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Research paper

Synthesis of sodium carboxymethyl cellulose using bleached crude cellulose fractionated from cornstalk

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ABSTRACT

In this study, crude cellulose derived from cornstalk, after bleaching, was used as raw material for the synthesis of sodium carboxymethyl cellulose (CMC) by reacting with the cellulose with NaOH and chloroacetic acid at 75 °C for 1.5 h. Effects of alkali dosage, concentration of chloroacetic acid on the physical and chemical properties of the CMC products were investigated. It was revealed that the reactants alkali reagent/chloroacetic acid/cellulose at the molar ratio of 4.6:2.8:1and 4:2.5:1, or at the molar ratio of NaOH/$ClCH_2COOH$ ≈ 1.6–1.64, resulted in CMC products of relatively high water solubility. The viscosity-average molecular weight M_v of these two CMC products obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1 is in the range of 1.94×10^4–2.48×10^4 g mol^{-1}, and the average DS of the two products are 0.57 and 0.85, respectively. As the solute concentration is above 2 wt%, the viscosity of the CMC-water solution exhibits nonlinear (exponential) increasing with increasing the solute concentration (typical of non-Newton fluids).

1. Introduction

Carboxymethyl cellulose (CMC) is one of the most widely used cellulose derivatives in the industry. CMC, a white-cream-colored powder, has wide applications in food, pharmaceutical, detergents and coatings [1,2,3]. CMC can also be utilized for paper or textile improvement as fibers [4,5]. It is an anionic linear polymer in which the original H atom in cellulose hydroxyl group is replaced by carboxymethyl substituent (−CH_2−COO−) [6,7]. CMC is extremely recommended as an additive in many commodity products due to its non-toxicity, high water solubility as well as the outstanding light and thermal stability [8]. Through the reaction of alkali cellulose in aqueous NaOH with monochloroacetic acid or its sodium salt, CMCs with different degree of substitution (generally in the range 0.5–1.4 for commercial products) can be produced [9,10]. Generally hydroxyl groups in cellulose are replaced by carboxymethyl groups in the order of C6 > C3 > C2 [11–13]. In heterogeneous carboxymethylation however the substitution takes place in the order C2 ≈ C6 > C3 [7,9,11–13]. For the CMC with the DS < 0.4, it is swelled but insoluble in water, while for DS of more than 0.4, CMC is fully soluble with its hydro-affinity, which increases with the raise of DS [14].

The continuously increasing demand of instant and defatted food in recent years makes the CMC market grow dramatically [15]. Generally purified cotton (α-cellulose>98.3 wt%) has been widely applied as the feedstock for CMC production [16] while usage of the expensive cotton as well as the purification treatment increase the cost of the product, which has thus become the limitation for the growth of CMC production. As such, there is a need for sustainable and inexpensive substitutes to cotton cellulose [17].

Cornstalk, containing cellulose (30–35 wt%), lignin (16–20 wt%) and hemicellulose (25–30 wt%), are very abundant in Canada. Canada produced 10.7 million tons of grain corn in 2011, accompanied with about 15 million tons of cornstalk. In 2015, more than 800,000 ha of grain corn were harvested [18] in Ontario Canada, producing approx. 8.8 million tons of grain corn. However,

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cornstalk and other agricultural lignocellulosic biomass have been paid little attention due to their limited applications mainly as organic fertilizer, silage for livestock and source for heat and electricity. Therefore, there is growing interest worldwide in transforming cornstalk or other crop residues into value-added bioproducts, such as CMC.

Effort have been made since 1980 in searching for less expensive alternatives to expensive cotton, such as various lignocellulosic biomasses (rich in cellulose), for production of CMC. According to the study of Mario et al. [19], banana pseudo stem, known as a potential cellulose source, was utilized for CMC synthesis. CMC product with DS, viscosity, purity and crystallinity of 0.75, 4033 mPas, 98.23 wt% and 38.33 wt% respectively, was achieved through alkalization using 15 wt% NaOH followed by etherification using sodium monochloracetate (MCA). Furthermore, sugar beet pulp was applied for production of CMC (with 0.667 DS) by reacting beet pulp with 30 wt% NaOH solution and sodium monochloracetate in isobutyl alcohol as the solvent [20]. Cellulose isolated from Lantana camara was converted to CMC (DS 1.22) by reacting with aqueous NaOH and MCA for 3.5 h at 55 °C in isopropyl alcohol solvent [21]. Moreover, cellulose derived from a variety of lignocellulosic biomasses, such as orange mesocarp, water hyacinth, sugarcane straw, corncob and cornstalk, etc. was utilized for the synthesis of CMC and other cellulose derivatives [22–26].

