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Starch modifications in supercritical CO₂

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Chapter 3

Insights in Starch Acetylation Reactions in Sub- and Supercritical Carbon Dioxide

Abstract

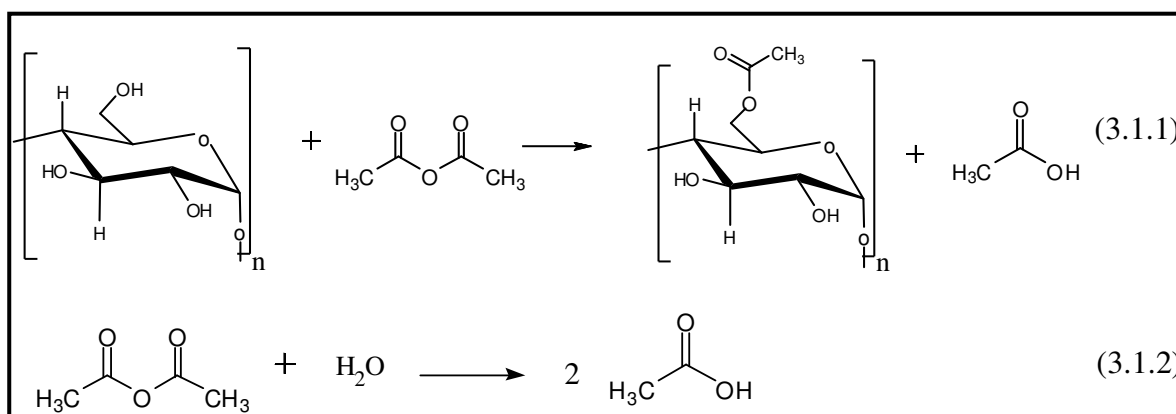
An in-depth study on the acetylation of starch with acetic anhydride (AAH) and sodium acetate (NaOAc) as the catalyst in pressurised carbon dioxide (scCO₂) in a broad pressure range (8 - 25 MPa) and a temperature of 90 °C is provided. Highest degrees of substitution (0.29) were found near the critical point of the mixture (15 MPa). The phase behavior of the system CO₂, starch and acetic anhydride (AAH) was studied in a high pressure view cell. The critical points were a clear function of the temperature and increased from the range of 9.4 – 10 MPa to 14.5 – 14.8 MPa when going from 50 to 90 °C (AAH mole fraction at the critical point in the range of 0.08 - 0.09). Acetylation experiments with a range of starch particles sizes showed a clear relation between the DS and the particle size.

Keywords: acetylation, potato starch, starch acetate, phase behavior, supercritical CO₂

3.1 Introduction

Starch esterification constitutes one of the most important modification reactions in the starch industry together with etherification and cross linking [1]. Among all starch esters, acetylated ones are most commercially produced [1] and used in many applications due to their favorable product properties compared to native starch. Examples are the use as thickening agents in a variety of food products, as sizing agents for the textile (wrap sizing) and paper (surface sizing) industry as well as gummed tape adhesives [2].

Starch-acetates are typically prepared by reacting native starch with an acetate source like acetic anhydride (AAH) in water (Scheme 3.1). Selectivity is a key issue and considerable amounts of acetic acid (AA) may be produced by the simultaneous hydrolysis reaction of the anhydride with water (Scheme 3.1). Another disadvantage is the high costs of water removal after reaction in the work-up/drying section of the process.



Scheme 3.1. Representative scheme of starch acetylation reaction using AAH as the reagent (for the sake of brevity only hydroxyl group substitution on position C-6 is shown).

To improve the selectivity, organic solvents such as pyridine and dimethylsulfoxide (DMSO) are used [3]. However, these solvents have a much higher environmental impact than water. Hence, there is a strong incentive to develop green, environmentally friendly solvents for starch modification reactions.

Supercritical CO₂ has shown to be an excellent solvent and processing aid for polymer processing [4, 5]. Supercritical CO₂ (scCO₂) is considered to be ‘green’, it is non-flammable, relatively non-toxic and inert. Another advantage is the ease of separation from the (reacting) system by simple depressurization [6-8]. Furthermore, supercritical conditions are not very extreme (T_c = 31°C, P_c = 7.38 MPa) which simplifies experimental studies on lab scale and subsequent industrial processing. As such, supercritical CO₂ could be an excellent solvent for chemical and physical modifications of starch [4, 9]. However,

remarkable little is known about starch modification reactions in supercritical CO₂ [4, 9]. We have recently performed exploratory studies on the synthesis of starch acetate in densified CO₂ at relatively low pressures (< 9.8 MPa) and a limited pressure effect was observed [10].

The aim of the present work is to investigate the influence of pressure on the acetylation reaction of starch in scCO₂ in a broader pressure window (8 MPa - 25 MPa) including supercritical mixture conditions. In addition, studies on the phase behavior of the system were performed in a high pressure view cell and the locus of reaction was established by performing acetylation reactions with a range of starch particle sizes.

3.2 Materials and Methods

3.2.1 Materials

Potato starch was kindly supplied by AVEBE (The Netherlands). The water content was determined by drying the potato starch in a vacuum oven at 50 °C until constant weight and was found to be 16.2 % wt/wt. Analytical grade acetic anhydride and sodium acetate were purchased from Merck (Germany). Dimethyl sulfoxide-d₆ (DMSO-d₆) was obtained from Aldrich. All chemicals were used as received without further purification. High purity CO₂ (≥ 99.7% volume) and N₂ (≥ 99.9% volume) were purchased from Hoekloos (The Netherlands).

