The Hydroxypropylation of Starch in a Self-Wiping Twin Screw Extruder

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ABSTRACT: Potato starch was chemically modified in an APV self-wiping twin screw extruder to produce hydroxypropylated starch. The product obtained had a molar degree of substitution (MS) between 0.06 and 0.26. The selectivity of the hydroxypropylation reaction varied between 50 and 95%, yields varied between 15 and 95%, and conversions between 30 and 91%. Using viscosity data of native and hydroxypropylated starch, together with extruder parameters like temperatures, residence time distribution, and shear rates, a model was set up to predict the MS values, conversions, and selectivities. With this model, interactions between temperature, reaction, and viscosity can be understood and predicted.

KEY WORDS: Modified starch, Processing, Reactive extrusion, Screw configuration

Introduction

Starch and its derivatives are used in many industrial processes nowadays. Their usage is no longer limited to food processing, but there are also...
applications in the paper, textile, pharmaceutical, and adhesive industry, which are becoming more numerous every year. In order to maintain this position, continuous innovation of the processes and products is essential. One important group of starch derivates are the starch ethers. In this work we focus on the modification of starch by propylene oxide forming hydroxypropylated starch. Hydroxypropyl starch (HPS) is a chemically modified starch with a wide range of applications. In HPS, part of the hydroxyl groups of the glucose monomers have been converted into \(-\alpha-(2\text{-hydroxypropyl})\) groups. A measure of the number of propylene oxide moles substituted to an anhydroglucose unit (AGU) is the molar substitution (MS). Since an AGU has three hydroxyl groups available for reaction, the maximum possible MS is 3. If substituent groups are able to react further with the reagent, thus forming oligomeric substituents, higher MSs are possible. MSs \(\leq 1\) are produced by reaction of starch with hydroxypropyl at temperatures below 320 K in aqueous slurries of starch granules. NaCl or Na\(_2\)SO\(_4\) is used as a swelling inhibiting salt, and NaOH is used as a catalyst. Producing HPS with MSs \(> 1\) in aqueous slurry becomes increasingly difficult. Increasing the MS lowers the gelatinization temperature of the starch granules. This type of reaction is performed in batch or continuous stirred tank reactors to overcome mixing problems. Starch polymers dissolve from their granular structure into water, forming a highly viscous paste. This process is initiated at temperatures above 60°C. As a consequence, starch suspensions are used with high salt and water concentrations and low reaction temperatures. The salt is used to inhibit the gelatinization process, allowing higher process temperatures. These mixing solutions give rise to extra costs because

- the salt has to be removed from the end product;
- a long residence time is needed to complete the reaction because of the low reaction temperatures;
- the excess of water used during the reaction results in low reaction selectivities.\(^1\)

A reactor that does not have these drawbacks is the extruder. Twin screw extruders can be used to produce modified starches continuously with a more constant product quality. Moreover, the extruder has the advantage of a good mixer for highly viscous fluids, enhanced heat transfer, and good plug flow characteristics. This paper describes how to perform the hydroxypropylation of starch in a self-wiping twin screw extruder. In order to understand the results of the measurement, a model is presented describing the interactions between extruder parameters, reaction, and viscosity.

## Theory

### KINETICS

The following reactions take place when gelatinized starch, NaOH, and propylene oxide are mixed:

\[
\text{ROH} + \text{OH}^- \leftrightarrow \text{RO}^- + \text{H}_2\text{O} \quad (a)
\]

The acidity constant of the hydroxyl groups on the starch molecules regulates the amount of RO\(^-\) formed. These RO\(^-\) groups are able to react with propylene oxide in the following way:

**Catalyzed reaction with starch:**

\[
\text{RO}^- + \text{CH}_2\text{CH}_{\text{CH}} \xrightarrow{\text{starch}} \text{ROCH}_2\text{CH}_{\text{CH}} \quad \text{slow}
\]

\[
\text{ROCH}_2\text{CH}_{\text{CH}} \xrightarrow{\text{water}} \text{ROCH}_2\text{CH} + \text{H}_2\text{O} \quad \text{fast}
\]

