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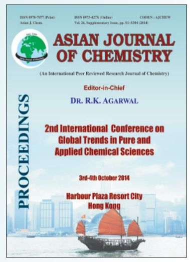

Synthesis of Carboxymethyl Cellulose Based on Pretreated Bamboo Shaving and Bagasse

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In this work, sodium carboxymethyl cellulose was prepared from compound of pretreated bamboo shaving and bagasse as raw materials, while the main reaction conditions affecting product properties such as viscosity and degree of substitution were studied. The results showed that the mass fraction ratio among these refined bamboo shaving and bagasse could be 60:40, the optimized reaction conditions were alkalified at 30 °C for 80 min and etherified at 55°C for 90 min. Afterwards, temperature was kept at 70 °C for 10 min. Under these conditions, viscosity of aqueous solution of 1 % carboxymethyl cellulose could always above 250 mPa·s, while most of the carboxymethyl cellulose samples reach 300 mPa s viscosity and DS ≥ 0.8. The content of chloride and moisture were less than 1.2 % and 10 %, respectively.

Keywords: Compound cellulose materials, Bamboo shaving, Bagasse, Sodium carboxymethyl cellulose, Preparation.

INTRODUCTION

Sodium carboxymethyl cellulose is a man-modified polysaccharide derivative. It's a kind of the principal cellulose ethers manufactured and consumed across the world. Due to its varied properties, such as biodegradability, non-toxicity, odorless, solubility, viscosity and water holding capacity, carboxymethyl cellulose is widely used in several industries. It could be applied in paper, food, pharmaceuticals, personal care, oil drilling and detergents. The main raw material of carboxymethyl cellulose synthesis is cotton fiber or wood pulp[1].

Commonly, all plant biomass consists of cellulose, hemicellulose, lignin, pectin and protein. About 33 % of all plant biomass is cellulose as the major component of the rigid cell walls. In recent years, there have been many researches to develop the raw materials of carboxymethyl cellulose manufacture, it was reported to be synthesized from diverse plant biomasses, such as sago waste[2], cavendish banana pseudo[3], flax pedicels[4] and sugar beet pulp stem[5], which contain rich cellulose (40-50 % on a dry basis). The synthesis of carboxymethyl cellulose from various agricultural waste cellulose sources have already been reported[6,7].

Bamboo shaving is a by-product of bamboo industry, commonly discarded or incinerated. It is an abundant lignocelluloses by-product in China. Bamboo shaving offers the advantages of being a kind of low-cost, plentiful materials for carboxymethyl cellulose production[8]. Bagasse is a fibrous residue obtained from sugarcane stalks after it is crushed to obtained juice used for sugar and ethanol production, sugarcane is widely cultivated in the earth[9]. Bamboo and bagasse have analogous components and contents, they consisted of more than 40 % of cellulose as the major component of the rigid cell walls (Table-1), but the degree of polymerization after pretreatment was distinctively different according to our analysis data.

The purpose of present research is to introduce the bamboo shaving and bagasse as the precursors to produce carboxymethyl cellulose. In an attempt to utilize these two waste for useful material production, this article seeks to determine the optimal conditions for bagasse and bamboo shaving pretreatment and carboxymethyl cellulose production from the pretreated materials. This will not only be helpful in the waste management but also be fruitful in saving the country revenue.

EXPERIMENTAL

Raw materials: Bamboo shaving was collected from Anji County, Zhejiang Province, China. Bagasse was collected from Congzuo, Guangxi Zhuang Autonomous Region, China. They were dried and used as raw materials for the experiments. The contents of cellulose, hemicellulose and lignin in bagasse and bamboo shaving were analyzed and list in Table-1.

TABLE-1
CONTENT OF CELLULOSE, HEMICELLULOSE AND LIGNIN IN BAGASSE AND BAMBOO SHAVING

Agricultural waste	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Bamboo shaving	43.2	25.1	15.2
Bagasse	40.5	26.7	18.3

Chemicals used during the present study were monochloro acetic acid, ethanol, sodium hydroxide, sulfuric acid, acetic acid, silver nitrate, ammonium carbonate, hydrochloric acid, *etc*. All the chemicals were AR grade or equivalent and used as received without further purification.

Bamboo shaving and bagasse pretreatment for cellulose extraction: Bagasse and bamboo shaving should be cut into small pieces (0.5-1 cm), then dried at 70 °C in a vacuum oven. The dried materials were ground into powder to pass through a 0.5 mm mesh sieve. Then the cellulose extraction conditions were optimized by orthogonal method separately. The powder was soaked in different concentration(5, 10 and 20 %) alkali at 1:6,1:8 or 1:10 (w/v) ratio of cellulose to solvent for 1, 2 or 3 h at 50, 70 or 95 °C. The obtained slurry was filtered and solid material was washed using distilled water, the extracted cellulose was dried at 60 °C in a vacuum oven. After pretreatment, the sample with best cellulose content should be selected and the degree of polymerization would be compared to determine the application method for carboxymethyl cellulose production.

