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NOVEL PROCESSES FOR THE CARBOXYMETHYLATION OF STARCH

Abstract

Two novel processes for the carboxymethylation of starch are presented, and are compared with respect to degree of substitution, substitution patterns, reaction times and yield. The first process is a gel process in a continuous static mixer reactor optimised for handling concentrated aqueous starch pastes. The second process is a slurry process which uses organic liquids as reaction medium. Based on experimental results for both processes it can be concluded that each process has its own characteristic advantages. The static mixer process gives a good selectivity, it has short residence times and superior controllability and safety. Benefits of the non-aqueous slurry process are the possibility to produce granular CMS with a high degree of substitution and a good selectivity.

Keywords: starch, carboxymethylation, Sulzer SMX static mixer, alcohol process, *i*-propanol

Introduction

Native starch is often chemically modified to give it superior properties for dedicated applications. Carboxymethyl starch (CMS) is commonly produced by reacting starch with the sodium salt of monochloracetic acid (SMCA) in an alkaline medium. One of the first papers on the carboxymethylation of starch was published in 1924 by Chowdhury [1].

Carboxymethyl starch has a wide range of applications [2, 3], see Fig. 1. CMS is used for paper making as a binder and as a water resistant coating (insoluble polyvalent metal salts of CMS). In the textile industry CMS is used as a thickener in printing pastes or dyes and in sizing, and in adhesives for water-washable tapes. CMS is also used as glue, as foaming agents, as a coating for seeds, and it is used in oil-well fracturing fluid. Degraded or oxidised CMS is used as detergent components. In the food industry CMS is applied as a fat substitute and as a stabiliser in ice-cream.

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An important characteristic of CMS is the degree of substitution, *DS*, which is defined as the average number of substituents per anhydroglucose unit (AGU), the monomer unit of starch. Each AGU has three hydroxyl groups, so the *DS* lies between zero and three.
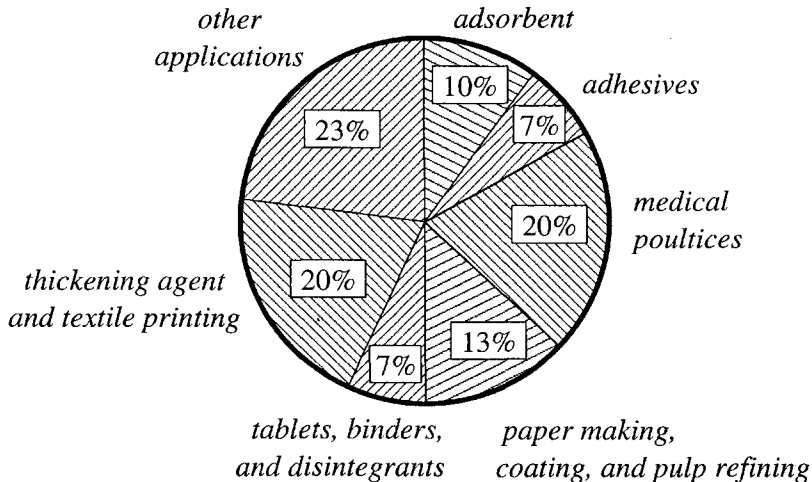

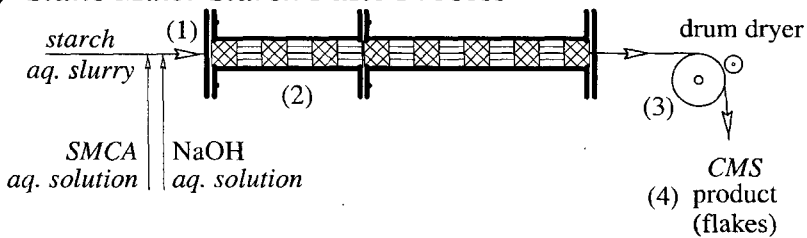Fig. 1. Pie diagram of the applications of CMS, after [3].

CMS can be manufactured in several ways. In an aqueous slurry the *DS* of CMS is limited to a value of about 0.03 [3]. At higher *DS* values the granules start to swell in water and become sticky which causes agglomeration. For many applications a *DS* > 0.03 is required. However, for a *DS* > 0.03 the starch granules become cold-water soluble which results in a highly viscous paste.

The traditionally used batch reactor with helical ribbon impeller for handling such a viscous starch paste has poor mixing and heat transfer characteristics. A homogeneous product asks for short mixing times relative to the reaction time. Therefore, a novel continuous reactor for the chemical modification of starch paste was developed in our laboratory [4]. This reactor has static mixing elements which provide good mixing, nearly plug flow behaviour and an enhanced heat transfer. The good radial mixing allows for faster reaction rates [5, 6] which results in a smaller reactor for the same production capacity. Other important aspects of a static mixer reactor are the good controllability and safety characteristics. We developed this novel type of reactor for the hydroxypropylation [4] and the carboxymethylation of starch [7]. In the static mixer process the starch loses its granular form and the paste has to be dried on a drum dryer to obtain dry CMS flakes.

To preserve the granular structure of the starch, various processes have been discussed [3, 8]. When salts are added to an aqueous slurry a *DS* of about 0.1 can be reached [8]. A slightly higher *DS* for granular CMS can be obtained after cross-linking of the starch [8]. In a relatively dry process, the maximum *DS* is 0.5 [3]. As a reactor for this dry process a bag at room temperature, a jacketed blender and a fluidized bed have been proposed [8].

Another process for the production of highly substituted granular CMS uses water-miscible organic liquids as a reaction medium. The organic liquids are used to prevent the gelatinisation of the starch granules and to provide a good reaction medium. This gives the possibility to wash and dry the starch easily, which is difficult when the starch is dissolved.

a) *Static Mixer Starch Paste Process*

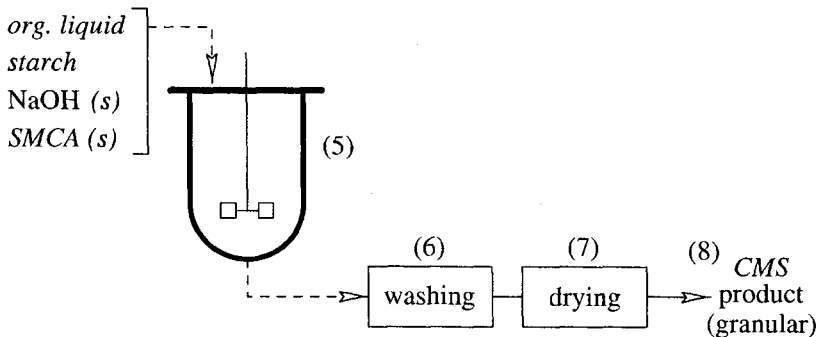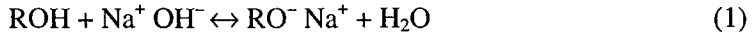### b) *Non-aqueous Batch Process*

Fig. 2. Schematic diagrams of the static mixer starch paste process (a) and the non-aqueous batch process (b). (1) Gelatinization of starch; (2) Reactor with static mixing elements; (3) Drying of the starch paste; (4) CMS product (flakes); (5) Non-aqueous slurry batch reactor; (6) Washing; (7) Drying of product; (8) Granular CMS product.

In this paper the novel static mixer starch paste process and the novel non-aqueous slurry process are described. Figure 2 shows the schematic flow diagrams of both processes. The advantages and disadvantages of both processes are discussed by comparing the results obtained with these processes.

Theory

Reaction equations

NaOH added to a solution or a slurry of starch gives the following equilibrium reaction with the hydroxyl groups of the starch:

$$ROH + Na^+ OH^- \leftrightarrow RO^- Na^+ + H_2O \tag{1}$$

The activated form of the starch hydroxyl groups, RO^-, is more reactive than the inactivated form ROH [9]. The main reaction is the carboxymethylation of starch:

$$ClCH_2COO^- Na^+ + RO^- Na^+ \rightarrow ROCH_2COO^- Na^+ + Na^+ Cl^- \tag{2}$$

SMCA can also react with OH^-, resulting in a competitive side reaction:

$$ClCH_2COO^- Na^+ + Na^+ OH^- \rightarrow HOCH_2COO^- Na^+ + Na^+ Cl^- \tag{3}$$

SMCA can also react with water, but in an aqueous solution the hydrolysis with OH^- dominates relative to H_2O for $c_{OH^-} > 0.0016$ kmol/m^3 [10].

Because in both the main and the side reaction Cl^- is formed, the conversion of SMCA (A), ζ_A, can be calculated from the chloride production:

$$\zeta_A = 1 - \frac{n_A}{n_{A_0}} = \frac{n_{Cl} - n_{Cl_0}}{n_{A_0}} \tag{4}$$

The selectivity of SMCA towards the product CMS (P) follows from the experimental *DS* and the number of moles Cl^- formed ($n_{Cl} - n_{Cl_0}$):

$$\sigma_p = \frac{n_P}{n_{A_0} - n_A} = \frac{n_{AGU}}{n_{Cl} - n_{Cl_0}} DS \tag{5}$$

The yield of the product CMS, η_P, is the ratio of the *DS* and the theoretical *DS*, DS_t, which is the *DS* at 100% selectivity and conversion based on the lowest molar amount of the reagents added (SMCA or NaOH):

$$\eta_p = \begin{cases} \text{if } n_{NaOH} \geq n_A & DS_t = n_{A_0}/n_{AGU} & \eta_P = \sigma_P \zeta_A \\ \text{if } n_{NaOH} < n_A & DS_t = n_{NaOH_0}/n_{AGU} & \eta_P = \sigma_P \zeta_{NaOH} \end{cases} \tag{6}$$

Substitution patterns of CMS

The mole fractions of mono-, di- and tri-substituted AGU were measured with HPLC. However, the technique is not sensitive enough to determine on which C-atom the carboxymethyl groups are situated. Spurlin [11] developed a 'rate of reaction' model which predicts these mole fractions as a function of the *DS* on the basis of three relative reaction rate constants k_2, k_3 and k_6 for the hydroxyl groups on carbon number C-2 , C-3 and C-6.

