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The reaction between granular arrowroot starch and sodium monochloroacetate (SMCA) in isopropanol-water mixtures has been studied in a systematic way using experimental design strategies. The effect of six factors, i.e. the theoretical degree of substitution (DS_t), reaction time, weight fraction of water in the mixture, NaOH/SMCA ratio, temperature and weight fraction of starch on three responses, i.e. the degree of substitution (DS), the conversion of SMCA and the selectivity of SMCA towards carboxymethyl starch, has been determined in a systematic manner. Granular carboxymethyl arrowroot starch with a maximum DS of 1.4 could be prepared in a single-step procedure. The results are compared with data obtained for potato starch. Similar trends for all responses were observed, suggesting close similarities between the chemical composition and the topochemistry of granular arrowroot- and potato-starch.

Keywords: Arrowroot starch; Modification; Carboxymethylation; Experimental design

1 Introduction

Native starches may be subjected to modification procedures to provide the desired properties for specific applications. Various types of modification procedures have been developed including physical, enzymatic and chemical modifications [1]. Examples of the latter are for instance oxidations, benzylations, ethoxylations and carboxymethylations. Carboxymethylation is commonly performed using sodium monochloroacetate (SMCA) and the product is carboxymethyl starch (CMS). The carboxymethylation reaction proceeds as follows:

$$ROH + NaOH \rightleftarrows RONa + H_2O \quad (1)$$

$$RONa + ClCH_2COONa \rightarrow ROCH_2COONa + NaCl \quad (2)$$

The reaction is carried out in the presence of a strong base to enhance the nucleophilicity of the hydroxyl group and to swell the starch particles. Sodium hydroxide is also playing a role in the undesired side-reaction occurring during the carboxymethylation process, that being the reaction between NaOH and SMCA to form sodium glycolate:

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl \quad (3)$$

Carboxymethyl starches are, in contrast to native starch, cold-water soluble provided that the degree of substitution (DS) is higher than about 0.2 [2]. Therefore, carboxymethylated starches have found applications in the area of paper making, textile printing, absorbents, pharmaceuticals, adhesives and medical poultices [3].

Various production methods have been developed to manufacture carboxymethyl starch [4]. With these methods, the final product is obtained either as a viscous paste or in a granular form. The latter form is preferable as it significantly simplifies product purification and drying. A well known procedure to obtain granular formed CMS is the application of organic solvents as the reaction medium. This process has been studies extensively to assess the effects of process conditions and reagent intake on the degree of substitution of the product [2, 5-7]. In our research group, *Tijsen* et al. [7, 8] studied the carboxymethylation process of granular potato-starch in more detail. The optimum reaction medium for the carboxymethylation process is a mixture of an alcohol, preferably isopropanol, and water (90:10 wt%). The maximum attainable DS by using this procedure is about 1.3.

This article describes the application of this procedure for the preparation of carboxymethyl arrowroot starch. Arrowroot could be a cheap alternative starch source for various starch production and starch modification companies in tropical countries. Arrowroot (*Marantha arundinacea*) is a tropical plant that grows in warm, swampy areas. The plant originates from the Caribbean region but is now widespread throughout the tropics. Until now, only a limited number of research papers have been published dealing with native or modified arrowroot starch. *Raja* et al. [9, 10] studied the properties of arrowroot starch treated with steam and aqueous HCl, whereas *Perez* [11] studied the gelatinization profiles for arrowroot starch. However, process studies on the carboxymethylation of arrowroot starch have not been reported yet. We here de-

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scribe our systematic studies on the carboxymethylation of arrowroot starch in an isopropanol-water mixture. The results will be compared with previous research performed on granular potato starch [7, 8, 12]. This study provides insights in the factors that affect the carboxymethylation process and allows determination of the optimum operating conditions to achieve carboxymethylated arrowroot starch with a high degree of substitution. In addition, it provides valuable input for the development of kinetic reactor models for this carboxymethylation process, that will be the subject of further studies.

2 Materials and Methods

2.1 Chemicals

Sodium hydroxide, isopropanol, sulfuric acid and $Ba(OH)_2$ were of technical grade and used without further purification. Technical grade SMCA was obtained from Akzo-Nobel (Arnhem, The Netherlands). Larger agglomerates of crystals were removed by sieving. Water purified by reverse osmosis was applied. The arrowroot starch applied in this investigation was isolated from arrowroots using a standard separation technique for native starches [13].

