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Analysis of Process Parameters Effect on Synthesis of Carboxymethylcellulose

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ABSTRACT

Synthesis of carboxymethylcellulose (CMC) from natural cellulose is an important industrial process. The effect of process parameters on the synthesis process is important information for the efficiency improvement of production process. Most of the previous studies on the effect of process parameters on the synthesis of CMC are based on the One-Factor-At-Time (OFAT); therefore, in this work, the response surface methodology (RSM) was used. Here, the cellulose was converted to CMC through carboxymethylation process using a technique of William etherification in heterogeneous system. The process parameters studied include the solvent ratio, reaction temperature and reactant ratio (molar ratio of NaOH to SMCA). Meanwhile, the analysis and optimization of the responses of the process, degree of substitution (DS) and yield were also performed using the response surface methodology. The validity of the synthesis process was identified by the determination of CMC spectrum using the fast Fourier infrared spectrometer (FTIR). The analysis of the results shows that carboxymethylation is strongly affected by combination of process parameters studied. The results obtained also show that the optimum responses, degree of substitution (DS) is 0.87 and yield is 1.80, whereas the optimum process parameters, solvent ratio is 0.70v/v, reaction temperature at 56.03°C, and molar ratio of NaOH to SMCA at 1.00mol/mol. These findings conclude that the DS and yield of carboxymethylation of cellulose are strongly affected by the combination of the process parameters.

Keywords: Carboxymethylcellulose, degree of substitution, one-factor-at-time, William etherification

ABBREVIATIONS

ANOVA	Analysis of Variance
CMC	Carboxymethylcellulose
DS	Degree of Substitution
FTIR	Fourier Transform Infrared
OFAT	One-Factor-At-Time
RSM	Response Surface Methodology

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INTRODUCTION

Modified cellulose is a form of cellulose which has become an important industrial polymer with a wide range of applications in many areas. Cellulose as raw material to cellulose derivatives production is a wonderful material in nature, and it can be found in all plant matters, including agricultural waste and forest debris to grass clippings. Intrinsic properties of this cellulose, which are unique in many ways, have caused its fundamental research and industrial applications to be hindered by its natural structures. As an example, the properties like high crystalline structure or less accessibility of its reactive sites often limit its dissolving characteristics in common organic solvents, and hence, restrict its accessibility for chemical reactions and biological and microbial treatments (McMurry, 1998). This leads to production of modified cellulose which generally enhances the functionalities of cellulose because more desirable properties are incorporated.

Various types of modified cellulose with their specific characteristic were developed. Commercial cellulose derivatives, such as cellulose diacetate, cellulose ethers, halodeoxycellulose having water solubility, organic-solvent solubility, ion-exchanging groups, or hydrophobic groups, are used as aqueous thickeners, plastics, column-supporting materials for chromatography, and others. The typical chemical modifications of the cellulose are etherification and etherification at hydroxyl groups of cellulose. One of the famous cellulose ether, which is carboxymethylcellulose, has gained its positions on the market due to its availability, economic efficiency, easy handling and low toxicity. CMC is used primarily in foods, drugs and cosmetics as a viscosifier, emulsion stabilizer, thickener and to improve texture. CMC is also used in detergent as an antiredeposition agent, textile warp-sizing aid, adhesives, latex paints and polishes.

Cellulose ethers are prepared based on the William etherification method by replacing the hydrogen on the cellulose hydroxyl groups with an alkyl group (Tijsen *et al*., 1999). The substitution reaction first involves the removal of the hydrogen by sodium hydroxide to make alkali cellulose. The alkali cellulose is then reacted with chloroacetic acid or sodium chloroacetic acid as the substituting agent. The degree of substitution (DS) is used to indicate the extent of the reaction. The DS is a major factor in the water solubility of Na CMC, below approximately 0.4 the polymer is swellable but insoluble; above this, the polymer is fully soluble with its hydro affinity increasing with increasing DS (Togrul and Arslan, 2003).

The dependence of reaction yield and degree of substitution on reagents concentration, reaction time, reaction temperature and solvent have been reported for carboxymethylation reaction using various sources of cellulose (Barai *et al*., 1996; Togrul and Arslan, 2003; Adinugrada *et al*., 2005; Dapia *et al.*, 2003; Varshney *et al*., 2006). Nonetheless, none of them analyzed the effects of the reaction parameters using response surface methodology. Most of them had analyzed based on the One-Factor-At-Times (OFAT) which is time consuming and lack information on the combined effect of the reaction parameters on carboxymethylation reaction. As compared to the OFAT, the response surface methodology involves a smaller number of runs, thereby reduces the cost and amount of time required for the experiment. The conclusions obtained from the response surface methodology include more accuracy since the OFAT may also miss out the best settings if the variables interact, that is, if the effect of a variable on the quality or performance of a process or product is dependent on the setting of another variables (Fabio *et al*., 2006; Myers and Montgomery, 1995; Bono *et al.*, 2007).

Process studies on the carboxymethylation of cellulose have not been well expanded to produce modified cellulosic materials for daily and industrial necessities. In fact, the production of this kind of product with various properties is possible, and will contribute to global economy. Most properties of the CMCs in actual applications, are dependent on a large extent, on three key parameters – molecular weight of the polymer, the average number of carboxymethyl substituents

per anhydroglucose unit (degree of substitution, DS), and the distribution of the carboxymethyl substituents along the polymer chain (Schult and Moe, 1997). In this work, the perception in the factors, which affect the carboxymethylation reaction and allow determination of the optimum operating condition using the RSM to achieve carboxymethylated cellulose with a high degree of substitution, was studied. This provides a valuable input for the development of kinetic models for the carboxymethylation process in future studies.