In our previous work published recently [27], a highly efficient organosolv fractionation approach was developed to fractionate cornstalk into cellulose and lignin using a mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v). The obtained crude cellulose can be a source of glucose for fuel ethanol production, but a more valuable application of the cornstalk-derived crude cellulose is as an inexpensive feedstock for bio-based materials. This work aimed to utilize the cornstalk-derived crude cellulose, after bleaching pretreatment, as a feedstock for the synthesis of CMC. This study centered on determination of best molar ratio of the reaction reagents (alkali reagent/etherifying reagent/cellulose) for the synthesis of CMC using cornstalk-derived cellulose. The chemical structure, water solubility, average DS as well as other physical properties such as viscosity of the CMC product were measured.

2. Materials and methods

2.1. Materials

Cornstalk used in this work was supplied by Ontario Federation of Agriculture (OFA), collected from a local farm in South Ontario. However, the chain of custody of the biomass feedstock is not available, hence it should be noted that the limited information may impose a reasonable degree of uncertainty on the reproducibility and repeatability of the study. The cornstalk was air-dried at room temperature to a moisture content of <10 wt%, and then ground into particles to pass 20 mesh sieve. Elemental composition and chemical components of oven-dried cornstalk are presented in Table 1. The contents of three major components in the cornstalk feedstock, i.e., Klason lignin (acid insoluble), α-cellulose and hemicellulose were determined in accordance with NREL/TP-510-42618 [28]. Briefly, the extractive content (EC) of oven dried raw cornstalk sample was first determined by soxhlet extraction in toluene/ethanol (2:1, v/v) for 24 h. The lignin content of the oven dried cornstalk sample was then determined by a sequential acid hydrolysis of the extracted cornstalk first with 72 wt% sulfuric acid at 30 °C for 120 min and then with 4 wt% diluted sulfuric acid at 121 °C for 60 min. The holocellulose content of oven-dried cornstalk was determined using a modified Chlorination method using the extracted cornstalk sample in water-acetic acid-sodium chlorite mixed solvent at 50–70 °C for more than 24 h to remove lignin. Based on the resulted solid residue, the holocellulose content (HC) was determined. Furthermore, the content of α-cellulose was determined by treating the obtained holocellulose sample with 17.5 wt% NaOH solution at room temperature to remove hemicellulose, while the content of hemicellulose was finally determined by difference. More detailed procedure to determine the contents of lignin, cellulose and hemicellulose was provided in the previous article [27].

The chemicals used in this study, such as sodium hydroxide (50 wt% solution), chloracetic acid (solid, 99 wt%), ethanol (95 vol%), hydrochloric acid (36.5–38 wt%), etc. were all purchased from Caledon Laboratory Chemicals, and were used as received.

2.2. Methods

2.2.1. Cornstalk fractionation

Fractionation of cornstalk was carried out in a 100 cm^3 autoclave reactor (Parr 4590), following the procedure detailed in our previous article [27]. In a typical run, briefly, 5.0 g air-dried cornstalk, 25 cm^3 mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) was added into the reactor. The reactor was then sealed, evacuated and pressurized to 1.0 MPa with N_2. The reactor was heated at the rate of approximately 10 °C min^{-1} to 90 °C under approximately 300 rpm stirring for 180 min. After reaction, the reactor was cooled to room temperature. The gas in the reactor was vented and the reactor was opened. The slurry in the reactor was poured into a 250 cm^3 glass beaker, and the reactor was rinsed with ethyl acetate. The spent ethyl acetate was also transferred to the 250 cm^3 glass beaker. After 15 min, mixture in the beaker was filtered, while the filter cake was further rinsed with ethyl acetate till the filtrate became colorless. The solid residue present in the filtration cake was then rinsed with distilled water, dried at 105 °C in an oven, and designated as crude cellulose.

2.2.2. Crude cellulose bleaching

Sodium chlorite was used for crude cellulose bleaching. Briefly, 2.5 g crude cellulose, 80 cm^3 hot distilled water (50 °C), 0.5 cm^3 acetic acid and 1.0 g sodium chlorite were added into a 250 cm^3 Erlenmeyer flask. The mixture was then heated under stirring

Table 1
Elemental composition and chemical components of oven-dried cornstalk.

Elemental composition (wt%)					Chemical components (wt%)			
C	H	O[a]	N	Ash[b]	Extractives[c]	Lignin[d]	Cellulose[d]	Hemi-Cellulose[e]
45.01 (0.24)[f]	5.67 (0.18)	45.38 (0.23)	1.50 (0.27)	2.44 (0.00)	1.34 (0.12)	18.57 (1.13)	35.31 (0.65)	32.58 (2.22)

[a] By difference assuming negligible sulfur content.
[b] Ashed at 575 °C.
[c] Soxhlet extraction in toluene/ethanol (2:1, v/v) for 24 h
[d] Determined in accordance with NREL/TP-510-42618 [28].
[e] By difference.
[f] values in parenthesis are relative errors from 2 to 3 measurements.