2.2 Isolation of arrowroot starch from arrowroot

The crude arrowroot was thoroughly washed with water to remove solid dirt. The arrowroot was subsequently cut into small pieces and, together with water (water: arrowroot = 3:1 vol/vol), mixed in a blender for 1 min. The mixture was sieved using a fine cotton cloth. Fibers remained on the cloth while the dispersed starch and the proteins passed through. The crude dispersed starch was washed with water (water: arrowroot = 6:1 vol/vol, three times in succession). The foam on top of the water layer (proteins) was removed. Subsequently, the starch was washed three times with water (water: arrowroot = 6:1 vol/vol) to remove other contaminants. The wet starch was dried in the air for at least one day. Further reduction of the water content is achieved by drying the sample in a vacuum stove. (55 °C, ca. 5 kPa) for about 24 h. Typical water contents of the starch samples obtained using this procedure are between 10-15%.

2.3 Analytical measurements

The DS was determined using high-performance liquid chromatography (HPLC) following a well established procedure [7, 14, 15]. The conversion of SMCA was calculated from the amount of chlorine ions present in the solution using a potentiometric titration with $AgNO_3$ [16]. The average size of the arrowroot starch granules was determined using electron microscopy and appeared to be 23 μm. The water content of the starch samples was determined using an IR-lamp placed on a balance [7].

2.4 Experiments

The experiments were carried out in 25-mL batch reactors equipped with a magnetic stirrer. The reaction vessels were placed in a thermostatic bath to ensure isothermal conditions within the reactor. The reaction vessel was filled with the appropriate amount of NaOH, followed by the predetermined amount of starch and the isopropanol-water mixture. Subsequently, the reactor was flushed with nitrogen to remove all air, closed and placed in the thermostatic bath. The mixture was stirred for 16 h. After these 16 h, the reaction was initiated by adding the appropriate amount of SMCA. The reaction was stopped at the predetermined reaction times by dropwise addition of concentrated sulfuric acid until a pH of about 1 was obtained.

2.5 Design of experiments

The experiments were conducted according to a Box-Behnken design [17] with six independent variables/factors. The design scheme consisted of 57 experiments, including seven center points to determine the experimental error. The selected independent variables including the applied levels are given in Tab. 1. The factor DS_t is the maximum attainable degree of substitution based on the molar intake of the limiting reactant (either SMCA or NaOH):

$$DS_t = \frac{n_{SMCA,0}}{n_{AGU,0}} \text{ if } n_{NaOH,0} \geq n_{SMCA,0}$$
$$DS_t = \frac{n_{NaOH,0}}{n_{AGU,0}} \text{ if } n_{NaOH,0} \geq n_{SMCA,0} \quad (4)$$

Tab. 1. Selected independent variables and experimental ranges.

Variable	DS_t	t [min]	w_{H_2O} [wt%]	NaOH/SMCA	T [°C]	w_{starch} [wt%]
Code	A	B	C	D	E	F
Low level	0.5	100	7.0	0.5	30	2.0
Middle level	1.75	300	11.0	1.25	40	7.0
High level	3.0	500	15.0	2.0	50	12.0

Tab. 2. Compilation of experiments and modeling results.