MATERIALS AND METHODS

Synthesis of Sodium Carboxymethylcellulose

The synthesis of the CMC was conducted in two steps, namely alkalization and etherification of cellulose under heterogeneous conditions. Alkalization work is a pre-treatment step for etherification reaction. The reaction was conducted in a temperature controlled water bath to maintain the reaction temperature at the required value. A motor running stirrer was also used to homogenize the solution and speed up the reaction. Oven was used to dry the resulted product. The dried product was blended into powder form for the DS analysis. Pure cellulose in adequate amount was suspended in 100ml of ethanol:isopropanol in an appropriate ratio under mechanical stirring. 10 ml of aqueous sodium hydroxide as swelling agent was added drop-wise and the solution then was stirred for an hour at room temperature (Pushpamalar *et al.,* 2006). Carboxymethylation reaction was started with an addition of sodium monochloroacetate (SMCA) with the reaction mixture placed in the temperature controlled water bath. The reaction mixture was then heated up to the reaction temperature and stirred for three hours of reaction time (Pushpamalar *et al*., 2006). This period of time is the optimum time for inducing better contacts between the etherifying agent and cellulose. Prolonged time increased degradation of the polymer which will lower the value of degree substitution (Bhattacharyya *et al*., 1995; Heinze and Pfeiffer, 1999). The slurry was neutralized with 90% acetic acid and then filtered. The CMC was purified by washing it with 70% ethanol four times to remove undesired byproducts. Then, the CMC was filtered and dried at 60^{o}C in an oven (Pushpamalar *et al.,* 2006).

Fourier Transform Infrared Spectroscopy of Sodium Carboxymethylcellulose

Fourier Transforms IR is a common instrument used to identify type of chemical bonds (functional group) in polysaccharides. Infrared absorption spectrum like molecular "fingerprint" was produced for this purpose. Different types of polysaccharides have distinct molecular "fingerprint" in the spectrum. With this fingerprint region, molecular compounds in polysaccharides such as cellulose and carboxymethylcellulose can be differentiated. Therefore, carboxymethylcellulose products were calibrated using the Fourier Transforms IR (FTIR) instrument in this research. The infrared spectra of the CMC samples were recorded with the FTIR. To get the spectra, a pellet made from the CMC samples was ground with KBr. Transmission was measured at the wave number range of 4000–400cm^{-1}.

Yield Measurement

Yield value is one of the responses to be optimized in this study. It indicates the amount of production based on the dry weight basis. An analytical balance was used for the yield measurement. The dry carboxymethylcellulose was weighed out and the net weight was divided with 5g of cellulose to get the yield value.

Determination of Degree of Substitution

The degree of substitution (DS) of the sample CMC was determined by the standard method (ASTM, 1961). 4 g of sample and 75ml. of 95% ethyl alcohol were agitated in 250ml. beaker for 5 min. 5 ml of nitric acid was then added. A hotplate was used to boil the solution, and this solution was then removed from the hotplate and further stirred for 10 minutes. Using a vacuum pump, liquid solution was decanted and washed 5 times with 80% ethyl alcohol (60ºC). Then, the precipitate was washed with a small quantity of anhydrous methanol and apply vacuum to remove the alcohol. Finally, the filter was dried at 105ºC for 3 hours and cooled in desiccators for half an hour. 1 to 1.5g of dry carboxymethylcellulose was added to 100ml of water and 25 ml of hydroxide 0.3N with agitation. The solution was heated to boil for 15 to 20 minutes. After the products dissolved, the mixture was titrated by 0.3N HCI. Phenolphthalein indicator was added to observe the colour change from Mexican pink (dark pink) to colourless.

To calculate the degree of substitution, equations (1) and (2) were used:

$$A = \frac{BC - DE}{F} \quad (1)$$

$$\text{Degree of substitution} = \frac{0.162 \times A}{1-(0.058 \times A)} \quad (2)$$

Where,
A = milli-equivalents of consumed acid per gram of specimen;
B = volume of Sodium hydroxide added;
C = concentration in normality of sodium hydroxide added;
D = volume of consumed chloric acid;
E = concentration in normality of Chloric acid used;
F = specimen grams used;

162 are the molecular weight of the anhydrous glucose unit and 58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

Optimization of the CMC Production

The response surface methodology (RSM), combined with a Box-Behnken design, was used to find out the relationship between the response functions and the process variables, and to determine the conditions of these variables able to optimize the carboxymethylation.

Therefore, to reduce the experimental runs in reasonable limit, some variables were fixed according to the literature review (Barai *et al*., 1996; Togrul and Arslan, 2003; Adinugrada *et al*., 2005; Dapia *et al*., 2003; Pushpamalar *et al*., 2006; Varshney *et al*., 2006). The variables used are shown in Table 1. Optimization was done through the response surface methodology (RSM) using Design Expert software. This software is a statistical tool to study the process optimization efficiently through a series of design and analysis. With the range of factors in Table 2, the DS and Yield were targeted to the maximum for the optimization purpose in the software using numerical optimization.

The reaction was optimized with respect to the DS and yield varying each of the reaction parameters. There reaction parameters optimized were the volume ratio of ethanol to isoprophyl alcohol, reaction temperature and molar ratio of NaOH to SMCA. Meanwhile, the range of factors is shown in Table 2. The DS and yield were selected as quantitative responses.

