CHAPTER 4

RESULTS AND DISCUSSION

In gereral, a good purification method is one with high yield obtained from each individual method used. The yield of purified cellulose obtained with certain conditions used in purification is always expressed in terms of percentage of α -, β - and γ -celluloses. In this experiment, α-cellulose is the major part that plays an important role in etherification for the preparation of Na-CMC. Therefore, the percentage of α -cellulose of 20 samples of purified cellulose obtained are determined and presented in Table 1. During purification, α -cellulose content in purified cellulose obtained is affected by some physical parameters involved as shown in graphical representation (see Figures 1-8) and in Table 1. Such parameters are pressure, time, alkali concentration and bleaching.

From Figures 1-4, the maximum yields of α -cellulose are obtained by digestion with about 3% NaOH. The α -cellulose contents are higher as alkali concentration increased from 1 to 3% but they are gradually lower as alkali concentration increased from 3 to 10%. The bleached samples of purified cellulose contain low α -cellulose content than unbleached ones at all points of alkali concentration ranged from 1 to 10%. From Table 1,

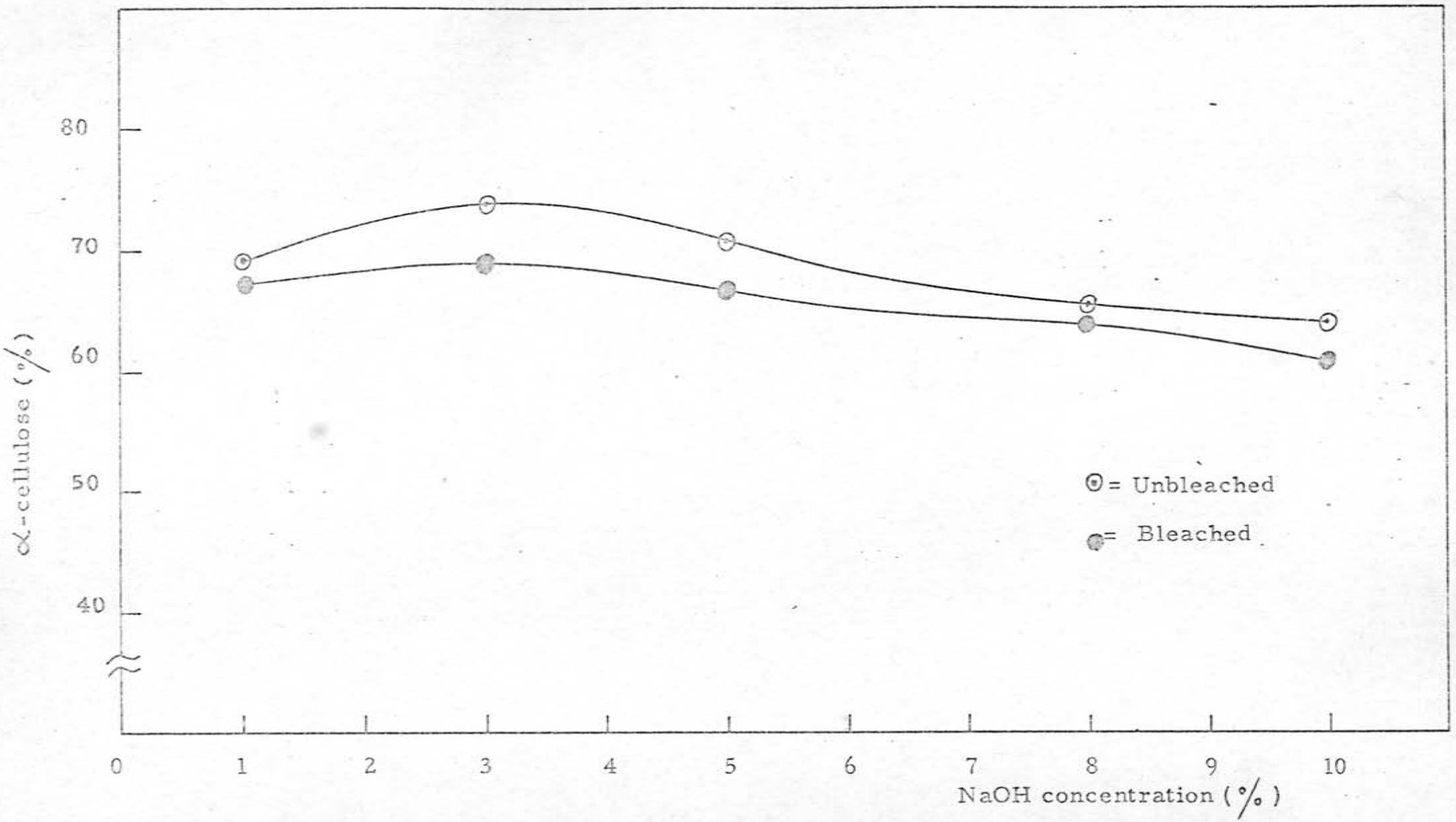

Figure 1. Graphical representation of alkali concentration vs. percentage of α-cellulose contained in both bleached and unbleached samples of purified cellulose (digestion for 2 hrs. with 10 lbs/in^2 pressure.)

