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Chemical Effects of Heat on Cellulose

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The mechanism of rupture of the glucosidic bond in the thermal decomposition of cellulose is examined, and data are given on the primary steps of formation of levoglycosan. The effect of inorganic components on carbon-carbon bond rupture and on the direction of decomposition is considered. Possible practical uses of the results are discussed.

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I. INTRODUCTION

The thermal decomposition of cellulose in a vacuum, with the formation of 1,6-anhydro-β-glucopyranose, was first accomplished in 1918 by Picter and Sarasin[1]. Interest in this process has continued to the present time; this can be ascribed to its importance from both scientific and practical points of view.

The thermal decomposition of cellulose to the monomeric levoglycosan involves formation of a new 1,6-anhydro-bond replacing the ruptured 1,4-carbon–oxygen–carbon bond (with preservation of the composition of the monomer unit of cellulose); during this process at 300° to 400°C cellulose retains its hydroxy-groups. Furthermore, thermal breakdown involves formation of a new conformation of the glucopyranose unit, with transition from $C-1$ to $1-C$ and of all the hydroxyls from equatorial to axial positions. Investigations of the thermal decomposition of cellulose are of interest for establishing its mechanism, in assessing the possibility of controlling thermal changes in cellulose (which may occur both in its extraction and in the exploitation of cellulosic materials), and also for producing new and more thermostable materials.

Surveys have been published[2,3] of research undertaken between 1918 and 1970 on the thermal decomposition of cellulose in a vacuum. However, Shafizadeh's review[2] has several important defects. In particular, it ignores results obtained on the mechanism[4-8], including data on the rates of the process and its possible retardation[5,8]. Furthermore, on the fundamental question of obtaining a high yield (up to 73%) of levoglycosan by the thermal decomposition of cellulose Shafizadeh refers to the work of Sandermann and Augustin published[9] in 1964, whereas analogous results had appeared[5] as early as 1960. Černý and Staněk's review[3] paid very little attention to the problem of obtaining levoglycosan by the thermal degradation of cellulose. The mechanism is not analysed, the reviewers merely mentioning that it should be analogous to that of the acid cleavage of glycosides. Rogovin's monograph[10] also makes a one-sided approach to the mechanism of the thermal breakdown of cellulose to levoglycosan. The author considers merely a radical mechanism on the basis of Arthur's results[11].

Thus until recently the mechanism of the thermal decomposition of cellulose to levoglycosan had not been sufficiently fully and objectively discussed. The aim of the present Review is to give the modern view of the mechanism of thermal breakdown with the formation of 1,6-anhydro-β-D-glucopyranose (levoglycosan) and other anhydro-sugars. Special attention will be paid to a critical assessment of work during the last five or six years, taking into account earlier investigations on these lines. Research on the further degradation of the monomer units of cellulose is not considered in this Review.

II. MECHANISM OF RUPTURE OF A GLUCOSIDIC BOND IN THE THERMAL DECOMPOSITION OF CELLULOSE

(*a*) Transglucosidation

Recent publications[12,13] reveal no generally accepted view on the mechanism of rupture of a glucosidic bond with subsequent formation of 1,6-anhydro-β-glucopyranose (levoglycosan) and other products of the action of heat on cellulose. Two mechanisms of cleavage of the cellulose molecule—homolytic with the formation of free radicals or heterolytic to give intermediate carbonium ions with subsequent formation of 1,2-, 1,4-, and 1,6-anhydrosugars—have been suggested. Shafizadeh and his coworkers[12,14,15] regard these mechanisms as somewhat hypothetical, and insufficient experimental evidence is available to support either. Furthermore, a single route for formation of each decomposition product is thought to be improbable under pyrolytic conditions. Under normal conditions chemical reactions follow the path of minimum energy consumption, and the solvent plays a considerable part in the transfer of ionic charges, while contributing to intramolecular interactions. During pyrolysis, however, many molecular rearrangements and reactions may be taking place simultaneously. It follows from general considerations that the pyrolytic degradation of the cellulose molecule should involve fission of a glucosidic bond or dehydration and breakdown of anhydroglucose units. Shafizadeh et al. used a combination of physical and chemical methods, including thermogravimetric analysis, to obtain a deeper insight into the complicated thermal reactions of hydrocarbons. Spectroscopic methods were also used, as well as modern methods of chemical and radiochemical analysis of the decomposition products. Radiochemical analysis was applied to the products obtained from levoglycosan labelled with carbon-14 and from its

polymer. The above combined approach was used initially to study the thermal decomposition of model compounds [16-18]. Several phenyl and substituted phenyl 2-amino-2-deoxy-β-D-glucopyranosides and various acetylated phenyl glucosides were examined with the aim of determining the effect of substituents in the sugar molecule and the accessibility of free hydroxy- and amino-groups [17].

Table 1. Analysis of volatile products of the pyrolysis of various phenyl glycosides [17].

