

## Application of thermochemical methods for the study of cellulose and cellulose esters

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### Abstract

In this research, the enthalpy of the interaction of cellulose and cellulose esters with various polar liquids was studied. Besides, the standard enthalpies of combustion and formation of cellulose and its esters were determined. It was shown that the absolute value of the standard exothermic enthalpy of the interaction of cellulose with the polar liquids is an indicator of the accessibility of the supramolecular structure for these liquids. It has been also established that the interaction enthalpy of cellulose materials with water, i.e., wetting enthalpy, is directly proportional to the content of non-crystalline domains and inversely proportional to the degree of cellulose crystallinity. In the case of cellulose esters, the wetting enthalpy characterizes their substitution degree and hydrophobicity, which are the higher, the lower the absolute value of the exothermic wetting enthalpy. The determination of the standard enthalpies of combustion and formation of cellulose and the melting heats of crystallites was carried out to evaluate the relative thermodynamic stability of CI, CII, CIII, and CIV crystalline forms and amorphous cellulose. For esters of cellulose, it was shown that an increase in the degree of substitution contributes to enhancing the exothermic enthalpy of the formation; thus, the esterification of cellulose is thermodynamically favorable.

**Keywords:** Cellulose; Cellulose Esters; Structure; Characterization; Enthalpy of Interaction; Wetting Enthalpy; Enthalpy of Combustion; Enthalpy of Formation

### 1. Introduction

Cellulose is a linear, stereoregular, semi-crystalline polysaccharide, the macromolecules of which consist of repeating cyclic anhydroglucose units (AGUs) in a "chair" conformation connected to each other by chemical 1,4- $\beta$ -glycosidic bonds of the "head-tail" type [1]. The degree of polymerization (DP) of natural cellulose in some plants can reach 30,000. However, during isolation and bleaching, the DP of cellulose decreases. A typical DP value for extracted cotton cellulose is 1500-3000 and for wood pulp 800-1200. During hydrolysis with dilute acids, the DP of cellulose can be reduced to 100-300 [2].

Each repeating unit of cellulose contains three hydroxyl functional groups, one primary, and two secondary hydroxyls. The hydroxyl groups of cellulose can be oxidized or substituted with various groups to obtain derivatives. In particular, when hydroxyls are replaced by acyl groups, then cellulose esters are formed [3].

Cellulose is a typical nanostructured polymer consisting of primary or elementary nanofibrils with lateral sizes of 3-20 nm, depending on the origin of cellulose [4, 5]. The lowest lateral size of elementary nanofibrils is observed for the cellulose of herbaceous plants, and the highest size is characteristic of the elementary nanofibrils of cellulose *Valonia* algae. Due to the high specific surface area, elementary nanofibrils are prone to aggregation with the formation of fibrillar bundles, called microfibrils.

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Cellulose nanofibrils contain crystallites and non-crystalline ("amorphous") domains [2]. Crystallites are relatively strong and inaccessible constituents, while non-crystalline ("amorphous") domains are weak and accessible places of the supramolecular structure of cellulose, which are responsible for the cellulose hydrophilicity, sorption of vapors, absorption of polar liquids, as well as for depolymerization during hydrolysis and oxidation.

Crystallites of natural cellulose belong to the CI-type crystal structure. It has been found that the unit cell CI can be in two different crystalline forms [6, 7]: triclinic CI $\alpha$  and monoclinic CI $\beta$ ; moreover, the CI $\alpha$  form is characteristic of the algae cellulose and bacterial cellulose, while the CI $\beta$  form dominates in the cellulose of terrestrial plants and "animal" (tunicate) cellulose. The CI $\alpha$  form is metastable and transforms into the more stable CI $\beta$  form after thermal treatment in an aqueous alkaline medium. As a result of the physicochemical modification of natural cellulose, it is possible to obtain samples with an altered crystalline structure of CII, CIII, or CIV type [6].

Cellulose and its derivatives have a variety of structures and properties, for the study of which various common methods are used such as X-ray diffraction (XRD), electron microscopy, NMR, FTIR, Raman-spectroscopy, and others. However, in the structural analysis by these conventional methods, a problem arises due to insufficient reproducibility of the obtained characteristics. It is known, for example, that different methods give different values of the crystallinity index (CrI) for the same cellulose sample; therefore, it is not clear which value of CrI should be preferred [8, 9]. Even applying the same method, e.g., XRD, also gave different CrI values for the same sample if different measurement techniques were used [10]. When studying the degree of substitution of cellulose derivatives, e.g., cellulose esters, large discrepancies in results can also be obtained if different methods or different techniques of the same method are applied.

To clarify the characteristics of cellulose and its derivatives and expand knowledge about the structure and properties of these polymers, a non-traditional approach is important, based, in particular, on the use of thermochemical methods. As is known [10-12], these methods provide the determination of the heat effects of various processes, as well as establish the relationship of these heat effects with various structural parameters of samples. The main purpose of this article was the application of various thermochemical methods in the study of cellulose and its derivatives such as cellulose esters.

