Optimization of Carboxymethylation of Starch in Organic Solvents

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A comparative study of the influence of ethanol, benzene, acetone, isopropanol, and mixtures of ethanol-acetone, ethanol-benzene, and ethanol-isopropanol as slurry media on the degree of substitution and viscosity of carboxymethyl starch during carboxymethylation is presented. It is shown that the degree of substitution increases with increasing acetone, isopropanol, or benzene content in the mixed solvent. After the same carboxymethylation steps the degree of substitution with ethanol/benzene mixture is higher than that with ethanol/isopropanol mixture.

INTRODUCTION

Carboxymethylation is a well-known derivatization process for polysaccharides, giving products in which the primary and/or secondary alcohol groups are etherified with carboxymethyl groups. These products have variety of promising properties. In general, the polysaccharide is activated with aqueous alkali hydroxide, mostly sodium hydroxide, and converted with monochloroacetic acid or its sodium salt to carboxymethyl polysaccharide derivative.

Starch is the main energy reserve polysaccharide in plants. Next to cellulose, starch is the most abundant carbohydrate in the world. The raw material is available in sufficient amounts and in high purity. Its total annual world production is estimated to be between 25 and 45 million tons [1]. Carboxymethyl starch (CMS) is known for a long time and was first made in 1924 by the reaction of starch in an alkaline solution with sodium monochloroacetate [2]. Figure 1 shows the reaction scheme of the carboxymethylation of starch.

The quality and solution properties of the produced carboxymethyl starch are mainly determined by the degree of substitution (DS), which is the average number of carboxymethyl functions in the polymer. It can be controlled by adjusting the reaction parameters during derivatization, which include the solvent system, its composition, concentration of alkali, anhydroglucose (AGU)/monochloroacetic acid (MCA) molar ratio, temperature, and duration of reaction. Various studies of the carboxymethylation of starch were carried out to optimize reaction conditions, that to increase product yield and reaction efficiency [3–6].

Carboxymethylation medium plays an important role in the reaction. Organic solvents are usually used for the preparation of CMC with higher DS [7]. In recent years, several studies have been performed on the effect of organic diluents on carboxymethylation process [8–12].

Recently, multi-step carboxymethylation of starch was investigated; products of DS of 0.36 have been obtained by Th. Heinze et al. [13–15] using methanol/water as the slurry medium in one step and a DS of up to 0.88 by two carhoxymethylation steps. CMS with a very high degree of substitution (DS = 2.1) was synthesized by multi-step carboxymethylation (10 steps) under heterogeneous reaction conditions in methanol/water with sodium hydroxide and monochloroacetic acid as an etherifying agent.

A benzene–ethanol–water mixture was used as the solvent medium in synthesizing of CMC with DS > 1.0 from cotton linter [16]. Olaru and Olaru [17] studied the reactivity of cellulose in organic solvents

R = H or CH$_2$COONa acording to DS
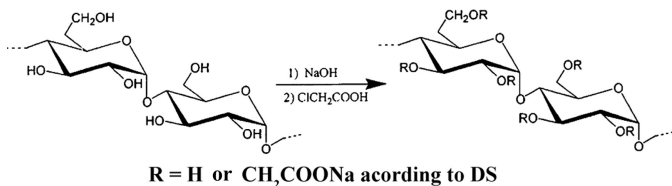
FIGURE 1 The reaction scheme of the carboxymethylation of starch.

such as ethanol, acetone, isopropanol, ethanol-acetone, and ethanol-isopropanol mixtures. They found that the presence of ethanol beside acetone or isopropanol, up to about 50% produces higher amounts of amorphous material. This improves the reactivity of cellulose toward carboxymethylation. In other studies, as that carried out by the same author [18], an ethanol–acetone 1:1 (w/w) mixture used as a reaction medium for carboxymethylation of wood pulp cellulose and cotton linters was found to give a higher DS than the pure solvents separately.

The present work studied the influence of various solvents, ethanol, acetone, isopropanol, benzene, and mixtures of ethanol-acetone, ethanol-isopropanol and ethanol-benzene, of various compositions as slurry media with different sodium hydroxide and monochloroacetic acid concentrations. Also, multistage carboxymethylation was used to get a product with high DS.