Because the position of the carboxymethyl groups is unknown it is impossible to discriminate between k_2, k_3 and k_6. Therefore, the k values are given subscripts a, b and

c. The three *k*-values can be determined separately only if experimental *DS* values are obtained in the full range from zero till three.

Experimental

Materials

Food grade quality potato starch, a slightly oxidised potato starch (Perfectamyl A-4692, AVEBE) and technical grade powder sodium monochloroacetate (SMCA) (Akzo-Nobel, Arnhem, The Netherlands) were a gift of AVEBE (Foxhol, The Netherlands). Elemental analysis of the SMCA showed that the contents of C, Cl, H and Na were 99.4 ± 0.3 wt%, 99.9 ± 0.2 wt%, 100.6 ± 1.7 wt% and 99.9 ± 0.2 wt% of the pure values, respectively ($n_r = 2$). The molar ratio of chloride and SMCA, was found to be $n_{Cl^-} / n_{SMCA} = 0.68 \times 10^{-3}$. H_2SO_4 used in the eluens of the HPLC analysis was of analytical grade.

Paste process

For the kinetic experiments in a batch reactor the starch was washed three times with demineralised water and dried in a vacuum oven at 55°C to a moisture content between 10–15 wt%. Native starch was used at low concentrations only ($c_{AGU} \leq 0.3$ kmol/m^3). For higher concentrations Perfectamyl was used. For experiments in the static mixers native potato starch from AVEBE was used. The concentration of NaOH in the NaOH-solution (33 wt%, technical grade, Chemproha) was always measured after dilution by titration with 1 N HCl (Titrisol, Merck). The HCl used for hydrolysis of the starch prior to HPLC analysis was of analytical grade.

Non-aqueous batch process

Before use, starch was washed three times with demineralised water and dried in a vacuum oven at 55°C to a moisture content between 10–15 wt%. NaOH pellets were of analytical grade. Dehydrated technical grade *i*-propanol with a purity >99% was used (Acros Chemica, Geel, Belgium). Ethanol, 96% pure, and acetone were both of technical grade. The other organic solvents, *i.e.* methanol, *n*-propanol, *n*-butanol, *s*-butanol and *t*-butanol, were of analytical grade. H_2SO_4 used for hydrolysis of the starch and $BaOH_2$ used for neutralisation of the HPLC samples were of analytical grade.

Experimental set-up for the paste process

The carboxymethylation of starch in aqueous solution was carried out in a batch reactor and in two continuous static mixer reactors of different scale (Static Mixer 1 and 2).

Batch reactor

A jacketed stainless steel batch reactor with a volume $V_r \approx 0.7 \times 10^{-3}$ m^3 and a stirrer with two turbine impellers ($D_{st}/D_{BR} \approx 0.5$) was used for the batch experiments. Native potato starch was used at concentrations up to $c_{AGU} \leq 0.3$ kmol/m^3. At higher starch concentrations the reaction mixture became too viscous, resulting in poor mixing of the reaction mixture. The use of a slightly oxidised potato starch (Perfectamyl) made it possible to use starch concentrations in the batch reactor of at least $c_{AGU} = 1.9$ kmol/m^3. For $c_{AGU} = 0.3$ kmol/m^3 Perfectamyl proved to have the same reactivity as native potato starch.

The experimental procedure was as follows. A weighed amount of starch with known moisture content together with a weighed amount of milliQ water was stirred in a beaker until no starch lumps could be seen. The beaker was closed with a lid and placed in a waterbath of about 90 °C. The starch slurry was stirred at 5 rps. After 15 minutes the starch started to gelatinise and the starch solution was stirred at 17 rps at 90°C during 45 minutes. The starch solution was weighed to determine the amount of evaporated water before pouring it into the batch reactor. The beaker was weighed again to determine the amount of starch solution in the reactor. Then a specific amount of SMCA powder was added together with a specific amount of water to reach the desired concentrations. The starch solution was brought to the desired reaction temperature with a thermostatic bath (Haake F3-S) which controlled the temperature in the reactor. The reactor was flushed with N$_2$ to remove O$_2$ and CO$_2$. The reaction was started by adding a specific amount of 33 wt% NaOH solution to the reactor with a 50 ml syringe. Sampling took place by suction of 5–20 ml of the reaction mixture into a 50 ml syringe with an extended nozzle and quenching in 100 ml 0.25 M HNO$_3$.

Small scale static mixer

Static Mixer 1 is a small tubular reactor ($D_t = 27.3$ mm and $L/D_t = 49$) filled with Sulzer SMX static mixing elements (see Fig. 3). Previously, it was used for the hydroxypropylation of starch [4]. For more details on this equipment and procedures, see [4, 7, 12].

Here the operation of the static mixer and some reactor features are discussed briefly. The starch slurry (with ≈12 wt% SMCA) was mixed with a 4.00 M ≈38 wt% SMCA-solution and a 11.2 M ≈33 wt% NaOH-solution in a pre-mixer (1) consisting of 10 Sulzer DN4 static mixing elements. A few seconds after leaving the pre-mixer the starch is gelatinised completely giving a viscous starch paste. Then the starch paste is heated to the desired temperature in a microwave heating section (2). The microwave oven (2.45 GHz) is amplitude controlled and has a tuning facility to maximise the coupling between the microwaves and the starch paste (3a).
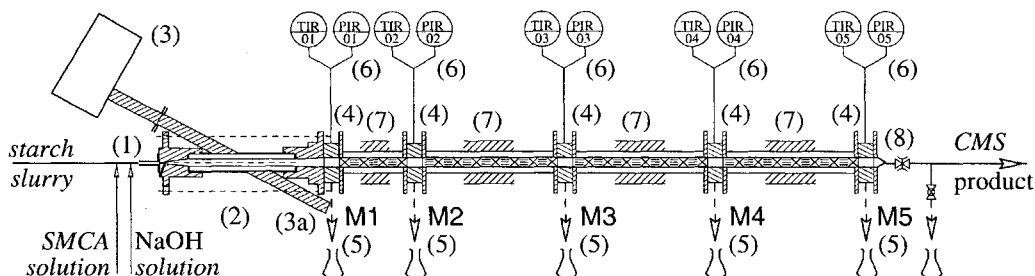
Fig. 3. Experimental setup of Static Mixer 1; (1) Pre-mixer: Sulzer SMX DN4 ($D_t = 4.8$ mm); (2) Microwave heating section; (3) Microwave generator (microwave tuning (3a)); (4) Measurement sections (M1–M5); (5) Sampling point; (6) Temperature and pressure measurement; (7) Reaction section (Sulzer SMX DN25; $D_t = 27.3$ mm); (8) Pneumatic valve.

The reactor consists of measurement (4) and reaction sections with Sulzer SMX DN25 static mixing elements (7). The temperature and pressure of the starch paste are measured in the measurement sections (6). A pneumatic valve at the end of the reactor (8) allows for sufficient pressure to take a sample from the last measurement section. Sampling (5) takes place through specially designed valves having a cleaning facility. The reaction was quenched with a stainless steel rod, cooled in liquid nitrogen. Subsequent acidification allowed for further handling of the samples.

Static Mixer 1 was originally designed with four reaction sections of the same length. Because the carboxymethylation of starch is an overall second order reaction the initial reaction rate is relatively high. Therefore, the first reaction section was replaced by a section with 7 instead of 14 SMX static mixing elements.

Larger scale static mixer

To investigate the scale-up of the static mixer reactor for the chemical modification of starch a larger static mixer was built with a 2.5 times larger internal diameter than Static Mixer 1 (Static Mixer 2: $D_t = 67.1$ mm and $L / D_t = 27$, see Fig. 4).

This reactor also has the possibility to sample (5) and measure temperature and pressure at several axial locations (6). The temperature of the starch paste can be measured at different radial distances and different angles with respect to the static mixing elements. This way, a radial temperature profile could be measured. A homogeneous temperature is important, because alkaline starch pastes are susceptible for thermal degradation.

