

An improved process for the preparation of sodium cellulose sulphate

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Abstract

Based on the reaction mechanism of cellulose sulphation, an improved process for the preparation of sodium cellulose sulphate (NaCS) was developed, in which the reaction solution could be regenerated by adding fuming H_2SO_4 (oleum) and/or normal H_2SO_4 and used many times. The NaCS prepared in this process showed the same qualities as that obtained with fresh reaction solution. This regeneration method successfully improved the process of production of NaCS, i.e. the costs of production and corrosive waste were greatly reduced. © 2000 Published by Elsevier Science S.A.

Keywords: Sodium cellulose sulphate; Cellulose sulphation; Poly-dimethyl-diallyl-ammonium-chloride; Immobilization

1. Introduction

Sodium cellulose sulphate (NaCS) and poly-dimethyl-diallyl-ammonium-chloride (PDMDAAC) can form a novel capsule for the immobilization of micro-organisms, enzymes, animal and plant cells etc. NaCS is a biologically compatible material [1–4]. From the viewpoint of immobilization, the preparation method of NaCS developed previously [5–7] is the only acceptable process. In this preparation, linters, which is a product of cotton processing, is used as the cellulose material and a mixture of H_2SO_4 and *n*-propanol is used as the reaction solution. As linters has a large ratio of volume to weight, more of reaction solution than cellulose is needed in the sulphation. Usually, 1 kg of cellulose requires at least 20 kg of reaction solution. Thus, a large amount of reaction solution is exhausted as waste after sulphation, leading to high costs of production and a heavy load for the environment. It is therefore important to reuse the reaction solution.

Based on positive results [8], in which the re-strained reaction solution was applied again without regeneration, the

sulphation mechanism and possible regeneration methods for the reaction solution (as well as the other three wastes in this work) are discussed, and a recycling process is established, in which the reaction can be carried out with the smallest quantity of waste and the lowest operating cost.

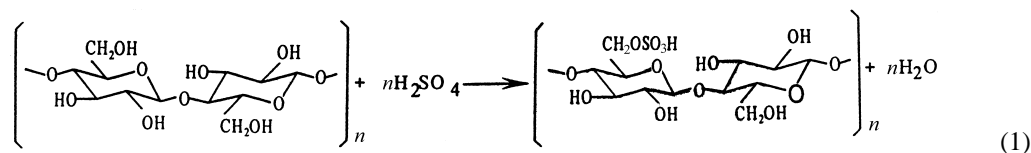
2. Description of process and mechanism of cellulose sulphation

2.1. Process for the preparation of NaCS

The improved process for the preparation of NaCS, in which a mixture of H_2SO_4 and *n*-propanol is used as the reaction solution, is presented in Fig. 1. In this process, the important point is the regeneration of the re-strained reaction solution and the recycling of other wastes.

2.2. Reaction mechanism of cellulose sulphation

Cellulose sulphation is the most important step in the preparation of NaCS. The reaction is



This reaction mechanism has been proven previously [9]. The conversion ratios of cellulose and the yield of NaCS

