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Design of a continuous process for the production of highly substituted granular carboxymethyl starch

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Abstract

A process design for the continuous production of highly substituted granular carboxymethyl starch (CMS) from potato starch is presented. Experiments in a batch reactor showed that aqueous isopropyl alcohol (IPA) is the optimal reaction medium to prevent the substituted starch from swelling and to keep it in a granular form. The degree of substitution (DS) that can be obtained in a single reaction step is limited to about 1.3. It is possible to increase the DS in a consecutive batch reaction where a lower water concentration is used. The continuous process consists of two continuous stirred tank reactors in series, each with a specific H_2O/IPA ratio. For a complete recycling of the organic reaction medium a hybrid dehydration section is evaluated. Based on this design, granular carboxymethyl potato starch with a DS of 1.5 or higher can be produced continuously. For an annual production of 3600 tons of CMS, the first CSTR should have: a starch content of 20% (w/w); a H_2O/IPA ratio of 10/90 w/w; a temperature of 40°C; a volume of 11 m³; and a residence time of 4.5 h. To increase the DS to 1.5, the intermediate CMS, with a DS of 0.8, is fed to the second CSTR, having a starch content of 20% (w/w); a H_2O/IPA ratio of 5/95 w/w; a temperature of 40°C; a volume of 7.4 m³; and a residence time of 3.6 h. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Process design; Starch; Continuous process

1. Introduction

In this paper, a process design for the continuous production of highly substituted carboxymethyl starch (CMS) from potato starch in aqueous isopropyl alcohol (IPA) is presented. The main advantage of using organic liquids is the fact that the granular structure of the starch will remain intact up to a high degree of substitution (DS). The granular form of CMS facilitates easy downstream processing, i.e. separation, purification and drying of the solid product, while the specific physical properties of a starch granule are preserved.

Starch consists of amylose and amylopectin, both polymers of anhydro-glucose units (AGU) as the monomer. Each AGU has one primary and two secondary hydroxyl groups, which can be modified. The number of substituted hydroxyl groups per AGU is defined as the DS. Therefore, the value for the DS is between zero and three.

CMS is a cold water-soluble starch ether which is mainly used in non-food applications (see Fig. 1 for an overview; Hofreiter, 1986). In the pharmaceutical industry, CMS is used as disintegrant under the name sodium starch glycolate (Bolhuis, Van Kamp, Lenk, Gelen, Arends & Stuut, 1984). This is a chemically crosslinked CMS with a DS of about 0.3. A specific application of highly substituted CMS is as a thickener in reactive dye printing on textile. The dye reacts with primary hydroxyl groups of the cellulose fibres of the textile and forms a chemical bond. Presently, sodium alginate, which does not contain primary hydroxyl groups, is mainly used as a thickener in reactive textile printing. As an alternative, the use of native and modified carbohydrates is now being explored. Native starch contains primary hydroxyl groups, and these cause a loss of the dye. Recently, it has been demonstrated that modified carbohydrates may have the same qualities as sodium alginate (Hebeish, Haggag, El-Kashouti, El-Zairy, Ragheb, Abd El Thalouth & Kantouch, 1995; Sostar & Schnieder, 1998). By selective substitution of the primary hydroxyl groups of starch with sodium monochloro acetate (SMCA) into carboxymethyl groups the loss of dye will be prevented. The fact that the primary hydroxyl groups are less reactive

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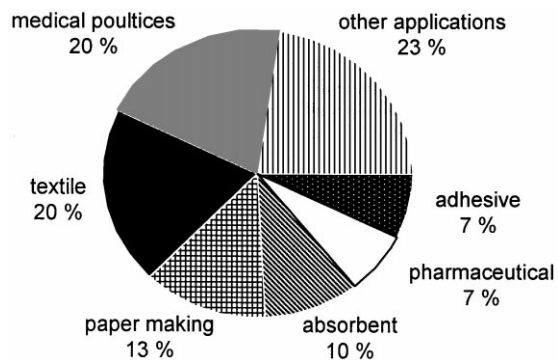*E-mail address:* jose.tijsen@akzonobel.com (C. J. Tijsen).

Fig. 1. Overview of the applications of carboxymethyl starch (taken from Hofreiter, 1986).

than the secondary ones means that a high DS is required.