Preparation of carboxymethyl cellulose: Preparation of carboxymethyl cellulose was carried out in two steps, alkalization and etherification under heterogeneous conditions. Optimization of the reaction was carried out varying the different reaction parameters such as concentration of alkali and monochloroacetic acid, temperature and time of the reaction. Alkalization was conducted at 20-45 °C in which 48 % NaOH (w/v) was added to vigorously stirred slurry of cellulose (20 g) in ethonal (240 mL) over a period of 0.5 h. Stirring was continued for another 1 h. Then monochloro acetic acid dissolved in ethonal was added under continuous stirring and the reaction mixture was heated up to the desired temperature (50-75 °C) and stirred at that temperature for desired duration (1-2 h) with 72 % ethanol followed by absolute ethanol and finally dried at 70 °C in vacuum oven.

The content of α-cellulose and degree of polymerization (DP) for cellulose extractions were determined by routine method. The degree of substitution (DS) were analyzed by potentiometric titration. The viscosity of 1.0 aqueous solution of carboxymethyl cellulose synthesized were determined using Ubbelohde type capillary viscometer immersed in a 30.0 ± 0.1 ºC thermostated water bath. The sodium content of carboxymethyl cellulose samples should be analyzed[10].

RESULTS AND DISCUSSION

α-Cellulose content of bagasse and bamboo shaving after pretreatment: The cellulose in bagasse was extracted using the described method and the results presented in Table-2. According to the results, the influence order of test conditions for each product was D > B >A > C, namely NaOH concentration > temperature > water bath time > water ratio and the best combination for bagasse pretreatment was 20 % NaOH at 1:6 (w/v) ratio of cellulose to solvent for 2 h at 95 °C, the content of α-cellulose reach to 94.80 %, while the average polymerization degree (DP) was 476, this data is close to pulp, one of the main material for carboxymethyl cellulose production. This experiment was repeated for 5 times with good reproducibility.

TABLE-2
ORTHOGONAL EXPERIMENT RESULTS FOR BAGASSE PRETREATMENT

Factor / No.	A: Time (h)	B: Temp. (°C)	C: Ratio of bagasse to solvent	D: NaOH concentration (%, W/V)	α-Cellulose content (%)
1	1	50	1:6	5	82.37
2	1	70	1:8	10	81.02
3	1	95	1:10	20	94.33
4	2	50	1:8	20	90.07
5	2	70	1:10	5	86.61
6	2	95	1:6	10	90.45
7	3	50	1:10	10	85.08
8	3	70	1:6	20	88.17
9	3	95	1:8	5	86.69
K1	257.72	257.52	260.99	255.67	–
K2	267.13	255.80	257.78	256.55	–
K3	259.94	271.47	252.71	272.57	–
R	9.41	15.67	8.28	16.90	–

Likely this experiment, bamboo shaving was also pretreated to meet the use for carboxymethyl cellulose preparation. The results showed the best combination for bamboo shaving pretreatment was 20 % NaOH at 1:8 (w/v) ratio of cellulose to solvent for 2 h at 95 °C, the content of α-cellulose reach to 93.45 %, but the average degree of polymerization (DP) was only 260.

Mass fraction ratio among refined bamboo shaving and bagasse for carboxymethyl cellulose production: According to the characteristics of the regional economy, bamboo shaving is more abundant than bagasse in the east of China. Results showed the cellulose content of the two pretreated materials could meet the demand of carboxymethyl cellulose production, while the degree of polymerization of pretreated bamboo shaving is not enough to be applied solely. Usually, the product with viscosity (of 1.0 % carboxymethyl cellulose) above 250 mPaos is necessary. Fig. 1 showed the experiments with different materials ratio under ordinary conditions for carboxymethyl cellulose preparation. The results displayed that mass fraction ratio among these refined bamboo shaving and bagasse could be 60:40, subsequent optimization studies were carried out at this material ratio.

Optimization conditions of carboxymethyl cellulose synthesis: In optimization process of carboxymethyl cellulose synthesis, each reaction parameter was varied one at one time. Some of the results were shown as Fig. 2-4.

