ELSEVIER

Carbohydrate Polymers 45 (2001) 219–226

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

An experimental study on the carboxymethylation of granular potato starch in non-aqueous media

C.J. Tijsen, H.J. Kolk, E.J. Stamhuis, A.A.C.M. Beenackers*

Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 30 November 1999; revised 1 April 2000; accepted 4 May 2000

Abstract

The optimal reaction conditions for the carboxymethylation of granular potato starch in mixtures of water and organic liquids were determined. The reaction was carried out with pellets of NaOH and sodium monochloro acetate (SMCA) powder as the carboxymethylation reagent. Different alcohols, from methyl alcohol up to the three isomers of butyl alcohol, and acetone were compared in terms of the degree of substitution, DS, and the reaction efficiency, RE. Gelatinisation of the starch granules was avoided at all times. For ethyl alcohol and isopropyl alcohol the effect of the water fraction was studied. The highest RE and the highest DS were obtained for isopropyl alcohol with 10 wt% water. For this system the effect of the temperature, the NaOH to SMCA molar ratio and the theoretical DS was studied in detail. The DS obtained in a single reaction step was limited to about 1.3, with an RE of 0.6. The modification was also carried out in three consecutive steps; resulting in granular carboxymethyl potato starch with a DS of 2.2. The results for the DS and the RE, obtained in this work, are considerably higher than the values reported in the literature.

Keywords: Starch; Carboxymethyl starch (CMS); Reaction conditions, Organic solvents

---

1. Introduction

Native starches are chemically modified to improve specific properties. In order to provide easy flow and handling, and to avoid excessive drying and separation costs, it is advantageous to keep the granular structure of the starch intact. Starch becomes cold water soluble by substituting the hydroxyl groups with sodium monochloro acetate (SMCA) to give carboxymethyl starch (CMS). To prevent gelatinisation of the starch granules, the reaction should be carried out in an organic medium. In this paper an experimental study is discussed on the use of organic liquids as a reaction medium for the production of highly substituted granular carboxymethyl potato starch.

The sodium salt of CMS, also called CMS, is mainly used as a thickening agent, with applications in both the food and non-food industry (Roberts, 1967). CMS is used as a disintegrant, called sodium starch glycolate, in the pharmaceutical industry (Bolhuis, Zuurman & te Wierik, 1997), and as a sizing and printing agent in the textile industry (Ragheb, El-Sayied & Hebeish, 1997).

CMS is produced by etherification of the hydroxyl groups with monochloro acetic acid or SMCA in the presence of alkali. The method is based on Williamson's ether synthesis (Ege, 1989). The first step in the carboxymethylation is an equilibrium reaction between NaOH and the hydroxyl groups of starch

$$\mathrm{ROH} + \mathrm{NaOH} \rightleftarrows \mathrm{RONa} + \mathrm{H_2O} \tag{1}$$

Here, R is the starch backbone. The second step is the actual formation of the carboxymethyl group by the substitution of SMCA

$$\mathrm{RONa} + \mathrm{ClCH_2COONa} \rightarrow \mathrm{ROCH_2COONa} + \mathrm{NaCl} \tag{2}$$

SMCA can also react, by an undesired side reaction, with NaOH to form sodium glycolate

$$\mathrm{NaOH} + \mathrm{ClCH_2COONa} \rightarrow \mathrm{HOCH_2COONa} + \mathrm{NaCl} \tag{3}$$

Sodium glycolate can react with itself or SMCA to give sodium diglycolate.

The amount of carboxymethyl groups formed is indicated by the degree of substitution, DS. The DS is defined as the average number of substituents per Anhydro Glucose Unit, AGU, the monomer unit of starch. Each AGU contains three hydroxyl groups, so the DS lies between zero and three. The reaction efficiency, RE, is a better parameter to optimise the reaction conditions. The RE is calculated by dividing the experimental DS by the theoretical DS. The theoretical

---

* Corresponding author. Tel.: +31-50-3634486; fax: +31-50-3634479.
E-mail address: a.a.c.m.beenackers@chem.rug.nl (A.A.C.M. Beenackers).