TABLE 1
Values of the reaction parameters used

Factors	Value
Cellulose	5g
Weight of solvent	100ml
Time	3hr
Alkalization time	1hr
Alkalization temperature	30°C
Sodium Monochloroacetate	6.0g

TABLE 2
Range of reaction parameters for optimization

Parameter	Range
Ethanol : Isoprophyl Alcohol (v:v)	0.50 – 2.00
Reaction Temperature (°C)	30 - 60
NaOH : SMCA (mol:mol)	1 - 3

RESULTS AND DISCUSSION

Carboxymethylation Process

Fig. 2 shows the IR spectrum of the sample carboxymethylcellulose at DS 0.731. This spectrum was compared with commercial CMC spectrum at DS 0.75-0.9 (*Fig. 1*). The two spectrums have similar bands at certain peaks, illustrating the fingerprint region (highlighted in oval) of the CMC. The IR spectra show the typical absorption of the cellulose backbone and the presence of the carboxymethyl ether group at 1600cm^{-1}. The area inside the oval is the fingerprint region for the CMC.

Based on the data presented in *Fig. 2*, the bands in the region 1350-1450cm^{-1} are due to symmetrical deformations of CH_2 and OH groups. In the fingerprint region, the bands showing the ether bonds in CMC are 1250-1050cm^{-1} (Georgelt, 1996). The presence of a new and strong absorption band at 1600 cm^{-1} is confirms the stretching vibration of the carboxyl group (COO^-) and 1415cm^{-1} is assigned to carboxyl groups as its salt.

The RSM Analysis of Carboxymethylation Reaction

The experimental results of degree of the substitution (DS) and the yield value were applied to obtain the regression models. Table 3 shows the experimental design compiled in the Design-Expert software. From the compilation, there are 17 runs needed in this study to determine the optimum reaction condition. From Table 3, 17 sets of run, with relevant parameter values, were studied. A statistical analysis was also performed on the experimental results.

The quality of the models was evaluated using ANOVA, in which the repetition supplied the freedom degree to obtain the pure error. Meanwhile, the regression analysis was performed to fit the response function and experimental data, and the ANOVA was required to evaluate the second

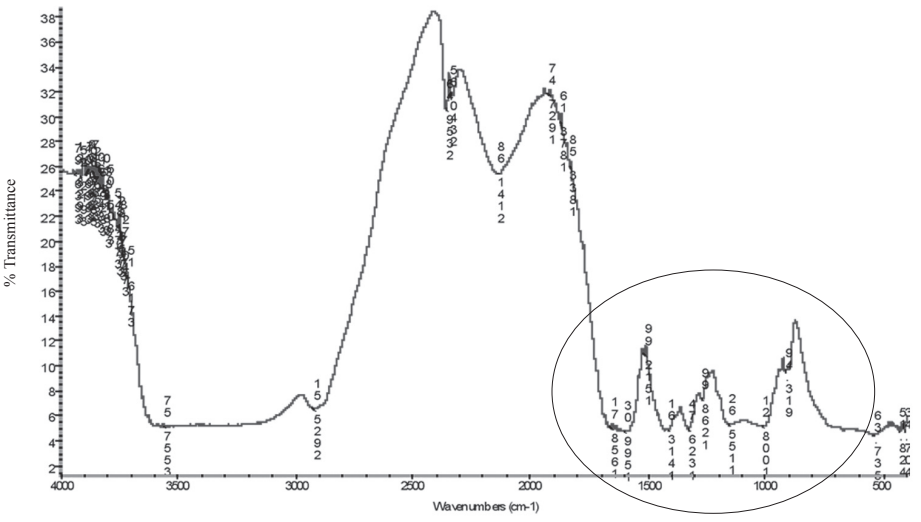

Fig. 1: FTIR spectrum for commercial CMC with DS at 0.75-0.9

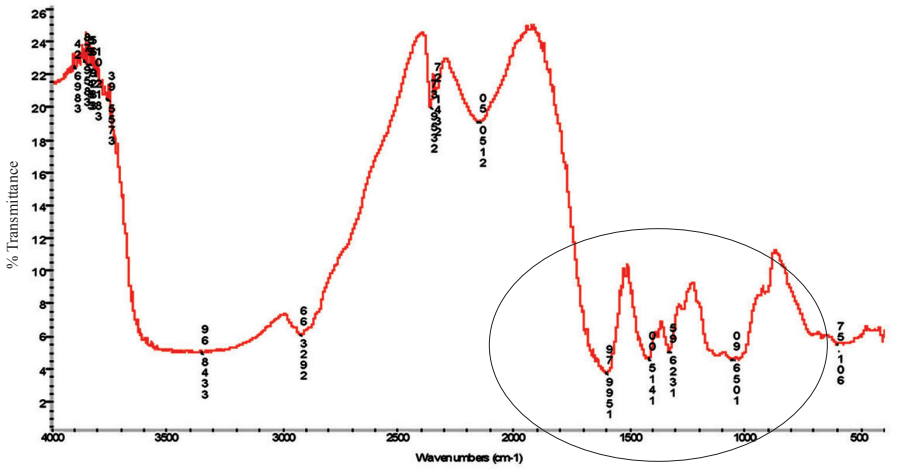

Fig. 2: FTIR spectrum for sample CMC with DS at 0.731

order model for both responses. From the ANOVA, the quadratic model for both responses was found to be significant. The quadratic models for the DS and yield, in terms of the coded factors, are shown in the following equations:

$$DS = 0.75-0.022A + 0.15B - 0.050C - 0.056A^2 - 0.16B^2 - 0.059C^2 + 0.012AB +0.071A-0.10BC \quad (3)$$

TABLE 3
Design Data for the analysis and optimization using the design expert software