Most important differences with Static Mixer 1 are the design of the microwave (3, 3a), the increasing lengths of the reaction sections (7) to obtain a steady increase in conversion at the subsequent measurement sections and the rotatable measurement section (M2) with a movable temperature measuring device inside.
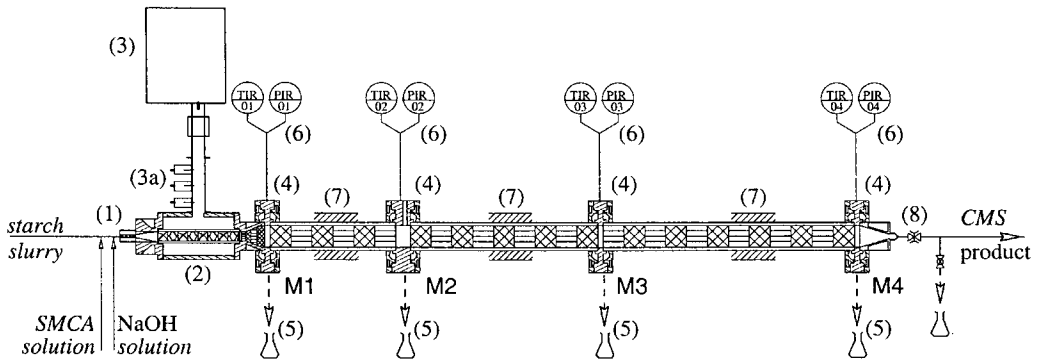
Fig. 4. Experimental setup of Static Mixer 2; (1) Pre-mixer: Sulzer SMX DN4 (D_i = 4.8 mm); (2) Micro-wave heating section; (3) Microwave generator (microwave tuning (3a)); (4) Measurement sections (M1–M4); (5) Sampling point; (6) Temperature and pressure measurement; (7) Reaction section (Sulzer SMX DN65; D_i = 67.1 mm); (8) Pneumatic valve.

The reactor can be thermostatted with water which circulates at high velocity through the jackets. With air filled jackets and good isolation the reactor can be operated nearly adiabatically.

Experimental set-up for the non-aqueous batch process

The carboxymethylation of granular starch in the non-aqueous batch process was carried out in two different reactors. In the large reactor the *DS* as function of the time was obtained. The conversion, the selectivity and the granular structure was studied in the small reaction vessels.

Large reactor

The organic liquid was first mixed with a specific amount of water. The granular potato starch and the reaction medium were added in a jacketed batch reactor (V_r = 1×10^{-3} m^3), followed by flushing with N_2. Also during the experiment a N_2 flow was used to prevent reaction of NaOH with CO_2 from the air. The reactor was equipped with a reflux cooler to prevent the loss of volatile liquid. Typically, after 15 minutes NaOH was added to the reaction mixture. Subsequently, the vessel was heated to the reaction temperature, and left overnight under stirring to assure equilibrium between the starch and the NaOH. The reaction was started by adding powder SMCA. At given times, a small sample was taken from the reaction suspension for analysis. The reaction was stopped by the addition of H_2SO_4.

Small reaction vessels

Experiments were carried out in magnetically stirred reactors ($V_r = 25 \times 10^{-6}$ m^3) placed in a thermostatic bath. First, NaOH pellets were added to the reactor. Then, the granular potato starch and the reaction medium, with a known composition, were mixed in the reaction vessel. Subsequently, the reaction vessels were heated to the reaction temperature and left overnight under stirring to assure equilibrium between the starch and the NaOH. The reaction was started by adding SMCA and stopped by adding H_2SO_4 to the samples.

Analytical procedures

Degree of substitution

The degree of substitution, DS, of the CMS was determined with HPLC [13, 14]. This technique requires hydrolysis of the starch into glucose units while keeping the carboxymethyl groups intact. Hydrolysis of the CMS gives eight possible molecules: glucose, three mono-CMG, three di-CMG and tri-CMG. For the starch paste process a 1 wt% sample was hydrolysed in 1 M HCl at 100°C during 4 hours. For the non-aqueous batch process 0.1 g of CMS was hydrolysed with 18 ml of 0.75 M H_2SO_4 at 100°C for 4 hours, and $BaOH_2$ was used to neutralise and precipitate the sulphate ions as $BaSO_4$.

The hydrolysed samples were injected on two Bio-Rad Aminex HPX-87H ion exclusion columns in series at 65 °C. As eluens 0.75 mM H_2SO_4 was used at a flow rate of 0.5 ml/min. The RI-detection (HP1047A) gave four separate peaks for tri-CMG, di-CMG, mono-CMG and glucose together with peaks for the salt, SMCA, glycolic acid and, if present, organic liquid. The mole fractions x_i of glucose ($i = 0$), mono-CMG ($i = 1$), di-CMG ($i = 2$) and tri-CMG ($i = 3$) and the DS were calculated with the following equations:

$$x_i = \frac{F_i A_i / M_i}{\sum_{j=0}^{3} F_j A_j / M_j} \quad \text{and} \quad DS = \sum_{i=0}^{3} i x_i \tag{7}$$

with the response factors: $F_0 = 1$, $F_1 = F_2 = F_3 = 1.03$ [15], the molecular masses are $M_0 = 180$, $M_1 = 237$, $M_2 = 294$ and $M_3 = 351$, and A_i are the peak areas in the chromatogram.

Chloride analysis

The amount of chloride, c_{Cl^-}, was determined by potentiometric titration with 0.1 M $AgNO_3$ and a combined Ag-electrode (Metrohm 6.0404.100) [16].

Results and discussion

Paste process

Reaction kinetics

Some results of a kinetic study in a batch reactor of the carboxymethylation of starch in aqueous solution are presented here [7]. The experimental conditions are given in Table 1 together with the selectivity, σ_P, obtained and the time required for a conversion of 50%, $t_{\zeta_A=0.5}$.

Table 1

Reaction conditions of the carboxymethylation of starch in aqueous solution in a batch reactor

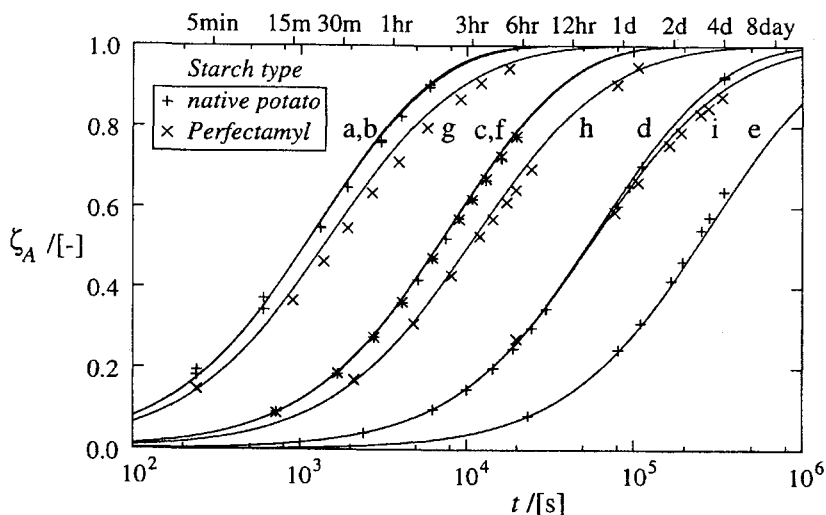| nr	Starch type	T °C	c_{AGU} kmol/m^3	c_{NaOH_0} kmol/m^3	c_{A_0} kmol/m^3	DS_t –	σ_P^e –	$t_{\zeta_A=0.5}$ 10^3 s
a	Native	84.9	0.296	0.654	0.514	1.74	0.210	1.04
b	Native	85.0	0.292	0.653	0.528	1.81	0.205	1.05
c	Native	65.0	0.297	0.665	0.526	1.77	0.235	6.65
d	Native	45.3	0.297	0.664	0.534	1.80	0.290	52.0
e	Native	32.1	0.295	0.672	0.525	1.78	0.320	235
f	Perfect.	65.1	0.300	0.659	0.525	1.75	0.236	6.63
g	Perfect.	64.9	1.87	1.32	1.22	0.652	0.770	1.36
h	Perfect.	45.0	1.89	1.32	1.23	0.651	0.750	10.1
i	Perfect.	30.3	1.85	1.32	1.21	0.654	0.850	53.4

Fig. 5. Conversion of SMCA, ζ_A, as a function of time t at several reaction conditions (see Table 1) for the carboxymethylation of starch in aqueous solution.