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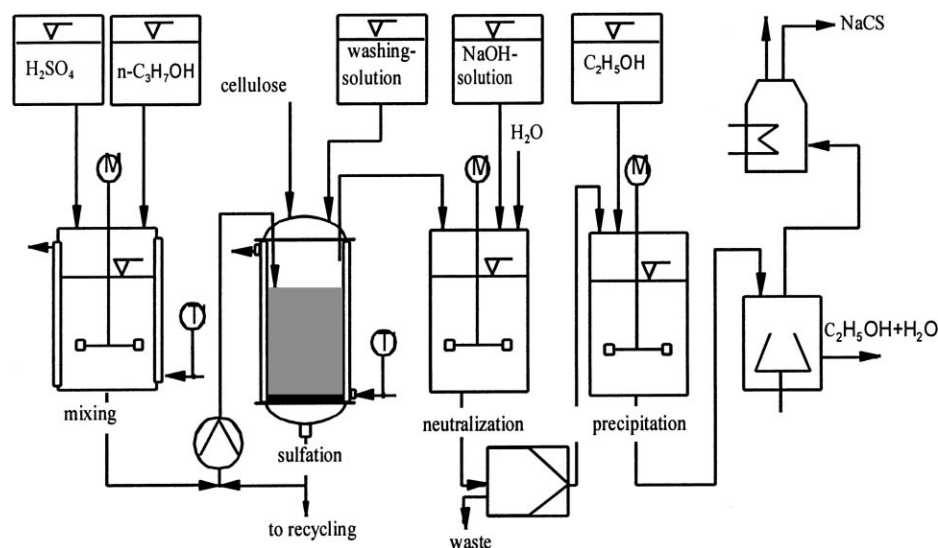
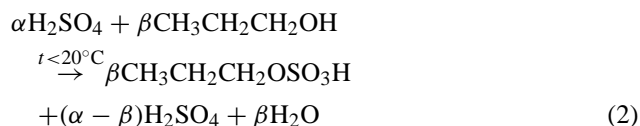


Fig. 1. Improved process for the preparation of sodium cellulose sulphate.

were increased with increasing concentration of H_2SO_4 (C_S) in the reaction solution. The reaction solution is formed as follows:



This mixture contains, in principle, four components: H_2SO_4 , $n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$, H_2O and $n\text{-C}_3\text{H}_7\text{OH}$. However, H_2SO_4 is surplus to $n\text{-C}_3\text{H}_7\text{OH}$, and thus, the content of $n\text{-C}_3\text{H}_7\text{OH}$ in the reaction solution is negligible. On account of the presence of H_2SO_4 and H_2O in the solution, undesired reactions, such as carbonization or hydrolysis etc., may take place during sulphation. However, these undesired reactions can be greatly reduced at the chosen experimental conditions of $T = -5\text{--}5^\circ\text{C}$, $t < 5\text{ h}$, $C_S = 20\text{--}35\%$ (w/w) and H_2O content $< 11\%$ (w/w).

2.3. Variation of composition in the reaction solution

Cellulose sulphation is a solid–liquid reaction, in which more than 20-fold in weight of the reaction solution than cellulose is required. Approximately 5% of H_2SO_4 is expended during sulphation, and approximately 75% of

the reaction solution is exhausted after sulphation. The re-strained reaction solution still has a high content of H_2SO_4 . Other compositions in the reaction solution change slightly.

In cellulose sulphation, shown in Eq. (1), part of H_2SO_4 is expended and an equivalent amount of H_2O is produced. The concentrations of all components in the regenerated reaction solution should be the same as those in fresh reaction solution. As these components, except for H_2SO_4 , only play a dilution role, a few changes in concentration will not affect the sulphation. Therefore, the main task of regeneration is that the concentration of H_2SO_4 must be recovered to the initial value in fresh reaction solution. The compositions of the reaction solution are listed in Table 1.

2.4. Regeneration of the reaction solution

If the re-strained reaction solution is to be renewed, the concentration in this solution $C_{b,j}$ ($j = \text{S, P, H}$ and E) ought to be regenerated to $C_{a,j}$, where a and b indicate the re-strained and fresh reaction solutions, respectively, and S, P, H and E indicate H_2SO_4 , $n\text{-C}_3\text{H}_7\text{OH}$, H_2O and $n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$, respectively.

The material balances of all components can be expressed in the following matrix:

Table 1
Changes in the composition of the reaction solution

	$n\text{-C}_3\text{H}_7\text{OH}$ (P)	H_2SO_4 (S) (mol)	H_2O (H) (mol)	$n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$ (E) (mol)
Before sulphation (a)	0	α	β	γ
After sulphation (b)	0	δ^a	$\beta + \delta$	γ

^a δ is the mole number of expended H_2SO_4 in the sulphation.

