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Optimization of Reaction Conditions for Preparing Carboxymethylcellulose

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Abstract: The cellulose powder was converted to carboxymethylcellulose (CMC) by etherification process using sodium monochloroacetate and sodium hydroxide. There are two reaction occur simultaneously during carboxymethylation that are the primary reaction which produces pure CMC and side reaction that produces undesired sodium glycolate. The carboxymethylation reaction was optimized against the reaction temperature, reaction time, SMCA concentration, NaOH concentration and the ratio solvent of ethanol:isopropanol. The Degree of Substitution (DS), viscosity and yield were analyzed with respect to the reaction conditions using response surface methodology. The method of analyzing the degree of substitution of CMC is back titration method. The produced CMC was identified by using Fourier Transform Infrared spectra (FTIR). The maximum DS obtained is 0.94, maximum yield is 22.0730 g and maximum viscosity 15.2 cP. After optimization of reaction conditions is carried out, the optimized DS obtained is 0.9424 and the optimized viscosity is 10.1 cP with yield is 22.1024 g.

Key words: Etherification, carboxymethylation, degree of substitution, viscosity, response surface methodology

INTRODUCTION

Modified cellulose is an important chemical that derives from modification of natural polymer, cellulose. Due to the abundant resources of natural polymer in the world, modified cellulose is now advancing in terms of productions and innovations.

Cellulose which is the raw material of generating modified cellulose is a common natural polymer can be found vastly in plants. Thus, the resources can range from woods to even the agricultural waste. The availability of cellulose in Malaysia is very wide with the abundant plantation of palm oil (Rosnah *et al*., 2004) which has good potentials in producing modified cellulose from their by-product. There have been quite numerous discoveries on the degree of substitution of CMC of different sources such as sago waste (Pushpamalar *et al*., 2006), water hyacinth (Barai *et al*., 1997), *Lantana camara* (Varshney *et al*., 2006), sugar cane bagasse cellulose (Rose *et al*., 2007) and other cellulose sources. The idea of producing useful component out of waste is indeed environmental friendly which the government has been trying to implement in most of the industries in Malaysia. This is a very good step in promoting Malaysia as being creative, innovative as well as contributing to form an environmental friendly atmosphere.

Williamson etherification is mostly applied in industries due to its low toxicity, wide availability, easy handling and its economic efficiency. Carboxymethyl cellulose or CMC is modified cellulose which is prepared by etherification of the hydroxyl groups with sodium monochloroacetate (SMCA) in the presence of aqueous alkali (Pushpamalar *et al*., 2006). CMC is important for its water soluble properties where vast applications are applied in food industry, cosmetics, pharmaceuticals, detergents, textiles, paper, drugs and as well as oil well drilling operation. The conversion of cellulose to carboxymethyl cellulose provides variety of usage due to its excellent characteristics. Among categories of applications of CMC that are in dissolved and dispersed forms are water binder, adhesives, film former, wet tact, binder, suspending aid and thickener (Heinze, 2005).

The properties of cellulose derivatives are mainly signified by the degree of substitution. An anhydroglucose unit of cellulose, the maximum degree of substitution can be achieved is 3 (Salmi *et al*., 1994). The selection of etherification condition is very essential in order to achieve high degree of substitution (Isogai, 2001). Most of the researches (He *et al*., 2009; Zhao *et al*., 2003) carried out obtained degree of substitution ranges from 0.5-2.0. In commercial CMC, the most common degree of substitution obtained is usually lower that is from 0.4 to 1.4 (Sara and Lo, 2003; Silva *et al*., 2004). Researchers are expanding their ways of gaining higher degree of substitution in order to acquire better commercial products.

