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Starch oxidation by hydrogen peroxide in the presence of an iron catalyst complex: process intensification and mathematical modelling

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PURPOSE OF THE ABSTRACT

Starch is a native macromolecule consisting of anhydroglucose units (AGU) linked together by α -glycosidic bonds. Native starch appears in two forms, amylose (linear) and amylopectin (branched). Oxidation of starch is a very interesting and challenging process, both from the viewpoints of science and technology. The goal is to oxidize some of the hydroxyl groups in starch to carbonyl and carboxyl groups. Oxidized starch has a much better water solubility than native starch and it is used in several applications, such as paper coating and sizing as well as in textile sizing, and in the alimentary industry as gelling agent.

Oxidized starch can be prepared by letting starch particles to react with hydrogen peroxide in the presence of an iron-based catalyst. The reaction scheme is depicted in Figure 1. An extensive series of kinetic experiments were carried out for oxidation of starch by hydrogen peroxide in the presence of an environmentally friendly homogeneous iron tetrasulphonatophtalocyanine (FePcS) catalyst shown in Figure 2. The experiments revealed that semi-batch reactor technology is the best one for the starch oxidation, because in this way the decomposition of hydrogen peroxide during the process can be minimized.

Process intensification efforts were taken to speed up the reaction. Ultrasound is known to be an efficient process intensification approach when solid particles are involved. The oxidation was enhanced by treating the starch particles with ultrasound before the reaction. Ultrasound caused cracks on the surface of the starch particles which made them more reactive in the oxidation. The positive effect of ultrasound was confirmed with a series of comparative experiments.

An advanced mathematical model was developed for the oxidation process. The model takes into account several experimentally confirmed observations, such as the oxidative formation of carbonyl and carboxyl groups in starch, as well as the decomposition of starch, catalyst and H₂O₂. The model is based on molecular mechanisms for the oxidation and decomposition reactions as well as on the dual structure of starch particles comprising an outer reaction layer and an internal porous layer, in which diffusion resistance retards the reaction rate. Adsorption of the catalyst on the starch surface is included in the model. The mathematical model explained very well the experimentally observed complex behavior of starch oxidation kinetics and hydrogen peroxide decomposition.

Keywords: Starch oxidation, FePcS catalyst, H₂O₂, kinetics, batch and semibatch reactor, mathematical model

Figure 1. Detailed reaction mechanisms for carboxyl group formation at position C6 (above), and carbonyl and

carboxyl group formation by C2-C3 bond cleavage (below). It should be noticed that the reaction schemes above do not represent complete stoichiometry.

Figure 2. The molecular structure of the water soluble iron catalyst complex FePcS for starch oxidation.

FIGURES

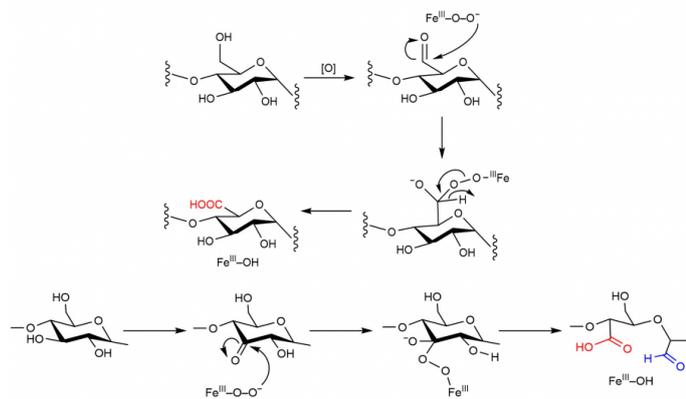


FIGURE 1

Figure 1

Detailed reaction mechanisms for carboxyl group formation at position C6 (above), and carbonyl and carboxyl group formation by C2-C3 bond cleavage (below). It should be noticed that the reaction schemes above do not represent complete stoichiometry.

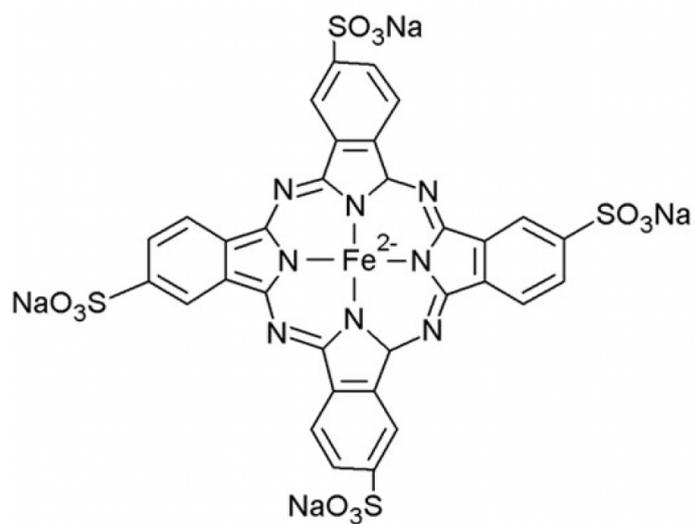


FIGURE 2

Figure 2

The molecular structure of the water soluble iron catalyst complex FePcS for starch oxidation.

KEYWORDS

Starch oxidation | FePcS catalyst | H₂O₂ | kinetics

BIBLIOGRAPHY