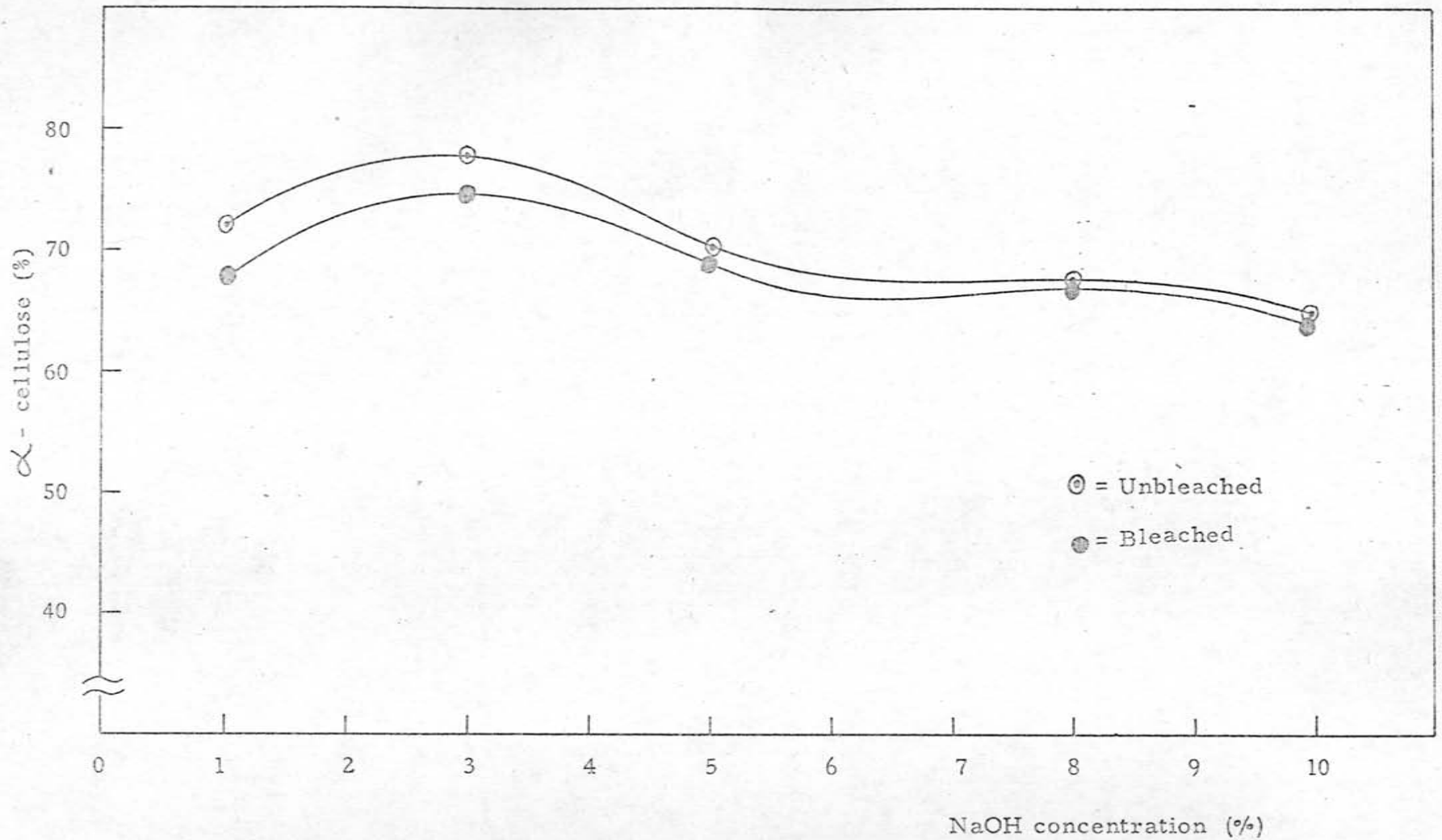

Figure 2. Graphical representation of alkali concentration vs. percentage of α-cellulose contained in both bleached and unbleached samples of purified cellulose (digestion for 2 hrs. with 20 lbs/in^2 pressure.)

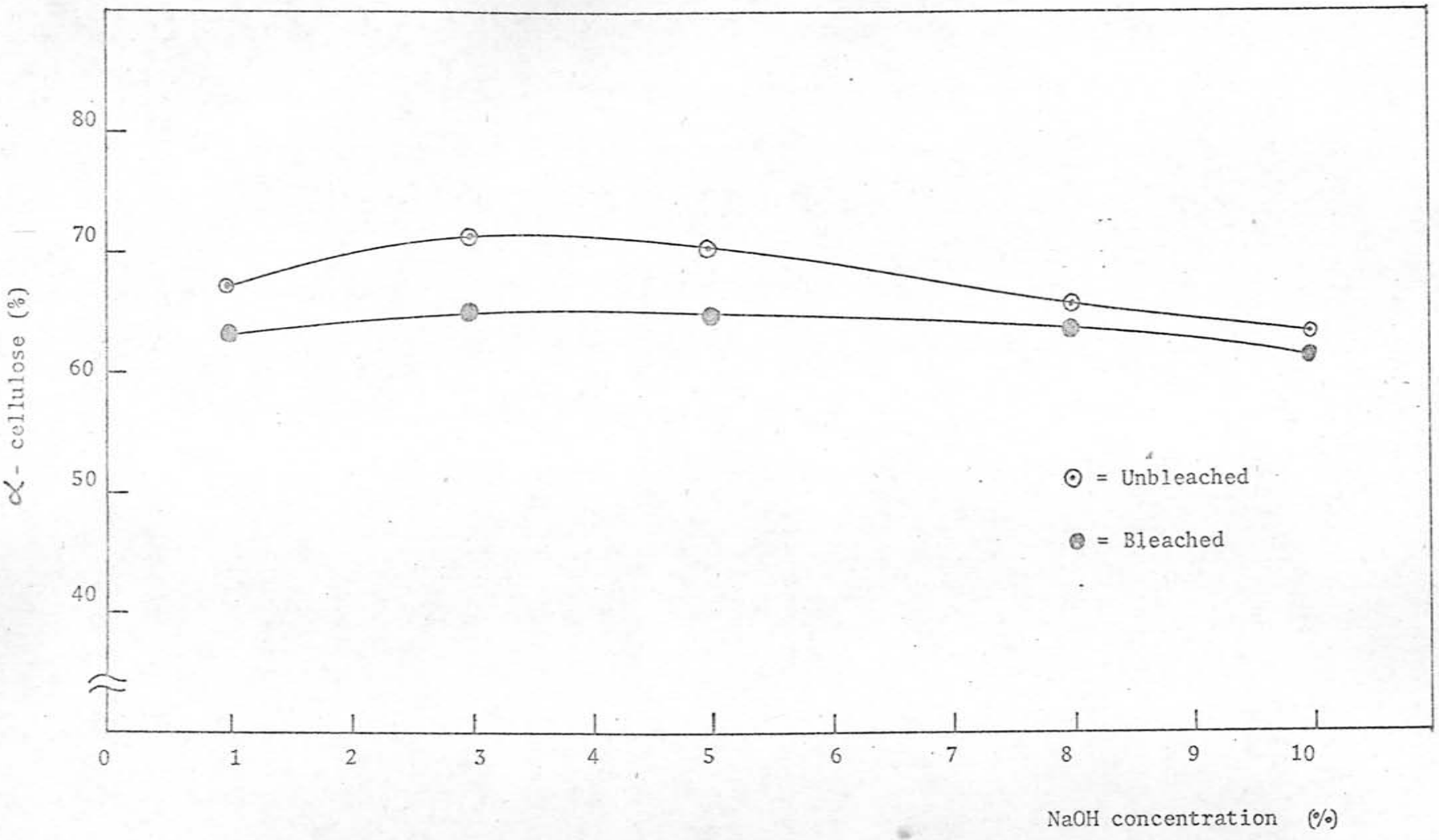

Figure 3. Graphical representation of alkali concentration vs. percentage of α-cellulose obtained in both bleached and unbleached samples of purified cellulose (digestion for 3 hrs. with 10 lbs/in^2 pressure.)