EXPERIMENTAL

Carboxymethylation

The synthesis of CMS with various DS was carried out based on the procedures of Heidrich and Ullmann [19] with some modification. 5 g of corn starch in 20 mL of solvent was stirred vigorously while 5 mL conc. aqueous sodium hydroxide solution was added during l5 min at room temperature. Stirring was continued for another 1 h at 40℃, and equimolar amount of monochloroacetic acid (dissolved in 5 mL organic solvent) was then added during a period of 15 min. The mixture was allowed to react for 4 h at 40℃. After carboxymethylation the mixture was filtered, suspended in methanol and neutralized with acetic acid. The product was collected after filtration, washed three times with 76% (w/w) aqueous methanol and pure methanol and then dried at 110℃ in vacuum oven. The DS was estimated according to Reference [20].

Multistage Carboxymethylation

The subsequent carboxymethylation steps were run in a similar procedure and under similar conditions for samples in which ethanol-isopropanol and ethanol-benzene mixtures were used as slurry medium.

The conditions used guaranteed that the reaction mixture could be mixed during the whole course of the reaction and that no gelation would occur.

Infrared Spectra

The infrared absorption spectra of starch and carboxymethyl starch were recorded on a Perkin Elmer Spectrometer using KBr pellet, from 4000 to $400\,\text{cm}^{-1}$.

Viscosity

The absolute viscosity of $1\,\text{wt}\%$ Na-CMS water solution was obtained by Ostwald viscometer at $20°\text{C}$.

RESULTS AND DISCUSSION

### Effect of Solvents and their Mixing Ratio

As mentioned in the Introduction, the DS of CMS depends on the reaction medium. The role of the solvent in the carboxymethylation reaction is to provide accessibility of the etherifying reagent to the reaction centers of the starch. So, the effect of composition of the reaction media ethanol, acetone, isopropanol, benzene, and their mixing ratio on the DS and solution viscosity is shown in Table 1. From this table, it is observed that the DS increases with increasing acetone, isopropanol or benzene content in the mixed solvent. In comparing of solvents as individual reaction media the DS is higher with benzene than other solvents whereas acetone and isopropanol have the same effect and higher than ethanol.

TABLE 1 Effect of Solvents and Their Mixing Ratio on the DS and Viscosity of CMS [AGU:NaOH (mol) = 1:2, AGU:MCA (mol) 1:1]

| Ethanol %	Acetone %	Isopropanol %	Benzene %	DS	η centipoises $\times 10^{-2}$
100	00	00	00	0.24	1977
75	25	00	00	0.36	2714
50	50	00	00	0.41	1766
25	75	00	00	0.39	1159
00	100	00	00	0.48	1298
75	00	25	00	0.29	1680
50	00	50	00	0.46	1488
25	00	75	00	0.46	1231
00	00	100	00	0.48	1780
75	00	00	25	0.26	2991
50	00	00	50	0.29	1600
25	00	00	75	0.29	2288
00	00	00	100	0.53	3647

Effect of Alkali Concentration

Because carboxymethylation process involves two competing reactions that take place simultaneously. The first reaction seems to prevail up to a certain NaOH concentration (Figure 1). Above this concentration, the second reaction predominates with the formation of a large amount of sodium glycolate as follows:

$$ClCH_2COOH + 2NaOH \longrightarrow HOCH_2COONa + NaCl + H_2O$$
$$\textbf{Sodium glycolate}$$
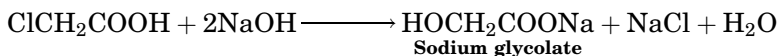
The formation of sodium glycolate decreases the DS.

We studied the effect of NaOH concentration on the DS and solution viscosity using ethanol-isopropanol (1:1) and ethanol-benzene (1:1) as the solvent media (Figure 2). It was observed that both the DS and solution viscosity increased by increasing NaOH concentration and reached maximum at 2 and 2.5 NaOH/AGU molar ratios with using ethanol-benzene and ethanol-isopropanol mixture, respectively.

