The Analysis of Boundary Functions of CMS Reaction Factors

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ABSTRACT: The mathematical model of nonlinear regression was established, describing the effect of sodium hydroxide, monocholroaceetic sodium, and reaction temperature on the synthesis of Carboxymethyl Starch (CMS); and the 23 groups of experiments were carried out. The relationship between the degree of substitution and boundary function of the three factors was discussed. [Nature and Science. 2005;3(2):79-81].

Key words: mathematical model; carboxymethy; boundary function

1   Introduction

Carboxymethyl Starch (CMS), which was first synthesized in 1924, is one of the most important modified starches widely used in textile, petroleum, food and pharmaceutical industries. Different methods for preparing CMS had been reported in literatures [3] [4] [5]. In the traditional method of synthesizing CMS, the degree of substitution (DS) of CMS is rather low, valued about from 0.01 to 0.1[1]. The products could not be dispersed in cold water, but they are soluble in 80% methanol to permit a reliable determination when the DS is above 0.5[2]. So attention was paid to the reaction ratio to increase DS. In this paper, the relationship between reaction factors of CMS and DS was discussed based on mathematical model.

2   Materials and Methods

2.1   Materials

All chemicals used were of analytical reagent grade; monochloroacetic acid, isopropyl alcohol, alcohol and sodium hydroxide were included; corn starch was produced by the Second Medicine Factory of Harbin.

2.2   Methods

Corn starch (0.5 g) is dissolved in absolute isopropyl alcohol (120 ml), sodium hydroxide was added according to Table 1, and the reaction time is 30 minutes; monochloroacetic sodium (MCAS, $ClCH_2COONa$) was then added (Table 1), and reacted another 60 minutes; then the products were cooled, neutralized, dried, and crushed.

3   Results and Discussion

3.1   Modeling

According to the figures given in the Table 1[6], series of experiments was carried out, using different quantities of aqueous sodium hydroxide and sodium salt of monochloroacetic under different reaction temperatures. The value of DS was got for 23 groups of products (Table 1). So mathematical model of DS of CMS preparations was established, and the three variables are reaction temperature, the dosage of sodium hydroxide and sodium salt of monochloroacetic (Model 1).

$y(x)=0.3451+0.0246x_1+0.1103x_2+0.0428x_3-0.0299x_1 x_2-0.0138 x_1 x_3+0.0225 x_2 x_3-0.0736 x_1^2-0.0253 x_2^2-0.0258x_3^2$ (Model 1).

F test for Modle1 was carried out, and the result was as followed.

$F_1=1.7010<F_{0.05}(5,8)=3.69$ [6]

$F_2=8.3121>F_{0.01}(9,13)=4.19$

The data of T-test were all higher than $t_{0.4}(1.3)=0.870$ [6]

It was showed that Model 1 was effective, the presence of variances in the equation was of value, and the model reflected the practical situation very well and could well reflect the law of the CMS preparation.

3.2   The relationship between the boundary function of every factors and DS value

Boundary function is that the value of DS changes a Δy with every factor changing a unit of ΔX near a certain level, the contribution of every factors near the level is then showed.

Table 1. Plan of Test and Results

No.	NaOH $X_1(g)$	Temp. $X_2(℃)$	MCAS $X_3(g)$	DS y
1	8	68	14	0.31
2	8	68	6	0.24
3	8	32	14	0.15
4	8	32	6	0.12
5	2	68	14	0.44
6	2	68	6	0.27
7	2	32	14	0.12
8	2	32	6	0.07
9	10	50	10	0.26
10	0	50	10	0.00
11	5	80.3	10	0.49
12	5	19.7	10	0.06
13	5	50	16.8	0.35
14	5	50	3.2	0.19
15	5	50	10	0.35
16	5	50	10	0.36
17	5	50	10	0.28
18	5	50	10	0.35
19	5	50	10	0.23
20	5	50	10	0.39
21	5	50	10	0.37
22	5	50	10	0.33
23	5	50	10	0.34

3.2.1 Analysis of boundary function of NaOH dosage

Reaction temperature (X_2) and $ClCH_2COONa$ dosage (X_3) were fixed in different levels in Model 1, the single factor model of NaOH dosage of were got, and the derivative of the model were calculated, the mathematical model of the boundary function of NaOH dosage to DS was gained.
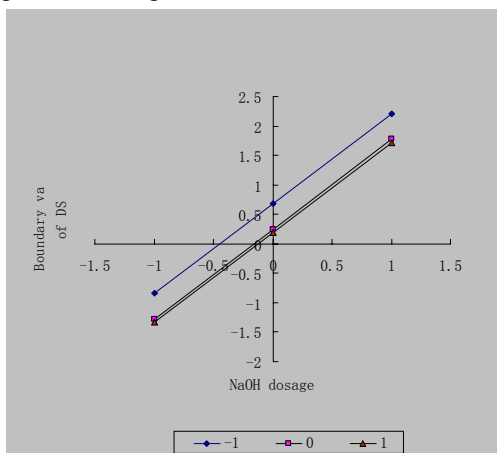

Figure 1. Relationship between DS Boundary Value and NaOH Dosage
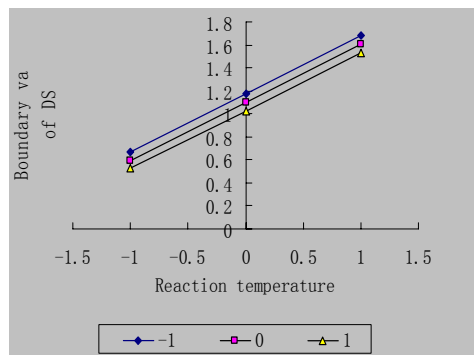

Figure 2. Relationship between DS Boundary Value and Reaction Temperature

When the code value of NaOH dosage was of different level in equation (A), DS of different NaOH dosage was got (Figure 1). The boundary function of NaOH dosage decreased with the increasing of dosage.

