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[e002]

Microwave assisted oxidative degradation of starch - estimation of degree of oxidation of the modified biopolymer.

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Abstract

Application of microwave irradiation (2.45GHz) to carrying out starch oxidation by hydrogen peroxide – sodium tungstate system was shown. A various methods of carboxyl content determination in the product were compared.

Keywords

Microwave irradiation, starch, oxidation, hydrogen peroxide, carboxyl content, degradation

Introduction

Microwave synthesis is a new technique for conducting chemical reactions. Acceleration of organic reactions by microwaves has been proven, and in many cases, microwave techniques have become more effective than conventionally conducted reactions. The phenomenon origins in: interaction of irradiation with the matter by means of dielectric and/or conducting mechanism [1].

Reaction of starch with aqueous system hydrogen peroxide – sodium tungstate effects oxidative degradation (depolymerization) of the biopolymer. There are two major paths of the reaction: 1) glycol-cleavage of the C2-C3 diol moieties in internal glucose unit (path C) and 2) stepwise decarboxylation at the reducing terminal glucose unit until glycosidic bond is reached (path A) (Figure 1) [2].

Therefore, the main factors describing oxidation-depolymerization process of starch are: dextrose equivalent, molecular weight and carboxyl content. Dextrose equivalent (DE) expresses amount of anhydroglucose end-units in polycarbohydrate chain (reducing end-group). According to the oxidation mechanism (Figure 1) some steps of oxidation can the value of DE increase, other decrease (Table 1).

