Theoretical Aspects of the Technology in Synthesis of Sodium Carboxymethyl Cellulose from Various Raw Materials

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Received 4 July 1999; accepted 27 January 2001

ABSTRACT

Some peculiarities of the technology in synthesis of sodium salt of carboxymethyl cellulose from various cellulose containing raw materials have been considered and discussed. The wastes of cotton-gin plants and their mixtures with viscose cellulose were used as raw materials. It has been predicted and experimentally confirmed that for preparation of product with high homogeneity on degree of substitution and molecular mass, the basic criterion is the rate of mass-diffusion of solid phase, providing approximately the same concentration of alkali exists in all points of cellulose raw materials during its treatment with aqueous solution of sodium alkali. The increase of mass-diffusion of raw materials by addition of microaccelerator has been predicted and experimentally proved. An adequate mathematical model of the relationship of the parameters of cellulose raw materials mass-diffusion and chemical reaction by taking into account the form coefficient of non-globular particles has been developed and examined. The practical confirmation for results of theoretical investigations has been presented.

Key Words: mass-diffusion, degree of substitution, product homogeneity, form coefficient, 100% alkali

INTRODUCTION

The interest in the technology of the synthesis of sodium-carboxymethyl cellulose (Na-CMC) has been developed, as it has a wide range of applications in medicine, oil-extraction, construction and domestic products. This is related to the fact that Na-CMC is water-soluble and a biodegradable polymer [1], which provides its ecological friendliness. These properties served as the basis for expansion of application fields of Na-CMC, in particular, the technology of granules capsulation of mineral fertilizers and other particulate materials [2].

The expensive viscose or cotton cellulose [3] is the raw materials for industrial production of Na-CMC. The substitution of the part of viscose cellulose

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by wastes of cotton-gin factories is important from the points of view both economy and ecology [4, 5]. That is why the development of scientific principles of the process of Na-CMC synthesis from various raw materials has an unquestionable theoretical and practical value.

Some theoretical and practical peculiarities for the technology of Na-CMC synthesis from viscose cellulose and wastes of cotton-cleaning plants and also from their mixtures are discussed in this paper.

The technology of the synthesis of Na-CMC from raw materials mixtures or cotton wastes has certain problems [6, 7] connected with low rate of the process and impossibility of preparation of product with high homogeneity on some qualitative indices due to low reactivity and mass-diffusion of cotton cellulose and cotton wastes during their treatment with aqueous solution of potassium hydroxide. It has been established as a result of experiments that, with the use of raw materials mixtures of complete cotton wastes, the arising problems may be solved by means of addition of microaccelerator for mass-diffusion.

Therefore, the development of mathematical model for regulation of the degree of substitution and molecular mass of Na-CMC, would provide the preparation condition for the most homogeneous products on the above-mentioned main indices can expand its practical application such as food industry.

EXPERIMENTAL

The experiments for preparation of laboratory parts of Na-CMC were carried out batchwise in mono apparatus system the scheme of which has been presented in Figure 1. For alkaline treatment of initial cellulose the estimated amount of aqueous solution of sodium alkali and for carboxymethylation of the prepared sodium cellulose-sodium monochloroacetate in solid form was used.

In all experiments to a given amount of cellulose in continuous mixing was added an aqueous solution of sodium hydroxide. The mixing was carried for 2.5 h at 40–45 °C, temperature of the reaction. Then, with the aim of alkylation of alkaline cellulose,

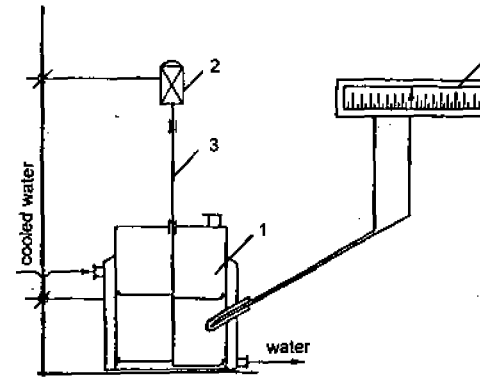

Figure 1. Laboratory apparatus for synthesis of Na-CMC: (1) reactor; (2) electromotor; (3) mixer; (4) device for temperature measurement.

sodium mono-chloroacetate was added after cooling the reaction mass to 22 °C. The final stage of the indicated reaction involved a 1 h esterification of the products of the reaction at temperature 70 °C accompanied with subsequent drying. The experimental samples of Na-CMC from viscose cellulose, cotton wastes and their mixtures in various ratios were synthesized in the laboratory apparatus.