Run	DS_t	w_{H_2O} [wt%]	NaOH/SMCA [mol/mo]l	w_{Starch} [wt%]	t [min]	T [°C]	DS_{exp}	DS_{model}	ζ_{exp}	ζ_{model}	σ_{exp}	σ_{model}
1	1.75	7	1.25	7	100	30	0.12	0.18	0.21	0.29	0.33	0.44
2	1.75	7	1.25	7	500	30	0.53	0.34	0.49	0.49	0.62	0.48
3	1.75	15	1.25	7	100	30	0.16	0.37	0.14	0.48	0.68	0.68
4	1.75	15	1.25	7	500	30	0.24	0.63	0.18	0.69	0.77	0.72
5	0.50	11	0.50	7	300	30	0.07	0.03	0.49	0.08	0.63	0.76
6	3.00	11	0.50	7	300	30	0.55	0.68	0.23	0.14	0.78	0.80
7	3.00	11	0.50	7	100	40	0.79	0.84	0.33	0.24	0.80	0.80
8	0.50	11	0.50	7	500	40	0.13	0.08	0.31	0.28	0.86	0.80
9	3.00	11	0.50	7	500	40	1.14	1.19	0.47	0.43	0.81	0.84
10	0.50	11	2.00	7	100	40	0.28	0.22	0.68	0.71	0.83	0.75
11	3.00	11	2.00	7	100	40	0.81	0.70	0.93	0.82	0.29	0.36
12	0.50	11	2.00	7	500	40	0.36	0.41	0.90	0.86	0.79	0.79
13	0.50	11	2.00	7	300	30	0.27	0.17	0.71	0.56	0.76	0.75
14	3.00	11	2.00	7	300	30	0.44	0.55	0.37	0.72	0.39	0.34
15	1.75	11	1.25	2	100	30	0.31	0.37	0.37	0.39	0.48	0.57
16	1.75	11	1.25	2	500	30	0.45	0.62	0.45	0.60	0.57	0.61
17	1.75	11	1.25	12	100	30	0.20	0.30	0.15	0.37	0.77	0.56
18	1.75	11	1.25	12	500	30	0.94	0.53	0.87	0.59	0.62	0.60
19	0.50	11	0.50	7	100	40	0.02	0.04	0.05	0.14	0.79	0.76
20	3.00	11	2.00	7	500	40	0.73	1.04	0.87	0.92	0.28	0.39
21	1.75	7	0.50	2	300	40	0.17	0.26	0.29	0.33	0.34	0.38
22	1.75	15	0.50	2	300	40	0.46	0.22	0.31	0.53	0.85	0.72
23	1.75	7	2.00	2	300	40	0.92	0.49	0.90	0.88	0.59	0.53
24	1.75	15	2.00	2	300	40	0.57	0.41	0.99	0.95	0.33	0.45
25	0.50	11	2.00	6	300	50	0.45	0.56	0.92	0.93	0.84	0.79
26	3.00	11	2.00	6	300	50	1.03	1.21	0.54	0.96	0.54	0.41
27	1.75	11	1.25	2	100	50	0.72	1.06	0.71	0.85	0.50	0.58
28	1.75	11	1.25	2	500	50	0.98	1.39	0.76	0.93	0.63	0.62
29	1.75	11	1.25	12	100	50	1.26	1.02	0.95	0.84	0.65	0.63
30	1.75	11	1.25	12	300	50	1.37	1.36	0.96	0.93	0.70	0.67
31	0.50	15	1.25	2	300	40	0.15	0.19	0.34	0.61	0.89	0.83
32	3.00	15	1.25	2	300	40	0.91	0.56	0.78	0.75	0.39	0.28
33	0.50	7	1.25	12	300	40	0.02	0.02	0.26	0.39	0.13	0.22
34	3.00	7	1.25	12	300	40	0.83	0.62	0.69	0.56	0.40	0.40
35	0.50	15	1.25	12	300	40	0.30	0.37	0.74	0.59	0.81	0.93
36	3.00	15	1.25	12	300	40	1.01	0.87	0.84	0.74	0.40	0.38
37	1.75	11	1.25	7	300	40	0.84	0.86	0.69	0.74	0.69	0.70
38	1.75	11	1.25	7	300	40	1.03	0.86	0.94	0.74	0.80	0.70
39	1.75	11	1.25	7	300	40	0.85	0.86	0.74	0.74	0.66	0.70
40	1.75	11	1.25	7	300	40	1.12	0.86	0.97	0.74	0.66	0.70
41	1.75	11	1.25	7	300	40	1.03	0.86	0.88	0.74	0.67	0.70
42	1.75	11	1.25	7	300	40	0.88	0.87	0.94	0.74	0.53	0.70
43	1.75	7	1.25	7	100	50	1.07	0.78	0.86	0.79	0.61	0.50
44	1.75	7	1.25	7	500	50	0.97	1.12	0.86	0.90	0.55	0.54
45	1.75	15	1.25	7	100	50	1.13	0.97	0.96	0.89	0.58	0.65
46	1.75	15	1.25	7	500	50	1.21	1.32	0.98	0.95	0.60	0.69
47	0.50	11	0.50	7	300	50	0.14	0.12	0.28	0.45	0.83	0.77
48	3.00	11	0.50	7	300	50	1.24	1.36	0.48	0.59	0.74	0.82
49	1.75	7	0.50	12	300	40	0.05	0.09	0.06	0.32	0.51	0.44
50	1.75	15	0.50	12	300	40	0.49	0.42	0.30	0.52	0.96	1.00
51	1.75	7	2.00	12	300	40	0.09	0.17	0.65	0.88	0.08	0.24
52	1.75	15	2.00	12	300	40	0.73	0.73	0.90	0.94	0.46	0.38
53	0.50	7	1.25	2	300	40	0.05	0.07	0.31	0.40	0.30	0.32
54	3.00	7	1.25	2	300	40	1.41	1.22	0.88	0.57	0.54	0.52
55	1.75	11	1.25	7	300	40	1.03	0.87	0.70	0.74	0.84	0.71
56	1.75	11	1.25	7	300	40	0.99	0.87	0.80	0.74	0.71	0.71
57	1.75	11	1.25	7	300	40	1.03	0.86	0.84	0.74	0.70	0.70

Here $n_{AGU,0}$ is the number of moles of anhydroglucose (AGU) units in the starch. The weight fraction of water (w_{H_2O}) and the weight fraction of starch (w_{starch}) are based on the intake of all components (solvents, starch and reagents). The w_{H_2O} is corrected for the amount of water in the starch.