PII: S0144-8617(00)00243-5

Nomenclature

A_i	peak area of component *i* (–)
AGU	Anhydro Glucose Unit (–)
DS	Degree of Substitution (–)
DS_t	theoretical DS (–)
CMS	CarboxyMethyl Starch (–)
Mw	molecular weight (g/mol)
M_l	liquid mass (kg)
n_i	number of moles of component *i* (–)
RE	Reaction Efficiency (–)
$RE_{overall}$	Overall Reaction Efficiency (–)
T	temperature (°C)
t	time (min, h)
W_{H_2O}	mass fraction water in the reaction medium (kg/kg)
W_{AGU}	mass fraction starch, i.e. the starch mass divided by the sum of the starch mass and the mass of the reaction medium (kg/kg)
V_{H_2O}	volume fraction water in the reaction medium (m^3/m^3)
V	volume reaction medium (dm^3)
ΔDS_t	added DS_t (–)

DS, DS_t, is the maximal DS obtained for complete conversion of the limiting reactant, either SMCA or NaOH, assuming that no side reaction occurs. The RE lies between zero and unity and is given by

$$RE = \frac{DS}{DS_t} \tag{4a}$$

with

$$DS_t = \frac{n_{A,0}}{n_{AGU,0}} \tag{4b}$$

The initial amount of moles of the limiting reactant is given by $n_{A,0}$, and $n_{AGU,0}$ is the initial amount of moles of starch.

Numerous studies discuss the influence of the reaction conditions, e.g. reagent concentration, reaction medium and temperature, on the carboxymethylation of starch. Hebeish and Khalil (1988), Khalil, Hashem and Hebeish (1990), Mofti, Hassan, Salma and El-Sabbah (1982) and Ravel, Patel, Patel and Patel (1994) studied the effect of the reagent concentration in an aqueous reaction medium. In an organic reaction medium Bhattacharyya, Singhal and Kulkarni (1995) and Jingwu, Dongli, Yuquan, Xiaohong and Dahua (1993) investigated the influence of the reagent concentrations. In all cases, an increase in the SMCA (or monochloro acetic acid) concentration resulted in an increase in the DS of the product, up to a constant value. While, an increase in the SMCA concentration decreases the RE and an increasing NaOH concentration gives an optimum in the DS and RE. In these studies the DS_t and the NaOH to SMCA ratio were varied simultaneously by varying either the NaOH or SMCA concentration. In our study these last two parameters are varied independently.

In the literature various organic liquids were used. Schrodt (1942) tested methyl alcohol for the carboxymethylation of potato starch. Ethyl alcohol was used by Sloan, Mehltretter and Senti (1962) for high amylose starch and by Thewlis (1969) for wheat starch. Mofti et al. (1982) also used ethyl alcohol but did not specify the type of starch used. Acetone was used by Čeh (1972) for the modification of corn starch. The effect of the water content in the organic reaction medium was studied by Bhattacharyya et al. (1995), Hebeish and Khalil (1988),

Table 1
Literature results for carboxymethylation of starch

References	Starch	Medium	Water (wt%)	DS (–)	RE (–)
Jingwu et al. (1993)	Corn	Isopropyl alcohol	24	0.53	0.3
Jingwu et al. (1993)	Potato	Isopropyl alcohol	12	0.9	–
	Corn	Isopropyl alcohol	22	1.15	–
Bhattacharyya et al. (1995)	Corn	Isopropyl alcohol	20	0.22	0.13
	Amaranth	Isopropyl alcohol	10	0.24	0.11
	Corn	Cyclohexane	20	0.24	0.14
	Amaranth	Cyclohexane	10	0.34	0.15

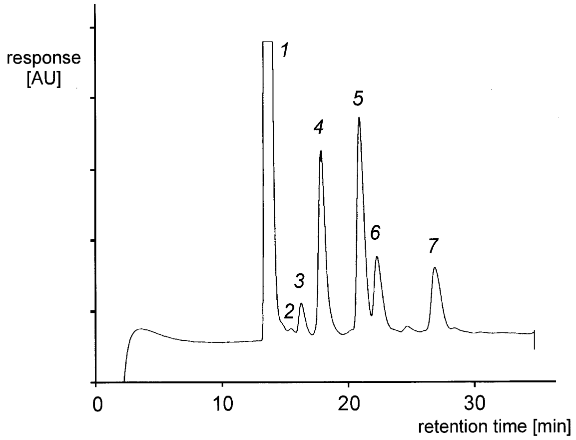

Fig. 1. HPLC chromatogram of carboxymethyl starch in isopropyl alcohol–water after hydrolysis; degree of substitution equals 0.6. 1: inorganic salts, 2: tri-carboxymethyl glucose, 3: di-carboxymethyl glucose, 4: mono-carboxymethyl glucose, 5: glucose, 6: sodium diglycolate and 7: sodium monochloro acetate and sodium glycolate.

Jingwu et al. (1993), Khalil et al. (1990) and Suzuki, Tadokoro and Taketomi (1961). In Table 1 an overview is given of the optimal reaction media found in the literature. The DS reported in the literature was transformed into an RE using the DS_t calculated from the reaction conditions. Unfortunately, Jingwu et al. (1993) did not report the concentration of the reagents used, so it is not possible to calculate the RE for their experiments. Most of the results reported have rather low DS and RE values, i.e. RE below 0.3. Furthermore, it is clear that the optimal amount of water in the system depends on the type of starch and organic liquid used.