Run	Block	Factor 1 A: Ethanol: Isoprophyl alcohol (v/v)	Factor 2 B: Reaction temp. (°C)	Factor 3 C: NaOH:SMCA (mol/mol)	DS	Yield
1	Block 1	1.25	45	2	0.729	1.551
2	Block 1	2.00	60	2	0.600	1.3696
3	Block 1	0.50	30	2	0.489	1.2496
4	Block 1	2.00	30	2	0.413	1.1316
5	Block 1	1.25	45	2	0.803	1.3530
6	Block 1	1.25	45	2	0.735	1.4188
7	Block 1	1.25	60	3	0.583	1.2802
8	Block 1	0.50	60	2	0.627	1.4100
9	Block 1	0.50	45	1	0.767	1.6698
10	Block 1	1.25	60	1	0.901	1.7988
11	Block 1	1.25	45	2	0.707	1.4466
12	Block 1	2.00	45	1	0.588	1.6876
13	Block 1	1.25	30	3	0.358	1.5484
14	Block 1	1.25	45	2	0.778	1.5011
15	Block 1	1.25	30	1	0.276	1.6154
16	Block 1	2.00	45	3	0.646	1.3214
17	Block 1	0.50	45	3	0.542	1.3072

$$\text{Yield} = 1.45 - 0.016A + 0.039B - 0.16C - 0.11A^2 - 0.050B^2 + 0.16C^2 + 0.019AB - 9.00\text{x}10^{-4}AC - 0.11BC \quad (4)$$

Where A represents volume ratio of ethanol to isoprophyl alcohol, B represents reaction temperature and C represents molar ratio of NaOH to SMCA.

Effect of Solvent on Carboxymethylation

The effects of the solvents on the DS and yield values, when the molar ratio of NaOH to SMCA and reaction temperature were selected at 2.00 and 45°C as the centre point, are shown in *Figs. 3* and *4*, respectively.

From the One Factor Plot in *Fig. 3*, it shows that there is an optimum DS value when the ratio of solvent medium was increased. The maximum value of the DS was found when the solvent ratio

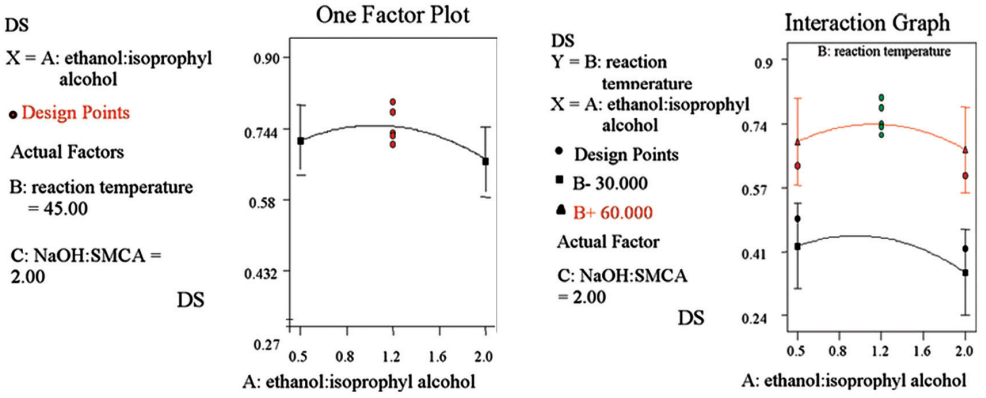

Fig. 3: The effect of the ratio between ethanol and isoprophyl alcohol on DS when the reaction temperature and molar ratio NaOH:SMCA were maintained at 45°C and 2, respectively

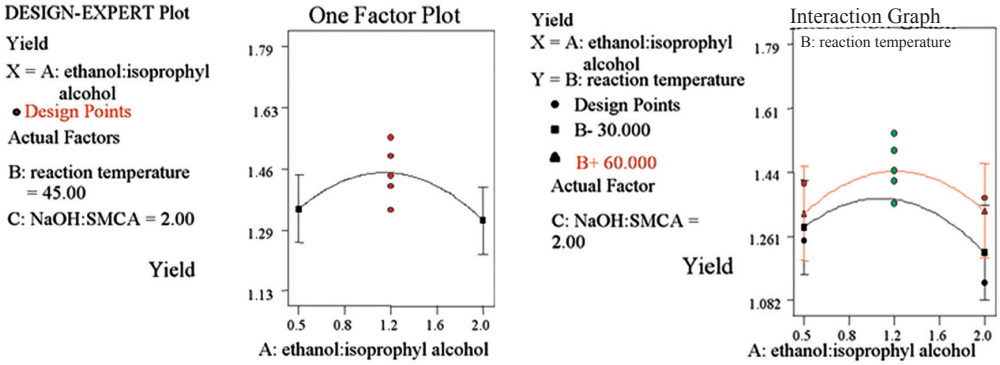

Fig. 4: The effect of the ratio between ethanol and isoprophyl alcohol on yield when the reaction temperature and molar ratio of NaOH:SMCA were maintained at 45°C and 2, respectively

near to 1.00 for reaction at 45°C. Above this value, the DS decreased. This indicates that the main reaction [equation 5(a) and 5(b)] is preferred when the concentration on ethanol and isopropanol is equal, while the interaction graph shows a simultaneous effect of the reaction temperature and solvent ratio on the DS value. It shows that the DS value is limited by the reaction temperature where the DS value can achieve the optimum points and then decreases with higher solvent ratio (higher preferences on isopropanol solvent).

From the One Factor Plot in *Fig. 4*, the yield curve shows a slight difference with the DS plot. However, the effect of the solvent ratio is the same with the DS where the yield value increases to optimum point and drops gradually with increasing solvent ratio. Nonetheless, the optimum point of the yield plot is closer to the solvent ratio at 1.25.