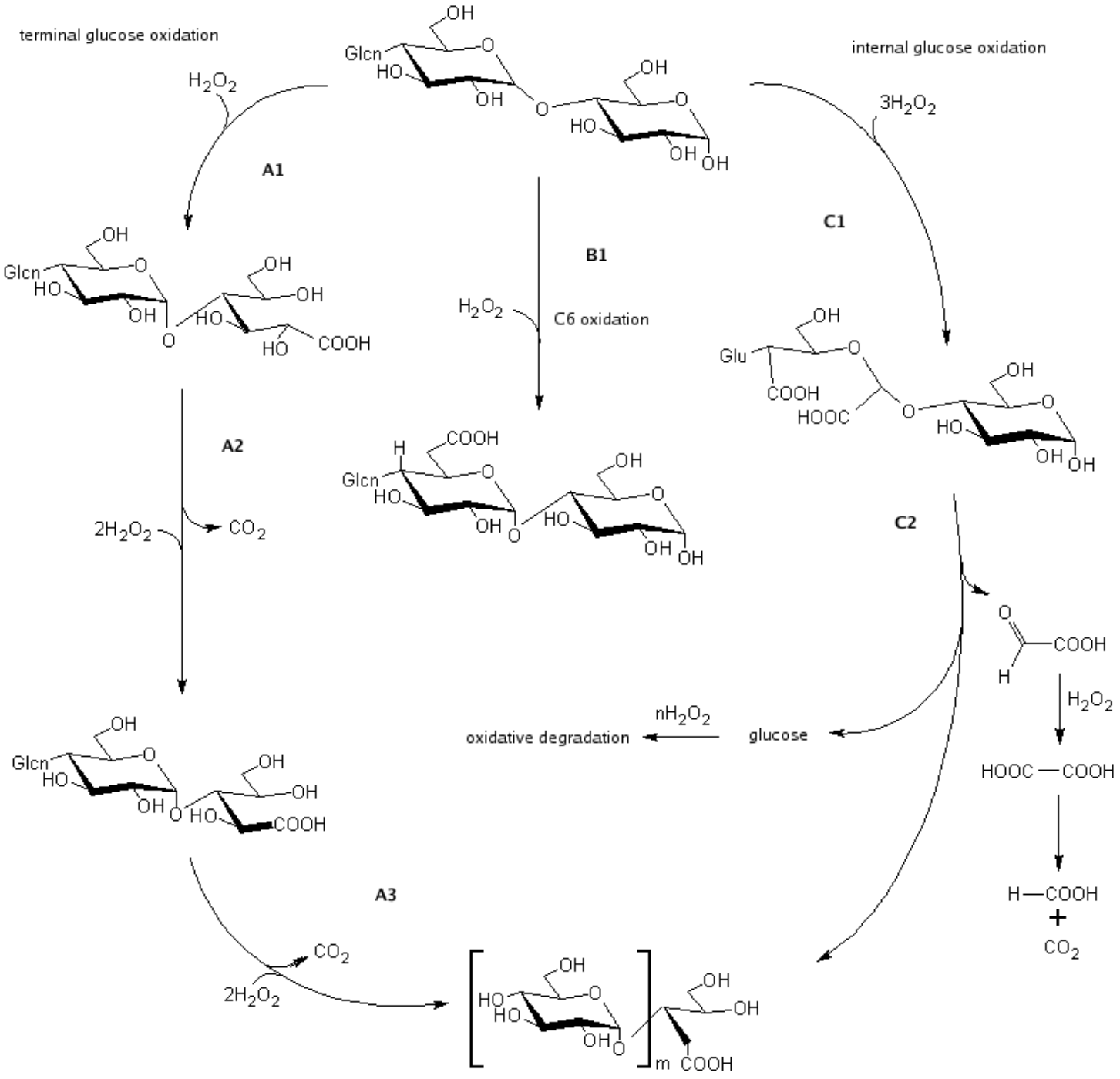

Figure 1. Simplified mechanism of tungstate catalyzed oxidation and degradation of starch by hydrogen peroxide [2]

Because of strong degradation of starch and presence of carboxyl groups in the polymer chains, solubility and swelling power in water of the product is much better than native starch. It affects experimental difficulties in estimation of carboxyl groups in oxidized starch. The well knows methods are useful to starches oxidized in granules suspension and the techniques require removing any metal cations (first of all sodium cation) from starch granules by means of flushing the sample with hydrochloric acid. In the case of highly degraded starches oxidized in gel form, applying of this method causes lost of part of the material, however remaining starch still stay contaminated with the cations. The results of the determination are not accurate. We have modified 'cation exchanger' method to adjust our requirements.

Table 1. The changes of DE value during the oxidation process (see also Figure 1)

Oxidation step	The influence on DE value

A1	decrease
A2	no influence
A3	no influence
B1	no influence
C1	no influence
C2	increase

Results and discussion

a) Microwave assisted synthesis

As can be seen (Table 2) during the oxidative degradation of starch molecular mass of the biopolymer decrease and the value of DE increase. Microwave irradiation helps to increase the oxidation degree. DE of microwave assisted oxidized starch is two times higher in comparison with starch oxidized in conventional condition at 90^{o}C for the same time. This phenomenon could be explained as an effect of thermal gradients inducted by microwave irradiation. Somewhat smaller effect of microwave irradiation can be noticed comparing the changes of molecular weight (Figure 2, Figure 3).

Table 2. DE value of oxidized starch at various conditions

Conventional condition, 60 min	Temperature,^{o}C	DE, %
	60	0.8
	70	0.8
	80	0.9
	90	1.3
Microwave condition, ~90°C	Time, min	DE, %
	20	1.0
	40	2.6
	60	2.9
	12	2.6