The selection of the experimental ranges for each factor is based on scouting experiments using arrowroot starch as well as related experimental studies on potato starch [7, 8]. An overview of all experiments carried out in the design window is given in Tab. 2.

The degree of substitution, the conversion of SMCA and the selectivity of SMCA for the reaction with arrowroot starch were selected as the quantitative responses. The conversion of SMCA (ζ_{SMCA}) is defined as:

$$\varsigma_{SMCA} = \frac{n_{SMCA,0} - n_{SMCA}}{n_{SMCA,0}} = \frac{n_{Cl} - n_{Cl,0}}{n_{SMCA,0}} \quad (5)$$

The selectivity of SMCA towards carboxymethyl starch is calculated from the experimental values of the DS and the conversion of SMCA according to the following equation:

$$\sigma = DS \frac{n_{AGU,0}}{n_{SMCA,0}\varsigma_{SMCA}} \quad (6)$$

The experimental results for each response were analyzed statistically using the Design Expert 5 software package (Stat-Ease). Responses are modeled using standard expressions:

$$y = b_0 + \sum_i b_i x_i + \sum_i b_{ii} x_i^2 + \sum_j \sum_k b_{jk} x_i x_k \quad (7)$$

Here, i = A to F, j = B to F and k = A to E with A-F representing the independent variables (see Tab. 1); b_i, b_{ii} and b_{jk} are the regression coefficients which are obtained by statistical analyses of the data. Significant factors were selected on the basis of their p value in the ANOVA analyses. Factors with a p value lower than 0.05 are regarded as significant and included in the response model. Backward elimination was applied to eliminate all statistically insignificant terms. After each elimination step, a new ANOVA table was generated to select the subsequent non-significant factor.

Of the three responses, both the DS and the conversion results had to be transformed to avoid negative model prediction. The experimental values were transformed using the logit function:

$$y_{tr} = \ln\left(\frac{y}{1-y}\right) \quad (8)$$

Transformation is only possible when the experimental values range between 0 and 1. This is always the case for the conversion and selectivity, but not for the DS. The experimental DS values were scaled between 0 and 1 by defining a DS_{ratio},

$$DS_{ratio} = \frac{DS_{experimental}}{2} \quad (9)$$

3 Results and Discussion

Carboxymethyl arrowroot starch is prepared by reacting the starch with SMCA in the presence of sodium hydroxide. The DS is dependent on process conditions such as temperature, starch loading, reaction time and solvent composition, as well as on reagent intakes. The quantitative effects of these variables on the DS as well as the conversion of SMCA and selectivity towards SMCA will be treated in the following sections. Here, the effect of changing one of the independent variables at a time on the responses is discussed, while all other independent variables are kept at standard values (Tab. 1). When relevant, the results obtained for the carboxymethylation of arrowroot starch will be compared with those obtained for potato starch [12]. The latter study was performed recently in our research group using a similar experimental design strategy (Box-Behnken design). The same independent variables were applied and the experimental ranges closely resemble those applied here for arrowroot starch.

3.1 Model analyses

The DS, SMCA conversion and selectivity obtained for all experiments within the design window are given in Tab. 2. The experimental DS values range between 0.02 and 1.41, the SMCA conversion between 0.05 and 0.96 and the selectivity towards carboxymethylation between 0.08 and 0.96. The experimental data were analyzed using statistical means. The values of the regression coefficients of the significant factors for the three responses are given in Tab. 3. Subsequently, parity plots were prepared to investigate the agreement between experimental values and model predictions (Figs. 1-3). These plots show

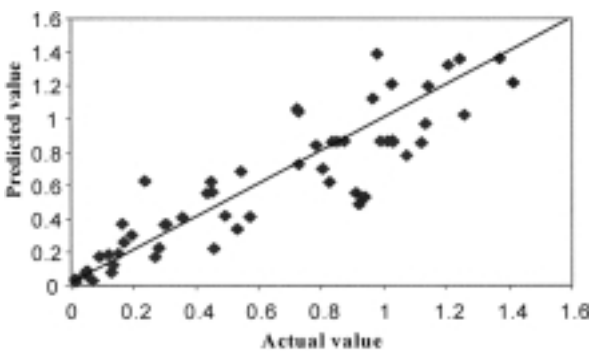

Fig. 1. Parity plot showing the modeled vs. experimental DS values.