The carboxymethylation reaction on starch proceeds in two steps. First, sodium hydroxide reacts with the hydroxyl groups of the starch (ROH) to give alkoxide groups:
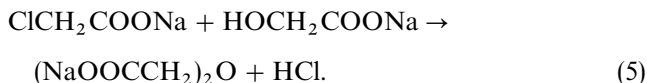
$$ROH + NaOH \rightleftharpoons RONa + H_2O. \tag{1}$$
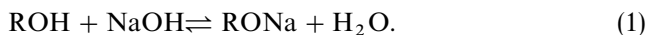
The carboxymethyl groups are formed in a S_N2 reaction between the starch alkoxide and the SMCA. This main reaction is given by

$$RONa + ClCH_2COONa \rightarrow ROCH_2COONa + NaCl. \tag{2}$$
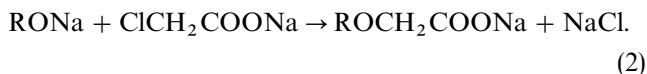
SMCA and sodium hydroxide can also form the side-product sodium glycolate, via the following reaction:

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl. \tag{3}$$
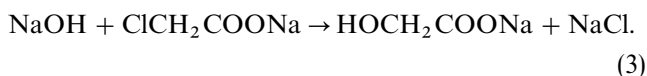
SMCA can also react with water, but this reaction is significantly slower than the reaction of SMCA with sodium hydroxide. For the conditions applied in this study the reaction with water can be neglected (Dawson & Pycock, 1934). Sodium glycolate can react further, either with itself or with SMCA, to give sodium diglycolate:

$$2HOCH_2COONa \rightarrow (NaOOCCH_2)_2O + H_2O, \tag{4}$$

$$ClCH_2COONa + HOCH_2COONa \rightarrow$$
$$(NaOOCCH_2)_2O + HCl. \tag{5}$$

The last two reactions are important in the presence of large amounts of sodium glycolate. This is relevant only if the selectivity of SMCA towards the product, CMS, is low.

There are a number of methods to produce CMS. The conventional process to modify starch is an aqueous suspension in a batch reactor, with 35–45% (w/w) solids. This method is applicable up to a DS of about 0.07,

above which the starch starts to gelatinise (Hofreiter, 1986). Modifications of starch as a paste, i.e. gelatinised starch, are also known. However, when this is done in a batch reactor often a heterogeneous product is obtained, due to the high viscosity of the paste. Recently, in our laboratory a static mixer reactor was tested for the continuous production of CMS paste (Lammers, Stamhuis & Beenackers, 1993; Visser, Rozendal, Hoogstraten & Beenackers, 1999). Another method is a dry process, where starch granules and SMCA powder are mixed with a 50% (w/w) caustic solution of sodium hydroxide (Rutenberg & Solarek, 1986). There are three main drawbacks for all these methods. First, the specific characteristics of the starch granules are lost in most of the above-mentioned processes. Second, the DS values that can be achieved with these methods are rather low, below 1 (Hofreiter, 1986). Third, the side products, sodium chloride and sodium (di-) glycolate, cannot be washed out easily when CMS is a paste. A method to overcome these drawbacks is to use an organic liquid as the reaction medium. It has been demonstrated that in a batch reactor, with aqueous IPA as the reaction medium, granular CMS can be produced with a DS higher than 1 (Tijsen, Kolk, Stamhuis & Beenackers, 2000). An extra advantage is that, because the granular form is preserved, the side-products can be washed out easily.

In this paper, a process design for the continuous production of highly substituted granular CMS in IPA is discussed in detail. The process contains unit operations to recover the salt-free granular CMS. An essential point is the purification of the IPA, so that it can be recycled. The sizing of the reactor and the downstream processing, for a given production capacity, are evaluated.

2. Process design

The process flow diagram for the continuous production of highly substituted granular CMS contains, in general, a reactor followed by downstream processing to separate the product from the reaction medium and the side-products. First, the optimal process conditions and the reactor set-up for the production of highly substituted CMS are discussed. Next, the units to recover the solid product subsequently to purify the IPA are outlined. The whole process should be explosion safe because IPA is used.

