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Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst

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ABSTRACT

Oxidized starch is heavily deployed as a surface sizing agent in the paper industry. The most common oxidation methods use transition metals as catalysts and perchlorines or iodates as oxidants, and thus a large amount of inorganic waste is produced. In the present work, iron tetrasulfophthalocyanine (FePcS), a cheap iron complex is used as a catalyst, and hydrogen peroxide (H_2O_2) as an oxidant, resulting in a waste free method for starch oxidation. The oxidation is performed in a semibatch mode, constantly feeding H_2O_2 into the reactor and the pH is kept constant by adding NaOH. Gas evolution was monitored by measuring gas flow in the outlet and performing mass spectrometric analysis. The samples were taken during experiments, and the carboxyl (COOH), carbonyl (CO) contents as well as hydrogen peroxide concentration, were analyzed resulting in kinetic data. At neutral pH (7), the catalyst is not well activated leading to accumulation of H_2O_2, whereas under alkaline reaction conditions (pH 10), the H_2O_2 was rapidly decomposed resulting in a COOH value of 1.6/100 AGU and CO value of 3.0/100 AGU, but with an extensive loss of the solid starch (yield = 67 wt.%) due to depolymerization and decomposition. Respectively, no carbon dioxide but only oxygen was detected in the formed outlet gas when using FePcS under alkaline solutions, whereas with $FeSO_4$ in acidic solutions only CO_2 was detected without any oxygen.

1. Introduction

Starch is an important and interesting biopolymer for the industries nowadays, due to its large availability and low cost. Thickening agents, stabilizers, emulsifiers, fuel ethanol, as well as bio-plastics, can be produced from native starch. In the paper industry, starch is heavily deployed as a sizing agent as it improves the mechanical and film-forming properties of paper, paper board and textiles by binding together the components of paper web (fibers, pigments, and fillers).

The main reason to chemically treat starch before the commercial use is to split the long glucose chains of the polymer molecules in order to reduce the high viscosity of unmodified starch solutions and thereby increase and maximize the possible starch amounts in technical applications. The reduction of the average chain length can be done – and also in practice is done – by numerous different ways. These include in addition to oxidation also, for example acid hydrolysis and enzymatic modification.

Thus, before starch can be used, it has to be modified by, e.g. oxidation. Numerous oxidation methods are known, e.g. wet-, semi-dry and dry-oxidation as well documented in [13]. Oxidation of starch allows carboxyl and carbonyl groups to be substituted on the polymer backbone, replacing the hydroxyl groups. Starch having a degree of substitution (DS) of 0.01–0.20 is of commercial interest. Traditionally, oxidation has been performed with heavy-metals (iron, copper, and tungsten) as catalysts, and NaOCl or N_2O_4 as oxidants, which all produce large quantities of inorganic waste. Thus, a new environmentally friendly method for starch oxidation was developed, by deploying a novel efficient iron complex as a catalyst and hydrogen peroxide as an oxidant [1]. Compared to the efficiency of iron (II) sulphate, 20 times less iron tetrasulfophthalocyanine (FePcS) (see Fig. 1) catalyst is needed to achieve the same oxidation degree. Additionally, the oxidized starch product contains practically the same iron content as the native potato starch, whereas prepared with iron salt as a catalyst the oxidized starch had a significant level of residual iron due to complexation, causing an undesirable coloration and loss of the catalyst [1].

The exact reaction paths in starch oxidation are not yet completely understood. Oxidative treatment can besides oxidizing hydroxyl groups to keto- and carboxyl-groups also cleave polymer. Therefore, studies with new catalytic systems in addition to kinetic investigations, which were in the focus of the present research, should also address viscosity and rheological properties of the oxidized starch.

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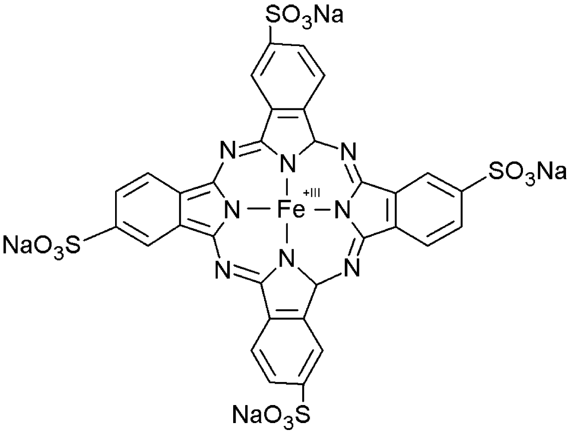

Fig. 1. Chemical structure of the catalyst.

Regarding oxidation of starch *per se* probably the most accepted reaction path is described by Floor et al. [2] in which two competing reaction paths take place. The relationship between the formation of carboxyl and carbonyl groups is unclear. It is reported, that hydroxyl groups in starch molecules are first oxidized to carbonyl groups and *then* to carboxyl groups, which primarily takes place at C-2, C-3, and C-6 [8,9]. This would indicate that the reaction path is consecutive with carbonyl groups as intermediates, which react further to carboxyl groups after prolonged reaction times. On the other hand, parallel reaction paths are, however, also reported. Depending on type of oxidant used, carbonyl groups are selectively formed by oxidation of the hydroxyl groups at the positions C_2 and C_3, whereas with another oxidant, the hydroxyl groups at the position C_6 form carboxyl groups [5].

