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LOW CONVERSION STARCH HYDROLYSATES

Summary

Starch liquefaction without significant increase in dextrose value was attempted. Potato, corn and pea high amylose starches were digested with thermostable alpha-amylase. Different reaction conditions (starch concentration, enzyme dosage, time reaction) were used in hydrolyses into DE < 10. Chemical and physical properties of obtained hydrolysates such as carbohydrate composition, iodine absorbance value, turbidity measurement, viscosity, gelling ability, swelling power were recognised. Comparison of properties of hydrolysates of similar DE indicated that the potato hydrolysates distinguish in the highest solubility and the lowest iodine absorbance. The high-amylose corn hydrolysates were characterised with the following properties: the highest swelling power and gelling ability. Pea hydrolysates had the highest viscosity.

Introduction

Starch hydrolysates are a mixture of reducing sugars. They are products a partial or total depolymerization of starch. Low converted starch hydrolysates (DE below 40) are usually produced by a two-stage process: the first stage of the hydrolysis – liquefaction – is carried out with acids or enzymes at elevated temperatures, the second stage of hydrolysis – saccharification – is carried with bacterial α-amylase to achieve a desired DE [2, 3, 4, 11, 12, 13, 20]. For many applications the functionality or suitability is enhanced when DE of the hydrolysates is relatively low (DE below 10). However, the production of these hydrolysates can be troublesome because of retrogradation of longer chain amylose fragments forming an insoluble haze.

The hydrolysates are commonly used in food industry as body agents, non-sweet fillers, carriers for synthetic sweeteners, flavour enhancers, additives for colouring

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agents and so on [1, 6, 14, 16]. Functional properties of low DE starch hydrolysates depend on their production technology and kind of source of starch. High amylose corn starch hydrolysates made by enzymatic hydrolysis having DE between 5 to 15 distinguish in good gel strength – important attribute in a fat replacer [5]. They are also prepared by hydrolysing of a granular amylose starch in a strongly acid aqueous slurry at a temperature above 70°C [7]. Low DE potato hydrolysates as Paselli SA2 (Avebe) with a DE of 2 [17], C*Pur 01906 (Cerestar) with a DE of 3 [21] and Lycadex® (Roquette Freres) with a DE of 5 [19] are prepared by an enzymatic degradation of starch and have plastic, fat-like characteristic increased with applied hydrolysate concentration. Combination of low degree of polymerisation of oat hydrolysates and beta-glucan content gives unique functional properties of the products [8,9].

In this research properties of various low converted starch hydrolysates obtained with alpha amylase are compared.

Materials and methods

Enzyme

Commercial enzyme Termamyl 120 L, a mixture of outstanding heat-stable alpha-amylase produced by selected strains of *Bacillus licheniformis*, was used. Its activity was 120 KNU/g, where 1 KNU was the amount of enzyme that hydrolysed 5.26 g starch per hour using Novo's standard method for determination of α amylase (substrate – soluble starch, calcium content of solvent – 0.0043 M, reaction time – 7–20 min, temperature - 37°C, pH – 5.6 [15].

Source of substrate

Potato starch (Potato Enterprise in Łobez), corn starch (National Starch and Chemical), pea starch (DPS, Starch Protein and Service), were used as a substrate for enzyme action (Tab. 1).

Table 1

Composition of starches used as substrates.

Starch components	Potato starch	Corn starch	Pea starch
Moisture (%)	13.0	12.6	11.0
Lipids (% d.s.)	0.04	0.29	0.24
Proteins (% d.s.)	0.05	0.64	0,79
Amylose (% d.s)	21	70	66
Amylopectin (% d.s)	79	30	34

Experimental procedure

Aqueous starch slurries of the concentration of 15 and 20% were prepared, their pH was adjusted to 6.5, and enzyme (0.013 –0.055 KNU/g d.s.) was admixed. The suspension was maintained at 95°C for 10 – 45 min. The inactivation of enzyme was conducted with citric acid. The reaction mixtures were analysed after 10, 20, 30 and 45 min hydrolysis.

The following analyses were performed for each sample:

- the amount of reducing groups by modified Schoorl-Rogenbogen method [18],
- carbohydrate composition by High Performance Liquid Chromatography. (HPLC apparatus (Waters 600E, USA) was used with a Aminex HPX – 42A column (7.8 x 250 mm), Bio-Rad. Elution of carbohydrate was detected with a differential refractometer. Samples (20 μl) were injected into the column and eluted with water at temperature 85° at a velocity of 0,5 ml/min),
- viscosity (Brookfield Model DV-II – spindle # 4 and 5 at 20,50 and 100 min^{-1}) was measured at 20% concentration at 25°C,
- iodine absorbance value defined as the optical density at 500 nm using a 4 cm cell in Pye Unican SP 500 Series 2 spectrophotometer,
- solubility and swelling power by Leach method 10],
- gelling ability (Instron 1140 – spindle 50, penetration speed – 100 rev/min, penetration depth – 50 mm).