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## 2. Materials and methods

### 2.1. Materials

Refined and bleached chemical Kraft pulp (KP) and cotton cellulose (CC) having CI $\beta$  allomorph were supplied from Buckeye Technologies, Inc. Sample of CI $\beta$  Avicel MCC PH-101 (MCC) was supplied from FMC. The CI $\beta$  samples were additionally purified by extraction with boiling 2% NaOH and boiling water; then samples were rinsed with deionized water, absolute ethanol and dried in a vacuum chamber at 378 K to constant weight. Amorphous cellulose (AC) was prepared by ball-milling of CC with ceramic balls for 10 h; then AC was rinsed with absolute ethanol and dried in a vacuum chamber at 378 K to constant weight.

To obtain CII allomorph, the CI $\beta$  sample of CC was mercerized with 20% NaOH at room temperature overnight; then the samples were washed with water, neutralized with 1% HCl, washed with water to neutral pH, rinsed with ethanol, and dried at 378 K to constant weight. Fibers of regenerated cellulose (RC) with CII allomorph were obtained from Rayonier Inc. The fibers of RC were additionally purified by extraction with boiling water; then samples were rinsed with absolute ethanol and dried in a vacuum chamber at 378 K to constant weight.

To prepare CIII, the CC sample was treated with anhydrous liquid ammonia at 239.7 K for 2 h, evaporated at room temperature, washed with absolute ethanol, and dried in a vacuum chamber at 378 K to constant weight. Samples with CIV allomorph were prepared by treatment of CIII samples in glycerol at 533 K for 30 min; then the treated samples were washed with water, absolute ethanol and dried in a vacuum chamber at 378 K to constant weight. The characteristics of the cellulose samples are shown in Table 1.

In addition, various mono-, di-, and triesters of cellulose having a non-crystalline phase state were studied. Theoretically, each repeating unit of these esters with a molar mass of **M** should contain acyl substituents with different numbers of carbon atoms, **N<sub>c</sub>** (Table 2).

**Table 1** Characteristics of the cellulose samples

Sample	Abbreviation	Allomorph	Cellulose, %	Ash, %	DP
Avicel PH-101	MCC	CI	>99	<0.01	220
Cotton cellulose	CC	CI	>99	<0.01	2700
Kraft pulp	KP	CI	>99	<0.02	1200
Amorphous cellulose	AC	CI	>97	<0.05	610
Mercerized CC	CCM	CII	>99	<0.01	2100
Regenerated cellulose	RC	CII	>99	<0.02	350
CC treated with liquid ammonia	CCA	CIII	>98	<0.02	2600
CCA treated with hot glycerol	CCAG	CIV	>98	<0.02	430

**Table 2** The studied cellulose esters

Esters of cellulose	Abbreviation	M	Nc	Formula of unit
Monoacetate	MAC	204	2	C <sub>8</sub> H <sub>12</sub> O <sub>6</sub>
Diacetate	DAC	246	4	C <sub>10</sub> H <sub>14</sub> O <sub>7</sub>
Triacetate	TAC	288	6	C <sub>12</sub> H <sub>16</sub> O <sub>8</sub>
Monopropionate	MPC	218	3	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>
Dipropionate	DPC	274	6	C <sub>12</sub> H <sub>18</sub> O <sub>7</sub>
Tripropionate	TPC	330	9	C <sub>15</sub> H <sub>22</sub> O <sub>8</sub>
Monobutyrate	MBC	232	4	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>
Dibutyrate	DBC	302	8	C <sub>14</sub> H <sub>22</sub> O <sub>7</sub>
Tributyrate	TBC	372	12	C <sub>18</sub> H <sub>28</sub> O <sub>8</sub>
Monovalerate	MVC	246	5	C <sub>11</sub> H <sub>18</sub> O <sub>6</sub>
Divalerate	DVC	330	10	C <sub>16</sub> H <sub>26</sub> O <sub>7</sub>
Trivalerate	TVC	414	15	C <sub>21</sub> H <sub>34</sub> O <sub>8</sub>
Monohexanoate	MHC	260	6	C <sub>12</sub> H <sub>20</sub> O <sub>6</sub>
Dihexanoate	DHC	358	12	C <sub>18</sub> H <sub>30</sub> O <sub>7</sub>
Trihexanoate	THC	456	18	C <sub>24</sub> H <sub>40</sub> O <sub>8</sub>
Monoanthanthate	MEC	274	7	C <sub>13</sub> H <sub>22</sub> O <sub>6</sub>
Dienanthate	DEC	386	14	C <sub>20</sub> H <sub>34</sub> O <sub>7</sub>
Trianthanthate	TEC	498	21	C <sub>27</sub> H <sub>46</sub> O <sub>8</sub>

The esterification of the initial cotton cellulose was carried out in the medium of trifluoroacetic acid (TFAA) served as a solvent and also a catalyst [13]. Cotton cellulose was mixed with TFAA while stirring at room temperature for 1 h and then treated with anhydrides of various aliphatic acids at 323 K for 1 h using a liquid-to-cellulose ratio of 50. The degree of substitution was adjusted using different molar ratios of anhydrides to cellulose. Finally, the cellulose esters were washed with water, rinsed with absolute ethanol, and dried in a vacuum chamber at 323 K to constant weight.