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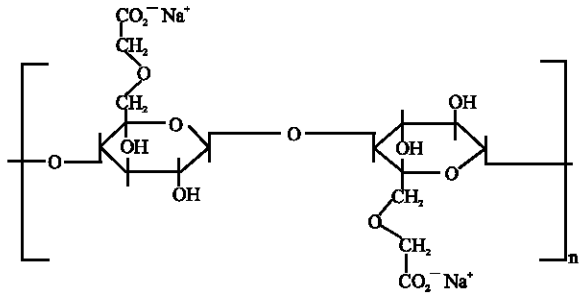

Fig. 1: Structure of carboxymethyl cellulose (Biswal and Singh, 2004)

Cellulose ether which is hydrophobically modified water soluble has created the CMC to have unique viscosity behavior in aqueous solutions. Viscosity is the measurement of any fluid resistance being deformed by shear stress which can be determined using Brookfield rotary viscometers. The rheological behavior of CMC solution studied using apparent viscosity as a measure of shear rate and temperature. There are several parameters that influencing the viscosity besides shear rate and temperature such as concentration, salts and molecular weight of polymers (Feller and Wilt, 1990).

Among the benefits can be acquired from this research are to achieve the optimum condition of the CMC in the analyzed reaction conditions which can be used commercially. Reaction condition in CMC preparing is the key factor in determination of the Degree of Substitution (DS) and viscosity. DS and viscosity are the two main properties of CMC that decide their end use in industry Figure 1 show structure of carboxymethyl cellulose.

MATERIALS AND METHODS

Materials: Cellulose was obtained from avicell in reagents grade, Sodium Monochloroacetate and sodium hydroxide powder in reagent grade, ethanol and isopropanol solution in reagent grade with corresponding purity. All the analysis materials is in reagent grade.

Preparation of carboxymethylcellulose: Preparation of CMC sample consists of two reactions which are alkalization and carboxymethylation reaction. Alkalization reaction begins after introduction of NaOH into 10 g of pure cellulose and mixing of ethanol and isopropanol solution under mechanical stirring for an hour. Then, carboxymethylation reaction start once the sodium monochloroacetate (SMCA) is added while the reaction continuously stirs at 400 rpm. Reaction temperature and reaction time are controlled in this reaction. The mixture then filtered and suspended in 200 mL of methanol overnight.

Table 1: Factors and corresponding range for BBD

Factors	Range
Reaction temp. (°C)	30-70
Reaction time (min)	60-240
SMCA concentration (v/v%)	6-14
NaOH concentration (w/v%)	15-45
Ethanol:Isopropanol (v/v)	0.25-1.75

The slurry was neutralized using glacial acetic acid. The samples undergo washing process using 70% ethanol solution for four times to remove undesired product. Lastly, the sample was dried in the oven at 60°C temperature.

Experimental design: Response surface methodology involving Box-Behnken design was employed for present study with application of Design Expert software (6.10 version). Table 1 becomes the design summary for BBD and 46 runs of experiment was carried out for the reaction conditions investigation. The design was chose based on it capability to provide accurate regression analysis and less runs needed for carboxymethylation reaction study as described by Tijsen *et al.* (1999).

Analytical procedures

FTIR identification: Carboxymethylcellulose product have to calibrate by using Fourier Transforms IR(FTIR) instrument in this research. Infrared spectra of the CMC samples were recorded with FTIR. Pellets were made from CMC samples ground with KBr. Transmission was measured at the wave number range of 4000-400 cm^{-1}.

DS determination: The DS of the sample CMC was determined by the standard method (ASTM, 1994). This wet chemistry method is known as back titration method and the below calculation is carried out for DS value:

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

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

Where:

DS = Degree of Substitution
A = Mili-equivalents of consumed acid per gram of specimen
B = Millimeters of added sodium hydroxide
C = Normal sodium hydroxide
D = Millimeters of consumed hydrochloric acid
E = Normal hydrochloric acid
F = Specimen gram used
162 = Molecular weight of the anhydrous glucose unit
58 = Net increment in the anhydrous glucose unit for every substituted carboxymethyl group

Viscosity measurement: To measure the viscosity of CMC solutions, 2% (w/w) solution of CMC is prepare in water. The viscosity is measure using Brookfield viscometer with spindle number 00 and UL adapter. The temperature is maintained at 30°C along the reaction. The solutions is stir with a magnetic stirrer to sure that all the material soluble (Usually 1 to 3 h is required). When solution is complete, immediately insert the spindle (with the guard attached) into the solution. Start the spindle rotating and allow it to rotate for three minutes before taking the reading. For shear rate analysis, the viscosity is measure in increasing shear rate by adjust the speed of the spindle.