Phenyl glycoside	Free phenols, %	Initial compound, %
β-D-Glucopyranoside	100	0
2-Amino-2-deoxy-β-D-glucopyranoside	82	2
2-Acetamido-2-deoxy-β-D-glucopyranoside	99	0
2-Deoxy-β-D-*arabino*-hexopyranoside	82	4
2-Acetamidotri-*O*-acetyl-2-deoxy-β-D-glucopyranoside	29	42
Tetra-*O*-acetyl-β-D-glucopyranoside	0	62
Tri-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside	0	63

We must consider in greater detail the experimental results on the thermal decomposition of phenyl glucosides, since they form the basis of the suggested mechanism of rupture of the glucosidic bond with subsequent formation of anhydro-sugars. Table 1 gives analyses of volatile products from the pyrolysis of various glucosides. The model compounds used show that the pyrolytic reactions involve rupture of glucosidic bonds. The aglycone group abstracts a proton with the liberation of phenol, which is removed, while the glycosyl group forms the anhydro-sugar or condenses to randomly combined oligosaccharides. Thermal analysis, together with analytical data on the pyrolysis products, indicates that acetylated phenyl glucosides are considerably more stable than the original compounds. Table 1 shows also that free hydroxyls play an important role in the thermolysis of glucosides: almost 100% of phenol is formed by rupture of the glucosidic bond in phenyl β-D-glucopyranoside; yet this bond is stable when the hydroxy-groups have been substituted (phenyl tetra-*O*-acetyl-β-D-glucopyranoside), and phenol is not formed, up to 62% of the starting material remaining unchanged.

From the thermal analysis together with an analysis of the distillation products it was concluded that thermolysis involved intramolecular transglucosidation. Since thermal reactions are less specific, various hydroxyls may take part. Substitution of hydroxyls in the aglucone or the glucosyl moiety may affect the accessibility, i.e. the reactivity, of the sites of glucosidation. Products of the pyrolysis of polymers obtained from levoglycosans labelled with carbon-14 at $C_{(1)}$, $C_{(2)}$, and $C_{(6)}$ were separated by thin-layer chromatography and then subjected to radiolysis [18]. The results suggested that thermal decomposition involved rupture of a glucosidic bond, opening of the cyclic structure, and subsequent fragmentation of the monomer unit of cellulose. The formation of two molecules of formaldehyde from the anhydroglucose unit was shown to result from the $C_{(1)}-C_{(5)}$ fragment of levoglycosan. It was found also that the production of a 3,6-anhydro-ring leads to the formation of furyl methyl ketone, whose decomposition yields furaldehyde from the $C_{(2)}-C_{(6)}$ fragment of the monomer unit. These investigations showed the identity of products obtained in the pyrolysis of cellulose and polymeric levoglycosan with analogous isotopic labelling.

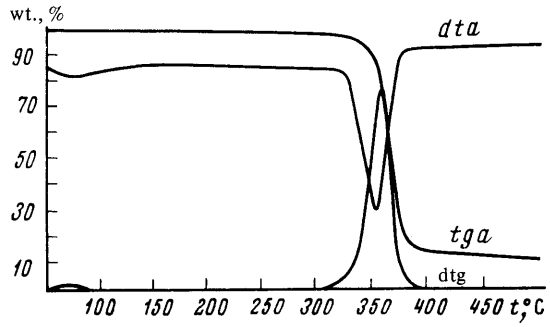


Figure 1. Thermogram of untreated cellulose.

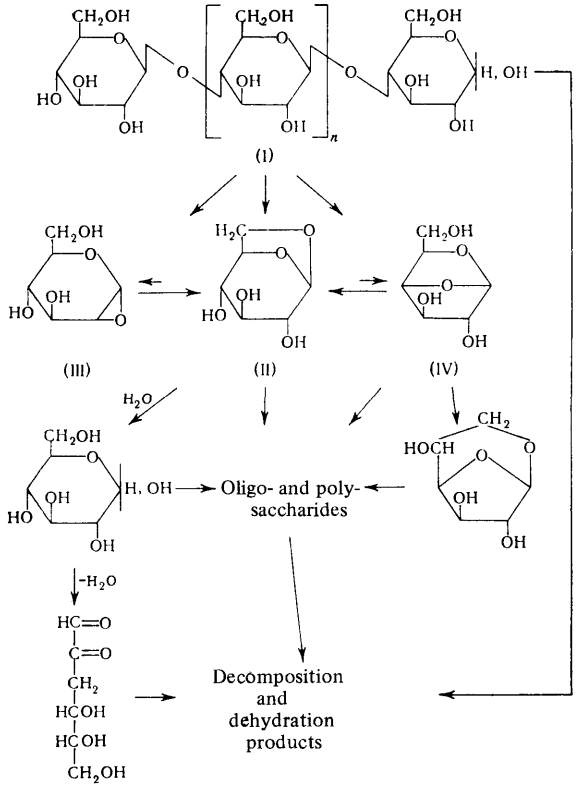


Figure 2. Pyrolysis of cellulose and transformation of products.