The needed chemicals (acids, alkalis, organic solvents) were acquired from Sigma-Aldrich Co.

## 2.2. Methods

### 2.2.1. Characterization of Samples

The content of cellulose in the samples was determined by NREL LAP 002 method [14], while the content of ash was analyzed by NREL LAP 005 method [15]. The average degree of polymerization (DP) was measured by the viscosity method using diluted cellulose solutions in Cadoxen [16]. Structural investigations of cellulose samples were carried out by the XRD method [2].

The substitution degree (SD) of esters was studied by a method of chemical analysis [17]. It was found that the SD of monoesters was 0.9-1.1, diesters 1.8-2.2, and triesters 2.8-3.0.

### 2.2.2. Enthalpy of Interaction

The standard enthalpies of the interaction of dry samples with various polar liquids ( $\Delta H_i$ ) were measured using a TAM Precision Solution Calorimeter [18]. Prior to starting the experiments, the air-dry samples were put into a special glass ampoule and dried in a vacuum at 378 K to constant weight. The glass ampoule containing the dry sample was sealed and introduced into the calorimetric cell filled with the liquid. The calorimeter was thermostated at 298.15 K to achieve an equilibrium state. Thereafter, the sealed ampoule with the dry sample was broken to ensure that the cellulose sample to contact with the liquid. The released exothermic heat effect was measured with accuracy  $\pm 0.01$  J. Three of the same sample were tested to calculate a reliable enthalpy value and standard deviation.

### 2.2.3. Enthalpy of Combustion and Formation

Combustion of the dry samples was carried out in a stainless-steel calorimetric bomb having a volume of 0.320 dm<sup>3</sup> at an oxygen pressure of 3.05 MPa with 1.00 cm<sup>3</sup> of deionized water added to the bomb. The combustion measurements were carried out by an isothermal water calorimeter at 298.15 K with an accuracy of  $\pm 0.001$  K. The value of the energy equivalent of the calorimeter determined by standard benzoic acid was 15802.3  $\pm$  0.9 J/K. The true mass of the sample used in each experiment was determined from the mass of the produced CO<sub>2</sub>. The correction of combustion energy for ignition and some other corrections were taken into account. To adjust the experimental combustion energy to standard conditions, T=298.15 K and P= 0.1 MPa, the Washburn correction was introduced. Finally, to calculate the standard enthalpy of combustion ( $\Delta H_c$ ), the correction for the change in the number of moles of gases before and after combustion was introduced. For each sample, five experiments were performed to calculate the reliable value of combustion enthalpy and standard deviation.

In addition, an average value of the combustion enthalpy can be calculated by the equation [19]:

$$\Delta H_c (Av) = E (C + k H - m O) \quad (1)$$

where energetic constant E= -413 kJ/mol, coefficients k=0.295, and m=0.42; while C, H, and O denote the numbers of corresponding atoms in one repeating unit of cellulose or its ester.

The standard enthalpy of formation ( $\Delta H_f$ ) of one mole of the repeating unit of cellulose or its derivative having formula C<sub>a</sub>H<sub>b</sub>O<sub>c</sub> can be calculated from the measured standard enthalpy of combustion,  $\Delta H_c$ , using the known Hess equation:

$$\Delta H_f = a \Delta H_f (CO_2, g) + 0.5b \Delta H_f (H_2O, l) - \Delta H_c \quad (2)$$

where  $\Delta H_f (CO_2, g) = -393.51$  kJ/mol and  $\Delta H_f (H_2O, l) = -285.83$  kJ/mol are standard enthalpies of the formation of carbon dioxide and liquid water, respectively.

## 3. Results and discussion

### 3.1. Study Enthalpies of Interaction of Cellulose and its Esters with Various Liquids

Various polar liquids were used for the experiments, namely, water, alcohols, alkalis, inorganic acids (orthophosphoric and nitric acids), organic acids (acetic and trifluoroacetic acid, TFAA), as well as organic solvents (amines, diamines, dimethylformamide, DMF, and dimethylsulfoxide, DMS). When the cellulose sample interacts with these polar liquids, an exothermic heat effect is released, called the enthalpy of interaction ( $\Delta H_i$ ). Using cotton cellulose (CC) as a standard sample, the following  $\Delta H_i$  values were obtained (Table 3).

