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Exploratory Studies on the Carboxymethylation of Cassava Starch in Water-miscible Organic Media

The carboxymethylation of cassava starch using sodium monochloroacetate (SMCA) as an etherification agent was investigated. Mixtures of water and water-miscible organic liquids were selected as carboxymethylation reaction medium to obtain a high degree of substitution (DS) without changing the granular form and to prevent gelatinization. Factors that affect the process of chemical modification of cassava starch, including the type of solvents, the mass percentage of water in the reaction medium, the mass percentage of starch, the molar ratio of NaOH to SMCA, the theoretical DS (DS_t), and the temperature were investigated experimentally. Isopropanol and *tert*-butanol appear to be the best solvents for the carboxymethylation process of cassava starch, and the optimum condition for this etherification reaction are a reaction medium consisting of about 10 wt% water, a reaction temperature between 50 and 55°C and a starch mass percentage between 4–8 wt%. When applying these conditions in combination with a DS_t of 2.5, granular modified cassava starch with a DS of 1.4 can be obtained. The experimental results will be compared with those reported for other types of granular starches.

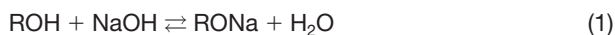
Keywords: Carboxymethylation; Cassava starch; Organic media

1 Introduction

Native starches have been used for a long time in food and industrial applications [1]. The shortcomings of native starch, such as the lack of free-flowing properties, insolubility in cold water, uncontrolled viscosity after cooking and the sensitivity of cooked starches to shear and low pH, limit their further use, for example, in the textile, papermaking and pharmaceutical industries [1].

Chemical modification of native starches can overcome these disadvantages. When the hydroxyl groups of starch are for instance (partly) substituted with sodium monochloroacetate (SMCA) to give carboxymethyl starch (CMS) [1], the starch becomes cold-water soluble. This modification procedure has a positive effect on the applicability in the mentioned areas. As such, this makes carboxymethylation a very successful modification reaction for various starches.

The chemical modification process of starch with SMCA involves a two-step consecutive reaction, accompanied by an undesired side reaction [1]. The main reaction of the carboxymethylation sequence is given by:



The side reaction is the formation of sodium glycolate from SMCA and sodium hydroxide according to:



To obtain granular products, the reactions are preferably carried out in organic solvents such as alcohols or acetone.

A number of experimental studies have been undertaken to determine the influence of the reaction conditions on the carboxymethylation of various types of starch with SMCA or the corresponding acid [2–9]. Surprisingly, only a limited amount of research has been carried out on the carboxymethylation of granular cassava starch. Cassava starch is an interesting feedstock for further derivatization processes to obtain value added products. The planting area and productivity of cassava (*Manihot esculenta*) all over the world is abundant and the underground storage organs of cassava are high in starch [10, 11]. Qui et al. [12] have reported the synthesis of carboxymethyl cassava starch using monochloroacetic acid in ethanol and have determined some of its product properties like the gelatinization temperature and clarity. A recent patent from Volkert et al. [13] describes the preparation of highly substituted carboxymethyl starches in organic reaction media including an example for cassava starch. However, exploratory studies to assess important features like the preferred solvents or solvent combinations for the process as well as more systematic studies to quantify and optimize the various factors affecting the carboxymethylation of cassava starch are lacking.

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Therefore, the objectives of this research are to investigate the feasibility of the carboxymethylation of cassava starch in water-miscible organic media to produce a modified cassava starch in the granular form with a high degree of substitution. All factors that are expected to affect the process of chemical modification are investigated in a systematic manner. These include the type of solvents, the mass percentage of water in the reaction medium, the starch mass percentage, the molar ratio of NaOH to SMCA, the theoretical DS (DS_t) and the temperature.

2 Materials and Methods

2.1 Materials

Cassava starch (Thailand, Stadex food grade quality) was kindly supplied by AVEBE (Foxhol, The Netherlands). Sodium monochloroacetate (SMCA), technical grade, was obtained from Akzo Nobel (Arnhem, The Netherlands). The NaOH pellets were obtained from Acros Organics (Geel, Belgium). Isopropanol (Lab-Scan), ethanol (Merck KGaA, Darmstadt, Germany), methanol (Lab-Scan, Hasselt, Belgium), 1-butanol, 2-butanol (Merck-KGaA, Germany) and H_2SO_4 (Merck KGaA, Germany) were of analytical grade and used without purification. *tert*-Butanol (synthesis quality) was obtained from Merck-Schuchardt.