The kinetics of starch oxidation reactions has not been previously studied, since most experiments were performed in batch reactors analyzing only the final product [1,2,4]. In some cases, experiments have been performed at different reaction times, and analysis data have been collected from each separate experiment to represent kinetic results of one single experiment [3,5,7]. This procedure is a straightforward but time consuming and expensive approach. Additionally, these methods lack the possibility to monitor changes of the solid to liquid ratios, gas phase analyses, and their dependencies on the oxidant concentration. In the present study, the aim was to monitor the progress of the reaction by taking several samples during experiments. This give the possibility to follow the formation of the two product types, carboxyl and carbonyl groups substituted to the backbone of the starch polymer during the reaction, revealing the pathways, which could be either consecutive or parallel. Such investigations of the starch oxidation kinetics using a semibatch reactor may be, however, challenging, since each sample has to contain at least 5–10 g of solid starch and thus the reactor size must be chosen accordingly.

To preserve the granular form of the starch, the reaction temperature cannot exceed the gelatinization temperature, which is specific to the origin of the starch. H_2O_2 decomposition which can take place during starch oxidation is highly exothermic (98.2 kJ/mole), which has to be taken into account to avoid gelatinization.

It is important that the granular structure of the starch remains intact during oxidation. Some applications allow the starch granules to be destroyed or gelatinized during oxidation but usually this is not the case. Also, possible residual iron content in the solid starch needs to be determined. Thus the solid starch product was analyzed with scanning electron microscopy (SEM).

The rate of starch decomposition is dependent on the temperature and concentration of the peroxide, as well as the pH and the presence of impurities and stabilizers. The decomposition occurs more rapidly under alkaline conditions, indicating that acid is often added as a stabilizer. In the presence of certain catalysts, such as Fe^{2+} or Ti^{3+}, the hydrogen peroxide decomposition may proceed via a different path, i.e. with free radicals such as $HO^{\bullet}$ (hydroxyl) and $HOO^{\bullet}$ being formed [10]. In the presence of iron tetrasulfophthalocyanine, H_2O_2 form nucleophilic species like $PcSFe^{III}–OOH$ and electrophilic species like $PcFe^{IV}{=}O$ or $PcFe^{V}{=}O$. These species are capable of degrading compounds that are resistant to, e.g. H_2O_2 oxidation [12].

The present work evaluates the effect of temperature, hydrogen peroxide concentration, and pH, on the oxidation of starch. Fur-

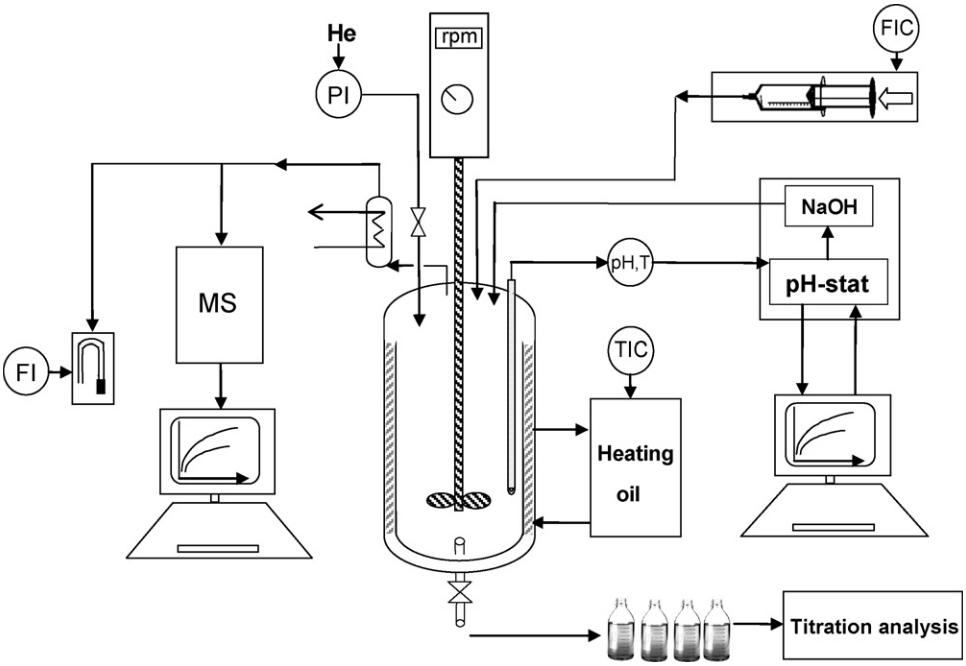

Fig. 2. Schematic figure of reactor setup.

thermore, the depolymerization of the starch to soluble starch, the formation of low molecular compounds, and the actual concentration of hydrogen peroxide were investigated.

2. Experimental

2.1. Materials

Native potato starch was purchased from Sigma–Aldrich, having a water content of 16%. Fresh 30% hydrogen peroxide produced by Merck was used as an oxidant. 2 M NaOH was used for pH stat control during experiment. 0.025 M NaOH was used for determining the carboxyl content by titration. 0.1 M HCl was used for determining carbonyl content. Potassium iodide, 2 M H_2SO_4 and 0.05 M $Na_2S_2O_3$ were used for determining the hydrogen peroxide content in the samples. Small amounts of water soluble iron tetrasulfophthalocyanine (see Fig. 1) were used as a homogeneous catalyst.

