A C T A A L I M E N T A R I A P O L O N I C A
Vol. VII (XXXI), No. 3-4 1981

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AUTOHYDROLYSIS OF HYDROGEN STARCH WITH LIMITED WATER CONTENT

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Key words: hydrogen starch, process of autohydrolysis, conditions of starch autohydrolysis, properties of starch preparations

Preparations of hydrogen starch and superior starch of all 2.5% 10.5% and 30.5% humidity levels were heated each at 120°C, 140°C and 170°C. All macro- and microscopic appearance, solubility, reducing value specific rotation and content of free phosphorus were studied in resulting preparations. It was found that the process of autohydrolysis takes place also in grains of hydrogen starch of limited water content Preparations obtained in our experiments are soluble in cold water.

Since introduction of modified starches to various industrial technological processes practical possibilities of utilizing physico-chemical properties of starch in man's economic activities expanded within recent years [4]. Modified starch preparations posses strictly defined properties dependend on the mode of modification most frequently carried out on chemical way.

Some considerably limited changes of physico-chemical properties of potato starch can also be induced by utilizing the ion-exchanging capacity of such starches. The potato starch has the properties of a polyelectrolite [3, 9] due to chemically-bound phosphoric acid present in it. The chemical analysis suggests such starch to be amylophosphoric acid. Depending on acidity of environment and concentration of cations it may appear in the form of the so-called cationic starches, i.e. of salts of amylophosphoric acid [6, 8, 12]. Such cationic starches should not be identified with cationic potato starches [4], which exhibit polyelectrolite properties in chemical processes.

Their properties depend on cation and its concentration influencing the degree of saturation of amylophosphoric acid with cation (the dissociation constant of the salt) [5, 13]. Among the cationic starches hydrogen starch, i.e. free amylophosphoric acid attracts most attention, because of its auto-

hydrolytic properties [7]. Our recent studies [1] proved, that the rate of the autohydrolysis of hydrogen starch depends on concentration of hydrogen ions, i.e. on the concentration of hydrogen starch in aqueous solution. Therefore we decided to examine the course of this process by increasing concentration of hydrogen starch in form of the lowest possible water content. Thus several hydrogen starches preparations were prepared with considerably varying water content. The autohydrolysis of the samples at above 100°C has been carried out maintaining conditions eliminating a possibility to alter their humidity. Significant changes in properties of hydrogen starch have been anticipated which could be considered as the inhibiting effect of water content in hydrogen starch on the process of its autohydrolysis.

MATERIALS AND METHODS

Hydrogen starch was prepared by the Winkler method [12] from potato superior starch with the content of total phosphorus of 55.5 mg P in 100 g dry mass.

The initial starch and hydrogen starch were conditioned at the room temperature in three different humidities:

1) in dessicator over P_2O_5
2) in regular laboratory conditions (dry room)
3) in atmosphere saturated with steam.

The following analyses were carried out:

1) determination of content of dry mass at 130°C over 1 hr in 1 g samples,
2) determination of reducing value, according to Meyer, with 3,5-dinitrosalicylic acid in Richter modification (10),
3) determination of free phosphorus according to Marsh (2).

EXPERIMENTAL

Superior starch (initial) and hydrogen starch prepared from it were taken into investigations. Characteristics of the resulting preparations are given in Table 1.

Table 1. Characteristic of starch preparations

Kind of starch	Content of total P in mg P/100 g d.s.	Water content %
superior starch	55.5	2.5 10.5 30.5
H-starch	56.3	2.5 10.5 30.5

Table 2. Macroscopic appearance of hydrogen starch preparation and starch

Water content %	Kind of starch	1 hour heating in temperatures		
		120°C	140°C	170°C
2.5	H-starch	unchanged	unchanged	light-yellow powder
	starch	unchanged	unchanged	light-cream powder
10.5	H-starch	unchanged	slightly lumped	lumped brown
	starch	unchanged	slightly lumped	lumped light-yellow
30.5	H-starch	lumped	lumped	light-brown, transparent "caramel"
	starch	lumped	lumped	yellow, transparent, "caramel"

About 500 mg samples of the materials sealed in glass tubes were heated for 1 hr in a laboratory drier at a 120°C, 140°C and 170°C.

After cooling the preparations were characterized macro- and microscopically, physical properties were examined and chemical analyses were preformed.

