrix any nitrogen from ammonia. The solid products give negative Lassaigne test. It may suggest that the residual content of nitrogen in the product obtained from potato starch is modified in some manner starch matrix contaminated with ammonium triphosphate from phosphoric acid residues present in this starch. The observations noted for potato starch are confirmed by results of similar processing of triticale and maize starch. However, changes on roasting in both last cases are less pronounced than in potato starch.

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TERMOLIZA SKROBI W ATMOSFERZE AMONIAKU

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S t r e s z c z e n i e

W przeciwieństwie do reakcji mono-, di- i oligosacharydów ze związkami azotowymi reakcje skrobi z tymi związkami są mało badane. W pracy wykazano, że skrobia ziemniaczana, kukurydziana i pszenżytnia różnią się między sobą reaktywnością z amoniakiem. Najbardziej podatna na tego rodzaju modyfikację skrobia ziemniaczana wiąże niewielkie ilości azotu, poczas gdy skrobia kukurydziana i pszenżytnia ulega modyfikacji bez wiązania azotu.

Najwyraźniej amoniak zapobiega termicznej degradacji skrobi do rozpuszczalnych dekstryn. Otrzymane produkty zmieniają swą podatność na retrogradację, nie zmieniają praktycznie temperatury kleikowania i redukcyjności. Reakcji modyfikacji matrycy skrobiowej towarzyszy tworzenie się heterocyklicznych związków azotowych, którym lotna frakcja modyfikowanego produktu zawdzięcza woń prażonych orzeszków ziemnych.