$$\begin{bmatrix} C_{b,S} & C_{S,S} & C_{P,S} - f C_{P,P} \frac{M_S}{M_P} \\ C_{b,H} & C_{S,H} & C_{P,H} + f C_{P,P} \frac{M_H}{M_P} \\ C_{b,P} & C_{S,P} & (1-f) C_{P,P} \\ C_{b,E} & C_{S,E} & C_{P,E} + f C_{P,P} \frac{M_E}{M_P} \end{bmatrix} \begin{bmatrix} W_b \\ W_S \\ W_P \end{bmatrix} = \begin{bmatrix} C_{a,S} W_a \\ C_{a,H} W_a \\ C_{a,P} W_a \\ C_{a,E} W_a \end{bmatrix} \quad (3)$$

where $C_{a,j}$, $C_{b,j}$ and $C_{i,j}$ ($i=S$ and P , $j=S$, P , H and E) are the concentrations of component j in the renewed reaction solution, in the re-strained reaction solution and in the row material i , respectively, M_j is the molecular weight of component j , W_a , W_b and W_i are the quantities of the renewed reaction solution, the re-strained reaction solution and the row material i , respectively, $W_{a,j}$, $W_{b,j}$ and $W_{i,j}$ are the quantities of component j in the renewed solution, the re-strained solution and the row material i , respectively, and f is the conversion factor from $n\text{-C}_3\text{H}_7\text{OH}$ to $n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$.

As $f=1$, and $C_{b,P}$, $C_{S,P}$, $C_{a,P}$, $C_{S,E}$, $C_{P,E}$, and $C_{P,S}$ are 0, Eq. (3) can be simplified to

$$\begin{bmatrix} C_{b,S} & C_{S,S} & C_{P,S} - C_{P,P} \frac{M_S}{M_P} \\ C_{b,H} & C_{S,H} & C_{P,H} + C_{P,P} \frac{M_H}{M_P} \\ C_{b,E} & 0 & C_{P,P} \frac{M_E}{M_P} \end{bmatrix} \begin{bmatrix} W_b \\ W_S \\ W_P \end{bmatrix} = \begin{bmatrix} C_{a,S} W_a \\ C_{b,H} W_a \\ C_{a,E} W_a \end{bmatrix} \quad (4)$$

$C_{b,S}$, $C_{S,S}$, $C_{P,S}$, $C_{P,P}$, $C_{b,H}$, $C_{S,H}$, $C_{P,H}$ and $C_{b,E}$ in Eq. (4) are known, and $C_{a,S}$, $C_{a,H}$ and $C_{a,P}$ are the objective concentrations. Three other variables, W_b , W_S and W_P , can be calculated in Eq. (4) with the given W_a . If W_b is known, W_S and W_P can also be determined in Eq. (4).

3. Materials and experimental details

3.1. Materials

Linters is chosen as the cellulose material (product of cotton) with $DP=1000\text{--}1600$. H_2SO_4 is used as an AP agent with a concentration of 95–97%. Oleum is 20% fuming sulphuric acid. $n\text{-C}_3\text{H}_7\text{OH}$ is also an AP agent with a purity of better than 99%.

Table 2

Composition of the reaction solution before and after sulphation

Component	Quantity (g)		Concentration (wt.%)		Concentration (mol l^{-1})	
	Before sulphation	After sulphation	Before sulphation	After sulphation	Before sulphation	After sulphation
$n\text{-C}_3\text{H}_7\text{OH}$	0	0	0	0	0	0
H_2SO_4	315.04	284.79	31.5	29.20	4.481	4.189
H_2O	104.66	110.22	10.47	11.30	8.102	8.601
$n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$	580.30	580.03	58.03	59.50	5.775	5.972

3.2. Regeneration of wastes

The reaction solution is the most important waste, which can be regenerated by adding H_2SO_4 , oleum or a mixture of H_2SO_4 and oleum. The unreacted cellulose can be sulphated again. The washing solution is neutralized to recover $n\text{-C}_3\text{H}_7\text{OH}$. The precipitation solution is distilled to recover ethanol.

