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## Synthesis of Higher Fatty Acid Starch Esters using Vinyl Laurate and Stearate as Reactants

This paper describes the synthesis of long-chain fatty esters of corn starch (starch laurate and starch stearate) with a broad range in degree of substitution (DS = 0.24–2.96). The fatty esters were prepared by reacting the starch with vinyl laurate or vinyl stearate in the presence of basic catalysts ( $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_2\text{CO}_3$ , and Na acetate) in DMSO at 110°C. The yellowish products were characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR and FT-IR. The DS of the products is a function of the carbon number of the fatty acid chain, vinyl ester to starch ratio and the type of catalyst. When performing the reactions using  $\text{Na}_2\text{HPO}_4$  as the catalyst, the DS for the starch laurate compounds is higher than for the corresponding starch stearates. For low vinyl ester to starch ratios, an increase in the vinyl ester concentration leads to higher product DS values. At higher ratios, the DS decreases, presumably due to a reduction of the polarity of the reaction medium.  $\text{K}_2\text{CO}_3$  and Na acetate are superior catalysts with respect to activity compared to  $\text{Na}_2\text{HPO}_4$  and products with DS values close to 3 were obtained.

**Keywords:** Corn starch; Esterification; Vinyl laurate; Vinyl stearate

### 1 Introduction

Green biodegradable polymers derived from natural resources are potentially very interesting substitutes for non-biodegradable petroleum-based polymers. An attractive field of application for these polymers is the use as packaging materials. For the current petrochemical-based products recycling is often neither practical nor economically feasible [1].

Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials. In particular starch is attractive as it is relatively cheap and abundantly available. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processibility (high viscosity), high brittleness, and incompatibility with hydrophobic polymers. Further modification of starch is therefore required to introduce hydrophobicity and to improve mechanical and moisture barrier properties.

Esterification of starch with low molecular weight fatty acid derivatives is one of the oldest modification technologies to improve starch properties. The first paper on the acetylation of starch was already published in 1865 [2]. However, most of the studies performed to date use

short-chain carboxylic acids ( $\text{C}_1$ – $\text{C}_4$ ), and particularly acetic acid derivatives ( $\text{C}_2$ ) [2–4].

The introduction of acetate groups on starch makes the product more hydrophobic, and consequently, more water-resistant products may be obtained [3, 4]. The hydrophobicity increases with the degree of acetate substitution (DS, defined as the moles of substituents per mole of anhydroglucose (AHG) units) [4]. However, the mechanical properties of high-DS starch derivatives of short-chain carboxylic acids still need considerable improvements before large-scale application as packaging materials becomes within reach. The major obstacle is the pronounced brittleness of the materials, even after the addition of plasticizers [5]. To improve the mechanical properties, higher carboxylic acid ( $\text{C}_4$ – $\text{C}_6$ ) [6], and even fatty acid derivatives ( $\text{C}_{12}$ – $\text{C}_{18}$ ) have been used in the modification reaction [5, 7], resulting in products with DS values up to 2.7 [1, 5]. The mechanical properties and hydrophobicity of the products were significantly improved when using these longer-chain fatty acid precursors [1, 5]. However, the fatty ester substituents [1, 5, 6] were introduced using fatty acid chloride reagents, that are relatively expensive and rather corrosive [7]. An alternative method using methyl and glyceryl laurate esters in the absence of solvent has been recently developed [7]. Relatively low-DS (0.34–0.61) products were obtained using this approach.

Recently *Mormann et al.* [8] explored the possibility of using vinyl esters and particularly vinyl acetate as reagents for the preparation of starch esters. Their re-

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search focused on the synthesis of starch acetates and only two examples of a reaction with a higher fatty acid vinyl ester were reported. The reactions were either performed in water or in DMSO using a basic catalyst ( $\text{Na}_2\text{HPO}_4$ ). The maximum attainable DS of starch acetate in water was below 1 and limited to 0.01, when using vinyl laurate. In DMSO, starch esters with a substantially higher DS value (up to 1.6 for starch acetate ester) were obtained. This solvent effect is likely caused by the higher solubility of the vinyl esters in DMSO than in water, leading to higher reaction rates.

In the following an investigation on the synthesis of higher fatty acid esters of starch is reported with an emphasis on the introduction of laurate and stearate ester side chains. The synthesis of starch stearate esters using vinyl ester reagents has, to the best of our knowledge, not been reported to date. The effects of the starch to vinyl ester ratio on the reaction rates and DS have been explored. In addition, the use of basic catalysts other than  $\text{Na}_2\text{HPO}_4$  has been investigated. The effect of the addition of a non-polar solvent (toluene) to the reaction medium to solubilise the products and thus to enhance the reaction rates has also been studied.

## 2 Materials and Methods

### 2.1 Materials

Corn starch (approx. 73% amylopectin and 27% amylose) was purchased from Sigma (Seelze, Germany). The starch was dried before use for 48 h at 105°C under vacuum (approx.  $\sim 0.1$  kPa), leading to a moisture content of 2% (w/w) (measured gravimetrically). Analytical grade vinyl stearate (Aldrich, Tokyo, Japan), vinyl laurate (Fluka, Seelze, Germany) and acetic anhydride (Merck, Darmstadt, Germany) were used without further purification. Potassium carbonate (Boom, Meppel, the Netherlands), sodium acetate (Merck) and disodium hydrogenphosphate (Merck) were used as received. Technical grade dimethyl sulfoxide (DMSO), 4-*N,N*-dimethylaminopyridine (DMAP), and tetrahydrofuran (THF) were supplied by Acros (Geel, Belgium) and were also used as received.