2.2. Reactor setup

Starch oxidation experiments were performed in a semibatch glass reactor with a liquid phase volume of 1000 ml (Figs. 2 and 3). Increased reactor volume was essential, since 6 samples, each of 50 ml, were taken during experiments. Catalyst to solid ratio remained constant due to homogeneous withdrawal of samples. *T* the temperature was kept constant with recirculating oil in the reactor wall. Rigorous stirring was necessary (700 rpm) to ensure sufficient heat and mass transfer, since the reaction temperature was close (2–3 °C) to the gelatinization temperature.

2.3. Oxidation of starch

2.3.1. H_2O_2 decomposition experiments

Experiments were performed in 50 ml bottles to study the effect of pH on the H_2O_2 decomposition with or without catalyst at elevated temperature (55 °C). Typically 2.50 g of starch was suspended in 21.25 g of water and 3.75 g H_2O_2 (30 wt.%), thereafter pH adjustment was performed and the catalyst (1.0 mg) was added. The bottle was gently flushed with argon, closed, and stirred (with magnetic stirrer) on oil bath for the desired time.

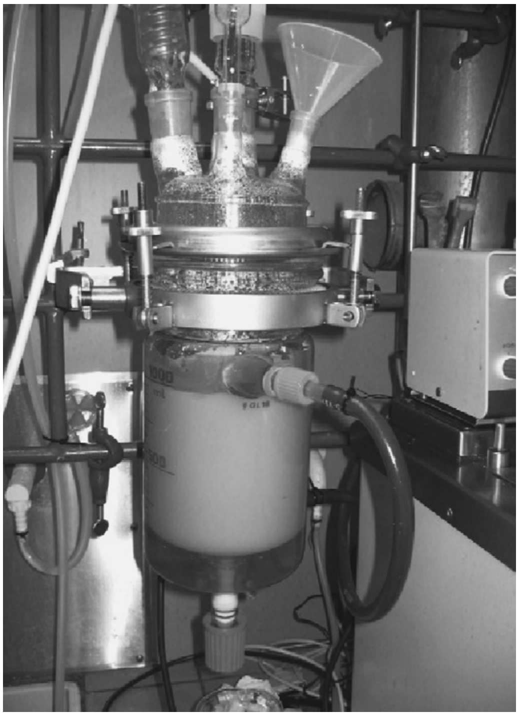

Fig. 3. Photo of the reactor.

2.3.2. Starch oxidation experiments

Typically 260 g of starch and 140 mg of FePcS catalyst were used in the experiments. Starch was suspended in warm distilled water and poured into the reactor. The volume was adjusted to an initial volume of 1000 ml with distilled water (totally 800 ml water was added). The pH was adjusted from the initial value of 7.3 to the desired value, if needed, before adding the catalyst and starting hydrogen peroxide feed. Gas flow out from the reactor system was monitored by a gas flow meter (Humonics 520). A mass spectrometer (Balzers Omnistar) was connected to the gas out let to analyze gas composition. The pH was kept constant with a titrino pH stat device using 2 M NaOH.

The length of the experiment was 7 h, and the samples were typically taken at 60, 120, 240, 300, 360 and 420 min. Although addition of H_2O_2 and NaOH increased the volume, gas evolution acted in the opposite direction resulting overall in a small decrease in the catalyst concentration. Thus it was important to calculate the theoretical and experimental solid to liquid ratio (see Fig. 8). Each sample (slurry) was transferred to a 50 ml glass bottle (0.2–2 of liquid phase taken for iodometric titration) and the alkaline solution was immediately neutralized to 5.8–6.0 with 0.1 M HCl, and then filtrated on a P4 glass filter funnel. The sample was then dried on paper overnight at room temperature and weighed the next day. After the experiment the remaining reactant was removed from the reactor, filtered and weighed in order to determine the mass balance and solid to liquid ratios of each sample.

Oxygen evolution was determined by titration of the remaining H_2O_2 in the reactor. A gas flow meter and mass spectrometer was used to determine the gas composition. The reactor was typically flushed with He carrier gas prior to an experiment in order to remove atmospheric gases, and a small flow of He (<50 ml/min) was maintained through the reactor system during experiments.

Reaction conditions were similar to the experiments performed in the previous studies [1]. Hydrogen peroxide (30 wt.%) was added to the reactor mixture with a continuous rate of 11 or 22 ml/h, corresponding to a total volume of diluted peroxide equal to 78 or 155 ml. The anhydroglucose unit (AGU) to H_2O_2 ratio was thus 1:0.72 or 1:1.43. AGU to catalyst ratio was 12,000:1.

2.4. Analysis by titration

Carboxyl and carbonyl titration was performed by Smith's method [6], with slight modifications. The remaining H_2O_2 concentrations in the samples were determined by means of iodometric titration. Depending on the estimated H_2O_2 concentration, 0.200–2.00 g of the aqueous phase of the sample was used. The titration was performed immediately after taking the sample, before neutralizing the H_2O_2 with HCl.