When no base is present the **noncatalyzed reaction** can occur:

\[
\text{ROH} + \text{CH}_2\text{CH} \xrightarrow{\text{water}} \text{ROCH}_2\text{CH} \quad (c)
\]

Also the propylene oxide is able to react with both NaOH (catalyzed reaction) and water (noncatalyzed reaction):

**Catalyzed hydrolysis:**

\[
\text{OH}^- + \text{CH}_2\text{CH}_{\text{CH}} \xrightarrow{\text{water}} \text{CH}_2\text{CH} + \text{H}_2\text{O} \quad \text{slow}
\]

\[
\text{OH}^- \xrightarrow{\text{water}} \text{OH}^- + \text{H}_2\text{O} \quad \text{fast}
\]

\[
\text{H}_2\text{O} + \text{CH}_2\text{CH}_{\text{CH}} \xrightarrow{\text{water}} \text{CH}_2\text{CH} + \text{OH}^- \quad \text{fast}
\]
HYDROXYPROPYLATION OF STARCH IN A SELF-WIPING TWIN SCREW EXTRUDER

Uncatalyzed hydrolysis:

\[ \text{H}_2\text{O} + \text{CH}_2\text{--CH} \rightarrow \text{CH}_2\text{--CH}_2 \text{ slow} \]  

The reactions proceed according to an S_N2 reaction mechanism.\(^1\)\(^2\) The reactants involved in the slow reaction step determine the reaction rate. The fast reaction steps are rapid, establishing acid–base reactions.\(^1\)\(^3\) The reaction rate equations of the reactions (b)–(e) can be written as

\[
\text{Catalyzed hydroxypropylation: } -R_{\text{PO}} = k_{1,0}c_{\text{RO}} - c_{\text{PO}} \\
\text{Uncatalyzed hydroxypropylation: } -R_{\text{PO}} = k_{1,1}c_{\text{ROH}}c_{\text{PO}} \\
\text{Catalyzed hydrolysis: } -R_{\text{PO}} = k_{2,0}c_{\text{OH}} - c_{\text{PO}} \\
\text{Uncatalyzed hydrolysis: } -R_{\text{PO}} = k_{2,1}c_{\text{H}_2\text{O}}c_{\text{PO}}
\]

In principle propylene oxide can react with 1,2-propanediol in a consecutive reaction to form 1,1′-oxybis-2-propanol in both hydroxide catalyzed and uncatalyzed conditions. According to measurements performed by Lammers et al.\(^1\)\(^4\) in a static mixer, less than 1% of the propylene oxide reacted towards 1,1′-oxybis-2-propanol. Therefore the contribution of this reaction to the overall conversion rate of propylene oxide was neglected.

The reaction constants of the above reactions have been determined by Lammers et al.\(^1\) The selectivity of the reaction towards HPS can be calculated from

\[
\sigma_{\text{HPS}} = \frac{k_{1,0}c_{\text{RO}} + k_{1,1}c_{\text{ROH}}}{k_{1,0}c_{\text{RO}} + k_{1,1}c_{\text{ROH}} + k_{2,0}c_{\text{OH}} + k_{2,1}c_{\text{H}_2\text{O}}}
\]

(1)

Figure 1 shows that the selectivity decreases at higher temperatures. Moreover there is an optimum in the selectivity curve depending on the amount of NaOH (catalyst) added.

Finally the ratio water to propylene oxide is of importance.\(^5\) Certain ratios are unfavorable, and so the degree of substitution is a function of the temperature, the water concentration, the NaOH concentration, the extruder pressure, and the propylene oxide concentration.

