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Preparation of carboxymethyl cellulose from corncob

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Abstract

In this paper, to find out the best technological conditions of extracting microcrystalline cellulose from corncob by using high pressure cooking method. The optimum concentration of NaOH of the extraction of microcrystalline cellulose is 50% with the method of high pressure cooking. Preparation of carboxymethyl cellulose (CMC) from microcrystalline cellulose was carried out by an etherification process, using NaOH and monochloroacetic acid (MCA), with ethanol and water as the supporting medium. The results indicated that the best reaction condition was that the microcrystalline cellulose were alkalized at 30 ℃ for 50 min and etherificated at 65 ℃ for 3 h, 85% ethanol as solvent with the molar ratio of cellulose/NaOH/MCA was 1:1:1. NaOH is added in three batches with total amount the ratio is 6:2.5:1.5. Under the optimized reaction conditions, the substitution degree (DS) of CMC is 1.02 and the viscosity is 6 mPa·s, which possessed special characteristics of low viscosity.

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Keywords: Corn cop; Microcrystalline cellulose; Carboxymethyl cellulose; High pressure cooking

1. Introduction

CMC is manmade modified cellulose, a linear, long-chain, water-soluble, anionic polysaccharide which is prepared by the reaction of MCA with alkali cellulose[1]. CMC has got ample scientific attention, especially due to its polyelectrolyte character and it is the most widely used cellulose ether today with applications in the detergent, food exploration, paper, textile, pharmaceutical and paint industries[2].The increasing environmental concerns have forced the researchers to obtain useful industrial materials from plant biomass. Recently the synthesis of CMC from different cellulosic sources have reported such as raw cellulose[3], paper sludge[4], wood residue[5], cotton linters[6,7], fibers[8] etc.

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China has a rich crop straw resources, (annual output is as high as 700 million tons[9]) which account for a considerable part of maize corncob that contains a large number of natural polymer materials such as cellulose, lignin and hemicellulose. Recently cultivation of corncob has tremendously increased in China and huge amounts of corncob are either thrown away as waste or burnt. However, these are applications with low added value, causing disposal as well as environment pollution problems[10]. If corncob can translate to low viscosity carboxymethyl cellulose[11] it could be effective use of biological resources, reduce environmental pollution and produce a great economic benefits and ecological benefits.

In this paper, microcrystalline cellulose was extracted with the method of high pressure cooking. CMC was prepared from microcrystalline cellulose carried out by an etherification process, using NaOH and MCA, with ethanol and water as the supporting medium.

2. 2. Materials and methods

2.1. Materials

Corn cop was collected from Hebei Yingtian Biology Science & Technology co; Ltd. Chemicals used during the study were NaOH (Yongda, Tianjin), MCA (Bodi, Tianjin), ethyl alcohol (Yongda, Tianjin), potassium dichromate (Bodi, Tianjin), ferrous ammonium sulfate (Damao, Tianjin), 1,10-Phenanthroline monohydrate (Yongda, Tianjin),ect.

2.2. Methods

- Extraction of cellulose

The corn cob samples were washed, dried and cut manually into small pieces about 1cm, then put it in the steam pressure pot with NaOH solution at 170 ℃ and 0.7 MP for 90 min. The cellulose residue was separated by filtration, washed thoroughly with water to neutral, dried and tested the cellulose content. H_2O_2 was added to bleach the crude cellulose, and then treated with HCl was to get microcrystalline cellulose.

- Synthesis of carboxymethyl cellulose

Microcrystalline cellulose was added to ethanol aqueous solution with magnetic stirring, 50 min later then, NaOH was added. The alkalization reaction was conducted at 30℃. After the alkalization reaction, MCA was added dropwise at 65 ℃ and stirred for 3 h. The solutions was then neutralized by HCl and filtered. The residue dried until reaching a constant weight.