2.5. Determining the water content

The water content of native and oxidized starch was determined by heating a specific amount of sample in an oven and then weighing the loss of evaporated water. Typically, a thin layer of sample (0.20–1.00 g) was placed on a glass plate and introduced in an oven (120 °C) for 3 min, cooled down at room temperature for 1 min and then weighed again. This was typically performed for the native starch and the final sample.

2.6. Analysis of structural changes and residual iron content

The structural changes on the starch granules of final samples, was followed by scanning electron microscopy (SEM, type Cambridge Instruments Stereoscan 360). The residual iron content in the solid oxidized starch was followed by scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA, ThermoNoran Vantage) and inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Reactions of hydrogen peroxide

Reactions of hydrogen peroxide are well known. H_2O_2 spontaneously decomposes to oxygen and water (Eq. (1)) and the rate of decomposition is dependent on the temperature, concentration and impurities. However, it can also, especially in the presence of any catalyst, form *hydroxyl radicals*. The peroxide is broken down into a hydroxide ion and a hydroxyl free radical (Eqs. (2) and (3)). Moreover, radical interactions can lead to recombination of hydrogen peroxide (Eq. (4)).

$$\text{Decomposition}: \quad 2\,H_2O_2 \rightarrow 2\,H_2O + O_2\,(g) \tag{1}$$

Formation of hydroxyl radicals :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{2}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^{+} \tag{3}$$

$$\text{Recombination} \quad {}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{4}$$

The reaction mechanisms of hydrogen peroxide with starch are very complex and may change when changing the reaction conditions. Generally, though, the reaction follows a mechanism similar to the one listed below, in which the formed hydroxyl radical formed oxidizes an alcohol group on the glucose unit forming a radical, which in turn reacts with the ferric ion, and finally with hydrogen peroxide [3,9]:

$$RCH_2OH + {}^{\bullet}OH \rightarrow R^{\bullet}CHOH + H_2O \tag{5}$$

$$R^{\bullet}CHOH + Fe^{3+} \rightarrow RCHO + H^{+} + Fe^{2+} \tag{6}$$

$$R^{\bullet}CHOH + H_2O_2 \rightarrow RCHO + {}^{\bullet}OH + H_2O \tag{7}$$

If the reaction is carried out to completion, then ultimately the organic molecules break down into CO_2 and water. If the pH is too high the iron can be precipitated as $Fe(OH)_3$ and at high pH H_2O_2 can decompose to oxygen and water. However, the homogeneous, water soluble FePcS catalyst does not precipitate at high pH and can thus be used in basic environment.

3.2. Results obtained from H_2O_2 decomposition

The decomposition of hydrogen peroxide was found out to be highly dependent on the pH and temperature (see Table 1). Hydrogen peroxide alone showed very slow decomposition at 55 °C and pH 5. When adding NaOH the decomposition increased; at pH 8.6 the yield (recovered solid starch) was 58% after 24 h, and at pH 10 the yield was only 36% after 8 h and 0% after 24 h, respectively (Table 1, entries 1–3b). Without a catalyst, there is no or hardly any carboxyl groups formed, see entries 4–6. In the presence of FePcS catalyst, H_2O_2 decomposes more rapidly, and the rate is increasing with increasing pH, see entries 7–10. Thus, if the solution is highly alkaline (pH 10), with the catalyst present all the H_2O_2 is decomposed in less than 1 h, or without the catalyst 73% of the H_2O_2 has decomposed after 8 h, while hardly any starch oxidation have occurred. However, 33% of the starch has decomposed at pH 10, see entry 6. Additionally, if having both the catalyst and starch at an initial pH level of 10 (see entry 13), all H_2O_2 is consumed while the carboxyl content is relatively low. DS was only 0.48 per 100 AGU units, while the solid starch yield had decreased to 87%.

This can be explained by the fact that the H_2O_2 is decomposed too fast, partly degrading the starch. The most interesting observation was that when starting with an initial pH of 8.6 in the presence of both starch and the catalyst (see entry 12), all the starch (97%) had become water soluble after 24 h. At the same time the pH had surprisingly dropped to 2.25 from the initial 8.6, indicating extensive carboxylic acid formation. There was 43% H_2O_2 left after the reaction and the carboxyl content was 3.90 per 100 AGU.

3.3. Kinetic experiments

Based on results obtained in the preliminary experiments, the most feasible reaction conditions for starch oxidation were chosen for kinetic experiments. The catalyst was shown to be active under alkaline reaction conditions. Too strong H_2O_2 concentrations caused starch depolymerization, in addition since the H_2O_2 reactions (decomposition and starch oxidation) are exothermic it is safer

Table 1
Preliminary experiments, reaction temperature 55 °C; initial H_2O_2 concentration of all experiments was 5.3 wt.%; AGU:cat molar ratio was 1000:1 in entries 7–14; AGU:H_2O_2 molar ratio was 1:2.5.

Entry	pH	*t* (h)	Starch	Catalyst	H_2O_2 yield %	DS_{COOH}/100 AGU	Solid starch yield %
1	5	24			98		
2	8.6	24			58		
3	10	8			34		
3b	10	24			0		
4	5	8	x		98	0	88
5	8.6	8	x		50	n.d.	n.d.
6	10	8	x		27	0.03	67
7[a]	5	24		x	99		
8	5	8		x	97		
9	8.6	8		x	50		
10	10	1		x	0		
11	5	8	x	x	88	0	75
12	8.6	8	x	x	43	3.90	3[b]
13	10	8	x	x	0	0.48	87
14	2	8	x	x[c]	51	n.d.	0

[a] Experiment at 20 °C.
[b] Solid insoluble starch was 3% left, 77% of water soluble starch recovered with acetone precipitation. Final pH 2.25.
[c] $FeSO_4$ used as catalyst with AGU: cat molar ratio 200:1; starch decomposed.