Figure 5 gives both the experimental and the modelled conversion of SMCA, ζ_A, as a function of time. The rate equation of Sergeev and Rad'ko [17] was applied for the side-reaction and a similar equation for the main reaction. The duplo measurements (a, b) nearly coincide, which shows that the reproducibility is good. Two experiments (c, f) were carried out under the same reaction conditions to compare the reactivity of Perfectamyl with that of native potato starch. The experimental points nearly coincide which proofs equal reactivity. The experiment with Perfectamyl at high concentration and temperature (g) shows the largest deviation from the modelled curve.
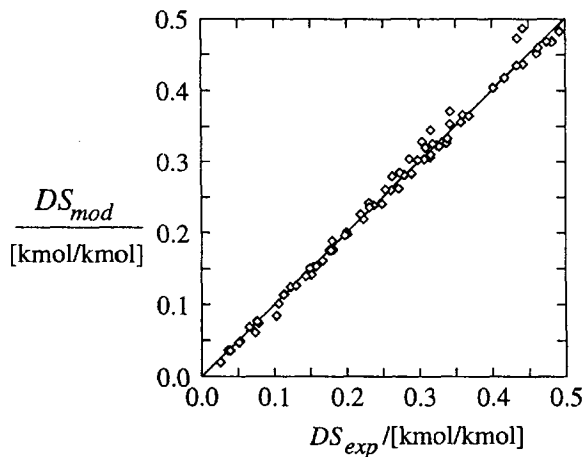

Fig. 6. Parity plot of the DS of the carboxymethylation of starch in aqueous solution in a batch reactor.
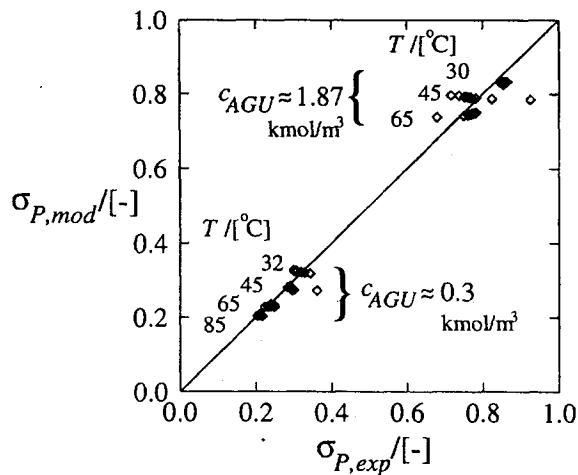

Fig. 7. Parity plot of the selectivity, σ_P, of the carboxymethylation of potato starch in aqueous solution in a batch reactor.

A parity plot for the *DS*, Fig. 6, shows that the modelled *DS* agrees well with the experimental values (MARR = 3.6%). Figure 7 shows a parity plot of the selectivity towards the product CMS, σ_P, for two starch concentrations, c_{AGU}, and several temperatures. It proves that σ_P is much higher for the higher ($c_{AGU} = 1.8$ kmol/m^3) than for the lower starch concentration ($c_{AGU} = 0.3$ kmol/m^3). At a high starch concentration, $c_{AGU} = 1.85$ kmol/m^3, and low temperature, $T = 30°C$, a selectivity of 0.85 can be reached (exp. i). At a higher temperature and nearly the same starch concentration the selectivity is somewhat lower, 0.77 for experiment g. Also for the low starch concentrations the selectivity decreases with increasing temperature, from 0.32 at 32°C to 0.21 at 85 °C (exp. a–e). Increasing *T* from 32°C to 65°C gives a 27% decrease in selectivity for the low starch concentration (exp. e → c) while for the high starch concentration the decrease appears to be 9% only (exp. i → g).

Small scale static mixer

The batch experiments showed that the selectivity, σ_P, was better at a higher starch concentration. Therefore the experiments in the static mixer were carried out with a high starch concentration, c_{AGU}. Table 2 gives the experimental conditions of some carboxymethylation experiments in Static Mixer 1.

T a b l e 2

Reaction conditions of the carboxymethylation of starch in aqueous solution in Static Mixer 1. (see Fig. 5 for labels a – d; ζ_{lim} is the conversion of the limiting reactant, SMCA or NaOH)

nr	T_c	c_{AGU}	c_{NaOH_0}	c_{A_0}	DS_{th}	$DS_{\zeta^e_{lim}=1}$	at measurement section M5				
							DS	ζ^e_{lim}	σ^e_P	η^e_P	τ
	°C	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{kmol}$	$\dfrac{kmol}{kmol}$	$\dfrac{kmol}{kmol}$	–	–	–	s
a	96	1.94	1.41	1.39	0.716	0.56	0.46	0.82	0.78	0.64	1075
b	84	1.95	1.40	1.39	0.713	0.51	0.40	0.78	0.72	0.56	1075
c	76	1.99	1.41	1.46	0.709	0.58	0.35	0.62	0.81	0.50	1069
d	67	1.94	1.37	1.20	0.619	0.45	0.26	0.58	0.73	0.42	1198

T_c is the temperature of the thermostatting water which circulates through the jackets of the reactor. Due to the heat of reaction the temperature of the starch paste is a few degrees higher. The initial starch, NaOH and SMCA concentrations and the mean residence time was approximately the same for all experiments (a – d). The theoretical *DS*, DS_t was calculated with Eq. (6) with the numbers of moles n_i substituted by the concentrations c_i.

The last 5 columns give the experimental values of the DS (see also Fig. 8), the conversion of the limiting reactant (either SMCA or NaOH), $\zeta^e_{\lim}$, the selectivity, σ^e_P, the yield, η^e_P, and the mean residence time, τ, at measurement section M5. The value $DS(\zeta^e_{\lim} = 1)$ is the DS which can be reached with a total conversion of the limiting reactant ($\zeta^e_{\lim} = 1$):

$$DS\left(\zeta^e_{\lim}\right) = \frac{DS}{\zeta^e_{\lim}}\Bigg|_{Mx} \tag{8}$$

with Mx the last measurement section.

Table 2 shows that the conversion at measurement section M5 decreases with decreasing temperature. The selectivity is approximately 0.75 and comparable with the values obtained in the batch experiments with approximately the same starch concentration.
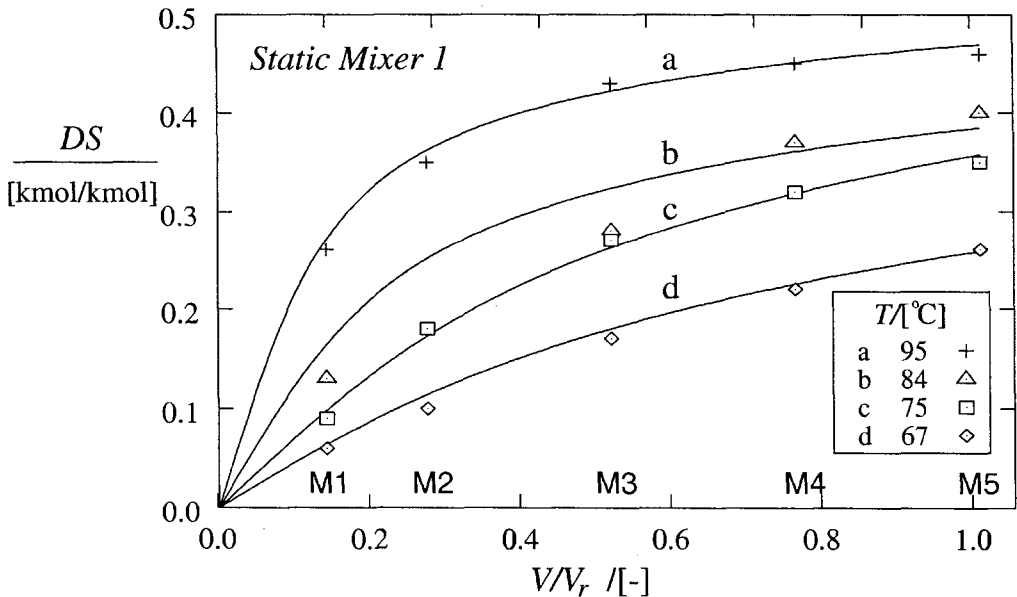

Fig. 8. The DS of CMS as a function of the axial position in the static mixer reactor (Static Mixer 1).

Figure 8 shows the DS as function of the position in the reactor, given as the ratio of the volume up to that position and the total volume of the reactor, V/V_r. The lines are simulated values of the DS on the basis of a model which describes the reactions and the heat transfer in the reactor [7]. The model predicts the experimental DS reasonably

good. Occasionally, experimental error, due to difficulties with sampling of the viscous starch paste, caused larger deviations from the predicted value.

Larger scale static mixer

Carboxymethylation of starch was carried out in Static Mixer 2 on a roughly 10 times larger scale than in Static Mixer 1. Two experiments to investigate the scale-up of the carboxymethylation in a static mixer reactor are discussed here. See Table 3 for the experimental conditions. Both experiments have approximately the same initial concentrations and hence the DS_t is almost the same.

Table 3

Reaction conditions of the carboxymethylation of starch in aqueous solution in Static Mixer 2. ($V_r = 6.38 \times 10^{-3}$ m^3; for exp. a: $w_{AGU} = 0.31$, $w_{NaOH_0} = 0.040$, $w_{A_0} = 0.13$ $w_{H_2O_0} = 0.52$)