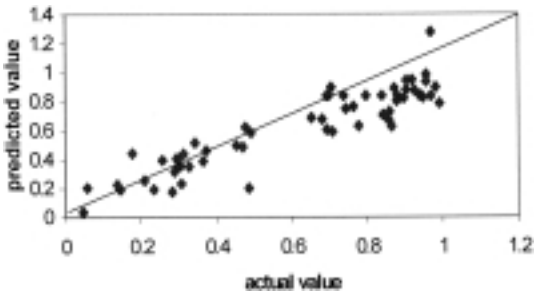

Fig. 2. Parity plot showing the modeled vs. experimental SMCA conversion values.

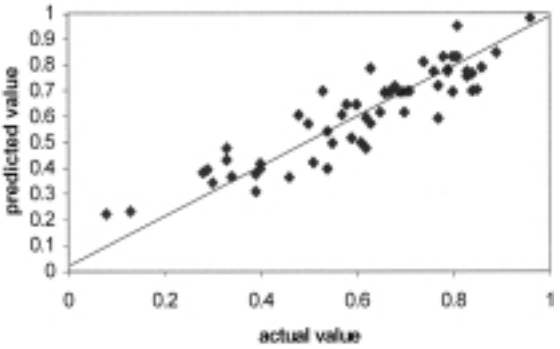

Fig. 3. Parity plot showing the modeled vs. experimental selectivity of SMCA towards carboxymethyl arrowroot starch.

that the agreement between experiments and models is satisfactory.

3.2 Effect of the reaction time on the DS, conversion and selectivity for arrowroot carboxymethylation

The degree of substitution of arrowroot starch increases at longer reaction times (Fig. 4). The design models predicts an increase in the DS from 0.8 to 1.2 when going from 100 to 500 min. Apparently, a large proportion of the substitution reaction already occurs within the first 100 min when applying the standard conditions as given in Tab. 1. This is also evident when looking at the SMCA conversion, which is already 0.76 after 100 min (Fig. 5). The selectivity for carboxymethylation appears to be rather independent of time and has a value of about 0.7 (Fig. 5). This observation is in line with the reaction

Tab. 3. Results for the regression coefficients for the models for the DS, conversion and selectivity.

Regression coefficient	DS model	Conversion model	Selectivity model
b_0	–16.1850	–9.2793	–1.8287
b_A	4.3118	1.9041	0.5474
b_B	0.0018	0.0022	0.0001
b_C	0.9359	0.1050	0.2572
b_D	4.1115	1.8113	0.5528
b_E	0.0679	0.1093	0.0023
b_F	–0.1329	–0.00488	0.0501
b_{AA}	–0.3350	–0.4664	–0.0178
b_{AB}			
b_{AC}	–0.129		–0.03756
b_{AD}	–0.5783		–0.1171
b_{AE}			
b_{AF}			
b_{BB}			
b_{BC}			
b_{BD}			
b_{BE}			
b_{BF}			
b_{CC}	–0.0360		–0.0062
b_{CD}			–0.0348
b_{CE}			
b_{CF}	0.0251		0.0028
b_{DD}	–1.0342		0.0157
b_{DE}			
b_{DF}			–0.0229
b_{EE}			
b_{EF}			
b_{FF}	–0.0117		–0.0037

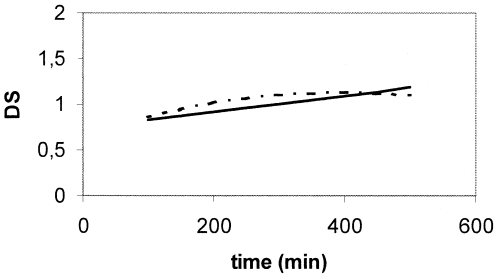

Fig. 4. Modeled DS vs. time for the carboxymethylation of arrowroot and (–) potato starch (– · –). All other independent values are set at standard conditions, see Tab. 1 for details.

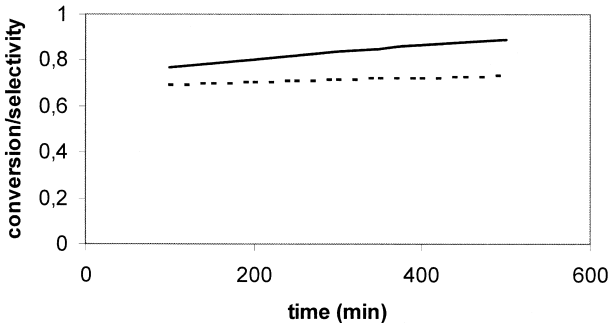

Fig. 5. Modeled conversion (–) and selectivity (- - -) vs. time for the carboxymethylation of arrowroot starch. All other independent values are set at standard conditions, see Tab. 1 for details.

scheme provided in Equations 1-3. Sodium monochloroacetate is involved in two parallel reactions and consequently, the concentration levels of the various components govern the selectivity of the process and the reaction time is of less importance. The effect of reaction time on the DS for arrowroot starch closely mimics the results obtained earlier in our laboratory for potato starch (Fig. 4) [12].