2.1. Process conditions

The carboxymethylation of starch is affected by a large number of process parameters, which have to be optimised simultaneously. Experimental design and response surface strategies have been used to optimise the operating conditions for the carboxymethylation in IPA (Tijsen, Scherpenkate, Stamhuis & Beenackers, 1999). An
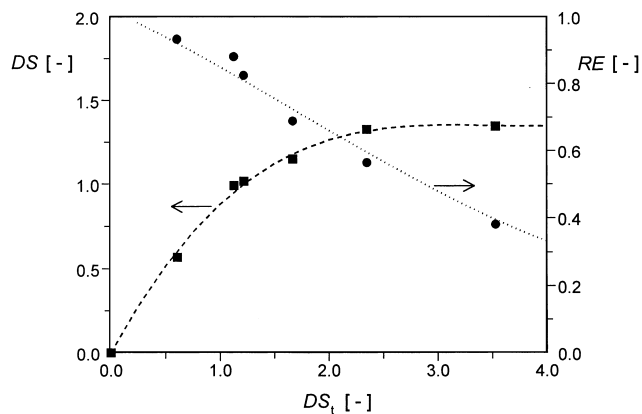
Fig. 2. The degree of substitution (DS, ■) and the reaction efficiency (RE, ●) as a function of the theoretical DS (DS_t) for the carboxymethylation of potato starch in one batch reaction. The reaction conditions are: H_2O/IPA = 10/90 w/w, w_{AGU} = 4% (w/w), t = 800 min, NaOH/SMCA = 1, and T = 40°C.

important parameter in the optimisation is the reaction efficiency (RE), which is defined as

$$RE = \frac{DS}{DS_t} \tag{6}$$

with DS_t being the theoretical DS. This is the maximum possible DS if all the reactants have been converted towards carboxymethyl groups. In other terms, the DS_t is calculated from

$$DS_t = \frac{\min(n_{NaOH}, n_{SMCA})}{n_{AGU}}. \tag{7}$$

In Eq. (7), n_{AGU} is the molar amount of the starch monomer units, n_{NaOH} is the molar amount of sodium hydroxide, and the molar amount of SMCA is given by n_{SMCA}. Fig. 2 shows the results for the DS and the RE as a function of DS_t under optimised conditions in a batch reactor. The graph shows that the RE decreases over the whole DS_t range. Above a DS_t of about 2 a further increase of reactants does not result in an increase in the DS of the product. The highest DS that could be realised in a single-batch reaction is about 1.3.

Recently, we have shown that a process with two consecutive reaction steps gave better results in terms of DS, conversion of SMCA and selectivity of SMCA towards CMS (Tijsen et al., 2000). An important point is that the H_2O/IPA ratio in the second reaction step must be lower, i.e. 5/95 w/w, than in the first step, i.e. 10/90 w/w. This strategy was tested both on a lab scale, in a 1 l batch reactor, and on a semi-technical scale, in a 180 l batch reactor. Results for the 1 l batch reactor are given in Tijsen et al. (2000). The results for the semi-technical scale, i.e. the DS as a function of reaction time and reaction conditions, are given in Fig. 3 and Table 1. It seems that the main reaction (see Fig. 3 and Eq. (2)) has first-order kinetics. Actually, this is an apparent first-
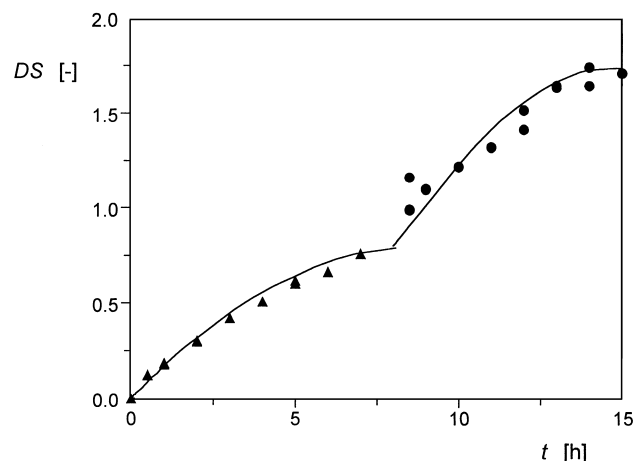

Fig. 3. The DS as a function of the batch reaction time (t) for the carboxymethylation of potato starch in a 180 l batch reactor: first reaction step: ▲, second reaction step: ●. The lines are obtained with a kinetic model for the reaction conditions and reaction rate constants given in Table 1.