RESULTS AND DISCUSSION

Characterization of CMC using FTIR: From Fig. 2, the bands in the region 1350-1450 cm^{-1} are due to symmetrical deformations of CH_2 and OH groups. In fingerprint region, bands that show the ether bonds in CMC are 1250-1050 cm^{-1}. The presence of a new and strong absorption band around 1600 cm^{-1} is confirms the stretching vibration of the carboxyl group (COO^-) and 1415 cm^{-1} is assigned to carboxyl groups as it salts.

Experimental design on DS and viscosity: Experimental data becomes the input for RSM design and this will generate a series of analysis on DS and viscosity model. The model is significant and R^2 value are in the acceptance level of 80% (Bas and Boyac, 2007) and corresponding significant conditions on responses will described in following section. RSM analysis on the effect of corresponding reaction conditions are discuss below by setting the reaction conditions at center point as shown in Table 2. The discussions were made for significant effects based on the ANOVA analysis.

Effect of reaction temperature on DS: From the Fig. 3, the effect of reaction temperature on DS increases rapidly with the increasing temperature until a maximum value of DS of 0.7913 at 60°C is obtained. When the maximum value of DS is achieved, the DS decreases with the further increment of reaction temperature. This also can be observed from several research conducted previously where there will be a maximum value of DS before the value of DS decreases. According to Varshney *et al.* (2006), further prolonging of carboxymethylation may cause the atmospheric oxidative degradation of CMC. Reaction of high temperature may cause degradation not only on CMC but also other products as well. The polymer structure of cellulose might degrade during the alkalization process hence the decrease in DS value with the increment of reaction temperature.

Effect of reaction time on DS: From Fig. 4, the DS increases with the increasing reaction time. The maximum value attained is 0.8696 at 240 min. This is because the longer the reaction time, the longer the alkalization process continues to substitute the functional groups of CMC which will further increase the value of DS.

Table 2: Reaction conditions value when it maintained at centre points

Reaction conditions at center point	Range
Reaction temp. (°C)	50
Reaction time (min)	150
SMCA (g)	10
NaOH (% w/v)	30
Solvent ratio (v/v)	1