**Table 3** Standard enthalpy of the interaction of CC with polar liquids

Liquid	$-\Delta H_i$ , kJ/mol AGUs
Acetic acid	1.6
n-Butanol	2.0
n-Propanol	2.8
Ethanol	3.5
Methanol	5.1
Water	8.2
DMF	10.0
DMSO	12.2
20% NaOH	25.1
Butylamine	26.0
Ethylenediamine	32.4
TFAA	40.5

As a result, the following relationship was established between the absolute value of the standard exothermic enthalpy of interaction and the accessibility of the cellulose structure to the liquid:

- If the absolute value  $[\Delta H_i]$  of the interaction enthalpy of 1 mole of AGUs of CC sample with the polar liquid does not exceed 4 kJ, then such a liquid (for example, n-butanol or n-propanol) can only penetrate into the capillary-porous system of cellulose
- If  $[\Delta H_i]$  is above 4 but below 15 kJ/mol, then a liquid (e.g., water) can penetrate into the non-crystalline ("amorphous") domains of cellulose, but the crystallites remain inaccessible to it. In this case, the enthalpy value becomes directly proportional to the content of non-crystalline domains and inversely proportional to the degree of cellulose crystallinity.
- If  $[\Delta H_i]$  is above 15 but below 35 kJ/mol, then an active polar liquid (for example, 20% NaOH) can penetrate both in non-crystalline ("amorphous") domains and crystallites of cellulose, causing inter-crystalline swelling and even partial decrystallization.
- If  $[\Delta H_i]$  is higher than 35 kJ/mol, then such an active polar liquid (for example, TFAA) can completely penetrate into the supramolecular structure of cellulose, causing complete decrystallization of crystallites, and even chemical modification of cellulose.

Cellulose is a typical hydrophilic biopolymer, so the interaction of cellulose with water is most common. Numerous studies in this area have shown [10, 11] that the standard enthalpy of cellulose interaction with water calling the wetting enthalpy ( $\Delta H_w$ ) is a linear function depending on the content of non-crystalline domains ( $Y=1-X$ ):

$$\Delta H_w = \Delta H_{w,nc} Y = \Delta H_{w,nc} (1-X) \quad (3)$$

where  $\Delta H_{w,nc} = -27.2$  kJ/mol is the standard wetting enthalpy of non-crystalline cellulose, and X is the degree of crystallinity.

As a result, the thermochemical method makes it possible to accurately and reliably determine the degree of cellulose crystallinity using the following equation:

$$X = 1 - (\Delta H_w / \Delta H_{w,nc}) \quad (4)$$

The X-values of the studied cellulose samples obtained by the thermochemical method are presented in Table 4.

**Table 4** Wetting enthalpy, crystallinity, and some characteristics of cellulose samples

Cellulose sample	$-\Delta H_w$ , kJ/mol AGUs	X	V, cm <sup>3</sup> /g	G, g/cm <sup>3</sup>	S, %
MCC	7.0 ±0.1	0.74±0.02	0.637	1.57	6.0
CC	8.2±0.1	0.70±0.02	0.640	1.56	6.9
KP	9.8±0.1	0.64±0.02	0.645	1.55	8.3
CCM	12.3±0.2	0.54±0.02	0.652	1.53	10.6
RC	16.9±0.2	0.38±0.02	0.665	1.50	14.4
CCA	17.1±0.2	0.37±0.02	0.665	1.50	14.5
CCAG	10.9±0.1	0.60±0.02	0.648	1.54	9.2

It is known that various physical methods such as X-ray diffraction, <sup>13</sup>C NMR, FTIR, Raman spectroscopy and others give only estimated and comparative crystallinity indices, which, even for the same cellulose sample, can vary within fairly wide limits depending on the used structural models, calculation algorithms, computer programs, calibration methods, and various corrections [8-10].

Unlike these physical methods, the thermochemical method is direct, simple, accurate, reliable, and reproducible, allowing unambiguous determination of the actual degree of cellulose crystallinity. Any type of precision calorimeter can be used to measure the enthalpy of interaction between samples and water. The thermochemical method does not require the use of special models, complex software, and complex calculations. In this method, there are no special requirements for the shape and size of the samples. It is possible to use cellulose samples with different morphology and crystal structure (CI, CII, CIII, or CIV) in the form of pieces, fibers, or powders. There are only two basic requirements for samples, namely, they must be chemically pure and dry. To remove moisture from cellulose samples, it is sufficient to use conventional vacuum drying at 378 K to constant weight.

After determining the degree of crystallinity of cellulose, it is possible to calculate various characteristics of this biopolymer (Table 4), such as specific volume (V, cm<sup>3</sup>/g), specific gravity (G, g/cm<sup>3</sup>), moisture sorption at 65% air humidity (S, %) and others using the following correlation equations [20]:

$$V = 0.694 - 0.077 X, \quad R^2=0.982 \quad (5)$$

$$G = 1/(0.694 - 0.077 X), \quad R^2=0.982 \quad (6)$$

$$S = 23 (1-X), \quad R^2=0.986 \quad (7)$$

For cellulose esters, the study of the standard wetting enthalpy allows one to determine the hydrophobicity degree (HD, %) using the equation:

$$HD = 100 + 3.68 \Delta H_w, \quad R^2=0.984 \quad (8)$$

In addition, the thermochemical method provides finding the substitution degree (SD) of a cellulose ester as follows:

$$SD = 3.78 + 0.14 \Delta H_w, \quad R^2=0.983 \quad (9)$$

**Table 5** Substitution degree and hydrophobicity degree of cellulose esters

Ester	$-\Delta H_w$ , kJ/mol	HD, %	SD	V <sub>m</sub> , cm <sup>3</sup> /mol	G, g/cm <sup>3</sup>
MAC	-20.0	26	1	149.4	1.36
DAC	-12.7	53	2	186.6	1.32
TAC	-5.4	80	3	223.8	1.28

For example, if  $\Delta H_w = -5.4$  kJ/mol, then it is a triester having a high degree of hydrophobicity, 80%; but if  $\Delta H_w = -20$  kJ/mol, then it is a monoester with the hydrophobicity degree of 26% only (Table 5).

