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The application of an advanced visualized method in synthesis process optimization of carboxymethyl hydroxyethyl starch

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ABSTRACT

Carboxymethyl hydroxyethyl starch with good transparency and high stability was prepared through two etherifications successively by adding 2-chloroethanol and chloroacetic acid as etherifying agents. A visualization method was used to optimize the proportion parameters and forecast the optimal process conditions. Carboxymethyl hydroxyethyl starch was prepared according to the optimal conditions, and the value of MS is about 0.3553 and DS is about 0.3412. It proves that visualization method is veracious and credible.

1. Introduction

Hydroxyethyl starch (HES) is a water soluble semisynthetic polysaccharide that the ether linkage will not part. It is hardly influenced by the electrolyte and the value of pH, and it could be used under a wide range of pH. It has been widely used in nonmedical industries, such as coating agents, thickeners, glues, etc. However, its poor-stability layer and transparence are not yet improved. Carboxymethyl starch (CMS) has excellent water-solubility, bond, expansion and decentralization functions, but it can be greatly affected by electrolytes and the value of pH. Therefore, a new multiplex starch — carboxymethyl hydroxyethyl starch should be prepared, which would have better water-solubility, viscosity stability, anti-temperature, anti-salt, and other characteristics. The preparation and properties of carboxymethyl hydroxyethyl starch are studied by the numbers. The aim is to prepare compound modified starch and to increase the value of the maize starch.

2. Results and discussion

2.1. Determination of initial points

In carboxymethyl hydroxyethyl starch design, the degree of molar substitution of hydroxyethyl group (MS) and degree of substitution of carboxymethyl group (DS) of starch are regarded as the most important properties. Many parameters, such as the amount of NaOH, 2-chlorine ethanol and chloroacetic acid, reaction time and temperature are directly related to the value of MS and DS. So, this paper takes MS and DS into consideration, which are universally accepted as general indexes of starch and the main design targets. The aim is to optimize the reaction parameters to get a good performance carboxymethyl hydroxyethyl starch.

A group of experimental data was collected according to uniform design. The experimental scheme and results are listed in Tables 1–3. There were six important factors influencing the value of MS and DS, namely, $NaOH_{(1)}$ (a), 2-chlorine ethanol (b), $NaOH_{(2)}$ (c), chloroacetic acid (d), reaction time (t) and reaction temperature (T).

2.2. Mapping results

Fig. 1 shows the mapping diagram for this problem. Sample data of carboxymethyl hydroxyethyl starch in multidimensional space were mapped and reduced to a two-dimensional plane, with 16 blue points (hollow points)[1] in figure representing 16 groups of carboxymethyl hydroxyethyl starch experiments, respectively. The contours of MS and DS were generated automatically on this plane. Real lines represent the contours of MS and dash-dotted lines are the contours of DS. The optimal proportions can be determined intuitively based on this plane. By means of an inversion mapping algorithm, optimal point in this plane can be mapped inversely to original multidimensional space and represented in terms of practical proportion data.

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[1] For interpretation of color mentioned in this figure the reader is referred to the web version of the article.

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Table 1
Uniform experimental scheme and results.

Entry	a (g)	b (g)	c (g)	d (g)	T (°C)	t (h)	Factors index	
							DS	MS
1	2.0	7.802	7.315	9.606	63	23.2	0.2559	0.0504
2	2.212	10.238	8.931	6.711	60	21.6	0.4337	0.0427
3	2.4	12.656	6.253	10.80	57	20.0	0.1956	0.2269
4	2.625	15.013	7.617	8.026	54	18.4	0.1859	0.1321
5	2.828	7.208	9.172	12.048	51	16.8	0.1202	0.2599
6	3.120	9.605	6.238	9.198	65	15.1	0.5596	0.1307
7	3.263	12.494	7.806	6.474	62	13.6	0.3867	0.1473
8	3.382	14.469	9.467	10.4	59	12.0	0.4098	0.1372
9	3.611	6.673	6.533	7.586	56	24.0	0.2979	0.1446
10	3.820	9.267	8.122	11.6	53	22.4	0.2765	0.1189
11	4.093	11.416	9.743	8.803	50	20.8	0.3415	0.1431
12	4.269	13.862	6.816	6.080	64	19.2	0.4839	0.1772
13	4.442	6.023	8.379	10.027	61	17.6	0.4826	0.112
14	4.642	8.418	10.063	7.223	58	16.0	0.2559	0.2117
15	4.786	10.831	7.063	11.256	55	14.4	0.4289	0.1433
16	5.018	13.259	8.667	8.400	52	12.8	0.2152	0.1603

Table 2
$L_{25}(5^6)$ orthogonal design.