3.3. Reaction kinetics

Cellulose sulphation kinetics in the regenerated reaction solution were measured in our apparatus [9]. Three tests were performed as follows:

1. The sulphation was carried out continuously three times with the reaction solution at -5°C . Only in the first test is the reaction solution fresh, and the reaction solutions in the second and third tests come from the preceding test. Correspondingly, the reaction time is increased by 30 min.
2. The sulphation was carried out with the reaction solution, which was regenerated by adding H_2SO_4 .
3. The sulphation was carried out with the reaction solution, which was regenerated by adding oleum.

3.4. Preparation of NaCS with the regenerated reaction solution

NaCS was prepared with the regenerated solution in the improved process shown in Fig. 1. Furthermore, the properties of NaCS were measured for comparison with those of NaCS produced with the fresh reaction solution.

4. Results and discussion

4.1. Regeneration of the reaction solution

It is known that the composition of the reaction solution varies throughout the sulphation. This variation is shown in Table 2 (here at a condition of 50 g of linters to 1000 g of reaction solution).

The general example, which is described in Eq. (5), is to add a mixture of oleum (=103.75% H_2SO_4) and H_2SO_4 (96%).

$$\begin{bmatrix} 29.20 & 96\alpha + 103.15(1 - \alpha) & -100 \times \frac{98}{60} \\ 11.30 & 4\alpha - 3.75(1 - \alpha) & 100 \times \frac{18}{60} \\ 59.50 & 0 & 100 \times \frac{140}{60} \end{bmatrix} \begin{bmatrix} W_b \\ W_S \\ W_P \end{bmatrix} = \begin{bmatrix} 31.50W_a \\ 10.47W_a \\ 58.03W_a \end{bmatrix} \quad (5)$$

$$\frac{K}{b\sqrt{(K/b)^2 + 4}} \ln \left[\frac{(\sqrt{(K/b)^2 + 4} + 2\sqrt{1 - X} + (K/b))(\sqrt{(K/b)^2 + 4} - 2 - (K/b))}{(\sqrt{(K/b)^2 + 4} + 2 + (K/b))(\sqrt{(K/b)^2 + 4} - 2\sqrt{1 - X} - (K/b))} \right] + \ln \left(\sqrt{1 - X} - \frac{bX}{K} \right) = -\ln \left(1 + \frac{b}{a}t \right) \quad (9)$$

where α (≤ 1) is the weight ratio of H_2SO_4 to oleum in the mixture. If $\alpha=1$, the mixture is composed of only H_2SO_4 , and if $\alpha=0$, the mixture is oleum. Three cases are discussed:

1. When $\alpha=0$, the solution of Eq. (5) is $W_b=0.9042W_a$, $W_P=0.0181W_a$ and $W_S=0.0777W_a$. If 1000 g of regenerated reaction solution (W_a) is to be regenerated, it requires 904.2 g of re-strained reaction solution, 181.1 g of 100% $n-C_3H_7OH$ and 77.7 g of oleum.
2. When $0 < \alpha < 1$, the calculated result is $W_b=0.8196W_a$, $W_P=0.0397W_a$ and $W_S=0.1407W_a$ at $\alpha=0.5$.
3. When $\alpha=1$, the reaction solution is regenerated by adding H_2SO_4 . The calculated result of Eq. (5) is $W_b=0.0W_a$, $W_P=0.2487W_a$ and $W_S=0.7513W_a$. This means that the regenerated solution does not need the re-strained solution, or it is not possible to recover the concentrations of all components back to the initial values, because the water content in the re-strained reaction solution is higher than that in the fresh reaction solution. In fact, the H_2SO_4 concentration is an important controlling component. If the concentrations of other compositions are not considered, Eq. (4) can be simplified as follows:

