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PHYSICO-CHEMICAL PROPERTIES OF STARCH HYDROLYSATES

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Key words: starch syrups, oxidized starch, acidic and enzymatic hydrolysis of starch

The physico-chemical properties of syrups obtained by acidic and enzymatic hydrolysis of potato starch were investigated. The content of high-molecular dextrans in enzymatically obtained starch syrups was increased by additions of oxidized starch "Sulinex". The enzymatically obtained starch syrups containing 6-10% "Sulinex" were used in caramel mass production.

The syrups produced by enzymatic hydrolysis of potato starch do not find application in the caramel industry because the caramel masses with their addition differ in physico-chemical properties from caramel masses containing starch syrups obtained by acidic hydrolysis of potato starch.

In the process of obtaining potato syrup by acidic hydrolysis of potato starch, at all stages of the hydrolysis the hydrolysate is composed of a mixture of the following saccharides: glucose, disaccharides, oligo-saccharides composed of 3-8 glucose residues, and dextrin [3, 7].

By applying suitable enzymes in the production of syrups by enzymatic hydrolysis of potato starch it is possible to obtain products with a predetermined ratio of glucose to maltose and dextrans. This is very important since the composition of the syrup has bearing on its sweetness, viscosity, hygroscopicity and osmotic pressure [1, 3, 4, 8, 11].

Meyer has found that the beginning of enzymatic hydrolysis of starch is chaotic. Greenwood confirms this claiming saying that the initial action of α -amylase on the substrate is "accidental" but that in the process of accumulation of reaction products, i.e. oligosaccharides containing 3-8 glucose residues in the molecule, their degradation is systematic in suitable conditions [10].

Hence, both the syrup obtained by acidic hydrolysis of starch and the syrup produced by enzymatic hydrolysis contain similar saccharides.

The aim of the work was the use of enzymatically obtained starch syrups in the production of caramel masses and the study of physico-chemical differences between syrups obtained as a result of acidic and of enzymatic hydrolysis of starch.

MATERIALS AND METHODS

The potato starch "Superior" manufactured by the Potato Industry Enterprise "Luboń" was used in the study. Its humidity was 19.5% and its dry matter contained: 0.184% ash, 0.39% protein and 0.104% phosphates (as phosphorus).

The syrup obtained by acidic hydrolysis of starch came from the Potato Industry Enterprise "Luboń". Its concentration was 81.7% dry substance and its reductivity 37 DE.

The syrups from enzymatic hydrolysis of starch were obtained by applying BAN L-60 preparation of bacterial α -amylase (Novo Industri, Denmark) of activity 2200 S.K.B. units/g dry substance of preparation. The enzymatic preparation used had a concentration of 0.15% in terms of d.s. starch. The starch milk was of 35% concentration and pH 6.5. After 5 h of hydrolysis at 85°C a hydrolysate with reductivity of 36.2 DE was obtained. The hydrolysate was boiled for 10 min in order to inactivate the enzyme and to dissolve the nonliquefied resistant small starch grains. The hydrolysate was purified by filtration, with an addition of activated carbon, through a diatomaceous earth filtration layer, and then condensed in an evaporator at reduced pressure till the syrup concentration attained 81.7% dry substance.

The modified starch "Sulinex" used in the work was manufactured by the Potato Industry Enterprise "Piła" and its content was 88.5% dry substance, mean molecular mass — 750 000, and carboxyl group content — 20.45 mval/100 g dry substance.

The enzymatic starch syrups with additions of the oxidized starch "Sulinex" were obtained by introducing 2-10 g dry substance of oxidized starch to 100 g dry substance of enzymatic hydrolysates. The syrups with "Sulinex" were boiled to gelatinize oxidized starch.

All of the starch syrups described above i.e. obtained by hydrolysing starch with acid, enzyme and enzyme together with oxidized starch, were used in production of caramel masses. Caramel syrups were made in the saccharose:starch syrup:water proportion of 1:0.5:0.25 parts by weight, by dissolving saccharose in boiling water, adding starch syrup and then boiling the solution to obtain a concentration of 83% dry substance. The caramel syrup was concentrated under reduced pressure until the water content was 1.2%, thereby obtaining caramel mass. After reducing the

temperature of the caramel mass to 20°C the content of water and of reducing sugars' DE was determined.

A part of the samples of the obtained caramel mass were wrapped in bobbin and label and stored for six months at 20°C and relative air humidity 60%. After 1, 2, 3, 4, 5 and 6 months of storage the caramel mass was studied hygroscopically by determining the water content in the samples.

