

Solid complex of hydrogen peroxide as a safe and green oxidant for polysaccharide modification

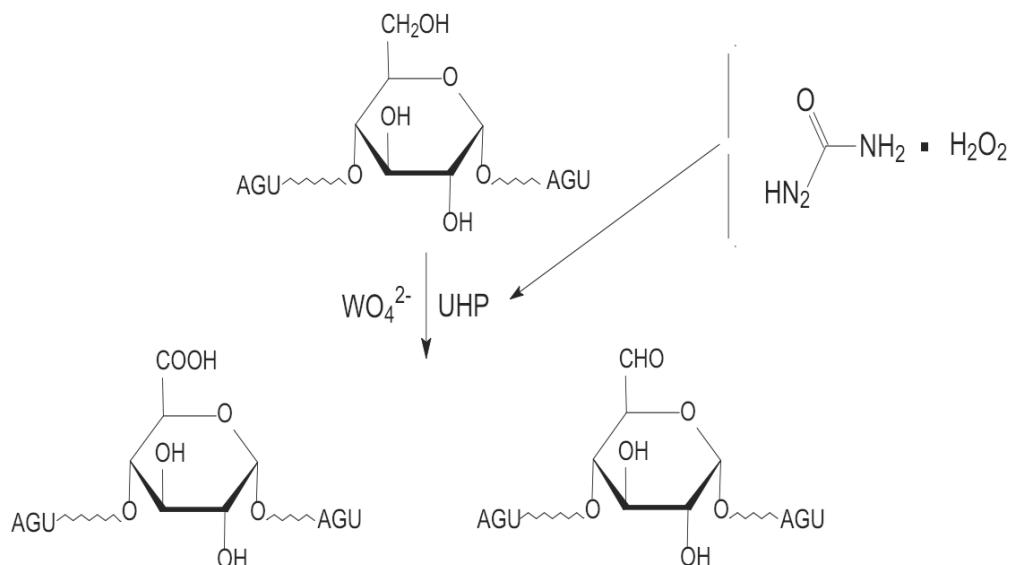
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Nowadays the bioresources including plant polysaccharides stay in focus of many researches according to ecological politics as well as oil reserves depleting. The well-known polysaccharide modification methods very often suffer from toxic by-products or difficult processing [1]. In order to solve the problem a new method for corn starch oxidation is presented. The process allows oxidizing the hydroxyl groups of anhydroglucose units of amylose and amylopectin (starch) by means of urea- hydrogen peroxide (UHP) action according to Scheme 1:



Scheme 1: UHP as the starch oxidant

Materials and Methods

The starting material was corn starch produced by Lubon S.A. (WPPZ Lubon S. A. Poland). Hypochlorite oxidized starch E1404 (WPPZ Lubon S. A. Poland) was used as commercial grade oxidized starch. All reagents used for oxidation reaction studies, as well as analyses of the products, were analytically pure and obtained from commercial suppliers (Sigma-Aldrich, POCh, Chempur, Fluka, Lach-Ner). All the chemicals were used as received.

Oxidation of starch

Oxidation of starch was conducted as follows. In a typical experiment 8.5g (correspondent to 50 mmol anhydroglucose units) of native corn starch was mixed with the 170mL of water. The mixture was slurried in water bath at 40°C and 60 40°C (15min). Then 0.9g (3 mmol) of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added. After 15min of intensive stirring urea hydrogen peroxide was added (28,2, 0.3 mol) and sample was heated in the water bath (40°C, or 60°C respectively). After the reaction was finished i.e. the conversion of hydrogen peroxide reached more than 90% (determined by permanganate titration as described earlier [2]), the reaction was stopped, the solution was cooled down and the starch was recovered by centrifugation and dried.

Hydrogen peroxide conversion

Reaction was monitored by checking the presence of H_2O_2 in the reaction mixture. Oxidant conversion was monitored by means of manganometric titration [2]. In specific periods of time a sample of about 500mg was taken from reaction mixture and weighted at analytical balance. To obtained sample water (200mL) and sulphuric acid (15mL) was added. The mixture was than titrated by permanganate solution (0.02mol/L).

