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Starch modifications in supercritical CO₂

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Summary

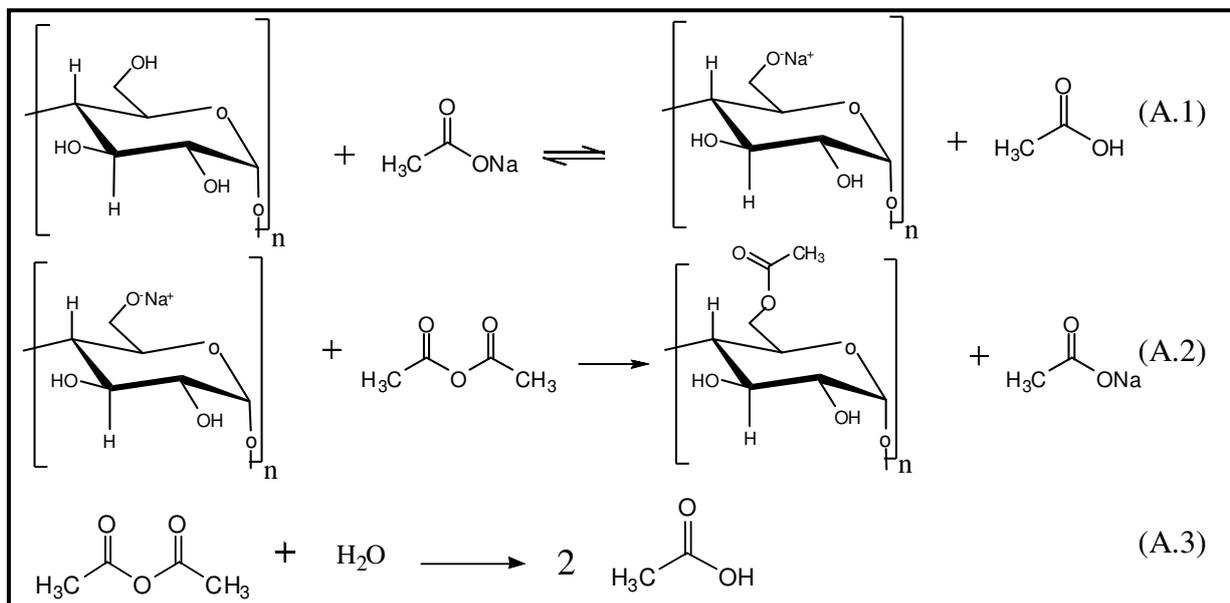
This thesis describes an exploratory study to determine the potential of supercritical carbon dioxide (scCO₂) as a solvent for chemical modification reactions of starch. The emphasis is on the acetylation of potato starch with acetic anhydride (AAH) and the esterification with fatty acid esters as reactants.

Acetylated starches are important commercial products. The common synthetic methodology involves the reaction of starch with AAH in water in the presence of an alkaline base like sodium acetate (NaOAc) as the catalyst (Scheme A). An undesired side reaction is the hydrolysis of AAH to form acetic acid (AA) (Scheme A.3). In conventional processes, only a relatively low starch concentration (between 35 and 42% w_t/w_t) is possible to avoid mixing problems and as a result the hydrolysis reaction also takes place to a considerable extent (Scheme A.3). Another serious drawback of the use of water is the high costs of water removal after reaction in the work-up/drying section of the process. To improve the selectivity, organic solvents such as pyridine and DMSO can be used. However, these solvents have a much higher environmental impact than water and are also difficult to separate from the product due to their relatively low volatility.

Fatty acid starch esters are accessible by reacting starch with carboxylic acids (C₄-C₁₆), fatty acid vinyl esters (i.e. vinyl laurate, vinyl stearate), fatty acid chlorides, or fatty acid methyl esters (i.e. methyl palmitate, methyl laurate) and basic salts as catalysts. Typically organic solvents such as pyridine or DMSO are applied. The use of these organic solvents is a serious drawback for further up-scaling of the process. Thus, for both starch

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modification reactions, the development and application of environmentally benign solvents is of prime importance (**Chapter 1**).



Scheme A. Representative scheme of starch acetylation using AAH as the reagent and NaOAc as a base catalyst.

Among the various green solvents, scCO_2 is considered a very promising option. It is not toxic, relatively inert and is known to have a positive effect on reaction rates and selectivities (**Chapter 1**). The goal of this project is to assess the application of supercritical carbon dioxide (scCO_2) as a solvent for the modification reactions of starch. The present research not only covers in-depth experimental and modeling studies on starch modification (**Chapters 2, 3, 4, and 5**) but also provides insights on a fundamental level on starch- CO_2 interactions (**Chapters 6 and 7**).