Determining the substitution degree provides the calculation of such characteristics of cellulose esters as the molar volume,  $V_m$ , cm<sup>3</sup>/mol, and specific gravity,  $G$ , g/cm<sup>3</sup> (see e.g., Table 5), using the following correlation equations [20]:

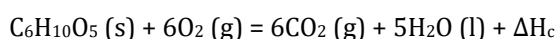
$$V_m = 112.2 + (37.2 + 15.85 N_{CH_2}) SD \quad R^2=0.980 \quad (10)$$

$$G = M/[112.2 + (37.2 + 15.85 N_{CH_2}) SD] \quad R^2=0.980 \quad (11)$$

where  $N_{CH_2}$  is the numbers of CH<sub>2</sub>-groups in one substituent, and  $M$  is the molecular mass of the one repeating unit of the ester.

### 3.2. Study of Enthalpy of Combustion and Formation of Cellulose

The combustion process of one mole of AGUs of cellulose can be described as follows:



where  $\Delta H_c$  is standard combustion enthalpy.

Based on this combustion process, the standard enthalpy of the formation of cellulose can be calculated relative to one mole of AGUs:

$$\Delta H_f = 6\Delta H_f(CO_2, g) + 5\Delta H_f(H_2O, l) - \Delta H_c$$

where standard enthalpies of the formation of carbon dioxide and water are:

$$\Delta H_f(CO_2, g) = -393.51 \text{ kJ/mol and } \Delta H_f(H_2O, l) = -285.83 \text{ kJ/mol.}$$

The results of the determination of the standard combustion and formation enthalpies of cellulose samples having different structural characteristics relative to one mole of AGUs are given in Table 6.

**Table 6** Standard thermodynamic characteristics of cellulose samples

Cellulose sample	Allomorph	X	$-\Delta H_c$ , kJ/mol	$-\Delta H_f$ , kJ/mol
MCC	CI	0.74±0.02	2820.0±2.0	970.2±2.0
CC	CI	0.70±0.02	2821.2±1.7	969.0±1.7
KP	CI	0.64±0.02	2823.7±2.2	966.5±2.2
CCM	CII	0.54±0.02	2823.3±1.8	966.9±1.8
RC	CII	0.38±0.02	2830.0±1.7	960.2±1.7
CCA	CIII	0.37±0.02	2836.4±2.3	953.8±2.3
CCAG	CIV	0.60±0.02	2825.0±2.1	965.2±2.1
AC	-	0	2847.8±2.4	942.4±2.4

The average value of the combustion enthalpy for various cellulose samples, calculated by eq. (1) is  $\Delta H_c (Av) = -2829$  (kJ/mol). A similar value of  $\Delta H_c (Av)$  can be received from the arithmetic mean of the experimental  $\Delta H_c$ -values of the studied samples shown in Table 6. Then, the average value of the enthalpy of formation of cellulose samples will be,  $\Delta H_f (Av) = -961$  (kJ/mol).

From the obtained experimental results, the thermodynamic characteristics of the crystalline domains (crystallites) were also calculated, as follows:

$$\Delta H_{cr} = \Delta H_{am} + (\Delta H_s - \Delta H_{am})/X \quad (12)$$

where  $\Delta H_s$  and  $\Delta H_{am}$  are standard enthalpies of the semicrystalline sample and amorphous cellulose, respectively.

Using three samples of CI, two samples of CII, and samples of CIII and CIV, the following thermodynamic characteristics of the crystalline domains of cellulose were evaluated (Table 7):

**Table 7** Thermodynamic characteristics of crystalline domains of cellulose

Allomorph	$-\Delta H_c$ , kJ/mol	$-\Delta H_f$ , kJ/mol	$\Delta H_m$ , kJ/mol
CI	2810.1	980.1	37.7
CII	2801.7	988.5	46.1
CIII	2817.0	973.2	30.8
CIV	2809.8	980.4	38.0

From the difference between the enthalpies of the formation of amorphous cellulose and crystalline domains, the heat of melting of cellulose crystallites ( $\Delta H_m$ ) with different crystal structures was also calculated.

