

Optimization of Sodium Carboxymethyl Cellulose Preparation from Bagasse by Response Surface Methodology

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Abstract. In this work, the process of sodium carboxymethyl cellulose (CMC) prepared from pretreated bagasse was studied. On the basis of single factor experiments, further research on the interaction among the significant elements was conducted by means of steepest ascent, Box-Behnken design and response surface methodology. Consequently, it turned out that the optimum carboxymethyl reaction factors were as follows: In ethanol-water solution, NaOH as basifier, alkalinized at 31.2 °C for 120min; chloroacetic acid as etherifying agent, etherified at 56 °C for 132min; afterwards, temperature was kept at 70 °C for 10min. Under these conditions, viscosity of 1% CMC aqueous solution reached 243 mPa s. Compared to that of the original value, it has an increase of 32.1%.

1. Introduction

Sodium carboxymethyl cellulose (CMC) is a kind of important cellulose derivatives synthesized and consumed in many countries. It has some properties such as solubility, viscosity, biodegradability, non-toxicity and water holding capacity. It could be applied in pharmaceuticals, paper, food, oil drilling, detergents, etc [1, 2].

Conventionally, CMC was synthesized from wood pulp or cotton fiber. Theoretically, CMC could be prepared by any plant biomasses with rich cellulose content. It was reported some agricultural waste were utilized to produce CMC [3, 4]. In fact, since the properties of these cellulose sources are different from wood pulp or cotton fiber, whatever polymerization degree or purification of cellulose, the synthesis process of CMC from the various cellulose sources should be studied.

Response surface methodology (RSM) is an efficient mathematical statistics approach with more economical and precise than that of usual methods [5, 6]. It could measure various factors in the mean time, and get information about the interaction among variables to gain a reasonable optimization result [7].

The purpose of this study was to determine the optimal carboxymethyl reaction factors for CMC synthesis from pretreated bagasse through RSM, and then increase the viscosity of CMC.

2. Materials and methods

2.1. Bagasse and its pretreatment

Bagasse (1.0 kg) was collected from supermarket in Hangzhou, China. After washed and cut into small pieces (0.5-1cm), then dried at 70 °C in a vacuum oven, ground into powder to pass through the 0.5 mm mesh sieve. After that, the bagasse powder should be submerged into 6% NaOH solution with the solid/solvent ratio of 1:10, mixed and kept at 95 °C for 2 h. After the process, the quality fraction of α -cellulose of pretreated bagasse increased from 42.01% to 90.23%.



2.2. Reagents

Chemicals used during the present study were sodium hydroxide, ethanol, monochloro acetic acid, acetic acid, etc. All these chemicals were used as original without further purification.

2.3. Preparation of CMC and optimization by RSM

CMC preparation from pretreated bagasse was carried out in alkalization and etherification successively under heterogeneous conditions. Single-factor experiment was used to determine the levels of each reaction conditions, and Plackett-Burman design (PBD) was used for significant effect factors screening. Path of steepest ascent experimental design and results were shown in Table 1. RSM was employed to optimize the most significant variable factors and find the relationship between the factors and viscosity. These independent factors were further studied by Box-Behnken design (BBD); the design and results were shown in Table 2. Statistical analysis of the model was evaluated by analysis of variance (ANOVA) with statistical software Design Expert version 7.0.0. The quality of the model was determined by the coefficient of determination R^2 ; the significance of the fitness polynomial equation for the response variables was evaluated by p value. The viscosity of 1% CMC solution was determined as the response value.

3. Results and discussion

PBD was finished on the basis of single-factor experiment. It was found that there was a wide variation of viscosity and alkalinity temperature (X_1), etherification temperature (X_2) and etherification time (X_3) were significant variables ($p < 0.05$). These three factors were selected for further optimization to gain a maximum response.

Path of steepest ascent experimental design and results were shown in Table 1, suggesting that point of Run 2 might be near the region of the maximum viscosity response, and can be chosen for further optimization.

Table 1. Experiment design and results of steepest ascent.

Run	alkalinity temperature (°C)	etherification temperature (°C)	etherification time (min)	Viscosity (mPa s)
1	27	50	100	80.8
2	30	55	115	189
3	33	60	130	136
4	36	65	145	95.2
5	39	70	160	96.0

RSM using BBD was applied to determine the optimal levels of the three selected variables that affected product's viscosity significantly. Table 2 showed the experimental design and corresponding results. The results were fitted with a second-order polynomial equation:

$$Y = +205.02 + 21.03 * X_1 + 12.56 * X_2 + 10.62 * X_3 + 3.38 * X_1 * X_2 + 5.13 * X_1 * X_3 + 4.13 * X_2 * X_3 - 31.79 * X_1^2 - 40.80 * X_2^2 - 11.01 * X_3^2$$

Table 2. Box-Behnken experiments design and results.

