**Chlorine-free oxidation of starch and its derivatives using alkaline hydrogen peroxide and water-soluble iron- and manganese-based catalysts**

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**Highlights**

* H2O2 combined with iron or manganese complex is an efficient system for starch oxidation
* Interplay between catalyst stability and applied process parameters dictates efficiency
* *In situ* Raman spectroscopic technique is developed to monitor catalyst stability
* Studies on model compounds provide insights into the mechanism of starch oxidation

**1. Introduction**

Oxidation is an attractive strategy to effectively reduce the high-molecular weight of native starch and improve its stability for various applications in paper and textile industries. Sodium hypochlorite (NaOCl) is a common oxidizing agent due to its efficiency in lowering the viscosity as well as introducing carbonyl/carboxyl functionality in the polysaccharide structure (**Figure 1, left**). However, it is highly desired to replace NaOCl with more environmentally-benign alternatives. In this work, H2O2 is used instead, in combination with iron (III) tetrasulfonatophthalocyanine (FePcS) or manganese (IV) 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) as the catalyst (**Figure 1, right**).







**Figure 1.** Catalytic oxidation of hydroxyl groups to carbonyl and carboxyl groups, and subsequent cleavage of the glycosidic bonds (left). Structure of iron and manganese complexes as catalysts used in this present work (right).

**2. Methods**

Typically, potato starch slurry in water (39 wt.%) was prepared and heated to the desired temperature. The pH was adjusted to 10 or 11 using NaOH. The catalyst was subsequently added, followed by H2O2. The influence of process parameters (i.e., time, temperature, oxidant, and catalyst and starch concentrations) for reactions carried out in both batch and continuous-flow set-ups on yield, viscosity, and degree of substitution (DS) was investigated. Yields were calculated based on the dry weight of product. Moisture content and urea viscosity were determined using a moisture analyzer and a rapid visco-analyzer, respectively. The carboxyl and carbonyl contents were determined by IR spectroscopy and by titration. Product properties were further characterized using various techniques including PXRD, SEM, FTIR, 2-D NMR HSQC, GPC, HPLC, and ESI-MS.

**3. Results and discussion**

At optimum batch conditions for the H2O2-FePcS system, a product yield of 91% was obtained with substantial degree of substitution (DSCO=0.41, DSCOOH=0.014), combined with degradation to lower molecular weight (197 mPa·s) (**Table 1**). However, high [H2O2] and temperature promoted the degradation of the FePcS catalyst (by *in situ* Raman spectroscopy). For the H2O2-Mn(tntacn) system, starch oxidation was a clear function of time and showed a linear dependency with respect to carboxyl group formation, whereas an exponential decay was found for starch degradation. H2O2 and catalyst concentrations of 2 wt.% and 20 ppm, respectively, were already sufficient to significantly reduce the viscosity of starch samples within benchmark specifications (144 mPa·s with DSCOOH=0.04). For both catalytic systems, the morphology and structure of the starch remained unchanged after oxidation. A clear shift of the cumulative weight fraction to lower regimes was also obtained (by GPC), consistent with the observed extent of depolymerization and formation of water-soluble oxidized compounds. Studies on model compounds (i.e., glucose, fructose, maltose, cellulobiose, beta-cyclodextrin, inulin, amylose, and amylopectin) provided insights into structure-property relationships as well as the mechanism of oxidation and depolymerization.

**Table 1.** Catalytic oxidation of native potato starch with FePcS and H2O2 at 50 °C and pH 10 in batch.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Entry | FePcS (μM) | H2O2 (M) | time  (min)*a* | Urea  viscosity  (mPa·s) | DSCOOH  (mol mol-1) | DSCO  (mol mol-1) | Yield  (wt.%)*b* |
| 1 | 331 | 0.2 | 135-80-72 | 3692 | 0.004 | 0.15 | 97.4 |
| 2 | 331 | 0.4 | 112-90-90 | 1360 | 0.011 | 0.22 | 95.2 |
| 3 | 166 | 0.4 | 180-120-120 | 1690 | 0.010 | 0.33 | 95.0 |
| 4 | 166 | 1.0 | 180-120-120 | 197 | 0.014 | 0.41 | 90.7 |
| 5*c* | 166 | 1.0 | 180-120-120 | 198 | 0.012 | 0.40 | 91.0 |

*a* H2O2 added in one or three steps dropwise with a concentration distribution of 30-35-35%.

*b* Weight of isolated oxidized starch divided by the initial weight of starch on a dry basis (total wt. 100 g).

*c* Upscale experiment of entry 4 with five moles (1000 g) of potato starch.

**4. Conclusions**

Environmentally-friendly oxidant, H2O2, in combination with low loadings of water-soluble Fe- and Mn-based catalysts are highly effective in the oxidation of abundant starch and starch derivatives. Some deactivation of FePcS was observed using *in* *situ* Raman spectroscopy depending on reaction conditions. These systems provide a promising alternative to hypochlorite (NaOCl) starch oxidation.