Developing their investigations on the thermal decomposition of carbohydrates [14-18], these workers used in a later study [12] a combined approach (previously applied to model compounds) to examine the mechanism of the thermal decomposition of cellulose. Fig. 1 illustrates the principal results, and Table 2 gives the composition of the pyrolysis products. The curves show that these reactions occur very slowly up to 300°C, after which they accelerate (when the temperature becomes high enough for rapid rupture of the glucosidic bond and distillation of the products). Thermogravimetric analysis (Fig. 1) and identification of the pyrolysis products from data obtained with model compounds [14-18] lead to the conclusion [12] that such rupture occurs by a transglucosidation mechanism involving one of the three free hydroxyls. Theoretically the 2-, 3-, or 6-hydroxyl might be involved in intramolecular transglucosidation, with fission of the $C_{(1)}-C_{(4)}$ polymer bond. This produces a new terminal group with an unsubstituted 4-hydroxyl, which in turn may be involved in further transglucosidation during pyrolysis. The suggested mechanism is set out in Fig. 2.

Table 2. Composition of pyrolysis products (% on initial quantity of cellulose) obtained in a stream of nitrogen at 300°C.

Product	Pressure	
	1 atm	5 mmHg
Product of distillation (tar)	19.1	55.8
Levoglycosan	3.57	28.1
1,6-Anhydro-β-D-glucofuranose	0.38	5.6
D-Glucose	traces	traces
Hydrolysable material	6.08	20.8

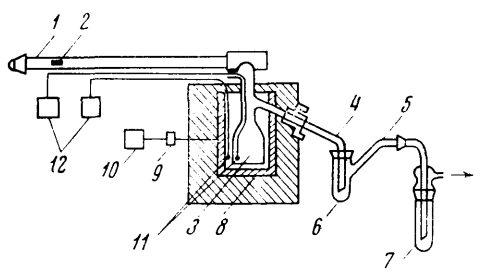


Figure 3. Diagram of apparatus for the thermal treatment of cellulose: 1) tube for keeping cellulose in a vacuum at room temperature; 2) core of magnet (for transferring cellulose to reaction vessel); 3) reaction vessel; 4) connecting tube with condenser; 5) connecting tube; 6) receiver for pasty distillate; 7) receiver for liquid and volatile products; 8) furnace block; 9) thermocouple for temperature control; 10) millivoltmeter; 11) measuring thermocouples; 12) d.c. potentiometer.

(*b*) Homolytic Rupture

A combination of different methods must be used to study the mechanism of thermal decomposition of a polymer, as is known from the chemistry of macromolecular compounds [19-21]: the mechanism can be assessed only from the totality of the results. Investigations on the thermal breakdown of cellulose took place in three stages.

The process was studied initially in a high vacuum (10^{-5} mmHg) by examining the effects of several factors—temperature, residual pressure, design of apparatus, degree of polymerisation of the original cellulose, and additions of glucose—on the yield of levoglycosan in the apparatus illustrated in Fig. 3 under conditions which ensured that this was the main product [4]. During an experiment the vacuum was maintained at 10^{-5} mmHg and the temperature at 305 ± 1°C (after the initial 5–10 min). The products were analysed after 10, 20, 40, 90, and 300 min, when the proportions of cellulose that had decomposed were 2–4%, 10%, 30%, 50%, and 80% respectively. The design of apparatus and the experimental conditions were published somewhat later [4]. The experiments established that conditions for obtaining a constant and quite high yield of levoglycosan (50–60% on the weight of cotton cellulose) [22,23]. The yield was independent of the degree of polymerisation of the initial cotton cellulose over the range 1000–150, [24] and was lowered considerably by the addition of glucose to the cellulose [25].

Subsequent investigations were aimed at establishing the mechanism of the thermal breakdown of cellulose to levoglycosan. It had originally been shown [27] that the yield of this compound from β-D-glucose and from cellobiose is far lower than from cellulose with degrees of polymerisation 1000–150 (respectively 14%, 5%, and 50%). [24] The addition of glucose to cellulose lowered the yield of levoglycosan [25]. Thus the hypothesis that levoglycosan is formed under pyrolytic conditions by the hydrolysis of cellulose to glucose followed by dehydration of the latter was not confirmed [27].

More recent examination [28] of the composition of the distillate from the thermal decomposition of cellulose has established that the formation of 3–4% of 1,6-anhydro-β-glucofuranose accompanies the levoglycosan. The former compound was present (8%) also among the thermal decomposition products from glucose, and was accompanied by 2–3% of phenols. Special experiments undertaken to establish the presence of 1,4-anhydroglucopyranose and of its 2,3,6-trimethyl derivative among the thermolysis products from cellulose and from trimethylcellulose respectively were unsuccessful. According to a personal communication, Shaw regards the formation of 1,4-anhydroglucopyranose and its trimethyl derivatives as impossible for steric reasons.

