Summary

Modification of starch by chemical derivation is of great industrial importance. A most significant group of modified starches are the hydroxyalkyl starches like hydroxyethyl and hydroxypropyl starch. The properties of these starches are determined by:

1. The native starch used to produce the modified product
2. The Molar Substitution (MS) of the product
3. The production method

The MS of a modified starch expresses the moles of substituent introduced per mole of anhydroglucose. Hydroxypropyl starch with a relatively low MS of about 0.1 finds large scale application in food products such as salad dressings, tomato ketchup and canned soups.

Higher substituted hydroxypropyl starches of MS = 0.3 to 0.5 are used as adhesives in the paper board industry and as an additive in textile printing. These products are produced by reaction of propylene oxide with starch in an aqueous solution using sodium hydroxide as a catalyst. The high MS products cannot be produced in an aqueous starch slurry because at MS = 0.3 the modified starch becomes cold water soluble. The production in solution has the disadvantage of a very high reaction mixture viscosity. Of course, viscosity can be reduced by using low starch concentrations but this decreases overall reaction selectivity. Nowadays, high MS hydroxypropyl starch is produced in batch processes. The high reaction mixture viscosity limits the scale of operation. Even in relatively small batch reactors, efficient mixing and optimal temperature control is problematic, resulting in undesired variations in product quality.

This thesis focuses on the development of a new continuous production process for high substituted hydroxypropyl starch using a static mixer reactor. Static mixers are in-line mixing devices, especially suited for mixing of viscous fluids. Use of such mixers in a chemical reactor is a relatively new development. Potential advantages of this reactor type are:

1. Good mixing of viscous fluids
2. Enhancement of heat transfer relative to empty tubes
3. Good plug flow characteristics

This thesis consists of 10 chapters. Chapter 1 presents an overview of different modified starch types and production methods and gives an outline of this thesis.

Chapter 2 reviews different types of commercially available static mixers and their properties with respect to mixing, pressure drop, heat transfer and residence time distribution. Based on these data, the Sulzer SMX static mixer elements were selected for the application studied here.
Chapter 3 presents experimental results on the kinetics of the four parallel reactions involved in the production of hydroxypropyl starch:

1. Catalysed reaction with starch:
   \[
   \text{ROH} + \text{OH}^- \rightleftharpoons \text{RO}^+ + \text{H}_2\text{O} \quad \text{fast}
   \]
   \[
   \text{RO}^+ + \text{CH}_2\text{-CHCH}_3 \rightarrow \text{ROCH}_2\text{CHCH}_3 \quad \text{slow}
   \]
   \[
   \text{ROCH}_2\text{CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{ROCH}_2\text{CHCH}_3 + \text{OH}^- \quad \text{fast}
   \]
   2-hydroxypropyl starch

2. Uncatalysed reaction with starch:
   \[
   \text{ROH} + \text{CH}_2\text{-CHCH}_3 \rightarrow \text{ROCH}_2\text{CHCH}_3
   \]

3. Catalysed hydrolysis:
   \[
   \text{CH}_2\text{-CHCH}_3 + \text{OH}^- \rightarrow \text{CH}_2\text{-CHCH}_3 \quad \text{slow}
   \]
   \[
   \text{OH} \quad \text{O}^- \quad \text{OH} \quad \text{O}^- \quad \text{OH} \quad \text{O}^- \quad \text{OH}
   \]
   \[
   \text{CH}_2\text{-CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{-CHCH}_3 + \text{OH}^- \quad \text{fast}
   \]
   propylene glycol

4. Uncatalysed hydrolysis:
   \[
   \text{CH}_2\text{-CHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{-CHCH}_3
   \]