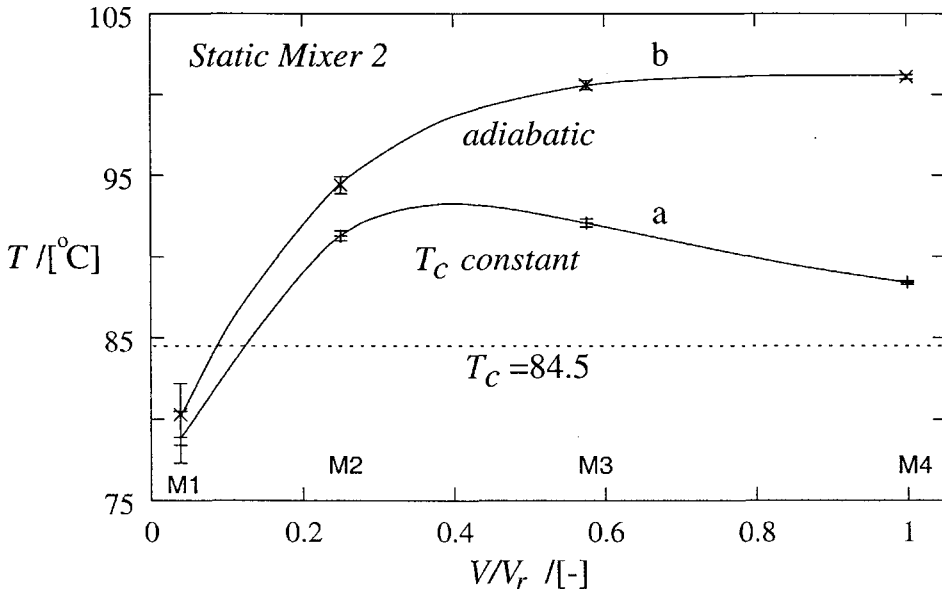| nr	T_c	c_{AGU}	c_{NaOH_0}	c_{A_0}	DS_{th}	$DS_{\zeta_{lim}^e=1}$	at measurement section M4				
							DS	ζ_{lim}^e	σ_P^e	η_P^e	τ
	°C	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{m^3}$	$\dfrac{kmol}{kmol}$	$\dfrac{kmol}{kmol}$	$\dfrac{kmol}{kmol}$	–	–	–	s
a	84.5	2.40	1.28	1.43	0.53	0.43	0.37	0.87	0.80	0.70	863
b	–	2.39	1.29	1.33	0.54	0.42	0.40	0.94	0.79	0.74	870

Fig. 9. Axial temperature profile of the reactor for pseudo-isothermal operation (T_c = constant) and for adiabatical operation (Static Mixer 2). The errorbars give the standard deviations of T due to instabilities in time.

   In experiment (a) the reactor was thermostatted with water of $84.5 \pm 0.1°C$. Experiment (b) was carried out adiabatically with approximately the same initial temperature as experiment (a). Figure 9 shows the axial temperature profiles of both experiments. In experiment (a) the temperature difference of the starch paste and the thermostatting water became maximal $8°C$ between measurement sections M2 and M3. The difference decreases further down in the reactor but is still $3.5°C$ at the outlet. In experiment (b) the temperature rises continuously until a temperature difference of $21°C$ is reached between M1 and M4. The slope of the temperature increase at M4 is very small which indicates a high conversion ($\zeta_{lim}^{e} = 0.94$).
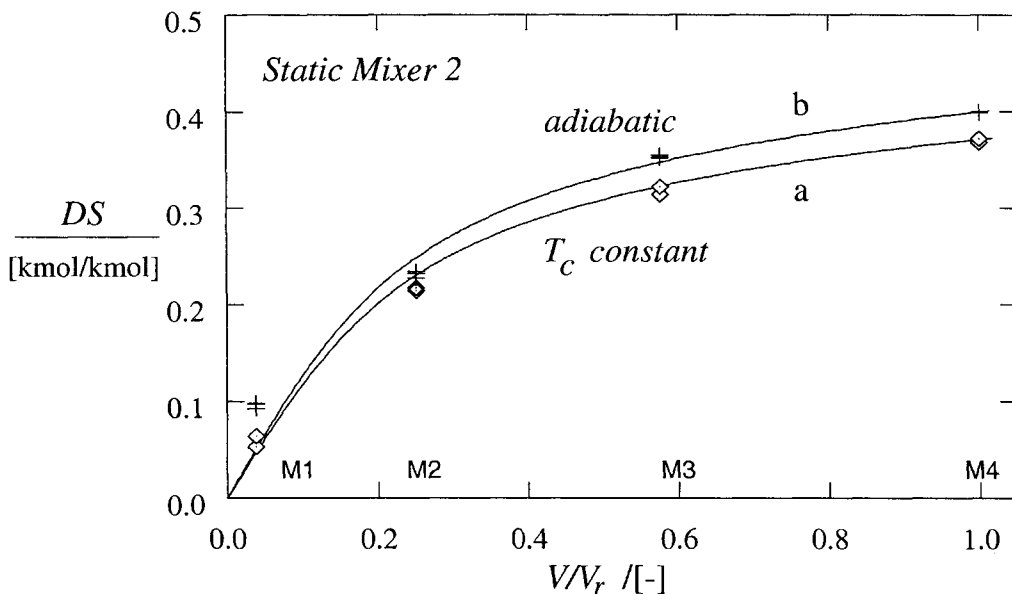

Fig. 10. The *DS* of CMS as function of the axial position in the static mixer reactor (Static Mixer 2). HPLC analysis of the *DS* in duplo.

   Figure 10 shows the *DS* as function of the axial position in the reactor for both experiments. In the adiabatic case (exp. b) a higher *DS* is reached due to the higher temperature and corresponding reaction rate. Both experiments gave a white coloured product CMS.

   The conversion for experiment (a) is 0.87 after 863 s while it was only 0.78 after 1075 s for experiment (b) in Static Mixer 1 which had approximately the same conditions (see Table 2). Due to the larger scale of Static Mixer 2 the removal of the heat of reaction becomes more difficult. This results in a larger temperature difference with the

thermostatting water. So the starch paste reaches a higher temperature which gives a higher reaction rate.

The selectivities of approximately 0.8 are somewhat higher than in the experiments with the small scale static mixer due to the higher starch concentration applied.

Experiment (a) showed that carboxymethylation in a static mixer with the scale of Static Mixer 2 and the short residence time of 863 s gave a notable temperature increase of 8 °C with respect to the thermostatting water. Experiment (b) proved that also in an adiabatic reactor a good selectivity can be achieved at a high conversion. This is important for the scale-up to commercial size equipment. The adiabatically operated reactor is easier to scale-up than the thermostatted reactor.

Substitution pattern

Figure 11 shows the molar fractions of glucose, mono-CMG and di-CMG as a function of *DS*. The dotted lines are calculated using an equal reactivity for the three hydroxyl groups in the AGU; this means $k_a = k_b = k_c$ in terms of the 'rates of reaction' model of Spurlin [11]. Apparently, the glucose, mono-CMG and di-CMG yields deviate substantially from these curves.
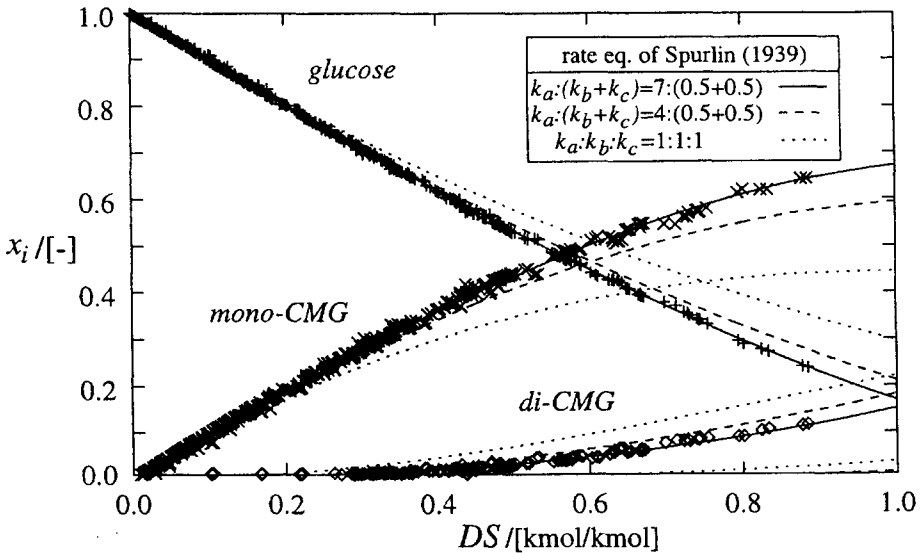

Fig. 11. Mole fractions of glucose, mono-CMG and di-CMG of monomer of carboxymethylated starch in aqueous solution as a function of *DS*, both in batch and in continuous static mixers. Reaction conditions: $30 < T/[°C] < 95$; $0.3 < c_{AGU}/[kmol/m^3] < 2.0$; $0.37 < c_{NaOH_0}/[kmol/m^3] < 2.0$; $0.37 < c_{A_0}/[kmol/m^3] < 1.9$; reaction time $t < 4.3 \times 10^5$ s.

Because the maximally obtained DS is in the order of one, k_b and k_c could not be determined separately. For the ratio of the reaction rate constants $k_a : (k_b + k_c)$ equal to 7 : 1 the model curves are in agreement with the experimental values. This means that one of the hydroxyl groups is 7 times more reactive than the sum of the other two. This also implies that under the experimental conditions applied, both in the batch reactor and in the two static mixers, there is no influence of T, c_{AGU}, c_{NaOH_0}, c_{A_0} and reaction time t on the measured substitution patterns. This is a strong indication that the hydroxyl groups of the starch are equally available in both the static mixers and in the batch process.