### 2.2 Analytical equipment

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a 400 MHz Varian AMX NMR machine (Varian, Palo Alto, CA, USA). The spectra were recorded at 50°C, as recommended by Laignel *et al.* [9]. IR spectra were recorded on a Spectrum 2000 FT-IR Spectrometer (Perkin Elmer, Norwalk, CT, USA). The products were placed directly on the

diamond plate and 50 scans with a resolution of  $4\text{ cm}^{-1}$  were recorded.

## 2.3 Methods

### 2.3.1 Typical example of the synthesis of laurate and stearate esters of corn starch

Corn starch (0.5 g) was first gelatinized in DMSO (5 mL) at 70°C for 3 h, resulting in the formation of a homogenous transparent solution. Subsequently, vinyl laurate or vinyl stearate (3 mol/mol AHG units in starch) and potassium carbonate catalyst (2%, w/w, with respect to starch) were added and the mixture was stirred at 110°C for 24 h. After cooling, the product was precipitated using methanol (100 mL) and separated from the liquid phase by decantation. The product was washed twice with methanol (50 and 25 mL, respectively). Finally, the product was dried in a vacuum oven (70°C, approximately 0.5 kPa) for 24 h until constant weight.

The samples were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and FT-IR. The atom numbering scheme is given in Fig. 1, typical spectra are given in Fig. 2 ( $^1\text{H}$ -NMR), Fig. 3 ( $^{13}\text{C}$ -NMR) and Fig. 4 (FT-IR).

Starch-laurate (Sample 15, Tab. 1, DS = 2.52):

$^1\text{H}$ -NMR (before peracetylation,  $\text{CDCl}_3$ ):  $\delta$  0.9 (t, 3H, (12), 1.1 (m, broad peaks, 16H, C4-11), 1.5 (m, 2H, C3), 2.4 (m, broad peaks, 2H, C2), 3-6 ppm (m, broad peaks, 7H, C1S-6S).

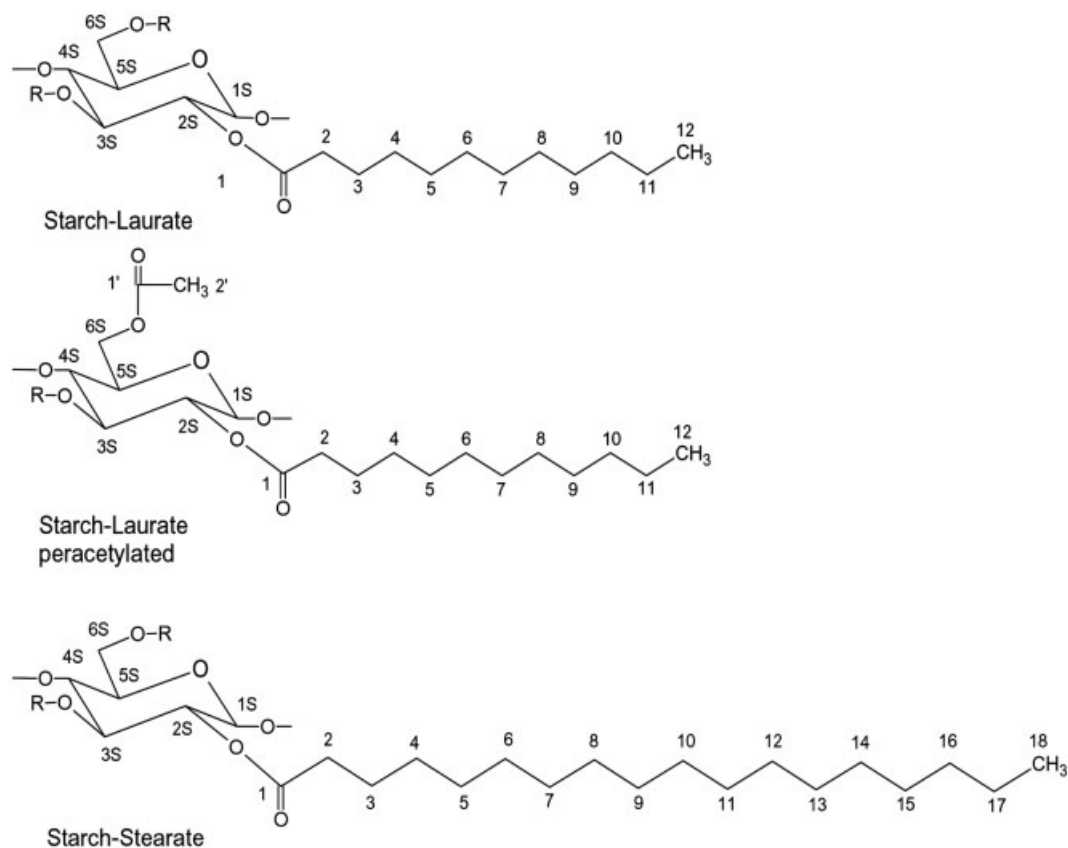
$^1\text{H}$ -NMR (after peracetylation,  $\text{CDCl}_3$ ):  $\delta$  0.9 (t, 3H, C12), 1.3 (m, broad peaks, 16H, C4-11), 1.5 (m, 2H, C3), 1.8-2.6 (m, broad peaks, 3H, C2'), 2.3 (m, 2H, C2), 3-6 ppm (m, 7H, C1S-6S).