Factor	a (g)	b (g)	c (g)	d (g)	T (°C)	t (h)
Level						
1#	a1(2)	b1(6)	c1(6)	d1(6)	T1(50)	t1(12)
2#	a2(3)	b2(8)	c2(7)	d2(7.5)	T2(53)	t2(15)
3#	a3(4)	b3(10)	c3(8)	d3(9)	T3(56)	t3(18)
4#	a4(5)	b4(12)	c4(9)	d4(10.5)	T4(59)	t4(21)
5#	a5(6)	b5(14)	c5(10)	d5(12)	T5(62)	t5(24)

Table 3
$L_{25}(5^6)$ orthogonal experiment.

Row	1	2	3	4	5	6		
Experiment							DS	MS
1#	a1	b1	c1	d1	T1	t1	0.363959	0.096182
2#	a1	b2	c2	d2	T2	t2	0.276482	0.079753
3#	a1	b3	c3	d3	T3	t3	0.386819	0.082615
4#	a1	b4	c4	d4	T4	t4	0.297863	0.067095
5#	a1	b5	c5	d5	T5	t5	0.276734	0.077955
6#	a2	b1	c2	d3	T4	t5	0.53384	0.078704
7#	a2	b2	c3	d4	T5	t1	0.276608	0.090704
8#	a2	b3	c4	d5	T1	t2	0.470436	0.172422
9#	a2	b4	c5	d1	T2	t3	0.276482	0.210881
10#	a2	b5	c1	d2	T3	t4	0.21533	0.087859
11#	a3	b1	c3	d5	T2	t4	0.409731	0.148255
12#	a3	b2	c4	d1	T3	t5	0.341212	0.159214
13#	a3	b3	c5	d2	T4	t1	0.297657	0.105416
14#	a3	b4	c1	d3	T5	t2	0.276545	0.181461
15#	a3	b5	c2	d4	T1	t3	0.255693	0.181436
16#	a4	b1	c4	d2	T5	t3	0.363787	0.212249
17#	a4	b2	c5	d3	T1	t4	0.255809	0.150384
18#	a4	b3	c1	d4	T2	t5	0.363787	0.331462
19#	a4	b4	c2	d5	T3	t1	0.559693	0.210336
20#	a4	b5	c3	d1	T4	t2	0.235281	0.146266
21#	a5	b1	c5	d4	T3	t2	0.341532	0.083468
22#	a5	b2	c1	d5	T4	t3	0.297657	0.17338
23#	a5	b3	c2	d1	T5	t4	0.276734	0.342388
24#	a5	b4	c3	d2	T1	t5	0.197726	0.21677
25#	a5	b5	c4	d3	T2	t1	0.235281	0.228998

2.3. Prediction and verification for the optimal proportion

As shown in Fig. 2, the value of both MS and DS could be controlled up to 0.3 in the direction of the arrow. Taking points 10 and 11 as references and step size as 1.3, a red asterisk predicted point was obtained through extrapolation in the direction of the arrow, and the values of MS and DS were gotten as 0.3513 and 0.3488 respectively. Therefore, this region can be determined as distribution area of optimum conditions and the red asterisk is the optimum point. The corresponding proportion parameters are listed in Table 4.

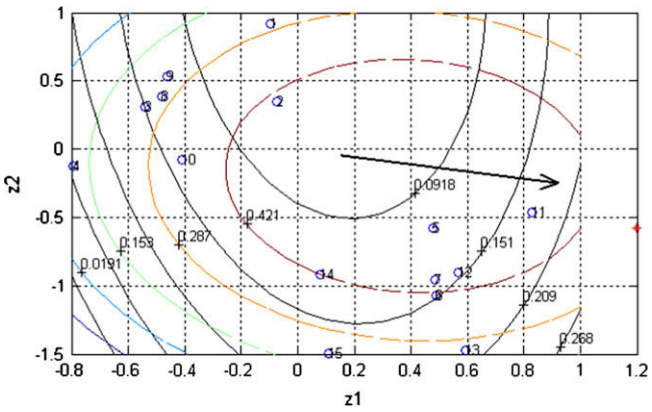

Fig. 1. Mapping figure (including optimal point).