3.2.2 Experimental set-ups

The high pressure reactor setup consists of a stirred batch reactor (Parr Instrument), an electrical heating element with temperature controller, a high pressure pump unit, and CO₂ and N₂ storage bottles (see Fig. 3.1a). The reactor has a capacity of 100 ml and may be operated in a temperature range from -10 °C to 350 °C and a maximum pressure of 35 MPa.

The CO₂ was supplied to the reactor using a membrane pump (Lewa) with a capacity of 60 kg/hr at a maximum pressure of 35 MPa. To prevent cavitation in the pump, the CO₂ is first cooled to 0 °C in a heat exchanger (Huber, The Netherlands). After pressurizing, a second heat exchanger with hot-oil is used to heat the CO₂ to the desired temperature.

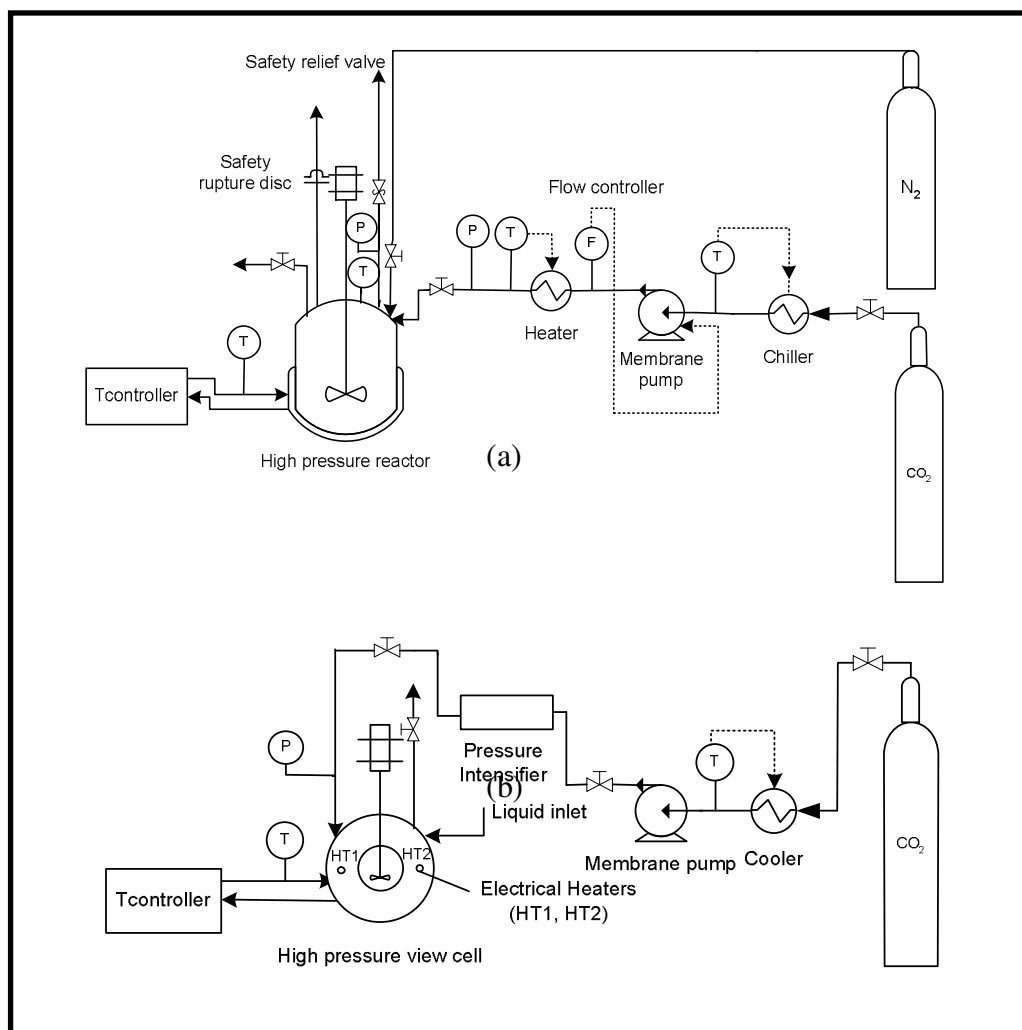


Figure 3.1. Schematic drawing of high pressure reactor set up (a) and high pressure view cell (b)

A high pressure view cell (Fig. 3.1b.) was used to determine the phase behavior of the system. It consists of a high pressure stirred view cell (NWA GmbH, Lorrach, Germany), equipped with a turbine type impeller, two stainless steel cartridge heaters (Firerod, WATLOW, Missouri, USA), a PID thermal controller (Eurotherm Controls Inc, Virginia, USA), a Bourdon type manometer (MQ1, OMET S.R.L., Milano, Italy), and a high pressure pump (NWA GmbH, Lorrach, Germany). The overall accuracy of the temperature and pressure measurements was estimated to be within ± 0.3 °C and ± 0.06 MPa, respectively. The cell has a capacity of 60 ml and may be operated at a maximum pressure of 75 MPa and a maximum temperature of 200 °C.