3.3 Effect of the theoretical DS on the DS, conversion and selectivity for arrowroot carboxymethylation

The molar ratio of SMCA/AGU at the start of the reaction (DS_t) is actually the maximum degree of substitution which can be obtained at 100% conversion and a SMCA selectivity of 1. As expected on the basis of this considerations, the DS increases when increasing the DS_t (Fig. 6). However, at higher values, the effect levels off. This may be explained when looking at the conversion and selectivity profiles as a function of the DS_t (Fig. 7). It is evident that both the selectivity and the conversion drop at higher values of DS_t. The effect on the DS is evident when considering the theoretical relation between the DS, conversion, selectivity and theoretical DS:

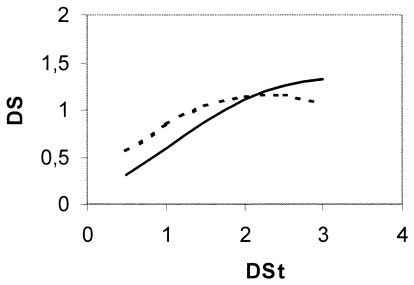

Fig. 6. Modeled DS vs. DS_t for the carboxymethylation of arrowroot (–) and potato starch (- - -).All other independent values are set at standard conditions, see Tab. 1 for details.

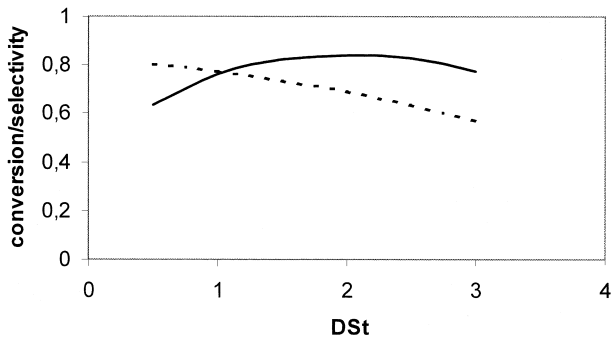

Fig. 7. Modeled conversion (–) and selectivity (- - -) vs. DS_t for the carboxymethylation of arrowroot starch. All other independent values are set at standard conditions, see Tab. 1 for details.

$$DS = \sigma \cdot \varsigma_{SMCA} \cdot DS_t \quad (10)$$

When the conversion and the selectivity decrease, as observed for higher DS_t values, the DS will, according to Equation 10, also be reduced substantially. The dramatic drop in the selectivity with increasing values of DS_t implies that the reaction rates of the main reactions (Eqs. 1-2) are significantly reduced compared to that of the undesired side-reaction (Eq. 3).

Similar trends for the effect of the DS_t on the DS were observed for potato starch (Fig. 6), although the effect for potato starch is less pronounced than for arrowroot [12].

3.4 Effect of the water fraction on the DS, conversion and selectivity for arrowroot carboxymethylation

The degree of substitution is a clear function of the water content (see Fig. 8). Within the design window, there appears to be an optimum water content of about 13% to achieve the highest DS. This optimum is close to the value found for potato starch (Fig. 8) [12]. Optimal water levels for the carboxymethylation of a number of other

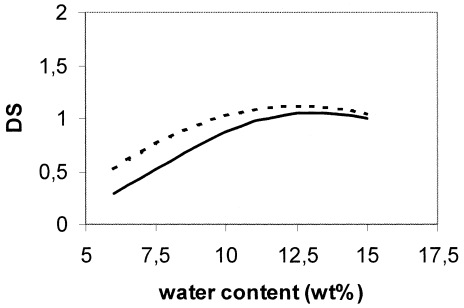

Fig. 8. Modeled DS vs. water content for the carboxymethylation of arrowroot (–) and potato starch (- - -). All other independent values are set at standard conditions, see Tab. 1 for details.

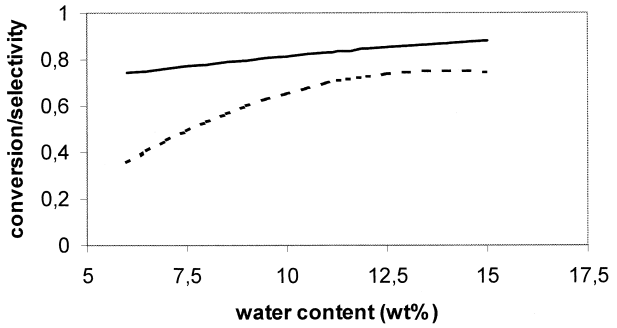

Fig. 9. Modeled conversion (–) and selectivity (- - -) vs. water content for the carboxymethylation of arrowroot starch. All other independent values are set at standard conditions, see Tab. 1 for details.