The coefficients of mass-diffusion of cellulose containing raw materials were determined in laboratory apparatus the scheme of which has been presented in Figure 2. For this the weight of cellulose containing material was placed into glass tube 1 with known cross-section and length.

Tubes were placed into glass 2 filled with alkaline solution with known concentration. By means of indicator paper diffusion time on length of tube and concentration of alkali in definite distances from phases contact surface were determined by method of acid titration. On the basis of experimental data on Feak equation the coefficients of mass-diffusion of raw materials were calculated.

For determination of molecular mass of the prepared Na-CMC and content of carboxymethyl groups in their macrochain the part of product was purified from sodium chloride and other impurities by method of dissolution in water and reprecipitation in

water-alcohol solution. The molecular masses of cellulose and synthesized Na-CMC were determined by Mark-Houwink method [8].

In all experiments the relative concentration of alkali which was calculated as ratio of mass of 100% alkali (pure non-aqueous alkali) to mass of absolutely dry initial cellulose has been used.

The adequacy of the models for real process (Figure 4) has been confirmed by comparing them to experimental and calculated data.

RESULTS AND DISCUSSION

With the aim of study of influence of mass-diffusion on homogeneity of the product, we analyzed differential curves of density distribution of Na-CMC (ρ) on degree of substitution in polymer macromolecule with carboxymethyl groups (n_i/n) presented in Figure 3. As it follows from this figure, density distribution of products prepared from viscose and cotton cellulose on degree of substitution is sharply differed. In the first case the narrow distribution (curve 1) represents rather high homogeneity of Na-CMC synthesized from viscose cellulose, but in the second case (curve 2) the wide distribution indicates a non-homogeneity of the product synthesized from cotton wastes. This is connected as noted above, with low mass-diffusion rate of cotton cellulose, which is explained with its crystalline structure. In this case the duration of diffusion of alkaline solution in internal space of cellulose raw materials considerably exceeds chemical reaction time of formation of sodium cellulose. In other words, mass-diffusion of the second component of raw materials mixtures limits the chemical reaction rate during treatment of raw materials by alkaline solution.

Consequently, for acceleration of total process as a whole and preparation of product with high homogeneity it is required an acceleration of mass-diffusion of cotton wastes, which has been obtained

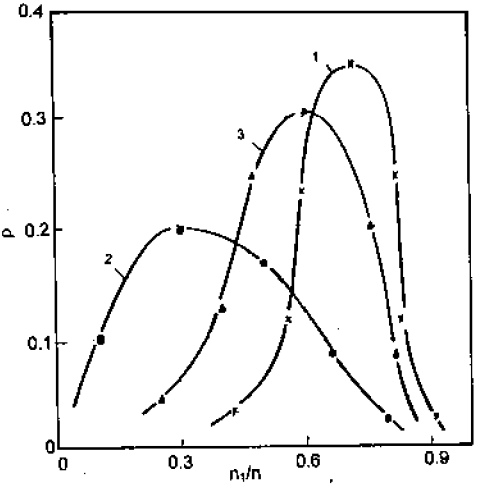

Figure 3. Differential curves of distribution density of Na-CMC on degree of substitution: (1) Na-CMC prepared from viscose cellulose; (2) from wastes of cotton-gin plants; (3) from wastes of cotton-gin plants with addition of mass-diffusion microaccelerator.

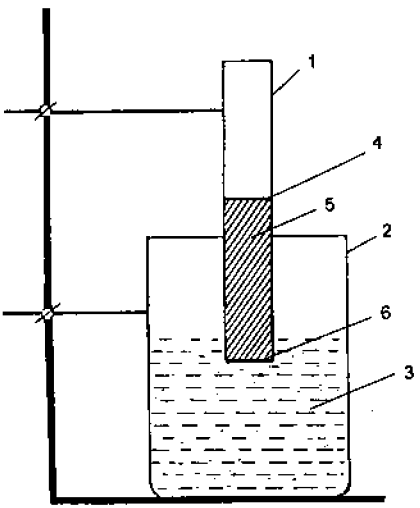

Figure 2. Laboratory apparatus for determination of coefficients of mass-diffusion, of cellulose raw materials in the systems -solid substance -liquid: (1) tube; (2) glass; (3) alkaline solution; (4) fixer of alkali; (5) cellulose containing material; (6) surface of phase contacts.

by means of addition of microaccelerator for molecular diffusion. The results of such approach have given the positive effects. As can be seen from curve 3 it is slightly differed from curve 1 on the range of density distribution.