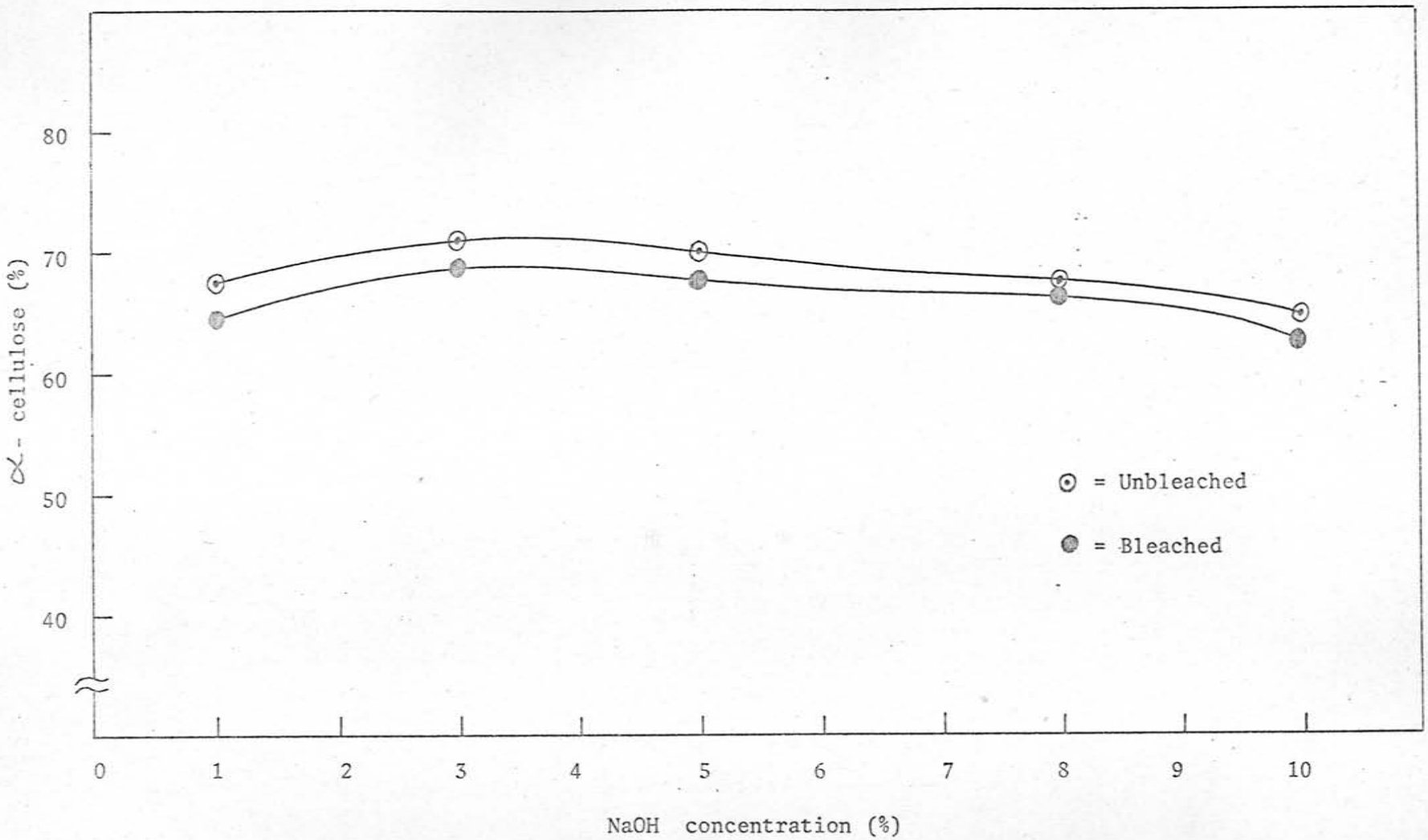

Figure 4. Graphical representation of alkali concentration vs. percentage of ∝ - cellulose contained in both bleached and unbleached samples of purified cellulose (digestion for 3 hrs. with 20 lbs/in^2 pressure.)

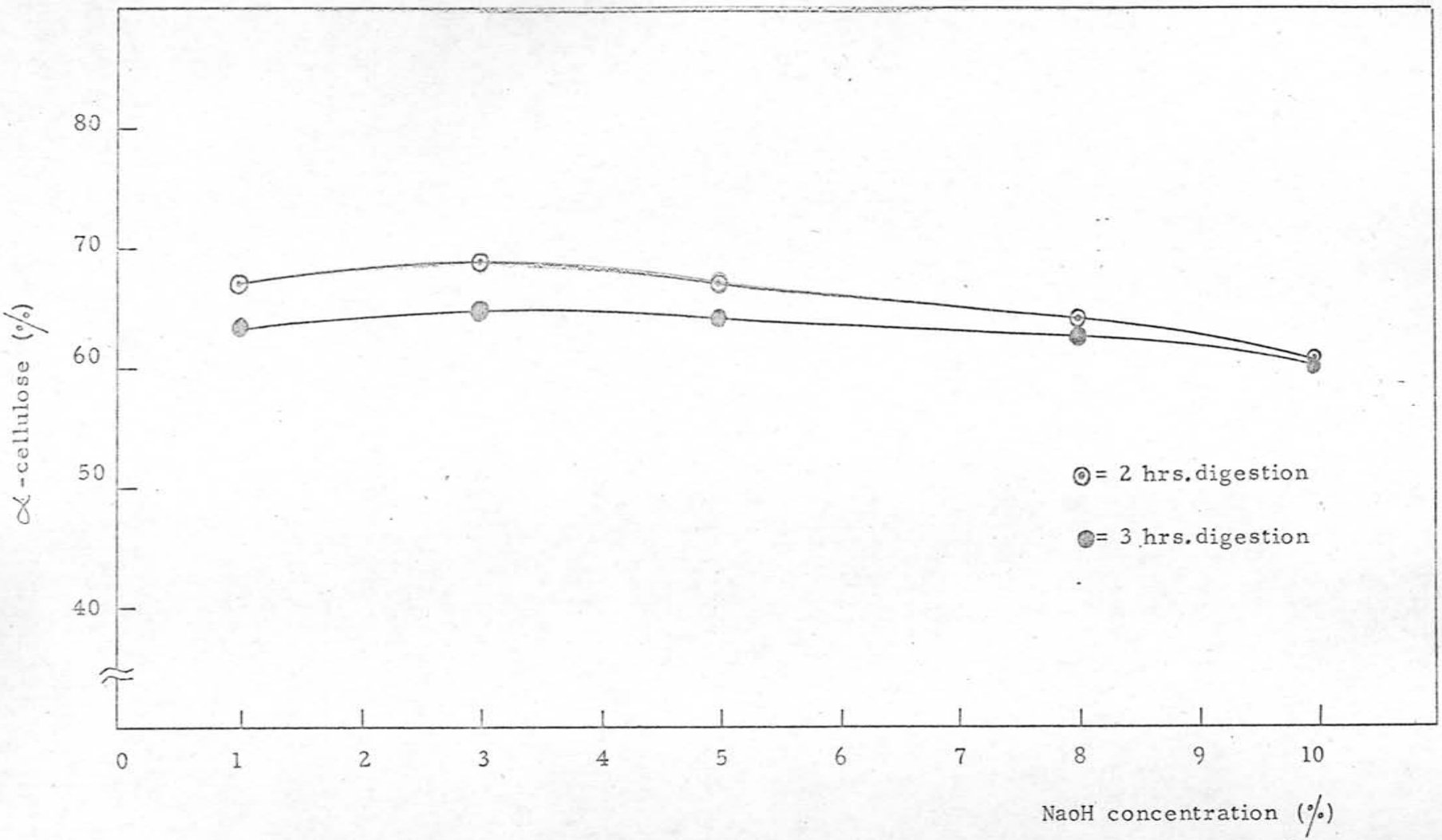

Figure 5. Graphical representation of alkali concentration vs. percentage of ∝-cellulose contained in bleached samples of purified cellulose (digestion under 10 lb/in^2 pressure for 2 and 3 hrs.)