The results for the DS and the RE reported in the literature for the production of granular CMS are rather low. Therefore, the initial aim of the present research is to produce routinely granular CMS with DS value above 1. The second aim is to realise these high DS values with an RE significantly above the low values known from the literature. To achieve this a systematic experimental program, for several organic liquids and various reaction conditions, was carried out.

2. Experimental

2.1. Materials

Potato starch, food grade quality, was obtained from AVEBE (Veendam, The Netherlands). Before usage 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%. Technical grade powder sodium monochloro acetate (SMCA) was obtained from Akzo Nobel (Arnhem, The Netherlands). The NaOH pellets were of analytical grade. Dehydrated isopropyl alcohol of a technical grade, purity higher than 99%, was obtained from Acros Chemica (Geel, Belgium). Ethyl alcohol, 96% pure, acetone and nitrogen were of technical grade. The other organic liquids, i.e. methyl alcohol, propyl alcohol, butyl alcohol, *sec*-butyl alcohol and *tert*-butyl alcohol, were of analytical grade.

2.2. Carboxymethylation experiments

The organic liquid was first mixed with a specific amount of water. Then the granular potato starch and the reaction medium were mixed in a 1 dm^3 jacketed reaction vessel, followed by flushing with nitrogen. During the experiments N_2 flushing continued to prevent any reaction of NaOH with CO_2 from the air. A reflux-cooler was used to prevent the loss of organic liquid. Typically, after 15 min 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 sodium hydroxide. Adding powder SMCA started the reaction. Periodically, a small sample was taken for analysis. The reaction was stopped by addition of sulphuric acid.

2.3. Analysis

The DS was determined with high-performance liquid chromatography, HPLC. This technique has been described for carboxymethyl cellulose (Heinze, Erler, Nehls & Klemm, 1994) and for carboxymethyl inulin (Verraest, Peters, Batelaan & van Bekkum, 1995). The method is applicable over the whole substitution range, $0 \leq DS \leq 3$, and requires the hydrolysis of the carbohydrate polymer into modified glucose units. About 0.1 g CMS was hydrolysed with 18 ml of 0.75 M sulphuric acid at 100°C for 4 h. The sample was neutralised by barium hydroxide resulting in precipitation of barium sulphate. Glucoses with zero, one, two or three carboxymethyl groups were separated on two Bio-Rad HPX-870 HPLC columns in series at 65°C, and were analysed with a refractive index detector. The flow rate of the eluent, 1.5 mM sulphuric acid, was 0.5 ml/min.

Fig. 1 gives a typical HPLC chromatogram of the hydrolysed CMS with a DS of 0.6. Seven peaks, in arbitrary units, are identified. The DS is calculated from the modified glucose peaks indicated by 2, 3, 4 and 5. Peak 1 consists of inorganic salts, mainly sulphate and chloride, peak 6 is sodium diglycolate and peak 7 is the unreacted SMCA and the side product sodium glycolate. The DS is calculated from

$$DS = \frac{\sum_{i=0}^{3} \frac{iA_i}{Mw_i}}{\sum_{i=0}^{3} \frac{A_i}{Mw_i}} \tag{5}$$

with A the relative peak area and Mw the molecular weight. For the various peaks, in Eq. (5), i is equal to 0 for glucose

Table 2
Standard reaction conditions

Amount of liquid (kg)	M_l	1.0
Mass fraction water (kg/kg)	w_{H_2O}	0.1
Temperature (°C)	T	40
Mass fraction starch (kg/kg)	w_{AGU}	0.04
NaOH/SMCA molar ratio (mol/mol)	–	1.0
Theoretical DS (mol/mol)	DS_t	1.1

(peak 5), 1 for mono- (peak 4), 2 for di- (peak 3) and 3 for tri-carboxymethyl glucose (peak 2).

3. Results and discussion

The effect of the reaction conditions on carboxymethylation was studied by varying one parameter at a time, while the other parameters were kept constant at the standard conditions given in Table 2. This in contrast to the statistical approach used in Tijsen, Scherpenkate, Stamhuis and Beenackers (1999). There, the parameters were varied according to an experimental design, to investigate the parameter interactions. The study presented here is required to obtain the optimal organic liquid as well as the relevant boundaries of the levels used in the experimental design study of Tijsen et al. (1999).

3.1. Comparison of organic media

Organic liquids used in the carboxymethylation of potato starch included: methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol and acetone, all diluted with 10 wt% water. In all these experiments the same DS_t was applied, i.e. the DS is proportional to the RE. For the alcohols tested Fig. 2 shows the RE as a function of reaction time. Under the conditions studied isopropyl alcohol gave the highest RE and the highest DS. In isopropyl alcohol, after about 460 min of reaction, an RE of 0.80 and a DS of 0.90 was obtained. For propyl alcohol and the three isomers of butyl alcohol, the RE was equal to 0.70, after about 450 min: i.e. 13% lower than for isopropyl alcohol. The lowest RE, 0.07 after 450 min, was obtained for methyl alcohol and ethyl alcohol. Reproducibility of the results appeared to be over 95%.