$^{13}\text{C}$ -NMR (before peracetylation,  $\text{CDCl}_3$ ):  $\delta$  14.0 (C12), 22.7 (C11), 24.9 (C3), 28-32 (C4-9), 31.9 (C10), 34.1 (C11), 61.9 (broad, C6S), 68-74 (broad, C2S, 3S, 5S), 76-78 ppm, overlap with  $\text{CDCl}_3$  (C4S), 95.4 (broad, C1S), 172-174 ppm (C=O, attached to O-C2S, O-C3S, and O-C6S).

FT-IR ( $\text{cm}^{-1}$ ): 2920 (C-H stretching), 2850 (C-H stretching), 1740 (C=O), 1455 ( $\text{CH}_2$ ), 1410 (C-H bending), 1370 (C-H bending), 1350 (C-H bending), 1295, 1230 (C-O stretching), 1150 (C-O stretching), 1110 (C-O stretching), 1020 (C-O stretching), 935 (C-O stretching), 760, 720.

Starch-stearate (Sample 17, Tab. 1, DS = 2.96)

$^1\text{H}$ -NMR (before peracetylation,  $\text{CDCl}_3$ ):  $\delta$  0.9 (t, 3H, C18), 1.0 (m, broad peaks, 28H, C4-C17), 1.5 (m, 2H, C3), 2.3 (m, broad peaks, 2H, C2), 3-6 ppm (m, broad peaks, 7H, C1S-6S).



**Fig. 1.** Numbering scheme for carbon atoms of products.

**Tab. 1.** Overview of the esterification of starch using vinyl-esters and basic catalysts<sup>a</sup>.

Exp.	Vinyl ester	Catalyst	Vinyl ester: AHG ratio [mol/mol]	Amount of toluene added [mL]	DS
1	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	2	-	1.13
2	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	3	-	1.23
3	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	6	-	0.90
4	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	2	5	0.99
5	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	3	5	1.07
6	Laurate	Na <sub>2</sub> HPO <sub>4</sub>	6	5	0.90
7	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	2	-	1.08
8	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	3	-	1.05
9	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	4	-	0.91
10	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	6	-	0.60
11	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	2	5	1.01
12	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	3	5	0.57
13	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	4	5	0.68
14	Stearate	Na <sub>2</sub> HPO <sub>4</sub>	6	5	0.24
15	Laurate	K <sub>2</sub> CO <sub>3</sub>	3	-	2.52
16	Laurate	CH <sub>3</sub> COONa	3	-	2.54
17	Stearate	K <sub>2</sub> CO <sub>3</sub>	3	-	2.96
18	Stearate	CH <sub>3</sub> COONa	3	-	2.44

<sup>a</sup> All experiments were performed at 24 h at 110°C in DMSO with a catalyst concentration of 2% (w/w) based on starch.

$^1\text{H-NMR}$  (after peracetylation,  $\text{CDCl}_3$ ):  $\delta$  0.9 (t, 3H, C18), 1.3 (m, broad peaks, 28H, C4–C17), 1.5 (m, 2H, C3), 1.8–2.6 (m, broad peaks, 3H, C2'), 2.4 (m, 2H, C2), 3–6 ppm (m, 7H, C1S–6S).

$^{13}\text{C-NMR}$  (before peracetylation,  $\text{CDCl}_3$ ):  $\delta$  14.0 (C18), 22.7 (C17), 25.0 (C3), 26–32 (C4–15), 32.0 (C16), 34.2 (C2), 61.4 (broad, C6S), 68–74 (broad, C2S, 3S, 5S), 75.7 (C4S), 95.5 (broad, C1S), 172–174 ppm (C=O, attached to O-C2S, O-C3S, and O-C6S).

FT-IR ( $\text{cm}^{-1}$ ): 2920 (C-H stretching), 2850 (C-H stretching), 1740 (C=O), 1455 ( $\text{CH}_2$ ), 1410 (C-H bending), 1370 (C-H bending), 1350 (C-H bending), 1295, 1150 (C-O stretching), 1100 (C-O stretching), 1020 (C-O stretching), 950 (C-O stretching), 865, 760, 720.

### 2.3.2 Peracetylation procedure

The presence of remaining hydroxyl groups in the products resulted in broad and overlapping starch resonances in  $^1\text{H-NMR}$  spectra [10] and hampered calculation of the DS. A peracetylation reaction to substitute all of the remaining hydroxyl groups with acetate groups was applied to obtain reliable DS data. The peracetylation procedure by *Einfeldt et al.* [11] was applied. Typically, the starch ester (0.1 g) was suspended in THF (4%, w/v) and stirred at  $55^\circ\text{C}$  until the starch was fully dissolved (typically 3 h). Subsequently, the peracetylating reagents (DMAP, acetic anhydride and pyridine in a DMAP: acetic anhydride: pyridine: AHG molar ratio of 1: 10: 22: 1) were added. The peracetylation reaction was conducted for 7 h at  $50^\circ\text{C}$ . The product was precipitated by the addition of methanol and washed several times with methanol. It was finally dried overnight in a vacuum oven at  $70^\circ\text{C}$  and 0.5 kPa until constant weight.