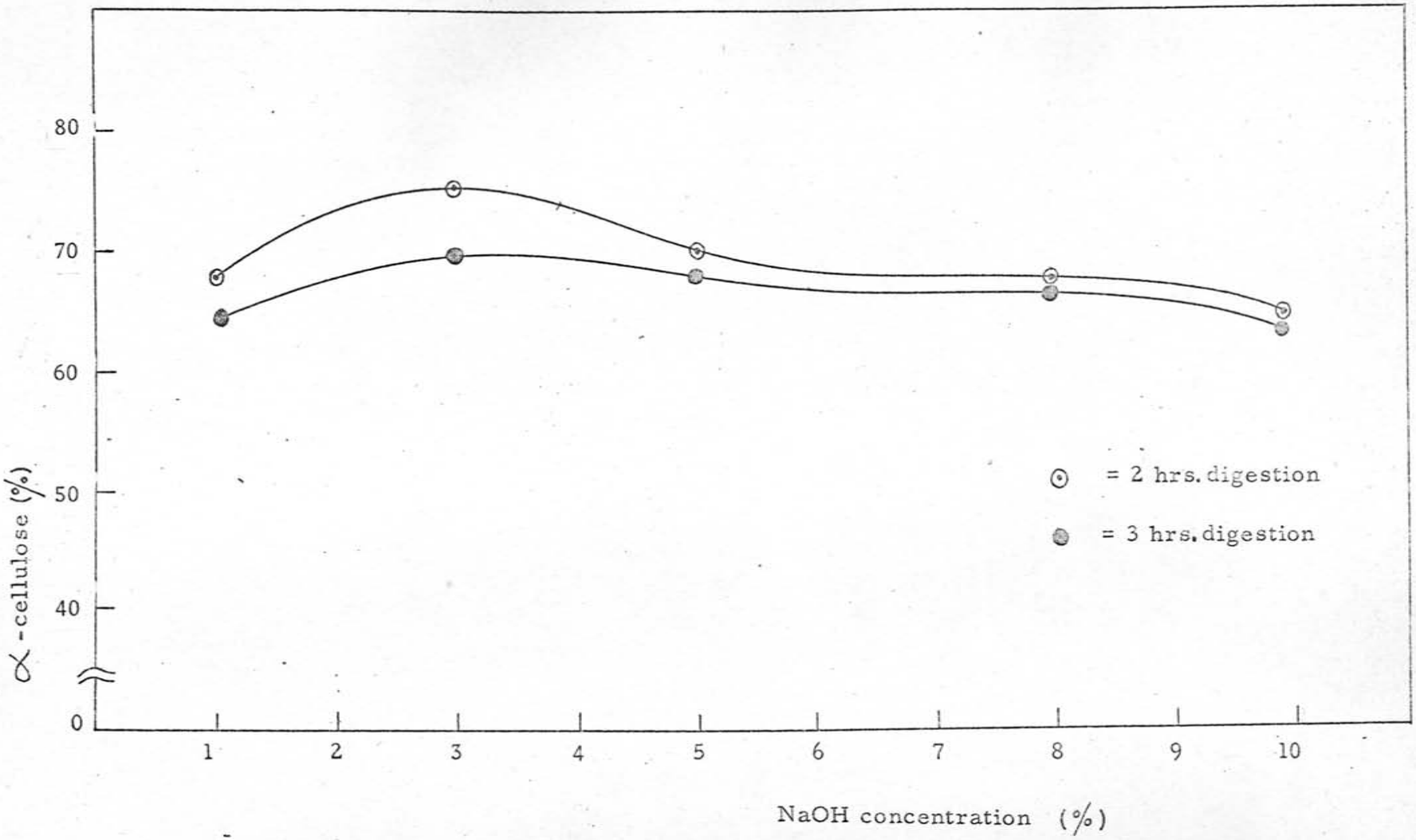

Figure 6. Graphical representation of alkali concentration vs. percentage of α-cellulose contained in bleached samples of purified cellulose (digestion under 20 lb/in^2 pressure for 2 and 3 hrs.)

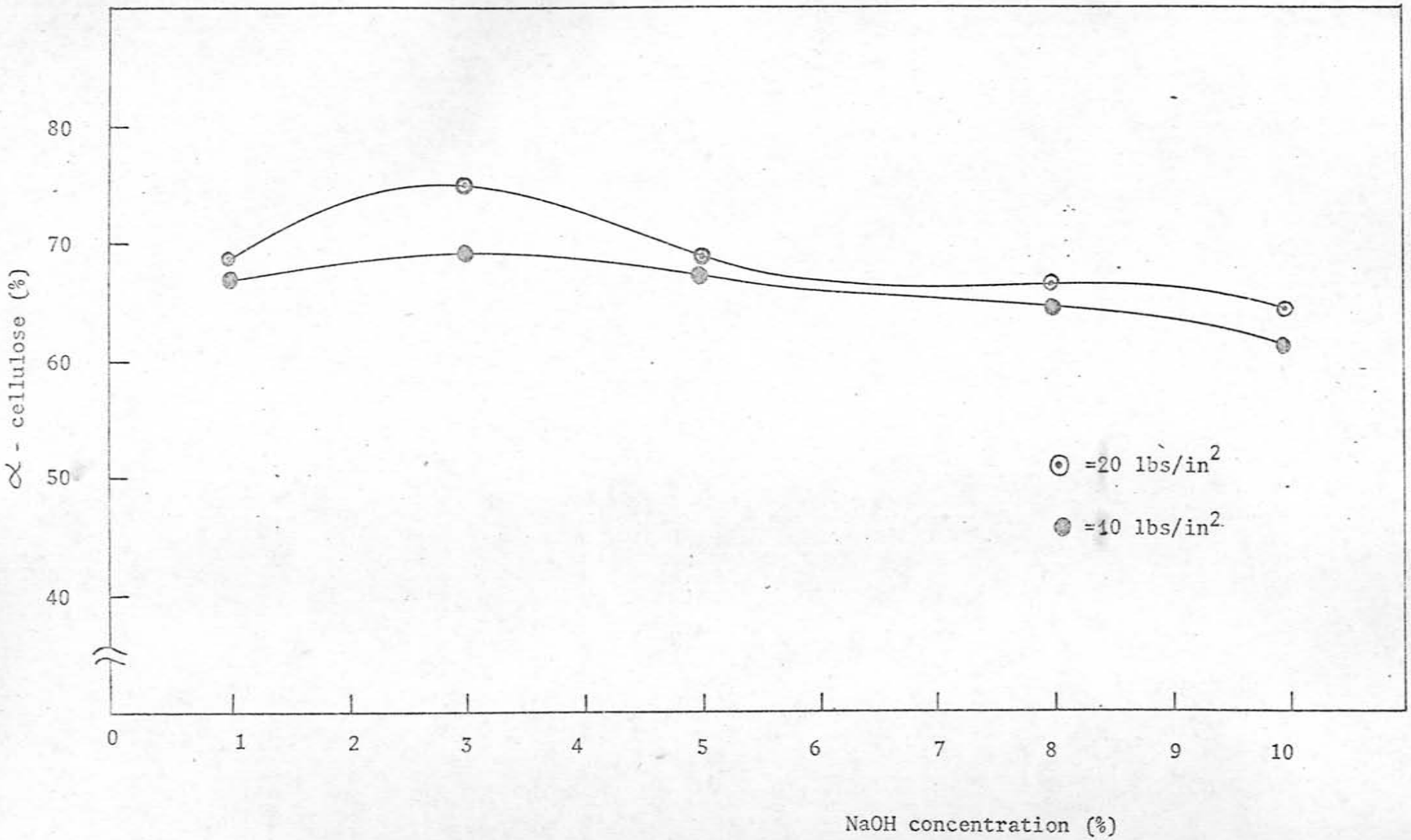

Figure 7. Graphical representation of alkali concentration vs. percentage of ∝ - cellulose contained in bleached samples of purified cellulose (digestion for 2 hrs. under pressure 10 lbs/in^2 and 20 lbs/in^2)