Table 1
Reaction conditions and results of the semi-technical batch experiments. I and II are the first and the second batch reaction, respectively. The solubility of SMCA and the reaction rate constants for the main and side reaction in the reaction medium at 40°C are given

		I	II
V_{liquid}	m³	144	160
T	°C	40	40
w_{H_2O}	kg/kg	0.10	0.05
C^*_{SMCA}	kmol/m³	0.20	0.03
w_{AGU}	kg/kg	0.23	0.21
w_{sol}	kg/kg	0.35	0.31
DS_t	mol/mol	0.99	1.75
NaOH/SMCA	mol/mol	1.25	1.25
t	h	7	7
k_{main}	m³/(kmol s)	3×10^{-5}	1×10^{-3}
k_{side}	m³/(kmol s)	3×10^{-4}	1×10^{-3}
$DS_{product}$	—	0.76	1.71
$RE_{overall}$	—	0.77	0.86

order behaviour, because the reaction is overall second order, first order in starch and first order in SMCA. However, for the conditions used, the reaction medium is saturated with SMCA, resulting in an apparent zero-order dependency in SMCA. The solubilities of SMCA (C^*_{SMCA}) were determined separately for the relevant reaction conditions (see Table 1). At the semi-technical scale, around 30 kg of granular CMS with a DS of about 1.7 were produced using two consecutive reaction steps.

2.2. Reactor selection

In the starch industry batch reactors are mostly used for modification reactions, merely based on historical

motives. For the production of granular CMS a continuous reactor seems more logical, because a constant product quality is desired. Furthermore, the system should be closed because a volatile organic liquid is used.

For the selection of a continuous reactor, first the orders of the reactions should be considered. Both the main and the side reaction, Eqs. (2) and (3), have overall second-order reaction kinetics. The main reaction is first order in both SMCA and starch alkoxide. The starch alkoxide concentration depends linearly on the NaOH concentration (Eq. (1)). The side reaction is first order in SMCA and in NaOH. Consequently, no particular type of operation (plug flow, cross-flow or ideal mixing) is preferred from a selectivity point of view.

An essential point is that the reaction mixture is a suspension. Furthermore, the reaction is rather slow and the rate is limited by the solubility of SMCA in the reaction medium, as can be seen from the apparent first-order kinetics in Fig. 3. Therefore, an important requirement is that the starch granules are prevented from settling even for long reaction times. A reactor that best suits the above considerations is the continuous, stirred tank reactor (CSTR).

The batch experiments showed that as the reaction proceeds, the amount of water in the reaction system must be reduced. This can be fulfilled easily with two CSTRs in series. The first and the second reactor operate with a reaction medium containing 10/90 w/w and 5/95 w/w H_2O/IPA, respectively. In between the two reactors, purification sections can be placed to remove the side-products and to recover the IPA. For suspensions the agitating apparatus are, in general, identical to the ones used for a standard stirred tank reactor. In this case, the reactor should not contain baffles. Batch experiments showed that between the baffles agglomeration of starch granules occurred. To prevent a vortex, the impeller should be placed just above the bottom of the reactor (Perry, Green & Maloney, 1984). The reaction is carried out at a relatively low temperature of 40°C, and due to the long reaction times (of the order of hours), a standard jacketed reactor will be sufficient to heat the reaction mixture.

Native starch is added as a suspension, in water and isopropyl alcohol, to the first reactor. The H_2O/IPA composition of the feed is not equal to that of the reaction medium, because water is produced in the starch–NaOH equilibrium (Eq. (1)). This is taken into account in the calculation of the inlet flows. Batch experiments showed that it is advantageous to add NaOH prior to SMCA. In that case, the NaOH–starch equilibrium is established first. Sodium hydroxide has a low solubility in alcohol (Seidell, 1940). Addition of water to isopropyl alcohol does not increase the solubility of NaOH, but results in a two-phase liquid system, consisting of a NaOH-rich water phase and a NaOH-poor organic phase (Mills & Hughes, 1957). Therefore, NaOH

is added as a solid to the native starch suspension before entering the first reactor. The reactant SMCA is added to the first reactor as a powder, because it has a low solubility in IPA (see Table 1). A screw conveyer is suggested for the addition of both the SMCA powder and the NaOH pellets.

For the second CSTR, the H_2O/IPA ratio is lower than for the first reactor and a CMS of intermediate DS is fed instead of native starch. The feed procedure for the second CSTR is similar to that of the first reactor.

2.3. Solid/liquid separation and product recovery

In the production of granular CMS, a salt-free dry product is desired and IPA has to be recovered. After the first CSTR the water content in the suspension has to be reduced and the salts have to be removed. Therefore, the intermediate CMS suspension is washed and thickened before it is transported to the second CSTR. The solids-free reaction liquid and the liquid used for the washing are transported to the IPA purification units (see Section 2.4). To obtain a salt-free dry CMS product the suspension leaving the second CSTR is washed, thickened and the final CMS granules are dried.