The physico-chemical analysis of syrups consisted in:

- a) determination of rheological properties with a Seibold revolving viscosimeter,
- b) determination of water content by the refractometric method [9],
- c) determination of dextrin content by the gravimetric method after removing protein from the samples and precipitating dextrans with 95% ethanol [6],
- d) determination of reducing sugars content with the Lane-Eynon method [9],
- e) determination of mean molecular mass of dextrans after precipitation of dextrans as in c) with 80% ethanol, and determination of molecular mass by determination of carbonyl groups with the use of hydroxylamine [5],
- f) determination of the quantitative composition of saccharides by the reflection spectroscopy method [7].

In the caramel masses there were determined:

- a) the content of reducing sugars by the method of Lane-Eynon [9],
- b) water content by the gravimetric method [9].

RESULTS AND DISCUSSION

The starch syrup obtained by acidic hydrolysis of starch and the syrups from enzymatic hydrolysis served as a substrate for the production of caramel masses which were obtained in identical conditions of time, temperature, pressure and concentration of components (i.e. saccharose and syrup). The caramel masses displayed differences as regards hygroscopicity during storage depending on whether they contained syrup from enzymatic or from acidic hydrolysis of potato starch. The caramel masses obtained with enzymatic syrups had a higher hygroscopicity than masses containing syrup obtained by acidic hydrolysis of starch (Table 3). This fact prompted the investigation of the chemical composition and physico-chemical properties of potato syrups obtained from starch by the two methods. The comparison of the two starch syrups involved an analysis of the respective contents of dry substance, reducing sugars and dextrans, of the quantitative composition of saccharides, of mean molecular mass of

dextrins and of rheological properties. The results of the analyses are collected in Tables 1 and 2.

Table 1. Chemical composition and physico-chemical properties of potato starch syrups

Kind of syrup	Content of				Mean molecular mass of dextrins	
	dry substance (%)	reducing sugars (DE)	total (%)	dextrins high-molecular (%)	total	high-molecular
After acidic hydrolysis of starch	81.7	37.0	28.0	11.5	320 000	450 000
After enzymatic hydrolysis of starch	81.7	36.2	21.0	16.8	180 000	250 000

Table 2. Carbohydrate composition of potato starch syrups

Kind of syrup	Content of saccharides in syrup (% dry substance)							
	glucose	maltose	maltotriose	maltotetrose	maltopentose	maltohexose	maltoseptose	total dextrins
After acidic hydrolysis of starch	22.0	13.0	11.0	9.0	7.0	6.0	5.0	28.0
After enzymatic hydrolysis of starch	5.0	10.5	15.5	12.5	13.5	16.0	6.0	21.0

The data contained in Tables 1 and 2 reveal differences in the quantitative composition of saccharides with small molecules and in the amount of dextrins contained in the studied syrups, which, in addition, differ also in the mean molecular mass of the dextrins. The syrups obtained enzymatically contained over four times less glucose and ca. 20% less maltose than the syrups obtained by acidic hydrolysis of starch. The total content of dextrins in "enzymatic" syrups was less by 1/3 than in "acidic" syrups, and their mean molecular mass in the former syrups was almost twice smaller (180 000/320 000) than in the latter ones. Similarly, the content of high-molecular dextrins in syrups produced with the use of enzymes was by about 1/3 less than in "acidic" syrups and the mean molecular mass of dextrins in the former is markedly lower (250 000/450 000) than in the latter. Both kinds of syrups differed markedly also in rheological properties (Figs. 1 and 2). Higher values of shearing stress and of apparent viscosity for the same shearing speed were demonstrated by syrups obtained by acidic hydrolysis of starch (curves A in Figs. 1 and 2; the values for syrups obtained with enzymes — curves G in the Figs.).