The rates of these 4 reactions were measured as:

\[
-R_{\text{PO1}} = k_{1,1}c_{\text{RO}^+}c_{\text{PO}^-}
\]

with:

\[
k_{1,1} = A e^{-E_A/RT}, A = 4.28 \times 10^7 \text{ m}^3/\text{kmol s and } E_A = 66.39 \text{ kJ/mol}
\]

\[
-R_{\text{PO2}} = k_{1,1}^* c_{\text{ROH}} c_{\text{PO}^-}
\]

with:

\[
k_{1,1}^* = A^* e^{-E_A^*/RT}, A^* = 39 \times 10^3 \text{ m}^3/\text{kmol s and } E_A^* = 71.2 \text{ kJ/mol}
\]

\[
-R_{\text{PO3}} = k_{1,1}^{**} c_{\text{OH}^-} c_{\text{PO}^-}
\]

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parallel reactions

with: 

\[ k_{1,1}^* = A^* e^{-\frac{E_A^*}{RT}} \]

\[ A^* = 3.28 \times 10^8 \text{ m}^3/\text{kmol s} \] and \[ E_A^* = 71.4 \text{ kJ/mol} \]

\[ -R_{PO4} = k_{1,1}^* c_{H_2O} c_{PO} \]

with: 

\[ k_{1,1}^* = A^{***} e^{-\frac{E_A^{***}}{RT}} \]

\[ A^{***} = 449.4 \times 10^3 \text{ m}^3/\text{kmol s} \] and \[ E_A^{***} = 77.15 \text{ kJ/mol} \]

These kinetic data, combined with experimental results on reaction selectivity, were used to calculate the acidity constant \( pK_a \) of the starch hydroxyl groups. Assuming that only one hydroxyl group per anhydroglucose unit dissociates, we found:

\[ pK_a = 2174 \frac{1}{T} + 6.06 \]

This relation can be used to calculate equilibrium concentrations of dissociated starch hydroxyl groups and hydroxide ions in alkaline aqueous starch solutions.

In Chapter 4 the experimental determination of the viscosity of concentrated starch pastes using a Couette viscometer is presented. Starch paste viscosity depends on starch concentration, shear rate and work performed on starch. A modified literature relation describing the experimental data is presented.

Based on results presented in Chapter 3 and 4, Chapter 5 discusses the possible design of a pilot plant scale static mixer reactor suitable for the continuous production of hydroxypropyl starch, see figure.

1: Starch slurry
2: Slurry pump
3: Pre-mixer
4: Heating section (microwave oven)
5: Reactor tube filled with SMX static mixers

Simplified scheme of the pilot plant scale static mixer reactor.
Summary

The reactor was used for a series of experiments on starch paste viscosity, residence time distribution, heat transfer and for the actual production of hydroxypropyl starch.

In Chapter 6 the rheological behaviour of starch pastes in the static mixer is discussed. Starch paste viscosity was determined by performing pressure drop measurements at various starch concentrations, temperatures and flow-rates. Experimental results could accurately be described by:

$$\eta_{app} = K e^{[B m_{starch} + C/T - D W + (n-1) \ln \dot{\gamma}]}$$

for: $0.2 \leq m_{starch} \leq 0.30$, $343 \leq T \leq 363$ K, $3.3 \leq W \leq 29.7$ kJ/kg and $2.71 \leq \dot{\gamma} \leq 10.84$ s$^{-1}$.

with: $\eta_{app}$ = apparent viscosity [Pa s]
$m_{starch}$ = mass fraction starch [-]
$T$ = temperature [K]
$W$ = work on starch [kJ/kg]
$\dot{\gamma}$ = shear rate [s$^{-1}$]
$K, B, C, D$ and $n$ are constants with values of $3.063 \times 10^{-4}$ Pas, $12.03$ [-], $4.134 \times 10^3$ K, $2.83 \times 10^{-2}$ kg/kJ and $0.494$ [-], respectively.

These results are in good agreement with those from rheological experiments presented in Chapter 4.

Chapter 7 discusses residence time distributions in the static mixer reactor as determined from step input response measurements using lithium chloride as a tracer. Experimental results were modelled using the axially dispersed plug flow model. The Péclet number $N_{Pe}$ proved to be independent from flow rate and starch concentration. The average value found was:

$$N_{Pe} = \frac{\nu L}{D} = 97$$

for: $0.16 \leq m_{starch} \leq 0.28$ and $1.6 \times 10^{-3} \leq \nu \leq 3.25 \times 10^{-3}$ m/s.

with: $L$ (length of reactor tube) = 1.58 m., $\nu$ = superficial fluid velocity and $D$ = axial dispersion coefficient.