In the literature there are a number of apparatus suggested for solid/liquid (S/L) separations. For selection we used the design guide based on particle size and concentration developed by Scarlett and Ward (1986). The average size by weight of a potato starch granule is 40 μm (Kuipers, 1995), and the fraction of starch is around 30% (w/w). According to Scarlett and Ward (1986), in this case cake filters, pressure or vacuum driven, can be used. On a continuous cake filter, the washing time and the volume of the wash liquid varies and need to be optimised. Hydrocyclones are often used as S/L separators in the potato starch industry (Verberne, 1977). The advantage of hydrocyclones is that there are no moving parts, and that the solids can be washed thoroughly. The disadvantage of hydrocyclones is that there is no blocking screen. In the carboxymethylation process this is very important, because if starch particles are present in the liquid it can cause blocking of the liquid purification section. For washing and thickening of the CMS suspension a continuously operated cake filter, with an optimised washing section, is proposed.

Drying of the final granular CMS product can be incorporated in the filtration apparatus used for the washing and thickening of the suspension. For the drying of the solids hot air is blown through the filter cake. Hot air has a low density and a low specific heat, and a rather large volume is required for a significant quantity of heat. A vacuum can be used as well, with the advantage that the IPA vapour can be collected, condensed and transported to the purification section. A drawback of the filter method is that a dry CMS cake is obtained which is

mechanically removed from the filter. This may cause damage to the granules, resulting in a loss of the specific granular properties. Another method of continuous drying of starch particles is flash drying. Flash dryers are used in potato starch manufacturing plants (Treadway, 1967). Tests on semi-technical scale in a batch Bolz dryer have shown that CMS granules have good fluidisation characteristics. Therefore, for the drying of the granular CMS product a flash dryer is proposed.

2.4. Recovery of the reaction liquid

The carboxymethylation is carried out in IPA with a small amount of water. For economical reasons it is desirable to recycle the IPA. In this process, the liquid outlet flows of both CSTRs have to be reconditioned. Besides IPA, both flows contain salts and water, the latter has to be removed only partly.

Purification of IPA is normally done with distillation. In this case, the concentration of the water is below the azeotropic point, therefore, azeotropic distillation should be used. The salts in the inlet flow change the azeotrope composition only slightly. Normally, an entrainer, e.g. cyclohexane, is used to break the azeotrope. A disadvantage is that the water flow becomes contaminated with the entrainer. If a Kubiersky distillation sequence, with three columns in series, is used the entrainer can be recycled (Ryan & Doherty, 1989). The first column is fed with the outlet flow of the CSTR and the azeotrope is broken. The bottom flow of this column has the specified H_2O/IPA composition. In the second column the entrainer is purified and in the third column water is separated from the entrainer. For the recovery of both IPA flows two Kubiersky sequences have to be used. For the first reactor giving a 10/90 w/w and for the second reactor giving a 5/95 w/w H_2O/IPA. The disadvantage of this distillation sequence is that the specified flow is the bottom flow of the first column so the salts will stay in this flow as well. Therefore, an alternative has to be considered.

Pervaporation is an attractive method for the dehydration of organic liquids, the permeate is mainly water and the retentate has the specified composition. In a literature study, the following types of membranes were compared: cellulose acetate (Deng, Shiyao, Sourirajan & Matsuura, 1990); Carboxymethyl cellulose (Atra, Vatai & Békássy-Molnár, 1999); polyetherimide (Huang & Feng, 1993); ceramic (Van Gemert & Cuperus, 1995); zeolite-filled PVA (Gao, Yue & Li, 1996); chitosan (Nawawi & Huang, 1997); and zeolite 4A (Jafar & Budd, 1997). The performance of a pervaporation unit depends on the fluxs and the selectivity. These properties depend on the type of membrane and are determined by the operating conditions, the temperature and vacuum at the permeate side. From the various membranes, the zeolite 4A membrane (Jafar & Budd, 1997) or the ceramic membrane (Van
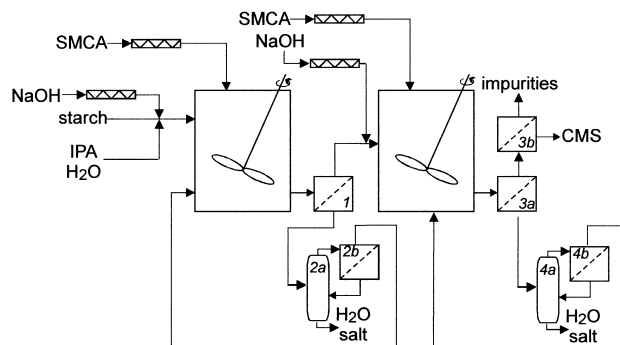

