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Natural Cellulose: Biosynthesis and Structural Changes

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Abstract

In this research the kinetics of cellulose accumulation in growing cotton fibers due to biosynthesis has been studied. The kinetic curve had initial slow stage (up to 15 days after flowering, AF), fast stage (15 to 35 days AF) and final very slow stage (above 35 days AF). To describe such complex kinetics, equation of Avrami-Kolmogorov-Erofeev (AKE) was used: $C_t/C_m = 1 – \exp [-K (t – t_o)^n]$, where C_t is amount of cellulose accumulated in fibers for time t AF; C_m is maximum amount of cellulose in mature cotton fibers; K is effective rate constant; n is effective order of the process; t is time AF and t_o is induction period. The calculated parameters of AKE-equation are: t_o= 7 days AF, K= 5.94 x 10^{-3} and n=1.72. Since n>1, the process of cellulose biosynthesis is not limited by diffusion of monomers. The kinetic curve calculated by AKE-equation coincide with the experimental points, which confirms the adequacy this equation for describing the biosynthesis process of natural cellulose. Structural studies have shown, that crystalline structure of cellulose in immature fibers is low-ordered. However, with increase in duration of cotton maturation, additional crystallization of cellulose occurs.

Keywords: Growing cotton fibers; Biosynthesis; Cellulose accumulation; Crystalline structure; Kinetics; kinetic AKE-equation

1 Introduction

As known cellulose is a natural semicrystalline polysaccharide having long linear chains consisting of repeat anhydroglucose units in a “chair” conformation [1, 2]. The linear macromolecules joined by hydrogen bonds form supermolecular structure of cellulose that consists of thread-like elementary nanofibrils and their bundles called microfibrils. Within the elementary fibrils, ordered crystallites and disordered non-crystalline domains are present. Cellulose is the most abundant organic matter on Earth. The total resources of cellulose in nature reach one trillion tons [3]. Moreover, as a result of photo- and biosynthesis the mass of this biopolymer in nature increases approximately by 100 billion tons annually [4]. Cellulose is present in all land plants and some algae; cellulose enters also into the composition of the shells of a number of animals (e.g. tunicates); in addition, cellulose is synthesized by several microorganisms (e.g. *Gluconacetobacter xylinus*). Important sources of natural cellulose are cotton fibers containing above 90% of cellulose [5].

In plants, monomers of cellulose are synthesized in chlorophyll pigment from carbon dioxide and water absorbing quanta of red and blue-violet light [6, 7]. Photosynthesis is a complex, multistage process that is proceeding in two phases - light and the dark. The light phase occurs in the presence of light in the thylakoid membranes of chlorophyll, with the participation of electron transfer proteins, specific carrier NADP and ATP-synthase, the result of which is photolysis of water molecules, binding of formed hydrogen by NADP and release of oxygen. The dark phase proceeds without light with use of NADP • H_2 complex and carbon dioxide and their transformation to monomeric sugars with the participation of ATP. Summary process of photosynthesis of monomeric C_6-sugars can be described as follows:

$$6CO_2 + 6H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6O_2$$

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Further the monomeric sugars are polymerized into cellulose chains under the action of terminal enzymatic complex having rosette shape [8, 9]. The rosettes provide both intracellular polymerization of monomers with formation of cellulose macromolecules and also extracellular assembly of formed chains into crystalline nanofibrils [10].

A convenient object for studying the formation of natural cellulose is cotton. It was found that the first signs of the appearance of cellulose in cotton are observed one week after flowering (AF) [11, 12]. At the starting growth stage, up to about 15-20 days AF, cotton fibers elongate, whereas the content of cellulose in formed thin primary cell wall is a quite low. At the developed growth stage, from 15-20 to about 35-40 days AF, the secondary cell wall of fibers is formed with a higher rate due to cellulose biosynthesis. At the final growth stage, above 35-40 days AF until complete maturation, the rate of cellulose formation slows down. Thus, the kinetic curve of cellulose formation in cotton fibers has S-shape [13].

Since this kinetics cannot be expressed by equations of first or second order, a special kinetic equation is needed, e.g. the equation of Avrami-Kolmogorov-Erofeev [14, 15], to describe the kinetics of cellulose accumulation during the growth of cotton fibers, which was the first purpose of this research. The second purpose was study the formation of crystalline structure of cellulose during the growth of cotton fibers.