These figures show that appropriate solvent ratio is needed to obtain the optimum value for the DS and yield. The effect of the solvent system on the extent of the reaction is related to miscibility, which is the ability to solubilise the etherifying agents and to swell the cellulose to improved

accessibility of the etherifying agent into the cellulose structure. The interaction graph is therefore important to show the simultaneous effect of the solvent and reaction temperature on reaction. *Figs. 3* and *4* provide information on the preferences of solvent in driving carboxymethylation reaction (equation 5a) to the right at different temperatures.

$$R_{cell}OH + NaOH \leftrightarrow R_{cell}\,OH.NaOH \quad (5a)$$

$$R_{cell}OH.NaOH + ClCH_2COONa \rightarrow R_{cell}OCH_2COONa + NaCl + H_2O \quad (5b)$$

Side Reaction

$$NaOH + ClCH_2COONa \rightarrow HOCH_2COONa + NaCl \quad (6)$$

The Effect of Molar Ratio of NaOH to SMCA on Carboxymethylation

By maintaining the solvent ratio and reaction temperature at 1.25 and 45°C respectively, the effects of alkali concentration on the DS and yield were studied (*Figs. 5* and *6*). Here, the effect of alkali on reaction was studied through One Factor Plot in the RSM. The yield and DS were responses distinctively with the alkali concentration (the concentration of the SMCA was maintained at 6.0 g in this work) which are described in the following paragraph.

It was observed that the degree of substitution showed an opposite effect with the yield response when the sodium hydroxide concentration was increased. From the One Factor Plot in *Fig. 5*, it is observed that the DS value responded distinctively with the concentration of the sodium hydroxide. When the sodium hydroxide concentration was increased, the DS value was found to increase gradually to the optimum point. At lower sodium hydroxide concentration, the DS curve sloped steeply and then dropped gradually with the increasing alkali concentration. However, the DS value at lower NaOH concentration was still higher as compared to the higher concentration of NaOH. The interaction plot shows the combined effect of solvent and molar ratio of NaOH:SMCA to DS. The graph shows that the solvent with appropriate amount of sodium hydroxide and SMCA gives a better product with higher DS.

Prior to alkylation, cellulose was treated with aqueous alkali, exposing the less crystalline regions to be attacked by the reagents, where heterogeneity of the product was the consequence. Carboxymethylation reaction involves two competing reactions which take place simultaneously (equations 5 and 6) (Pushpamalar *et al*., 2006). The first reaction was between cellulose and monochloroacetic acid in the presence of alkali (equation 5). The second one was the reaction between sodium hydroxide with monochloroacetic acid to form sodium glycolate (equation 6). The first reaction seemed to prevail up to a certain NaOH concentration. Above this concentration, the second reaction was predominated with the formation of a larger amount of sodium glycolate, which decreased the DS value. By looking at the One Factor Plot in *Fig. 5*, the reaction is therefore preferential for lower NaOH concentration.

Based on the One Factor Plot in *Fig. 6*, the relationship between the sodium hydroxide concentration and yield was the opposite of the DS. In particular, higher yield was obtained at lower NaOH concentration. At particular alkali strength, the yield was decreased to minimum and then started increasing. Higher yield at lower NaOH concentration might be due to the formation of sodium glycolate which was difficult to be removed from the sample. The interaction plot gave important information, i.e. the interaction between solvent and NaOH produces the maximum yield of product.

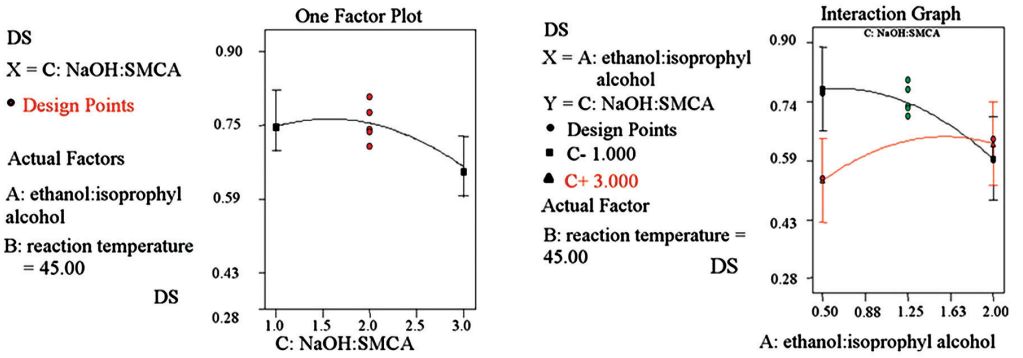

Fig. 5: The effect of the molar ratio NaOH:SMCA on DS when the ratio between ethanol and isoprophyl alcohol and the reaction temperature were maintained at 1.25 and 45°C, respectively

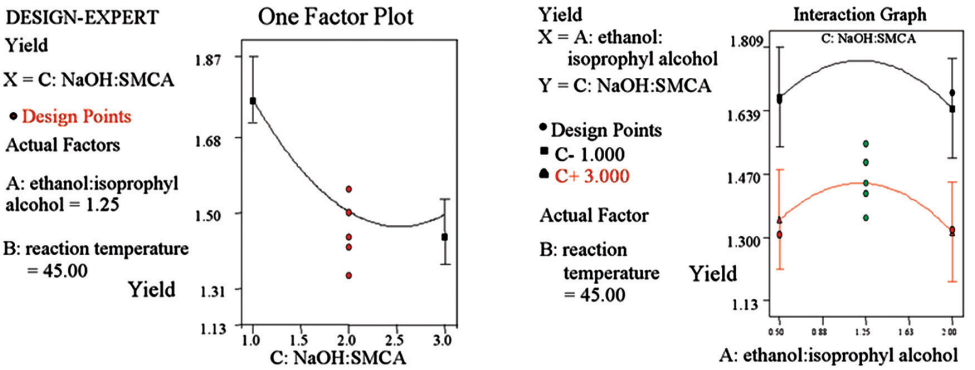

Fig. 6: The effect of the molar ratio NaOH:SMCA on yield when the ratio between ethanol and isoprophyl alcohol and the reaction temperature were maintained at 1.25 and 45°C, respectively

Effect of Reaction Temperature on Carboxymethylation

Figs. 7 and *8* show the effect of the reaction temperature on the degree of substitution and yield when the solvent ratio was maintained at 1.25 and the molar ratio of NaOH to SMCA was maintained at 2.00. It was also observed that the responses were increased by increasing the reaction temperature until the optimum point was achieved. The response values were decreased with the increasing temperature.