It was thus established that under certain conditions levoglycosan is the main product of the thermal decomposition of cellulose. However, neither the results nor the identification of volatile products were sufficient to assess the mechanism of breakdown of the polymeric molecule. Subsequent studies were therefore concerned with the changes in the cellulose molecule itself produced by heat and with the distillation products. Attention was concentrated on the following characteristics—(i) the quantity of chemically unchanged monomer units in the cellulose, (ii) the degree of polymerisation, (iii) the content of formyl and carboxyl functional groups, (iv) the physical structure of heat-treated specimens, (v) the yield of levoglycosan, and (vi) the rate of the process (and its possible inhibition).

A marked difference in yields of levoglycosan—50% and 3–4% respectively—was found when cotton cellulose and cellulose hydrate were heated [4]. This was originally attributed to a difference in the physical structure of the celluloses, but it was subsequently demonstrated [5] that the quantity and the composition of ash elements present in

the cellulose affect the path of decomposition and hence the yield of products. After the ash content of both specimens had been reduced to < 0.002%, the yield of monomer on thermal decomposition amounted to 73% of the cellulose decomposed for both modifications[5]. The results indicated that a hydroxylated polymer (cellulose) is capable of thermal depolymerisation at the glucosidic bonds[5] and permitted an approach to a study of the mechanism (apart from the effect of salt cations, whose role has been discussed separately[5,30,31]).

Table 3. Thermal decomposition of cotton cellulose (ash content 0.05%)*.

N, %	*W*, %	*n*	*M*, %	Content	
				C, %	H, %
0	—	2000—700	99.4	44.4	6.17
2	5	400	99.4	44.4	6.17
3	10	200	87.0	44.4	6.17
10	40	200	80.4	44.9	6.17
36	50	200	80.4	45.0	6.2
64	45	200	52.7	51.5	5.5
86	40	200	7.7	67.5	4.7

*N = degree of decomposition (% on initial cellulose);
W = yield of levoglycosan (% on cellulose decomposed);
n = degree of polymerisation;
M = content of chemically unchanged monomer units.

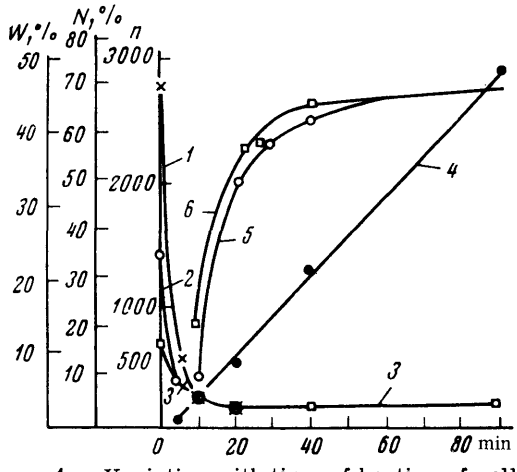


Figure 4. Variation with time of heating of cellulose [see footnote to Table 3)]: 1) n (initially 2800); 2) n (1500); 3) n (700); 4) N; 5) W (n = 2800); 6) W (700 obtained by partial hydrolysis).

Table 3 presents data on the quantity of cellulosic units remaining unchanged in specimens that have been heated for various times. A striking fact is that levoglycosan is formed in low yield (5—10% of the cellulose decomposed) from a cellulose containing 99.4% of monomer units chemically unchanged in the initial stages of decomposition. Quite a high proportion of monomer units remain chemically unchanged almost throughout the decomposition of cellulose: only at ~90% decomposition does the quantity of unchanged units fall to ~8%.[4,5]

Results for the time variation of the degree of polymerisation of cellulose[4,6] are given in Table 3 and illustrated by Figs. 4 and 5. The latter show that decomposition begins with a sharp decrease in n with losses in weight of 5% and 20—30% for cotton cellulose and cellulose hydrate respectively. After this, the degree of polymerisation remains constant up to 80% decomposition, at 200—300 and 30—50 for the two modifications[5]. These limiting values of n agree with those obtained in the heterogeneous hydrolysis of cellulose. The first stage of the process is characterised by a low yield of levoglycosan and a sharp drop in the degree of polymerisation; the second stage gives a high yield, which n remains constant.

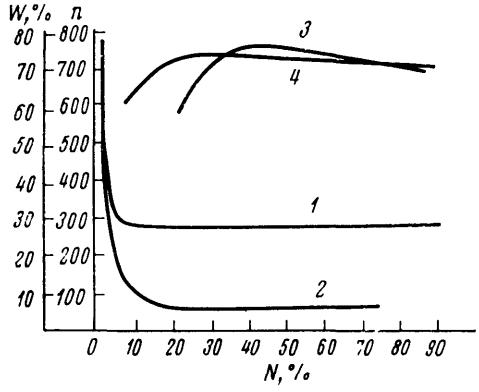


Figure 5. Influence of degree of decomposition N on: 1) n for cotton cellulose; 2) n for cellulose hydrate; 3) W for cotton cellulose; 4) W for cellulose hydrate (ash content < 0.002%).