It was observed that viscosity is very low at low alkalization temperature and it increased with temperature increasing from 20 to 30 °C and there after decreased considerably (Fig. 2). So the optimum alkalization temperature was found to be 30 °C. The optimized reaction conditions for carboxymethyl cellulose synthesis were alkalified at 30 °C for 70 min and etherified at 55 °C for 90 min (Figs. 3 and 4); afterwards,

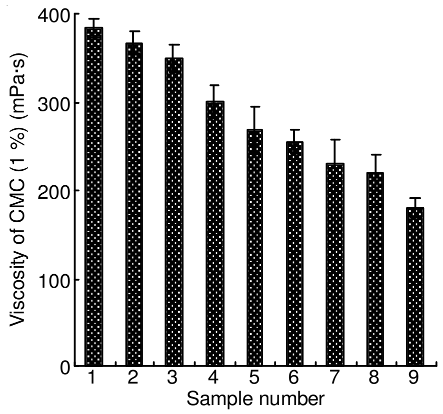

Fig. 1. Different mass fraction ratio among refined bamboo shaving and bagasse as the materials for carboxymethyl cellulose production. Samples from No. 1-9 showed different ratio of refined bagasse: bamboo shaving were 10: 0, 8: 2, 7: 3, 6: 4, 5: 5, 4: 6, 3: 7, 2: 8, 0: 10. Reaction conditions: alkalified at 30 °C for 60 min and etherified at 50 °C for 90 min

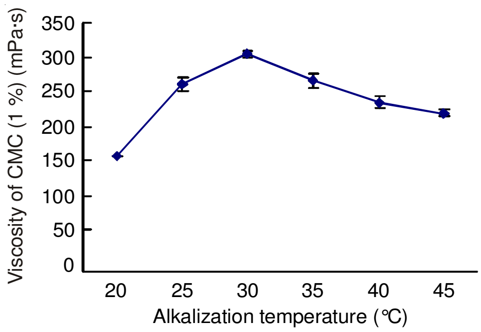

Fig. 2. Viscosity of carboxymethyl cellulose synthesized with various alkalization temperature. The other reaction conditions: alkalified for 60 min and etherified at 50 °C for 90 min

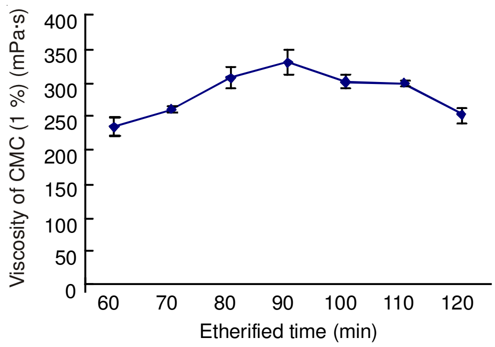

Fig. 3. Viscosity of carboxymethyl cellulose synthesized with various etherified time. The other reaction conditions: alkalified at 30 °C for 60 min and etherified at 60 °C

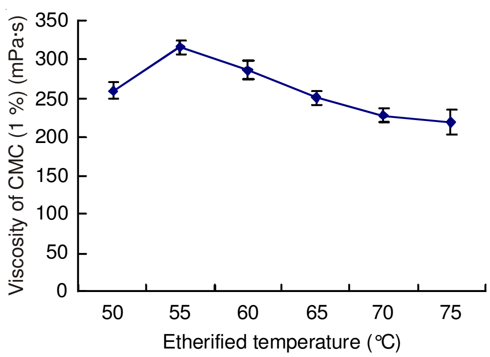

Fig. 4. Viscosity of carboxymethyl cellulose synthesized with various etherified temperature. The other reaction conditions: alkalified 30 °C for 60 min and etherified for 90 min

temperature was kept at 70 °C for 10 min. Under these conditions, viscosity of 1 % carboxymethyl cellulose aqueous solution was all above 250 mPa·s and most carboxymethyl cellulose samples reached to 300 mPa·s and DS ≥ 0.8. The content of chloride and moisture were less than 1.2 and 10 %, respectively.

Conclusion

This study introduced a successful method for carboxymethyl cellulose synthesis utilizing two kinds of sustainable cellulose sources-bamboo shaving and bagasse as raw materials. Conclusively, cellulose isolated from bamboo and bagasse lignocellulosic biomass could be derivatized by carboxymethylating modification reactions. The results showed that mass fraction ratio among these refined bamboo shaving and bagasse could be 60:40, the optimized reaction conditions were alkalified at 30 °C for 80 min and etherified at 55 °C for 90 min; afterwards, temperature was kept at 70 °C for 10 min. Under these conditions, viscosity of 1 % carboxymethyl cellulose aqueous solution could be insured above 250 mPa·s with DS ≥ 0.8, while some of the carboxymethyl cellulose sample reached to 300 mPa·s. Since the content of chloride and moisture were less than 1.2 and 10 %, respectively, the product could meet the market demand. These materials seem to be potential feedstocks for producing this derivative for a variety of applications. This study introduced a novel method for recycling wastes.

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