3.2.3 Experimental Procedure

3.2.3.1 Starch acetylation reactions in scCO₂

Potato starch was acetylated in the high pressure set-up by reacting native potato starch with AAH and an alkaline base salt as the catalyst. Native potato starch (3.53 g), AAH (4.35 mol/mol AGU), and the NaOAc (0.1 mol/mol AGU) were charged to the reactor. The reactor was flushed with N₂ to remove traces of air. Next, the autoclave was pressurized with CO₂ and heated till the desired temperature. CO₂ was added to increase the pressure to the desired level. The reaction was performed at a stirring rate of 1750 rpm. After reaction, the reactor was cooled to room temperature, depressurized and the solid products were separated from the liquid phase using a syringe. The solid product was washed several times with water (approximately 1.5 liter) to remove acetic acid and unreacted acetic anhydride, filtered, and dried in a vacuum oven (5 mbar) at 50°C until constant weight. The products were collected for further analyses. The amount of unreacted AAH in the liquid phase after reaction was determined using gas chromatography (GC).

3.2.3.2 Phase behavior studies

Phase behavior studies were carried out in the high pressure view cell. The molar ratio of AAH - starch – CO₂ was similar as in the acetylation experiments in the high pressure batch reactor. Native starch (1.7 g) was first charged in the view cell followed by the pre-determined amount of liquid acetic anhydride (4.35 mol/molAGU). The view cell was heated to the desired temperature and CO₂ was added to reach the pre-determined pressure value. The critical point of the mixture was visually determined as the point at which the biphasic AAH-CO₂ mixtures became a single (supercritical) phase. For confirmation, the cell was subsequently pressurized with CO₂ to a value approximately 10 MPa higher than the critical point. Then, the cell was carefully depressurized and the pressure at which the supercritical state changed to a biphasic state was again recorded. The critical points as determined by both measurements were equal within 0.04 MPa, confirming that thermodynamic equilibrium was indeed achieved. The AAH mole fraction (y_{AAH}) at the critical point was calculated using the following equation:

$$y_{AAH} = \frac{n_{AAH,o}}{(n_{AAH,o} + n_{CO_2,o})} \quad (3.1)$$

In Eq. 3.1 $n_{AAH,0}$ is the initial moles of AAH, $n_{CO_2,0}$ is the molar intake of CO_2 at a given pressure and temperature. Inhere, it is assumed that adsorption of both CO_2 and AAH in the starch is limited compared to the intake. To determine the molar intake of CO_2 , the density needs to be known at different pressures and temperatures. These values were obtained from the Span and Wagner EOS [11-14].

3.2.4 Analytical equipment

The product DS was determined using 1H -NMR measurements performed on an Oxford NMR AS 400 spectrometer operating at 400 MHz. The products (25 mg) were dissolved in DMSO- d_6 (2 g). The spectra were measured at 60 °C with 64 scans.

The chemical composition of the liquid phase after reaction was determined using a gas chromatograph (GC) HP 5890 series II equipped with a FID detector and HP 5 column (length = 30 m and I.D. = 0.25 mm). The GC was operated at an injector temperature of 280 °C, an oven temperature of 100 °C, a detector temperature of 300 °C, and an inlet pressure of 86 kPa. Helium was used as the carrier gas with a flow rate of 2.2 ml/min. The average particle sizes of the starch samples were determined using a Sympatec Helos/BF laser diffraction instrument equipped with Rodos dry dispersion unit.

3.2.5 Determination of the product DS

The DS of the acetylated products was calculated by comparing the unit area of the acetate protons (A_{H-ace} , at δ 1.9 – 2.1 ppm) with the unit area of the starch protons (A_{H-agu} , at δ 3.6 – 5.6 ppm) using the following equation [15, 16] :

$$DS = \frac{7A_{H-ace}}{3A_{H-agu}} \quad (3.2)$$

where A_{H-ace} is the area of the methyl signals and A_{H-agu} is the area of the proton signals of the anhydroglucose unit.

3.2.6 Determination of total AAH conversion (X_{AAH}) and product selectivity (S_{SA})

The X_{AAH} and S_{SA} were calculated on the basis of the chemical composition of the liquid phase after reaction (GC analyses). Here, X_{AAH} and S_{SA} are defined as:

$$X_{AAH} = \frac{n_{AAH,o} - n_{AAH}}{n_{AAH,o}} \times 100 \% = \frac{n_{AAH,reacted}}{n_{AAH,o}} \times 100 \% \quad (3.3)$$

$$S_{SA} = \frac{n_{AAH,p}}{n_{AAH,reacted}} \times 100 \% \quad (3.4)$$

In Eq. 3.3 and Eq. 3.4, $n_{AAH,o}$ is the initial moles of AAH, n_{AAH} is the moles of unreacted AAH, and $n_{AAH,p}$ and $n_{AAH,reacted}$ are the moles of acetate in the starch acetate product and the total moles of reacted AAH, respectively.

3.3 Results and Discussion

3.3.1 Screening experiments

A number of experiments were performed with acetic anhydride (AAH) (4.35 mol/mol AGU) as the reactant and NaOAc (0.1 mol/mol AGU) as the basic catalyst at various pressures (8-25 MPa) and two reaction times (1 and 24 h). The temperature was maintained at 90°C. After reaction, the product was washed thoroughly with water to remove un-reacted reagents and catalyst and dried at 50°C and 5 mbar till constant weight. After work-up, the products were obtained as white granular powders. The DS of the products was subsequently determined by ¹H-NMR.