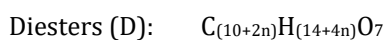
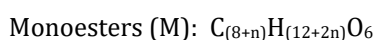
Based on the obtained results, a conclusion was made regarding the relative thermodynamic stability of various crystalline forms of cellulose and amorphous cellulose. It was found that this thermodynamic stability increases in the following order: AC < CIII < CI  $\leq$  CIV < CII.

Amorphous cellulose is the least thermodynamically stable; therefore, during thermo-moisture treatment, AC usually crystallizes into the most stable CII crystalline structure [21]. Among the crystalline forms, the least thermodynamically stable is CIII, which can be recrystallized into more stable crystalline forms [22, 23].

The most thermodynamically stable is the crystalline form CII. However, the use of cellulose samples containing stable CII crystallites causes numerous problems. It is known, for example, that after the transformation of the crystalline structure of CI into CII as a result of mercerization, the solubility of cellulose worsens [24]. As a result, the transparency and filterability of cellulose solutions containing CII are reduced. The presence of stable CII crystallites is also a major factor in the reduced reactivity of cellulose samples during acetylation, nitration, and the spinning of viscose [24-26].

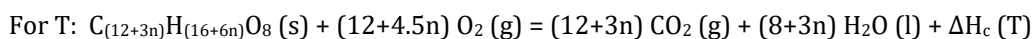
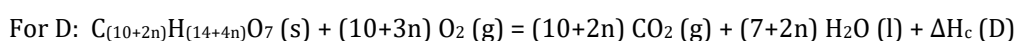
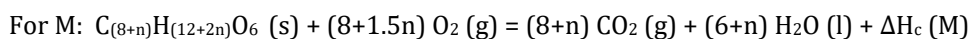
### 3.3. Study of Enthalpy of Combustion and Formation of Cellulose Esters

The one repeating unit of cellulose esters can be described by the following general formulas.

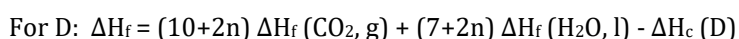
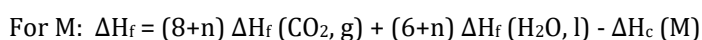


where n is the numbers of CH<sub>2</sub>-groups in one substitute.

Then, the combustion process of one mole of repeating units of esters will be as follows.



Accordingly, standard enthalpies of the formation of these esters can be calculated, as follows.





$$\text{For T: } \Delta H_f = (12+3n) \Delta H_f(\text{CO}_2, \text{g}) + (8+3n) \Delta H_f(\text{H}_2\text{O}, \text{l}) - \Delta H_c(\text{T})$$

where  $\Delta H_f(\text{CO}_2, \text{g}) = -393.51(\text{kJ/mol})$  is the standard enthalpy of the formation of gaseous carbon dioxide, and  $\Delta H_f(\text{H}_2\text{O}, \text{l}) = -285.83(\text{kJ/mol})$  is the standard enthalpy of the formation of liquid water.

The experimentally determined thermodynamic characteristics of cellulose esters are collected in Table 8. The study showed that these characteristics are linear functions of numbers of carbon atoms ( $N_c$ ) in the acyl substituents (Figures 1 and 2).

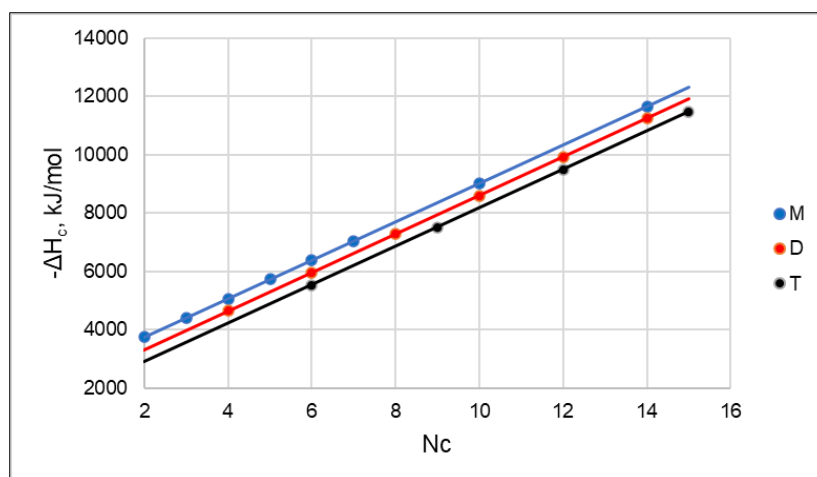
**Table 8** Thermodynamic characteristics of cellulose esters