RESULTS AND DISCUSSION

Data in Table 2 present characteristics of macroscopic appearance of hydrogen starch preparations in comparison with relevant data for initial starch (potato superior). No differences in external looks of H-starch and superior at 120°C and 140°C are observed. Stronger thermal effect revealed is realized just at 170°C. It is manifested by browning of the preparations. At this temperature samples with higher humidity (30.5% H_2O) lost their powder consistency and turned into transparent glassy mas resembling "caramel". The yellowish coloring or even browning of hydrogen starch preparations can be accounted for a more pronounced carmelization process during heating. Microscopic observation (Table 3) reveals stronger destructive effects of higher temperatures (140° and 170°C) on grains of hydrogen starch. These changes are particularly strong at 170°C. In consequence of such treatment hydrogen starch yields preparations entirely soluble in cold water (Table 4). The transformations can be interpreted as the result of intensive hydrolysis which occurs while heating of hydrogen starch [7]. This assumption is supported by a significant increase of reducibility of hydrogen starch.

It is interesting to compare the reducibility of H-starch preparations soluble in cold water — see Tables 4 and 5. Thus a water-soluble hydrogen starch preparation of 2.5% humidity posesses much lower reducibility (which is an indicator of degree of hydrolysis of this polysaccharide) than water soluble preparation of much higher humidity and these heated to lower temperatures. This fact delivers an evidence for the thermal decomposition of starch at 170°C to have stronger influence on solubility of the polysaccharide than the hydrolysis process. It can also be deduced from the data in Table 5 that autohydrolysis of hydrogen starch may also proceed in preparations with very low content of water. The evidence for this comes from higher values of reducibility of these preparations in comparison with superior starch, in which autohydrolysis does not take place. The increased reducibility which is observed in superior starch only at higher temperatures seems to be due to thermally induced depolymerization.

It has to be noted that an appropriate volume of water is necessary for the hydrolysis of starch. Theoretical calculations lead to the value of 11% of water necessary to complete the hydrolysis of starch into glucose.

Table 3. Microscopic appearance of hydrogen starchpreparation and starch

Water contnet %	Kind of starch	1 hour heating in temperature:		
		120°C	140°C	170°C
2.5	H-starch starch	unchanged unchanged	grains become diffuse internal structure of grains diffuse	soluble preparation slightly delineated internal structure
10.5	H-starch starch	sporadic grains imperfect sporadic imperfect grains	strongly loosened layers internal structure of grains diffuse	soluble preparation strong "corrosion" of grains
30.5	H-starch starch	few imperfact grains few imperfact grains	soluble preparation strong "corrosion" of grains	soluble preparation soluble preparation

Table 4. Solubility in water of hydrogen starch and starch (suspension 2%)

Water content %	Kind of starch	1 hour heating in temperature		
		120°C	140°C	170°C
2.5	H-starch	very dense paste, gelatinizes in 62°C	gelatinizes in 56°C, liquefy in 63°C	cold-soluble in water
	starch	very dense paste, gelatinizes in 61°C	very dense paste, gelatinizes in 60°C	gelatinizes in 64°C, does not liquefy
10.5	H-starch	very dense paste, gelatinizes in 61°C	gelatinizes in 65°C, liquefy in 78°C	cold-soluble in water
	starch	gelatinizes in 61°C	gelatinizes in 67°C	partly cold-soluble in water
30.5	H-starch	gelatinizes in 85°C does not liquefy	partly cold-soluble in water	cold-soluble in water
	starch	very dense paste, gelatinizes in 83°C, does not liquefy	gelatinizes in 95°C does not liquefy	cold-soluble in water

Since water residing in starch may participate in a hydrolytic decomposition of this polysaccharide an assumption should be made that the hydrogen starch preparations with 30.5% H_2O contained water in excess, that with 10.5% of H_2O contained an amount of water being sufficient for its hydrolysis in 95%, whereas starch with 2.5% of H_2O contained water sufficient only for its 22.5% hydrolysis.