The acetylation of potato starch with acetic anhydride (AAH) and a number of base catalysts in a batch reactor set-up is described in **Chapter 2, 3, and 4**. The acetylation reaction was initially studied at relatively low pressures (6 – 9.8 MPa) (**Chapter 2**). Later studies revealed that these experiments were actually performed in the sub-critical state. At

these conditions, acetylated potato starch with a range of degree of substitutions (DS) (0.01 - 0.46) were obtained. Other important reaction parameters such as the anhydride conversion (X_{AAH}) (10 % - 80%), and the selectivity of the reaction (S_{SA}) (2 % - 18 %) were also determined. Statistically adequate (R^2 and R^2_{adj} of 0.9 - 0.98) models correlating the effect of the process variables to the DS, X_{AAH} and S_{SA} were developed. The models indicate that the temperature, water content and NaOAc to starch ratio play a significant role while the effect of pressure within the experimental window (6 - 9.8 MPa) is rather limited. To evaluate the performance of CO_2 , a number of experiments were performed in water and the results confirm that densified CO_2 is a good solvent for starch acetylation.

When employing a broader CO_2 pressure range (8 - 25 MPa) at a temperature of 90 °C and a NaOAc to starch ratio of 4.35 mole/mole AGU (**Chapter 3**), the pressure has a profound effect on the DS, X_{AAH} , and S_{SA} values. This implies that pressure is a suitable process parameter to tune the DS to the desired value for a given application. The highest DS values (0.29) were found near the critical point of the mixture (15 MPa). This value was determined by parallel experiments using a high pressure view cell. Furthermore, additional experiments with a range of starch particles sizes showed a clear relation between the DS and the particle size. This implies that mass transfer inside the particle is limiting the overall conversion rates and is more important than intrinsic kinetic effects. Further studies are required to quantify the complex interaction between intra-particle mass transfer and the acetylation kinetics.

In **Chapter 4**, a systematic study was performed to quantify the effects of process conditions and particularly the effect of pressure on the acetylation of starch in pressurized CO_2 using various basic catalysts and AAH as the reagent. The highest DS value (0.49) was obtained using potassium carbonate (K_2CO_3) as the catalyst at 90 °C, 15 MPa pressure, and a catalyst to starch ratio of 0.5 mole/mole AGU. The experimental data of 22

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experiments were analysed using non-linear multivariable regression to quantify the effects of process conditions on important reaction parameters like the DS and X_{AAH} . The models predict a positive influence of temperature and catalyst ratio on the product DS, whereas an optimum is observed for the pressure. Important product properties of the products prepared in CO₂ (viscosity in water and relevant thermal properties) were determined and compared with the typical products prepared in water. The results show remarkable differences both in thermal stability and viscosity profiles.

Chapter 5 describes an experimental study on a novel synthetic method for fatty acids/potato starch esters using supercritical carbon dioxide (scCO₂) in a broad pressure range (6 – 25 MPa), temperatures between 120 and 150 °C and various basic catalysts and fatty acid derivatives (methyl and vinyl esters and anhydrides). Products with a broad range of DS values (0.01 - 0.31) were obtained, the actual values depending on process conditions, type of catalyst and the fatty acid reagent. The combination of K₂CO₃ and vinyl laurate gave the highest DS values (DS = 0.31 at 150 °C, 8 MPa). The DS of the products is a clear function of the temperature and pressure. While the DS increases with temperature, a maximum DS value is obtained at 8 MPa (**Chapter 5**). Apparently, two opposing effects play a role here. In the low pressure range (below 8 MPa), a higher pressure leads to a higher solubility of CO₂ in the starch matrix and thus enhances the rate of diffusion of the reactants, ultimately leading to higher DS values. However in the high pressure regime (above 8 MPa), a compressive effect dominates which leads to lower diffusion rates of the reactants into the starch granules. Relevant product properties were determined and evaluated and it was shown that the introduction of fatty acid chains on the starch backbone has a profound effect on product properties like hydrophobicity and thermal behavior.

An in depth study on the degree of gelatinization of potato starch by a scCO₂ treatment at elevated temperatures (from 50 to 90 °C) and pressures (from 0.1 to 25 MPa) at relatively low water contents is reported in **Chapter 6**. Upon treatment with CO₂, starch granules are plasticized, swelled and gelatinized as observed by *in situ* FT-IR, XRD, and DSC measurements. A series of experiments under N₂ pressure confirms that scCO₂ plays a special role in the gelatinization process. Quantification of the degree of gelatinization (DG) by DSC measurements indicates that starch gelatinization is induced by both temperature and pressure (**Chapter 6**).

The solubility of CO₂ in native potato starch (NPS) and potato starch acetate (SA) at two different temperatures (50 °C and 120 °C) and various pressures (up to 25 MPa) was determined experimentally using a magnetic suspension balance (MSB) (**Chapter 7**). The CO₂ sorption behavior is highly depending on the temperature and pressure. In this thermodynamic study, it is shown that the DG and the CO₂ sorption in the starch granules are correlated. The extent of DG is a function of the amount of CO₂ present in the starch matrix and *vice versa*, a higher DG will also increase the accessibility of CO₂ inside the starch matrix (**Chapters 6 and 7**). Another important finding is the existence of the specific intermolecular interaction between the carbonyl group of starch acetate (SA) and CO₂ as established by FT-IR. This favorable interaction may explain the higher CO₂ solubility in SA compared to NPS. In addition, the experimental solubility data and the degree of swelling (S_w) for both native potato starch and SA were successfully modeled using the Sanchez Lacombe equation of state (S-L EOS) (**Chapter 7**).