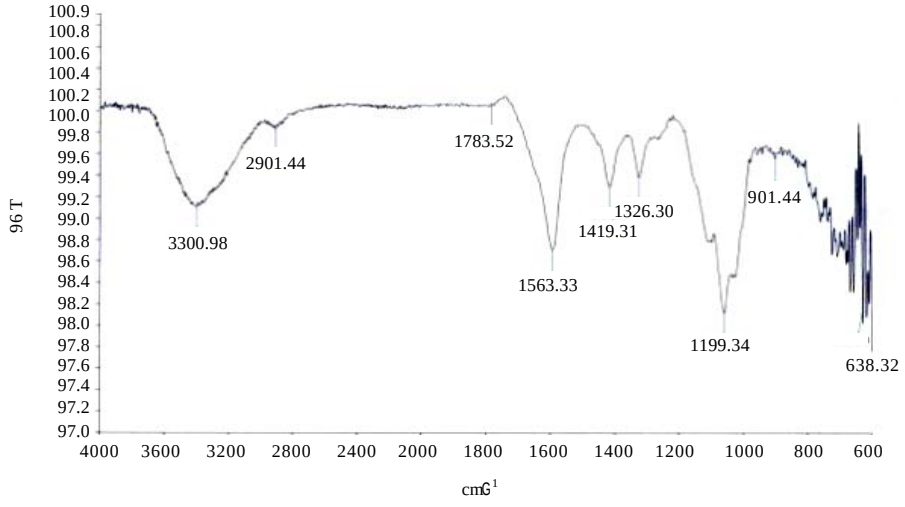

Fig. 2: FTIR spectra of optimized sample

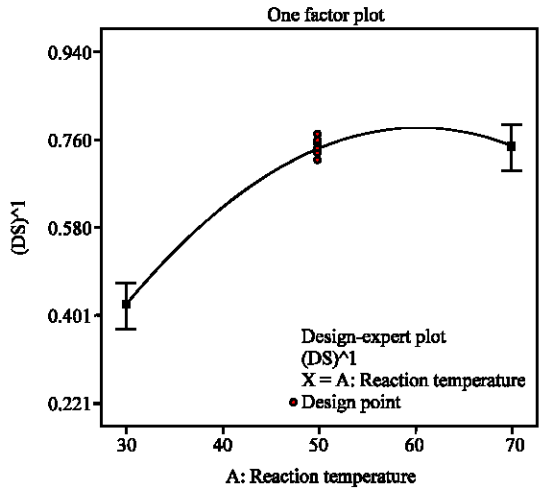

Fig. 3: The effect of reaction temperature on DS

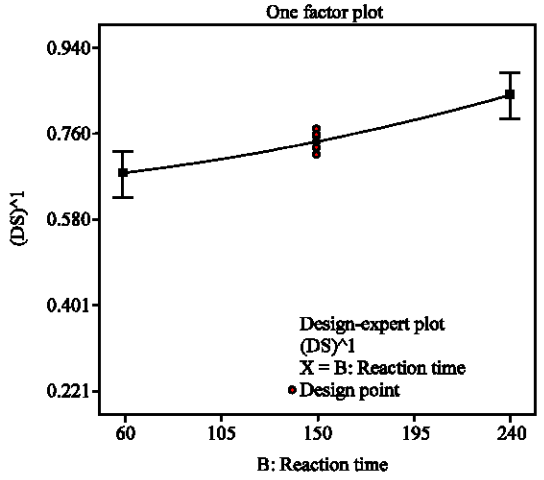

Fig. 4: The effect of reaction time on DS

Effect of SMCA concentration on DS: From Fig. 5, the higher the SMCA concentration, the higher content of functional groups of CMC thus more substitution of functional groups will occur. The maximum DS obtained is 0.9009 at 14 g of SMCA. However, the SMCA concentration is impeded by other reaction conditions such as NaOH concentration. The side reaction of SMCA concentration with NaOH will tend to produce sodium glycolate which is the by-product (Eq. 4).

Main reaction:

$$R_{cell}OH + ClCH_2COOH + NaOH \rightarrow R_{cell}OCH_2COONa + NaCl + H_2O \quad (3)$$