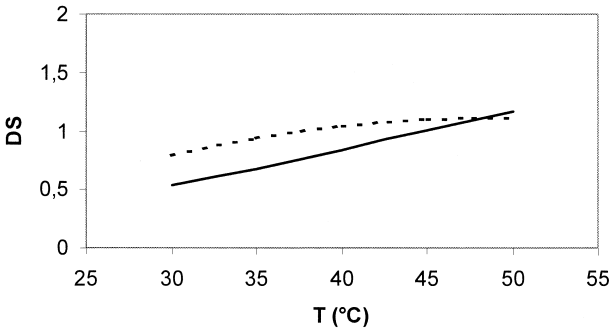

Fig. 10. Modeled DS vs. temperature for the carboxymethylation of arrowroot (–) and potato starch (- - -). All other independent values are set at standard conditions, see Tab. 1 for details.

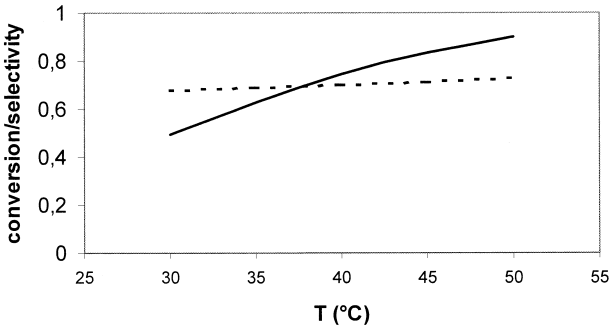

Fig. 11. Modeled conversion (–) and selectivity (- - -) vs. temperature for the carboxymethylation of arrowroot starch. All other independent values are set at standard conditions, see Tab. 1 for details.

starches in isopropanol-water media have been reported [7, 18-20]. Typically, these are between 10 and 20 % (w/w) water. Water is required to swell the starch particles to make them more accessible for the reagents. Furthermore, water affects the distribution of the various components between the bulk liquid phase and the starch particles. Fig. 9 clearly illustrates that the selectivity increases with increasing water content but levels off and even slightly reduces at the high end of the water range. A gradual increase in the conversion upon increasing the water content is observed. Evidently, the observed maximum in the DS versus the water content graph is a selectivity effect, suggesting the side-reaction (Eq. 3) with the formation of sodium glycolate is slightly promoted at higher water fractions.

3.5 Effect of the temperature on the DS, conversion and selectivity for arrowroot carboxymethylation

Within the design window (30-50 °C), the DS increases with increasing temperature (Fig. 10). For instance, upon going from 30 °C to 50 °C, the DS increases from 0.5 to 1.2. A similar trend has been observed for potato starch, although the DS for potato starch appears to be higher at the low end of the temperature range (Fig. 10). For corn and amaranth starches, optimum temperatures were observed at 65 and 30 °C, respectively [20], indicating that the optimal reaction temperature for carboxymethylation depends on the type of starch used. The effect of the temperature on the DS is solely a conversion effect. The conversion increases when increasing the temperature (Fig. 11). Surprisingly, the selectivity is independent of the temperature, implying that the activation energies for the desired and undesired reactions are of the same order (Fig. 11).

3.6 Effect of the NaOH/SMCA ratio on the DS, conversion and selectivity for arrowroot carboxymethylation

The model predicts an optimum value for the NaOH/SMCA ratio to achieve the highest value for the DS (Fig. 12). A similar trend was observed for potato starch (Fig. 12). At

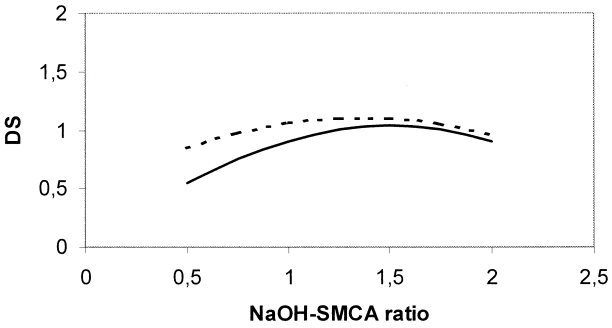

Fig. 12. Modeled DS vs. NaOH/SMCA ratio for the carboxymethylation of arrowroot (–) and potato starch (- - -). All other independent values are set at standard conditions, see Tab. 1 for details.