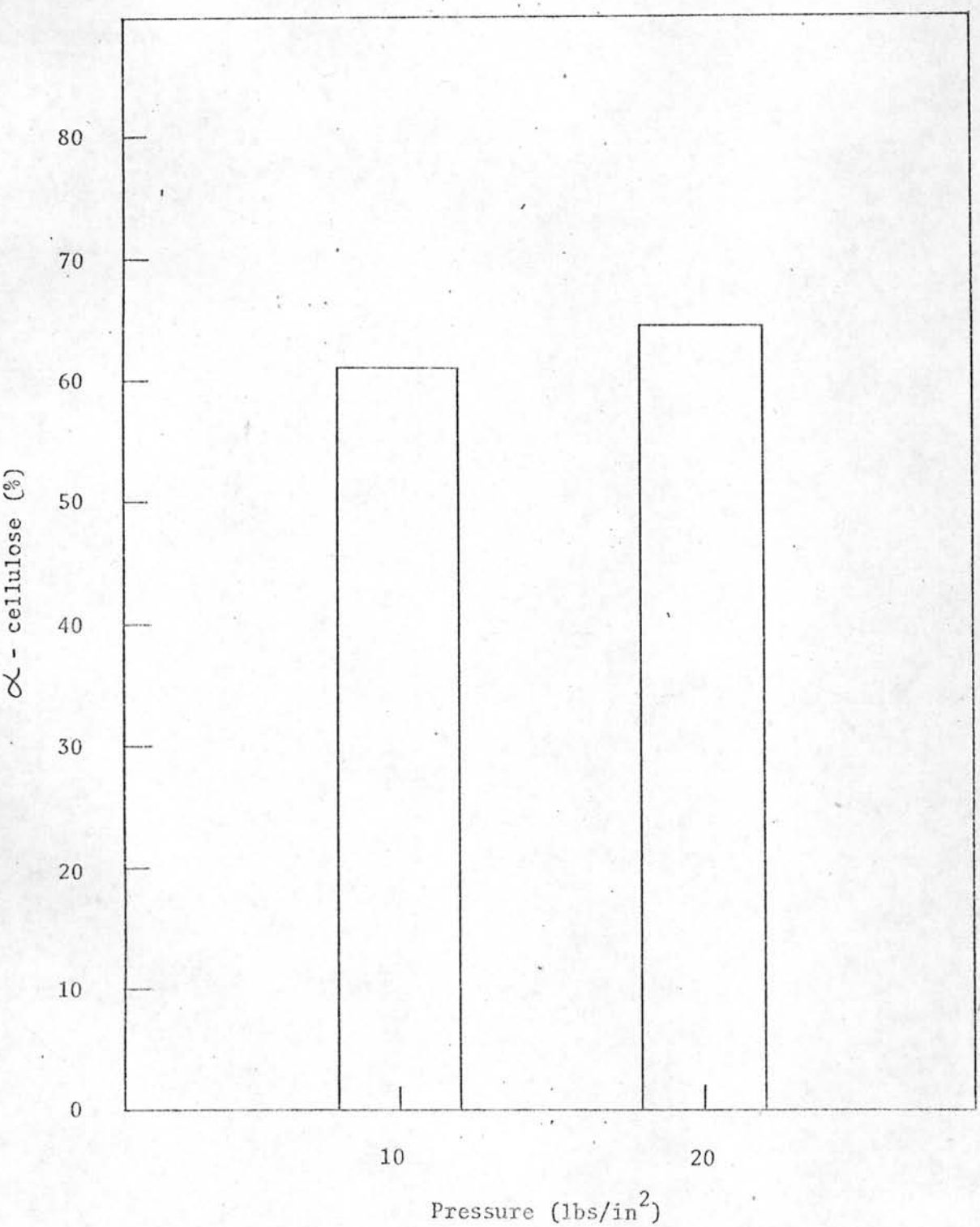

Figure 8. Histogram showing percentages of ∝ - cellulose in bleached samples of purified cellulose (digestion with 10 % NaOH for 2 hrs.)

two sets of samples were listed as unbleached and bleached ones. The content of α-cellulose of the second one is from 60.91 to 75.17% (see sample no. 15 and 7 in Table 1). Bleaching of purified cellulose, in addition, found to be a factor involved in decreasing of α-cellulose content. However, bleaching is necessary in purification process for fading unwanted color and for ease removal of tiny seed hull particles attached to cellulose fiber in order to obtain suitable raw material for the preparation of Na-CMC.

By keeping pressure constant at 10 and at 20 lbs/in^2, percentage of α-cellulose of bleached samples obtained with 2 hours digestion is higher than one with 3 hours digestion at all points of various alkali concentration (see Figures 5 and 6). For the same digestion time (2 hours) and with different pressures, the contents of α-cellulose are varied with pressure at each equal alkali concentration (see Figure 7). It is found that the cellulose contents of ones with 20 lbs/in^2 pressure are higher than ones with 10 lbs/in^2.

According to Figures 1, 2, 3 and 4 the maxima are at 3% NaOH concentration. Among these maxima, the highest content of α-cellulose is 75.17% for sample no.7 (see Table 2). As previously mentioned, good purification method is one with high yield. It could possibly say that the purification method

under conditions used for sample no. 7 is to be the one with the most favor. It fact, it is not true in this case.

Table 2. A list of four highest percentages of α-cellulose in bleached samples of purified cellulose derived from various purifying conditions.

Sample no.	Purifying condition		% α-cellulose
	3% NaOH		
	Time	Pressure	
7	2 hrs	20 lbs/in^2	75.17±0.80
2	2 hrs	10 lbs/in^2	68.85±0.74
17	3 hrs	20 lbs/in^2	69.07±0.74
12	3 hrs	10 lbs/in^2	64.61±0.70

Because of poor visual and physical appearance and of difficulty in getting rid of foreign matters, condition used in sample no. 7 is, thus, rejected and not chosen as good purification procedure. As regards to visual inspection and to ease of manual removal of foreign matters, the conditions used for purification of samples no. 5 and 10 are preferred for purification of cellulose from cotton fuzz though their

α-cellulose contents are lower than one of sample no. 7. Such conditions used are 10% NaOH with 2 hours digestion under pressur 10 lbs/in^2 and under 20 lbs/in^2. The purified cellulose obtained from samples no. 5 and 10 are white and completely free from contaminants, and their percentages of α-cellulose are 60.99 and 64.60 respectively.

Though α-cellulose content of sample no. 5 is less than one of sample no. 10 as shown in Figure 8, both samples were used as source of cellulose for the preparation of Na-CMC. In various ratio of mixtures of benzene and ethyl alcohol (B-EtOH) and of methyl ethyl ketone and ethyl alcohol (ME-EtOH) as reaction media, products of Na-CMC were prepared and their degrees of substitution (D.S.'s) of the first etherification step were determined as shown in Table 3 and in graphical representation (see Figure 9). The purpose of increasing D.S. of the products was attempted by conducting multistep of etherification and their D.S.'s were, then, determined after each step in accordance with Tables 4-5 and Figures 10-12.

According to Table 3, D.S.'s of Na-CMC derived from sample no. 5 as raw material are 0.587-0.837 for B-EtOH as reaction medium and 0.731-0.817 for ME-EtOH as reaction medium whereas ones from sample no. 10 as raw material are 0.564-0.621 and 0.663-0.687 for B-EtOH and ME-EtOH as reaction media respectively. From Figure 9, the highest D.S. obtained is one from sample no. 5 as raw material and with 50:50 B-EtOH as reaction medium.

Table 3 A list of degrees of substitution of sodium carboxymethylcellulose obtained from the first etherification step using various ratio of mixed reaction media

Raw material	Reaction medium (B-EtOH)	D.S.	Reaction medium (ME-EtOH)	D.S.
sample no. 5	50:50	0.837±0.010	50:50	0.731±0.009
(purified cellulose	60:40	0.762±0.009	60:40	0.783±0.009
obtained from 10% NaOH	70:30	0.747±0.009	70:30	0.795±0.009
digestion at 10 lbs/in^2	80:20	0.716±0.009	80:20	0.817±0.010
pressure for 2 hours)	90:10	0.587±0.007	90:10	0.816±0.010
sample no. 10	50:50	0.605±0.007	50:50	0.664±0.008
(purified cellulose	60:40	0.564±0.007	60:40	0.667±0.008
obtained from 10% NaOH	70:30	0.621±0.007	70:30	0.663±0.008
digestion at 20 lbs/in^2	80:20	0.614±0.007	80:20	0.675±0.008
pressure for 2 hours)	90:10	0.608±0.007	90:10	0.687±0.008