- Determination of carboxymethyl cellulose

The substitution degree of CMC was determined by the method of complexometric titration[12] and the viscosity of the mass fraction of 1% CMC was measured by using the NDJ-5S type rotary viscosity meter.

3. Results and discussion

3.1. Effect of NaOH dosage on the extraction of cellulose

As is shown in Fig. 1, the effect of NaOH concentration was tested in different concentration of the NaOH solution. It was observed that the cellulose content of solid increased with NaOH concentration and attained a maximum content of 79.08% at an alkali dosage of 50% (by dry corncob meter). At particular alkali strength, the cellulose content reached maximum after which it started declining. This observation can be explained that cellulose molecules were hydrolyzed with the increase of dosage of alkali.

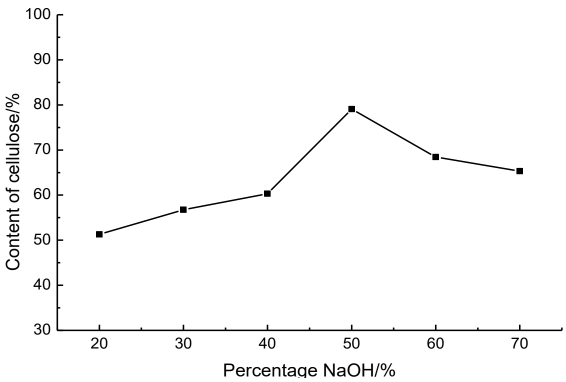

Fig. 1. Effects of various percentage NaOH on content of cellulose

3.2. Effect of etherification agent

The results are plotted in Fig. 2. There was an increase in the DS up to 1:1 (cellulose: MCA) and then it decreased. Excessive amounts of etherifying agent will changes the pH of reaction system and glycolate formation seems to be favored, so the reaction efficiency decreases [13, 14]. Therefore, chloroacetic acid dosage was: m (cellulose): m (MCA) = 1:1.

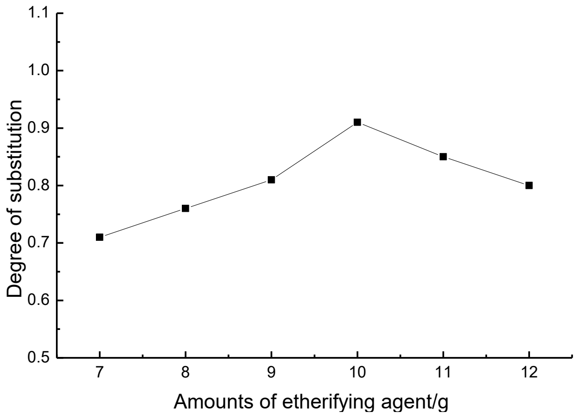

Fig. 2. Effects of amounts of etherifying agent on degree of substitution of carboxymethyl cellulose

3.3 Effect of alkali dosage

As shown in Fig. 3, that the DS increased with increasing the concentration from 4 g to 10 g and thereafter decreased considerably. The higher dosage of alkali is not preferable as it is reported in literature that, at a particular alkali strength, the DS will be maxi-mum after which it will decline. At higher concentrations sodium hydroxide reacts with sodium monochloroacetate to form sodium glycolate resulting in the inactivation of the monochloroacetate [13]. So the optimum dosage of NaOH was found to be 10 g (by dry corncob meter).

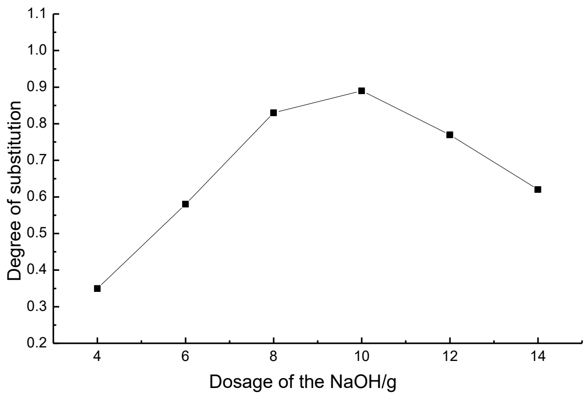

Fig. 3. Effects of dosage of NaOH on degree of substitution of carboxymethyl cellulose