The effect of pressure on the DS of the product for a 1 h reaction time is given in Figure 3.2a. The DS varies between 0.22 and 0.29. The highest DS was observed at 15 MPa pressure. The limited effect of pressure in the lower pressure regime (8 – 10 MPa, Fig 3.2) is in agreement with recent work from our group on the acetylation of starch in the subcritical pressure regime [10]. Pressure effects seem to be more important at relatively higher pressure values (> 10 MPa) and actually show a maximum in this high pressure regime. Based on literature precedents for a wide variety of chemical reactions in supercritical CO₂, the highest reaction rates and thus highest DS are expected close to the supercritical point of the reaction mixture [8, 17-19]. This indicates that the supercritical state of the reaction mixture is likely attained at about 15 MPa pressure. Further confirmation for this statement comes from phase behavior measurements in the high pressure view cell (*vide infra*).

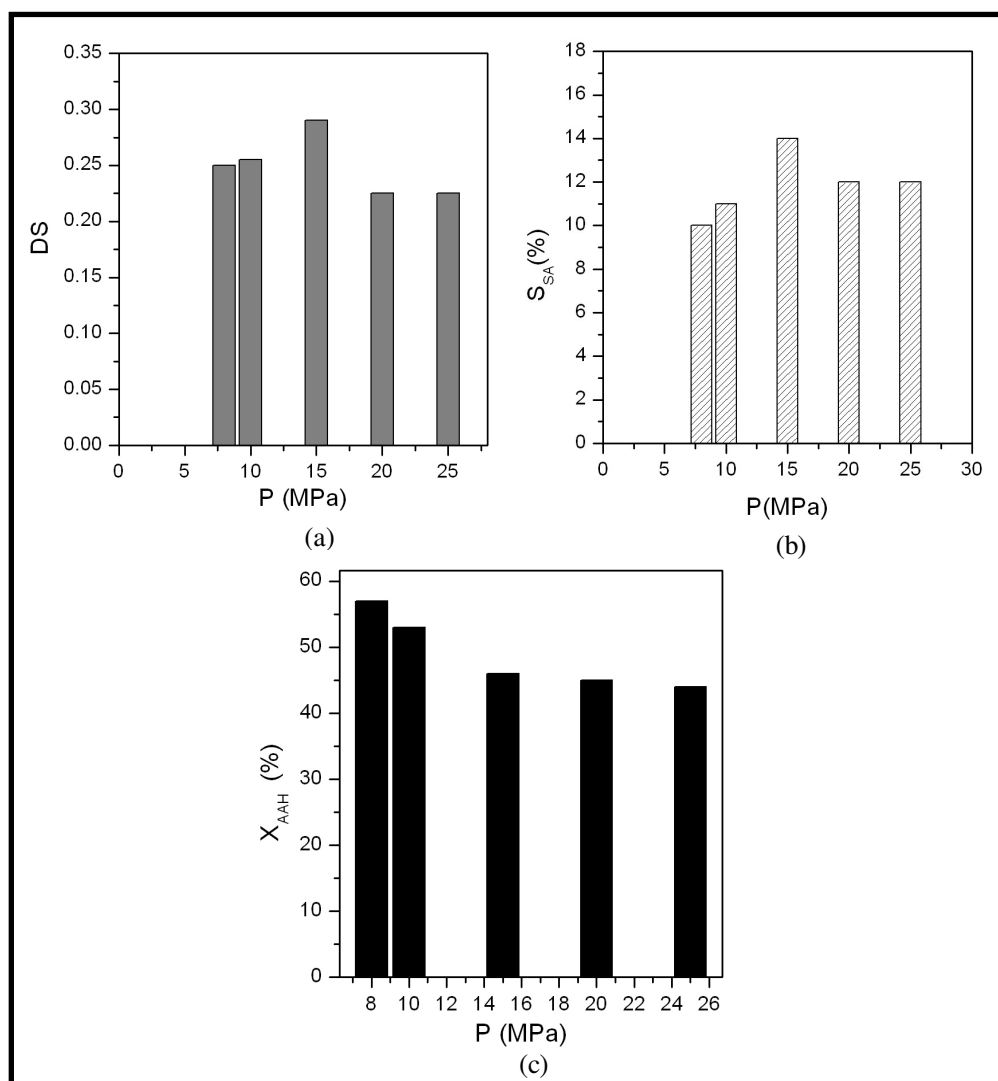


Figure 3.2. The effect of pressure on the DS (a), S_{SA} (b) and X_{AAH} (c) for 1 h reaction times at 90°C.

The X_{AAH} varies between 44 and 57%, an indication that a reaction time of 1 h is not yet sufficient to achieve full AAH conversion. AAH conversion is highest at the lowest pressures. The selectivity for the starch acetylation reaction (S_{SA}) varies between 10 and 14%, implying that the hydrolysis reaction is dominant (Figure 3.2b). The S_{SA} is highest at 15 MPa, and coincides with the highest DS value in the pressure range. The hydrolysis reaction is due to the presence of water in the starch source (16.2 wt%). It is of interest to determine the water conversion after 1 h by considering the known amount of AAH in the liquid phase (GC) after reaction and the mass balance for the system (Table 3.1).

Table 3.1. Reactivity of AAH for the starch acetylation and hydrolysis reaction^a.

P (MPa)	Water intake (x 10 ⁻³ mol)	AAH Intake (x 10 ⁻³ mol)	AAH reacted with water (x 10 ⁻³ mol)	AAH reacted with starch (x 10 ⁻³ mol)	X _{water} (%)
15	32.7	81	31.8	5.4	97
20	32.7	81	32	4.2	98

^aExperiments at 90 °C, 1 h reaction time.

It is clear that the water conversion is essentially quantitative after 1 h. Thus, it appears that in the initial phase (< 1 h), the predominant reaction is hydrolysis of AAH by residual water in the starch and that the rate for the desired acetylation reaction is considerably slower.