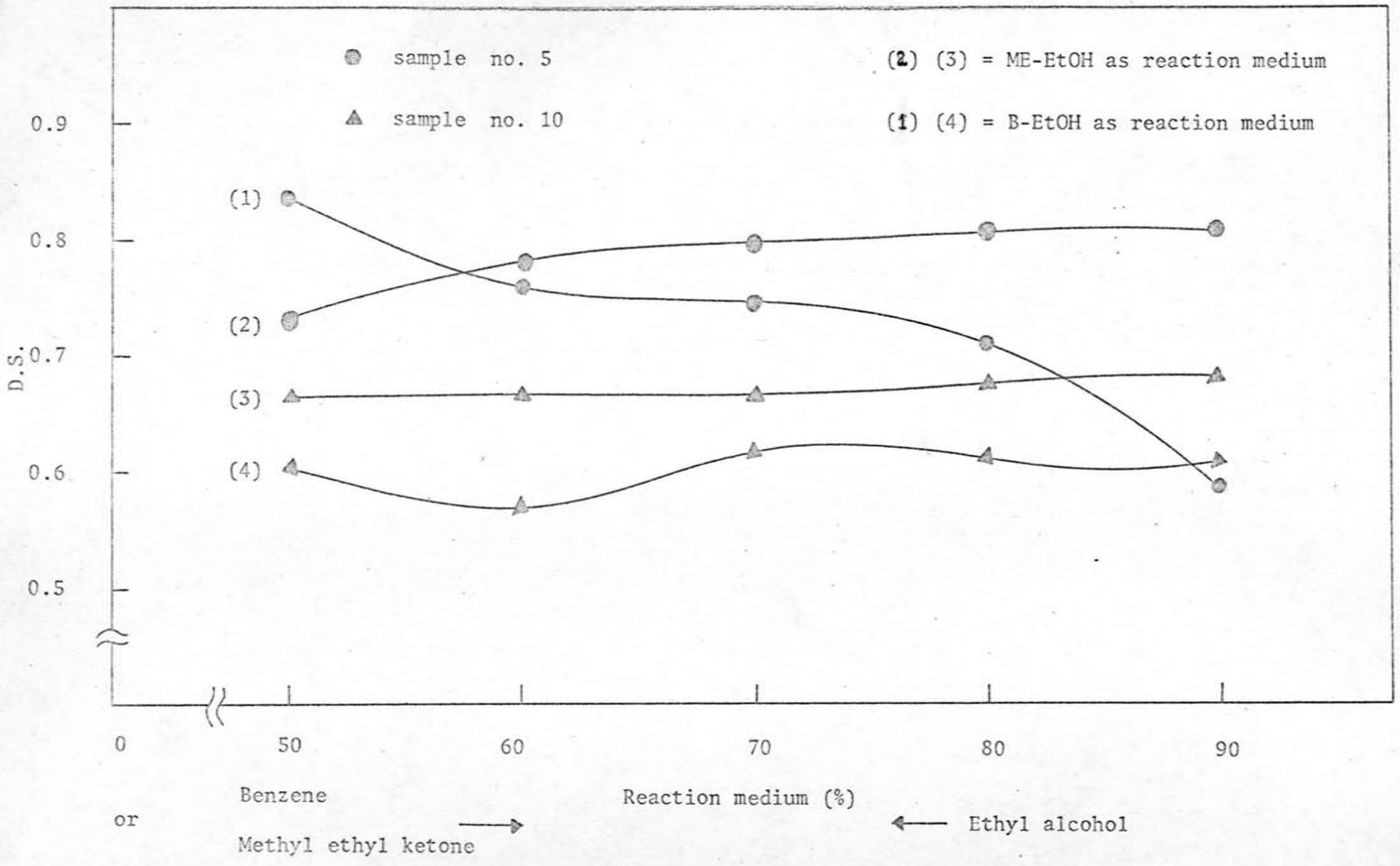

Figure 9. Graphical representation of various percentages of mixed reaction media vs. degrees of substitution of etherification products.

The second high D.S. of Na-CMC is one from the same raw material but with 80:20 ME-EtOH as reaction medium. It is also found that most D.S.'s of the etherification products obtained from sample no. 5 in either B-EtOH or ME-EtOH as reaction medium are higher than one from sample no. 10 (except one from sample no. 5 in 90:10 B-EtOH). In B-EtOH medium, the change of D.S. can not be certainly predicted by mixing ratio of benzene and ethyl alcohol in the mixture as regards to the fluctuation of the curve pattern (see curve no. (4) in Figure 9). For ME-EtOH as reaction medium, D.S.'s of Na-CMC considerably increase with increasing percentage of methyl ethyl ketone in the mixture of both samples (no. 5 and 10) used as raw material (see curves no. (2) and (3) in Figure 9).

Since sample no. 10 considerably represented raw material for Na-CMC with low D.S., sample no. 5 is then used as starting raw material for the preparation of Na-CMC with expected high D.S. . In addition, various concentration of B-EtOH (including 90:10 B-EtOH) and of ME-EtOH are chosen as reaction media. Therefore, techniques for increasing D.S. of etherification product were then performed by multistep of etherification and by using sample no. 5 as starting raw material in B-EtOH and in ME-EtOH. The results of multistep of etherification

performed in B-EtOH and in ME-EtOH are shown in Table 4 and in graphical representation (see Figure 10 and 11).

For B-EtOH as reaction medium, D.S.'s of Na-CMC are about twice increasing from the first to the second steps and slightly even up from the second to the fourth steps. After the fourth step of etherification, D.S.'s of the etherification product are 1.782, 1.689, 1.712, 1.703 and 1.480 (see Table 4 and Figure 10). That is D.S.'s of Na-CMC seem to be higher with 4 repetitions of etherification (see curve no. (1)-(5) in Figure 10). However, the increasing of D.S.'s are considerably slow and time consumed in order to obtain the products with expected high D.S..

Considering ME-EtOH as reaction medium, the change of D.S.'s of Na-CMC from the first to second steps is approximately two times as ones obtained with B-EtOH as reaction medium (see Table 4). It is also found that the change of D.S.'s of the products from various mixing ratio of methyl ethyl ketone with ethyl alcohol does not follow the same appearance as one previously described (see Figures 10 and 11). After the second step of etherification, some D.S. values of Na-CMC declines with repetition of etherification, (see Figure 11). The interpretation of our experimental result are as follows:

(a) For 50:50 ME-EtOH as reaction medium, the D.S.'s of Na-CMC increase from 0.731 to 1.825 with 3 repetitions of etherification but it is lower to 1.756 at the fourth step. Thus, the etherification has to be discontinued.

Table 4 A list of degrees of substitution of sodium carboxymethylcellulose obtained by multistep of etherification of purified cellulose derived from 10% NaOH digestion at 10 lbs /in^2 pressure for 2 hours.

Etherification step	D.S.				
	Mixing ratio of reaction medium				
	50:50	60:40	70:30	80:20	90:10
Benzene : Ethyl alcohol					
1	0.837±0.010	0.762±0.009	0.747±0.009	0.716±0.009	0.587±0.007
2	1.646±0.018	1.460±0.016	1.494±0.017	1.469±0.016	1.213±0.014
3	1.724±0.019	1.632±0.018	1.645±0.018	1.641±0.018	1.471±0.016
4	1.782±0.010	1.689±0.019	1.712±0.019	1.703±0.019	1.480±0.015
5	-	-	-	-	-
Methyl ethyl ketone : Ethyl alcohol					
1	0.731±0.009	0.783±0.009	0.795±0.009	0.817±0.010	0.816±0.010
2	1.748±0.019	1.675±0.019	1.786±0.020	1.895±0.021	1.720±0.019
3	1.825±0.020	1.746±0.019	1.626±0.018	1.730±0.019	1.632±0.018
4	1.756±0.020	1.834±0.020	-	-	-
5	-	-	-	-	-