### 2.3.3 Determination of the degree of substitution

The DS of the product was calculated using  $^1\text{H-NMR}$  spectra of the products after peracetylation. The DS of the fatty acid esters was calculated from the DS of the products after peracetylation (Eq. 1).

$$\text{DS}_{\text{fattyester}} = 3 - \text{DS}_{\text{acetate}} \quad (1)$$

The DS of the acetate groups of the products may be calculated by comparing the unit area of the acetate protons ( $A_{\text{H-acetate}}$ ) to the unit area of the starch protons (calculated from the intensity of the starch peaks at  $\delta$  3.6–5.6 ppm). The procedure was described earlier by *Elomaa et al.* [10] and the relevant equations are given below:

$$\text{DS}_{\text{acetate}} = \frac{A_{\text{H-acetate}}}{A_{\text{H-starch}}} \quad (2)$$

$$A_{\text{H-starch}} = \frac{A_{3.6-5.6}}{7} \quad (3)$$

Determination of the unit area of the acetate H-atoms ( $A_{\text{H-acetate}}$ ) is hampered by peak overlap with the H-atoms attached to C2 ( $A_{\text{C2}}$ ) of the fatty acid chains ( $\delta$  1.8–2.6 ppm range) and a correction has to be made (Eq. 4).

$$A_{\text{H-acetate}} = \frac{A_{1.8-2.6} - A_{\text{C2}}}{3} \quad (4)$$

$$A_{\text{C2}} = 2 \times A_{\text{H-fattyester}} \quad (5)$$

The  $A_{\text{C2}}$  values of both the laurate and stearate side chains were calculated from the peak intensity in the range  $\delta$  0.5–1.8 ppm (protons attached to the fatty acid carbons C3–C12 for laurate and C3–C18 for stearate) using Equations 5, 6 and 7:

$$A_{\text{H-fattyester}} = \frac{A_{\text{C3-C12}}}{21} = \frac{A_{0.5-1.8}}{21} \text{ (laurate)} \quad (6)$$

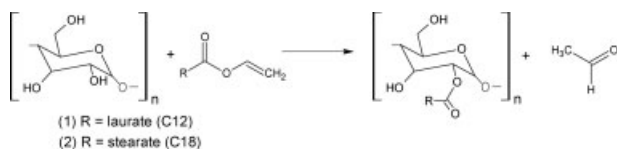
$$A_{\text{H-fattyester}} = \frac{A_{\text{C3-C18}}}{33} = \frac{A_{0.5-1.8}}{33} \text{ (stearate)} \quad (7)$$

In Equations (3)–(7),  $A_{x-y}$  stands for the peak area in the range  $\delta$   $x$ - $y$  ppm, while  $A_{\text{Cx-Cy}}$  is the area of the H-atoms attached to carbons in the range  $\text{C}_x$ - $\text{C}_y$  (carbon numbering scheme is given in Fig. 1).

## 3 Results and Discussion

### 3.1 Exploratory experiments

A number of exploratory experiments were carried out with vinyl laurate and vinyl stearate (vinyl ester: AHG molar ratio of 3: 1) at  $110^\circ\text{C}$  for 24 h in DMSO using  $\text{K}_2\text{CO}_3$  as the catalyst. A schematic representation of the esterification reaction of starch with the vinyl esters is provided in Scheme 1.



The reaction was performed in two discrete steps. Initially, the starch was gelatinised in DMSO at  $70^\circ\text{C}$  for 3 h to make the hydroxyl groups of starch more accessible for reaction. Subsequently, the vinyl ester and the catalyst were added and the reaction mixture was heated to  $110^\circ\text{C}$ . After 2–3 h, the esterified starch started to separate from the medium in the form of a gel. After 24 h, the brownish gel was precipitated with methanol and the product was collected after vacuum drying in the form of a transparent, light yellow solid. The products of these

exploratory reactions are insoluble in water and DMSO, but swell in organic solvents such as toluene and THF.

The DS of the products was determined by using NMR (see above). When using a vinyl laurate: AHG molar ratio of 3 and  $K_2CO_3$  as the catalyst, a product DS of 2.52 was obtained. A reaction with vinyl stearate at similar conditions resulted in a stearate starch ester with a DS of 2.96.