2.2 Reactor set-up

The carboxymethylation process of cassava starch was studied in a 1 L glass jacketed batch reactor with nitrogen flushing to prevent any reaction of NaOH with carbon dioxide in the air. The reactor was equipped with a reflux cooler to prevent the loss of organic liquid.

A speed adjustable impeller was used to stir the reaction medium. The stirrer speed was set at 1000 rpm for all experiments.

2.3 Procedure

The organic solvent was first mixed with a specific amount of water to a total volume of about 750 mL. Subsequently, the granular cassava starch was added and the reaction medium was mixed in the glass reactor at room temperature. The reactor contents were heated to the desired temperature while stirring. Subsequently, the appropriate amount of NaOH in the form of pellets was added to the reaction mixture. After 15 min, addition of the appropriate amount of SMCA powder started the etherification reaction. Periodically, samples were taken from the reactor for analysis. Specific intakes for each experiment are given in Tab. 1.

2.4 Analysis of the DS

The DS is defined as the average number of substituents per anhydroglucose unit (AGU) and varies between 0 and 3. The DS was determined by High Performance Liquid Chromatography (HPLC) using a literature procedure [5, 6, 14]. A sample (4 mL) was taken from the reactor and the solid fraction was collected by centrifugation. This solid residue was hydrolyzed with 20 mL of 0.75 M H_2SO_4 at 100°C for 4 h and then neutralized using $Ba(OH)_2$, resulting in precipitation of $BaSO_4$. The mole fractions of glucose, monosubstituted carboxymethyl glucose (mono-CMG), disubstituted carboxymethyl glucose (di-CMG) and trisubstituted carboxymethyl glucose (tri-CMG) were determined with HPLC (HP3396) using two Bio-Rad HPX-870 HPLC columns in series at 65°C, and analyzed with a refractive index detector. The flow

Tab. 1. Overview of experimental conditions.

	Symbol	Solvent screening	Water fraction	Temperature effect	Starch loading	NaOH/SMCA ratio	DS_t effect ratio
Mass fraction water [wt%]	w_{H_2O}	10.0	4–16	10.0	12.0	12.0	12.0
Temperature [°C]	T	40	35	30–55	50	50	55
Mass fraction starch [wt%]	w_{AGU}	4.0	4.0	4.0	2–8	6.0	6.0
NaOH/SMCA ratio [mol/mol]	n_{NaOH}/n_{SMCA}	1.0	1.0	1.0	1.0	0.75–1.5	1.0
Theoretical DS [mol/mol]	DS_t	1.1	1.1	1.1	1.1	1.1	0.75–2.5

rate of the eluent (0.008 M aqueous H₂SO₄) was set at 0.54 mL/min. The DS and the mole fraction, x_i , of the hydrolyzed monomers were calculated from a HPLC chromatogram with the following relation

$$DS = \sum_{i=0}^3 i \cdot x_i \quad (4)$$

and

$$x_i = \frac{F_i A_i}{\sum_{i=0}^3 F_i A_i} \quad (5)$$

with $i = 0$ for glucose, 1 for mono-CMG, 2 for di-CMG and 3 for tri-CMG. F_i is the response factor of component i , $M_{w,i}$ is the molar mass of fragment i and A_i is the HPLC peak area of component i .

3 Results and Discussion

The effect of the following parameters on the carboxymethylation process and especially on the DS were investigated: type of organic solvent, amount of water in the organic solvent, temperature, starch loading, NaOH/SMCA ratio and the theoretical DS (DS_t). The effects of the reaction conditions on the carboxymethylation were studied by varying one parameter at a time while the others were maintained at standard conditions.

The DS_t is the maximal DS when the limiting reactant (either SMCA or NaOH) is completely converted without the occurrence of the side reaction to glycolate (Eq. 3). The DS_t is expressed as follows:

$$DS_t = \frac{n_{SMCA,0}}{n_{AGU,0}} \quad \text{if } n_{NaOH,0} \geq n_{SMCA,0} \quad (6)$$

$$DS_t = \frac{n_{NaOH,0}}{n_{AGU,0}} \quad \text{if } n_{NaOH,0} < n_{SMCA,0}$$

An important parameter for evaluation of the reaction is the reaction efficiency (RE), which is defined as:

$$RE = \frac{DS}{DS_t} \quad (7)$$

3.1 Solvent screening studies

Solvent screening studies were performed with a range of alcohols: methanol, ethanol, isopropanol, 1-butanol, 2-butanol, and *tert*-butanol. When performing this study, the values of the other parameters were kept constant and these values are given in Tab. 1. The reactions were carried out in the presence of 10 wt% of water. The carboxymethylation results are given in Fig. 1. It is evident that the highest values for the DS are obtained in isopro-