From *Fig. 7*, One Factor Plot quadratic curve was obtained for the DS plot. There was a significant and drastic increase in the degree of substitution with temperature, within the range between 30°C – 52.50°C for the molar ratio of NaOH to SMCA at 2.00. The increased of the DS might be due to the fact that there was a better environment created that favoured the reaction to the right (equation 5). Similarly with the DS, the effect of reaction temperature on the yield at higher NaOH concentration was increased with the reaction temperature until a maximum value thereafter decreased *(Fig. 8)*. However, the curve is not as steep as in the DS plot. This might be due to the cellulose degradation causing lost of water from cellulose (Pushpamalar *et al*., 2006). These provide information which indicates that the reaction temperature is an important factor to influence the carboxymethylation reaction for desired product.

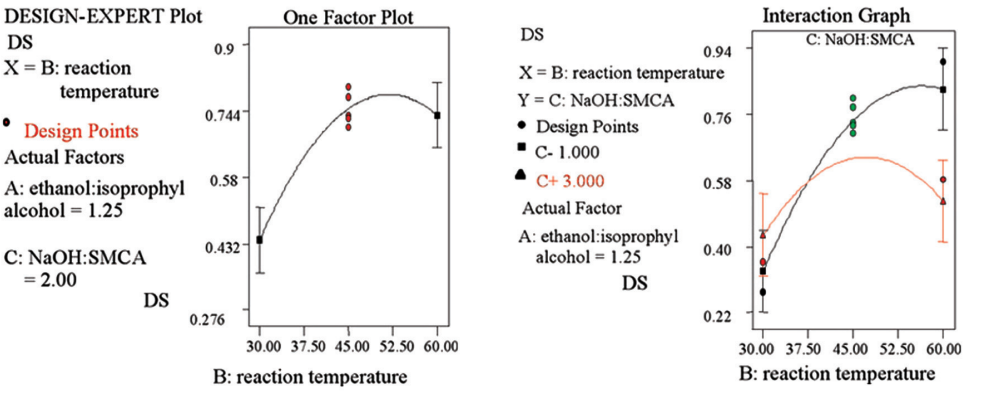

Fig. 7: The effect of the reaction temperature on DS when the ratio between ethanol and isoprophyl alcohol and the molar ratio of NaOH:SMCA were maintained at 1.25 and 2.00, respectively

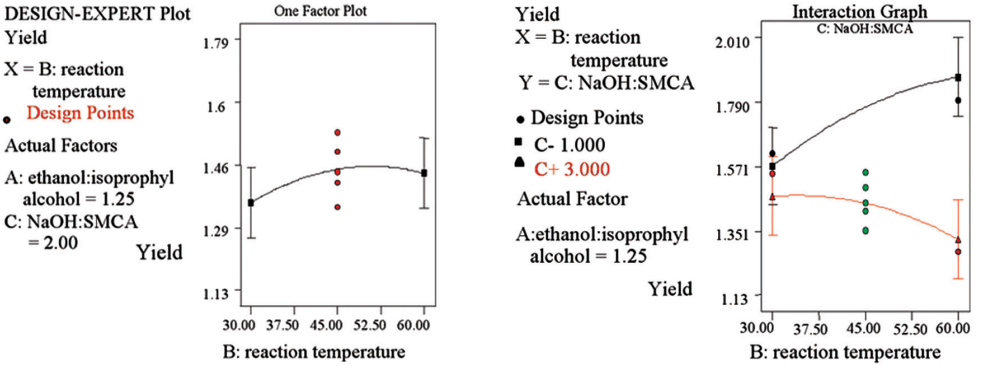

Fig. 8: The effect of the reaction temperature on yield when the ratio between ethanol and isoprophyl alcohol and the molar ratio of NaOH:SMCA were maintained at 1.25 and 2.00, respectively

From both plots, it shows that the reaction temperature gives the same effect on the responses, while they may be shown differently when the interaction with other factors are considered, as shown in the interaction graph in *Figs. 7* and *8*. Looking at the Interaction Plot depicted in *Fig. 7*, lower concentration of molar ratio NaOH:SMCA performs better in higher reaction temperature for the carboxymethylation reaction to occur. Where it could be observed that the curve sloped steeply at lower concentration of molar ratio of NaOH:SMCA when the reaction temperature increased. Similar to the DS responses, the yield value was higher when carboxymethylation reaction occurred in lower concentration and higher temperature.

Optimization of Process Parameters on Carboxymethylation Process

Based on the model, the relationship between the response and the variables is visualized by a response surface or contour plot to indicate the relative influence of the parameters, find an optimum parameter combination, and predict the experimental results for other parameter combinations. The numerical optimization was carried out with the help of Design Expert v.6.0.10, considering each value of response and three solutions were obtained, as shown in Table 4.