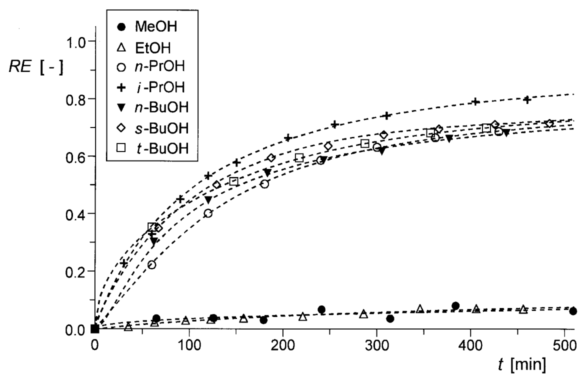

Fig. 2. The reaction efficiency, RE, of carboxymethyl potato starch in various alcohols as a function of reaction time, *t*. Organic liquids: methyl alcohol (MeOH), ethyl alcohol (EtOH), propyl alcohol (*n*-PrOH), isopropyl alcohol (*i*-PrOH), butyl alcohol (*n*-BuOH), *sec*-butyl alcohol (*s*-BuOH) and *tert*-butyl alcohol (*t*-BuOH). The reaction conditions are given in Table 2.

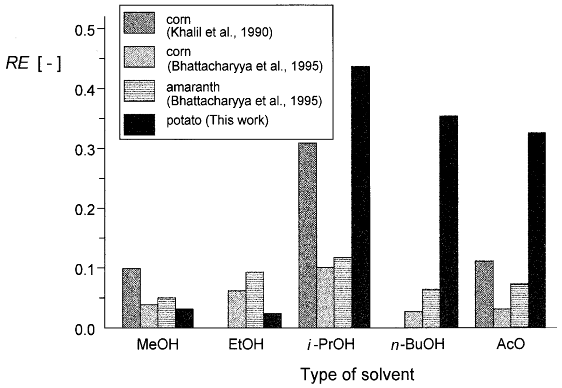

Fig. 3. Effect of various organic liquids on the reaction efficiency of carboxymethyl potato starch, obtained in this work, compared with literature results for corn, amaranth starch (Bhattacharyya et al., 1995) and corn starch (Khalil et al., 1990). Organic liquids: methyl alcohol (MeOH), ethyl alcohol (EtOH), isopropyl alcohol (*i*-PrOH), butyl alcohol (*n*-BuOH) and acetone (AcO). For the reaction conditions see Table 3.

The good performance of isopropyl alcohol for the carboxymethylation of potato starch is in agreement with results reported for other types of starch, see Table 1. A comparison between the performance of the various organic media obtained in this work and the performance reported in the literature is made in Fig. 3. Table 3 gives an overview of the various reaction conditions applied. The quantities reported in the literature are based on volume fractions, whereas mass fractions are used in this study. From Fig. 3 it can be concluded that for the different liquids applied, the highest RE is obtained for potato starch in isopropyl alcohol. With butyl alcohol and acetone, potato starch also appears to give the highest RE. In contrast, potato starch appeared to give the poorest results in methyl alcohol and ethyl alcohol. The significant difference between the results for corn starch from Bhattacharyya et al. (1995) and Khalil et al. (1990) are most likely to be caused by the different reaction conditions and the experimental method used.

Our experimental method to prepare CMS differs from procedures reported in the literature. Bhattacharyya et al. (1995) and Khalil et al. (1990) added aqueous NaOH dropwise prior to the reaction. Jingwu et al. (1993) added a NaOH solution during the reaction. In our study all the NaOH was added as pellets at least 12 h before the carboxymethylation reaction was started by addition of SMCA. Jingwu et al. (1993) suggested that the addition of aqueous NaOH in two steps increased the RE and reduced the formation of sodium glycolate. Unfortunately, Jingwu et al. (1993) did not report the reagent concentration, so, it is not possible to compare their RE with our results. Furthermore, a mixture of isopropyl alcohol, NaOH and water can

Table 3
Overview of the experimental conditions, used for the comparison of the reaction efficiency (RE) given in Fig. 3