## 3.2 Product characterisation

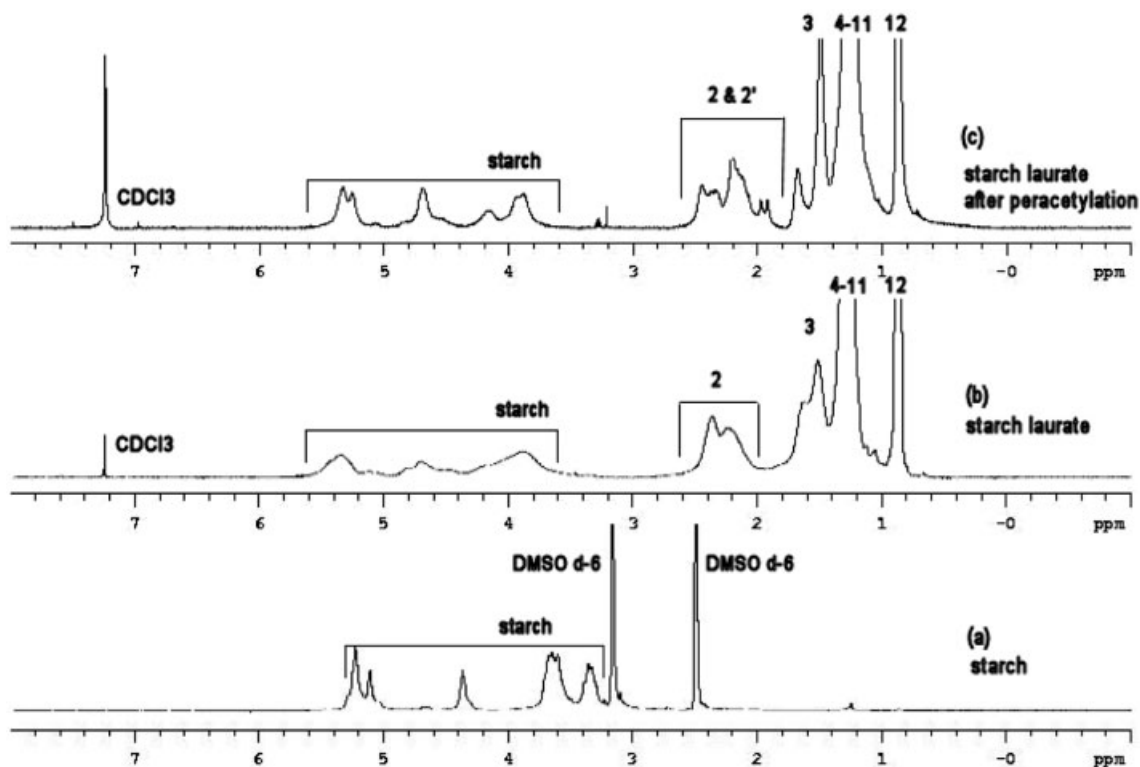
### 3.2.1 $^1H$ - and $^{13}C$ -NMR analyses

The solubility of the products in common NMR solvents ( $DMSO-d_6$  or  $CDCl_3$ ) is a function of the product DS. Medium-DS starch laurate and starch stearate ( $1 < DS < 2$ ) dissolve poorly in  $DMSO-d_6$  and  $CDCl_3$ , even at higher temperatures ( $50^\circ C$ ). Higher DS products have a higher solubility in  $CDCl_3$  and good-quality  $^1H$ - and  $^{13}C$ -NMR spectra could be obtained (Figs. 2 and 3).

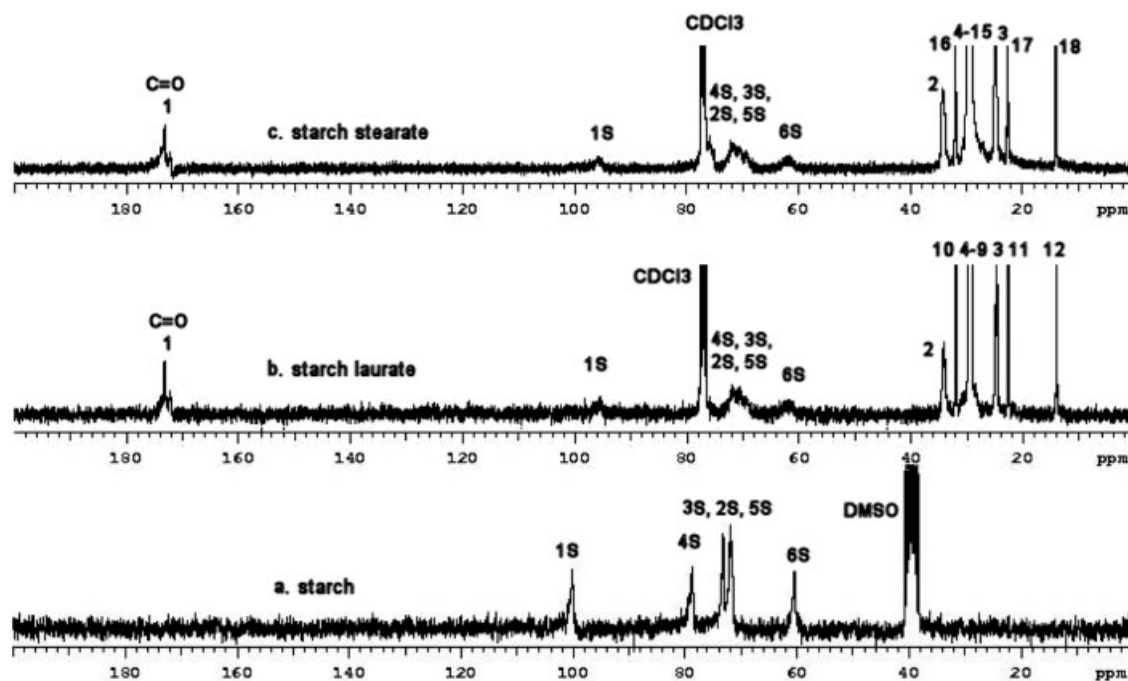
A typical  $^1H$ -NMR spectrum of starch laurate is shown in Fig. 2. Clearly visible are the peaks arising from starch and the aliphatic hydrogen atoms of the fatty acid chain ( $\delta$  0.8–2.5 ppm). The starch peaks ( $\delta$  3–5.5 ppm) are broad and