Temperature homogeneity in a static mixer

In the large static mixer reactor the temperature profile was measured over half of the cross section after six SMX static mixing elements. A temperature difference between the incoming starch paste and the wall of 15°C was applied. Without static mixing elements the temperature profile would have a parabolic shape. Due to the radial mixing by the static mixing elements the temperature profile appears to be flattened (see Fig. 12).
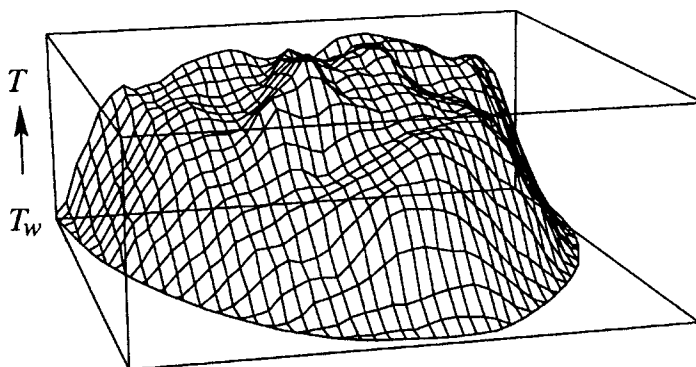

Fig. 12.Measured temperature profile of half the cross section after six SMX elements (Static Mixer 2).

Non-aqueous batch process

For the carboxymethylation of starch in the non-aqueous slurry process first the best media was to be selected, then the optimal amount of water in the system was determined. To obtain highly substituted CMS at a good selectivity, the theoretical DS, DS_t, was varied. The optimal reaction temperature, which is a sensitive parameter because of gelatinisation, was selected with experimental design and logistic regression

[18]. Finally, the obtained substitution patterns were compared with models known from the literature.

Best media

The results reported in the literature [19–28] suggest that i-propanol is the best organic liquid, but the DS and the selectivity, σ_P, values reported are rather low ($DS <$ 0.5 and $\sigma_P < 0.3$).

The organic liquids we tested for the carboxymethylation of potato starch were methanol, ethanol, n-propanol, i-propanol, n-butanol, s-butanol, t-butanol and acetone, all with 10 wt% water. Figure 13 shows the experimental yield, η_P, as a function of time for the different organic liquids. Under the conditions studied, see Table 4, i-propanol gave the highest yield and in this case also the highest DS. Because the same theoretical DS was used for all liquids, DS_t was equal to 1.1.

Table 4

Standard reaction conditions for the carboxymethylation of starch in the non-aqueous batch process

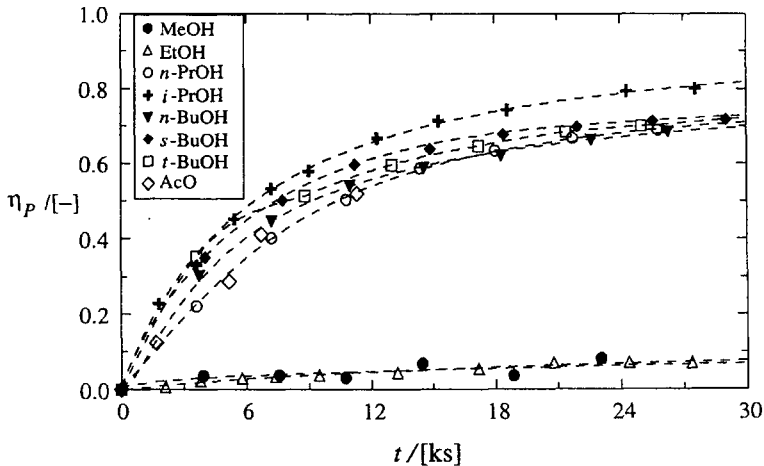| amount of organic liquid	m_l	kg	1.0
water mass fraction	w_{H_2O}	kg/kg	0.1
temperature	T	°C	40
starch mass fraction	w_{AGU}	kg/kg	0.04
NaOH / SMCA molar ratio	–	kmol/kmol	1.0
theoretical DS	DS_t	kmol/kmol	1.1

Fig. 13. The yield, η_P, of carboxymethyl potato starch in various organic liquids as a function of reaction time, t. Reaction conditions: $T = 40$ °C, 4 wt% starch, 10 wt% water, $n_{NaOH}/n_{SMCA} = 1.0$, and $DS_t = 1.1$.

After about 30×10^3 s, the yield is equal to 0.80 in i-propanol. Acetone, n-propanol and the three isomers of butanol gave a slightly lower value of $\eta_P = 0.70$ whereas methanol and ethanol gave $\eta_P = 0.07$, all after a reaction time of 30×10^3 s. A reasonable reproducibility was obtained, triplo results with the same reaction medium differed by 5%, at the most.

It can be concluded that our results confirm the superior behaviour of i-propanol known from the literature. However, the DS and the yield obtained in this study are much higher than reported in the literature.

Effect of water fraction

The effect of the water fraction on the carboxymethylation was studied in more detail for i-propanol. The moisture content of the starch granules was included in the total water fraction in the system. Figure 14 shows the DS as a function of time for four i-propanol-water mixtures. Because the same DS_t was used in all cases, the DS is directly comparable to the yield. The optimal water fraction for i-propanol is about 0.1. After 30×10^3 s, the DS is equal to 0.91 and the yield is equal to 0.80. After more than 24 hours of reaction the DS is 1.0 and the yield, η_P, is 0.88. For the production of granular carboxymethyl potato starch i-propanol with 10 wt% is the best reaction medium.
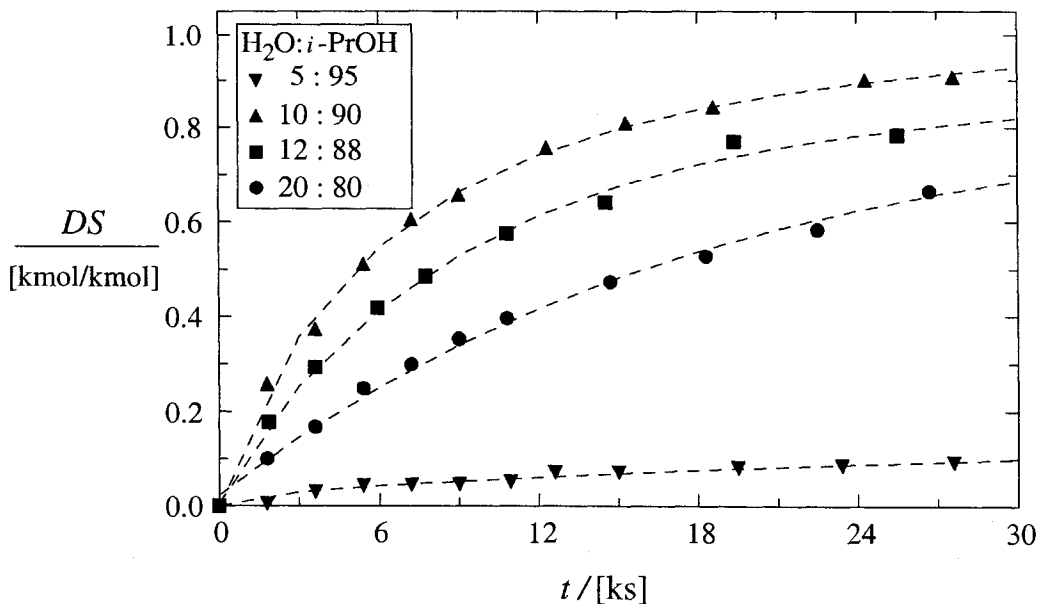

Fig. 14. Effect of the water fraction on the carboxymethylation of potato starch in i-propanol; DS as function of the reaction time t. The reaction conditions are given in Table 4.

Theoretical degree of substitution

From Eqs (1)–(3) it is clear that the DS_t (which is either n_A/n_{AGU} or n_{NaOH}/n_{AGU}, whichever is lower) will influence the final DS. Figure 15 shows the final DS and the yield as a function of the theoretical degree of substitution. The DS increases monotonously with an increase in the DS_t, until a constant level is reached of 1.3. The yield, η_P, decreases monotonously over the whole range.
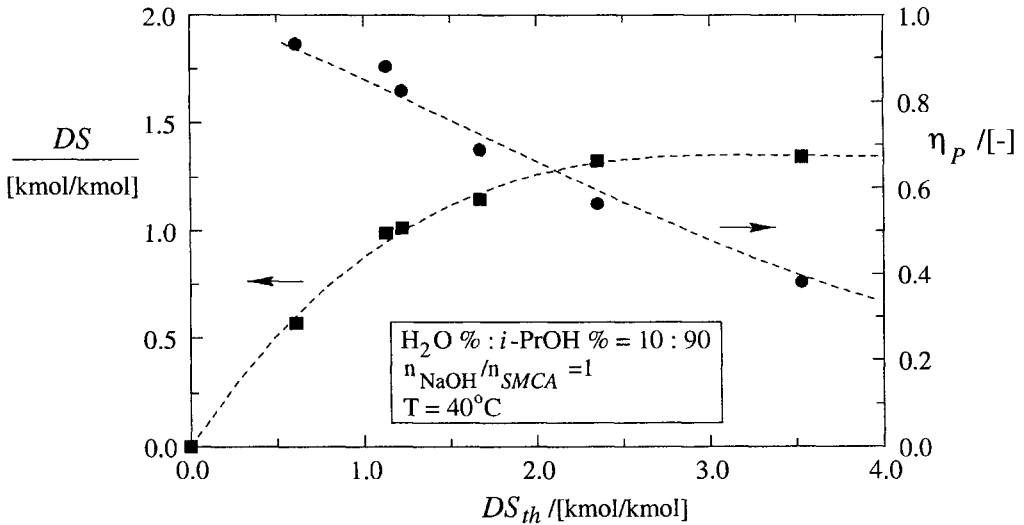

Fig. 15. Final DS and yield, η_P, as a function of theoretical DS, DS_t, for i-propanol.