The holding time $V_i/\Phi_i$ was in good agreement with the experimentally observed average residence time $\bar{t}$.

An experimental study on heat transfer in a tube filled with Sulzer SMX elements is presented in Chapter 8. Data were obtained from measuring radial temperature profiles at the in- and outlet of a specially designed heat transfer section. The results were
modelled with both a one- and a two-dimensional heat transfer model. From the one-dimensional model the following relation for the Nusselt number was found:

$$N_{Nu} = 1.87 \left( N\text{Pe}_{h,t} \right)^{0.44}$$

for: \( 270 \leq N\text{Pe}_{h,t} \leq 1439 \).

with: \( N_{Nu} = \frac{\alpha_{1,1} d_t}{\lambda_{fl}}, N\text{Pe}_{h,t} = \frac{\rho_{fl} c_{p,fl} v d_t}{\lambda_{fl}} \)

\( \alpha_{1,1} \) = inside tube heat transfer coefficient \([\text{W/m}^2 \text{K}]\), \( d_t \) = tube diameter \([\text{m}]\),
\( \lambda_{fl} \) = fluid thermal conductivity \([\text{W/m K}]\), \( \rho_{fl} \) = fluid specific density \([\text{kg/m}^3]\),
\( c_{p,fl} \) = fluid specific heat \([\text{J/kg K}]\).

This result is in good agreement with literature data.

As a novel approach heat transfer was also modelled with the two-dimensional heat transfer model, commonly used in the modelling of packed bed reactors. For the effective radial thermal conductivity, \( \lambda^{*}{e,r} \), and the inside tube heat transfer coefficient, \( \alpha_{1,2} \), the following relations were found:

\( \lambda^{*}{e,r} = \lambda^{*}_{sm,0} + K_{sm} N\text{Pe}_{h,t} \)

\( \alpha^{*}_{w} = 98.5 \left[\text{-}\right] \)

for: \( 270 \leq N\text{Pe}_{h,t} \leq 1439 \).

with: \( \lambda^{*}_{sm,0} = 1.25 \left[\text{-}\right] \)
\( K_{sm} = 1.16 \times 10^{-2} \left[\text{-}\right] \)

\( \alpha^{*}_{1,2} = \frac{\alpha_{1,2} d_t}{\lambda_{fl}} \)

\( \lambda^{*}_{e,r} = \frac{\lambda_{e,r}}{\lambda_{fl}} \)

Experiments involving actual pilot plant scale production of hydroxypropyl starch are described in Chapter 9. Experimental conversion of propylene oxide was in good agreement with results from model calculations both from a one- and a two-dimensional reactor model. The increase of reaction selectivity with reaction mixture starch concentration was less than expected from the kinetic data obtained in Chapter 3. The experimental data give an indication that this is caused by a decrease in the effective acidity of the starch hydroxyl groups at high starch concentrations.

Based on the results described above, a rational design of a commercial scale static mixer reactor suitable for the production of 600 kg/hr hydroxypropyl starch is discussed in
Chapter 10. Based on reaction selectivity and equipment costs considerations, adiabatic operation is preferred for the commercial scale reactor.

The experimental work described in this thesis has shown that use of a continuous static mixer reactor for chemical derivation of concentrated starch solutions is very promising. The prototype reactor proved to be a robust tool due to the mechanical simplicity of the design. Relatively high reaction temperatures could be applied without undesired brown colouring of the product due to the low residence time in the reactor, relative to a batch process. Furthermore, the continuous well controlled production process compares favourable to batch processing with respect to good manufacturing practices because it enables continuous monitoring of product quality and fits well in the down stream process steps of product purification and drying.

The new production method presented here gives incentive for a larger role of products from renewable resources in the field of adhesives and textile print additives and opens perspectives for new applications.