Results and discussion

Role of enzyme concentration and reaction time

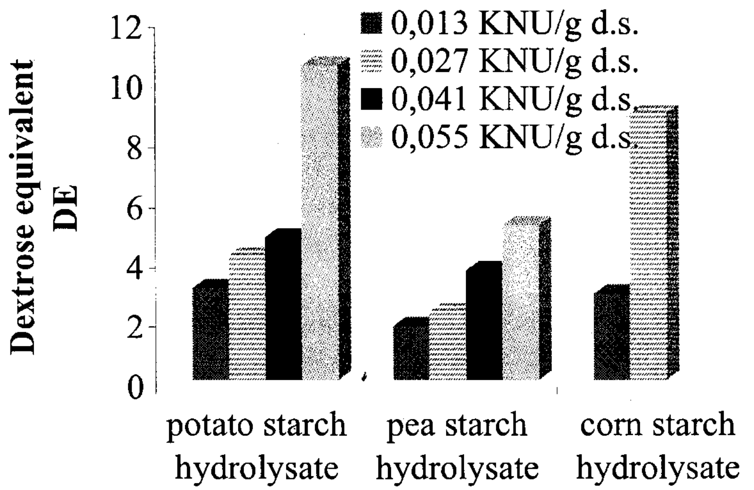
Starch hydrolysates were obtained by means of α-amylase treatment of potato starch, high amylose corn starch, and pea starch. The applied enzyme dose varied from 0.013 to 0.055 KNU/g d.s. As low enzyme dosage as 0.013 KNU/g d.s. produced hydrolysates of DE from 2 to 4 (Fig. 1A).

Production of these hydrolysates required different reaction time, this is, 10, 20, and 30 min for potato, corn, and pea starch, respectively (Fig. 1B).

Viscosity

The tested starches were treated by α-amylase in dosage 0.013 KNU/g d.s. within 30 min. Comparison of viscosity value for hydrolysates obtained from the starches characterised similar DE indicated that the highest viscosity shown the pea hydrolysate.

A)



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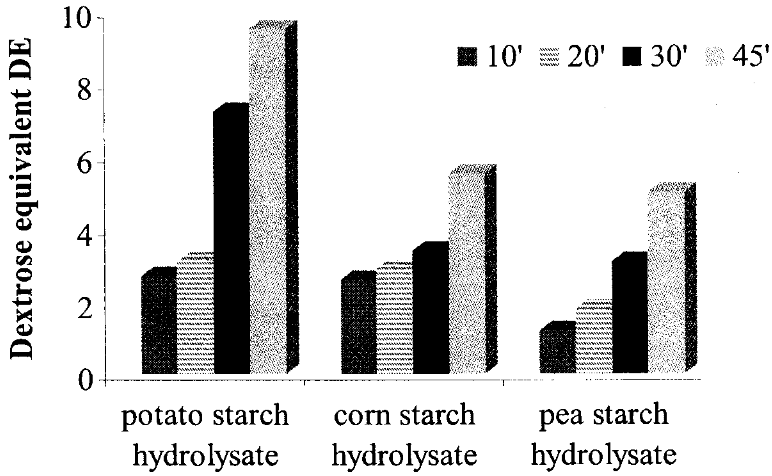

Fig. 1. The influence of enzyme dosage and reaction time on the level of reducing sugars (substrate: 15–20% d.s.; temperature: 95°C; pH 6,5; A – reaction time 20 minutes; B – enzyme dosage: 0.013 KNU/g d.s.).

Obtained results of research confirmed the rule created in literature: the decrease of viscosity followed by the increase of starch depolimerization [5, 22].

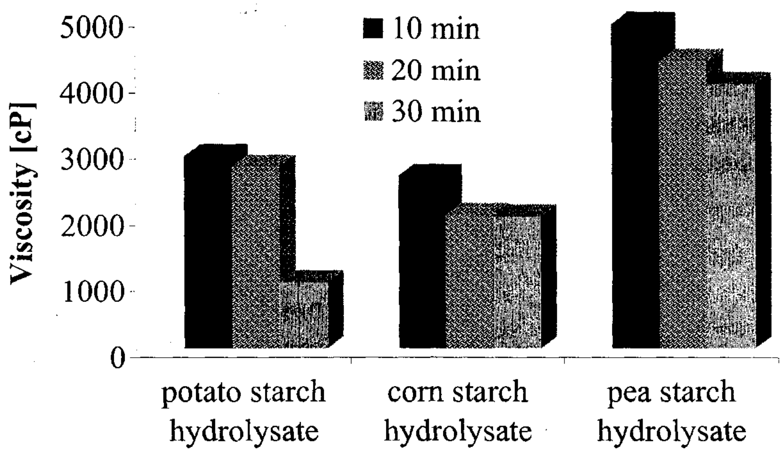

Fig. 2. The influence of reaction time on starch hydrolysate viscosity (substrate: 15–20 –% d.s.; temperature: 95°C; pH 6,5; enzyme dosage 0,013 KNU/g d.s.).