To investigate the production of granular carboxymethyl potato starch with a DS above 1.3, a novel method was developed. At 40°C granular CMS could be produced with a DS as high as 2.2 with a yield of 0.56.

Granular structure

The experimental conditions are restricted because gelatinisation must be avoided. An experimental design study was undertaken to determine the boundaries of the operation conditions. For this study 25 ml vessels were used. Swelling of the starch was checked visually. The study showed that in i-propanol the temperature, the water fraction, w_{H2O}, and the fraction of starch, w_{AGU}, were the most sensitive parameters for gelatinisation. In Fig. 16 the operation window is shown where the CMS remains in the granular form. It can be concluded that the operating flexibility with respect to the temperature and the water fraction increases with an increase in the starch fraction.
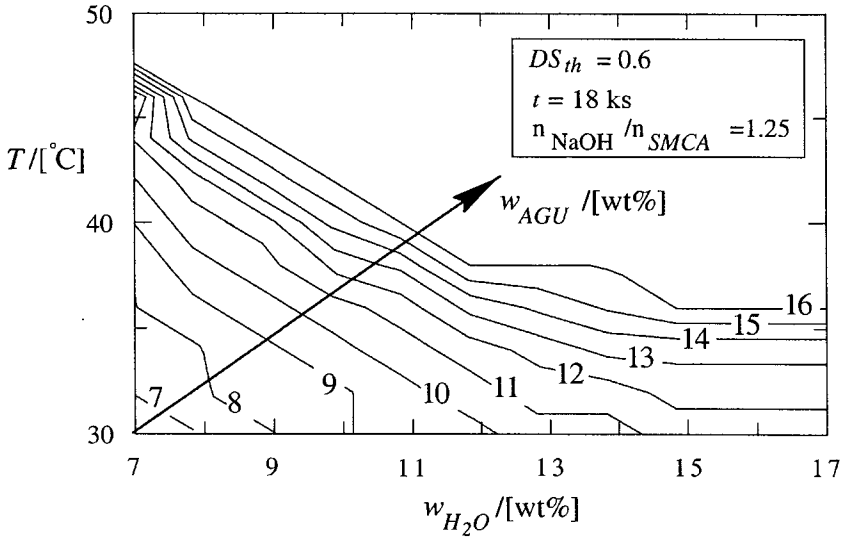
Fig. 16. Contour plot of the starch structure as function of T, w_{H2O}, and w_{AGU}.

Selectivity

The selectivity of SMCA for the main reaction as function of the temperature, the n_{NaOH}/n_{SMCA} ratio, and the DS_t was studied in 25 ml reaction vessels. Figure 17 shows that the selectivity improves with increasing reaction time, leading to $0.7 < \sigma_P < 0.9$ after 6×10^3 s. An important factor for the selectivity is the NaOH concentration. The selectivity decreases with increasing NaOH concentration.

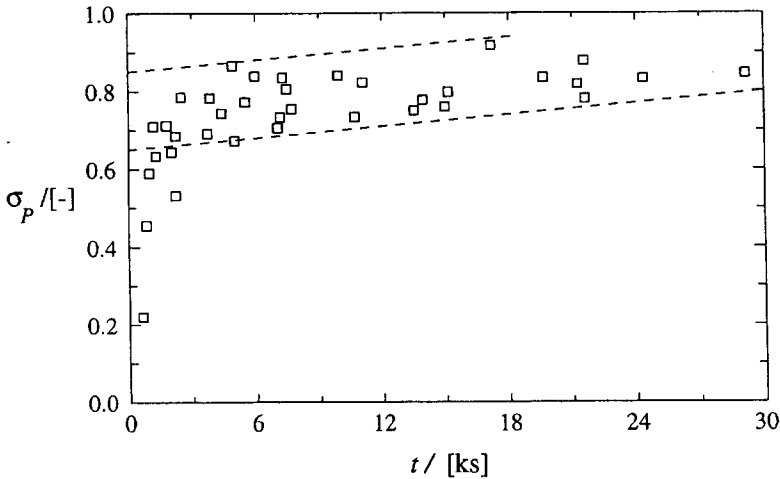Fig. 17 Selectivity of SMCA towards the product CMS, σ_P, as a function of time. Reaction conditions: i-propanol, 10 wt% water, $30 \leq T/[°C] \leq 50$, 4 wt% starch, $0.5 \leq n_{NaOH}/n_{SMCA} \leq 1.2$, and $0.6 \leq DS_t \leq 1.2$.

Substitution pattern

Figure 18 shows the experimental monomer product distribution obtained in the non-aqueous batch process. A comparison is made with distributions calculated from rate equations presented in the literature [11]. The line for $k_a : (k_b + k_c) = 4 : 1$ is in good agreement with the experimental results. This means that one of the hydroxyl groups is 4 times more reactive than the sum of the other two. Because the maximal DS, in Fig. 18, is in the order of unity, k_b and k_c could not be determined separately.

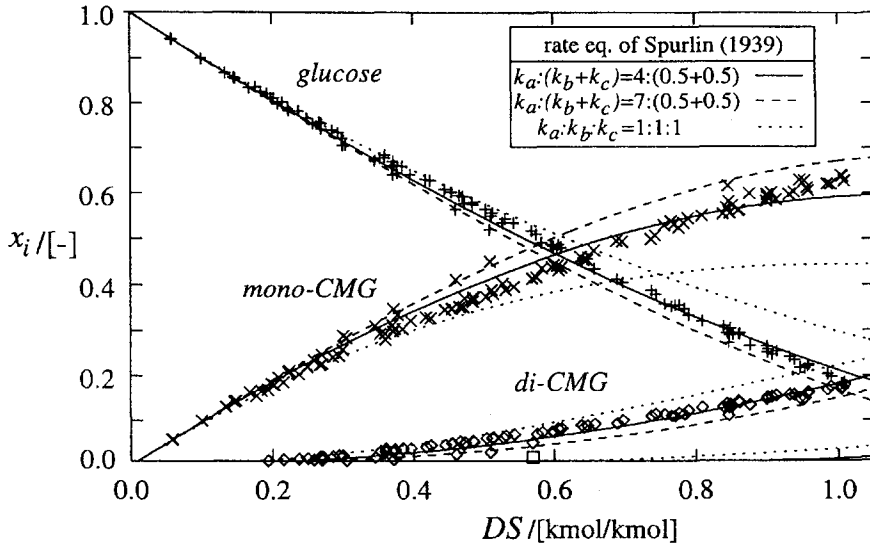Fig. 18.Mole fractions of glucose, mono-CMG, di-CMG, and tri-CMG of monomer of carboxymethyl starch as function of *DS* for the non-aqueous batch process.

Comparison of both processes

Here, a qualitative comparison is made between the static mixer paste process and the granular non-aqueous batch process for the carboxymethylation of starch. The characteristics of the two processes are compared in Table 5.

Table 5

Comparison between the carboxymethylation of a starch paste in a continuous static mixer reactor and of starch granules in a non-aqueous batch process

	static mixer	non-aqueous batch process
operating mode	continuous	batch
starch form	gelatinised	granular
$t_{\zeta_A=0.5}$ [s] $(T = 40°C)$	17.3×10^3	4.5×10^3
typical reaction temperature, T_{typ} [°C]	85–90	40
typical reaction time, t [s], at T_{typ}	900	18×10^3
maximal DS [–]	0.9	1.3
maximal selectivity, σ_P [–]	0.80	0.87
$k_a : (k_b + k_c)$ [–]	7 : 1	4 : 1
economics	higher investments	higher variable costs
capacity per m^3 reactor	high	lower
maximal mass fraction starch	0.32	0.10
environmental	water	i-propanol

Reaction time

The reaction time of both processes is compared by means of the half-time conversion of SMCA, $t_{\zeta_A=0.5}$. From Fig. 13 $t_{\zeta_A=0.5}$ for the carboxymethylation at 40°C in i-propanol is estimated as 4.5×10^3 s. $t_{\zeta_A=0.5}$ in the starch paste process at 40°C is calculated as $t_{\zeta_A=0.5} = 17.3 \times 10^3$ s (based on reaction times of exp. h and i, see Table 1). The latter value is almost four times higher than for the non-aqueous batch process.

However, raising the temperature to decrease the reaction time is limited in the non-aqueous batch process where gelatinisation has to be avoided. In the starch paste process a higher temperature is even desired to lower the viscosity. But a drawback of a higher temperature is the lower selectivity (see Table 1 and Fig. 7). $t_{\zeta_A=0.5}$ at 85°C at the high starch and reactant concentrations ($c_{AGU} \approx 1.9$, $c_{NaOH_0} \approx 1.3$, $c_{A_0} \approx 1.2$ kmol/m^3, see Table 1) becomes 236 s only. Such short reaction times are possible only if the mixing times are even shorter. Here, the static mixer reactor is superior because of the high intensity mixing characteristics.