Run	X1 Alkalinity temperature (°C)	X2 Etherification temperature(°C)	X3 Etherification time (min)	Viscosity (mPa s)
1	30.0	55.0	100.0	182
2	33.0	50.0	140.0	136
3	30.0	55.0	153.6	198
4	30.0	55.0	120.0	209
5	30.0	55.0	120.0	197
6	25.0	55.0	120.0	87.0
7	30.0	55.0	120.0	215
8	35.0	55.0	120.0	149
9	27.0	50.0	140.0	93.0
10	30.0	55.0	120.0	209
11	30.0	55.0	120.0	197
12	30.0	46.6	120.0	65.0
13	27.0	60.0	100.0	98.0
14	27.0	60.0	140.0	108
15	33.0	60.0	140.0	177
16	27.0	50.0	100.0	87.0
17	30.0	55.0	120.0	203
18	33.0	50.0	100.0	122
19	33.0	60.0	100.0	134
20	30.0	63.4	120.0	120

The ANOVA for the model was shown in Table 3. The value of coefficient of determination R-Squared was 0.9858. In a normal way, a regression model of R-Squared higher than 0.9 illustrated a high correction, it was suggested that 98.58% of the total variance could be explained by the model. The adjusted determination coefficient ($Adj R^2=0.9731$) was also high enough to confirm the significance of the model. The p - value of this model was less than 0.0001, which indicated that the model fitness was extremely significant. Furthermore, the lack of fit value of the model was 0.3219 (non-significant), implied that the model was adequate to predict the response and explain the effect of variables on the response.

The three-dimensional (3D) response surface plots were employed to illustrate the interaction among the variables on CMC viscosity (Figure 1, Figure 2 and Figure 3). Each 3D plot represented combinations of the two test variables, while the other variables maintained at the center level. An elliptical contour or saddle nature of the contour plots suggested that there has a significant interaction between two variables, such as alkalinity temperature and etherification temperature (Table 3 and Figure 1), as well as etherification temperature and etherification time (Table 3 and Figure 2). The quadratic model predicted the maximum enzyme activity was 233.36 mPa s, when the coded level of alkalinity temperature, etherification temperature and etherification time were 31.2 °C, 56.0 °C and 132.2min, respectively.

Table 3. ANOVA of quadratic model for CMC viscosity.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	46805.87	9	5200.65	77.35	< 0.0001 significant
X ₁	6042.73	1	6042.73	89.88	< 0.0001
X ₂	2153.63	1	2153.63	32.03	0.0002
X ₃	1200.63	1	1200.63	17.86	0.0018
X ₁ X ₂	91.13	1	91.13	1.36	0.2714
X ₁ X ₃	210.13	1	210.13	3.13	0.1075
X ₂ X ₃	136.13	1	136.13	2.02	0.1852
X ₁ ²	14683.07	1	14683.07	218.39	< 0.0001
X ₂ ²	24193.51	1	24193.51	359.84	< 0.0001
X ₃ ²	1097.14	1	1097.14	16.32	0.0024
Residual	672.33	10	67.23		
Lack of Fit	408.33	5	81.67	1.55	0.3219 not significant
Pure Error	264.00	5	52.80		
Cor Total	47478.20	19			
R-Squared	0.9858				
C.V. %	5.49				
Adj R ²	0.9731				
Pred R ²	0.9117				

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

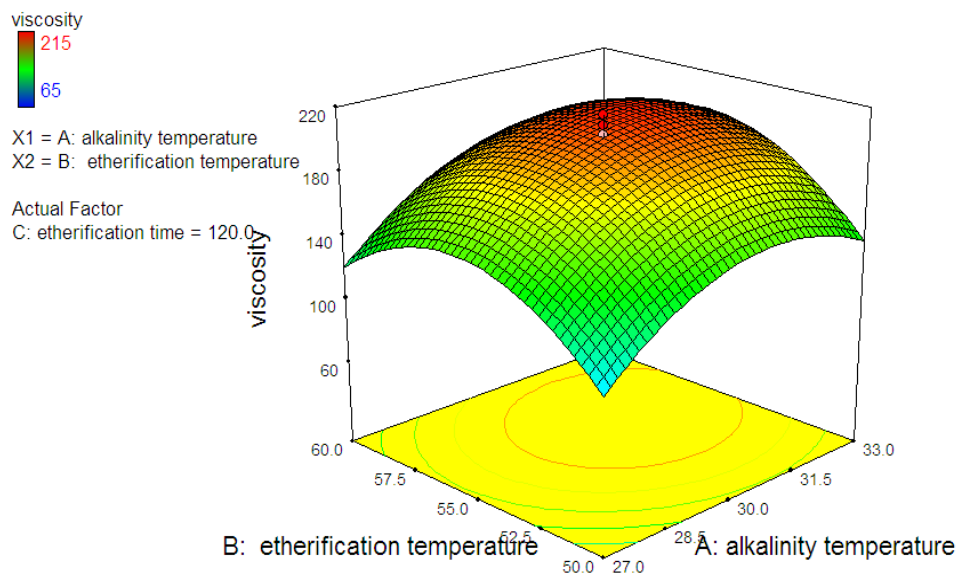


Figure 1. Response surface plots of viscosity responses to alkalinity temperature and etherification temperature.