Table 5. Reducing value of hydrogen starch preparation and starch (in % glucose per dry substance)

Water content %	Kind of starch	1 hour heating in temperature					
		120°C		140°C		170°C	
2.5 st	H-starch	3.9		7.6		9.7	
	starch		1.6		1.3		3.3
10,5	H-starch	4.6		18.4		29.4	
	starch		1.0		1.4		13.1
30.5	H-starch	13.0		47.2		73.9	
	starch		1.2		3.0		54.2

Reducibility values quoted in Table 5 show that in none of the investigated starch preparations including H-starch containing 2.5% H_2O hydrolysis was completed. The results indicate that autohydrolysis of hydrogen starch may occur even in the case of the samples of lower humidity content in the grains. In such case inhibiting effect of water being deficiency on the course of autohydrolysis can be observed.

Table 6 presents data on preparations soluble in cold water. The characteristics reveals suitability of hydrogen starch for manufacturing of water soluble starch preparations. Parameters like humidity of H-starch and temperature can be adjusted to obtain preparations with demanded degree of depolymerization.

DISCUSSION

The presented study is aimed at drawning attention to a potential application of hydrogen starch in industrial practice. Due to introduction of hydrogen ions into aquaeous solutions it can undergo autohydrolysis by hydrolyzing its own glycoside bonds. Conscious control of this process permits us to obtain starch preparations of grainy structure and characterized by easy solubility even in cold water.

Results of the present study have also theoretical value. In our former work [1] we used in analyses a hydrogen starch with the lowest level of water being 7.4%. This time we were able to obtain an hydrogen starch

Table 6. Properties cold water soluble starch preparations

Kind of starch	Water content %	Heating temperature in °C	Macroscopic of appearance of preparations	Solution appearance	Reducing value of preparations in % of glucose	Content of free P in mg % P
H-starch	2.5	170	light-yellow powder	yellow colour	9.7	12.1
H-starch	30.5	140	white lumped	strong opalescent	47.2	15.1
H-starch	30.5	170	brown "Caramel" transparent	yellow opalescent	73.9	52.1
Starch	30.5	170	yellow "Caramel" transparent	yellow opalescent	54.2	57.5

preparation of exceptionally low level of moisture: 2.5%. In spite of such an insignificant content of water the starch reveals typical autohydrolytic properties. This is evidenced by a multiple increase of reducibility in relation to the initial superior starch treated under the same conditions.

The rate of this reaction is strongly affected by water content in starch. It seems that within the investigated range of humidity $\leqslant 30\%$ H_2O we deal with an inhibiting influence of this component of starch on the rate of hydrogen starch hydrolysis, what if used consciously and intentionally may also have practical significance.

CONCLUSIONS

1) Autohydrolysis process of hydrogen starch can occur also in grains of H-starch with limited content of water. In this case the rate of autohydrolysis is proportional to humidity of hydrogen starch preparations.

2) The selection of parameters of all hydrogen starch humidity, temperature and heating period allows to obtain the starch preparations soluble in cold water.

3) Under the same experimental conditions hydrogen starch was subject to stronger depolymerization transformations than superior starch. The rate of this reaction is proportional to the water content in hydrogen starch preparations.

4) The liberation of free phosphorus from starch by healting at 120-170°C is faster in superior starch than in hydrogen starch. The water content in starch plays an important role in this reaction.

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Manuscript received: April, 1980
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AUTOHYDROLIZA SKROBI WODOROWEJ O OGRANICZONEJ ZAWARTOŚCI WODY

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Streszczenie

Skrobię wodorową oraz krochmal superior o różnej wilgotności: 2,5%, 10,5%, 30,5% ogrzewano w temperaturach: 120°C, 140°C i 170°C (tab. 1). Otrzymane preparaty badano pod względem wyglądu makro- i mikroskopowego (tab. 2, 3), rozpuszczalności (tab. 4), redukcyjności (tab. 5) oraz zawartości fosforu wolnego (tab. 6). Uzyskane wyniki świadczą, że nawet w ziarnach skrobii wodorowej o niskiej zawartości wody zachodzi proces autohydrolizy. Świadczy o tym wzrost redukcyjności w wyniku hydrolitycznej depolimeryzacji cząstek tego polisacharydu oraz zwiększenie się zawartości fosforu wolnego wskutek hydrolizy wiązania estrowego kwasu amylofosforowego. Szybkość autohydrolizy zależy od zawartości wody w skrobi (zależność wprost proporcjonalna) i oczywiście od temperatury.

Z przeprowadzonych badań wynika również, że zmieniając odpowiednio wilgotność i temperaturę skrobi wodorowej można otrzymać preparaty rozpuszczalne w zimnej wodzie. Preparaty te mogą mieć znaczenie praktyczne.