overlapping [10]. This feature hampers the DS determination by NMR, and therefore a peracetylation procedure to substitute all of the remaining OH groups with acetate groups was applied [8, 10, 11]. The  $^1H$ -NMR spectrum of a typical peracetylated starch laurate is shown in Fig. 2c. NMR spectra of the peracetylated products are considerably improved in terms of peak resolution and allow a more reliable calculation of the DS. The proton signals of the acetate methyl group, required for DS determinations, are together with the  $CH_2$  groups of the acid chain adjacent to the ester moiety in the range  $\delta$  1.8–2.3 ppm.

Typical  $^{13}C$ -NMR spectra of the products are given in Fig. 3. Clearly visible are the carbon resonances of the fatty ester chains ( $\delta$  10–35 ppm) and the C atom of the ester group ( $\delta$  170–175 ppm). The resonances arising from the anhydroglucose unit of starch are broadened. Two of the carbon resonances (1S and 4S) are considerably shifted compared to native starch. The same phenomenon was observed by Dicke for starch acetate [12]. The shift of the starch peaks and the presence of peaks arising from the fatty ester chains clearly indicate that the esterification reaction with vinyl laurate and vinyl stearate was successful.



**Fig. 2.** Typical  $^1H$ -NMR spectrum of (a) native starch in  $DMSO-d_6$  at  $60^\circ C$ ; (b) starch laurate, DS = 2.52 (Sample 17, Tab. 1) in  $CDCl_3$  at  $50^\circ C$ ; (c) peracetylated starch laurate, DS = 2.52 (Sample 17, Tab. 1) in  $CDCl_3$  at  $50^\circ C$ . For atom numbering scheme: see Fig. 1.



**Fig. 3.** Typical  $^{13}\text{C}$ -NMR spectra of: (a) native starch, in  $\text{DMSO-}d_6$  at  $60^\circ\text{C}$ ; (b) starch laurate, DS = 2.52 (Sample 15) in  $\text{CDCl}_3$  at  $50^\circ\text{C}$ ; (c) starch stearate, DS = 2.96 (Sample 17) in  $\text{CDCl}_3$  at  $50^\circ\text{C}$ . For atom numbering scheme: see Fig. 1.

### 3.2.2 FT-IR measurements

The FT-IR spectra of starch laurate and starch stearate are shown in Figs. 4b and c. For comparison, a spectrum of native starch (Fig. 4a) is also included.

FT-IR spectra of both starch laurate and starch stearate (Fig. 4b and c) show characteristic bands of the carbonyl group of the fatty esters in the  $1750\text{--}1700\text{ cm}^{-1}$  region. In addition, the C-H stretching vibrations of the alkyl groups of the fatty ester chain are clearly present at  $2920$  and  $2850\text{ cm}^{-1}$ . Characteristic peaks of the polysaccharide backbone are visible in the  $1250\text{--}900\text{ cm}^{-1}$  region (C-O stretching) [13]. The near absence of remaining hydroxyl vibrations in the range  $3000\text{--}3600\text{ cm}^{-1}$  and at  $1640\text{ cm}^{-1}$  indicates that the DS of the product is high, in line with the NMR data.

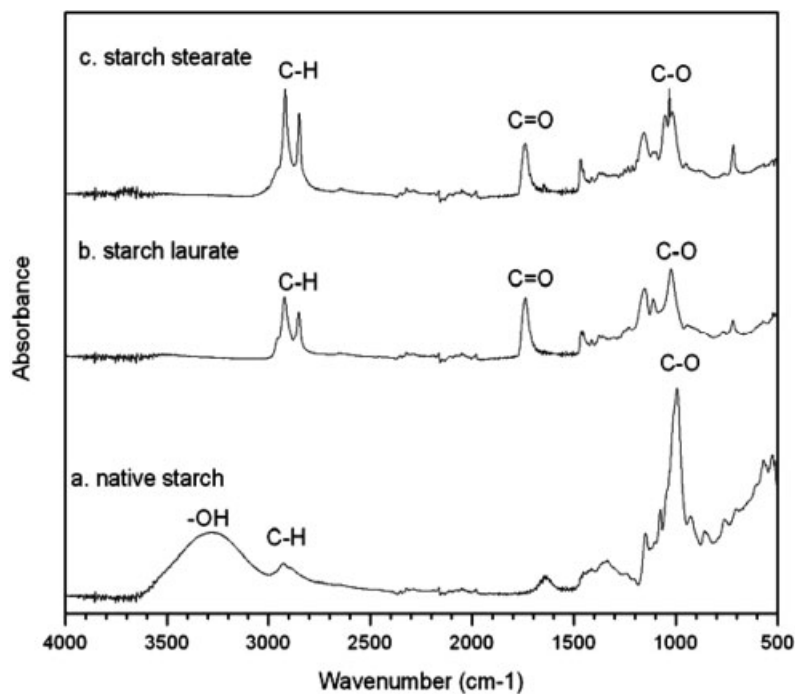
### 3.3 Systematic studies

The effect of important process variables like the vinyl ester to AHG ratio, type of catalyst and the effect of the addition of co-solvents on the product DS was studied in more detail. Most of the experiments (14) were performed using  $\text{Na}_2\text{HPO}_4$  as the catalyst. In addition, four experiments were performed with two alternative basic catalysts ( $\text{K}_2\text{CO}_3$  and Na acetate). The results are shown in Tab. 1.