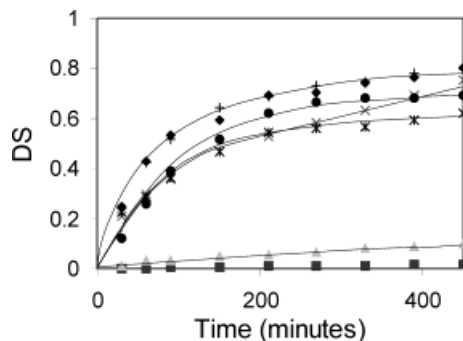


Fig. 1. DS of cassava starch for different solvents as a function of the reaction time. Organic liquids: methanol (■), ethanol (▲), 1-butanol (x), 2-butanol (*), 1-propanol (●), *tert*-butanol (+), isopropanol (◆).

panol and *tert*-butanol. At given conditions and 450 min of reaction time, the DS of cassava starch can reach values as high as 0.81 with isopropanol and *tert*-butanol as the solvents. This corresponds with an RE of 0.74. Inferior results were obtained in methanol and ethanol. Here, the RE's after 450 min were less than 0.10. Solvent effects, especially the effect of different alcohols, on the carboxymethylation process have been studied for various types of starches [3–9]. The results for methanol and isopropanol, the two extremes with respect to performance in this study, for a number of starches are given in Fig. 2. Despite the fact that the experimental conditions for each study differ considerably (Tab. 2), it is evident that the performance in isopropanol is substantially better than in methanol. It may be concluded that isopropanol is the solvent of choice for the carboxymethylation process. The observed solvent trend for cassava is also in agreement with the results obtained in our group for the carboxymethylation of potato starch, although here the performance in *tert*-butanol was slightly less than in isopropanol [5, 6].

In all experiments, the granular structure of the cassava starch remained intact and gelatinization did not occur to a significant extent. Based on these solvent screening results, further experimental studies on the carboxymethylation of cassava starch were carried out with isopropanol as the solvent of choice.

3.2 Effect of the water loading on the DS

The effect of the water content of the organic reaction medium was investigated using the conditions given in Tab. 1. Five isopropanol-water mixtures ranging in water fractions between 4–16 wt% were tested and the results are graphically presented in Fig. 3. It can be concluded that the optimal water mass percentage is in the range of