A significant increase in the DS value was observed (Fig 3.3) when the reactions were performed for a prolonged time (24 h). The DS increases from 0.29 for 1 h reaction time to 0.62 at 24 h (15 MPa), see Figures 3.2a and 3.3 for details. For the 24 h runs, there is a clear pressure effect as well. The DS value at 15 MPa (0.62) is considerably higher than that at 20 MPa (0.36), in line with the reactions for 1 h reaction time (Fig 3.2a).

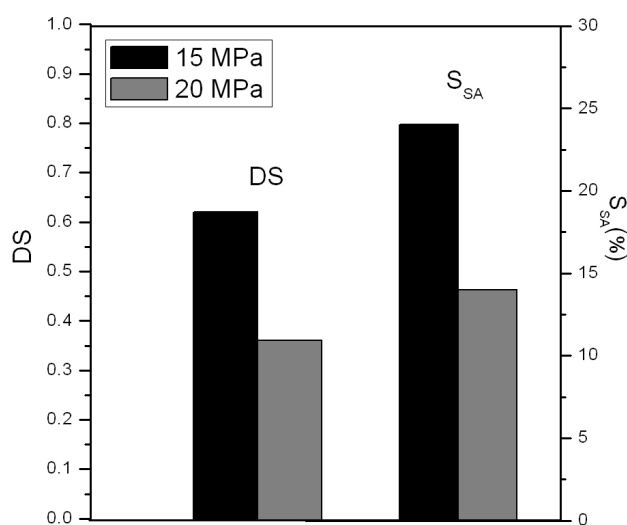


Figure 3.3. The effect of pressure on the DS and S_{SA} for 24 h reaction times.

The X_{AAH} value after 24 h (60%, 15 MPa and 54%, 20 MPa) is considerably higher than after 1 h (46% at 15 MPa and 45% at 20 MPa) (Figure not shown for brevity). However, the conversion is still far from quantitative. Based on the observation that all the water in the system is consumed by the hydrolysis reaction after 1 h (Table 3.1) and that hydrolysis thus is not occurring to a great extent anymore, we anticipated that the S_{SA} would increase when going from 1 to 24 h reaction time. This indeed proved to be the case and the S_{SA} at

24 h reaction time (24%, 15 MPa) is considerably higher than at 1 h (14%). Thus, a comparison between the 1 and 24 h runs indicate that the reaction between AAH and water is much faster than the desired acetylation reaction and that starch acetylation occurs to a considerable extent when all water has reacted.

3.3.2 Discussion

The system under study is complex in nature and should either be regarded as a solid/scCO₂ system or a solid/gas/liquid system. The actual state will depend on whether the CO₂/AAH mixture is actually in the supercritical state or present as a separate gas and liquid phase. In such multiphase systems, not only the intrinsic kinetics of the reactions determine the activity and selectivity of the desired acetylation reaction but mass transfer and solubility effects may play a major and even decisive role [17, 20]. The relative rate of chemical reaction compared to the rate of mass transfer in the starch particle determines the locus of reaction (mainly surface or uniformly inside the particle). The locus of the undesired hydrolysis reaction may be either in the liquid phase/supercritical state outside a starch particle or inside the starch particle and this further complicates the analyses. To gain insights in the locus of the reaction and the phase behavior at different temperatures and pressure, separate experiments in a high pressure view cell and using starch particles with a smaller average sizes were performed and will be presented in the following.

3.3.2.1 Phase behavior of the CO₂/AAH/starch mixture as a function of temperature and pressure

The phase behavior of the solid starch/CO₂/AAH mixtures was investigated in a high pressure view cell (Fig 3.1b) that enabled visual observation of the phase changes in the system at different pressures (4 – 25 MPa) and temperatures (50 – 90 °C). The system was studied in the absence of catalyst. The critical point of the mixtures was assessed by increasing the system pressure to 10 MPa higher than the supercritical state, followed by a gradual decrease of the pressure. In the first step (increasing the system pressure), the critical point was determined as the point at which the biphasic AAH-CO₂ mixtures became a single (supercritical) state, while in the second step (decreasing the system pressure) the occurrence of a biphasic AAH-CO₂ mixture from the single supercritical state was marked as the critical point of the mixtures. The critical points as determined from both steps should be equal in case thermodynamic equilibrium is reached after every step.

The observations of the phase changes in the first step are visualized in Figure 3.4 (from 8 to 15 MPa at 90 °C and from 8 to 10 MPa at 50 °C). It is clear that the fluids change from a gas-liquid AAH – CO₂ mixture (from 8 to 14.5 MPa) to a mono-phasic (supercritical) region at about 15 MPa. A further increase of the pressure to 25 MPa followed by a decrease in pressure results in the formation of a separate gas- and liquid phase at 15 MPa, a confirmation that the supercritical state is indeed achieved at about 15 MPa. On the basis of the intakes, it may be calculated that the AAH mole fraction (y_{AAH}), in the supercritical fluid is about 0.09 (Eq 3.1). The critical point as visually observed is in agreement with the literature values, where the critical point of an AAH-CO₂ mixture (y_{AAH} of 0.097) at 90 °C was found at 14.84 MPa [21].