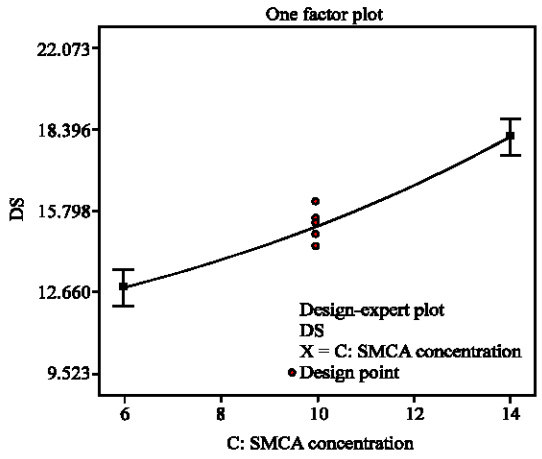

Fig. 5: The effect of SMCA concentration on DS

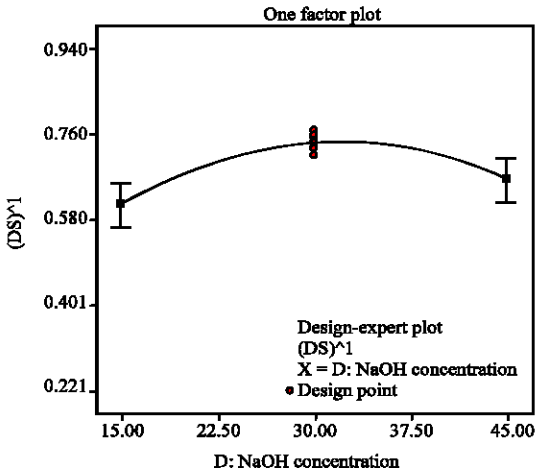

Fig. 6: The effect of NaOH concentration on DS

Side reaction:

$$ClCH_2COONa + NaOH \rightarrow HOCH_2COONa + NaCl \quad (4)$$

The effect of NaOH concentration on DS: The NaOH concentration plays great role in determining the production of CMC and the by-product. The proportion of NaOH concentration and SMCA concentration must be at optimum to obtain high value of DS. From Fig. 6, the DS increases steadily with the increment of NaOH concentration and when maximum value is attained, the DS decreases gradually. The maximum value of DS obtained is 0.7443 at 30% w/v. This shows that the optimum condition for carboxymethylation of cellulose is at 30% w/v. Further increment of NaOH concentration will not yield the pure product of CMC instead by-product sodium glycolate. Hence, the environment created will

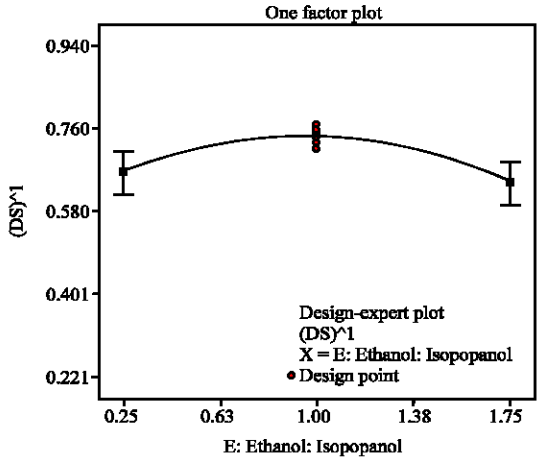

Fig. 7: The effect of solvent ratio on DS

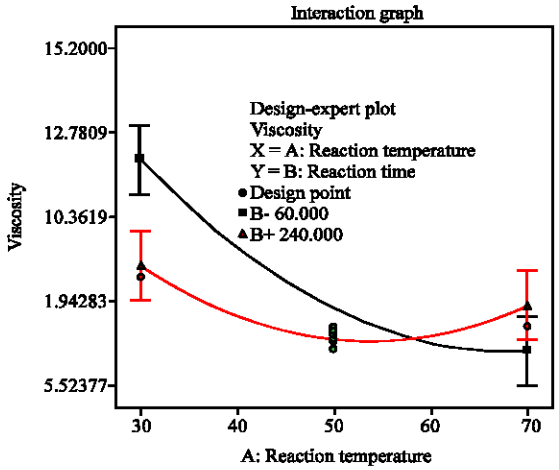

Fig. 8: Effect of reaction temperature and time on viscosity

determine either main or side reaction overcome each other.

Effect of solvent ratio on DS: The ratio of solvent volume ethanol:isopropanol is one of the vital aspect in obtaining optimum DS value. The solvent is used as a medium for the substitution of CMC functional groups to take place. The effect of the solvent system with regard to the reaction is related to its miscibility, the ability to dissolve the etherifying agents and to swell the cellulose to improve the accessibility of the etherifying agent into cellulose structure (Silva *et al*., 2004; Khullar *et al*., 2005). Without solvent, the reaction will be deterred. The accurate ratio of solvent will enhance the substitution reaction and if the ratio is not appropriate, the substitution reaction will be impeded. From Fig. 7, the optimum ratio of ethanol:isopropanol is 1.00:1.00 with DS of 0.7443. Higher DS is obtained due to the lower swelling in high organic solvent. The polarity of the solvent decreases as the number of carbon atoms increases in the solvent.