3.4 Effect of reaction temperature

As shown in Fig. 4, the temperature parameter study was carried out in six different reaction temperatures. A maximum DS of 1.02 was obtained with 65 ℃ as the reaction temperature. There was an increase in the DS with reaction temperature up to 65℃ thereafter it decreases. The increase may be due to the fact that there is better reaction environment created for carboxymethylation. The decrease of the DSwhich beyonds 65℃ may be due to the cellulose degradation where chemical elimination of water from cellulose originates primarily from an intramolecular elimination leading to C2, C3 unsaturation or a ketone group on C2 [15]. Concurrently, there might be intermolecular elimination among hydroxyl groups of neighboring chains giving rise to cross-linking by ether linkages, thus decreasing the sites of –OH groups for carboxymethylation [15].

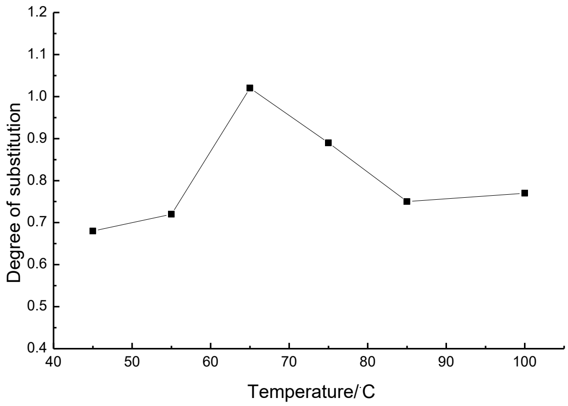

Fig. 4. Effects of various reaction temperatures on degree of substitution of carboxymethyl cellulose

3.5 Effect of ethanol concentration

As shown in Fig. 5, the carboxymethylation reaction was carried out in six different ethanol concentration. It is observed that the increase in the ratio of organic solvent increases the DS of the CMC produced. A maximum of 0.92 was obtained with 85% ethanol. So the ethanol concentration was 85%.

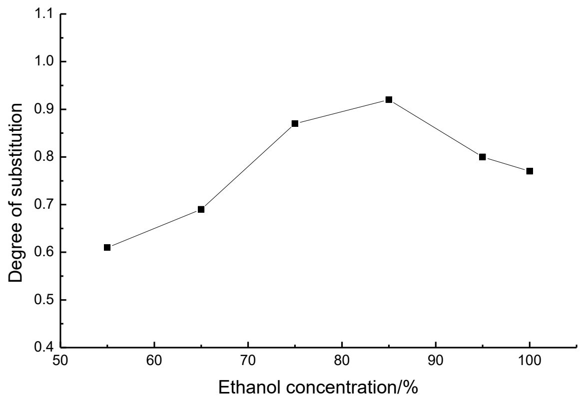

Fig. 5. Effects of dosage of ethanol concentration on degree of substitution of carboxymethyl cellulose

4. Conclusions

The results show that the optimum concentration of NaOH of the extraction of microcrystalline cellulose is 50% with the method of high pressure cooking. The optimum condition of carboxymethylation cellulose from microcrystalline cellulose was that the microcrystalline cellulose were alkalizated at 30 ℃ for 50 min and etherificated at 65 ℃ for 3 h, 85% ethanol as solvent with the molar ratio of cellulose/NaOH/MCA was 1:1:1. NaOH is added in three batches with total amount the ratio is 6:2.5:1.5. Under the optimized reaction conditions, the substitution degree (DS) of CMC is 1.02 and the viscosity is 6 mPa·s, which possessed special characteristics of low viscosity.

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