Ester	Formula of unit	$N_c$	$-\Delta H_c, \text{kJ/mol}$	$-\Delta H_f, \text{kJ/mol}$
MAC	$\text{C}_8\text{H}_{12}\text{O}_6$	2	3747.6	1115.5
DAC	$\text{C}_{10}\text{H}_{14}\text{O}_7$	4	4647.5	1288.4
TAC	$\text{C}_{12}\text{H}_{16}\text{O}_8$	6	5547.4	1461.3
MPC	$\text{C}_9\text{H}_{14}\text{O}_6$	3	4408.0	1134.5
DPC	$\text{C}_{12}\text{H}_{18}\text{O}_7$	6	5968.3	1326.3
TPC	$\text{C}_{15}\text{H}_{22}\text{O}_8$	9	7528.6	1518.2
MBC	$\text{C}_{10}\text{H}_{16}\text{O}_6$	4	5068.3	1153.4
DBC	$\text{C}_{14}\text{H}_{22}\text{O}_7$	8	7289.0	1364.2
TBC	$\text{C}_{18}\text{H}_{28}\text{O}_8$	12	9509.7	1575.1
MVC	$\text{C}_{11}\text{H}_{18}\text{O}_6$	5	5728.7	1172.4
DVC	$\text{C}_{16}\text{H}_{26}\text{O}_7$	10	8609.8	1402.1
TVC	$\text{C}_{21}\text{H}_{34}\text{O}_8$	15	11490.9	1631.9
MHC	$\text{C}_{12}\text{H}_{20}\text{O}_6$	6	6389.1	1191.3
DHC	$\text{C}_{18}\text{H}_{30}\text{O}_7$	12	9930.6	1440
THC	$\text{C}_{24}\text{H}_{40}\text{O}_8$	18	13472.1	1688.7
MEC	$\text{C}_{13}\text{H}_{22}\text{O}_6$	7	7049.5	1210.3
DEC	$\text{C}_{20}\text{H}_{34}\text{O}_7$	14	11251.4	1477.9
TEC	$\text{C}_{27}\text{H}_{46}\text{O}_8$	21	15453.2	1745.7

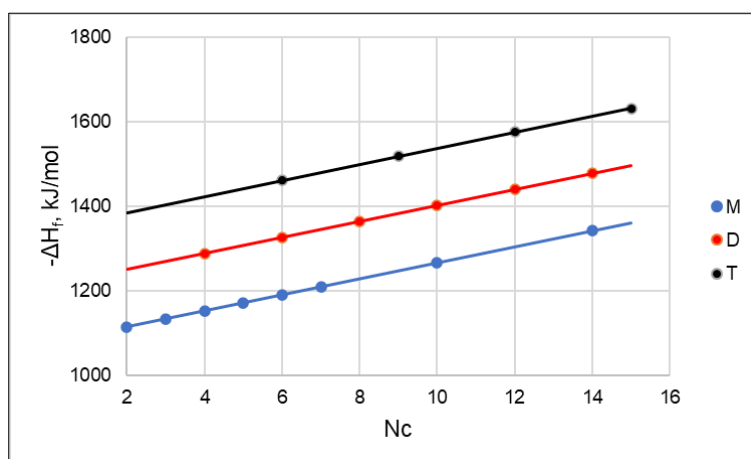
The obtained linear dependences can be described by the following correlation equations (Table 9).

**Table 9** Correlation equations  $\Delta H = F(N_c)$

Ester	Equations	$R^2$
M	$-\Delta H_c = 660.4 N_c + 2427$	0.997
	$-\Delta H_f = 19 N_c + 1077$	0.997
D	$-\Delta H_c = 660.4 N_c + 2006$	0.998
	$-\Delta H_f = 19 N_c + 1212$	0.998
T	$-\Delta H_c = 660.4 N_c + 1585$	0.996
	$-\Delta H_f = 19 N_c + 1347$	0.996



**Figure 1** Linear dependence of combustion enthalpy on numbers of carbon atoms in substituents for mono- (M), di- (D), and triesters (T)



**Figure 2** Linear dependence of enthalpy of formation on numbers of carbon atoms in substituents for mono- (M), di- (D), and triesters (T)

These results show that increasing the degree of substitution and the length of the substituent contributes to enhancing the exothermic enthalpy of formation; thus, cellulose esterification is thermodynamically favorable.

#### 4. Conclusions

It was shown that the absolute value of the standard enthalpy of the interaction of cellulose with the polar liquids is an indicator of the accessibility of the supramolecular structure for these liquids. If the absolute value  $[\Delta H_i]$  of the interaction enthalpy of 1 mole of AGUs of standard cotton cellulose with the polar liquid does not exceed 4 kJ, then such a liquid can only penetrate into the capillary-porous system of cellulose. If  $[\Delta H_i]$  is above 4 but below 15 kJ/mol, then a liquid can penetrate into the non-crystalline domains of cellulose, but the crystallites remain inaccessible to it. In this case, the enthalpy value becomes directly proportional to the content of non-crystalline domains and inversely proportional to the degree of cellulose crystallinity. If  $[\Delta H_i]$  is above 15, but below 35 kJ/mol, then an active polar liquid can penetrate both in non-crystalline domains and crystallites of cellulose, causing inter-crystalline swelling and even partial decrystallization. But if  $[\Delta H_i]$  is higher than 35 kJ/mol, then such an active polar liquid can completely penetrate into the supramolecular structure of cellulose, causing complete decrystallization of crystallites, and even chemical modification of cellulose.