THE COROTATING SELF-WIPING TWIN SCREW EXTRUDER

The geometry of the screws of this extruder type can be described as an “eight”-shaped chamber with a rather large tetrahedral gap. Because of this gap, the mean transport mechanism in a corotating self-wiping twin screw extruder is drag flow\(^6\)\(^7\), implying that back pressure can have a large effect on the actual throughput. The simplest approximation considers the channel to have a rectangular cross-sectional shape, with average height \(H\) and width \(W\). The barrel wall is treated as moving with a velocity \(U_w\) over the screw channel under an angle \(\phi\), the pitch angle. The real throughput equals the sum of the maximum drag flow and the pressure flow\(^7\)\(^8\):

\[
Q_{\text{real}} = Q_d - Q_p
\]

or

\[
Q_{\text{real}} = \frac{1}{2}(2m - 1)U_wWHF_p
- (2m - 1)\frac{WH^3}{12\eta}\left(\frac{dP}{dz}\right)F_p
\]

(2)

For a given extruder geometry and an iso-viscous fluid, the drag flow and pressure flow are therefore
determined by the screw rotation rate and the real throughput. In case of rectangular screw channels, analytical solutions for the shape factor $F_d$ and $F_p$ can be obtained. However, for the complex screw geometry of a self-wiping extruder, $F_d$ and $F_p$ can only be calculated numerically or measured.

**VISCOSITY**

An important aspect is the influence of the viscosity. Usually non-Newtonian flow behavior of starchy materials is to be expected in extruders. Not only the starch materials but also the chemical reactions performed with these materials influence the viscosity function. In our case two viscosity functions were derived, describing the behavior of concentrated starch pastes and of the hydroxypropylated starch.

In case of a concentrated starch paste the viscosity is a function of strain, strain history, temperature, and the amount of water. The strain history $W(t)$ is introduced into the viscosity equation, using an exponential dependency of the apparent viscosity on the amount of work performed on the paste:

$$W(t) = \frac{1}{\rho_p w_{starch}} \int_0^t \eta(t) \gamma \, dt \quad \text{[kJ kg}^{-1} \text{ dry starch]}$$

(3)

The viscosity equation is a modified version of that presented by van Zuilichem and Janssen and Dolan and Steffe, and reads as follows:

$$\eta_{app} = \eta_0 e^{\left\{A_{hps} T + B_{hps} w_{hps} - C W(t) + (n_{hps} - 1) \ln \dot{\gamma}\right\}}$$

(4)

Here $\eta_0$, $A$, $B$, $C$, and $n$ are fit parameters as noted in the literature. $w_{starch}$ is the amount of pure starch in the gel, $\dot{\gamma}$ is the shear rate, $W(t)$ is the amount of work performed on the starch granule, and $T$ is the temperature of the gel. The viscosity of hydroxypropylated starch was described in the same way as for the concentrated starch pastes. From our own measurements it was observed that the $\eta_{app}$ of hydroxypropylated starch (MS > 0.25) is not dependent on the strain history, which reduces Eq. (3) to

$$\eta_{app,hps} = \eta_{0,hps} e^{\left\{B_{hps} w_{hps} + (n_{hps} - 1) \ln \dot{\gamma}\right\}}$$

(5)

The parameters were measured using a Brabender Rheoteron Couette Viscometer. The samples were prepared by dissolving hydroxypropylated starch (MS = 0.25) in water. Samples with a total starch concentration of 5.2, 10.0, 14.8, 20.0, and 24.8 mass% were tested in the viscometer thermostated at 27.54, 35.14, and 40.14°C. The samples were completely gelatinized. In Table I the measurements are tabulated. Experimental data were fitted with Eq. (5), using the Marquadt–Levenberg method. In Table II the parameters of the fit are shown.
TABLE II: Values and Standard Deviations of the Parameters \(\eta_0, A_{hp}, B_{hp}, n_{hp}\) as Measured for HPS in the Couette Rheometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\eta_0, hp)</td>
<td>(4.52 \times 10^{-7})</td>
<td>(1.23 \times 10^{-8})</td>
</tr>
<tr>
<td>(A_{hp})</td>
<td>(2.277 \times 10^{3})</td>
<td>(3.2)</td>
</tr>
<tr>
<td>(B_{hp})</td>
<td>22.4</td>
<td>(1 \times 10^{-2})</td>
</tr>
<tr>
<td>(n_{hp})</td>
<td>0.835</td>
<td>(1.3 \times 10^{-3})</td>
</tr>
</tbody>
</table>