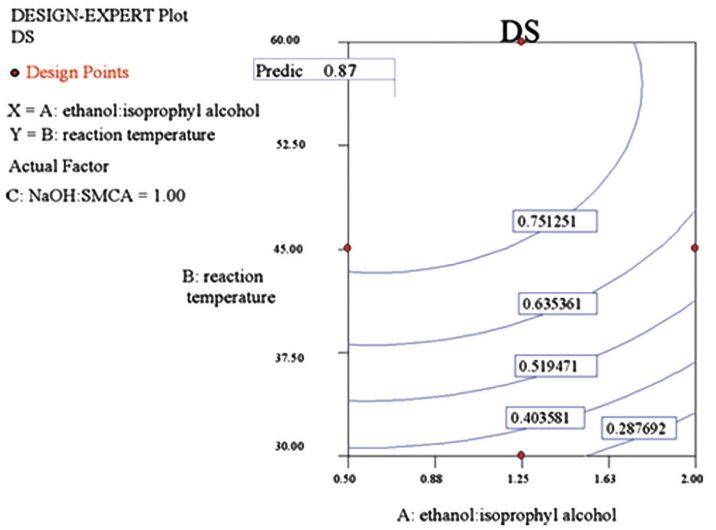

Fig. 9: Optimization contour plot on the DS value when NaOH:SMCA remained constant at 1.00

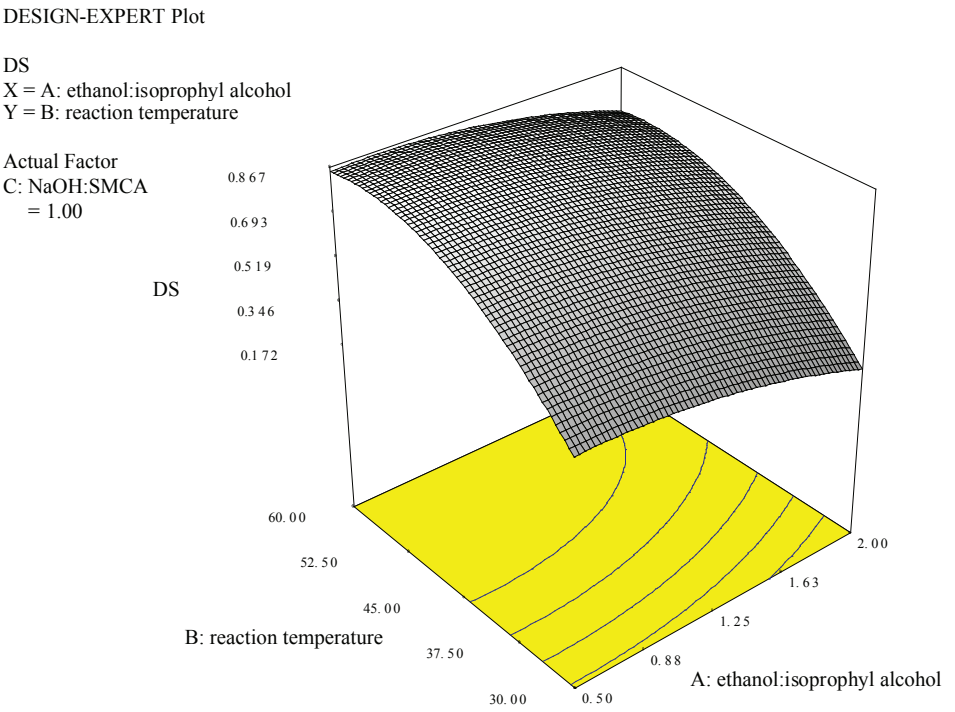

Fig. 10: Optimization of the 3D response surface on the DS value when NaOH: SMCA remained constant at 1.00

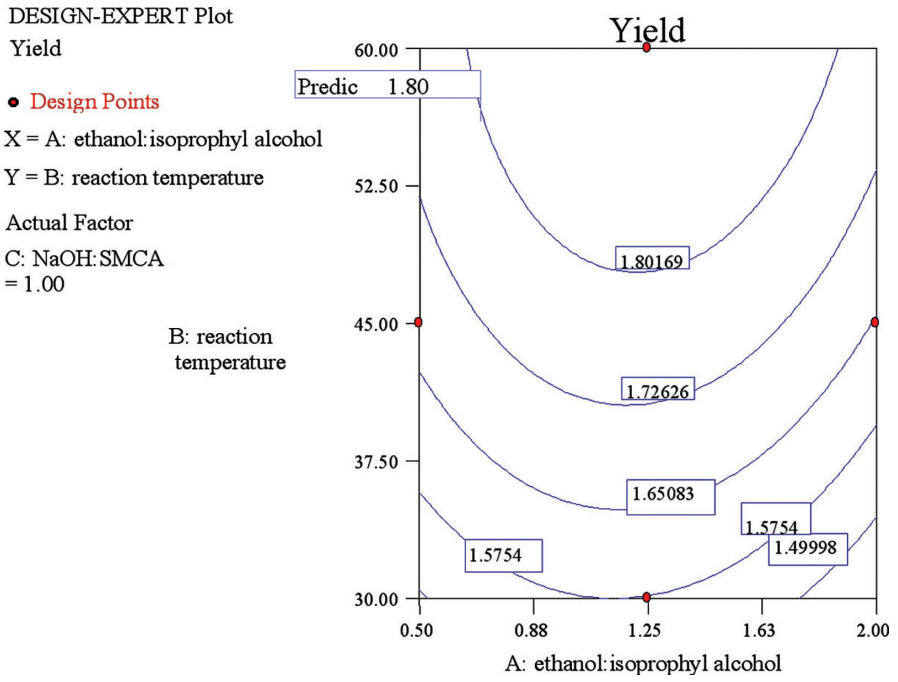

Fig. 11: Optimization contour plot on yield when NaOH:SMCA remained constant at 1.00

TABLE 4
Solutions of optimization on DS and yield

Name	Goal	Lower Limit	Upper Limit
ethanol:isoprophyl alcohol	is in range	0.5	2
reaction temperature	is in range	30	60
NaOH:SMCA	is in range	1	3
DS	Maximize	0.2760	0.901
Yield	Maximize	1.1316	1.7988