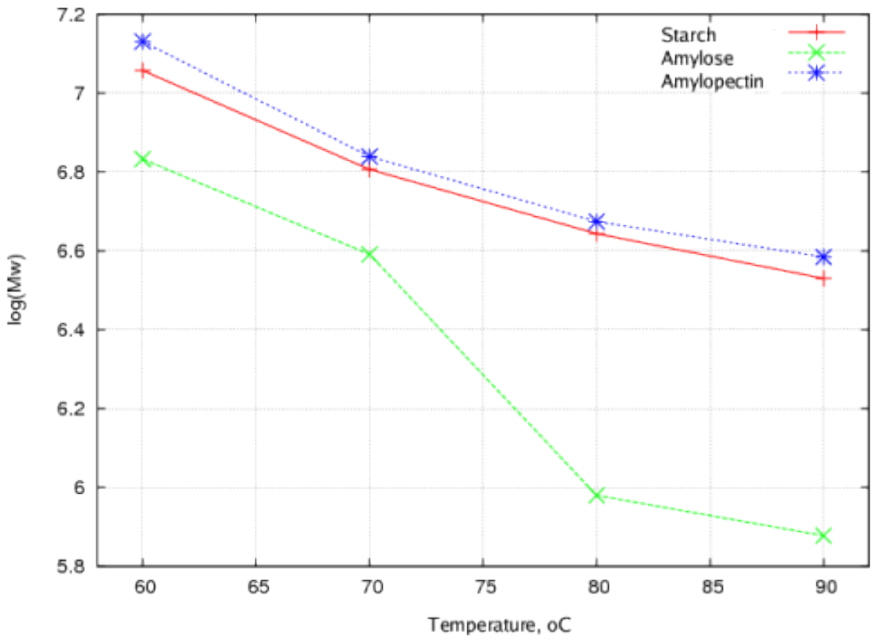

Figure 2. The dependence of molecular weight of starch and starch fractions: amylose and amylopectin on temperature of oxidation process at conventional conditions

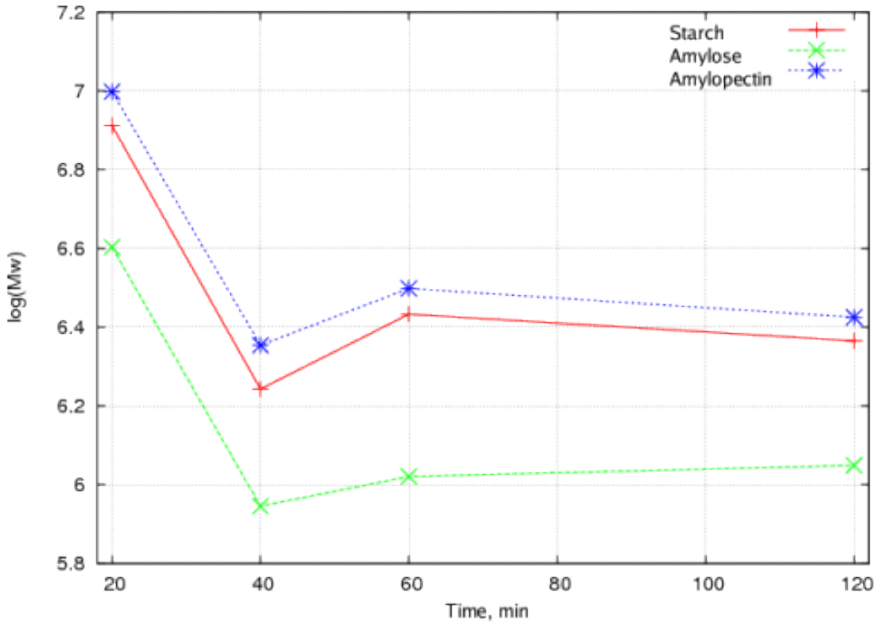

Figure 3. The dependence of molecular weight of starch and starch fractions: amylose and amylopectin on time of oxidation process at microwave conditions

b) The carboxyl group content estimation

For comparison three methods of carboxyl content determinations were applied (Table 3). As can be seen standard method and 'cation exchanger' give comparable results. However, back titration shows an overestimation. It is interesting to note, that total acidity of hydrogen peroxide oxidized starch (7.4 mmol/100g) is lower than native starch (8.4mmol/100g). It may suggest that during oxidative degradation of starch, rate of hydrolysis of phosphate ester of amylopectin is higher than overall rate of carboxyl group formation.

*Table 3. Results of carboxyl content determination with various titration methods. * - mean value from two measurements, ** - developed method, *** - carboxyl content was not*

estimated because of experimental difficulties, see Introduction for detailed explanation.