A plot of the apparent viscosity versus strain and HPS concentrations is given in Fig. 2. The viscosity dependency of hydroxypropylated starch having MS values lower than 0.25 is assumed to behave in an exponential way. The \(\eta_{app}\) can be calculated from

\[
\eta_{app} = \eta_{hp}\left[\frac{\eta(\text{MS} = 0.25)}{\eta(\text{MS} = 0)}\right] e^{[\text{MS}/0.25]} \tag{6}
\]

**HEAT TRANSFER**

Knowledge of heat generation and transfer during reactive extrusion is essential for obtaining good products. Several processes like heat transfer through the barrel wall, generation of heat due to viscous dissipation, and generation of heat by the reaction take place. In order to determine which process has the largest influence on the reaction, dimensionless numbers can be used. The Brinkman number determines the ratio between mechanical energy by viscous dissipation and the heat due to conductive heat transfer. It is given by

\[
Br = \frac{\eta_{app} u^2}{\lambda \Delta T} \tag{7}
\]

Here \(\eta_{app}\) is the apparent viscosity of the material, \(u\) is the velocity, \(\lambda\) is the thermal conductivity, and \(\Delta T\) is the temperature difference between the barrel and the material. By Lamers et al. found that \(\lambda\) is independent of the starch concentration and the viscosity.\(^{18}\) The ratio between the heat generated by the reaction and the heat generated by viscous dissipation is equal to the \(Br\) number divided by the Damköhler IV number (ratio of heat generated by the reaction and the conductive transport of heat):

\[
R \text{ number} = \frac{Br}{Da IV} = \frac{\eta_{app} u^2}{\Delta H_r(\Delta RPO_{\text{ov}})} \tag{8}
\]

Here \(\Delta H_r\) is the reaction enthalpy (\(\Delta H_r = 88\) kJ mol\(^{-1}\) at 25.15°C).\(^{14}\) Based on the similarity of the functional groups involved in the reaction, the reaction enthalpy, \(\Delta H_r\), of the hydroxypropylation reaction was assumed to be equal to \(\Delta H_r\) of the hydrolysis reaction. \(RPO_{\text{ov}}\) is the reaction rate of propylene oxide.

\[
-RPO_{\text{ov}} = cPO(k_{10}cROH + k_{11}cRO) + k_{20}cOH^{-} + k_{21}cH_2O) \tag{9}
\]

In Figs. 3 and 4 both dimensionless groups are shown. It can be concluded that during the reaction the heat generation process changes. In the case of a high material temperature and a low shear
rate (Fig. 3), heat generated by the reaction is the main heat source (assuming that when the R number equals 1 both processes are equally important). Not only the temperature and the shear rate are important, but also the MS of the end product (Fig. 4).

**HEAT TRANSFER FROM THE BARREL TO THE PROCESSED MATERIAL**

During the last decades, different heat transfer theories have been proposed. They mostly depend on the one-dimensional diffusion equation for instationary heat transfer in a stagnant medium, as proposed by Jepson. Recently Tenge and Mewes and Todd have proposed newer concepts concerning heat transfer in extruders. In our case the extruder is assumed to behave as a scraped heat exchanger. This means that after every pass of a screw flight along the barrel a new polymer layer is deposited at the barrel wall. This layer is penetrated by heat for a certain time after which it is renewed and mixed with the bulk. Another approach is to consider the heat transfer to a semi-infinite flowing medium. Both approaches have been used in our model.

Heat is also generated because of viscous dissipation. Yacu and van Zuilichem describe a method for modeling this heat generation. The extruder is divided into a solid conveying zone, a melt-pumping zone, and a melt-shearing zone. It is assumed that in the first section because of the reasonably good mixing in self-wiping twin screw extruders, heat transfer is controlled by convection. A pseudo heat transfer coefficient $U_s$ is used to replace the characteristic conductivity property of the granular material in the feed section.