Solutions	1 (Selected)	2	3
ethanol:isoprophyl alcohol	0.70	0.77	0.87
reaction temperature	56.03	55.91	49.25
NaOH:SMCA	1.00	1.00	1.00
DS	0.87	0.87	0.83
Yield	1.80	1.81	1.79
Desirability	0.98	0.97	0.94

TABLE 5
Previous study on the carboxymethylation reaction condition

Reference	Reaction temp.	Reaction time (min)	NaOH	SMCA (g)	Cellulose (g)	Solvent (ml)	DS
Barai *et al.,* 1996 (water hyacinth)[a]	75* 30-75	360* 60-360	10% (2.5M)*	0.92 : 1(w/w)*		Isopropanol - 110	0.72*
Pushpamalar *et al.,* 2006 (sago waste)[a]	45*	180*	10ml of 25%*	6.0*	5	Pure isopropanol	0.821*
Togrul and Arslan, 2003 (sugar beet pulp cellulose)[a]	70*	360*	30% in 20ml*	3.0*	2.0	Isobutyl alcohol	0.667*
Zhao *et al.,* 2003 (cotton linter)[a]	50-60	30	NaOH/AGU: 2:1(mol)	MCA/AGU: 1.5:1(mol)	100	Benzene-ethanol	1.10*
Varshney *et al.,* 2006 (Lantana camara)[a]	55* (35-65)	210*	3.24mol/AGU, 20% (w/v)* (10-40%)	2.05*mol/AGU (1.55-2.30)	3	Isoprophyl alcohol	1.22*

*Optimized value

[a]Cellulose source

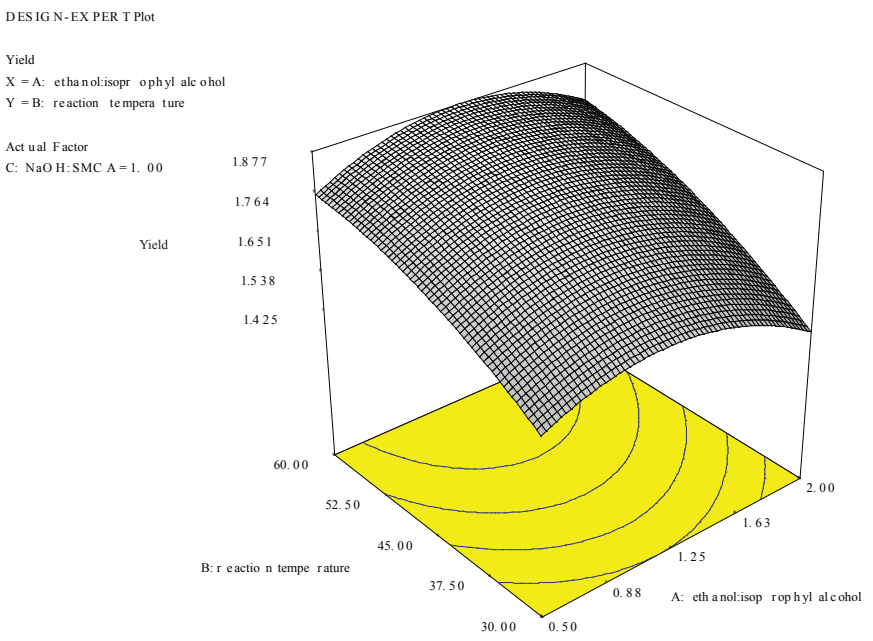

Fig. 12: Optimization of 3D response surface on Yield when NaOH:SMCA remained constant at 1.00

From Table 4, there are three solutions suggested from the numerical optimization. The best results of the DS value and yield obtained under optimized condition, selected among the three, were 0.87 and 1.80g/g, respectively. The optimized conditions were the volume ratio of ethanol to isoprophyl alcohol at 0.70, the reaction temperature at 56.03ºC, and the molar ratio of NaOH to SMCA at 1.00.

Figs. 9 through *12* show the response surfaces and the contour plot of the optimization result on the DS and yield under optimized condition. Based on these figures, the effects of the reaction condition on the responses were studied. The point identified by the flag in the contour plot was chosen in the graph, as a representative of the optimized area corresponding to the reaction condition. The contour plot in *Fig. 10* shows an elliptical and inclined profile implying the interaction effects between the reaction factors on the CMCs yield.

Table 5 shows the process parameters of carboxymethylation reaction in the previous study. These authors studied the production of carboxymethylcellulose from different sources of cellulose. However, none of them optimized the reaction condition using the RSM as in the present study. Instead, they used the one-factor-at-time (OFAT) to optimize the process parameters. However, the results reported (Table 5) were similar to the result obtained in the present study. The difference in the optimum condition could be attributed to the variation of the cellulose sources, the solvent used and the different reaction times. Nonetheless, the optimum DS obtained in the present study, which is 0.87, is similar to the previous study (0.6-1.3). This shows that the value obtained from the RSM analysis is reliable.

CONCLUSIONS

The conversion of cellulose to CMC was completed done using the carboxymethylation process of William etherification. The analysis results using the RSM show that the effects of reaction parameters are easily interpreted with less experimental runs, as compared to the OFAT conducted by most of the previous studies. The effects of the reaction parameters on the yield and DS were studied by performing the one factor plot, interaction plot, contour plot and surface plot. The results show that the DS and yield varies with the variation of combination of process parameters. The numerical optimization results also suggest that the optimum value of the DS and yield are 0.87 and 1.80, respectively, whereas the optimum condition of the process parameters, solvent ratio is 0.70v/v, reaction temperature at 56^{o}C, and the molar ratio of NaOH to SMCA at 1.00mol/mol.

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