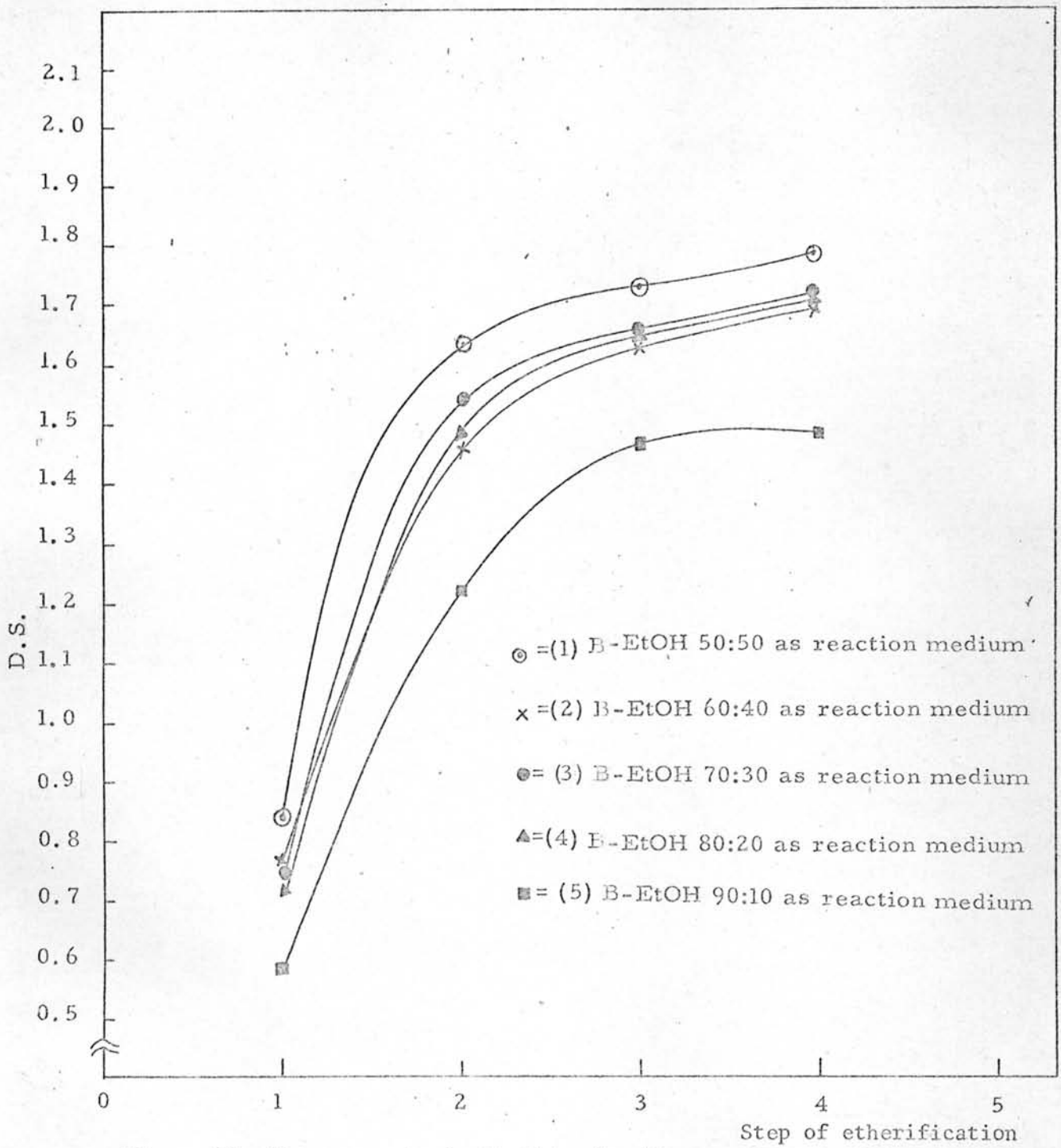

Figure 10. Degrees of substitution of sodium carboxymethylcellulose obtained from multistep of etherification, using mixture of benzene and ethyl alcohol as reaction media and 7 days for each etherification step.

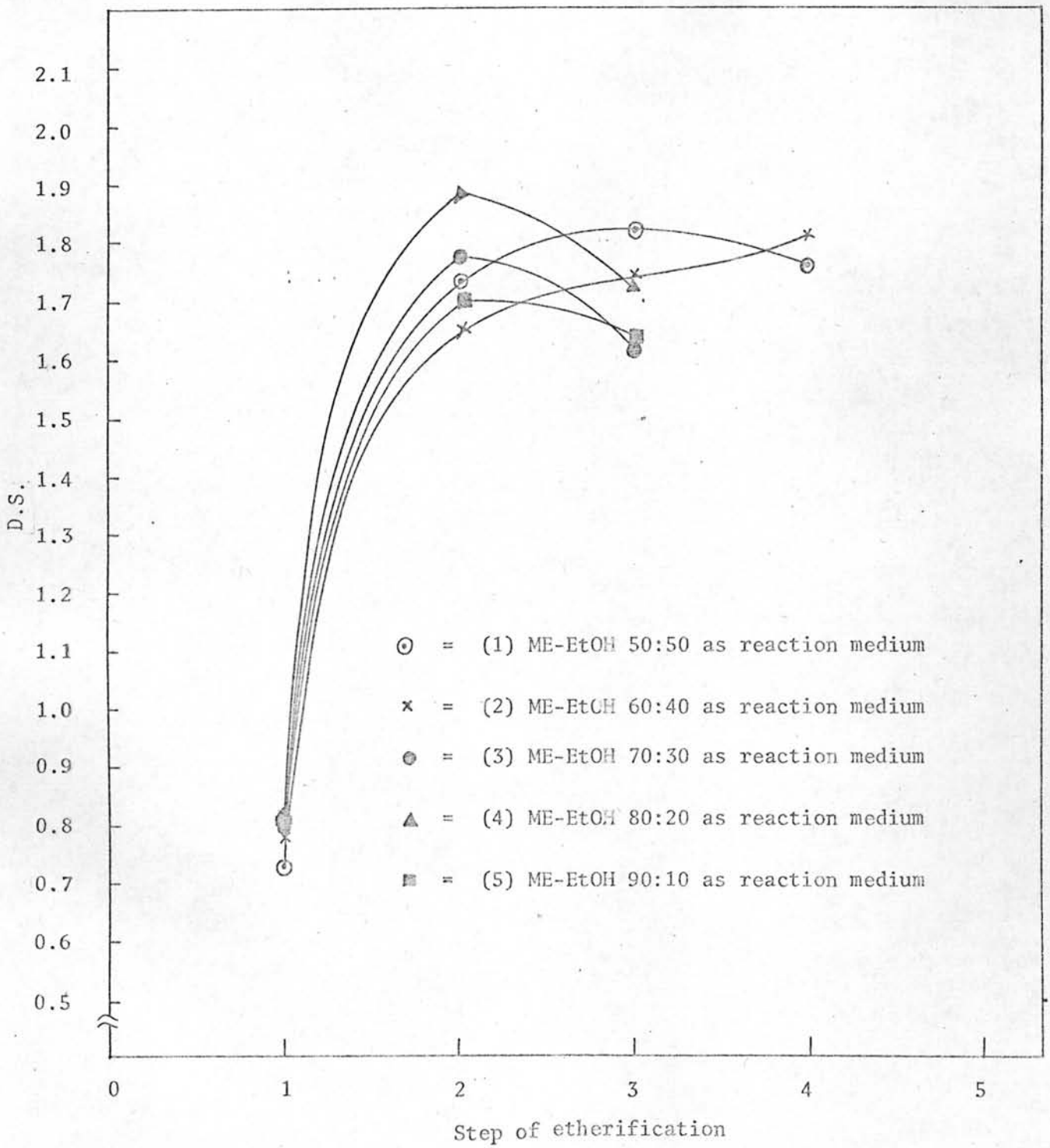

Figure 11. Degrees of substitution of sodium carboxymethylcellulose obtained from multistep of etherification, using mixture of methyl ethyl ketone and ethyl alcohol as reaction media and 7 days for each etherification step.

(b) For 60:40 ME-EtOH as reaction medium, D.S.'s of the products increase with 4 repetitions of etherification as similar to ones obtained in B-EtOH (see curve no. (2) in Figure 11). Though D.S. of the product seems to increase with repetition of etherification, the lump-formation of Na-CMC occurs after the fourth step which is very difficult for being etherified. It is, therefore, ceased to cary on further step of etherification.

