STUDY OF A PROCEDURE FOR THE OBTAINMENT OF METHYLCELLULOSE FROM MECHANIC PULP IN HOMOGENEOUS MEDIA

CRISTIAN TAPIA[1], JAIME SAPAG HAGAR, PEDRO SICHES, FERNANDO VALENZUELA and CARLOS BASUALTO.

Laboratorio de Operaciones Unitarias, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago , P.O.Box 233, Santiago 1, Chile.

Keywords: Methylcellulose. Mechanic pulp etherification. Homogeneous reaction. Factorial experimental design. Cellulose ether.

Abstract

The etherification reaction of mechanic pulp (MP) with dimethylsulphate (DMS) in homogeneous media was studied using a 2^{5-1} fractional factorial experimental design. In according to this model the quantity of DMS/2 g of dissolved MP and the interaction between reaction temperature and reaction time were established as reaction critical factors.

The results obtained under different reaction conditions showed a low mass yield (around of 20%) and a low percentage of methoxylation (%MeO) (around of 0.5%). The reasons that could explain this low performance of reaction would be a low NaOH solubility in the mixture solvent dimethylacetamide - lithium chloride (DMAc/LiCl) which would produce a poor cellulose activation, and the heterogeneous composition of MP which contains besides cellulose, hemicelluloses and lignin, which also could react with DMS.

1. Introduction

The traditional procedure for the obtainment of Methylcellulose (MC) is based on the Williamson etherification reaction, using alkyl halide, generally methylchloride or DMS which react with alkalicellulose (Greminger, 1979). The technical problems associated with this procedure are: i) The difficulty to get uniform substitution since the reaction is heterogeneous. ii) Low yield reaction because side reactions between water and etherificant agent (Utz, 1989). If the reactions were carried out in homogeneous media the cellulose substitution would be more uniform and, if the mixture solvent were completely water free, the side reactions which consume etherificant would be avoided. The main problem for this homogeneous procedure is to find a good cellulose solvent (Philipp et al, 1977; Turbak et al, 1980).

One of the solvent mixtures proposed for homogeneous etherification of cellulose is the mixture DMAc/LiCl, since this mixture has a low degradation effect over the cellulose dissolved along time (Mc Cormick, 1981, Mc Cormick et al, 1985).

In a previous paper (Sapag-Hagar et al, 1994) the dissolution of MP in the mixture DMAc/LiCl was studied. Two procedures for the dissolution of MP were tested. A first one working at high temperature in which around 63.5 % of the pulp was dissolved, and a second one working at low temperature by solvent interchange, in which only 10.1 % of the pulp was dissolved. The high temperature dissolution method was chosen.

The aim of this work was on the one hand to obtain the critical factors of the homogeneous etherification of MP using a factorial experimental design and on the other hand to establish the performance of the homogeneous procedure for the obtainment of MC from MP.

2. Experimental

2.1 Reagents

The MP (from P. radiata) was obtained from INFORSA plant of CMPC, Chile. The dried MP was milled in a hammer mill (DIAF A/S) provided with 1 mm diameter stainless steel screen. Then, the product was milled again in a balls mill by 8 hours. After that, the MP was classified by sieving (60-80-100-120 Test sieves, ASTM) for 10 minutes. The milled MP had an average size particle of 148 μm. The MP analysis by detergent fiber acid method (AOAC, 1990) showed the following composition: lignocellulose: 69.2% ; cellulose: 53.2% ; lignin

[1]Author to whom mail should be addressed

10.9% ; insoluble ashes: 5.1% . All the reagents used were of commercial reagent grade.

2.2 Methods

Dissolution of MP in the solvent mixture DMAc/LiCl

1.000 g of MP was suspended in 100 mL of the solvent mixture 10% LiCl in DMAc. The suspension was heated to 150°C and maintained at this temperature for 1 hour, and then permitted to cool off to room temperature, applying after that heating/cooling cycles (100/150°C). The portion not dissolved was separated through centrifuge decantation. (Sapag-Hagar et al, 1994).