Effect of reaction temperature and time on viscosity: The interaction graph shows that the viscosity is decreasing with reaction temperature and time. Minimum reaction time and temperature will favor on the effect of the swellability of cellulose as well as diffusion and adsorption of reactants (Fig. 8). This condition may provide better environment for carboxymethylation reaction as well as to obtain higher viscosity of CMC solutions. In contrast, higher temperature and prolonged time may significantly cause the degradation of cellulose chain and CMC structure.

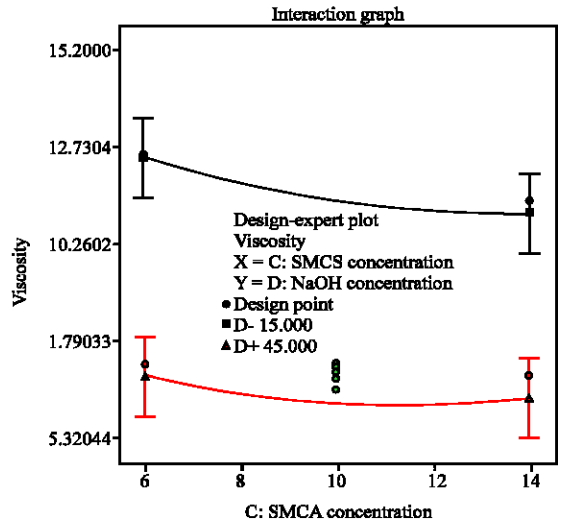

Fig. 9: Effect of SMCA concentration and NaOH concentration on viscosity

Effect of SMCA and NaOH concentration on viscosity: higher NaOH concentration will decrease the SMCA concentration and the viscosity of the CMC solution. This fact is due to the side reaction which takes place and results in the formation of sodium glycolate from SMCA and NaOH (Fig. 9). A side reaction is a two competitive reaction in carboxymethylation process which converts the sodium chloroacetate to sodium glycolate. The formation of sodium glycolate will increase if the concentration of NaOH is higher. It is because the monochloroacetis acid molecules tend to react with NaOH which lead to the destruction of cellulose chain or CMC polymer and decomposition of SMCA.

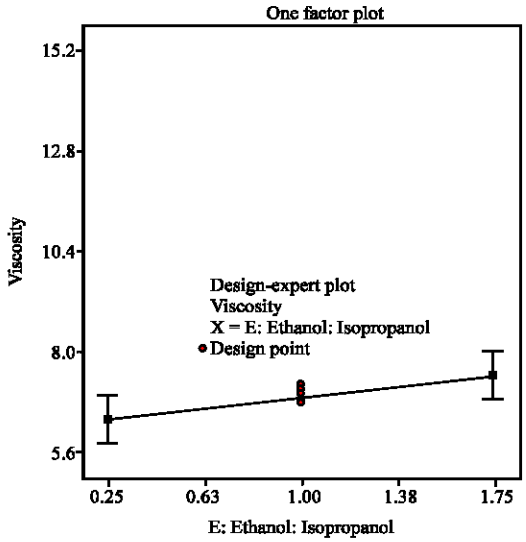

Fig. 10: Effect of solvent ratio on viscosity

Effect of solvent ratio on viscosity: The use of the solvent during the synthesis is to alter the pattern of the cellulosic hydrogen bonds and the hydrophobic interactions of the methylated blocks for destroying the gel structure that may be formed during the synthesis in heterogeneous conditions. Through one factor plot in Fig. 10, isopropanol is the medium that may adjust the polarity of the solvent system which driven the main reaction to occur. Lower polar solvents make the hydrated sodium ion become easier to access the cellulose chains and break the crystalline structure. Higher mixing ratio in volume of ethanol to isopropanol is favorable since it provide higher efficiency in the diffusion of the etherifying reagent into the reaction of cellulose chains.