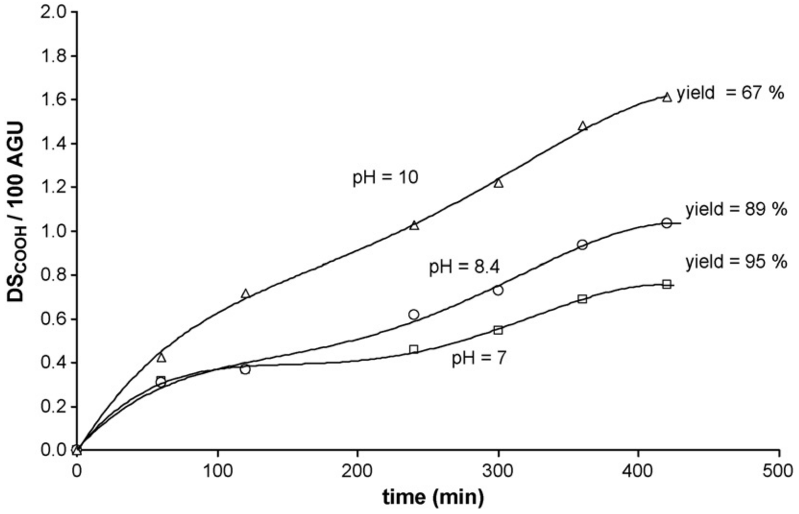

Fig. 4. The kinetics of the carboxyl formation at different pH levels (7–10) when using AGU/cat ratio of 12,000:1 and H_2O_2 flow of 22 ml/min at temperature of 55 °C. Yield corresponds to the amount of recovered solid starch at the end of the experiment.

to add small amounts of H_2O_2 continuously than the whole amount at once.

The kinetic experiments were performed under alkaline pH. The selected three pH levels were 7, 8.4 and 10. The carboxyl and carbonyl contents, as well as H_2O_2 and the gas evolution were determined. Carboxyl groups were formed at the highest rate at the highest pH 10 (Fig. 4), but at the same time starch decomposed to low molecular weight products. After 7 h, the carboxyl DS was 1.7 per 100 AGU units, but 33% of the starch was lost. When decreasing the pH, less COOH groups were formed compared to the experiment performed at pH 10, and the starch recovery was at a reasonable level (only 10% solid starch lost at pH 8.6 and 5% at pH 7, respectively).

The formation of carbonyl product showed a behavior different compared to the carboxyl formation at different pH levels (Fig. 5). The highest formation of $C{=}O$ groups was not found at the highest pH (10), but at pH 8.4. The formation of H_2O_2 hydroxyl radicals is probably higher at this pH level, while the decomposing reaction to water and oxygen is more prominent at pH 10 than at lower pH levels (compare Table 1, entries 10 and 12), which could explain this phenomenon.

In both the carboxyl and carbonyl formation there are clearly two separate phenomena. At the beginning (0–240 min), the products are mainly formed on the surface of the starch granules, while later (240–420 min) partial degradation allows reaction inside the granule and the reaction rate increases again.

The DS values achieved corresponds well to the DS values obtained in the previous studies at similar reaction conditions [1]. In Table 2, the performed kinetic experiments are compared with some results from the literature, which also employed hydrogen peroxide as an oxidant. At pH 7, $DS_{COOH} = 1.85$ and $DS_{CO} = 5.46$ where reported whereas in our study $DS_{COOH} = 0.75$ and $DS_{CO} = 2.05$ (Table 2, entries 3 and 5) are recorded. The slightly lower values in our study can be explained by the fact that in the work of Sorokin et al. [1], the temperature was 58 °C compared to 55 °C in this study. A few degrees may in fact have a big influence meaning that the reaction temperature can be in the gelatinization zone or slightly below it. Moreover in the current investigation samples were taken during the course of the reaction, influencing the solid to liquid ratio. When comparing the effect of the H_2O_2 flow rate, it can be noticed that when reducing the flow by half, also the DS_{COOH} is reduced by the same amount while DS_{CO} is reduced by 2/3 (Table 2, entries 2 and 4).