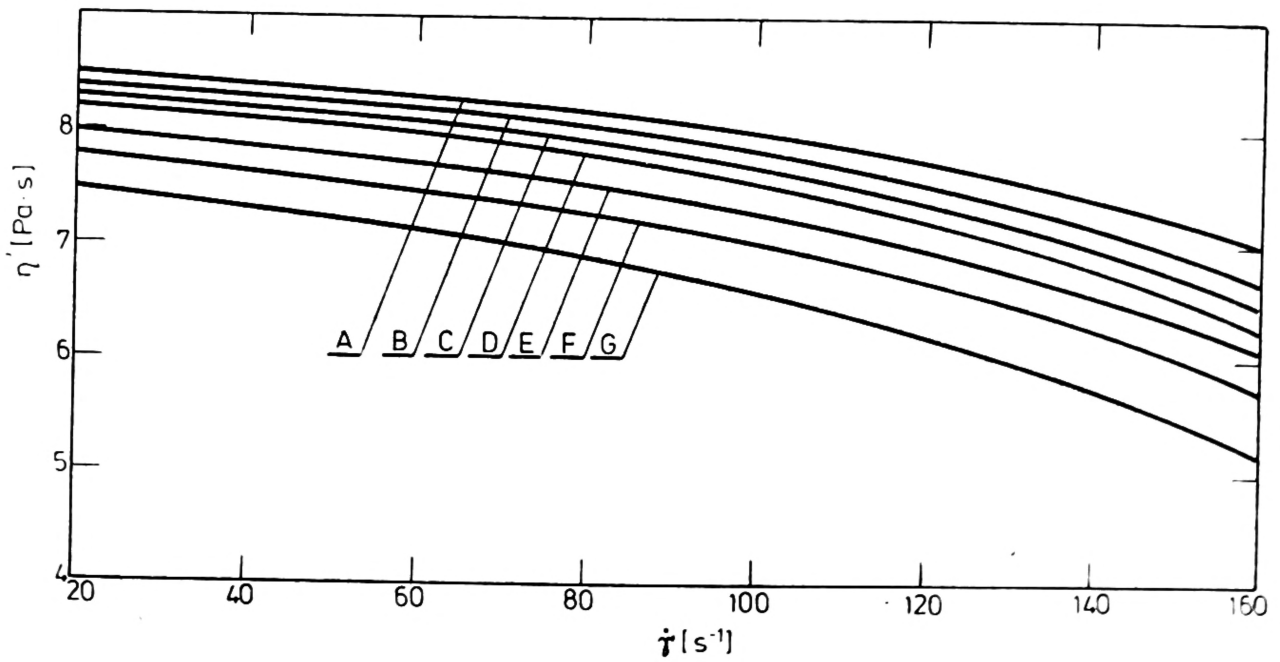


Fig. 1. Dependence of apparent viscosity on shearing speed for starch syrups; kinds of syrup: A — after acidic hydrolysis of starch, G — after enzymatic hydrolysis of starch, B-F — after enzymatic hydrolysis of starch with "Sulinex" additions in amounts of 10% (B), 8% (C), 6% (D), 4% (E) and 2% (F)