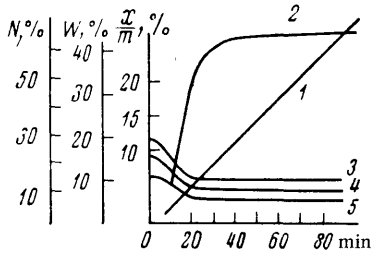


Figure 6. Time variation of: 1) N; 2) W; and sorption capacity x/m (where x is the quantity of moisture and m the weight of the specimen) at different relative humidities (p_1/p_0, %): 3) 90; 4) 80; 5) 60.

The results can be interpreted on the basis that the cellulose molecule is a periodic aggregation of segments of differing structure. The first stage of thermal decomposition involves rupture of the chain links with the accumulation of fragments having degrees of polymerisation of 200—300 and 30—50 for cotton cellulose and cellulose hydrate respectively. Dehydration predominates at this stage, followed by far-reaching breakdown of the

monomer unit with the formation of volatile products (yield of levoglycosan only 5–10%) (Figs. 4 and 5). The yield of levoglycosan reaches its maximum value in the second stage, after the degree of polymerisation has become constant, when thermal decomposition involves the consecutive chemical conversion of monomer units of the cellulose fragment accompanied by detachment of a monomer unit, which is converted by internal isomerisation into levoglycosan. The degree of polymerisation is maintained at 200 with degrees of decomposition of the cellulose from 4% to 70–80% (Table 3), and remains unchanged in a vacuum at 300°C for 80 min.

In this connection it is interesting to consider the light thrown on the physical structure of cotton cellulose by the water-vapour sorption isotherms obtained during heat-treatment [32]. Fig. 6 shows that the sharp drop in the degree of polymerisation to limiting values (which represents a sharp increase in the yield of levoglycosan) is accompanied by a fall in the sorption capacity of cellulose during the first few minutes of heat-treatment. Both the sorption capacity and the yield of levoglycosan then remain constant. These facts indicate that in the first stage the cellulose chain breaks down mainly in amorphous regions.

Table 4. Variation in content of carboxyl and carbonyl groups during the thermal decomposition of cotton cellulose [4].

N, %	Content, %		n	N, %	Content, %		n
	COOH	CO			COOH	CO	
0	0.02	0.26	800	3	0.05	0.80	200
1	0.02	0.35	400	7	0.10	0.78	200
2	0.03	0.75	200	30	0.32	0.87	200

In order to characterise the two-stage breakdown of cellulose to limiting degrees of polymerisation it was important to trace the variation in the content of functional groups with the time of heat-treatment under conditions of maximum inhibition of oxidising processes (10^{-5} mmHg vacuum). [4] Table 4 shows that the rapid change in degree of polymerisation in the first stage of decomposition is not accompanied by a change in the content of functional groups. In the second stage the numbers of carboxyl and carbonyl groups increase, while the degree of polymerisation remains constant. Thus these groups do not become weak points in the cellulose molecule right until limiting degrees of polymerisation.

The rate of the process was then studied [5] by means of a McBain spring balance specially equipped for decomposition studies at 300–400°C. Figs. 7 and 8 show the rate curves for cotton cellulose and for cellulose hydrate with an ash content < 0.002%, when the curves are similar in shape with maxima within the same limits of decomposition. Decomposition occurs quite fast, with maximum rates per minute of 2% and 3% respectively for the cotton cellulose and cellulose hydrate decomposed. Fig. 9 illustrates the possibility of slowing down the thermal decomposition of cellulose, such retardation being accompanied by an intensification of secondary processes of extensive decomposition [8].

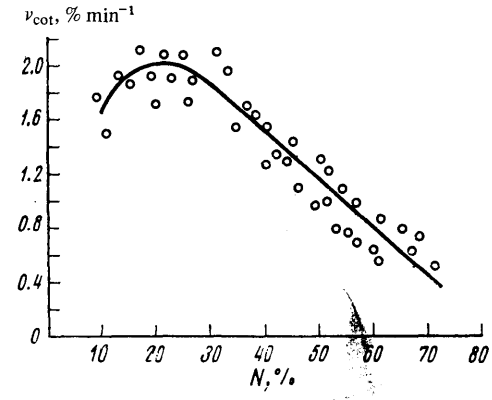


Figure 7. Rate v_{cot} of thermal decomposition of cotton cellulose (ash content < 0.002%).

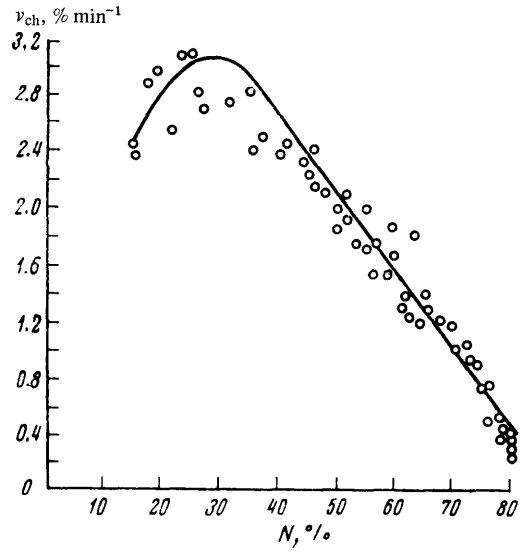


Figure 8. Rate v_{ch} of thermal decomposition of cellulose hydrate (ash content < 0.002%).