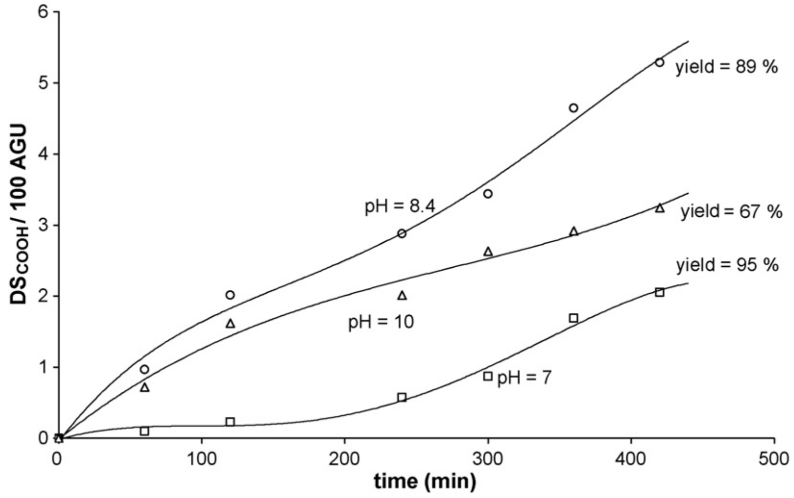

Fig. 5. The kinetics of the carbonyl formation at different pH levels (7–10) when using AGU/cat ratio of 12,000:1 and H_2O_2 flow of 22 ml/min at temperature of 55 °C. Yield corresponds to the amount of recovered solid starch at the end of the experiment.

Table 2
Comparison of performed kinetic experiments (entries 1–4) and DS values from the literature.

Entry #	Reaction conditions				DS_{COOH}/100 AGU	DS_{CO}/100 AGU	Yield[a] %	Ref. #
	T (°C)	pH	H_2O_2 flow	Catalyst				
1	55	10	22	FePcS	1.61	3.24	67	
2	55	8.4	22	FePcS	1.03	5.28	89	
3	55	7.0	22	FePcS	0.75	2.05	95	
4	55	8.4	11	FePcS	0.46	1.87	96	
5[b]	58	7		FePcS	1.85	5.46		[1]
6[c]	58	3		$FeSO_4$	0.00	0.00		[1]
7[d]	40	10		$FeSO_4$	0.90	6.40	91	[3]
8	40	Acidic		$FeSO_4$	0.59	0.87		[11]
9[e]	90	2.0		WO_4^{2-}	24.4	–		[2]

[a] Yield = total amount of recovered solid starch.
[b] Reaction temperature 58 °C, FePcS as catalyst AGU/catalyst ratio = 12,900:1, reaction time 7 h, hydr. per. flow equivalent to entry 4.
[c] Reaction temperature 58 °C, $FeSO_4$ as catalyst, AGU/catalyst ratio = 12,900:1, reaction time 7 h, hydr. per. flow equivalent to entry 4.
[d] Reaction temperature 40 °C, $FeSO_4$ amount 0.1 wt.% based on dry starch, reaction time 4 h, hydr. per. added in beginning of experiment.
[e] Starch gelatinized and reaction performed at 90 °C.

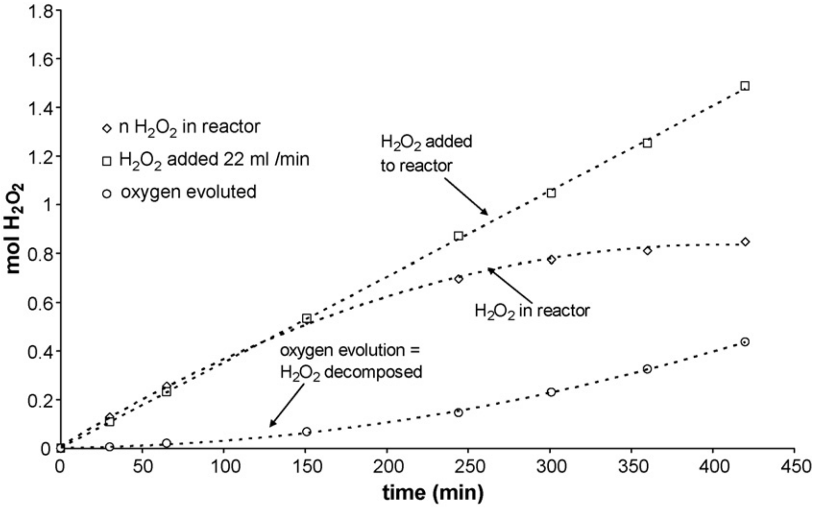

Fig. 6. Hydrogen peroxide evolution at pH 8.4 when using AGU/cat ratio of 12,000:1 and H_2O_2 flow of 22 ml/min at temperature of 55 °C.

As can bee seen (Table 2, entry 6), if using $FeSO_4$ with same AGU/catalyst ratio as FePcS, no starch oxidation occurs [1]. If the reaction temperature is high and gelatinization is allowed, then it is possible to achieve much higher substitution degrees (entry 9), since the reaction solution have higher surface contact with the starch. In contrast to the result obtained in the H_2O_2 decomposition experiments (Table 1), maintaining the pH at 8.4 with pH stat does convert the starch into soluble starch as it was in the case of only adjusting *initial* reaction media to pH 8.6 (Table 1, entry 12). The pH dropped to a final 2.25 due to formation of low molecular carboxylic