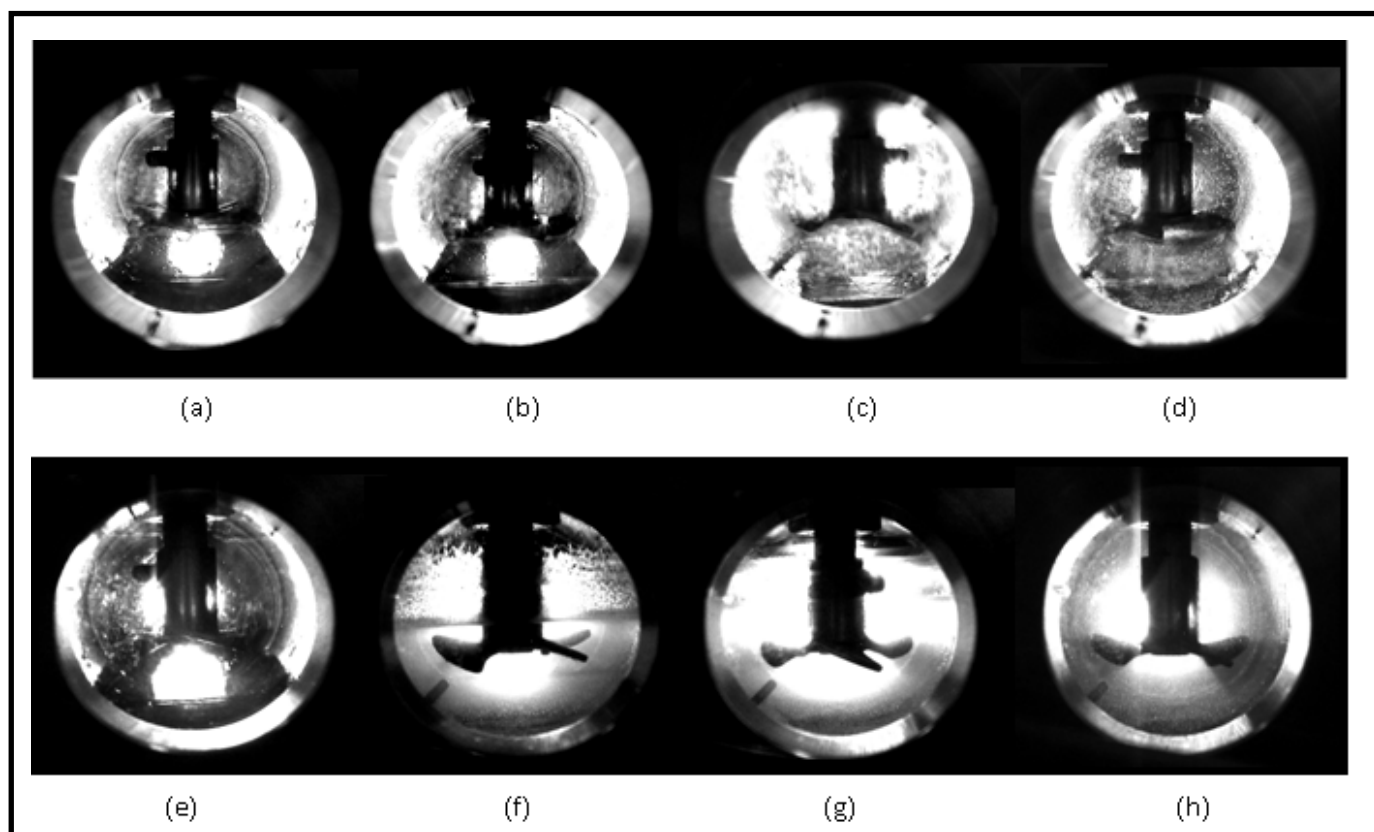


Figure 3.4. Phase behavior of starch-acetic anhydride-scCO₂ mixtures at 90°C with pressure of 8 MPa (a) 9.8 MPa (b) 14.5 MPa (c) and 15 MPa (d) and at 50°C with pressure of 8 MPa (e) 9.4 MPa (f) 9.9 MPa (g) 10 MPa (h)

A similar behavior was observed at 50 °C (Figure 3.4). Here, the gas-liquid mixture becomes a single phase at 10 MPa (Fig 3.4h) which indicates that the critical pressure of the mixtures is in the range from 9.4 – 10 MPa (y_{AAH} of 0.08). Moreover, the critical

pressure of the same mixtures at a temperature of 70 °C (y_{AAH} of 0.09, calculated using Eq 3.1) was also determined experimentally and found in the range between 12.4 and 12.6 MPa (figures not shown for brevity). Thus, the observations in the high pressure view cell clearly show that the critical conditions (P and T) for binary CO₂/AAH mixtures are a function of temperature of the system (Table 3.2) and generally higher than those of pure CO₂.

Table 3.2. The critical region of AAH-CO₂ mixtures at different temperatures

No	T (°C)	Critical region (MPa)	y_{AAH}
1	50	9.4 – 9.8	0.08
2	70	12.4 – 12.6	0.09
3	90	14.5 – 14.8	0.09

3.3.2.2 Acetylation reactions using starch samples with different particle sizes

The locus of the acetylation reaction (mainly surface or uniformly inside the starch particle) in scCO₂ was studied by performing experiments with a range of starch particle sizes at two conditions (50 °C, 8 MPa and 90 °C, 15 MPa). The various particle size fractions were prepared by fractionation of the granular starch feed into four different size fractions (Table 3.3). The fraction with a particle size < 36 μm was discarded as the amount in a standard sieve experiment was by far too limited to perform an acetylation experiment. The volume based particle size distribution of each fraction was determined using laser diffraction combined with a theoretical model-based matrix such as Fraunhofer or Mie [22]. The average particle sizes were determined from the particle size distribution.