The change of material in the second section from solid powder to a fluid melt is assumed to take place abruptly. In the third section four regions are defined where energy is converted. For every region an energy term can be defined:

- the screw channel ($E_{\text{screw}}$)
- between the flight tip and the screw barrel ($E_{fb}$)
- between the flight tip of one screw and the bottom of the channel of the other screw ($E_{fbo}$)
- between the flights of opposite screws parallel to each other ($E_{ff}$)

Per screw turn the total energy converted per channel can be expressed as

$$E_{\text{tot}} = E_{\text{screw}} + E_{fb} + E_{fbo} + E_{ff} = E_{pt} \eta N^2$$  \hspace{1cm} (10)

**DETERMINATION OF THE AMOUNT OF SHEAR DURING PROCESSING**

The shear imposed on the processed material is assumed to take place in the screw channel ($\dot{\gamma}_c$) and between screw flights and the barrel wall ($\dot{\gamma}_f$). The shear rate over the flight and in the screw channel can be approximated by

$$\dot{\gamma}_f = \frac{u}{\delta} = \frac{\pi DN}{\delta} \quad \dot{\gamma}_c = \frac{u}{H} = \frac{\pi DN}{H}$$  \hspace{1cm} (11)

in which $\delta$ is the flight clearance and $H$ is the channel height. The residence time in the screw channel is

$$t_{\text{channel}} = \frac{L_{\text{channel}} S_{\text{channel}}}{\phi v}$$

while the residence time in the flight section is

$$t_{\text{flight}} = \frac{V_{\text{flight}}}{\phi_{\text{flight}}}$$  \hspace{1cm} (12)

The (averaged) total shear on the material, together with the number of (tangential) passes over the tip of the kneading flight $\nu$ ($=m N t_{\text{flight}}$), is

$$\dot{\gamma}_t = (\dot{\gamma}_f t_{\text{flight}} + \dot{\gamma}_c t_{\text{channel}}) \nu$$  \hspace{1cm} (13)

**MODELING**

The reactor hydrodynamics in a self-wiping twin screw extruder has a plug flow character, as has been verified by van Zuilichem and de Graaf. Assuming that all materials are perfectly mixed in the radial direction of the channel the following balances can
be derived:

\[ \frac{d c_{PO}}{dz} = -\frac{R_{PO,ov} S}{\phi_v} \]  
(14)

Heat balance:

\[ \frac{dT}{dz} = -\frac{R_{PO,ov} \Delta H_s S - T - T_b + E_{tot}\eta_{app}}{\rho c_p \phi_v} \]  
(15)

Pressure buildup:

\[ \frac{dp}{dz} = \frac{(-1.5\eta_{app}(Q_{real} - A))}{B} \]  
(16)

Total shear:

\[ \frac{d\gamma}{dz} = \dot{\gamma} \]  
(17)

The axial temperature profile, pressure buildup, MS, and selectivity can be calculated by solving the above set of differential mass and heat balances using a fourth-order Runge-Kutta procedure.\textsuperscript{17} During this process the viscosity of the material has to be corrected for the amount of work performed on the material and the increased shear rate. The amount of work performed on the starch over a small part of the channel is assumed to be

\[ W = \frac{\Delta p}{\rho \text{reaction mixture} m_{starch}} \]  
(18)

in which \( \Delta p \) is the pressure drop over a small part of the extruder channel. Using Eqs. (5) and (6) the viscosity of the material is calculated as function of the MS, shear, and work performed. The die used consisted of two round capillaries. During the experiments a fixed diameter was used. In the model the die pressure was calculated according to the following equation:

\[ p_{die} = \frac{Q_{real}\eta_{app}}{K} \]  
(19)

in which \( K (2 \times 10^{-11}) \) is the die resistant and \( \eta_{app} \) is the viscosity in the die. Furthermore, it was assumed that the reaction in the partially filled zone is negligible and that no diffusion limitation between the propylene oxide phase and the starch gel exists.