Reactor volume

The ratio of the reactor volumes for both processes is calculated on basis of the same production rate of CMS with $DS = 0.5$ with typical reaction times ($\tau_{SM} = 900$ s; $\tau_{NABP} = 18 \times 10^3$ s), starch mass fractions ($w_{AGU,SM} = 0.32$; $w_{AGU,NABP} = 0.10$) and tem-

peratures (T_{SM} = 85°C; T_{NABP} = 40°C) of each process (see Table 5). The volume ratio becomes:

$$\frac{V_{NABP}}{V_{SM}} \propto \frac{\tau}{\tau} \frac{w_{AGU,SM}}{w_{AGU,NABP}} = \frac{18\cdot 10^3}{900} \frac{0.32}{0.10} = 64 \tag{9}$$

Selectivity

High selectivity in the aqueous starch paste process requires a high concentration of starch as shown in Fig. 7. In the starch paste batch reactor a selectivity of 0.77 (T = 65°C) and in the static mixers a selectivity of 0.8 is reached. The concentrations of starch and reactants in the static mixer are limited by the pumps and by the fact that SMCA is a salt. So, for the static mixer a selectivity of almost 0.8 is maximal.

The selectivities reached in *i*-propanol with 10 wt% water are, beside some initial low values, between 65% and 87% (see Fig. 17). This is higher than in the aqueous starch paste process under the conditions applied.

Both process give a good selectivity which results in a relatively low cost of raw material.

Degree of substitution

In the starch paste process a *DS* of about 0.56 at ζ_{lim} = 1 with $\sigma_P \approx 0.78$ can be reached, see Table 2. A *DS* of 0.9 is possible, Fig. 11, but with a lower selectivity. A further increase of the *DS* requires additional feeding of SMCA and NaOH to the starch paste. To maintain a good selectivity the dilution of the starch paste by this addition should be kept minimal.

The non-aqueous batch process has a larger maximal reachable *DS* than the starch paste process.

Substitution pattern

The experimentally obtained mole fractions of glucose, mono-CMG, and di-CMG in both processes were compared as a function of the *DS* with the 'rate of reaction' model of Spurlin [11], see Fig. 11 and 18. The mole fractions of both processes deviate from the model with equal reactivity for all three hydroxylgroups, *i.e.* $k_a = k_b = k_c$. For the starch paste process the ratio $k_a : (k_b + k_c)$ = 7 : 1 agreed with experiment while for the non-aqueous batch process this was $k_a : (k_b + k_c)$ = 4 : 1. This means that in the starch paste process the most reactive hydroxylgroup appears to be relatively more reactive than in the non-aqueous batch process.

Economical aspects

Besides the technical differences between both processes discussed above, there are substantial economical differences too. The starch paste process in a static mixer

reactor requires relatively higher investments though these will hardly affect process economics. Evaporation of the water in the starch paste with a drum dryer brings substantial variable costs. A benefit is the lower personnel costs because the process is continuous. Further, such a continuous process can be better controlled leading to lower variations in product specifications. The non-aqueous batch process has the advantage of the optional removal of by-products from the CMS, which is hardly possible in the paste process. Also, the batch process has lower drying costs than the paste process. However, the costs of purification of the non-aqueous liquid are substantial. To minimise these costs the non-aqueous liquid must be circulated as much as possible.

Summary

Each process has its own characteristics (see Table 5). The static mixer process is a continuous process and is therefore appropriate for high production rates with a constant product quality. Although the *DS* in one reaction step with this process is limited. The reaction time can be relatively short at relatively high reaction temperatures due to the short mixing times in the Static Mixer. With the non-aqueous process it is possible to produce granular CMS with a *DS* of 1.3. Purification of the granules is possible. An advantage of the non-aqueous batch process is that the starch granules can be easily separated from the reaction medium. For a particular application a quantitative economic analysis will be required. The result will depend on production capacity, the *DS* required and the need to purify the product.

Conclusions

For the production of carboxymethyl starch, a continuous static mixer process and a batch-wise process with an optimal organic reaction medium preventing starch gelatinisation were compared. Both processes have their own characteristics and the optimal choice of a production method of CMS will depend particularly on the plant capacity desired, the *DS* required and on whether product purification is necessary.

The main technical differences are the way of operation and the form of the CMS product. With the static mixer process a paste is produced and in the non-aqueous batch process the granular form of the starch is preserved. With the static mixer process it is possible to have a higher production rate than with the non-aqueous batch process. For the non-aqueous batch process the low production rate is caused by the limitations in the temperature and the fraction of starch in the reactor. In the paste process, purification of CMS is difficult. In the non-aqueous batch process the separation of the granular CMS from the reaction liquid is easy and purification of the granular product is possible. The maximal selectivity, σ_P, and *DS* are higher in the non-aqueous batch process than in the paste process.

Both processes have their own substitution pattern. In the starch paste process the mole fraction of mono substituted CMG is higher than in the non-aqueous batch process for an equal *DS*.

Notation

c_i	Concentration of species i, kmol/m³.
D_t	Internal diameter of the static mixer tube, m.
DS	Degree of substitution, ratio of moles substituent to moles AGU, kmol/kmol.
DS_t	Theoretical *DS* at 100% selectivity of the limiting reactant towards the product CMS, kmol/kmol.
$DS\left(\zeta^e_{\text{lim}} = 1\right)$	Final degree of substitution with total conversion of limiting reactant: $DS\left(\zeta^e_{\text{lim}} = 1\right) = DS/\zeta^e_{\text{lim}}\big|_{\text{Mx}}$, with Mx the last measurement section (M5 for SM1 and M4 for SM2).
F_i	Response factor of mono- ($i = 1$), di- ($i = 2$) and tri-CMG ($i = 3$) with respect to glucose ($i = 0$).
k_i	Reaction rate constant, with $i = a$, b and c for the three hydroxylgroups of AGU.
L	Length of the reactor, m.
MARR	Mean absolute relative residual, MARR $= \frac{1}{N}\sum_{i=1}^{N}\left|\left(y^e_i - y^m_i\right)\big/y^e_i\right|$, for all non-zero y^e_i.
M_i	Molecular weight of species i, kg/kmol.
M	Molarity, kmol/m³.
m	Mass, kg.
n_r	Number of repetitions.
n_i	Number of moles of species i, kmol.
ROH	Hydroxyl group of an AGU.
RO⁻	Dissociated hydroxyl group of an AGU.
rps	Revolutions per second, s⁻¹.
T	Temperature, °C.
T_c	Temperature of thermostatting water, °C.
t	Time, s or h.
V	Volume in reactor from entrance up to a certain axial position, m³.
V_r	Volume of the reactor, m³.
w_i	Weigth fraction of species i, $w_i = m_i / m_{tot}$; except for non-aqueous batch process: $w_{\text{H}_2\text{O}} = m\text{H}_2\text{O} / (m_{\text{H}_2\text{O}} + m_{\text{org}})$; $w_{\text{AGU}} = m_{\text{AGU}} / (m_{\text{AGU}} + m_{\text{H}_2\text{O}} + m_{\text{org}})$.
x_i	Molar fraction of species i.
y^e_i, y^m_i	Quantity obtained by experiment or by model, respectively (e.g. c_{Cl^-}, DS) used in MARR.

Greek

η_P	Yield of product CMS based on limiting reactant.
ζ_i	Conversion of species i.
σ_P	Selectivity of SMCA towards CMS.
τ	Mean residence time, s.

Subscript

A	SMCA.
BR	Batch reactor.
exp, mod	Experimental and modelled, respectively.
i, j	Species i, j.
l	liquid.
lim	Limiting reactant, SMCA or NaOH.
NABP	Non-aqueous batch process.
org	Organic liquid.
P	Product (CMS) .
SM	Static Mixer process.
st	Stirrer.
tot	Total.
typ	Typical.
0	Initial value ($t = 0$).

Superscript

e, m	Experimental and modelled, respectively.

Abbreviations

AGU	Anhydroglucose unit.
CMG	Carboxymethyl glucose.
CMS	Carboxymethyl starch.
M1 – M5	Measurement sections of the static mixer reactor.
PIR	Pressure indication and registration.
RI	Refraction Index.
SM	Static Mixer.
SMCA	Sodium monochloroacetate ($ClCH_2COONa$).
TIR	Temperature indication and registration.

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NOWE PROCESY DO KARBOKSYMETYLOWANIA SKROBI

Streszczenie

Przedstawiono dwa nowe procesy służące do karboksymetylowania skrobi. Porównano je pod względem dającego się uzyskać stopnia podstawienia, miejsc podstawiania, niezbędnego czasu reakcji i wydajności. Pierwszy proces wymaga skrobi zżelowanej i odbywa się w statycznym, pracującym w ruchu ciągłym reaktorze z mieszaniem, który zoptymalizowano w celu otrzymywania stężonych wodnych past skrobiowych. Drugi proces zachodzi w zawiesinie w rozpuszczalnikach organicznych.

W oparciu o dane doświadczalne z obu procesów można stwierdzić, że każdy z procesów ma swe specyficzne zalety. Proces w reaktorze statycznym z mieszaniem zapewnia dobrą selektywność, jest krótszy bardzo łatwo jest go kontrolować i jest bezpieczny. Korzyścią wynikającą ze stosowania procesu w zawiesinie w rozpuszczalnikach organicznych jest zachowanie gałeczkowej struktury kaboksymetyloskrobi nawet przy wysokim stopniu podstawienia i dobrej selektywności. ▨