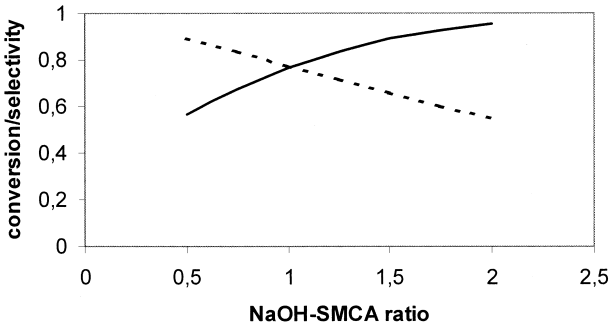

Fig. 13. Modeled conversion (–) and selectivity (- - -) vs. NaOH/SMCA ratio for the carboxymethylation of arrowroot and potato starch. All other independent values are set at standard conditions, see Tab. 1 for details.

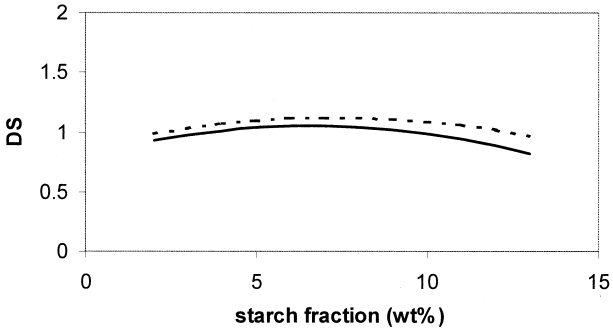

Fig. 14. Modeled DS vs. starch mass fraction for the carboxymethylation of arrowroot (–) and potato starch (- - -). All other independent values are set at standard conditions, see Tab. 1 for details.

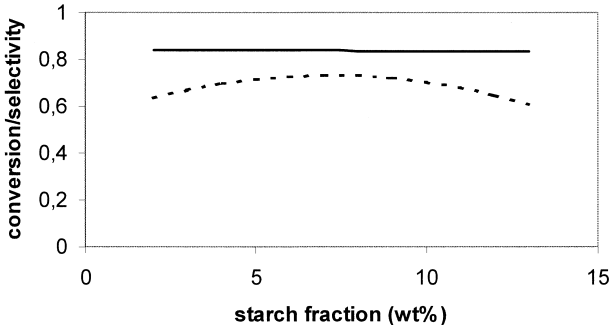

Fig. 15. Modeled conversion (–) and selectivity (- - -) as a function of the starch mass fraction for the carboxymethylation of arrowroot starch. All other independent values are set at standard conditions, see Tab. 1 for details.

higher values, the selectivity towards carboxymethylation drops dramatically (Fig. 13), whereas the conversion shows a gradual increase.

3.7 Effect of the mass fraction of starch on the DS, conversion and selectivity for arrowroot carboxymethylation

The DS of the carboxymethylated arrowroot starch depends on the starch fraction. This is clearly illustrated in Fig. 14. The DS shows a maximum for starch loadings between 6-8 %, (w/w) leading to a DS of about 1. Inspection of the effect of the starch fraction on the selectivity and conversion (Fig. 15) implies that the SMCA conversion is not affected by the starch loading. The primary cause for the observation of an optimum DS value is a change in the selectivity. Apparently, the undesired side-reaction is slightly favored at higher starch fractions. Although speculative, this effect may be related to the distribution of water and isopropanol over the bulk liquid and starch phase. It is well known that starch has a high affinity for water. At higher starch intakes, the composition of the liquid phase will change and becomes richer in isopropanol. This affects the partitioning of the reactants over the starch and bulk liquid phase. The kinetic constants of various reactions are known to be a function of the solvent composition [7] and as a consequence the selectivity may change.

4 Conclusions

The effect of process conditions such as temperature, starch loading, reaction time and solvent composition, as well as reagent intakes on the carboxymethylation of arrowroot starch have been assessed quantitatively using experimental design strategies. The results provide valuable insights in the carboxymethylation process of arrowroot starch and allow optimization of the process conditions to prepare carboxymethyl starch with a desired DS.

A key issue is the selectivity of the process. Data analyses were performed to obtain information on the selectivity of the process and to determine conditions to suppress

the undesired side-reaction to glycolate. It turns out that the selectivity towards carboxymethyl arrowrootstarch decreases when increasing the DS_t and the NaOH/SMCA ratio. Temperature and reaction time only have a minor effect whereas optimum values were observed for the water content and the starch loading. The results obtained in this study will be valuable input for the development of kinetic models for the carboxymethylation process of arrowroot starch and other tropical starches. These activities are currently being undertaken and will be reported in due course.

The results obtained for arrowroot starch closely mimic those obtained earlier in our laboratory for potato starch, suggesting strong similarities in composition and topochemical features between both types of starches.

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