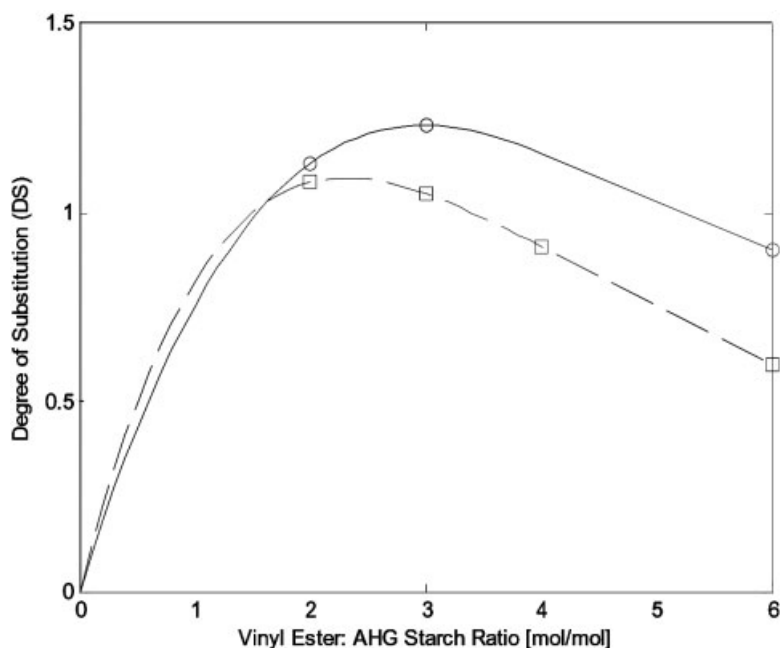
### 3.3.1 Effect of vinyl ester to AHG ratio on the product DS

The effect of the vinyl ester to AHG molar ratio on the product DS was determined for both types of vinyl esters with  $\text{Na}_2\text{HPO}_4$  as catalyst (samples 1–3, 7–10). The results are presented in Fig. 5. The highest DS value was 1.23 for vinyl laurate at an intermediate vinyl ester: AHG ratio of 3.

The DS of the products is a clear function of the vinyl laurate and stearate ester levels (Fig. 5). The DS values are increasing with higher vinyl ester: AHG molar ratio until a certain maximum. A further increase leads to a reduction in the DS. This behaviour is likely the result of two opposing effects. Higher concentrations of vinyl esters are expected to lead to higher esterification reaction rates. At low to medium vinyl ester: AHG ratios (0–3) this positive effect dominates the reaction rate and the DS of the products will therefore increase at higher vinyl ester intakes. A further increase in the vinyl ester concentration leads to a reduction in the DS. This is likely due to a reduction of the polarity of the reaction medium. At a ratio of 1:6, the ester concentration is equal on a weight basis to the DMSO concentration. This reduced polarity is expected to lead to a lowering of the reaction rates due to a reduction of the solubility and degree of ionisation of the starch reactant as well as the base catalysts. These negative effects dominate the reaction performance at higher vinyl ester: AHG ratios and lead to a reduction in the DS values.



**Fig. 4.** FT-IR Spectra of starch laurate (DS = 2.52, Sample 15, Tab. 1), starch stearate (DS = 2.96, Sample 17, Tab. 1) and native starch.



**Fig. 5.** DS of the product as a function of the type of vinyl ester and the vinyl ester: starch ratio (24 h reaction time, 110°C, 2% (w/w) catalyst intake on starch). ○ : starch laurate; □ : starch stearate. Lines for illustrative purposes only.

When using  $\text{Na}_2\text{HPO}_4$  as the catalyst, the starch laurate esters display higher DS values than the starch stearates. This effect is particularly evident at higher vinyl ester: AHG ratios (>3) (Fig. 5). Thus, the DS of the product is also a function of the chain length of the fatty acid, with high carbon numbers leading to a reduction in the DS. *Aburto et al.* [14] reported the synthesis of fatty esters of starch using alkanoyl chloride reactants

( $\text{C}_8$ – $\text{C}_{18}$ ) with reactant ratios of 6 mol alkanoyl chloride: mol AHG. *Aburto et al.* observed a similar trend in reactivity pattern and the DS decreased from 1.7 for lauroyl chloride to 0.8 for stearoyl chloride. The difference was explained by assuming that the reaction rate is reduced for larger reagents due to steric effects and this explanation likely also holds for the reactions with the vinyl esters [14].



### 3.3.2 Effect of the addition of toluene as a co-solvent

A number of reactions were performed using a co-solvent. In this case, the reactions were initiated in DMSO and toluene was added after 12 h reaction time to re-dissolve the poorly soluble partially-esterified starch products (entry 4–6, 11–14 in Tab. 1). A similar procedure was proposed by *Nouvel* *et al.* [15] for the silylation of starch. Here, the addition of co-solvents (toluene/ THF) led to an increase in the DS. These findings were rationalised by assuming that the co-solvents increase the solubility of the silylated products, leading to enhanced reactivity.