It was established that the interaction enthalpy of cellulose materials with water, i.e., wetting enthalpy, is directly proportional to the content of non-crystalline domains and inversely proportional to the degree of crystallinity. As a result, the degree of crystallinity of cellulose can be determined by thermochemical method. In the case of cellulose esters, the wetting enthalpy characterizes their substitution degree and hydrophobicity, which are the higher, the lower the absolute value of the exothermic wetting enthalpy.

The determination of the standard enthalpies of combustion and formation of cellulose and the melting heats of crystallites was carried out to evaluate the relative thermodynamic stability of CI, CII, CIII, and CIV crystalline forms and amorphous cellulose (AC). As a result, it was found that this thermodynamic stability increases in the following order: AC < CIII < CI ≤ CIV < CII

For esters of cellulose, it was shown that increasing the degree of substitution and the length of the substituent contributes to enhancing the exothermic enthalpy of formation. Thus, cellulose esterification is thermodynamically favorable

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## References

- [1] Krässig HA. Cellulose, Structure, Accessibility and Reactivity. Philadelphia: Gordon and Breach Publishers; 1993.
- [2] Ioelovich M. Models of supramolecular structure and properties of cellulose. *J. Polym. Sci. Ser. A.* 2016; 58: 925–943.
- [3] Zugenmaier P. Crystalline Cellulose and Derivatives. Characterization and Structure. Berlin & Heidelberg: Springer-Verlag; 2008.
- [4] Ioelovich M. Cellulose: Nanostructured Natural Polymer. Saarbrücken: LAP; 2015.
- [5] Klemm D., Heublein B., Fink HP., Bohn A. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem.* 2005; 44: 2–37.
- [6] O'Sullivan A. Cellulose: the structure slowly unravels. *Cellulose.* 1997; 4: 173-207.
- [7] Sugiyama J., Vuong R., Chanzy H. Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall. *Macromolecules.* 1991; 24: 4168-4175.
- [8] Park S., Baker J.O., Himmel ME., et al. Cellulose crystallinity index: Measurement techniques and their impact on interpreting cellulase performance. *Biotechnol. Biofuels* 2010; 3: 1–10.
- [9] Terinte N., Ibbett, R., Schuster KC. Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): Comparison between measurement techniques. *Lenzing. Ber.* 2011; 89: 118–131.
- [10] Ioelovich M. Application of thermochemical method to determine the crystallinity degree of cellulose materials. *Appl. Sci.* 2023; 13: 2387.
- [11] Uryash V. F., Larina VN., Kokurina NY., Novoselova NV. The thermochemical characteristics of cellulose and its mixtures with water. *J. Phys. Chem.* 2010; 84: 1023–1029.
- [12] Goldberg RN., Schliesser J., Mittal A., et al. A thermodynamic investigation of the cellulose allomorphs: Cellulose(am), cellulose Ib(cr), cellulose II(cr), and cellulose III(cr). *J. Chem. Thermodynamics* 2015; 81: 184–226.
- [13] Ioelovich M. Adjustment of hydrophobic properties of cellulose materials. *Polymers.* 2021; 13: 1241.
- [14] NREL CAT Task LAP 002. Two Stage Sulfuric Acid Hydrolysis for Determination of Carbohydrates.
- [15] NREL CAT Task LAP 005. Standard Method for Ash in Biomass.
- [16] Ioelovich M., Leykin A. Nano-cellulose and its application. *SITA,* 2004; 6: 17-24.
- [17] Freire CSR., Silvestre AJD., Neto CP., Rocha RMA. An efficient method for determination of the degree of substitution of cellulose esters of long-chain aliphatic acids. *Cellulose* 2005; 12: 449–458.
- [18] Harjunen P., Lehto VP., Koivisto M., et al. Determination of amorphous content of lactose samples by solution calorimetry. *Drug Dev Ind Pharm.* 2004; 30: 809-815.
- [19] Ioelovich M. Energy potential of natural, synthetic polymers and waste materials –a review. *Acad. J. Polymer Sci.* 2018; 1: 1-15.

- [20] Ioelovich M. Progress in Characterization of Cellulose and Cellulose Esters. Eliva Press Chisinau; 2023.
- [21] Wadehra IL., Manley RSJ. Recrystallization of amorphous cellulose. J. Appl. Polym. Sci. 1965; 9: 2627-2630.
- [22] Wada M. In situ observation of the crystalline transformation from cellulose IIII to I $\beta$  Macromolec. 2001; 34: 3271-3275.
- [23] Kulshreshth K. A review of the literature on the formation of cellulose IV, its structure, and its significance in the technology of rayon manufacture. J. Text. Inst. 1979; 70: 13-18.
- [24] Ioelovich M., Karlivan VP. Effect of structural characteristics on reactivity of cellulose. Wood Chem. 1986; 1: 18-25.
- [25] Ioelovich M. Crystalline structure of alkali-celluloses and its influence on viscose forming process. Wood Chem. 1990; 2: 8-15.
- [26] Klenkova NI. Structure and Reactivity of Cellulose. Lgrad: Science; 1976.