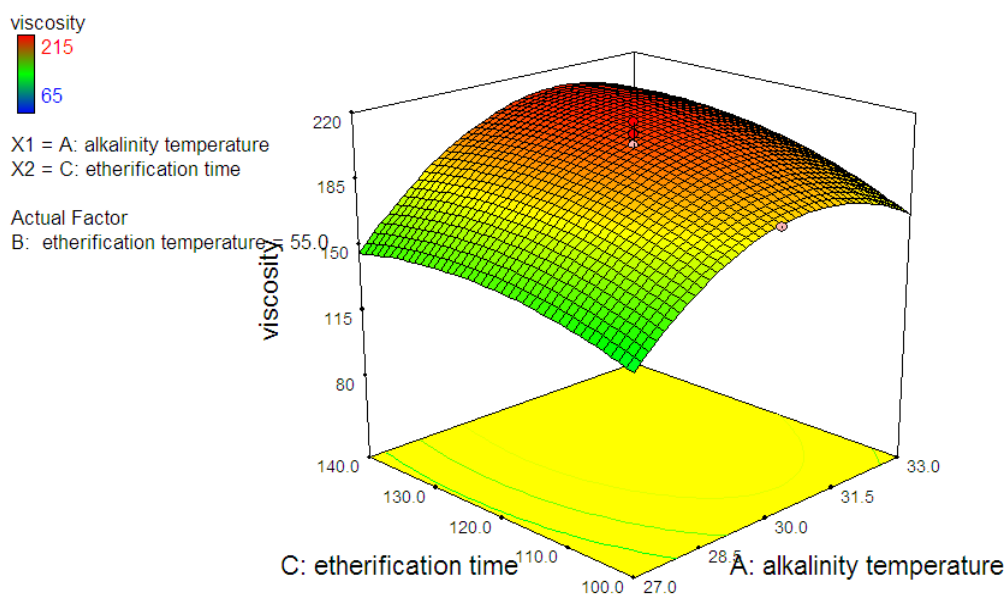


Figure 2. Response surface plots of viscosity responses to alkalinity temperature and etherification time.

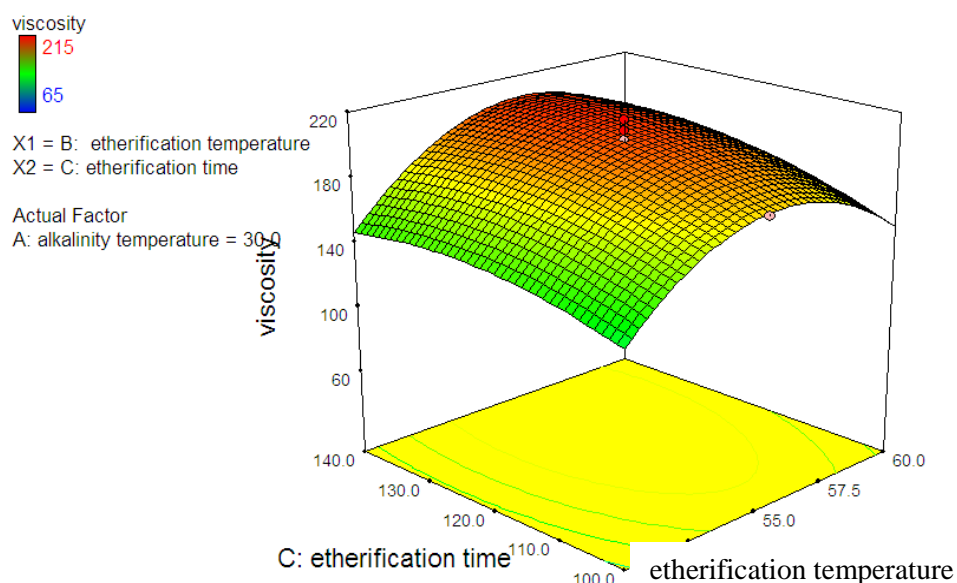


Figure 3. Response surface plots of viscosity responses to etherification temperature and etherification time.

The other reaction factors were fixed at follows: 5 g of the sample was alkalinized for 2 h in a shaking water bath with 5 % NaOH in 100mL of ethanol as a solvent. After this process over, 6.5 mL 75% monochloro acetic acid dissolved in ethanol was added under continuous stirring and etherified, then kept at 70 °C for 10min. The slurry was neutralized with 90% of acetic acid and then filtrated. The solid obtained as CMC was washed by 70% ethanol for twice to remove undesirable byproducts. The obtained CMC was dried at 60 °C in an oven. In order to confirm the model adequacy for predicting the maximum response, a validation experiment was conducted with five tests. Under such optimum conditions, the experimentally generated mean value of 234 mPa s (236 mPa s, 228 mPa s, 228 mPa s,

243 mPa s, 233 mPa s, respectively), which was excellent agreement with the model prediction value. The viscosity was increased by 32.1% in comparison with that of original viscosity.

4. Conclusions

In this work, the progress of CMC preparation from pretreated bagasse was improved by response surface methodology. The high quality of a mathematical model indicated that RSM could be used to optimize the factors of the carboxymethyl reation for enhancing the viscosity of CMC product, which increased by 32.1% compared with that of the initial process factors.

5. Acknowledgement

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6. References

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