The addition of toluene for the esterification of starch with vinyl esters surprisingly did not lead to improved DS values. The products have about the same DS value for vinyl laurate when using only DMSO and even reduced DS values for vinyl stearate (see Tab. 1). Although toluene may positively affect the reaction by (partly) re-dissolving starch ester precipitates, it also results in a dilution of the reaction mixture and a reduction in the polarity. The latter factors appears to have a strong effect on reaction rates (see above), with reductions in polarity leading to lower reaction rates.

### 3.3.3 Catalysts screening

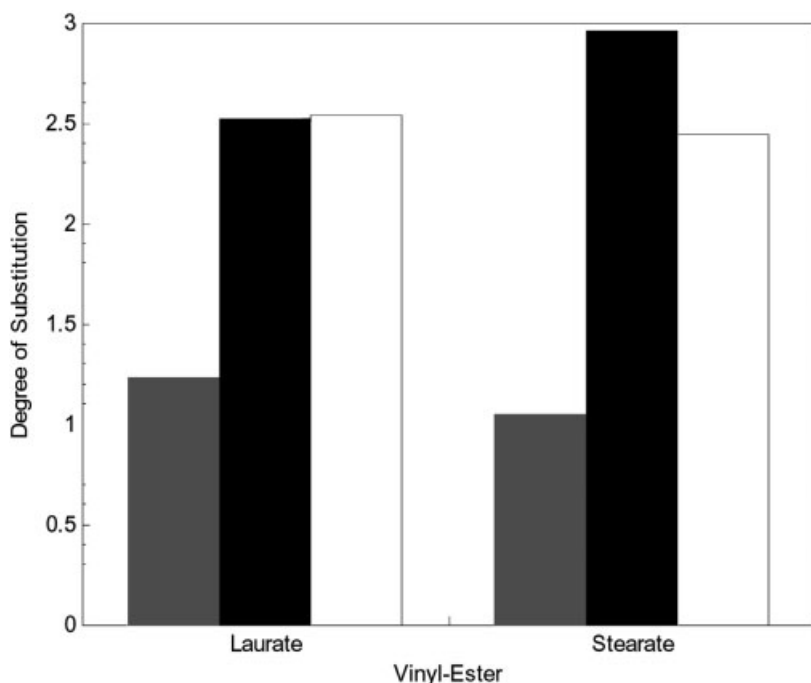
A number of alternative basic catalysts for  $\text{Na}_2\text{HPO}_4$ , i.e.  $\text{K}_2\text{CO}_3$  and Na acetate were tested. The results are given

in Tab. 1 and illustrated in Fig. 6. It is clear that Na acetate and  $\text{K}_2\text{CO}_3$  are considerably more active than  $\text{Na}_2\text{HPO}_4$  and products with a significantly higher DS were obtained. For starch laurate esterification, the two catalysts are equally effective and products with a DS of about 2.5 were obtained. For starch stearate,  $\text{K}_2\text{CO}_3$  gave products with a significantly higher DS (2.96) compared to Na acetate (DS=2.44). Thus, the DS of the product is also tunable by proper catalyst selection.

The DS of the laurate ester when using Na acetate is higher than for the stearate ester (Tab. 1 and Fig. 6), in line with the findings for  $\text{NaH}_2\text{PO}_4$ . However, when using  $\text{K}_2\text{CO}_3$  as the catalyst, the DS for the laurate ester is lower than the stearate ester. Apparently, the statement that the DS for the laurate esters is always higher than for the stearate esters is not generally valid and among others a function of the type of catalyst.

## 4 Conclusions

A study on the synthesis of corn starch fatty acid esters with high DS values is reported. The products were synthesised in DMSO using vinyl esters in the presence of basic catalysts ( $\text{Na}_2\text{HPO}_4$ ,  $\text{K}_2\text{CO}_3$ , and Na acetate). The yellow products were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, and FTIR and confirm the presence of chemically bound fatty acid chains. The DS of the products is a clear function of the chain length of the fatty ester and the type of catalyst.  $\text{K}_2\text{CO}_3$  and Na acetate are superior



**Fig. 6.** Comparison of DS values with different catalysts (vinyl ester: AHG molar ratio = 3:1, catalyst amount = 2% (w/w), 110°C, DMSO). Gray:  $\text{Na}_2\text{HPO}_4$ ; black:  $\text{K}_2\text{CO}_3$ ; white: Na acetate.

with respect to activity when compared with  $\text{Na}_2\text{HPO}_4$ . With these catalysts, products with a DS > 2.4 could be obtained for both laurate and stearate esters.

The DS of the products may also be tuned with the vinyl ester: AHG molar ratio. At low vinyl ester: AHG ratio, the DS of the product increases at higher vinyl ester intakes. A maximum was observed at a vinyl ester: AHG ratio between 2 and 4. Higher ratios led to a reduction in the DS, presumably due to a reduction of the polarity of the reaction medium. We are currently determining important product properties of the products and setting up structure-performance relations. These results will be provided in forthcoming papers.

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