It is noteworthy that, while cellulose hydrate has degrees of polymerisation of 30–50, compared with the 200–300 of cotton cellulose, its rate of decomposition exceeds that of the latter by 50%. This indicates the importance of the absolute number of terminal monomer units in thermal decomposition. All segments of the polymer molecule are equally accessible to the action of heat in both modifications, so that the differences observed in the quantities of cellulose decomposed at the first stage, in the limiting degrees of polymerisation, and hence in the rates of the process are determined by the structural inhomogeneity of the cellulose macromolecules themselves and by their different proportions of amorphous and crystalline regions. Formation of levoglycosan—the principal route of thermal decomposition—takes place in the second stage (with the degree of polymerisation constant) after removal of the amorphous regions of the cellulose.

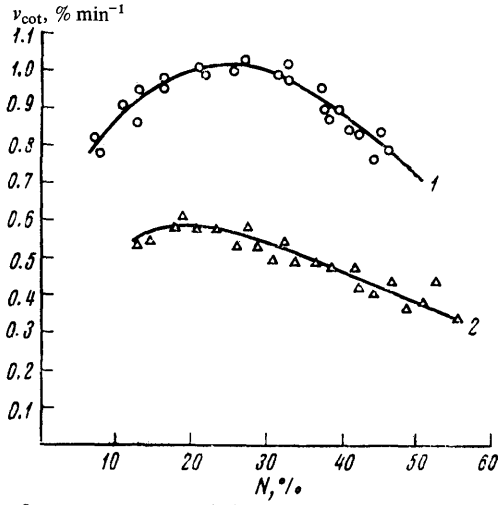


Figure 9. Rates v_{cot} of thermal decomposition of cotton cellulose: 1) in absence of an inhibitor; 2) in presence of an inhibitor.

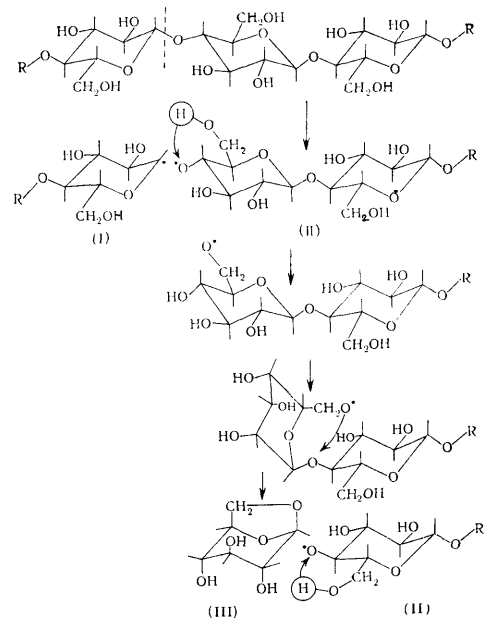


Figure 10. Scheme of depolymerisation of cellulose by a radical–chain mechanism, in which (I) and (II) are radicals.

The high rates with a high yield of levoglycosan, the constancy of the degree of polymerisation of cellulose throughout the decomposition following an initial sharp fall to a limiting value, and also the possibility of slowing down the process by means of radical inhibitors suggest that the thermal depolymerisation of cellulose can be regarded as a radical–chain process which, having begun in some activated region of the macromolecule, leads to the complete breakdown of cellulose with the detachment of one glucose anhydride molecule after the other from the initiated end of the chain. It was suggested[5,7] that the appearance of an active centre in a monomer unit tends to weaken the glucosidic bond nearest to the glucose unit, and its rupture leads to the appearance of a new active centre (Fig. 10). Change in conformation of the monomer unit makes isomerisation possible, leading to the formation of glucose anhydride (levoglycosan) molecules.

Table 5. Effect of an inhibitor (di-2′-naphthylphenylenediamine) on yield of levoglycosan from the pyrolysis of cellulose[35].