### Experimental

#### Extrusion

During the experiments a self-wiping twin screw extruder was used. This APV Baker extruder (type M.P.F. 160) has an L/D of 24 and a length of 122.5 cm. It was mounted with three pressure transducers with a range of 0–50 bar. Two different heat profiles were imposed on the barrel (Fig. 5). The potato starch was delivered by AVEBE (The Netherlands) (Food grade, production year 1991). Merck manufactured the propylene oxide and the NaOH. Because propylene oxide is a gas at 32°C and the extruder operating conditions are above 32°C, a special screw configuration was chosen (Fig. 5). After starch, water, and NaOH had been fed, a pressure was built up by means of pressure-inducing elements. This pressure was reduced using 4D of kneading discs in a staggered position. Because there was no transport action in these kneading discs, this part of the extruder could be fully filled with gelatinized starch. Propylene oxide was injected after this gel slot. Because of the gel slot, gasified propylene oxide could not leak back to the starch inlet. From this point on two different screw geometries were used. The first, low shear, geometry (Screw I) consisted of only transporting elements. The second, high shear, geometry (Screw II) consisted of transporting elements and kneading elements. Besides this screw geometry, the screw rotation, the PO throughput, the amount of NaOH, the starch throughput, and the temperature could be varied. In Tables III and IV an overview is given of the parameters during the extruder runs with Screws I and II.

### Analysis

The extrudate was analyzed on the molar degree of substitution (MS) and the conversion of propylene oxide into propylene glycol. The MS was determined as described by de Graaf et al.\textsuperscript{25} To calculate the selectivity of hydroxypropyl towards starch, the amount of propylene oxide left and the amount of propylene glycol formed has to be measured. This was done using gas chromatography. Part of the extrudate was dissolved in water and neutralized with HCl (0.1 mol l\(^{-1}\)). As an internal standard propanol was added.

### Results and Discussion

In this section, experimental results on MS values, propylene oxide conversions, and selectivities toward the desired product HPS are compared with results obtained from model calculations.
FIGURE 5. Screw I (upper screw) and Screw II (lower screw) geometry together with the temperature profiles used. The die is situated at 122.5 cm.

MODEL

In order to determine the importance of viscous dissipation, MS values as modeled both with and without viscous dissipation are compared with experiments (Figs. 6 and 8). By examining these graphs it becomes obvious that viscous dissipation has a pronounced effect on the reaction and cannot be neglected. Besides the effect of viscous dissipation it was also examined which heat transfer model predicted MS values the best. In Fig. 6 the outcomes for both models are set out in a parity plot of the calculated MS values versus the measured MS values. Both models do not differ much from each other, leading to the conclusion that both models can be used in this particular case.

EXPERIMENTS

In Fig. 7 the influence of temperature (constant temperature along the barrel) and screw speed on the MS values is set out. An increased temperature means a higher reaction velocity and thus a higher MS. The screw speed does not have a pronounced effect on the MS. In this case the model predicted the same MS values and did not show an effect of the screw speed on the MS as well. In Fig. 8 the modeled values of Experiment 1 (Table III) are set out versus the dimensionless reaction length. A steep decline in the viscosity is noticed as a result of the increase of the temperature and the MS (a higher MS results in a lower viscosity, Eq. (6)). In this case the viscosity drop influences the reaction rate by influencing the temperature.