Etherification stage

This procedure was based on Mc Cormick's patent (Mc Cormick, 1981). A scheme of combined activation and etherification is showed in Fig.1.

The etherification reaction was done in a 250 mL glass reactor provided with mechanical anchor stirrer.

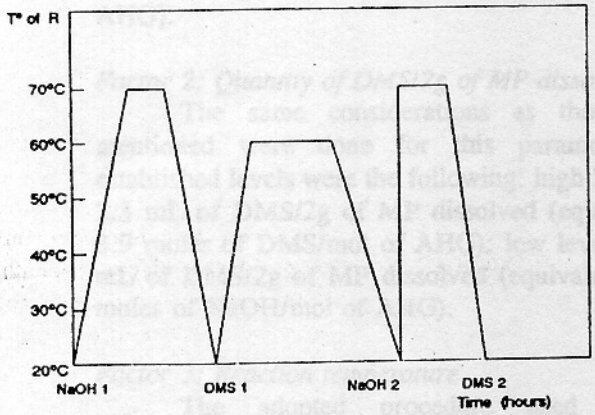

Fig.1. *Scheme of the etherification reaction with DMS over dissolved MP in DMAc/LiCl.*

Product separation stage

The reaction product was separated by the addition of 40 mL of methanol. A solid product was obtained which was separated from the solvent mixture by vacuum filtration. The product was then washed with a mixture of methanol/acetic acid/water = 85/5/10, and then with methanol. Later, this washed product was suspended in water where it partially dissolved. The suspension was filtered under vacuum and a solution was obtained. Finally, the water was removed by vacuum evaporation (10.1 kPa, 65°C) and a film of raw product was obtained.

Product purification stage

The film of raw product was dissolved in 20 mL of distilled water and placed into a dialysis tubing (cellulose dialysis tubing, Sigma). The dialysis tubing was submerged into 900 mL of distilled water. The product was dialyzed with agitation by 8 hours. Then, the water from the dialyzated solution was eliminated by vacuum evaporation (10.1 kPa, 65°C) and a film of MC dialyzated was obtained.

Determination of methoxylation percentage (%MeO) by gas chromatography

It was used the procedure described by Hodges (Hodges et al, 1979).

Experimental design

A 2^{5-1} fractional factorial experimental design (Box et al, 1978) was used for the determination of the reaction critical factors. The factors and its levels considered are showed in Table 1.

Table 1. *Parameters considered and its levels in the factorial experimental design.*

Factor	Parameters	Levels
1	quantity of NaOH (g/2 g of dissolved MP)	0.50 0.70 0.90
2	quantity of DMS (mL/2 g of dissolved MP)	1.40 1.80 2.30
3	reaction temperature (°C)	45.0 60.0 75.0
4	reaction time (h)	6.0 8.0 10.0
5	stirring speed (rpm)	80 120 160

The standard deviation of the experimental error was estimated from the standard deviation of five run experiments carried out at the medium level of each parameter.

3. Results and Discussion

The etherification procedure used by us was based on Mc Cormick's patent (Mc Cormick, 1981). In this procedure the activation with NaOH and etherification with DMS were carried out in one step. For the study of this procedure a 2^{5-1} factorial fractional design was proposed (Fig.1). This design considered 5 factors and 2 levels for each factor. The criteria used for the factors selection and levels established were the following:

Factor 1: Quantity of NaOH/2g of MP dissolved

The quantity of NaOH used in the procedure is very important because cellulose react with NaOH forming alkalicellulose, reactive species, which is able to react with DMS.

The reactive unit of cellulose is the anhydroglucose (AHG) which has three hydroxyl groups. Then, theoretically, it would be necessary 3 moles of NaOH for each mol of AHG for a complete activation of cellulose. Assuming that a 2% w/v MP solution is equivalent to a 1%w/v cellulose solution, the following levels for this parameter were established: high level (+): 0.90 g of NaOH/2g of MP dissolved (equivalent to 3.6 moles of NaOH/mol of AHG): low level (-): 0.50 g of NaOH/2g of MP dissolved (equivalent to 2.0 moles of NaOH/mol of AHG).