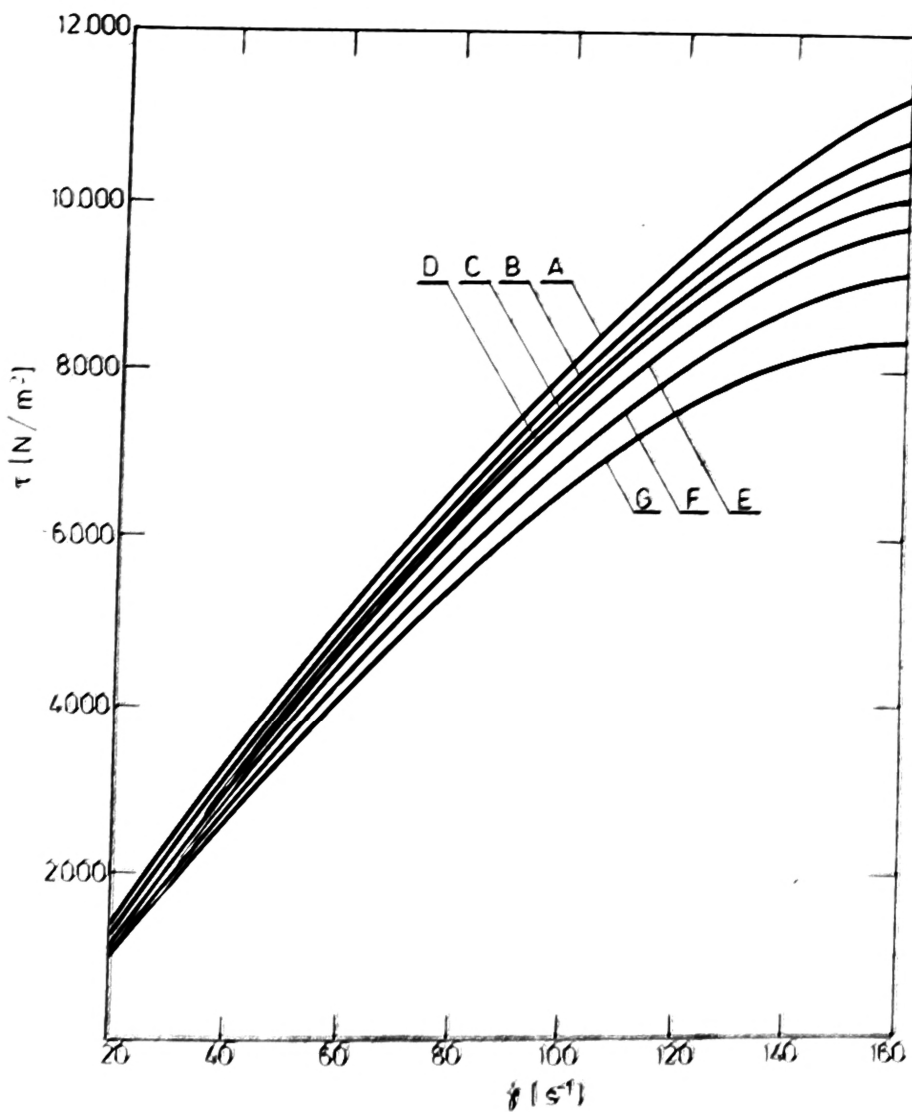


Fig. 2. Dependence of shearing stress on shearing speed for starch syrups; denotations as in Fig. 1

Table 3. Effect of storage time on humidity of carmel mass (conditions of storage: temperature 20°C, air humidity 60%, period of storage 6 months)

Kind of syrup	Syrups			Caramel masses							Remarks			
	"Sulinex" concentration (%)	reductivity (DE)	dry mass (%)	reductivity (DE)	after content (%) after storage for (months)									
					0	1	2	3	4	5		6		
After acidic hydrolysis of starch	0	37.0	81.7	14.5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	no changes
	0	36.2		14.2	1.2	1.2	1.3	1.4	1.4	1.4	1.5	1.5	1.5	mass begins to stick to paper after 3 months
After enzymatic hydrolysis of starch	2	35.5		14.0	1.2	1.2	1.2	1.3	1.3	1.3	1.4	1.4	1.4	sticks to paper after 5 months
	4	34.8	81.7	13.7	1.2	1.2	1.2	1.2	1.3	1.3	1.3	1.4	1.4	slightly sticks to paper after 6 months
	6	34.1		13.5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	no changes
	8	33.3		13.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	no changes
	10	32.6		13.1	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	no changes

In order to increase the content of high-molecular polysaccharides in syrups obtained by enzymatic hydrolysis of starch, the chemical composition of the syrups was altered by an addition of "Sulinex" oxidized starch. It was expected that the "Sulinex" addition would improve such physico-chemical properties of the syrups as viscosity and hydrophilicity [2]. This was proved to be true by measurements of shearing stress and apparent viscosity (curves B-F in Figs. 1 and 2).

The obtained syrups with the "Sulinex" addition were used as substrates for the production of caramel syrups which in turn were processed into caramel masses. The proportions of components and the method of obtaining caramel masses were analogous to those in the case of obtaining such masses from syrups produced by acidic and enzymatic hydrolysis of starch.

Samples of caramel masses obtained from all of the syrup kinds described above were stored for 6 months. The results of hygroscopicity studies (Table 3) show that caramel masses made of the "enzymatic" syrups with 6-10% additions of the "Sulinex" oxidized starch were non-hygroscopic, since during the six-month storage period their water content did not increase.

CONCLUSIONS

1. Starch syrups obtained by enzymatic hydrolysis of potato starch are an unfavourable substrate for the production of caramel mass. The dextrans contained in these syrups have lower molecular mass than dextrans occurring in syrups obtained by acidic hydrolysis of starch.

2. The lower molecular mass of dextrans and their smaller content in enzymatic starch syrups cause a decrease of apparent viscosity of these syrups as compared to the syrups produced by acidic hydrolysis of starch.

3. It was observed that caramel masses containing starch syrup obtained enzymatically are more hygroscopic than masses with syrups obtained by acidic hydrolysis of starch.

4. The undesired properties of enzymatic starch syrups may be prevented by an addition of 6-10% of "Sulinex" oxidized starch.

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FIZYKOCHEMICZNE WŁAŚCIWOŚCI HYDROLIZATÓW SKROBIOWYCH

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Streszczenie

Zbadano właściwości fizykochemiczne syropów otrzymywanych w wyniku kwasowej i enzymatycznej hydrolizy skrobi ziemniaczanej. W wymienionych rodzajach syropów stwierdzono istotną różnicę w wartościach średnich mas cząsteczkowych dekstryn i wynikające stąd różnice w lepkościach pozornych tych syropów. Zawartość dekstryn wielkocząsteczkowych w enzymatycznie otrzymywanych syropach skrobiowych zwiększano dodając do nich skrobię utlenioną "Sulinex". Enzymatycznie otrzymywane syropy skrobiowe, zawierające 6-10% "Sulinexu" zastosowano do wyrobu mas karmelowych, które wykazywały właściwą higroskopijność podczas sześciomiesięcznego czasu przechowywania.