2 Experimental

2.1 Materials and Chemicals

Bolls of cotton "Acala" were collected with age of 5 to 70 days AF. The needed chemicals were supplied from Sigma-Aldrich Co.

2.3 Methods

Content of cellulose and some other components in cotton fibers were analyzed in accordance with standard NREL methods [16, 17]. Crystalline structure of cotton cellulose was investigated using method of wide-angle X-ray scattering [18]. Crystallinity degree of cellulose itself (X) in growing cotton was calculated by the equation [1]:

$$X = X_s (1 + K(w^{-1} - 1) \quad (1)$$

where X_s is relative crystallinity of cotton sample, w is content of cellulose in cotton fibers expressed in weight parts, K is coefficient.

Lateral sizes (D) of cellulose crystallites in direction perpendicularly to [200] planes of crystalline unit cell were calculated by modified Scherrer equation taking into account the contribution of instrumental factor and lattice distortions to width of crystalline peak [1, 18]. Interplanar spacing (d) in direction perpendicularly to [200] planes of crystalline unit cell was calculated by the Bragg equation.

3 Results and Discussion

The study showed that the kinetic curve of cellulose accumulation in cotton fibers due to biosynthesis has a typical S-shape (Figure 1). This kinetics is characterized by initial slow stage (up to 15 days AF), fast stage (15 to 35 days AF) and final very slow stage (above 35 days AF).

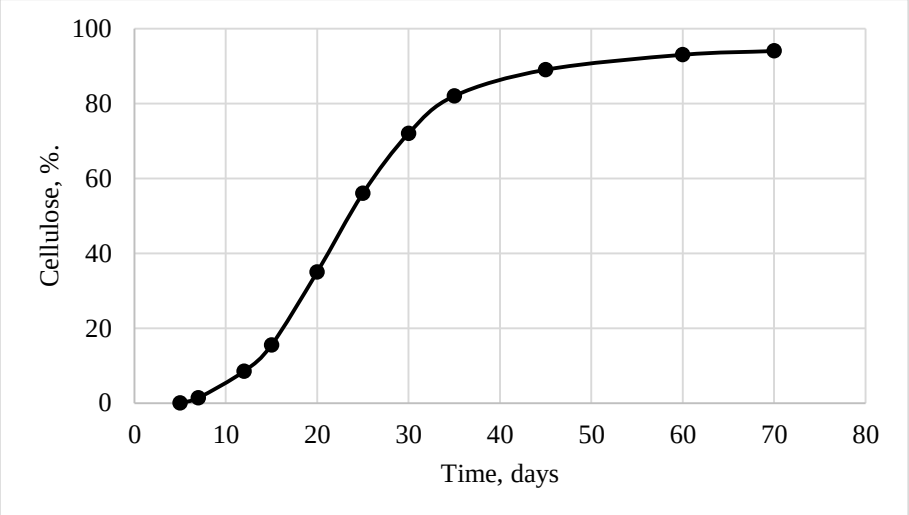

Fig. 1. Kinetic curve of cellulose accumulation in growing cotton fibers

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At the initial stage of biosynthesis, when the primary cell wall is formed, the cellulose content in the immature fibers is low ≤10% (Table 1). After completion of formation of secondary cell wall, the cellulose content in mature cotton fibers reaches the maximum value, 94%.

Table 1. Chemical composition of cotton fibers (CF) in %

Components	Immature CF	Mature CF
Cellulose	9.8	94.1
NCP*	60.2	2.5
Lipids	5.1	1.2
Proteins	8.6	0.5
Ash	2.3	1.1
Others	14.0	0.6

*NCP denotes non-cellulosic polysaccharides (hemicelluloses, pectin, etc.)

To determine the kinetic parameters for such a complex process as biosynthesis, it is recommend to use the kinetic equation of Avrami-Kolmogorov-Erofeev (AKE) [14, 15]:

$$\alpha = 1 - \exp [-K (t - t_o)^n] \quad (2)$$

or in the logarithmic form:

$$\ln(1- \alpha) = -K (t - t_o)^n \quad (3)$$

where **α** is completeness degree of process (for process of cellulose accumulation **α** = C_t/C_m; C_t is percentage of cellulose at time t AF and C_m is maximum percentage of cellulose in mature cotton fibers); **K** is effective rate constant; **t** is time; $\mathbf{t_o}$ is induction period at which **α=0;** and **n** is effective order of the process that reflects the kinetic mechanism. If **n**=0.5, then it is a diffusion process; if **n** is in the range from 0.5 to 1, then it is a diffusion-limited process; and if **n** >1, then this process is not limited by diffusion.