Factor 2: Quantity of DMS/2g of MP dissolved

The same considerations as those above mentioned were done for this parameter. The established levels were the following: high level (+): 2.3 mL of DMS/2g of MP dissolved (equivalent to 3.9 moles of DMS/mol of AHG): low level (-): 1.4 mL of DMS/2g of MP dissolved (equivalent to 2.4 moles of NaOH/mol of AHG).

Factor 3: Reaction temperature

The adopted procedure used different temperatures during the reaction see Fig.1. The temperature that was considered as reaction temperature correspond to the temperature at which was maintained the solution after added the first portion of DMS (DMS_1 in Fig.1.). This temperature was chosen as reaction temperature because it fixs the top energetic level to which the cellulose partially activated is submitted after the first portion of NaOH was added ($NaOH_1$ in Fig.1.). By the other hand, after the second portion of DMS was added (DMS_2 in Fig.1.), the temperature was not changed and was maintained at room temperature . The high and low levels were established considering the patent temperature as reference (60°C) $\pm$ 33.3% respectively.

Factor 4: Reaction time

The period after the second portion of DMS (DMS_2 in Fig.1.) was added to the solution was considered as reaction time. The high and low levels were established considering the patent time as reference (8 hours) $\pm$ 25% respectively.

Factor 5: Stirring speed

This parameter was considered important because the diffusion of reactants and heat transfer between the bulk of solution and its surroundings are controlled by stirring speed. There was no patent indication about this parameter. The levels were established empirically according to size reactor, liquid level and solution viscosity.

The obtained products under different experimental conditions established by the experimental design were partially soluble in water, which pointed out that the product would had a low percentage of methoxylation. Besides, the products were contaminated by salts. The qualitative and quantitative analysis of these salts showed that the main contaminant was LiCl (Tapia, 1993).

Study of a procedure for the raw product purification by dialysis

Since that MC is a polymer soluble in water an LiCl is also soluble in this solvent, a product purification procedure by dialysis was developed.

A MC solution (25 cP, Sigma) contaminated with LiCl was prepared as following: 20 mL of a solution containing 200 mg of MC and 85.71 mg of LiCl (equivalent to 13.95 mg of Li), which is equivalent to 30% LiCl contamination, was prepared. The assay was done in duplicate. The sampling was done without reposition, taking every 1 hour 10 mL of water from the dialysis bath, during 8 hours. Finally, a sample was taken after 23 hour of dialysis. Li was determined for each sample. Figure 2 shows that after 8 hours of dialysis over 94% of LiCl had been eliminated. Besides, the MC recuperation from dialysis tubing after 23 hours of dialysis was 99.2 %.

Once the procedure of purification by dialysis was established, the raw products were purified by this method bringing out LiCl contamination for each sample. The raw products showed a variable and high contamination of LiCl (between 7.6% and 53.5% of LiCl) which pointed out that the purification procedure based on methanol washing as proposed by Mc Cormick was inefficient.

The dialyzated product showed lower weight than raw product. This difference was not explained by LiCl contamination which indicate that there were other products that passed through the dialysis membrane. These products could be low molecular

weight cellulose fragments produced by the effect of reaction conditions over the cellulose chain. Reducing sugars were searched in the dialysis bath using the Fehling's method for each run experiment. The results showed that most of them gave positive results which means that cellulose degradation effectively occurs.

Statistical analysis of the experimental design applied to etherification stage

The results, considering mass yield and % MeO as system response are shown in Table 2.

Table 2. *Experimental design applied. The system response was measured as mass yield of MC dialyzated and %MeO.*

Experiment (%)	Parameter 1 2 3 4 5	Mass Yield (%)	%MeO (%)▲
1	LLLLH	22.0	0.42
2	HLLLL	17.6	0.59
3	LHLLL	19.6	0.54
4	HHLLH	7.3	0.49
5	LLHLL	17.7	0.49
6	HLHLH	12.6	0.60
7	LHHLH	16.9	0.74
8	HHHLL	14.7	0.85
9	LLLHL	23.2	0.43
10	HLLHH	17.0	0.50
11	LHLHH	25.3	0.45
12	HHLHL	12.6	0.78
13	LLHHH	19.4	0.44
14	HLHHL	22.2	0.18
15	LHHHL	13.6	0.38
16	HHHHH	16.8	0.62
17	MMMMM	21.8	0.43
18	MMMMM	22.9	0.60
19	MMMMM	18.3	0.44
20	MMMMM	18.4	0.46
21	MMMMM	14.7	0.50