$$C_{a,S}W_a = C_{b,S}W_b + C_{S,S}W_S - C_{P,P} \frac{M_S}{M_P} W_P \quad (6)$$

$$W_a = W_b + W_S + W_P \quad (7)$$

$$100 = C_{a,S} + C_{a,H} + C_{a,E} \quad (8)$$

If $W_b/W_a=0.75$ (i.e. 75% reaction solution is re-strained after sulphation), then $W_P=0.0555W_a$ and $W_S=0.1945W_a$; thus, the concentrations of the regenerated reaction solution are $C_{a,S}=31.50\%$, $C_{a,H}=10.92\%$ and $C_{a,E}=57.58\%$. By comparison of the concentrations in this solution with those in the fresh reaction solution, 0.45% of the concentration of H_2O is increased, 0.45% of the concentration of ester is reduced and the concentration of H_2SO_4 is maintained constant. These small changes should not affect further sulphation. However, the advantage is clear, i.e. all parts of the

re-strained reaction solution are applied again in the process of the preparation of NaCS.

4.2. Kinetics of cellulose sulphation with the regenerated reaction solution

The kinetic model developed for cellulose sulphation, which is described in Eq. (9), satisfies cellulose sulphation with the fresh reaction solution:

where

$$K = 2.5159 \times 10^{10} \exp \left(-\frac{77386.7}{RT} \right) C_S^3 \quad (10)$$

$$a = 5.43 \times 10^{-2} + 3.67 \times 10^{-4}(T - 273.15) + [-0.107 + 4.58 \times 10^{-4}(T - 273.15)]C_S \quad (11)$$

$$b = -3.17 \times 10^{-3} + 1.09 \times 10^{-5}(T - 273.15) + [-3.60 \times 10^{-3} + 1.47 \times 10^{-5}(T - 273.15)]C_S \quad (12)$$

It will be proven, using three different experiments, whether Eq. (9) is valid for the recycled reaction solution:

1. The sulphation was carried out continuously three times with the reaction solution at $-5^\circ C$.
The fresh reaction solution was used in the first test. The reaction solutions in the second and third tests came from the preceding test. Correspondingly, the reaction time was increased by 30 min. The conversion ratios of cellulose in the three tests are shown by the filled bars in Fig. 2, and the values calculated by Eq. (9) are also shown in Fig. 2. The sulphation can be carried out with the re-strained reaction solution.
2. The sulphation was carried out with the solution regenerated by adding H_2SO_4 at $T=-5^\circ C$ for 150 min. The conversion ratios are shown in Fig. 3.
3. The sulphation was carried out with the solution regenerated by adding oleum. The conversion ratios are increased with increasing quantity of oleum as shown in Fig. 3.

At the same time, the yield of NaCS and the degree of substitution (DS) for the above three cases were measured and calculated, and they showed the same tendency.

The results from the three tests illustrate that the re-strained solution can be applied in the preparation of cellulose sulphate not only by increasing the reaction time but also by regeneration by adding H_2SO_4 and/or oleum. Furthermore, it is proven that the presented kinetic model can be calculated in many cases of cellulose sulphation.

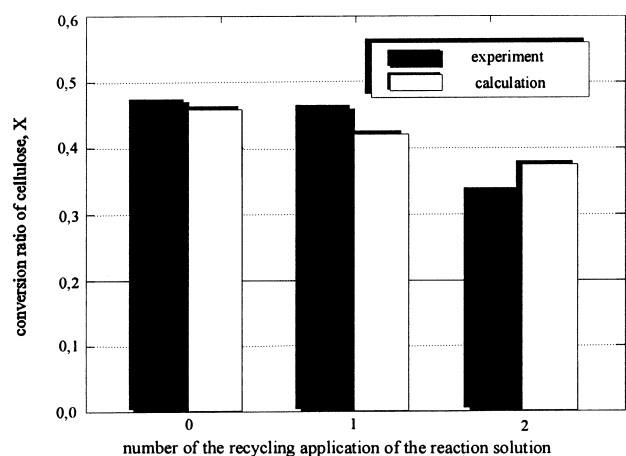


Fig. 2. Conversion ratios of cellulose with the non-regenerated reaction solution by increasing the reaction time.