At higher NaOH concentration, due to alkaline hydrolysis, starch chains degrade so that the average molecular weight decreases, which lead to decreased solution viscosity of CMS at these NaOH concentrations.
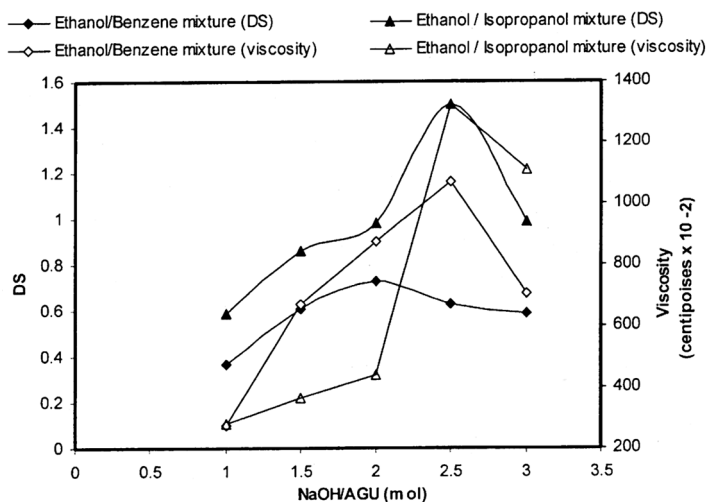
FIGURE 2 Effect of alkali concentration on DS and viscosity [McAc/AGU (mol) = 2:1, solvent ratio = 1:1 vol/vol].
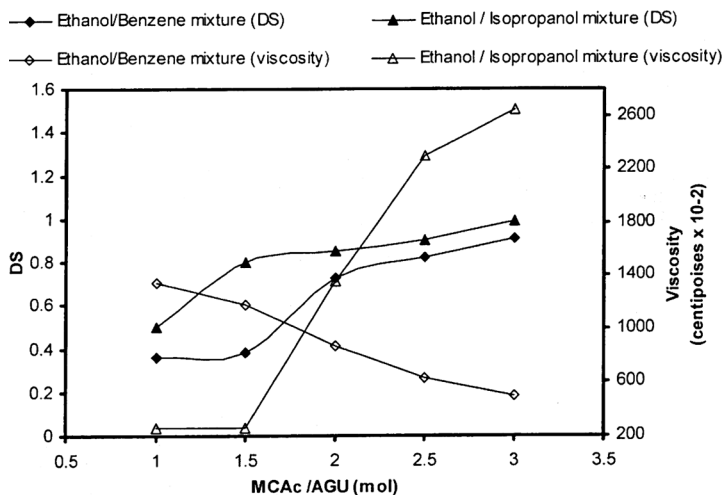
FIGURE 3 Effect of etherifying agent concentration on DS and viscosity [NaOH/AGU (mol) = 2:1, solvent ratio = 1:1 vol/vol].

## Effect of Etherifying Reagent Concentration

To study the effect of monochloroacetic on the DS of the produced CMS, the ratio of starch to NaOH and solvent ratio of 1:1 by volume ethanol-isopropanol or ethanol-benzene were kept constant; the amount of monochloroacetic acid was varied to reach different DS values.

Figure 3 shows that the DS increases with increasing monochloroacetic acid while the solution viscosity decreases in using ethanol-benzene mixture and increases with ethanol-isopropanol mixture. This may be due to increased monochloroacetic acid concentration; especially when the molar ratio of $ClCH_2COOH/AGU = 2$, the structure of starch is seriously destroyed and becomes amorphous. This improves the diffusion of monochloroacetic acid and therefore increases the degree of substitution.