In our case for preparation of more homogeneous Na-CMC the relative concentration of 100% sodium alkali in all points of volume of cellulose raw materials must not be less than 0.25 kg/kg which, mainly, depends on diffusion rate of the solution. Therefore, with the aim of study of some theoretical aspects of the advanced assumptions the necessity of the analysis of experimental curves of mass-diffusion of various cellulose-containing materials presented in Figure 4 arises. From these curves constructed without taking into account any chemical reaction, it is seen that in the course of diffusion depending on distance of phase surface, contact the concentration of sodium alkali is exponentially decreased. In this case for achievement in all points of raw materials of relative concentration of 100% alkali >0.25:kg/kg the high concentrations in the range of phase contact and values of mass-transfer coefficient of raw materials are necessary to achieve.

In Figure 4 the line 1 characterizes a theoretical case when diffusion rate is extremely high ($D=\infty$, $dC/dl\neq 0$) and in momentary time the equal concentrations of alkali (line 1, C=const, dC=0; $dl\neq 0$, dC/dl=0 are established in all points of raw materials. The direct line on Y-axis belongs to materials in which D=0, i.e. alkali diffusion is generally absent in high values of C_o. Between these lines all infinitely exponentially decreased curves characterize the real processes of internal mass-transfer of various materials. If the indicated curves are close to line 1, this shows a rather high mass-transfer rate of materials. Here, curve 2 characterizes the course of internal mass-diffusion of viscose cellulose, which confirms a sufficient high mass-diffusion rate of these raw materials. The curves 3 and 4 characterize the course of mass-diffusion of cotton cellulose without and with addition of micro-accelerator.

As it follows from analysis of these curves after addition of microaccelerator the mass-diffusion rate of cotton cellulose (curve 4) is displaced to the side of curve 2 which means approximate flattening of mass-diffusion rates of components of raw materials mixtures by means of rising of cotton component. It is theoretically possible to prepare absolute homogeneous product in high mass-diffusion rate which would be momentarily providing the same concentrations of alkali in any point of cellulose raw materials (curve 1). But this is practically impossible.

An analysis of data on mass-diffusion shows that the values of mass-transfer coefficient of viscose cellulose are three orders higher than that of cotton cellulose. However, after addition of microaccelerator these coefficients are approximately become equal.

A diffusion and chemical reaction are consecutive stages of total process of treatment of cellulose with sodium alkali. Therefore, in accordance with well-known method in this field, for studying the limiting stage they are first analyzed separately and then in combination.

Differential Feak equation on mass-transfer for analyzed systems is in the following form:

$$m_l \cdot C = -D \cdot \frac{dc}{dl} \cdot F_c \cdot \tau_d \qquad (1)$$

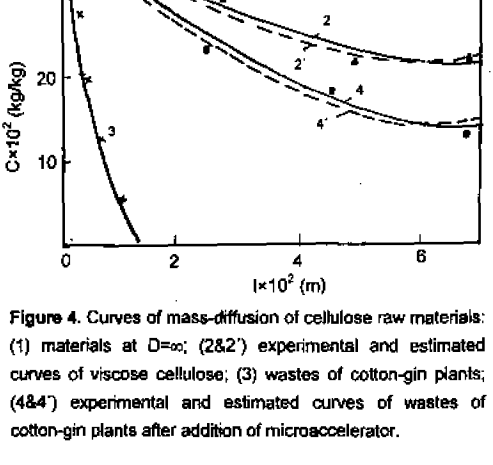

Figure 4. Curves of mass-diffusion of cellulose raw materials: (1) materials at $D=\infty$; (2&2') experimental and estimated curves of viscose cellulose; (3) wastes of cotton-gin plants; (4&4') experimental and estimated curves of wastes of cotton-gin plants after addition of microaccelerator.