	Khalil et al. (1990)	Bhattacharyya et al. (1995)		This work
Starch	Corn	Corn	Amaranth	Potato
T (°C)	60	65	30	40
DS_t (–)	1.71	1.71	2.57	1.1
NaOH/(S)MCA (mol/mol)	1.89	1.27	1.73	1.0
W_{H_2O} (kg/kg)	0.21–0.24	0.20	0.10	0.10
V_{H_2O} (m^3/m^3)	0.20	0.16–0.180	0.08–0.09	0.08–0.09
W_{AGU} (kg/kg)	0.04–0.05	0.0625	0.12	0.04
AGU (g)	4	4	4	40
V (dm^3)	0.1	0.06	0.03	0.98–1.02
t (min)	120	90	90	100

reportedly form a two-phase liquid system (Mills & Hughes, 1957; Yokota, 1985). Consequently, when an aqueous NaOH solution is added to a starch–isopropyl alcohol suspension, a two-phase liquid system can be formed with a localised high NaOH concentration. If so, SMCA may react with NaOH to form sodium glycolate before the main reaction proceeds. The formation of a two-phase liquid system seems to be avoided with our experimental method.

3.2. *Effect of water*

The effect of the water fraction on the carboxymethylation was studied in more detail for isopropyl alcohol and ethyl alcohol. The moisture content of the starch granules was included in the total water fraction. Fig. 4a shows the RE as a function of time for four isopropyl alcohol–water mixtures. In all these experiments the same DS_t was applied, i.e. the DS is proportional to the RE. The optimal water fraction for isopropyl alcohol appeared to be about 0.1. Fig. 4b gives similar results for three ethyl alcohol–water systems. The highest DS in ethyl alcohol is obtained for a water fraction of 0.2. However, in the latter case, after about 250 min the starch gelatinised at a DS of about 0.26 with an RE of 0.23. Apparently, with isopropyl alcohol it is possible to have a granular product with a high DS and a high RE, over a broad range of conditions.

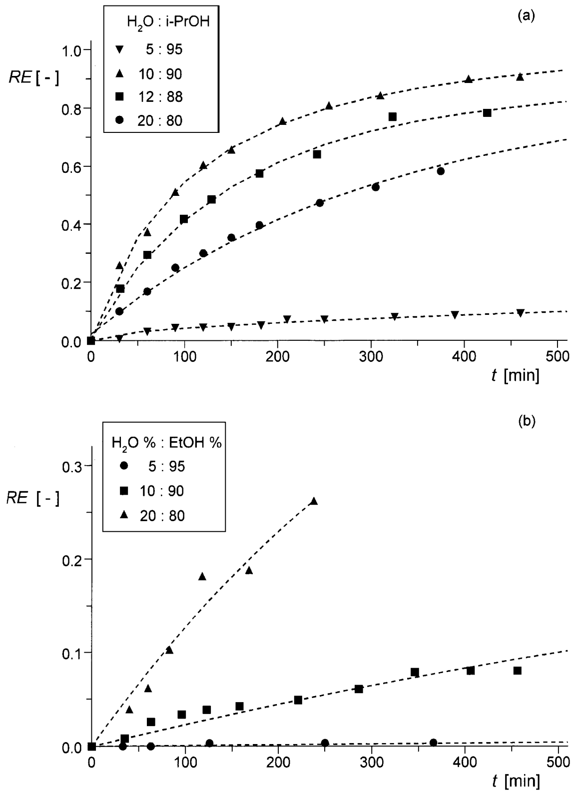

Fig. 4. The effect of the water fraction on the reaction efficiency, RE, of carboxymethyl potato starch as a function of time, *t*: (a) isopropyl alcohol; (b) ethyl alcohol. For the reaction conditions see Table 2.

From the results presented in Figs. 3 and 4 it follows that the optimal amount of water in the organic reaction medium depends on the type of starch as well as on the type of alcohol. We found that for potato starch a water fraction of 0.1 in isopropyl alcohol is optimal. Bhattacharyya et al. (1995) also found that for amaranth starch isopropyl alcohol with a water fraction of 0.1 is optimal. For corn starch the optimal water fraction in isopropyl alcohol is about 0.2 (Bhattacharyya et al., 1995; Khalil et al., 1990). For ethyl alcohol we found an optimal water fraction of 0.2 for potato starch. In methyl alcohol the optimum water fraction is 0.24 for corn starch (Khalil et al., 1990). The optimal amount of water appeared to increase with decreasing carbon number of the alcohol. This is confirmed by Filbert (1952), who studied the carboxymethylation of various carbohydrates, including potato starch, gum and cellulose, and reported optimal water fractions of 0.28 for ethyl alcohol and 0.22 for propyl alcohol. These values are somewhat higher than our results. However, Filbert (1952) did not discuss a dependency of the optimal water fraction on the type of carbohydrate.

3.3. *Reaction conditions for isopropyl alcohol*

In this section the other reaction conditions are optimised for the carboxymethylation reaction in the optimal liquid system, i.e. isopropyl alcohol with about 10 wt% water.