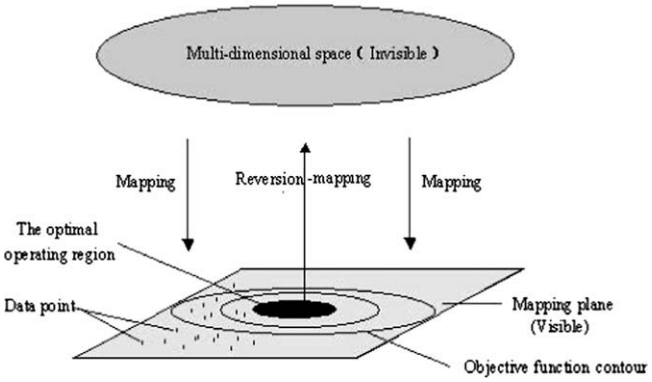

Fig. 2. Principles of visual optimization method.

The predicted proportions of carboxymethyl hydroxyethyl starch were tested via a group of verification experiments. Table 4 shows the comparison of the test results and prediction results, in the value of MS and DS, which demonstrates the availability of the VM.

2.4. Performance test

Carboxymethyl hydroxyethyl starch sample has been prepared according to the above predicted proportions. Some properties, such as transparency, retrogradation and paste viscosity, were determined and listed in Table 5.

2.5. Comparison of VM and orthogonal design

Compared with the best results of $L_{25}(5^6)$ orthogonal experiment which also has been used to prepare carboxymethyl hydroxyethyl starch — the value of MS is about 0.3316 and DS is about 0.3414, the results of VM are better than the results of orthogonal design, and the number of text times (16 times) is far smaller than that of orthogonal design (25 times).

Table 4
Comparison of test results and prediction results.

Entry	a (g)	b (g)	c (g)	d (g)	T (°C)	t (h)	Factors index	
							DS	MS
Predicted	5.2975	15.674	5.7585	5.7645	66	18	0.3488	0.3513
Test	5.3012	15.635	5.7585	5.7729	66	18	0.3553	0.3412

Table 5
Comparison of different starch.

Species[a]	Transparency (%)	Retrogradation (ml)	Paste viscosity (Pa s)
CMS	63.40	98	0.298
HES	26.91	7.8	0.02
Carboxymethyl hydroxyethyl starch	69.22	100	0.075

[a] The tested solution is 2% aqueous solution and total volume is 100 ml.

3. Conclusion

Herein, we have shown a synthetic process of a new modified starch (carboxymethyl hydroxyethyl starch). VM was used to optimize its process conditions and compared with orthogonal design. A custom reactor was designed and made to solve the problem of determination of MS. MS and DS were mapped in a plane simultaneously, and the optimal proportions region was determined intuitively according to the contours distribution. Through extrapolation or interpolation with step size in the optimal region, an optimal proportion point could be located. This study demonstrates the availability of the VM method in optimization MS and DS on carboxymethyl hydroxyethyl starch proportion parameters. About 2% aqueous solution of starch is configured with optimal sample, which has good transparency and high stability.

4. Experiment

4.1. Materials

Corn starch was purchased from the Hebei Yufeng Starch Sugar Industry Co., Ltd, China. Other chemicals were all of reagent grade and used without further treatment.

4.2. Etherification procedure

The etherifications were carried out in 250 ml three-necked stoppered bottle equipped with a mechanical stirrer. Corn starch (25 g) was suspended in 80% aqueous solution of methanol (50 ml) and reflux condensation. NaOH pellet was weighed and added for alkalization treatment. Then 2-chloroethanol was dripped into the starch suspension at 45 °C. 16–24 h later, the reaction was stopped and 80% aqueous solution of methanol (80 ml) was added. When the temperature of starch emulsion dropped to room temperature, a certain amount of NaOH solid was added and pretreated for 30 min. After that, chloroacetic acid was added at 50–65 °C for 4 h. And then, neutralisation was carried out with 2 mol/l aqueous HCl. The solution was filtered and the filter-cake (the neutralized starch) was washed with 80% aqueous solution of methanol and dried at 50 °C for 6 h.