In comparing the ethanol-isopropanol with ethanol-benzene as slurry media, it is noted that the rate of increasing of DS is higher with using ethanol-benzene mixture than ethanol-isopropanol mixture.
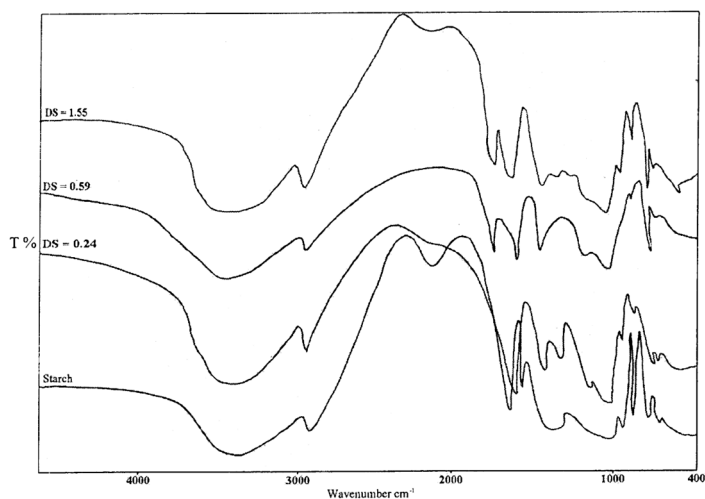
Multi-step Carboxymethylation of Starch

One possible way to increase the DS of CMS is multi-carboxymethylation of starch. As found in Figure 4 an increase in the MCA/AGU molar ratio up to 2 led to slightly increased DS of CMS. The CMS samples with
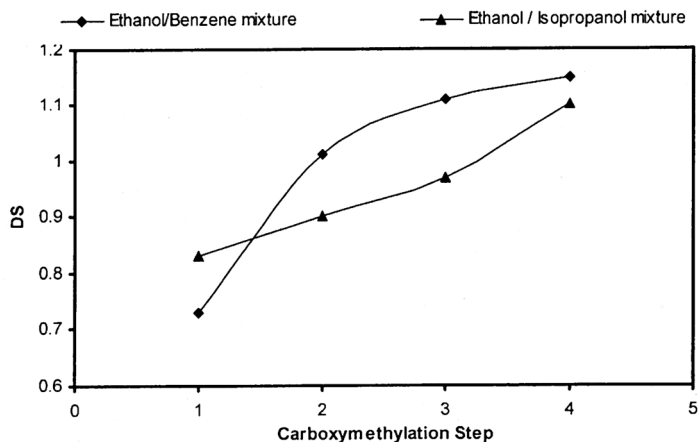
FIGURE 4 Dependence of DS on the number of carboxymethylation steps [NaOH/AGU (mol) = 2:1, McAc/AGU (mol) = 2:1, solvent ratio = 1:1 vol/vol].

DS = 0.7 and 0.8 (ethanol/isoprene and ethanol/benzene mixtures, respectively) were activated and allowed to react with about 2:1 MCA/AGU under similar conditions yielding CMS with DS = 0.8 and 1.01 (ethanol/isoprene, ethanol/benzene mixtures, respectively). Subsequently, additional carboxymethylation reactions were carried out three

FIGURE 5 IR spectra of starch and CMS.

times with CMS obtained in the previous step. After four carboxymethylation steps, samples with DS = 1.01 and 1.05 were obtained. After the same carboxymethylation steps the DS with ethanol/benzene mixture is higher than that with ethanol/isopropanol mixture.

Infrared Spectra

The FTIR spectra of native and etherified starch (DS = 0.24–1.55) are shown in Figure 5. In the spectra of the etherification products, compared with that of native starch, strong absorption bands at $740 \, cm^{-1}$ were observed that can be ascribed to the $\nu_{c=O}$ of acetate groups. All CMS have a high intensity IR band at about $1600 \, cm^{-1}$ due to COO^- ion stretching [21]. The characteristic band between 3000–$3400 \, cm^{-1}$ originates from hydroxyl bond stretching. The intensity of this band decreases in the etherified derivatives [22].

CONCLUSIONS

- The DS increases with increasing acetone, isopropanol, or benzene content in the mixed solvent. In comparing of solvents as individual reaction media the DS is higher with benzene than other solvents whereas acetone and isopropanol have the same effect and higher than ethanol.
- The DS and solution viscosity increased by increasing NaOH concentration and reached maximum at 2 and 2.5 NaOH/AGU molar ratios with using ethanol-benzene and ethanol-isopropanol mixture, respectively.
- After the same carboxymethylation steps the DS with ethanol-benzene mixture is higher than that with ethanol-isopropanol mixture.
- All CMS have a high intensity IR band at about $1600 \, cm^{-1}$ due to COO^- ion stretching.

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