Sample	Id	Method	Total acidity*, mmol/100g
Native potato starch	1	Standard	4.5
	2	Back titration	15.0
	3	Cation exchanger**	8.4
E1404, commercial available, sodium hypochlorite oxidized starch	4	Standard	8.4
	5	Standard, without removing of the cations	2.9
	6	Back titration	28.8
	7	Cation exchanger	11.7
Hydrogen peroxide oxidized starch, 80^{o}C, conventional condition	8	Standard	not estimated***
	9	Back titration	not estimated***
	10	Cation exchanger	7.4

Conclusion

As a conclusion we would like to point out that application of microwave heating for oxidation of potato starch guides to the higher conversion by means of DE value. Probably it might be explained by thermal gradients in the reaction mixture. The differences are detectable even in the short reaction time i.e. 60 minutes. However further and detailed study on reaction mechanism (rate of hydrogen peroxide consumption, reaction kinetics) as well as differences in final product properties (rheology, texture, molecular mass distribution, etc.) comparing to so called conventional conditions are needed. Developed method of carboxyl group determination in oxidized starch, based on Floor at al. work [2], is very promising, but validation of the technique is needed before common use.

Experimental part

Starch oxidation was carried in multimode microwave reactor Moulinet FM A945GS. Temperature was measured by means of two channel fiberoptic thermometer Reflex RFX-2, Neoptix, Canada.

Oxidation of starch was conducted as follows: 40g of 'native' potato starch was put into the 400mL of water. The mixture was pasted at 90^{o}C during 15min. Obtained paste was cooled down to 30^{o}C and than 2.0g of Na_2WO_4 was added. After the 15min of intensive stirring hydrogen peroxide was added (83.4mL of 30% water solution) and sample was irradiated by microwaves at the power of approximately 90W or placed into the water bath to heat in the conventional way (at 60, 70, 80, and 90^{o}C). When reaction was finished the solution was cooled down and the starch was recover by precipitation in water/MeOH/25%NH_3 (1:1:0.1 volume ratio) mixture. Precipitated starch was centrifuged and dried. In order to remove from the biopolymer of some traces of oxidant or catalyst sample was autoclaving and precipitated in acetone two times.

Degradation progress was estimated by reducing power (dextrose equivalent – DE, DNS

method), molecular weight measurements as well as carboxyl content in the product. Carboxyl content was estimated by means of a few methods: standard [3], back titration [4] and based of 'cation-exchanger' method [2] as follows. 1g of starch was gelatinized in 100ml of deionized water at 90^{o}C for 20 min. Next the sample was cooled down and passed thought a column filled with strong cation exchanger (Amberlite IR120). Effluent was titrated by 0.02M NaOH to pH 8.3 (phenolphthalein). Molecular mass distributions were performed by means of Gel Permeation Chromatography (GPC). The following chromatographic system was used: four columns connected in series, filled with Sephacryl gels (Pharmacia, Sweden): S-200, 0.470 m; S-200, 0.940 m; S-500, 0.860 m; S-1000, 0.830 m. Internal diameter of all columns was 16 mm. As eluent Na_2CO_3 solution (5 mmol/L) was used. Flow rate was 0.128ml/min. The molecular mass and molecular mass distribution was estimated using anthrone method applied for every single fraction collected after elution.

References

[1] D. Bogdal, S. Bednarz, M. Lukasiewicz, Tetrahedron, **2006**, 62, 9440; Marcin Lukasiewicz, Bohdan Achremowicz, Szczepan Bednarz, ECSOC-9; Sz. Bednarz, M. Lukasiewicz, B. Achremowicz, M. Grzesik, D. Bogdal, The 5th International Congress of Food Technology, 9-11 March **2007**, Thessaloniki, Greece; M. Lukasiewicz, Sz. Bednarz, A. Ptaszek, B. Achremowicz, D. Bogdal, M. Grzesik, P. Tomasik, XV International Starch Convention, 19-21 June **2007**, Moscow, Russia
[2] M. Floor, K.M. Schenk, A.P.G. Kieboom, H. van Bekkum, Starch, **1989**, *41*, 303
[3] P. Parovuori, A. Hamunen, P. Forssell, K. Autio, K. Poutanen, Starch, **1995**, *47*, 19
[4] R.E. Wing, J.L. Willett, Industrial Crops and Products, **1997**, *7*, 45

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