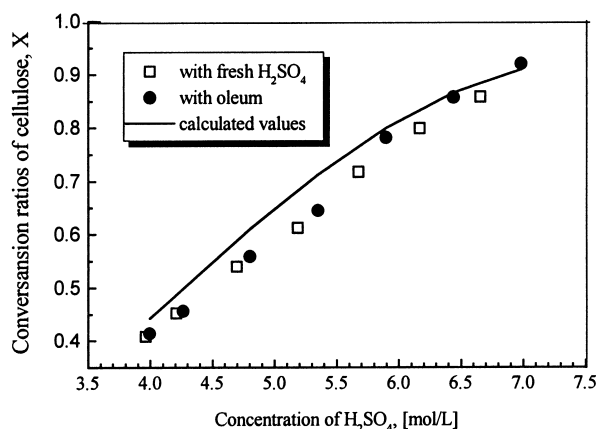


Fig. 3. Conversion ratios of cellulose using the regenerated reaction solution by adding different quantities of H₂SO₄ and oleum.

4.3. Production of NaCS with regenerated reaction solution

NaCS was prepared with the regenerated reaction solution under suitable reaction conditions. The average values of the conversion ratios, yields and DS from six tests are listed in Table 3, and they are almost the same as those with fresh reaction solution. The other properties of the prepared NaCS, such as the viscosity of an NaCS aqueous solution, the mechanical stability of an NaCS–PDMDAAC

Table 3
Conversion ratios of cellulose, yield of NaCS and degree of substitution with fresh and regenerated reaction solution

	With fresh reaction solution	With regenerated reaction solution	Calculated values
Conversion ratios of cellulose, X	0.5066	0.4943	0.5442
Yield of NaCS, Y	0.6330	0.6139	0.6878
Degree of substitution, DS	0.396	0.377	0.419

capsule and the transfer behaviour of glucose through an NaCS–PDMDAAC membrane, were determined and they show similar results [1,10].

Based on the above results, a larger apparatus was designed, in which 1 kg NaCS could be produced and the reaction solution was regenerated according to the above method. Five batches of NaCS were produced and they showed similar behaviour.

4.4. Recycling of other wastes

The recycling of cellulose material is not successful because of the lower viscosity and poor encapsulation properties of the prepared NaCS. However, it is clean and non-toxic, and represents a minor load on the environment. The washing solution can be either regenerated to the reaction solution by adding H₂SO₄ and/or oleum or neutralized to recover *n*-C₃H₇OH. The precipitation solution contains a large amount of ethanol and more than 70% ethanol can easily be recovered. The results are satisfactory.

5. Conclusions

An important point in the modern chemical industry is that processes should be carried out under conditions which yield little or no load on the environment. The biggest problem in the scale-up of NaCS production is the recycling of the reaction solution and other wastes. Therefore, the regeneration method in this work is a successful step in the achievement of this goal. The advantages are clear: similar quality of product, small environmental load and low production costs. It has been proven by the results obtained that regeneration of the re-strained reaction solution is valuable both in theory and in practice.

6. Nomenclature

$C_{a,j}$	concentration of component j in the renewed solution (kg kg ⁻¹)
$C_{b,j}$	concentration of component j in the re-strained solution (kg kg ⁻¹)
$C_{i,j}$	concentration of component j in row material i ($i=S$ and P , $j=S$, P , H and E) (kg kg ⁻¹)
f	coefficient of the conversion of n -C ₃ H ₇ OH to n -C ₃ H ₇ OSO ₃ H
M_j	molecular weight of component j
W_a	quantity of the renewed solution (kg)
W_b	quantity of the re-strained solution (kg)
W_i	quantity of the row material i (kg)
$W_{a,j}$	quantity of component j in the renewed solution (kg)
$W_{b,j}$	quantity of component j in the re-strained solution (kg)
$W_{i,j}$	quantity of component j in row material i (kg)

Subscripts

a	the renewed solution
b	the re-strained solution
E	$n\text{-C}_3\text{H}_7\text{OSO}_3\text{H}$
H	H_2O
P	$n\text{-C}_3\text{H}_7\text{OH}$
S	H_2SO_4

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