By integration of eqn (1) taking into account the range in changes of variables we would have:

$$\ln\frac{C_d}{C_0} = -\frac{m_1 \cdot l_c}{D \cdot F_c \cdot \tau_d} \quad (2)$$

By solving eqn (2) with respect to C_d and τ_d we have:

$$C_d = C_0 \cdot \exp(-\frac{m_1 \cdot l_c}{D \cdot F_c \cdot \tau_d}) \quad (3)$$

$$\tau_d = -\frac{m_1 \cdot l_c}{2.3 \cdot D \cdot F \cdot \log\frac{C_d}{C_0}} \quad (4)$$

where

C: relative concentration of 100% sodium alkali (kg/kg); C_0 and C_d: relative concentrations of 100% sodium alkali on phase contact surface and in distance from surface contact (kg/kg); m_1: mass of layer in apparatus (kg); D: diffusion coefficient (kg/m.s); F_c: surface of phase contact in layer (m^2); τ_d: duration of the processes of intraphase transfer of sodium alkali (s); l_c: current distance from phase contact surface on direction of mass-transfer (m).

If surface of phase contact of a layer (F_c) is non-constant then it is changed depending on l_c. Then for particle of raw materials of any form the eqn (1) taking into account their coefficients may be in the following forms:

$$m_p \cdot C = -D \cdot \frac{dC}{dl} \cdot \frac{Fg}{\phi} \cdot \tau_d \quad (5)$$

$$\frac{4}{3} \cdot \pi \cdot R^3 \cdot \rho_r \cdot C = -D \cdot \frac{dC}{dR} \cdot \frac{4\pi R^2}{\phi} \cdot \tau_d \quad (6)$$

After simplification, division of variable and integration of differential eqn (6) we would have:

$$\ln\frac{C_d}{C_0} = -\frac{\rho_c \cdot \Phi}{6 \cdot D \cdot \tau_d}(R_0^2 - R_c^2) \quad (7)$$

Solving eqn (7) with respect to C_d or τ_d leads to the following expressions:

$$C_d = C_0 \cdot \exp[-\frac{\rho_c \cdot \Phi}{6.D.\tau_d}(R_0^2 - R_c^2)] \quad (8)$$

$$\tau_d = -\frac{\rho_c \cdot \Phi}{6 \cdot D \cdot 2.3 \log\frac{C_d}{C_0}}(R_0^2 - R_c^2) \quad (9)$$

where

Φ: coefficient of particles' form; F_g surface of globular particles of raw materials (m^2); m_p: mass of particles of raw materials (kg); R_0, R_c: initial and current radii of presented globular particles of raw materials (m). ρ_r: density of cellulose raw materials (kg/m^3).

When the particles of raw materials have a globular form, then in eqns (7), (8) and (9) it is necessary to have Φ=1. The eqns (7) and (9) describe the dependence of concentration of diffused alkali (C_d) and duration of mass-transfer in the particles of raw materials (τ_d) on technological and geometrical parameters of stage of alkali treatment of raw materials.

In the real conditions, the stage of treatment of cellulose raw materials with solution of sodium alkali proceeds in complicated manner. It consists of two consecutively proceeding processes: -internal transfer of alkaline solution and -chemical reaction with formation of sodium cellulose. As noted above, after addition of microaccelerator of mass-transfer, the physical process rate does not limit the total process. In this case as presented in eqn (3) the relative concentration of 100% alkali on surface of phase contact (C_0) providing the given concentrations (C_d>C_r) in all internal points of particles of raw materials necessary for proceeding the chemical process with normal rate are met. The kinetics of chemical reaction for the preparation of sodium cellulose in the first assumption may be described by equation of the first order [9]:

$$C_f = C_d \exp(-k\tau_r) \quad (10)$$

$$\tau_r = -\frac{1}{k} \cdot 2.3 \log\frac{C_f}{C_d} \quad (11)$$

where:

τ_r: duration of the process for chemical reaction in alkaline treatment of cellulose raw materials (s); K: rate constant of the chemical process (1/s); C_r: concentration of alkali necessary for proceeding of chemical process (kg/kg); C_f: final concentration of alkali (kg/kg). It might be noted that alkaline solution on eqn (3) is firstly transferred inside particles of cellulose material and then after achievement of alkali concentration >0.25 kg/kg its basic part as a result of chemical reaction is consumed for formation of sodium cellulose. Taking into account of the eqn (8), the expression (10) is transformed as the following:

$$C_f = C_0 \exp\{-[-\frac{\rho_c \cdot \Phi}{6 \cdot D \cdot \tau_d}(R_0^2 - R_c^2) + k\tau_r]\} \qquad (12)$$