Carbohydrate composition

Carbohydrate composition of the starch hydrolysates changed dependence on the depolimerisation degree of starch. Enhancement of the depolimerisation degree was associated with the increase of simple sugar amount and the decrease in the oligosacharides content [16].

The influence of enzyme dosage and reaction time on carbohydrate composition of tested hydrolysates is presented in Table 2.

Table 2

Carbohydrate composition of tested hydrolysates of starch.

Hydrolysate type	Enzyme dosage KNU/g d.s.	Glucose [%]			Maltose[%]			Higher sugar [%]		
		Reaction time [min]								
		10	20	30	10	20	30	10	20	30
Potato starch hydrolysate	1.3	0.5	1.0	5.9	1.0	1.0	10.0	98.5	98,0	84,1
	2.7	1.0	2.7	6.0	2.7	3.1	10.1	96.3	94.2	83.9
	4.1	1.3	3.0	6.3	3.0	3.6	11.8	95.8	93.4	81.9
Corn starch hydrolysate	1.3	0.2	0.2	0.3	1.8	2.6	4.3	98.1	97.2	95.4
	2.7	1.0	3.4	3.5	2.1	7.0	7.3	97.0	89.6	89.2
Pea starch hydrolysate	1.3	0.6	1.0	2.8	1.9	4.1	9.1	97.5	94.8	88.1
	2.7	1.3	2.8	3.2	2.9	7.6	9.2	95.8	89.7	87.6

Iodine absorbance

Fig. 3. illustrates the correlation between DE of different starch hydrolysates and iodine absorbance value. This hydrolysate property determines the degree of hydrolysate transparency. Potato starch hydrolysates indicated the lowest iodine absorbance whereas pea starch hydrolysates had it the highest.

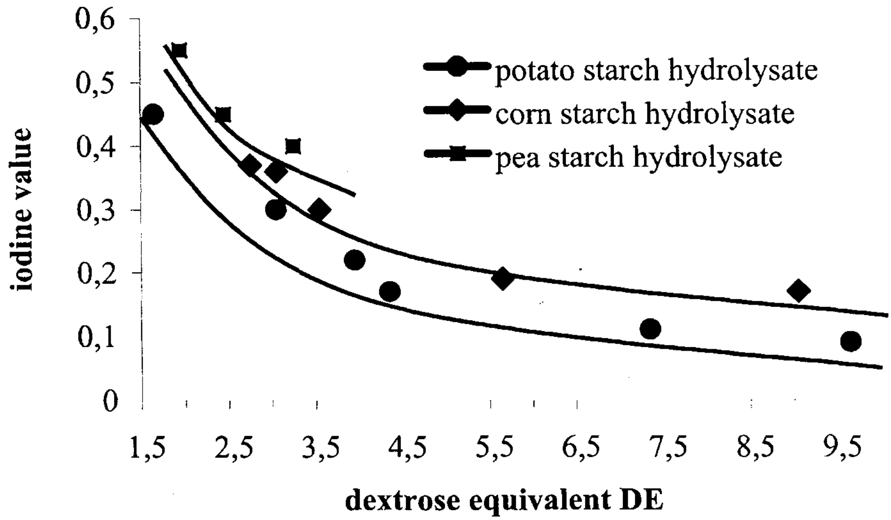

Fig. 3. Correlation between DE of different starch hydrolysates and iodine absorbance (substrate: 15-20% d.s.; temperature: 95°C; pH 6,5; enzyme dosage 0.013 KNU/g d.s.; reaction time 20 min.).

Solubility and swelling

Hydrolysed starches were dried in a spray dryer and subjected to further studies. The influence of dextrose equivalent on solubility and swelling power of the dry hydrolysates is shown in Fig. 4. Results of research indicated that solubility of the dry hydrolysates depended on DE; solubility increased moderately to DE increase. For example: 52% potato starch hydrolysates dissolved in water in the case of hydrolysate with 2.9 DE but hydrolysates of 9.5 DE dissolved already in 91%.

Water solubility of the hydrolysates also depended on type of starch. Solubility of hydrolysates with similar DE (2.9 DE) was as follows:

potato starch hydrolysate – 51%,
corn starch hydrolysate – 47%,
pea starch hydrolysate – 29%.

Swelling power of hydrolysates was associated with DE and type of starch. Corn starch hydrolysates had the highest swelling power whereas pea starch hydrolysates had it the lowest.