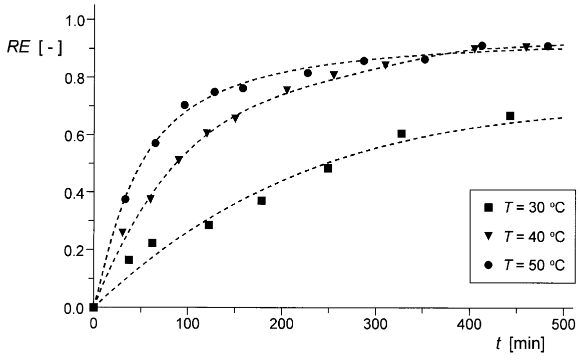

Fig. 5. The effect of temperature on the carboxymethylation rate of granular potato starch, given in terms of the reaction efficiency, RE, as a function of time, *t*. Experiments in isopropyl alcohol–water with the reaction conditions given in Table 2.

Except when indicated otherwise, the experimental conditions are given in Table 2.

3.3.1. Temperature

The influence of the reaction temperature is shown in Fig. 5. As expected the highest reaction rate is observed for the highest temperature. An interesting point is that the final DS and RE appeared to be independent of reaction temperature. After 24 h of reaction the DS obtained at all three reaction temperatures appeared to be 1.0 with an RE of 0.91. These results indicate that the activation energy for the main and the side reaction are equal.

Therefore, the choice for the optimal reaction temperature can be based on the highest reaction rate in the absence of gelatinisation. For potato starch in water, gelatinisation occurs approximately at 60°C (Schoch & Maywald, 1967). It is known that the gelatinisation temperature is higher in organic liquids. However, the gelatinisation temperature for CMS will be lower than for native starch and is a strong function of the DS. Differential Scanning Calorimetry (DSC) and Rapid Visco Analysis (RVA) were used to determine the gelatinisation temperature of starch and CMS in organic liquids. It was found that no thermal transition occurred in the DSC curves. The RVA technique had the disadvantage that the organic liquids evaporated when the temperature was increased. So, also with this second technique no gelatinisation temperature could be determined. During the carboxymethylation reactions, at a temperature higher than 45°C, the diameter of the CMS granules appeared to increase, which indicated irreversible swelling.

To avoid gelatinisation and irreversible swelling, and to have a relatively high initial reaction rate, a temperature of 40°C was selected as the optimal reaction temperature. Bhattacharyya et al. (1995) studied the influence of the temperature on the carboxymethylation in isopropyl alcohol and found that the optimal temperature for amaranth and corn starches were 30°C and 65°C, respectively. This indicates that the optimal reaction temperature depends on the type of starch used.

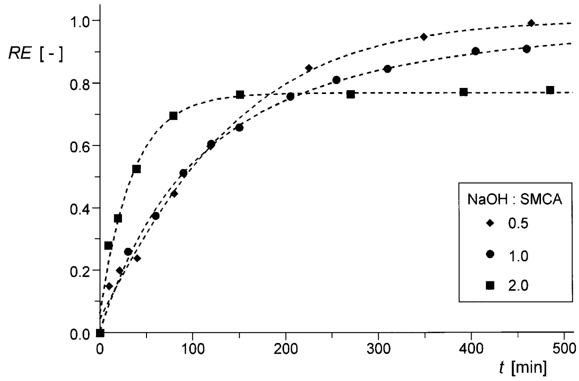

Fig. 6. The reaction efficiency, RE, as a function of time, *t*, for three sodium hydroxide to sodium monochloro acetate (SMCA) molar ratios. Experiments in isopropyl alcohol–water with the reaction conditions given in Table 2.

3.3.2. Sodium hydroxide to sodium monochloro acetate ratio

At a constant value of DS_t, the NaOH to SMCA ratio was varied by changing either the amount NaOH or the amount SMCA. The observed RE as a function of time is shown in Fig. 6 for three NaOH/SMCA ratios. Increasing the NaOH to SMCA ratio from 0.5 to 2.0 resulted in a decrease in the final DS from about 0.99 to 0.77, although the highest initial reactivity is observed for the highest NaOH to SMCA ratio. The latter is a consequence of the starch NaOH equilibrium (see Eq. (1)). At a higher NaOH concentration more RONa is present, resulting in a higher reaction rate of the main reaction (see Eq. (2)). The fact that the final DS decreases with an increase in the NaOH to SMCA ratio is caused by the competition between the main and the side reaction. An increase in the NaOH concentration also enhances the formation of sodium glycolate (see Eq. (3)) resulting in a lower final DS.