L: low level ; H: high level ; M: medium level
▲: (g of MC dialyzated/2 g of MP dissolved)* 100

For both, the analysis of results was done using the contrast table (Box et al, 1978). When the mass yield of MC dialyzated was considered, all factors and interactions were into the experimental error at 5% level of confidence . Thus, using this response it was not possible to know the reaction critical factors. By the other hand, when %MeO was considered, the following critical factors were established: quantity of DMS/2g of MP dissolved and the interaction between reaction temperature and reaction time see Fig.3.

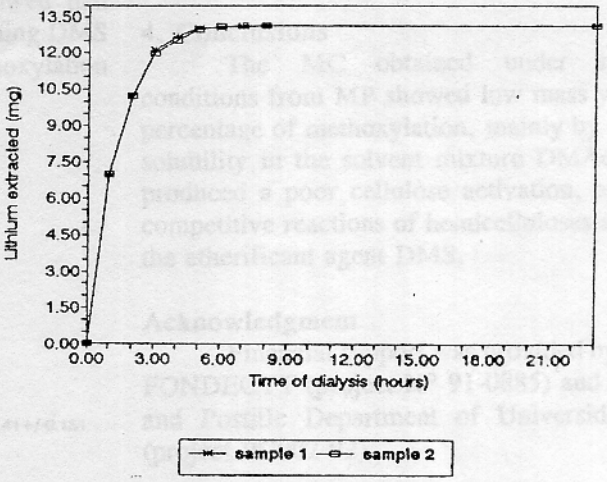

Fig.2. *Curve of Lithium extraction from MC samples solution contaminated with LiCl, by dialysis.*

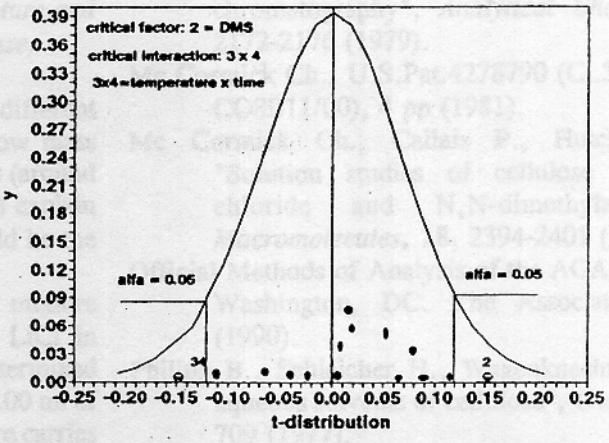

Fig.3. *Main effect and interaction related to t-distribution as reference at 5% level of confidence with 16 degrees of freedom and a scale factor of 6.91E-02, considering %MeO as response.*

Thus, when the quantity of DMS/2 g of MP dissolved was increased from 1.4 mL to 2.3 mL, the %MeO just increased in 0.15%, independent of the other factor levels. This poor result could be explained

by a poor cellulose activation and side reactions which consume etherificant agent.

The analysis of interaction (see Fig.4) shows that when the reaction time was increased at the high level for reaction temperature, the % MeO disminished significantly. This results showed that under these conditions side reactions consuming DMS were developed, giving a low cellulose methoxylation degree.