Fig. 4. Process flow diagram for the continuous production of highly substituted granular CMS. The units are: 1: S/L separation, thickening and washing of the intermediate CMS suspension. 2: hybrid system for the dehydration of isopropyl alcohol with 2a: distillation and 2b: pervaporation. 3: S/L separations, 3a: thickening and washing of the final CMS suspension and 3b: drying of the solid CMS granules. 4: hybrid system for the dehydration of isopropyl alcohol with 4a: distillation and 4b: pervaporation.

Gemert & Cuperus, 1995) seem to be the most suited. These type of membranes require the smallest membrane area and are the most resistant against contamination. For the zeolite 4A membrane the best separation is at a temperature of 70°C. It is known that salts influences the dehydration performance of a pervaporation section. If salts stay in the dehydrated IPA flow that is recycled, they will accumulate in the process.

The difficulties with the salts can be overcome by using a hybrid system, i.e. combining normal distillation with pervaporation (Mulder, 1996). The top flow of the distillation column has the azeotropic composition, $H_2O/IPA = 13/87$ w/w, and is fed to the pervaporation system. The retentate leaving the pervaporation system has the specified H_2O/IPA composition and the permeate is mainly water that is fed back to the distillation column. The bottom flow of the distillation column is water with the salt. If necessary, it can be purified, e.g. by reverse osmosis.

2.5. Complete flow sheet and sizing

In Fig. 4, the process flow diagram for the continuous production of highly substituted granular carboxymethyl starch is given. The design consists of two CSTRs in series with unit operations to purify the final product and to recondition the IPA. In the first CSTR, operating at 40°C with a H_2O/IPA ratio of 10/90 w/w, an intermediate CMS is produced. The second CSTR, operating at 40°C with a H_2O/IPA ratio of 5/95 w/w, produces the final CMS product. The Units 1 and 3a, in Fig. 4, are continuous cake filters for thickening and washing of the intermediate CMS suspension and the final CMS suspension, respectively. The two aqueous IPA flows are dehydrated by a hybrid system, Units 2 and 4. The hybrid

systems contain each a distillation column, Units 2a and 4a, and a pervaporation section, Units 2b and 4b. Each purified IPA flow is recycled to their original CSTR. The washed intermediate CMS from Unit 1, is fed to the second CSTR together with NaOH and SMCA. The final CMS product leaving the continuous cake filter, Unit 3a, is fed to a flash dryer, Unit 3b. After the flash dryer salt-free granular CMS is obtained.

The production capacity of the continuous carboxymethylation process for a specific DS is determined by the starch fraction in the reactor, the reactor volume and the residence time in the reactor. The starch fraction in the reactor is limited by the total solids content. Batch experiments showed that the maximum solids content in a stirred tank reactor is around 35% (w/w), resulting in a maximum starch fraction of around 25% (w/w). Therefore, these quantities are suggested for the continuous process as well. For the carboxymethylation process low residence times, high conversions of SMCA and high selectivities of SMCA towards the produced CMS are desired. The kinetic model described in Tijsen et al. (1999) has been used to calculate the residence time and to find the optimal reaction conditions in the reactors. The reaction rate constants and the partition coefficients were determined from batch experiments (see also Table 1).

To produce CMS with a final DS of 1.5, intermediate CMS with a DS of 0.8 is produced in the first CSTR and the DS is increased to 1.5 in the second CSTR. For the first CSTR, the residence time, the conversion of SMCA and the selectivity of SMCA towards the intermediate CMS as a function of the NaOH/SMCA molar ratio are given in Fig. 5a. Here the DS_t was kept constant at 1.25, in other words a constant SMCA/AGU ratio was taken (see Eq. (7)), whereas the reaction was modelled for a DS of 0.8. In Fig. 5b the residence time, the conversion and the selectivity are given as a function of DS_t for the first reactor, with NaOH/SMCA kept constant at 1.25 and again with a DS equal to 0.8. It is noted that the numerical results are influenced by the constant values chosen for either DS_t in Fig. 5a and NaOH/SMCA in Fig. 5b, though the general trends remain the same for other DS_t and NaOH/SMCA ratios.