To calculate the kinetic parameters the experimental kinetic curve was linearized using a double logarithms of AKE-equation, as follows:

$$\ln F = \ln K + n \ln(t - t_o) \quad (4)$$

where $F = -\ln(1-\alpha)$; and $t_o \approx 7$ days.

The verification confirmed that experimental kinetic can be linearized really in coordinates of the eq. (5), as shown in Figure 2.

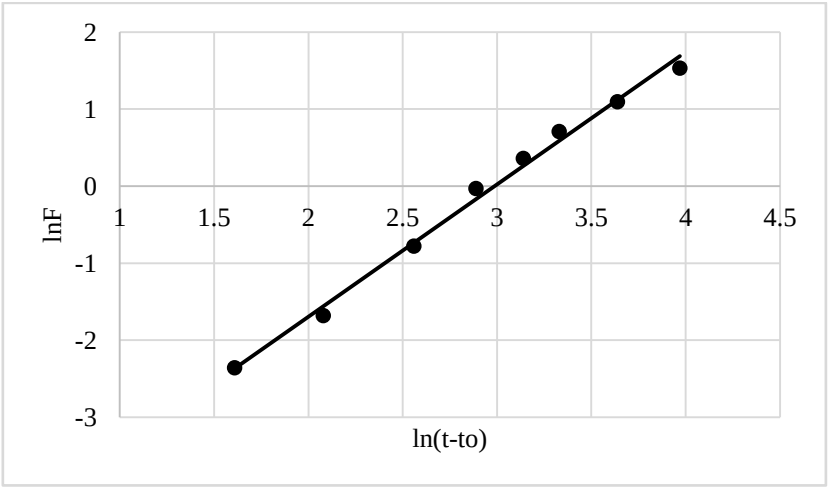

Fig. 2. Linearized kinetic curve of cellulose accumulation

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The calculated parameters of AKE-equation for the process of cellulose formation in growing cotton fibers are: effective rate constant **K**= 5.94 x 10^{-3}, whereas the coefficient **n**=1.72. Since **n**>1 this indicates that the process of cellulose biosynthesis is not limited by diffusion of monomers. The found kinetic parameters permit to calculate the completeness degree of cellulose biosynthesis by the equation (5):

$$\alpha = 1\text{-Antiln}\,[-K(t - t_o)^n] \qquad (5)$$

As can see from Figure 3, the calculated results coincide with the experimental points, which confirms the adequacy of AKE-equation for describing the kinetic curve.

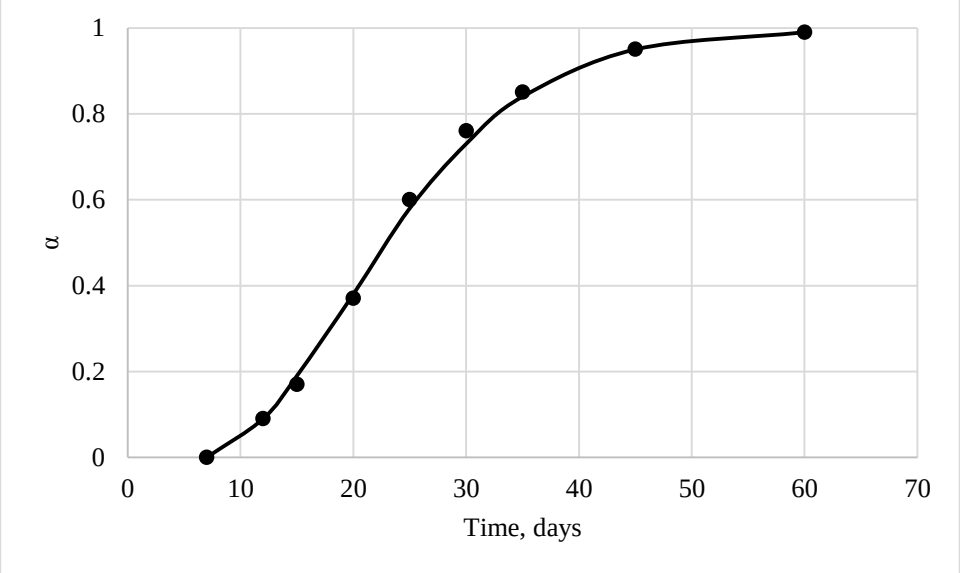

Fig. 3. Calculated kinetic curve and experimental points

Structural studies have shown, that crystalline structure of cellulose in immature fibers is less ordered than the cellulose of mature fibers (Figure 4, Table 2).