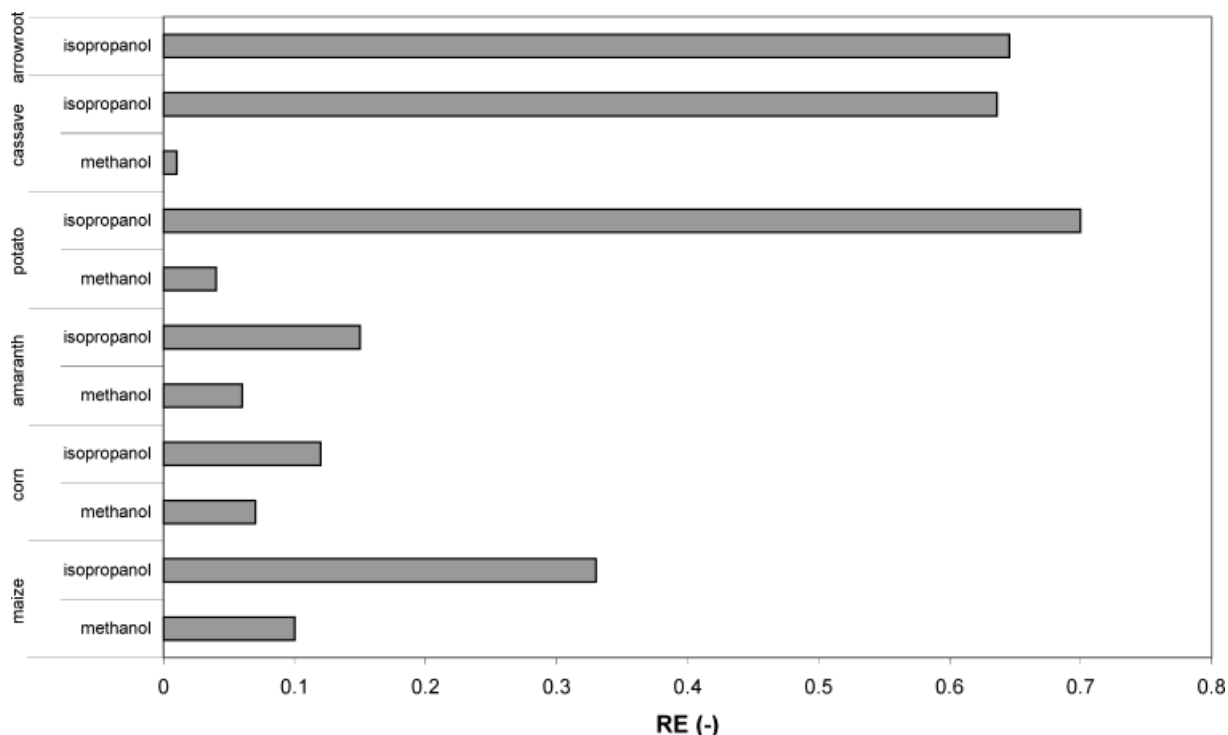


Fig 2. RE's for the carboxymethylation of various starches in methanol and isopropanol. Experimental conditions are given in Tab. 2.

Tab. 2. Overview of the carboxymethylation conditions and RE's for various types of starches.

Starch		Cas-sava	Cas-sava	Arrow-root	Potato	Potato	Maize	Maize	Corn	Corn	Ama-ranth	Ama-ranth
Solvent ^a		1	2	2	1	2	1	2	1	2	1	2
RE	(-)	0.01	0.64	0.65	0.04	0.7	0.1	0.33	0.07	0.12	0.06	0.15
<i>T</i>	°C	40	55	50	40	50	60	60	65	65	30	30
DS _t	(-)	1.1	1.1	1.75	1.1	1.1	1.71	1.71	1.71	1.71	2.57	2.57
$n_{\text{NaOH}}/n_{\text{SMCA}}$	(-)	1	1	1.25	1	1	1.89	1.89	1.27	1.27	1.73	1.73
$w_{\text{H}_2\text{O}}$	wt%	10	10	10	10	10	21–24	21–24	20	20	10	10
w_{AGU}	wt%	4	4	7	4	4	4–5	4–5	6.2	6.2	12	12
V_{reactor}	dm ³	1	1	0.025	1	1	0.1	0.1	0.06	0.06	0.03	0.03
<i>t</i>	min	100	100	100	100	100	120	120	90	90	90	90
Reference		This work	This work	15	5,6	5,6	3	3	7	7	7	7

^a 1 = methanol; 2 = isopropanol.

7–13%, with an optimum at around 10 wt%. Apparently, water is essential for the carboxymethylation reaction. It is well known that starch particles swell in the presence of water and in this way facilitate mass transfer of the reactant into the starch particles [1, 3]. Moreover, the addition of water to isopropanol results in a dramatic improvement

of the solubility of both reagents (SMCA, NaOH) and also affects the partitioning of the reagents between the bulk liquid phase and the starch particles [6]. The optimal isopropanol-water ratios reported for other types of starches are given in Tab. 3. It may be concluded that the optimum organic solvent-water ratio depends on the type of starch.

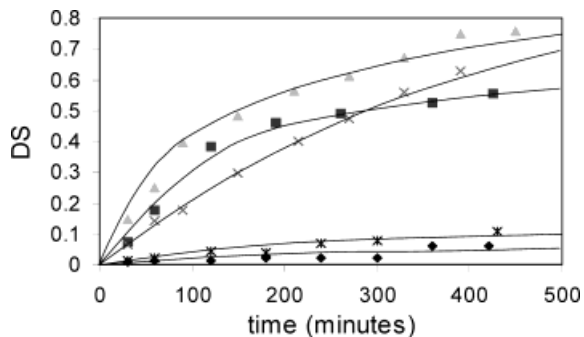


Fig. 3. DS as a function of the reaction time for different water intakes. 4% H₂O (◆), 7% H₂O (■), 10% H₂O (▲), 13% H₂O (x), 16% H₂O (*).