On the basis of the eqns (9) and (11), the expression describing total duration of alkaline treatment of raw materials may be prepared:

$$\tau_t = \tau_d + \tau_r = -[\frac{\rho_r \cdot \Phi}{6D.2.3 \log\frac{C_d}{C_0}} \cdot (R_0^2 - R_c^2) + \frac{1}{k} \cdot 2.3 \log\frac{C_f}{C_d}] \qquad (13)$$

In eqn (10) with the constant values C_o, C_d and τ_r providing the reaction at temperatures 40–45 °C, the rate constant values (K) of the reaction for sodium alkali and cellulose raw materials presented also in Table 1 are calculated. The concluding analysis of data of this table shows that mass-transfer coefficient (D) for all raw materials and also for cotton cellulose after addition of microaccelerator is approximately one order higher than rate constants of the chemical process (K). This creates the favorable conditions for normal proceeding of total process according to consecutive mechanism with formation of highly homogeneous product. An insignificant difference between rate constant values of the chemical process for preparation of sodium cellulose from various raw materials is an evidence for that with the exception of diffusion barrier on the problem of homogeneity of

Table 1. Mass-diffusion coefficients and reaction rate constants in alkaline treatment of raw materials.

Cellulose containing materials	D (kg/m.s.)	K (s^{-1})
Viscose cellulose	2.03×10^{-2}	0.53×10^{-3}
Cotton wastes without addition of microaccelerator	1.25×10^{-5}	0.184×10^{-3}
Cotton wastes with addition of microaccelerator	0.69×10^{-2}	–
Raw materials mixtures after addition of microaccelerator	1.37×10^{-3}	0.45×10^{-3}

product may be successfully solved.

The balance equation for apparatus of continuous action may be presented as:

$$m_0 C_0 = m_l \frac{dC}{d\tau} + m_0 C_f \qquad (14)$$

$$m_0 C_0 = m_l \cdot k \cdot C_d + m_0 C_f \qquad (15)$$

By solving eqn (15) with respect to m_c we will have:

$$m_l = \frac{m_0(C_0 - C_f)}{k.C_d} \qquad (16)$$

where:

m_0: mass consumption of raw materials in apparatus (kg/s).

Eqn (16) allows the calculation of the mass of layer of cellulose material in apparatus (m_s) of continuous action providing existence of loaded reagents (m_0) in it with estimated time (τ_n).

With the aim of practical confirmation of theoretical precondition the laboratory experiments for the synthesis of Na-CMC by using three types of cellulose as raw materials have been carried out. The results have been presented in Table 2.

An analysis of data in Table 2 shows that with the same relative concentrations of 100% alkali on surface of phase contact (0.37 kg/kg) the duration of the process of alkaline treatment of cotton wastes without addition of microaccelerator is much higher in comparison with treatment of viscose cellulose and

Table 2. Some indices of the synthesized sodium carboxymethyl cellulose.

Raw materials	Duration of alkaline treatment (s)	Average degree of substitution (n/n)	Solubility in water (% by mass)	Content of basic material (% by mass)
Viscose cellulose without addition of micro-accelerator	54×10^2	0.74	99.8	62
Raw materials mixture (on 50% viscose and cotton cellulose) with addition of micro-accelerator	54×10^2	0.72	98.3	60
Cotton wastes with addition of micro-accelerator	54×10^2	0.70	98.1	59
Cotton wastes without addition of micro-accelerator	864×10^2	0.57	71.3	42

cotton wastes by addition of a microaccelerator. The effect of microaccelerator is also evident on the values of other qualitative indices presented in Table 2.

CONCLUSION

The wastes of cotton-gin plants of the Republic of Azerbaijan have been used as raw materials and the method of preparation of qualitative product with their use has been developed. It has been predicted and experimentally confirmed that an influence of mass-diffusion of raw materials in their alkaline treatment on homogeneity of CMC on qualitative indices; the decrease of mass-diffusion of raw materials by addition of a microaccelerator has been predicted and experimentally confirmed.

The limiting stage of total process of alkaline treatment of cotton wastes by comparison of coefficients of diffusion with reaction rate constants has been established. The mathematical model of total process taking into account the coefficient of form of non-globular particles and the interrelation between parameters of mass-diffusion of raw materials with the chemical reaction being developed.

The adequacy of model by comparison of the estimated and experimental curves has been confirmed, and the laboratory apparatus and the methods for determination of coefficients of mass-diffusion (diffusion of alkaline solution) of raw materials are created.

ACKNOWLEDGEMENTS

The authors of the paper thank professor A.A. Efendiev for discussion and valuable advices.

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