Both Fig. 5a and b show that the selectivity of SMCA towards the intermediate product decreases with increasing NaOH/SMCA ratio and DS_t. Furthermore, the conversion of SMCA increases as the NaOH/SMCA ratio is increased, and the conversion has a minimum as a function of DS_t. The NaOH/SMCA ratio has an asymptote for the residence time, caused by a decrease of the selectivity as the NaOH/SMCA ratio is increased. Apparently for a DS_t equal to 1.25, a NaOH/SMCA ratio greater than 1.8 results in too much SMCA hydrolysis to make a DS of 0.8 possible. It can be concluded that a high selectivity means a low DS_t and a low NaOH/SMCA ratio. A high conversion means a low DS_t but a high NaOH/SMCA ratio. A short residence time means a me-
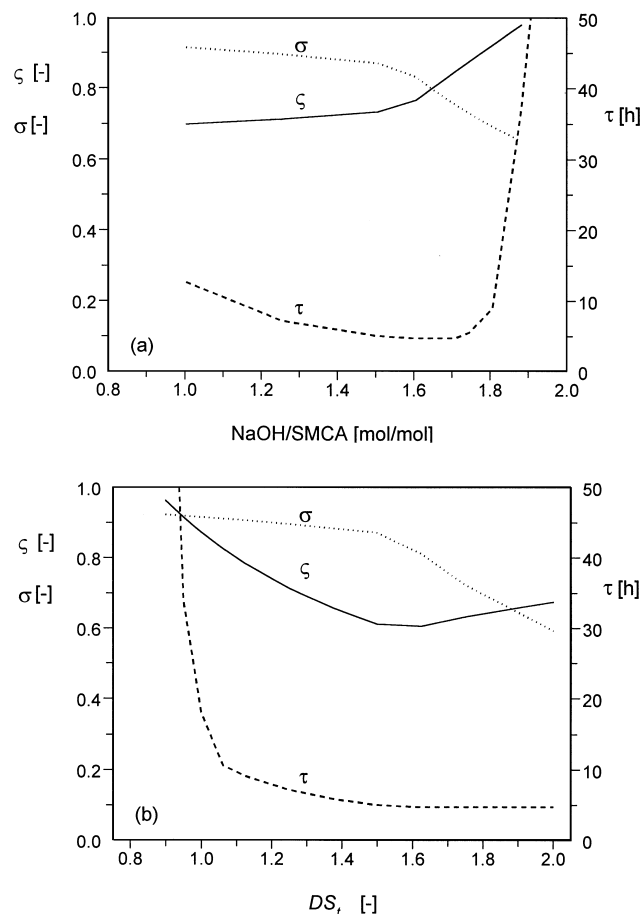

Fig. 5. The conversion of SMCA (ς), the selectivity of SMCA toward CMS (σ) and the residence time (τ) as a function of (a) the NaOH/SMCA molar ratio for $DS_t = 1.25$, (b) the DS_t for NaOH/SMCA $= 1.25$, all for the production of CMS with a DS of 0.8. For both figures $T = 40°C$, $w_{AGU} = 17\%$ (w/w), $w_{sol} = 35\%$ (w/w) and $H_2O/IPA = 10/90$ w/w.

dium DS_t and a medium NaOH/SMCA ratio. Therefore, not all constrains can be fulfilled at the same conditions. For the second reactor, the residence time, conversion of SMCA and the selectivity of SMCA towards the final product have a similar dependency on the DS_t and the NaOH/SMCA ratio as observed for the first reactor.

In Fig. 6 the production capacity of CMS, with a final DS of 1.5, as a function of the volume of the second reactor is calculated for three cases. The conditions for each case are given in the figure caption. For a high production rate, i.e. a relative short residence time, a concession in the selectivity has to be made. Nevertheless, for the highest production rate, i.e. Case III, the selectivity in the second reactor is still as high as 0.97. The conditions of Case III were used to calculate the residence time and reactor volume for an annual production of 3600 tons. The first CSTR should have a residence time of 4.5 h and a volume of 10.25 m³, to produce intermediate CMS with a DS of 0.8, with a solids fraction of 35% (w/w) and