Tab. 3. Overview of the optimum water fraction for the carboxymethylation of various types of starches in isopropanol/water mixtures.

Type of starch	Optimum water fraction [wt%]	Reference
Potato	10	5, 6, 9
Amaranth	10	7
Corn	20	7
Arrowroot	13	15
Cassava	10	this work

3.3 The effect of temperature on the DS

The conditions applied to determine the effect of temperature on the carboxymethylation reaction and particularly the DS are presented in Tab. 1. The temperature was varied between 35 and 55°C. The results are given in Fig. 4. It is obvious that the highest reaction rate, leading to the highest DS values, occurs at the highest temperature. At 55°C, the DS becomes constant after about 300 min, an indication for complete SMCA conversion. Experiments at temperatures exceeding 55°C, which appear to be favorable for high reaction rates, were not performed to

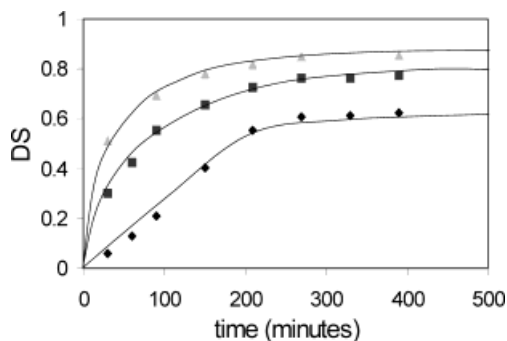


Fig. 4. DS as a function of the reaction time for different temperatures. 55°C (▲), 45°C (■), 35°C (◆).

prevent gelatinization of the cassava starch leading to an undesirable destruction of the granular structure. The gelatinization temperature range for cassava, as determined by differential scanning calorimetry (DSC) is between 62–84°C with a peak temperature of about 69°C for cassava originating from Venezuela [11]. For a number of Nigerian cassava starches, onset temperatures between 55–62°C and peak temperatures between 63–69°C were reported [10]. Based on these considerations, the optimum carboxymethylation temperature i.e. the temperature to obtain high reaction rates without gelatinization is about 55°C.

3.4 Effect of the starch loading on the DS

Experiments aiming to assess the effect of different starch loading on the carboxymethylation reaction were carried out using the conditions given in Tab. 1. A total of four experiments were conducted with starch loading varying between 2 and 8 wt%. Experiments at higher loading were not performed to prevent mixing problems due to an anticipated high apparent viscosity of the reaction medium. From Fig. 5, it can be concluded that the DS is rather insensitive to the starch loading for values between 4–8 wt%. However, a significant reduction in the DS is observed when the reaction is performed at 2 wt% of starch. Apparently, the reaction rates are significantly lower at this low starch intake. These results may be explained by realizing that the intakes of the reactants NaOH and SMCA are also significantly lower when the reaction is carried out at a low starch loading with constant DS_t and NaOH/SMCA ratios. This will evidently lead to lower reaction rates. However, based on this consideration, it is expected that the reaction rates for a 8 wt% starch intake will be higher than that for 4 wt% and this is not experimentally observed. These observations may be explained by realizing that the water-isopropanol ratio of the bulk liquid as well as that inside a starch

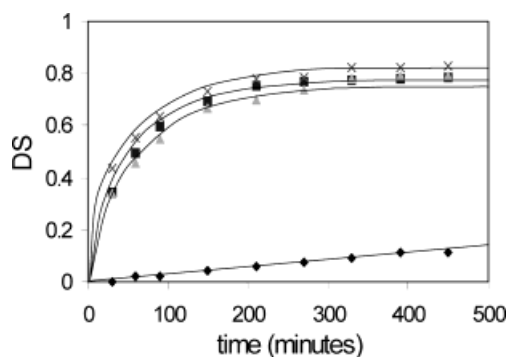


Fig. 5. DS at different starch loading as a function of the reaction time. Starch fraction: 2% starch (◆), 4% starch (■), 6% starch (▲), 8% starch (x).

particle is a function of the starch intake. This is due to the preferential absorption of water in the starch particles [16]. As such, the reaction medium becomes more organic-like at higher starch loadings and this will affect the solubility of both reagents (NaOH, SMCA) in the bulk organic phase as well as the distribution coefficients of both SMCA and NaOH between the bulk organic phase and the starch particle [6]. This in turn will affect the reaction rates of both the main- and side-reactions significantly. The observation that the DS is nearly independent on the starch loading for 4–8 wt% suggests that all effects apparently counterbalance in this range.