The DS values of the products after the acetylation reaction of the four different particle fractions for both experimental conditions are given in Table 3.3. For both reactions, the DS is a clear function of the average particle size and reactions with larger average particle size leads to a lower DS value. This suggests that the surface area plays an important role during the acetylation reaction in pressurized CO₂. It implies that the starch acetylation reaction rate under sub- and supercritical conditions is faster than mass transfer of the substrates/catalyst inside the starch granules [23]. Furthermore, it also emphasizes that the intrinsic kinetics of the chemical reaction are of less relevance for the overall conversion rates.

Table 3.3. The comparison of DS of various particle sizes at different reaction condition

Particle sizes ^a (μm)	Average Particle Size (d_v) ^b (μm)	Condition I ^c	Condition II ^d
		DS	DS
36 - 45	43.64	0.21	0.51
45 - 56	52.33	0.18	0.48
56 - 63	62.55	0.18	0.46
> 63	73.5	0.15	0.29

^a fractionated with specified sieve trays, ^b determined by laser diffraction ^cExperiments at 50 °C, 8 MPa , ^dExperiments at 90 °C, 15 MPa

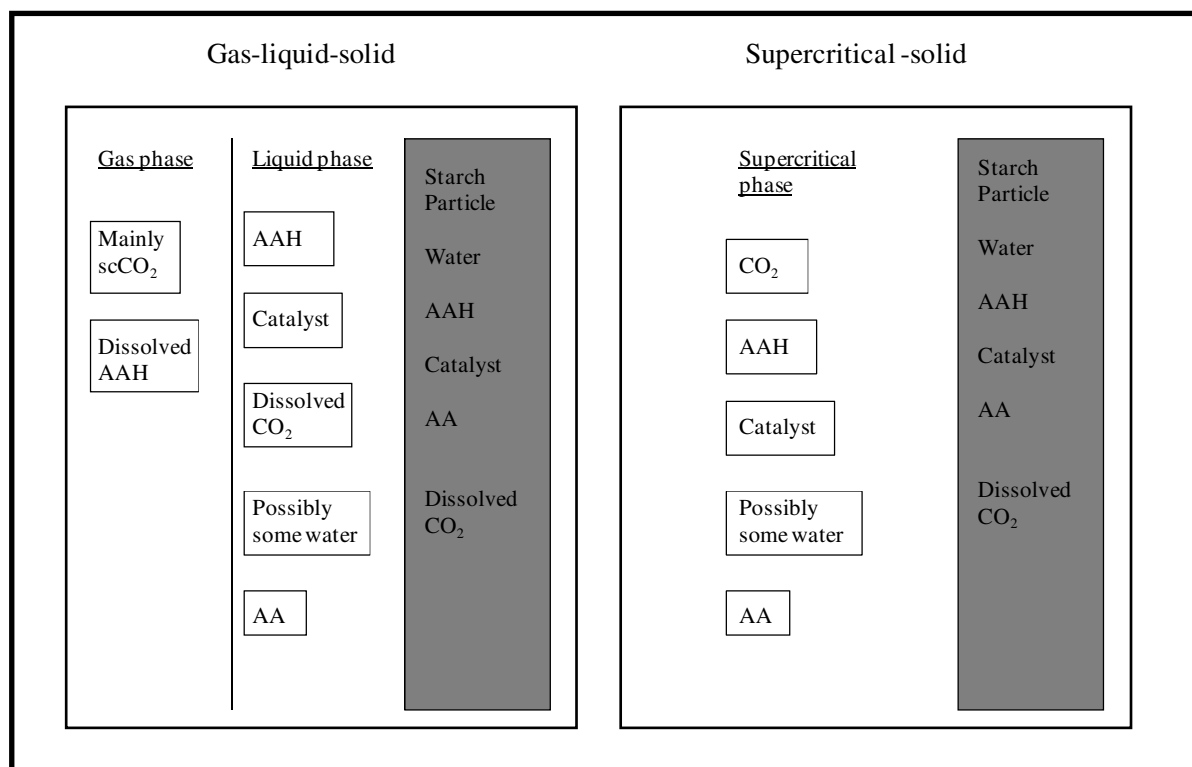
Elegant studies by Steeneken and Woortman (2008) for the acetylation of potato starch using acetic anhydride in water have also shown a clear effect of the particle sizes on the product DS [23]. Similar results were obtained by Chen et al. (2004) for acetylated potato starch synthesized in water with the same reagents [24]. Thus, a limitation of the overall reaction rates by intra-particle mass transfer effects seems valid for both water and CO₂.

3.3.2.3 The effect of pressure and temperature on the starch acetylation reaction

With the available data for the supercritical points of the mixture and the observation that the starch acetylation reaction is strongly intra-particle mass transfer controlled leading to DS gradients in any given particle, the major factors that determine the reactivity of the system may be discussed and rationalized. The system characteristics will be evaluated in the subcritical state (gas-liquid-solid system) and above the critical state (Scheme 3.2).