Inhibitor, mole %	Yield, %
0.00	34±3.0
0.90	26.0±2.0
2.25	17.4±3.0
4.50	4.4±2.0

Kislitsyn and his coworkers[33–36] paid special attention to the choice of a suitable inhibitor for the thermal decomposition of cellulose, and selected di-2′-naphthylphenylene-diamine, a well known inhibitor of free-radical reactions. With an inhibitor concentration of 4.5 mole % the yield of levoglycosan is 4.9% on the cellulose, instead of the 36.4% obtained in a control experiment (Table 5). The justification of the transition of a monomer unit from the $C-1$ to the $1-C$ conformation[34] is especially interesting. Kislitsyn remarks that the very fact of the formation of levoglycosan in the $1-C$ conformation is convincing evidence of the changes occurring during thermolysis. The energy barriers opposing the transitions are low, and are easily overcome even by thermal motion. The difference in energy observed between the chair and boat conformations of cyclohexane is only 5.3 ± 0.3 kcal.[35,36] The main problem is whether the terminal monomer unit is situated in the limited space of the crystallite between the cellulose chains after transition to the $1-C$ conformation. In a crystalline zone the planes containing the chains are 3.95 Å apart[34]. Calculations and measurements on a model show that after such a transition the terminal unit is located about 2.5 Å above the plane of the chain. A vacant space >1 Å high separates the adjacent planes. Conformational changes can therefore occur without steric hindrance.

(*c*) Mechanism of Rupture of a Glucosidic Bond in the Thermal Decomposition of Cellulose

Recent results have led to a denial[12] of a homolytic mechanism for rupture of the glucosidic bond, which was attributed to intramolecular rearrangements, i.e. transglucosidation of a free hydroxy-group with subsequent formation of levoglycosan. This mechanism was based mainly on experiments with model compounds[15–18] and also on thermographic results and identification of the thermal decomposition products from cellulose. It is extremely significant that the role of free hydroxyls in the thermal rupture of a glucosidic bond was shown convincingly on model compounds having different degrees of substitution

of their hydroxy-groups. The results provide a good illustration that protecting the hydroxy-groups almost changes the direction of the process.

These results will also explain the different directions of thermal decomposition in amorphous and in crystalline regions of cellulose[6,32], where the change in direction depends on the blocking of hydroxy-groups by hydrogen bonds. Thus intramolecular rearrangement may predominate in monosaccharides and probably disaccharides, in which hydrogen bonds are absent, and the glucosidic bond may be ruptured by the mechanism shown in Fig. 2.

These conclusions are consistent with the hypothesis[6] that the thermal decomposition of cellulose takes place in two stages. In the first stage (in the amorphous regions) dehydration occurs, and a small quantity of levoglycosan (5–10% based on the cellulose decomposed) may be formed by transglucosidation at the carbon-(6) atom[5,6,32]. This stage involves a decrease in the molecular weight to that corresponding to the limiting degree of polymerisation. The postulate that all hydroxyls are equivalent in decomposition by a transglucosidation mechanism would have suggested a continuous decrease in the molecular weight of cellulose, which is not observed in practice. A second characteristic feature[5] is the increasing rate of the process, which passes through a maximum. With equal accessibility of the hydroxy-groups (Fig. 2) there is no reason to expect intramolecular rearrangements to show a maximum rate. Extremely significant evidence of a homolytic process is provided by the possibility of slowing down decomposition[8,34,35], which could not be achieved with a heterolytic process.

The mechanism shown in Fig. 2 is based on extremely interesting results[17] on the thermal decomposition of phenyl glucosides and their derivatives. The monomer units of cellulose were considered[12] in isolation from the actual polymer and existing intermolecular interactions, and the mechanism of the formation of levoglycosan was regarded as analogous to reactions occurring in monosaccharides. However, there is little justification for transferring the mechanism of rupture of a glucosidic bond in a monomeric compound to the cellulose polymer, with its supermolecular structure, inhomogeneity of physical structure, and hydrogen bonds blocking hydroxyls in crystalline regions. The absence of radicals in the thermal decomposition of corresponding model compounds of anhydro-sugars[12] is no proof of their absence in the rupture of a glucosidic bond in cellulose. Decomposition of the latter, because of its polymeric nature, may take place by a mechanism differing from that of the degradation of a disaccharide. As noted above, the yields of levoglycosan from cellulose and from cellobiose under the same conditions were respectively 50% and 4%.[26] Such a difference in behaviour between a dimer and a polymer was explained by the influence of the supermolecular structure of the latter (hydrogen bonds and other intermolecular interactions). The effect of hydrogen bonds on the reactivity of hydroxyls in oxidation, etherification, etc. is well known.

Identification of the products of thermal decomposition has also suggested a mechanism. Using modern methods (chromatography, mass spectrometry, etc.) Shafizadeh et al. detected in the distillate 1,6-anhydro-β-D-glucopyranose and also 1,6-anhydro-β-D-glucofuranose, which had been found previously[28,37]. The presence of 3-deoxy-D-*erythro*-hexulose in the distillate has been established for the first time; it is assumed to be formed from glucose (Fig. 2). Thirty-seven different volatile products—among them acids (lactic, acetic, formic), aldehydes, ketones, water, carbon monoxide, and carbon dioxide—had been detected somewhat earlier[38], also by gas–liquid chromatography, among the products of the pyrolysis of cellulose at 375°C.