Carboxyl group content

Carboxyl content was estimated based on cation-exchanger method [3] with some modification as follows: 1g of starch was pasted in 100ml of deionized water at 130°C (0.2MPa) for 20 min. Next, the sample was cooled down and passed through a column filled with strong cation exchange resin (Amberlite IR120, H⁺ form). The effluent was titrated by 0.02M NaOH to pH 8.3. A blank sample was titrated as well.

Carbonyl group content

Hydroxylamine method was used to investigate the carbonyl groups content in the samples. No modification was applied in this case [4].

Molecular mass and molecular mass distribution

Molecular weight distributions were performed by means of Gel Permeation Chromatography (GPC). The system of two columns Ultrahydrogel-2000 and Ultrahydrogel-500 (Waters) connected in a series and RI detector (Knauer) was used. As an eluent 0.1 mol/L NaNO₃ and 0.02% NaN₃ solution in water was applied. Flow rate was set to 0.6ml/min and sample volume of 100µl was injected. The sample concentration was c.a. 5mg/ml. A calibration using pullulan standards was performed.

Results and Discussion

As a result of investigation a series of oxidized starches was obtained. As it was shown on Figure 1 and 2 the overall decomposition of UHP is strongly temperature dependent. The reaction carried out at 40°C do not result in significant UHP conversion. The oxidant consumption at 60°C was completed after about 120min. According to that it is worth to emphasize that decomposition of oxidant is slow and gentle. At temperature higher than 40°C the changes in UHP and hydrogen peroxide concentration are noticeable. It result in starch oxidation. The gentle oxidant utilization allows to perform deeper oxidation of AGU units in starch and lower oxidant consumption. Additionally losses of active oxygen are far lower to those for liquid solutions of hydrogen peroxide.

When glucan product were stand in focus (see Table 1) one can see that proposed starch processing allows to obtained an oxidized starch with rather high oxidation degree. Oxidation degree may be measured as carbonyl and carboxyl group content. Both of them are the result of primary hydroxyl oxidation at C6.