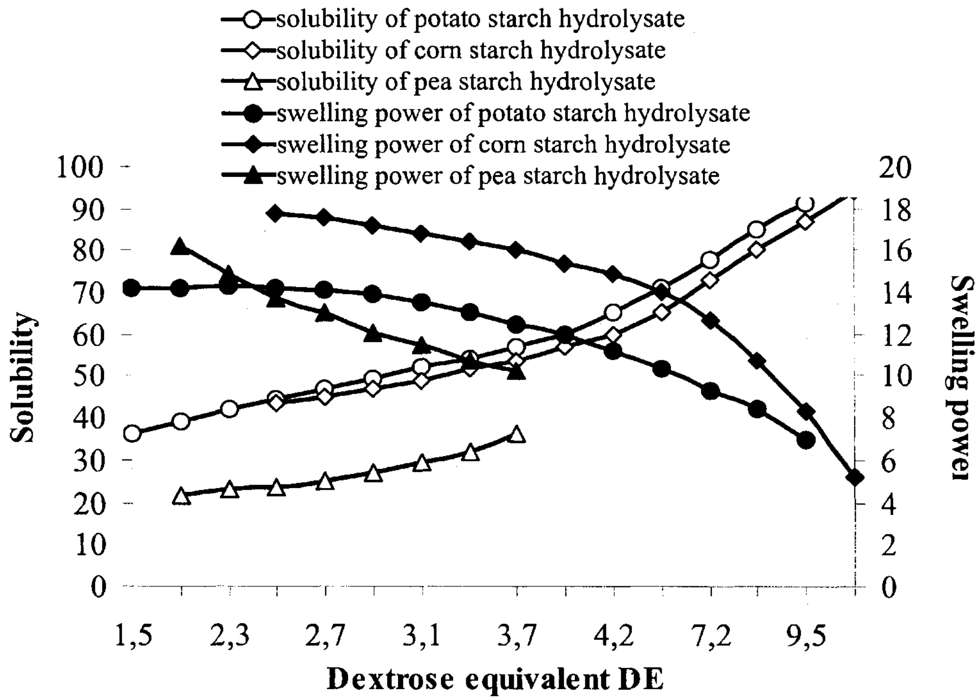

Fig. 4. Solubility and swelling power and DE of tested hydrolysates (substrate: 15-20 % d.s.; temperature: 95°C; pH 6,5; enzyme dosage: 0.013 KNU/g d.s.; reaction time: 20 minutes)

Gelling ability

Corn hydrolysates had the highest gelling ability among hydrolysates with similar DE (Tab. 3). This result fitted suggestion that starches with high amount of amylose form strong gels [22].

Table3

Characteristics of starch hydrolysates

Hydrolysate type	DE	Gelling ability
Potato starch hydrolysate	3.1	1.614
Corn starch hydrolysate	2.9	3.003
Pea starch hydrolysate	3.1	1.843

Conclusion

The tested starches treated by alpha-amylase show their different enzymatic susceptibility. In production of starch hydrolysates with 3.1-3.4 DE it is necessary to apply different reaction conditions: enzyme dosage – 0.013 KNU/g d.s. of starch and reaction time – 10 min for potato starch, 20 min for corn starch and 30 min for pea starch.

Comparison of starch hydrolysates with similar DE indicate that:

- Potato starch hydrolysates have the lowest iodine absorbance and the highest solubility. They can be used in pasteurised or cold prepared foods.
- Corn starch hydrolysates characterise the highest swelling power and gelling ability – properties compatible with fats and oil. They can be indicated as the best fat replacers.
- Pea starch hydrolysates have the highest viscosity – important factor for improvement emulsion stabilising properties.

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NISKOSCUKRZONE HYDROLIZATY SKROBIOWE

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

Badania dotyczyły upłynniania trzech rodzajów skrobi: ziemniaczanej i dwóch amylozowych- kukurydzianej i grochowej. Proces hydrolizy skrobi termostabilną alfa-amylazą (Termamyl 120L) prowadzony był przy zastosowaniu zmiennych parametrów procesu (stężenie skrobi, dawka enzymu, czas reakcji), prowadzących do uzyskania hydrolizatów o zbliżonej wartości DE (DE < 10). Uzyskane hydrolizaty poddawane były ocenie fizykochemicznej przy wykorzystaniu metod analitycznych określających: skład węglowodanowy, zdolność absorbji jodu, rozpuszczalność, zdolność żelowania, lepkość, siłę pęcznienia. Badania wykazały, że hydrolizaty ziemniaczane charakteryzują się najwyższą rozpuszczalnością. Natomiast hydrolizaty wysokoamylozowe kukurydziane cechuje najwyższa siła pęcznienia i zdolność żelowania, a hydrolizaty grochowe wykazują najwyższą lepkość.