Rheological behaviour of carboxymethylcellulose solution: Rheological characterization is important information to study the aqueous environment created by CMC. A simple study on it is reported here for optimized sample. The study was carried out by measuring the apparent viscosity at 2% concentration. The viscosity value categorized the CMC sample produced in this research as low viscosity CMC. The solution viscosity is a measurement of chain length as well as molecular weight of CMC in solution. In order to study the shear thinning behavior of CMC aqueous solution, a plot of apparent viscosity versus shear rate was figure out as show in Fig. 11. The solution of the optimized sample exhibit non-Newtonian rheology where no linear relation is observed between a variety of mechanical stresses on the liquid and the resulting flow properties (Dapia *et al*., 2005). The CMC solution character is pseudoplastic, where viscosity is decrease with increasing shear rate.

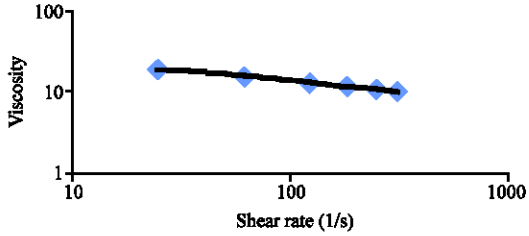

Fig. 11: The viscosity versus shear rate graph

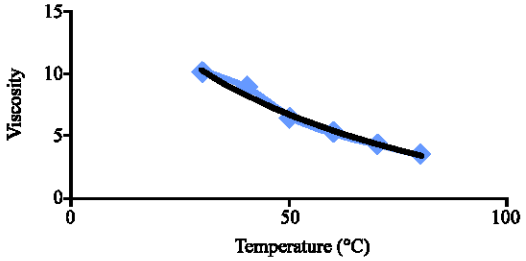

Fig. 12: The viscosity versus temperature graph

Table 3: Optimized DS and the respective conditions

Conditions	Values
Reaction temp. (°C)	68.200
Reaction time (min)	130.000
SMCA concentration (v/v%)	13.990
NaOH concentration (w/v %)	37.090
Ethanol:Isopropanol	1.740
DS	0.516

Figure 12 explains the study of temperature on viscosity that shows the viscosity of CMC decreases with increasing temperature like most water soluble polymers. Prolonged heating at extremely high temperatures will permanently degrade the cellulose chains or depolymerization which results in a decreasing of viscosity. Besides that, the strong alkaline conditions used in the preparation process could attribute to the structural changes. High alkaline conditions at elevated temperature are well known to cause degradation in carbohydrate molecules.

Optimization using response surface methodology: Through the DS and viscosity model with the understanding of the dependency of reaction conditions on DS and RE as done in previously section had shown the importance of the conditions. Hence, numerical optimization was carried out considering each value of response and the goal of DS and viscosity are set to maximum. Result of the numerical optimization based on our target yield few set of solutions and selected solutions were presented in Table 3 and 4.

The viscosity obtained from the study almost equal to the predicted optimized result. The obtained value for the viscosity is 10.1 cP with 3% error. However, the

Table 4: The optimum viscosity with corresponding conditions

Conditions	Values
Reaction temp. (°C)	40.51
Reaction time (min)	149.10
SMCA concentration (v/v %)	6.85
NaOH concentration (w/v %)	26.50
Ethanol:Isopropanol	1.16
Viscosity predicted	9.84

obtained DS is 0.516 with 45% error which is due to the purification problem and miscalculation of DS model regression. This error can be reduce through backward elimination technique of RSM.

CONCLUSION

There are many optimum conditions can be obtained to achieve high DS, yield and viscosity by using numerical optimization in RSM. There are more than 10 optimized result obtained from the raw data and 1 particular data was selected to be carried out. The optimized conditions results are 0.9424 for DS, 10.1 cP for viscosity and 22.1024 g for yield.

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