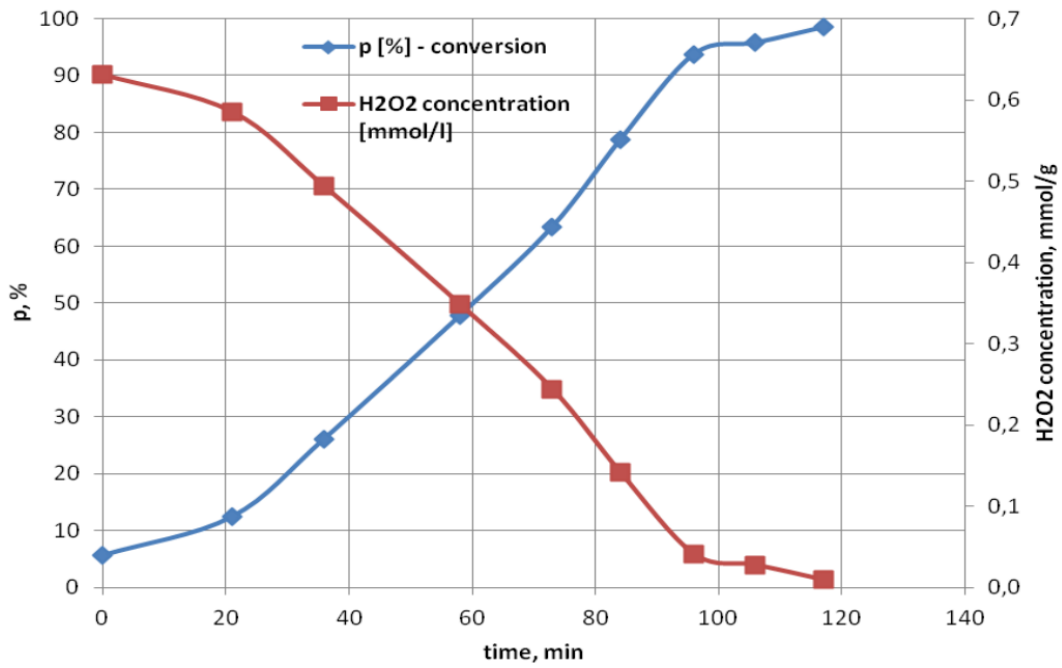


Figure 1: UHP conversion at 40°C

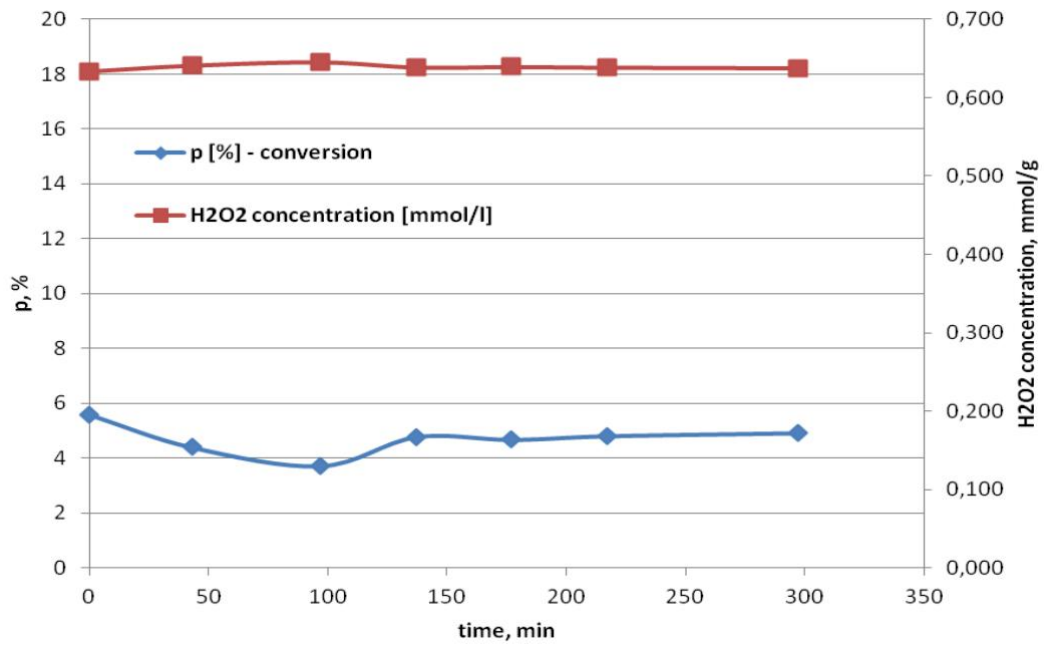


Figure 2: UHP conversion at 40°C

It is easy to see that starch oxidized at 40°C is similar to native ones by means of COOH group content. When temperature of the process is higher i.e. 60°C the overall COOH content is much higher even when compared to commercial oxidized starch E1404.

Table 1. Molecular parameters of oxidized starch

ID	COOH	CHO	Mw	Pd
	mmol/100g		g/mol	
Native	2,11	0,68	0,86	18,72
E1404	9,01	3,22	0,50	11,35
40	1,89	17,76	1,11	19,80
40+	1,89	5,66	1,26	16,51
60	15,98	12,89	0,91	14,01
60+	10,16	9,53	0,61	21,03

Interesting results were obtained also when CHO group content was investigated. It was observed that carbonyl content increase rapidly even at low temperature. Comparing reactions at 40 and 60°C shows the decrease in CHO what is probably result of deeper oxidation of starch i.e. CHO to COOH conversion. In each case the reaction performed using sodium tungstate as a peroxide activator show lower degree of oxidation. It may be result of changes in reaction mechanism or to fast oxidant utilization. The phenomenon needs deeper investigation.

One of the most important structural parameter when modifying polysaccharides are glucan chain degradation. Each known modification method result in glycosidic bond hydrolysis. So the average molecular mass of the product is lower than native polysaccharide. In Table 1 weight average molecular masses of obtained oxidized starches were presented including dispersity of the polymer. It is easy to see that proposed starch processing allows to get the less degraded product with higher Mw molecular mass. On the other hand the dispersity factor is higher in this

case what may testify on specific degradation mechanism resulting in statistical changes in polymer chains length.