Changing the total throughput (Fig. 9, constant barrel temperature and concentration ratios) results in a small increase in the measured MS at higher throughputs. The model predicts the opposite. At an increased throughput and a constant screw speed, the leakage flow decreases ($Q_{\text{leak}} = Q_{\text{th}} - Q_{\text{real}}$) resulting in a decreasing mean residence time (MRT).
### TABLE III
Extruder Parameters Used for Screw I Configuration

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<tr>
<th>No</th>
<th>N (rpm)</th>
<th>( \phi_m, \text{starch} ) (g min(^{-1}))</th>
<th>( \phi_m, \text{water} ) (g min(^{-1}))</th>
<th>( \phi_m, \text{PO} ) (g min(^{-1}))</th>
<th>( c_{\text{NaOH}} ) (mol dm(^{-3}))</th>
<th>T (°C)</th>
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### TABLE IV
Extruder Parameters Used for Screw II Configuration

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<thead>
<tr>
<th>No</th>
<th>N (rpm)</th>
<th>( \phi_m, \text{starch} ) (g min(^{-1}))</th>
<th>( \phi_m, \text{water} ) (g min(^{-1}))</th>
<th>( \phi_m, \text{PO} ) (g min(^{-1}))</th>
<th>( c_{\text{NaOH}} ) (mol dm(^{-3}))</th>
<th>T (°C)</th>
</tr>
</thead>
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HYDROXYPROPYLATION OF STARCH IN A SELF-WIPING TWIN SCREW EXTRUDER

FIGURE 6. Parity plot of the measured and modeled MS values (Table III). □: Model without viscous dissipation taking into account; ◊: modeled values with penetration theory; O: modeled values with Leveque solution.

and conversion. Still the measured and calculated MS values are within the accuracy of the analysis method. In this graph also the modeled selectivity, conversion, and mixture end temperature are set out. The calculated lines agree to what is expected from theory: a decreased reaction time due to a decreasing MRT results in a decreasing conversion. There is almost no influence on the selectivity and the reaction end temperature.

Increasing the throughput of propylene oxide (Fig. 10) results in a higher MS because of an increased concentration in the starch gel and a lower initial viscosity. Furthermore the temperature rises because of the increased reaction heat, which in turn lowers the viscosity. A lower viscosity means that the fully filled length increases, resulting in an increased MRT. All these effects lead to higher MS values and conversions.

Until now only transport elements have been used in the screw geometry. In Figs. 10–12 measurements with the Screw II geometry are shown. The alkali amount was 1.5 mol l⁻¹, which is about three times lower than the alkali amount in the former screw geometry. Also a different temperature profile was used (Fig. 5). In the first kneading section, the temperature profile was kept the same for all experiments. From that point on the temperature profile

FIGURE 7. MS of HPS as a function of the extruder screw speed. ◊: T = 70°C; ▲: T = 80°C; ■: T = 90°C. Modeled values (only for T = (70°C) and (90°C)).

FIGURE 8. Simulated PO conversion, starch viscosity, and reaction temperature vs. the dimensionless reaction length.

FIGURE 9. The MS of HPS as a function of the throughput; the screw speed remained constant (Screw I). ◊: Measured MS of HPS; –: modeled MS; ◊: ζ to HPS; O: σ of PO; △: end T.

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was changed for the different experiments. Because of the neutral elements in the first kneading section (Fig. 5) the filled length was significantly larger in comparison to the case where only transport elements were used. This resulted in almost the same MS values compared to the MS values obtained with a Screw I configuration despite the lower alkali concentration. Figure 10 indicates that MS increases with an increase in $\phi_m$PO (all other parameters remained constant). The decay of MS values at increasing propylene oxide throughputs is a result of the demixing of propylene oxide and water at higher propylene oxide concentrations.26 Figures 11 and 12 show the effect of increasing screw speeds.

Again no significant influence was found on the conversion, the selectivity, or the MS. (It should be noted that during these measurements both the MS and the conversion of propylene oxide into propylene glycol were determined.) By comparing the measured selectivities and conversions with the calculated selectivities and conversions a good similarity becomes apparent.

## Conclusions

The reaction rate of the hydroxypropylation of starch is relatively slow. Besides that, propylene oxide is also a gas at 40°C. As is proven in this article, these two factors are no problems for the process. Choosing the right screw design, extruder type, and extruder parameters, the process is able to reach high MSs, high selectivities, and conversions. Examining the extruder experiments and the modeling more thoroughly, it can be concluded that besides reactant concentrations, heat transport and material viscosity are major parameters influencing the conversion. Instead of using high extruder temperatures it is also possible to use the viscous dissipation to heat the reaction mixture.