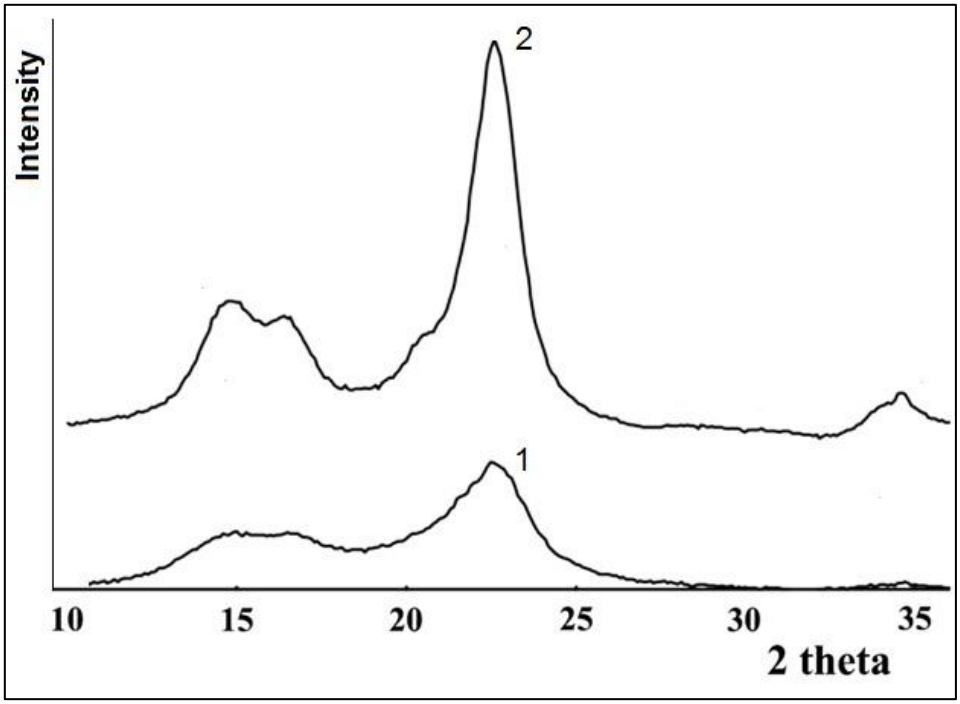

Fig. 4. X-ray diffractograms of cellulose in immature (1) and mature cotton fibers

Table 2. Parameters of crystalline structure of cotton fibers (CF)

Parameters	Immature CF	Mature CF
Crystalline allomorph	CIβ	CIβ
Crystallinity degree: X, %	52	68
Lateral size of crystallites: D, nm	4.0	6.1
Interplanar spacing: d, nm	0.393	0.390

The accumulation of cellulose in growing cotton fibers is accompanied by rise in the degree of crystallinity and increase in the size of crystallites (Figures 5, 6).

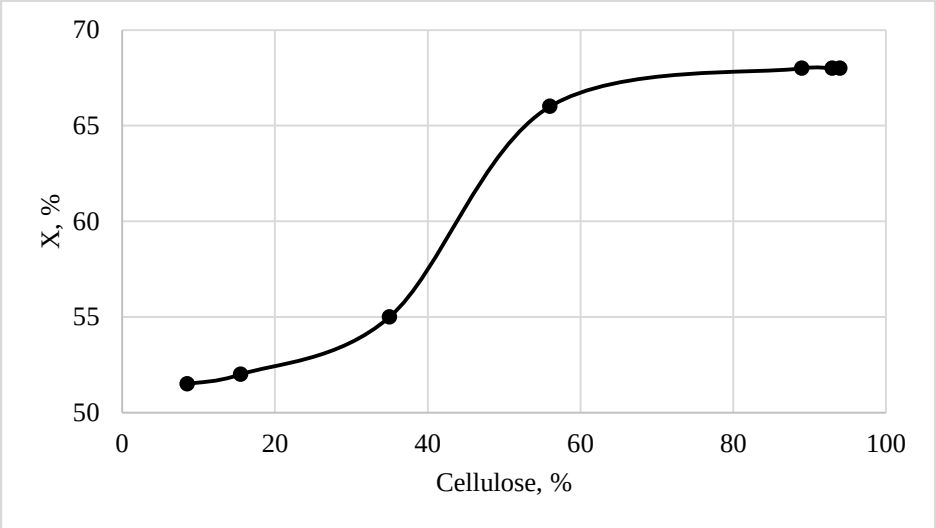

Fig. 5. Dependence of crystallinity degree (X, %) on percentage of cellulose in growing cotton fibers