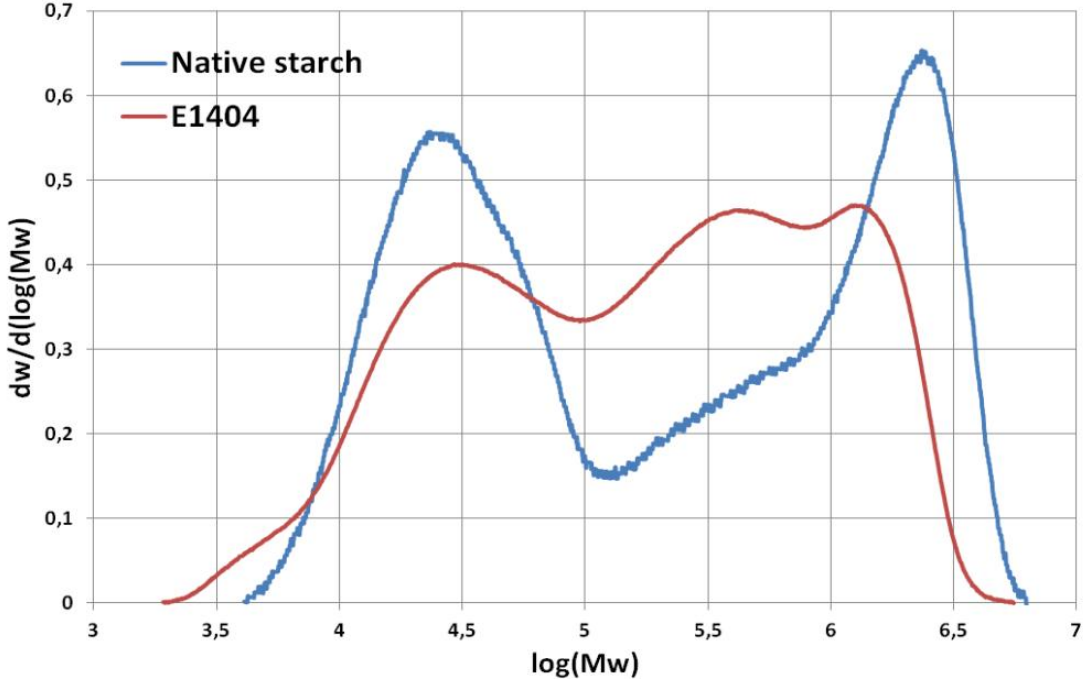


Figure 3: Molecular mass distribution of standard materials

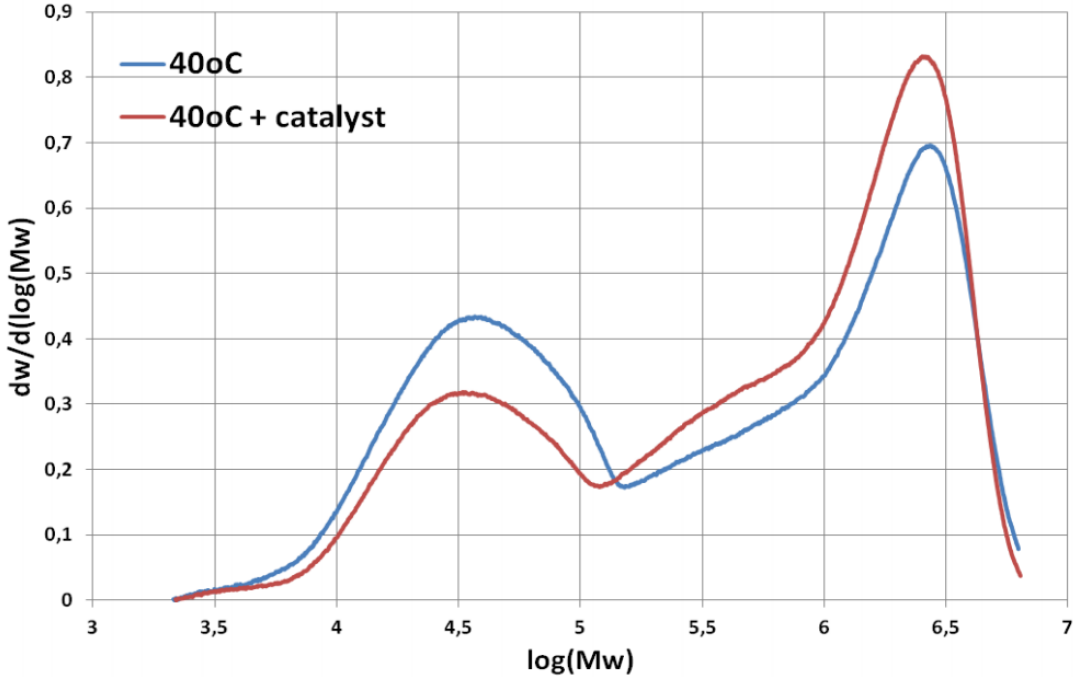


Figure 4: Molecular mass distribution of starches oxidized at 40°C

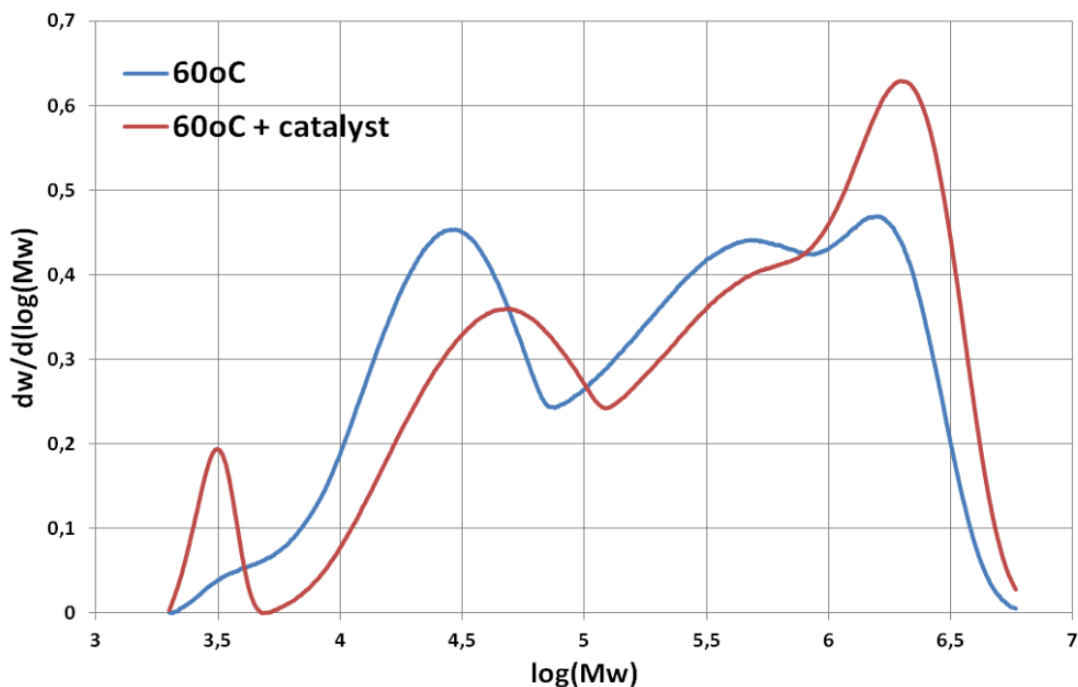


Figure 5: Molecular mass distribution of starches oxidized at 60°C

The molecular mass distributions of all investigated materials are presented on Figure 3 to 5. One can see that oxidation performed at 40°C does not influence on molecular mass distribution.

When the reaction was carried out in higher temperature degradation cannot be omitted however in noncatalytic process more shallow than for commercial E1404

Conclusions

As a conclusion it is worth to point out that urea - hydrogen peroxide adduct looks very promising as the starch oxidant. During the oxidation course the significant amount of carbonyl and carboxyl groups are introduced into the polymer macrochain. In fact the application of hydrogen peroxide activator is less efficient than uncatalysed processes. In both cases the amount of oxidized primary hydroxyl groups is higher to those observed for commercial oxidized starch. On the other hand the molecular parameters of starch oxidized using UHP are far higher than for E1404 what means that the oxidation is more gentle and the degradation of starch chains are lower than in case of sodium hypochlorite oxidation processes. The granular structure of starch is preserved in that case in better way when UHP is used as oxidant.

Presented preliminary studies show the strong need for further investigation including starch granule topography, pasting (rheological) properties and detailed molecular study including the mechanism and kinetics of starch and starch glucan oxidation.

References

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