Table 2
Process conditions required for an annual production of 3600 tons granular CMS with a DS of 1.5. I and II are first and second CSTR, respectively

|		I-in	I-out	II-in	II-out
Φ_m	kg/s	0.65	0.65	0.70	0.70
w_{sol}	kg/kg	0.35	0.31	0.35	0.31
w_{AGU} or w_{CMS}	kg/kg	0.17	0.23	0.23	0.26
w_{H_2O}	kg/kg	0.10	0.14	0.05	0.09
x_{NaOH}	mol/mol	0.100	0.002	0.099	0.004
x_{SMCA}	mol/mol	0.067	0.018	0.055	0.015
x_{AGU} or x_{CMS}	mol/mol	0.053	0.053	0.056	0.056
x_{H_2O}	mol/mol	0.211	0.303	0.118	0.213
x_{IPA}	mol/mol	0.568	0.568	0.672	0.672
x_{NaCl}	mol/mol	0.000	0.049	0.000	0.040
$x_{glycolate}$	mol/mol	0.000	0.006	0.000	0.001
$V_{reactor}$	m³	10.25	—	7.41	—
τ	h	4.49	—	3.57	—
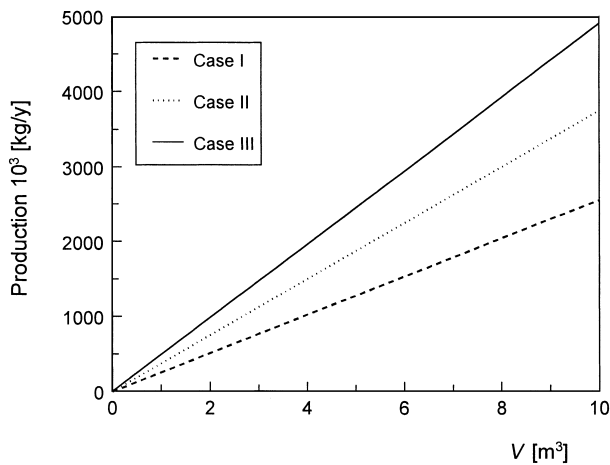
Fig. 6. Annual production of the CMS product as a function of the reactor volume of the second CSTR for Case I: $DS_t = 1.8$, NaOH/SMCA = 1.25, $\varsigma = 0.72$ and $\sigma = 0.99$; Case II: $DS_t = 2.0$, NaOH/SMCA = 1.25, $\varsigma = 0.60$ and $\sigma = 0.98$; Case III: $DS_t = 1.8$, NaOH/SMCA = 1.80, $\varsigma = 0.73$ and $\sigma = 0.97$. For all cases $T = 40°C$, $w_{CMS} = 23\%$ (w/w), $w_{sol} = 35\%$ (w/w) and H_2O/IPA = 5/95 w/w.

a starch fraction of 17% (w/w). For this production capacity the second CSTR should have a volume of 7.41 m³ with a residence time of 3.6 h to increase the DS from 0.8 to 1.5, with a solids fraction of 35% (w/w) and a starch fraction of 23% (w/w). In Table 2, the mole fractions and mass flows are given for the first and the second CSTR.

3. Conclusions

A novel process is proposed for the continuous production of highly substituted granular CMS, in aqueous IPA, with a DS typically of 1.5. A special feature of the process is that by selecting the optimal H_2O/IPA ratio,

the CMS remains granular despite the high DS. This allows for an easy product separation and purification. The isopropyl alcohol can be kept in the system by a nearly 100% recovery.

Notation

C^*_{SMCA}	maximum solubility of SMCA, kmol/m³
DS	degree of substitution
DS_t	theoretical degree of substitution
k	second-order reaction rate constant, m³/(kmol s)
n	molar amount, mol
RE	reaction efficiency
T	temperature, °C
t	time, min or h
V	volume, m³
w_{AGU}	starch mass over mass starch and mass liquid, w/w
w_{H_2O}	water mass over mass liquid, w/w
w_{sol}	solids mass over mass solids and mass liquid, w/w
x	mole fraction, mol/mol

Greek letters

ς	conversion of SMCA
τ	residence time in CSTR, h
σ	selectivity of SMCA towards CMS
Φ_m	mass flow, kg/s

Subscripts and superscripts

AGU	anhydro-glucose unit
CMS	carboxymethyl starch
IPA	isopropyl alcohol
liquid	liquid, i.e. water and IPA
main	main reaction, Eq. (2)
overall	for all reaction steps involved

product   carboxymethyl starch, CMS
side   side reaction, Eq. (3)
SMCA   sodium monochloro acetate

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