When the system is below the critical point, it consist of a CO₂ rich gas phase, a liquid phase of mainly AAH and solid starch particles (Scheme 3.2, left). A complicating factor is the presence of water in the starch granule, which may distribute between the three phases. Based on the high affinity of starch for water, it is assumed that most of the water resides in the starch particles [25, 26]. CO₂ is slightly soluble in starch, and about 5-50 mg CO₂/g starch (T = 40 – 120 °C) is expected to be present in the subcritical state below 8 MPa based on literature data [27-29]. These values were measured for the binary system CO₂/starch and may change when AAH is present. The starch acetylation reaction takes place mainly on the surface of the starch particles and is limited by mass transfer of reactants inside the starch granule. The undesired hydrolysis reaction occurs likely inside the starch particle (high water concentration), though it cannot be excluded that the reaction takes place also in the liquid (AAH) phase. The undesired reaction between AAH

and water is much faster than the reaction between starch and AAH as it is evident from the low S_{SA} values (max 11% at a pressure of 10 MPa, 90 °C, see Figure 3.2).



Scheme 3.2. Schematic representation of the various phases for the system CO₂/AAH/starch (left: below supercritical state; right: above critical state).

In this situation, one could argue whether there is a positive effect of the presence of CO₂ in the system. Further evidence comes from earlier studies in our group on the acetylation reaction at subcritical conditions and indeed showed a positive effect of CO₂ [30]. For this purpose, the reactions were carried out in CO₂ and N₂ under otherwise similar conditions (50 °C and a pressure of 8 MPa). The DS of the products made in CO₂ were twice that of in N₂, confirming a positive effect of CO₂ on the starch acetylation reaction.

The positive influence of CO₂ pressure is thus most probably related to higher mass transfer rates of AAH inside the starch particle and possibly also of the catalyst due to plasticization, swelling and gelatinization of the starch particle. The special role of scCO₂ on the gelatinization of starch has been reported elsewhere [31, 32].

In the subcritical region, pressure effects are evident on the DS, X_{AAH} and the S_{SA} (Figure 3.2). When increasing the pressure in the subcritical pressure range from 8 to 15 MPa, the DS and S_{SA} increase and the X_{AAH} is reduced (1 h reaction time). Thus, the rate

of starch acetylation is enhanced compared to the rate of the undesired hydrolysis reaction. It is reasonable to assume that the rate of the fast hydrolysis reaction is reduced at higher pressures in the subcritical region (in line with a lower X_{AAH}) compared to the acetylation reaction, leading to a lower X_{AAH} , higher DS and S_{SA} . At this stage, we do not have a sound explanation at molecular level for these experimental observations.

In the supercritical regime (Scheme 3.2, right), the liquid AAH is miscible with the CO₂ gas phase and forms a single supercritical phase. The DS value is highest at the critical point of the system and then reduces again (Figure 3.2). This is likely caused by compressive effects at higher pressure which lead to a reduction of the free volume in the starch particle [31]. Thus, contrary to the plasticizing effect, the compressive effect will lead to a reduction of the CO₂ solubility and thus to a lower diffusion rate of the reactants into the starch granules (lower mass transfer rate), leading to lower DS values [31, 33]. In addition, the highest DS value at the critical point may be due to a higher intrinsic reaction rate at the critical point, as observed in the literature [8, 17-19]. The effect is rather limited (DS from 0.25 at 8 MPa to 0.31 at 15 MPa), which is due to the fact that the overall reaction rate for the starch acetylation reaction is dominated by mass transfer effects (*vide supra*).

The X_{AAH} is rather insensitive to the pressure above the critical point whereas the S_{SA} is reduced (Figure 3.2). In the supercritical regime, the AAH outside the starch particle is diluted and distributes between the supercritical phase and the starch particles. Compared to the subcritical state, where AAH is present as a separate phase, this is expected to lead to a lower reactivity for particularly the fast hydrolysis reaction, independent whether the reaction occurs in the starch particle or outside. Indeed, experimentally the X_{AAH} was found to be a function of the pressure, with a lower value in the supercritical state than in the subcritical state (Figure 3.2).

The rate of the undesired reaction between AAH and water in the supercritical regime is, like in the subcritical state, much faster than the reaction between starch and AAH as evident from the low S_{SA} values (max 0.14 at a pressure of 15 MPa, 90 °C, 1 h see Figure 3.2).

The experimental findings reported here in combination with literature data have provided insights in the acetylation reaction of starch in pressurised CO₂. However, a full description of the system and quantification in the form of a chemical reaction engineering model is far from reality. It will require detailed information on phase composition of all components in both regimes, the intrinsic kinetics of the hydrolysis reaction and the

acetylation reaction in the relevant process window. A further complication not discussed here in detail is a change in the physical properties of the starch particles during the acetylation reaction. Acetylated starch is known to have a higher CO₂ solubility [29] and this will lead to changes in intra-particle mass transfer rates of AAH and catalyst within the starch particle.

3.4 Conclusions

This paper describes an in-depth study to evaluate the effects of pressure, temperature and reaction time on the acetylation of starch with acetic anhydride and NaOAc as the catalyst in pressurized CO₂. The relevant process parameters (DS, X_{AAH}, S_{SA}) were shown to be a clear function of the process variables. The DS values showed a clear pressure effect, indicating that pressure is a very suitable process parameter to tune the DS to the desired value for a given application. This is a unique feature of the CO₂ system. The experimental results were explained qualitatively for two regimes of operation (sub- and supercritical). Here, it is particularly relevant to mention that the supercritical conditions were attained at a much higher pressures than for pure CO₂ only. Furthermore, it was proven that the rate of the desired acetylation reaction in the starch particle is mainly governed by mass transfer effects and that the intrinsic kinetics are of less importance. Further studies using chemical reactor engineering principles will be required to quantify the complex interactions between mass transfer and the overall acetylation kinetics.

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