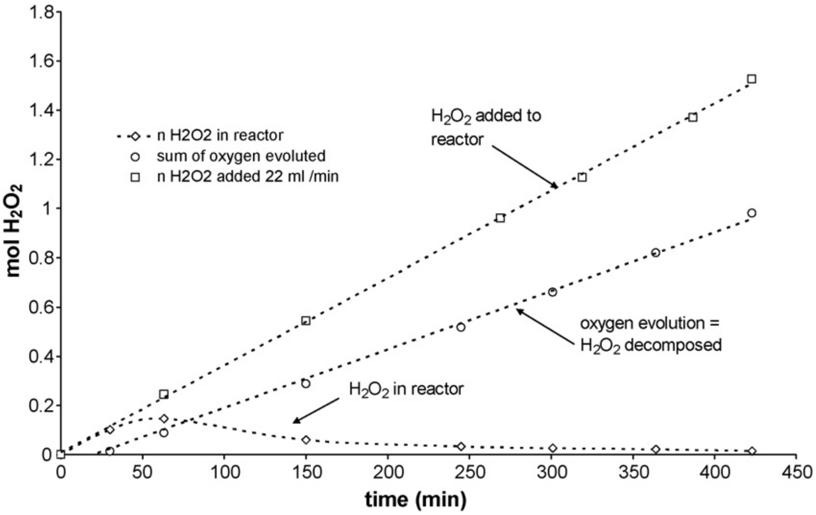

Fig. 7. Hydrogen peroxide evolution at pH 10 when using AGU/cat ratio of 12,000:1 and H_2O_2 flow of 22 ml/min at temperature of 55 °C.

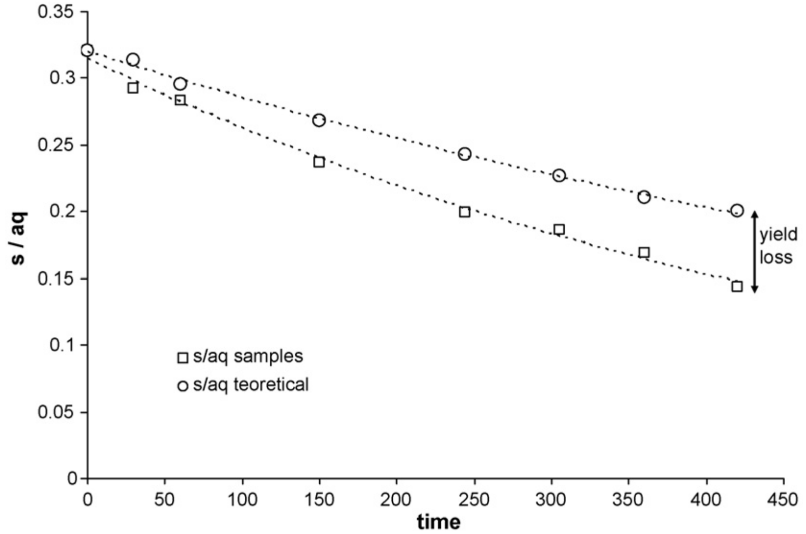

Fig. 8. Theoretical and experimental values of solid to liquid ratios as a function of time. Reaction conditions: pH 10, $T = 55\,^{\circ}\text{C}$.

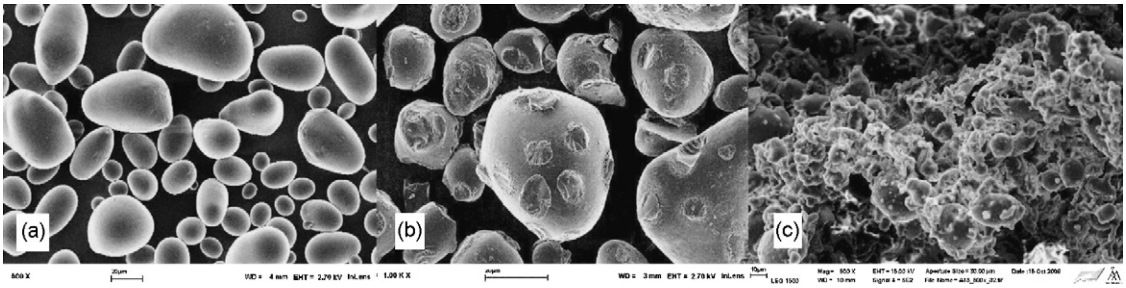

Fig. 9. SEM pictures of (a) native potato starch, (b) oxidized starch at pH 10 and (c) and water soluble starch (see Table 1, entry 12).

acids. The solid starch was heavily depolymerized (as can be seen in SEM analysis, Fig. 9c), thus increasing the surface area, which could explain the high DS_{COOH} in this experiment.

The oxygen evolution could be determined by observing the H_2O_2 added to the reactor, and H_2O_2 concentration in the reactor at specific reaction time (by titration of samples), by monitoring the gas flow out of the reactor and analyzing it by MS. The results of the oxygen evolution can be seen in Figs. 6 and 7 at two different pH values, 8.4 and 10, respectively. At pH 7, the gas formed was too small to be detectable. At pH 8.4 the oxygen mass balance is substantially different compared to pH 10. The H_2O_2 is accumulating in the reactor to a final level of 0.8 mol/L and then maintained at that level, while the gas evolution starts to increase in the final phase of the experiments. At the pH level of 10, the H_2O_2 is not accumulated at all but is remaining at very low level during the experiment (see Fig. 7).

The part of the starch that was decomposing and reacting further to low molecular compounds was found out to be of significant level when the pH was 10 (33% of the solid starch was lost). The loss of the solid material can be seen during the experiment at pH 10 (Fig. 8). Both the theoretical and the observed ratios were decreasing due to the fact that solid starch was withdrawn and liquids were fed in, however there was a clear difference between experimental and theoretical values. The experimental ratio was 29% lower than the theoretical ratio at the final sample, which was in a good agreement with the total solid starch loss of 33 wt.% (=67% solid starch yield).