3.5 The influence of NaOH and SMCA molar ratio on the DS

The $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio is known to have a significant effect on the rate of reactions and the final DS of the modified starches [3–9]. For a proper comparison, the $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio has been varied at a constant value of the DS_t (1.1, see Tab. 1). Three different $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratios were applied (0.75, 1.0, 1.5), all by varying the intake of NaOH at a constant SMCA intake. Fig. 6 illustrates that an increase in the $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio leads to a higher final DS of the products. In addition, the DS at a fixed time is higher when applying a higher NaOH concentration. Similar observations were reported for potato [6] and arrowroot starch [15]. These results may be explained when considering the various reactions taking place during the carboxymethylation process (Eq. 1–2). At higher NaOH concentrations, the reaction rates will increase and the starch-NaOH equilibrium (Eq. 1) will shift to the right. As a consequence, the DS is expected to increase at higher NaOH concentrations, which is in accordance with the experimental observations.

It is expected that the rate of the side reaction will also be promoted by an increase in the NaOH concentration. This indeed has been observed for the carboxymethylation of

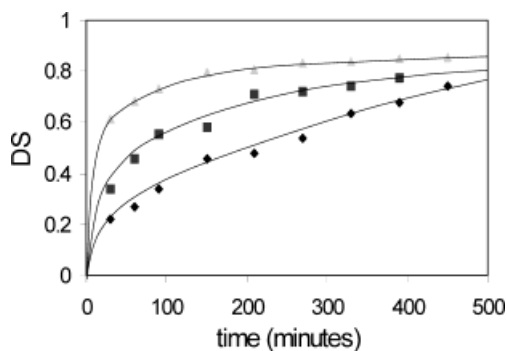


Fig. 6. DS at different $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratios as a function of the reaction time. $n_{\text{NaOH}}/n_{\text{SMCA}}$: 0.75 (◆), 1.0 (■), 1.50 (▲).

potato [6] and arrowroot starch [15] where an increase in the $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio from 0.5 to 2 led to a reduction in the selectivity towards carboxymethylation. Similar effects are expected for cassava starch. However, due to the incomplete conversions at lower $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratios within the time window of this study, it is not possible to draw conclusions on the effects of the $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio on the selectivity of the carboxymethylation process for cassava.

3.6 The effect of the DS_t on the DS

Besides the $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio, the DS_t of the product is also expected to be a function of the reagent-starch ratio (DS_t). A number of experiments were performed using variable reagent-starch ratios at a constant $n_{\text{NaOH}}/n_{\text{SMCA}}$ ratio of 1.0 (see Tab. 1 for other conditions) to quantify this effect. An increase in value of the DS_t , i.e. an increase of the NaOH and SMCA concentration at a fixed starch intake, results in a dramatic increase in the DS of the final product (Fig. 7). These observations are anticipated on the basis of the reaction equations (Eq. 1–2) and are in line with other studies [3–9]. In addition, the time required to reach the maximum value for the DS is also significantly lower at high DS_t values, suggesting that the rate of the carboxymethylation reaction is also significantly higher at higher values of the DS_t . In Fig. 8, the DS of the product after 450 min of reaction time is plotted as a function of the DS_t . It can be seen that with increasing DS_t , the DS increases continuously until a value for the DS_t of about 2.0. At higher values, the DS seems to level off, a trend which has also been observed for the carboxymethylation of potato [6] and arrowroot starch [15]. This observation is likely due to a decrease of the selectivity of the process and the formation of larger amounts of the glycolate (Eq. 3). Unfortunately, the selectivity for cassava carbox-

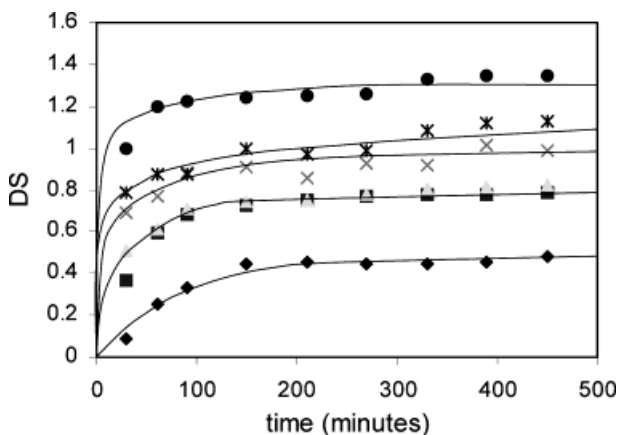


Fig. 7. DS at different DS_t levels as function of the reaction time. DS_t : 0.8 (◆), 1.1 (■), 1.2 (▲), 1.4 (×), 1.6 (*), 2.5 (●).