Increasing the alkali molality increases the reaction rate considerably, giving high conversions while the selectivity drops only slightly. Both experiments and calculations show selectivities above 50% (these values can be higher at different extruder conditions), which is good compared to selectivities
reached with processes used nowadays (<50%). Complete conversion of propylene oxide can be achieved. This is very important because of the price and toxic character of this reactant. Comparing the results of using extra kneading elements, it can be concluded that they have no significant effect on the selectivity or conversion.

### Nomenclature

- **c**: Concentration (mol m\(^{-3}\))
- **\(E_a\)**: Activation energy (J mol\(^{-1}\))
- **\(\Delta H_r\)**: Molar reaction heat (J mol\(^{-1}\))
- **k**: Reaction rate constant (m\(^3\) mol\(^{-1}\) s\(^{-1}\))
- **m**: Mass (kg)
- **M**: Molar mass (kg kmol\(^{-1}\))
- **MS**: Molar degree of substitution (–)
- **n**: Amount of screw threads (–)
- **N**: Screw speed (s\(^{-1}\))
- **P**: Pressure (bar)
- **Q\(_d\)**: Drag flow (m\(^3\) s\(^{-1}\))
- **Q\(_{real}\)**: Real throughput (m\(^3\) s\(^{-1}\))
- **R\(_{a}\)**: Screw radius (m)
- **R\(_{PO}\)**: Reaction rate of propylene oxide (mol m\(^3\))
- **r\(^2\)**: Regression coefficient (least-squares method) (–)
- **S**: Cross-sectional channel area (m\(^2\))
- **T**: Temperature (°C)
- **t**: Time (s)
- **u**: Velocity (m s\(^{-1}\))
- **U\(_s\)**: Pseudo heat transfer coefficient (J s\(^{-1}\) m\(^{-2}\) K\(^{-1}\))
- **V\(_c\)**: Chamber volume (m\(^3\))
- **w**: Weight fraction (–)
- **W**: Channel width (m)
- **x**: Mole fraction (–)
- **x**: \(x\)-Coordinate channel (m)
- **\(\alpha\)**: Heat transfer coefficient (J s\(^{-1}\) m\(^{-2}\) K\(^{-1}\))
- **\(\alpha\)**: Filling degree (–)
- **\(\beta\)**: Distance between screw axis (m)
- **\(\gamma\)**: Shear rate (s\(^{-1}\))
- **\(\delta\)**: Flight clearance (m)
- **\(\varepsilon\)**: Clearance between flight tip and channel bottom of 2 opposite screws (m)
- **\(\lambda\)**: Thermal conductivity (J m\(^{-1}\) s\(^{-1}\) K\(^{-1}\))
- **\(\nu\)**: Number of fully filled chambers (–)
- **\(\zeta\)**: Conversion (%)
- **\(\eta\)**: Viscosity (Pa s)
- **\(\rho\)**: Density (kg m\(^{-3}\))
- **\(\sigma_{hps}\)**: Selectivity towards hydroxypropylated starch (–)
- **\(\sigma\)**: Clearance between flights of opposite screws parallel to each other (m)
- **\(\varphi\)**: Pitch angle (rad)
- **\(\phi_m\)**: Mass feed rate (kg s\(^{-1}\))
- **\(\phi_v\)**: Volumetric feed rate (m\(^3\) s\(^{-1}\))
- **\(\phi_w\)**: Heat flux (J m\(^{-1}\))
- **\(\tau_{xz}\)**: Shear stress (N m\(^{-2}\))
- **NaOH**: Sodium hydroxide
- **OH\(^-\)**: Hydroxide ion
- **HPS**: Hydroxypropyl starch
- **PO**: Propylene oxide
- **PG**: Propylene glycol
- **ROH**: Starch hydroxyl group
- **RO\(^-\)**: Dissociated starch hydroxyl group

### References