The code number of NaOH dosage was of different quantity rank in equation A, and the boundary DS of different NaOH dosages was calculated after number conversion (Figure 1). It was clear that the boundary function of NaOH dosage decreased with increasing of NaOH dosage in Figure 1. The boundary DS was high while NaOH dosage was relatively low; and the boundary DS decreased with the increase of NaOH dosage. The critical point of boundary value of NaOH dosage moved backward with the increasing of other factors, while the NaOH dosage changing from positive value to negative value. When the other factors increased from –1 to 1, their critical point values were around 6.35, 5.48 and 5.36 separately. It was showed that NaOH dosage limited the DS of CMS, and the DS was stable only if every factor was of certain value.

a: $(x_1, -1, -1)$ $dy/dx = -0.1526 x_1 + 0.0683$
b: $(x_1, 0, 0)$ $dy/dx = -0.1526 x_1 + 0.0246$ (A)
c: $(x_1, 1, 1)$ $dy/dx = -0.1526 x_1 + 0.0190$

3.2.2 Analysis of boundary function of reaction temperature

The boundary function of the reaction temperature to the degree of substitution of CMS was in model B and Figure 2.

a: $(-1, x_2, -1)$ $dy/dx = -0.0506 x_2 + 0.1177$
b: $(0, x_2, 0)$ $dy/dx = -0.0506 x_2 + 0.1103$ (B)
c: $(1, x_2, 1)$ $dy/dx = -0.0506 x_2 + 0.1029$

The contributive ratio of reaction temperature to CMS decreased with the increase of temperature, and was positive. It was showed that the increase of reaction temperature do benefit no the synthesis of CMS. When a unit of ΔX_2 was changed in the low temperature

district, the value of DS increased greatly, while it increased slowly in the high temperature district. The degree of DS increasing led by the increase of reaction temperature was weakened when the dosage of $ClCH_2COONa$ and NaOH were increased.

3.2.3 Analysis of boundary function of $ClCH_2COONa$ dosage

The boundary function of the $ClCH_2COONa$ dosage to the degree of substitution of CMS was in model C and Figure 3.

$$a: (-1,-1,x_3) \quad dy/dx = -0.0516\, x_3 + 0.0341$$
$$b: (0, 0\, x_3) \quad dy/dx = -0.0516\, x_3 + 0.0426 \quad (C)$$
$$c: (1, 1,x_3) \quad dy/dx = -0.0516\, x_{31} + 0.0515$$

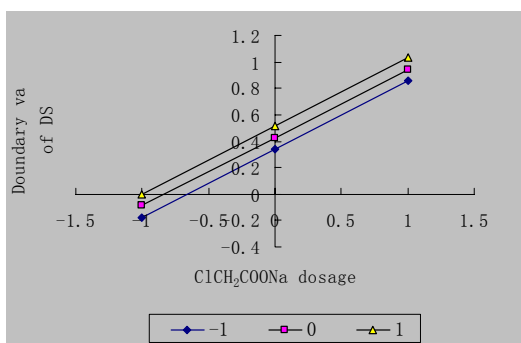**Figure 3. Relationship between DS Boundary Value and $ClCH_2COONa$ Dosage**

The change ratio of the degree of subsitition of CMS decreased with the increase of the $ClCH_2COONa$ dosage, and it changed from positive to negetive. That is, the increasing of the $ClCH_2COONa$ dosage did not do benefit on the CMS product with high DS. When other factors were in the level of -1, 0 and 1 separately, the optimum $ClCH_2COONa$ dosage (critical value) was 12.64, 13.32 and 14.00 separately. It was clear that the contributive ratio of the $ClCH_2COONa$ dosage was limited by the taken value of other factors, the critical vale increased with the increasing of the taken value of other factors, and the negative effect led by the increasing of the $ClCH_2COONa$ dosage was decreased.

4 Conclusions

(1) The degree of subsitition of CMS changed with the change of NaOH dosage. It was of the highest value while the NaOH dosage was proper, and lower while the NaOH dosage was too much or small. The limiting function was stable when other factors were fixed.

(2) The reaction temperature was of positive effect to the starch carboxymethylization in the test. The degree of subsitition of CMS increased with the increasing of temperature.

(3) The degree of subsitition of CMS was also affected by the $ClCH_2COONa$ dosage. The $ClCH_2COONa$ dosage had positive effect when the dosage was proper, while it had negative effect when the dosage was too much, but the limiting function decreased with the increasing of other factors' levels.

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