(c) For 70:30 ME-EtOH, 80:20 ME-EtOH and 90:10 ME-EtOH as reaction media, D.S.'s of the products leading to their maxima after the second step of etherification are 1.786, 1.895 and 1.720 respectively (see Table 4). Again, decreasing of D.S.'s occurs after performing 3 repetitions of etherification (see curves no. (3), (4) and (5) in Figure 11).

According to (a), (b) and (c),it seems to fail to use the technique of multistep of etherification in order to increase D.S. to one that close to the theoretical maximum value (D.S. = 3.0). The higest D.S. obtained at this point is less than 2.0. It is only 1.895 from 80:20 ME-EtOH as reaction medium and it is not satisfactory.

After considering the results obtained in Table 4, the 3 values of high D.S. are 1.895, 1.834 and 1.825 from 80:20 ME-EtOH, 60:40 ME-EtOH and 50:50 ME-EtOH as reaction media respectively. It is no doubt that the rest of D.S. values presented in Table 4 are not of interest. Among the 3 values of high D.S., the conditions used for one with D.S. 1.895 is our first choice of consideration for finding a way in order to

raise the D.S. value. The reason is not only the highest D.S. value but also the preparation required less period of time. That is, 14 days of reaction time is needed for product with D.S. 1.895 whereas 28 and 21 days of reaction times are required for products with D.S.'s 1.834 and 1.825 respectively. Besides, Na-CMC lump with D.S. 1.834 is not suitable for using as starting raw material for further etherification. In addition, the product with D.S. 1.825 is decreased its D.S. value after repetition of etherification (1.825 to 1.756). Because of less time consuming and of less chemical and reagent expense, it may be a worth decision to use product with D.S. 1.895 as starting raw material. In other words, the best choice should be one with not only good yield but also economic.

Since product with D.S. 1.895 is one of our interest, the condition and physical parameters involved in the process of preparation must be carefully considered in order to obtain a suitable condition for preparing Na-CMC with high D.S.. However, the 80:20 mixing ratio of methyl ethyl ketone with ethyl alcohol is favor for using as reaction medium . According to Table 4. and curve no. (4) in Figure 11, D.S. value of the product decreases from 1.895 to 1.730 and lump formation of Na-CMC occurs. Therefore, it is obviously impossible to even up the D.S. value by technique of multistep of etherification with keeping reaction condition unchanged. Because of lump

formation of Na-CMC and after careful considering the physical parameters involved in the process of preparation, shorter period of reaction time of each step is first decided as one of reaction conditions for conducting an other new experiment. At this step, the reaction conditions used for multistep of etherification are 80:20 ME-EtOH as reaction medium with 5 day reaction time for each step of etherification and the etherification product must be oven-dried in order to prevent lump-formation of the product. The results obtained under new reaction conditions with multistep of etherification are shown in Table 5 and in graphical representation (see Figure 12).

Table 5 A list of degrees of substitution of sodium carboxymethylcellulose obtained after 5 days for each etherification step and with 80:20 ME-EtOH as reaction medium

	Step 1	Step 2	Step 3	Step 4	Step 5
D.S.	0.811±0.009	1.740±0.020	2.564±0.030	2.665±0.030	2.767±0.031

The D.S. values of the products are sharply increased from the first step through the third step and then about 3.94 to 3.84% increasing from the third step to the fourth step and

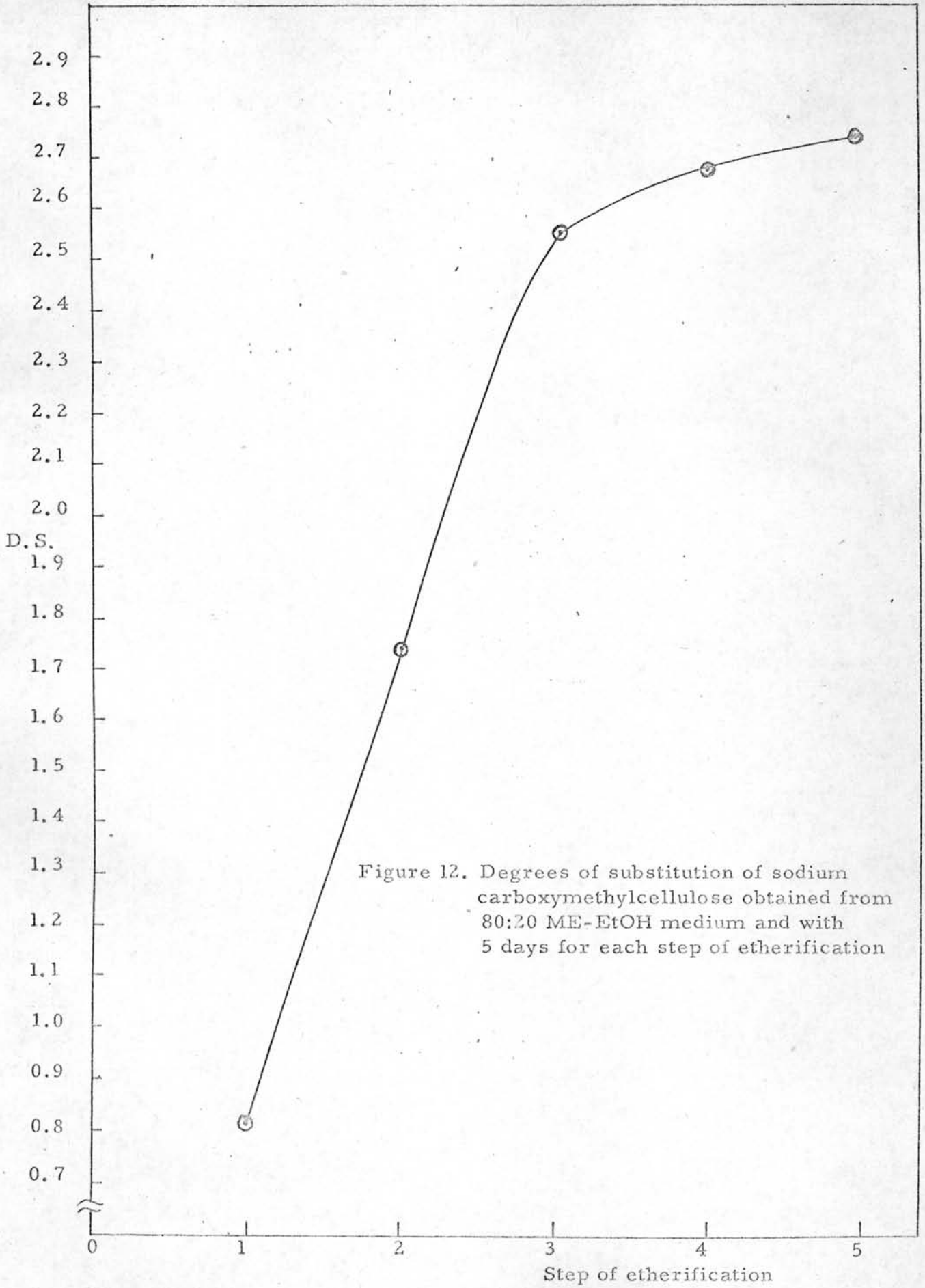

Figure 12. Degrees of substitution of sodium carboxymethylcellulose obtained from 80:20 ME-EtOH medium and with 5 days for each step of etherification

from the fourth step to the fifth step respectively. After the fifth step, the product is hard lump with D.S. = 2.767±0.131. Though its D.S. can not be brought closely to a theoretical maximum D.S. for substitution of cellulose (D.S. = 3.0), the result at this step is satisfactory because its D.S. value is 0.233 less than such theoretical value and much higher than one of generally commercial available Na-CMC (0.65 to 0.85). The product obtained is easily totally soluble in water to give a clear and homogeneous solution.