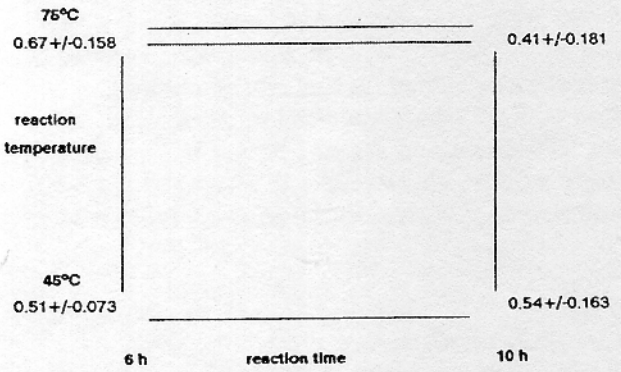

Fig.4. *Interaction between reaction temperature and reaction time, considering % MeO as response.*

The results obtained under different experimental studied conditions showed a low mass yield product (around 20%) and a low %MeO (around 0.5% ; DS = 0.026). The reasons that could explain this low performance for the procedure would be the following factors:

a) the low NaOH solubility in the solvent mixture DMAc/LiCl. The NaOH solubility in 9% LiCl in DMAc solution at 70°C was determined experimentally given 5.93 x 10^{-3}g of NaOH/100 ml of solution. By contrast, the traditional procedure carries out the cellulose activation in a 40% NaOH aqueous solution, which is equivalent to 57.2 g of NaOH/100 ml of solution. This low NaOH solubility in the mixture solvent DMAc/LiCl would produce a poor cellulose activation, which explain a low yield of the etherification reaction; b) MP is a heterogeneous product which contains cellulose, hemicelluloses and lignin. Hemicelluloses and lignin can react with DMS, then side reactions could take place between them which would disminish the reaction extent between cellulose and DMS. This matrix effect was studied experimentally. Thus, the reaction in homogeneous media carried out using cellulose instead of MP, under similar experimental conditions, gave a 7.52% MeO (DS = 0.407) product instead of a 0.5% MeO (DS = 0.026) obtained for MP.

4. Conclusions

The MC obtained under homogeneous conditions from MP showed low mass yield and low percentage of methoxylation, mainly by a low NaOH solubility in the solvent mixture DMAc/LiCl which produced a poor cellulose activation, as well as by competitive reactions of hemicelluloses and lignin for the etherificant agent DMS.

Acknowledgment

Financial support was provided by grants from FONDECYT (project N° 91-0885) and Postgraduate and Postitle Department of Universidad de Chile (project PG002-92).

References

Box G., Hunter W., Hunter J., *Statistics for experimenters*, N.Y. Wiley, 374-449 (1978).

Greminger G.K.,*Cellulose derivatives, ethers in Encyclopedia of Chemical Technology*, Kirk-Othmer 5, N.Y. John Wiley & Sons, 149-153 (1979).

Hodges K., Kester W., Wiederrich D., Grover J., "Determination of alkoxyl substitution in cellulose ethers by Ziesel-gas chromatography", *Analytical Chemistry* 51, 2172-2176 (1979).

Mc Cormick Ch., U.S.Pat.4278790 (Cl.536-84; CO8B11/00), 4 pp (1981).

Mc Cormick Ch., Callais P., Hutchinson B., "Solution studies of cellulose in lithium chloride and N,N-dimethylacetamide", *Macromolecules*, 18, 2394-2401 (1985).

Official Methods of Analysis of the AOAC. 15th ed. Washington, DC. The Association, 82-83 (1990).

Philipp B., Schleicher H., Wagenknecht W.,"Non-aqueous solvents of cellulose", *Chemtech* 702-709 (1977).

Sapag-Hagar J., Tapia C., Valenzuela F., Maeda M., Coromina M .,"Dissolution studies of mechanic pulp in the mixture dimethyl acetamide/lithium chloride (DMAc/LiCl)" *Bol. Soc. Chil. Quím.* 39, 161-164 (1994).

Tapia C., *Preparation of methylcellulose in homogeneous media directly from mechanic pulp*, Master Thesis in Pharmaceutical Sciences, Universidad de Chile, 35-37 (1993).

Turbak A., Hammer R., Davies R., Hergert H.,

"Cellulose solvents" *Chemtech*, 51-57 (1980).

Utz H., *Cellulose ethers-synthesis, application and analytical aspects in Derivatisation of Wood. In cellulose sources and exploitation*, Kennedy J.F., Phillips. G.O., Williams P.A (editors), 273-283 (1989).