CO_2 can be formed by a terminal glucose oxidation route via decarboxylation, producing CO_2 [2]. The outlet gas composition was analyzed in this work online with MS. The only gas at pH 8–10 was oxygen, while no CO_2 was detected. In a comparable experiment with $FeSO_4$ as a catalyst using pH 2.8–3.0, only CO_2 was observed and no O_2. Clearly there was no terminal glucose oxidation occurring at the experiments performed in the alkaline solution with FePcS as the catalyst, but only internal glucose oxidation, which in turn formed low molecular compounds (such as erythronic, glyoxylic, and formic acids).

3.4. Analysis of the granular structures and residual iron content by SEM-EDXA

The structure of the oxidized starch granules is important. Although some applications allow the starch granules to be destroyed or gelatinized during oxidation, usually this is not the case. Thus the solid starch product was analyzed with scanning electron microscopy (Fig. 9).

The microphotographs made with SEM show a loss of smoothness on the surface of the starch granules (Fig. 9b). When the starch is allowed to react further to water soluble starch (Table 1, entry 12), the major part of the granules is still intact, but clustered together (Fig. 9c). When analyzed with SEM-EDXA, the residual iron content of the FePcS oxidized starch was too low to be detected, whereas oxidized starch obtained with $FeSO_4$ was measured to have up to 0.20 ± 0.05 wt.% iron content. When analyzed with ICP-MS, the iron content was measured to 2.1 mg/kg for native starch, 9.5–15.4 mg/kg (pH 8.4 and pH 10) for FePcS oxidized starch, and 292 mg/kg for $FeSO_4$ oxidized starch, respectively. Moreover, the color of the FePcS oxidized starch was white, whereas the $FeSO_4$ showed a light brown discoloration.

4. Conclusions

The starch oxidation kinetics with H_2O_2 was studied at different pH levels by determining the substitution of carboxyl and carbonyl groups, as well as the hydrogen peroxide concentration and oxygen evolution. The maximum DS of carboxyl groups was obtained at the highest pH (10), whereas the highest DS of carbonyls were obtained at pH 8.4, which could be explained by a more effective radical formation at lower pH level. The yield of the recovered solid starch was higher at more neutral pH levels. Moreover, it was found that at independent on the pH level, initially the oxidation reaction occurs mainly on the surface of starch granules, while later on partial degradation allows reactions inside the granule. The only gas product formed at alkaline reaction conditions was oxygen.

References

[1] A.B. Sorokin, S.L. Kachkarova-Sorokina, C. Donzé, C. Pinel, P. Gallezot, From native starch to hydrophilic and hydrophobic products: a catalytic approach, Topics Catal. 27 (2004) 67–76.

[2] M. Floor, K.M. Schenk, A.P.G. Kieboom, H. van Bekkum, Oxidation of maltodextrins and starch by the system tungstate-hydrogen peroxide, Starch/Stärke 41 (1989) 303–309.

[3] P. Parovuori, A. Hamunen, P. Forssell, K. Autio, K. Poutanen, Oxidation of potato starch by hydrogen peroxide, Starch/Stärke 47 (1995) 19–23.

[4] P. Mischnick-Lübbecke, W.A. König, Bestimmung der Substitionsmuster von chemisch modifizierten Stärken, Starch/Stärke 39 (1987) 425–431.

[5] S.M. Butrim, T.D. Bil'dyukevich, T.L. Yurkshtovich, Kinetics of starch oxidation in the system nitrogen (IV) oxide-tetrachloromethane, Russ. J. Appl. Chem. 74 (2001) 2106–2110.

[6] R.J. Smith, Characterization and analysis of starches, in: R.I. Whistler, E.F. Paschall (Eds.), Starch: Chemistry and technology, Vol. II, Academic Press, Inc., New York, 1967, pp. 620–625.

[7] S. Veelaert, D. de Wit, H. Tournois, An improved model for the periodate oxidation of starch, Polymer 35 (1994) 5091–5097.

[8] D. Kuakpetoon, Y.-J. Wang, Locations of hypochlorite oxidation in corn starches varying in amylose content, Carbohydr. Res. 343 (2008) 90–100.

[9] H.S. Isbell, H.L. Frush, Mechanisms for hydroperoxide degradation of disaccharides and related compounds, Carbohydr. Res. 161 (1987) 181–193.

[10] W. Armstrong, Relative rate constants for reactions of hydroxyl radicals from the reactions of iron (II) or titanium (III) with hydrogen peroxide, Can. J. Chem. 47 (1969) 3737–3744.

[11] S. Pietrzyk, T. Fortuna, Ł. Raś, The influence of pH and Fe (II) ions on physicochemical properties of oxidized potato starch, Electron. J. Polish Agric. Univ. 10 (4) (2007) 16.

[12] A. Sorokin, B. Meunier, Oxidation of polycyclic aromatic hydrocarbons catalyzed by iron tetrasulfophthalocyanine FePcS: inverse isotope effects and oxygen labeling studies, Eur. J. Inorg. Chem. 9 (1998) 1269–1281.

[13] P. Tomasik, C.H. Schilling, Chemical modification of starch, Adv. Carbohydr. Chem. Biochem. 59 (2004) 175–403.