4.3. Degree of molar substitution of hydroxyethyl group

The degree of molar substitution of hydroxyethyl group is the total mole number of reagent combined with the starch per anhydroglucose (Wurzburg, 1987). It was measured by gas chromatography according to the reported method (Hu & Ji, 1995; Li, 1981; Lortz, 1956; Xiang & Yu, 1990; Zhang, Li, & Lin, 1994). The degree of substitution can be calculated by following equations:

$$\text{iodoethane}\% = \frac{44.05 \times \text{iodoethane found in mg}}{155.97 \times \text{sample weight in mg}} \times 100 \quad (1)$$

$$\text{MS} = \frac{\text{iodoethane}\%}{(1 - \text{iodoethane}\%)} \times \frac{162.14}{44.05} \quad (2)$$

where: MS = degree of molar substitution.

A custom reactor was adopted in the analysis of molar substitution, which could keep good gas tightness during pyroreaction. The reactor body is a cylindrical stainless steel tube with PTFE lining. The pinhole in the centre of the lid is to facilitate sampling. The instrument drawing is shown in Fig. 3.

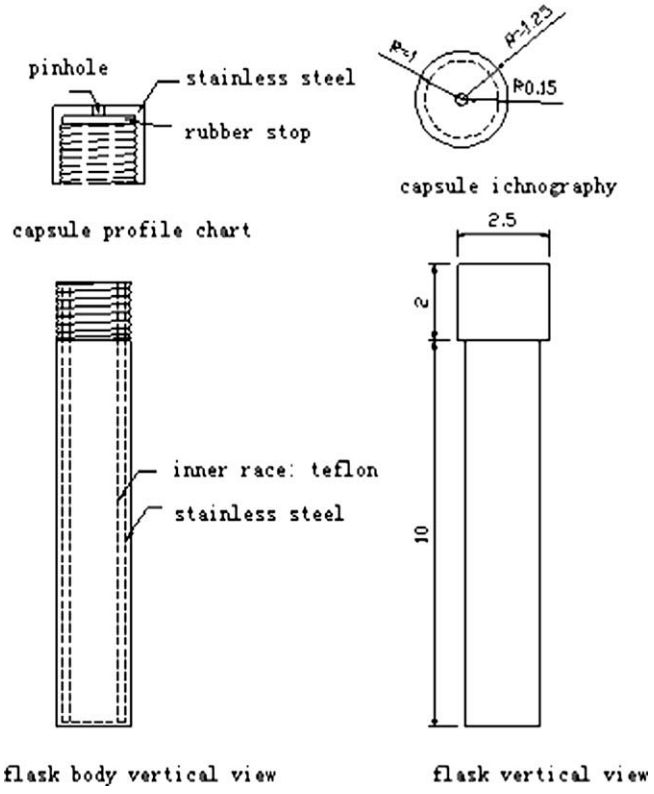

Fig. 3. The profile of custom reactor.

4.4. Degree of substitution of carboxymethyl group

The degree of substitution of carboxymethyl group was determined by EDTA copper salt titration and calculated by following equations:

$$A = \frac{c \times (v_0 - v_1) \times 2 \times 81 \times 100}{m \times v \times 1000} \quad (3)$$

$$\mathrm{DS} = \frac{162A}{8100 - 80A} \quad (4)$$

4.5. The basic principles of visualization method

The visualization method is an effective method for finding the optimized operating region and the near-optimal operating point based on practical production data or experimental data. The basic principles of this method are shown in Fig. 2. Firstly, the simple data in multidimensional space are mapped to a two-dimensional plane with a mapping model; meanwhile, the contours of the objective function or functions are generated automatically in this plane. Then, the optimized operating direction or region can be located intuitively according to the distribution of the contours. Finally, a point found in this region, which, although not strictly optimal, is near-optimal, can be mapped back to the original multidimensional space with an inversion mapping method, and will be represented in terms of original variables. It is beneficial as a guide for practical production and scientific experiments (Yan & Bogle, 2007).

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