3.3.3. Theoretical degree of substitution

From Eqs. (1)–(3) it is clear that besides the NaOH to SMCA ratio also the ratio of starch to NaOH and to SMCA will influence the final DS. In Fig. 7 the final DS and the RE, after 500 min of reaction, are given as a function of DS_t for an NaOH to SMCA ratio equal to 1.0. It is seen that for an increase in the DS_t the DS increases monotonously to a constant level whereas the RE decreases over the whole range studied. So, there is an optimal situation for the production of highly substituted potato CMS. It can be concluded that the highest DS that can be reached in a single step is about 1.33 obtained at a DS_t of 2.35 with an RE of 0.57.

3.4. Step-wise modification

To produce granular CMS with a DS greater than 1.33, a so-called step-wise modification procedure was applied. Bhattacharyya et al. (1995) and Mofti et al. (1982) have reported this procedure. Bhattacharyya et al. (1995)

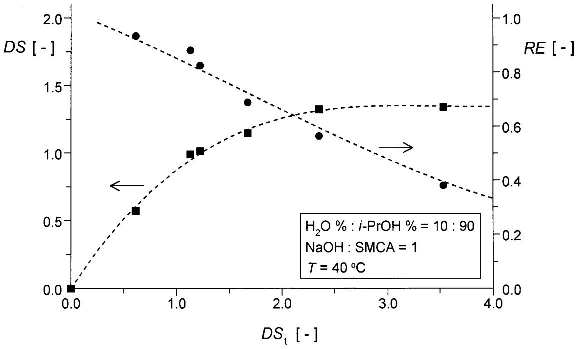

Fig. 7. The degree of substitution, DS, and the reaction efficiency, RE, as a function of the theoretical degree of substitution, DS_t, for isopropyl alcohol–water. For the reaction conditions see Table 2.

Table 4
Experimental conditions used in the three-step modification of granular potato starch in isopropyl alcohol–water and the results for the degree of substitution (DS) and the reaction efficiency (RE)

	Step 1	Step 2	Step 3
W_{H_2O} (kg/kg)	0.10	0.05	0.05
W_{AGU} (kg/kg)	0.04	0.04	0.04
NaOH/SMCA (mol/mol)	1.0	1.0	1.0
T (°C)	40	40	40
ΔDS_t (−)	1.0	1.6	1.3
DS_t (−)	1.0	2.1	2.8
t (h)	2.5	7	26.5
DS (−)	0.50	1.50	2.20
RE (−)	0.50	0.71	0.79
$RE_{overall}$ (−)	0.50	0.58	0.56

optimised the reaction conditions for a single reaction step and used these, in a multiple-step reaction strategy, to produced granular amaranth CMS with a DS of 0.43. They reported that after a third reaction step the amaranth CMS, with a DS of 0.46, was gelatinised. The reaction conditions and the DS obtained in this work, in three reaction steps, are given in Table 4. For step two and three the DS_t is the sum of the DS obtained in the previous step and the ΔDS_t which takes into account the amount of the reagents added in the that step. For the second reaction step the ΔDS_t was 1.6 and the DS of the feed stock, potato CMS, was 0.5. This corresponds to a DS_t of 2.1. In the final reaction step DS_t was equal to 2.8, i.e. a ΔDS_t of 1.3 and a DS of the feed stock of 1.5. In the case of step-wise modifications besides an RE for a single reaction step, also an overall RE can be used, $RE_{overall}$, which is defined as

$$\mathrm{RE}_{\mathrm{overall},n} = \frac{\mathrm{DS}_n}{\sum_{i=1}^{n} \Delta \mathrm{DS}_{\mathrm{t},i}} \tag{6}$$

with n equal to 1, 2 or 3 for the first, second or third reaction step.

To ensure that the granular structure of the CMS was maintained, the first reaction step was stopped after 2.5 h. This resulted in a relatively low RE of 0.5. In contrast to the studies reported in the literature we adjusted the reaction medium to avoid gelatinisation of the product. In the second and the third reaction step isopropyl alcohol with a water fraction of 0.05 was used. In this way, it is possible to produce CMS with a DS as high as 2.20. In contrast, the highest DS found in the literature for granular CMS is 1.2 (Jingwu et al., 1993). The final $RE_{overall}$ is equal to 0.56. Clearly, it is advantageous, in terms of both the RE and the DS, to perform the carboxymethylation in a step-wise manner.

4. Conclusions

The optimal reaction medium for the carboxymethylation of granular potato starch is isopropyl alcohol with a 0.1 mass fraction of water. By adding the NaOH pellets separately from the organic liquid–water mixture, at least 10 h before SMCA is added, much higher values of both RE and DS could be realised, as compared to the literature. An increase in the molar ratio of NaOH to SMCA resulted in a decrease in the RE. The DS of granular CMS obtained in a single reaction step, in isopropyl alcohol with 0.1 mass fraction water, appears to be limited to about 1.3. This is obtained for a DS_t of 2.4, which corresponds to an RE of 0.6. The temperature has a minor effect on the reaction performance, the best suited temperature is about 40°C. It has been demonstrated that using a three-step reaction procedure, granular potato CMS with a DS as high as 2.2 could be obtained, with an overall RE of 0.6.