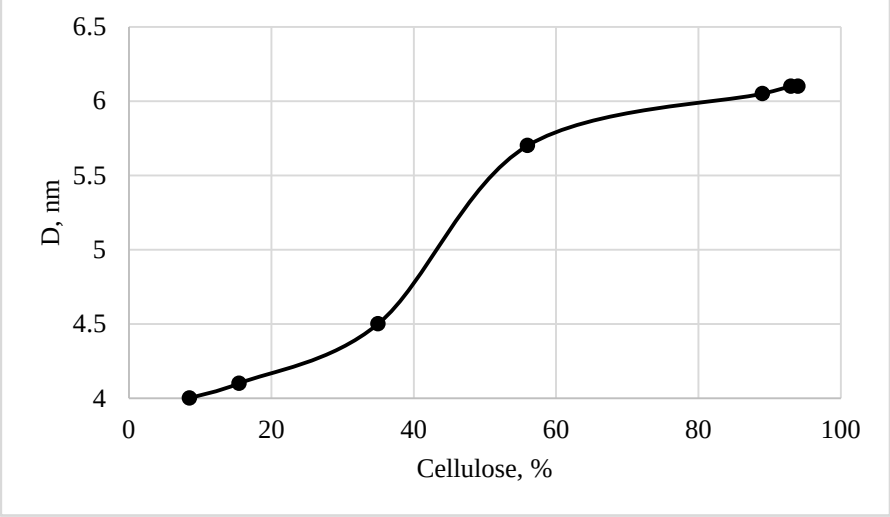

Fig. 6. Dependence of lateral size of crystallites (D, nm) on percentage of cellulose in growing cotton fibers

Thus, with the increase in duration of cotton maturation and cellulose accumulation, additional crystallization of cellulose occurs, as a result of which a rise in degree of crystallinity and size of crystallites is observed.

4 Conclusion

It is confirmed that the kinetic curve of cellulose accumulation in cotton fibers due to biosynthesis is S-shaped. This kinetics cannot be expressed by equations of first or second order, and therefore special kinetic equation such as the

equation of Avrami-Kolmogorov-Erofeev (AKE) was used to describe the kinetics of cellulose biosynthesis in growing cotton fibers:

$C_t/C_m = 1 - \exp [-K (t - t_o)^n]$

where C_t is amount of cellulose accumulated in fibers for time **t** AF; C_m is maximum amount of cellulose in mature cotton fibers; **K** is effective rate constant; **n** is effective order of the process; **t** is time AF and $\mathbf{t_o}$ is induction period. The calculated parameters of AKE-equation are: $\mathbf{t_o}$= 7 days AF, **K**= 5.94 x 10^{-3} and **n**=1.72.

Since **n**>1, the process of cellulose biosynthesis is not limited by diffusion of monomers. The kinetic curve calculated by AKE-equation coincide with the experimental points, which confirms the adequacy this equation for describing the biosynthesis process of natural cellulose.

Structural studies have shown, that crystalline structure of cellulose in immature fibers is low-ordered. However, with increase in duration of cotton maturation, additional crystallization of cellulose occurs.

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Prof. M. Ioelovich published 13 monographs and book chapters, and more than 400 scientific publications in field of structure, chemistry, physics, technology and nanotechnology of biomass, cellulose and synthetic polymers, as well as biochemicals and bioenergy. He is also authors of 14 patents. Prof. M. Ioelovich is member of editorial board of Energy and Ecology, Int. Res. J., J. Polymer Chemistry, J. Research in Industrial and Engineering Chemistry, S. Asian Res. J. of Natural Products, as well as official reviewer of various scientific journals such as Bioresources, BioScience, Energy and Ecology, Green Energy, Material Letter, Carbohydrate Polymers, Cellulose, etc.