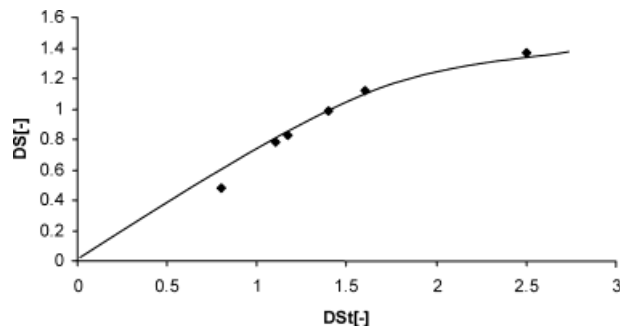


Fig. 8. DS as a function of the DS_t at $t = 450$ min.

ymethylation has not been measured separately to strengthen this explanation. However, selectivity has been determined for a recent study on the carboxymethylation of arrowroot starch [15] and here it was indeed demonstrated that the selectivity decreases when increasing the DS_t.

3.7 Carboxymethylation of various starches in isopropanol-water media, a comparison

Carboxymethylation results in isopropanol-water as the reaction medium for a number of starches have been reported in the literature [3–9]. A comparison between the performance of cassava starch and other starches is given in Tab. 2 and graphically represented in Fig. 2. Significant differences were observed in the reaction efficiencies and values between 0.1 and 0.7 have been reported. Unfortunately, it is very difficult to compare the results properly as the experimental conditions differ considerably (Tab. 2). In addition, different dosing procedures for NaOH addition were applied, which is expected to have a significant effect on the selectivity and, as a consequence, the RE of the process. Furthermore, different analytical procedures were applied to determine the DS of the products, which might also bias the results.

However, the carboxymethylation results for cassava, potato and arrowroot starch were obtained under similar experimental conditions and using a HPLC method to determine the DS, allowing for a proper comparison. The RE values for the three starches are in the same range and vary between 0.64 and 0.70. Although somewhat speculative at this stage, this comparison suggests that the outcome of the carboxymethylation process (RE, DS) is a strong function of process conditions and less depending on the type of starch applied.

Despite a possible overriding effect of process conditions, it would still be interesting to find correlations between the physico-chemical properties of the various starches and the reaction efficiency of the carboxymethylation process.

The carboxymethylation reaction is assumed to be a function of the chemical composition (e.g. amylose-amylopectin ratio, levels of impurities), associated structural properties (e.g. crystallinity) and geometrical features (shape, size) [1, 7, 17]. Typical values for the average particle size and the amylose content for cassava, arrowroot and potato starch are given in Tab. 4. Unfortunately, the current dataset is too limited to correlate these properties with the reaction efficiency of the carboxymethylation process and to draw statistically sound conclusions.

Tab. 4. Properties of cassava, arrowroot and potato starch.

Starch	Average granule size [μm]	Granule size range [μm]	Amylose content ^a [%]	RE ^b
Cassava	14	3–30	17	0.64
Arrowroot	23	9–40	21	0.65
Potato	36	10–100	21	0.7

^a Typical value, content varies according to starch variety, geographic position and planting season.

^b Conditions are given in Tab. 2.

4 Conclusions

We have performed an exploratory investigation in a batch set-up to gain insights in the carboxymethylation of cassava starch using SMCA to obtain granular carboxymethyl cassava starch. Solvent screening studies indicate that higher alcohols like isopropanol and *tert*-butanol give the best results provided that 10 wt% of water is present in the reaction mixture. The DS is rather insensitive to the starch loading, in a range of 4–8 wt%. The highest DS obtained in a single step was about 1.4, for a DS_t of 2.5, a reaction temperature of 55°C and a reaction time of 300 min. Higher reaction temperatures were not applied to prevent degradation of the granule and subsequent gelatinization. The observed trends for cassava starch closely mimic those reported for the carboxymethylation of potato and arrowroot starch. The results obtained in this study will serve as valuable input for subsequent kinetic studies and reactor models to assess the effects of all variables in an integrated way.

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