Acknowledgements

The authors would like to thank AVEBE B.A. (Veendam, The Netherlands) for supporting this project.

References

Bhattacharyya, D., Singhal, R. S., & Kulkarni, P. R. (1995). A comparative account of conditions for synthesis of sodium carboxymethyl starch from corn and amaranth starch. *Carbohydrate Polymers*, *27*, 247–253.

Bolhuis, G. K., Zuurman, K., & te Wierik, G. H. P. (1997). Improvement of dissolution of poorly soluble drugs by solid deposition on a super disintegrant. II. The choice of super disintegrants and effect of granulation. *European Journal of Pharmaceutical Science*, *5*, 63–69.

Čeh, M. (1972). Darstellung der Carboxymethylstärke. *Starch/Stärke*, *24*, 124–127.

Ege, S. N. (1989). *Organic chemistry* (2nd ed.). (pp. 446–447). Lexington. MA., DC: Heath and Company.

Filbert, W.F. (1952). Du Point de Nemours & Co. US Pat. 2,599,620; *Chem. Abstracts* 11732b, Vol. *46*.

Hebeish, A., & Khalil, M. I. (1988). Chemical factors affecting preparation of carboxymethyl starch. *Starch/Stärke*, *40*, 147–150.

Heinze, T., Erler, U., Nehls, I., & Klemm, D. (1994). Determination of the substituent pattern of heterogeneously and homogeneously synthesized carboxymethyl cellulose by using high-performance liquid chromatography. *Angewandte Macromolecularae Chemie*, *215*, 93–106.

Jingwu, Z., Dongli, L., Yuquan, S., Xiaohong, Z., & Dahua, W. (1993). The study on the effect of alkalization on the carboxymethylation of starch. *Journal of Tianjin University*, *1*, 124–131.

Khalil, M. I., Hashem, A., & Hebeish, A. (1990). Carboxymethylation of maize starch. *Starch/Stärke*, *42*, 60–63.

Mills, A. L., & Hughes, F. (1957). Liquid–liquid equilibria from alcohol–sodium hydroxide–water system. *Chemical Engineering Data Series*, *2*, 35–37.

Mofti, A., Hassan, E. A., Salama, J. Y., & El-Sabbah, M. M. B. (1982). Synthesis and study of polyacids from soluble starch and chloroacetic acids. *Starch/Stärke*, *34*, 375–379.

Ravel, D. K., Patel, S. P., Patel, R. G., & Patel, V. S. (1994). A study on reaction influencing factors in carboxymethylation of *Leucaena glauca* seed gum. *Starch/Stärke*, *46*, 399–402.

Ragheb, A. A., El-Sayied, H. S., & Hebeish, A. (1997). Preparation and characterization of carboxymethyl starch (CMS) products and their utilization in textile printing. *Starch/Stärke*, *49*, 238–245.

Roberts, H. J. (1967). Starch derivatives. In R. L. Whistler & E. F. Paschall, *Starch: chemistry and technology* (pp. 293–350). New York: Academic Press.

Schoch, T. J., & Maywald, E. C. (1967). Industrial microscopy of starches. In R. L. Whistler & E. F. Paschall, *Starch: chemistry and technology* (pp. 637–647). New York: Academic Press.

Schrodt, A. (1942). Chemische Fabrik Pfersee G.m.b.H., Ger. Pat. 717275; *Chem. Abstracts* 2520, Vol. *38*, 1944.

Sloan, J. W., Mehltretter, C. L., & Senti, R. F. (1962). Carboxymethyl high-amylose starch. *Journal of Chemical Engineering Data*, *7*, 156–158.

Suzuki, H., Tadokoro, Y., & Taketomi, N. (1961). Starch derivatives. I. Carboxymethylation of starch by monochloracetic acid, *Denpun Kogyo Gakkaishi*, *9*, 33–42. *Chem. Abstracts* 8784e, Vol. *57*, 1962.

Tijsen, C. J., Scherpenkate, H. J., Stamhuis, E. J., & Beenackers, A. A. C. M. (1999). Optimisation of the process conditions for the modification of starch. *Chemical Engineering Science*, *54*, 2765–2772.

Thewlis, B. H. (1969). Carboxymethylation of wheat starch. *Starch/Stärke*, *21*, 21–24.

Verraest, D. L., Peters, J. A., Batelaan, J. G., & Van Bekkum, H. (1995). Carboxymethylation of inulin. *Carbohydrate Research*, *271*, 101–112.

Yokota, H. (1985). The mechanism of cellulose alkalization in the isopropyl alcohol–water–sodium hydroxide–cellulose system. *Journal of Applied Polymer Science*, *30*, 263–277.