However, conclusions on the mechanism of the depolymerisation of cellulose and on the primary steps in the formation of levoglycosan cannot be based on the composition of the distillation products. Yet Shafizadeh and Fu[12] have made the completely valid remark that electron spin resonance data showing the presence in the reaction medium of free radicals, which in the opinion of other workers[10,11] support a homolytic mechanism of rupture of glucosidic bonds in the thermal decomposition of cellulose, cannot provide direct evidence of the mechanism of bond rupture, since thermal depolymerisation may be accompanied by far-reaching decomposition by a radical mechanism.

The results of the comprehensive investigations on the complicated pyrolytic process involved in the thermal decomposition of cellulose support a radical–chain mechanism of the thermal depolymerisation of cellulose.

III. PRIMARY STEPS IN THE FORMATION OF LEVOGLYCOSAN IN THERMAL DECOMPOSITION

Hypotheses on the primary steps in the thermal depolymerisation of cellulose with the formation of levoglycosan cannot yet be confirmed experimentally. The usual methods of labelled atoms and deuterium exchange are inapplicable to cellulose, since no methods are yet available for introducing labelled hydrogen or oxygen into its molecule. Several possible schemes of primary reactions have been suggested, and are examined below.

Shafizadeh et al., on the assumption that rupture of a 1,4-polymeric (glucosidic) bond in cellulose is a consequence of intermolecular transglucosidation, consider that this reaction produces new terminal groups with unblocked 4-hydroxyls, which in turn may be involved in further transglucosidation on the continuation of the pyrolysis. Thus levoglycosan may be formed either directly from cellulose or via the intermediate formation of 1,2- or 1,4-anhydroglucopyranose (Fig. 2). The formation of 1,6-anhydroglucofuranose (in 3–4% yield) in addition to the main product—1,6-anhydroglucopyranose (yield 36%)—is regarded by these workers as direct proof of the intermediate formation of 1,4-anhydroglucopyranose, which may be converted into the 1,6-isomer. These workers assume that pyrolytic reactions can occur by various routes: 1,4-reaction does not exclude the direct involvement of 6-hydroxyls; formation of 1,2-anhydroglucopyranose is entirely possible, although thermal decomposition with formation of levoglycosan takes place when the 2-hydroxyl has been methylated just as in a control experiment without protection of this hydroxy-group[39]. The Reviewer regards the intermediate formation of 1,4-anhydroglucopyranose as improbable; this is supported by the failure of attempts to detect this compound among the distillation products from the thermal decomposition of cellulose. Special studies also showed that 1,4-anhydro-2,3,6-trimethylglucose was not the main product of the thermolysis of 2,3,6-trimethylcellulose. An earlier report[40] of the presence of 2,3,6-trimethylglucosan among hydrolysis products from the thermal decomposition of trimethylcellulose quite obviously does not prove the presence of 1,4-anhydroglucopyranose. This report[40] produced the objection by Shaw that, according to theoretical calculations, 1,4-anhydroglucopyranose cannot be

formed either as intermediate or as final product. Thus a mechanism of transglucosidation suggests that levoglycosan can be formed only directly via the 6-hydroxyl, by hydrogen transfer to the glucosidic oxygen, and only from amorphous segments of cellulose, in which the hydroxy-groups are not blocked by hydrogen bonds.

Gardiner [37] and Madorsky [41], who favoured the hypothesis that cleavage of a glucosidic bond occurred by a heterolytic mechanism, assumed that terminal units having a levoglycosan structure were formed via a 1,2-oxiran ring appearing with detachment of part of the cellulose molecule. However, this mechanism is inconsistent with the above features of depolymerisation, which show it to be a radical–chain process. Kilzer and Broido [42] assume that the thermal decomposition of cellulose is a chain process, with initial formation of an active oxygen anion in a terminal glucoside unit. The glucosidic 1-oxygen atom is replaced by the 4-oxygen of the same unit by an S_N2 type of reaction. The 1,4-anhydroglucopyranose formed as intermediate is then converted into either levoglucosan or 1,6-anhydroglucofuranose, while the active centre of the anion migrates to the next unit in the chain. However, this transition is impossible from steric considerations, since carbon atom (1) would be attacked on the side opposite to the primary hydroxy-group [35]. Furthermore, the formation of levoglycosan via 1,4-anhydroglucopyranose cannot be regarded as proved (see above).

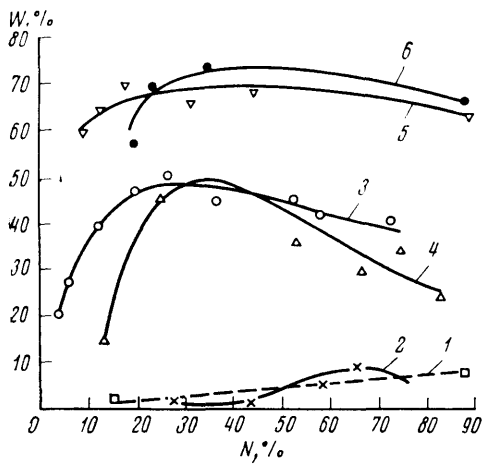


Figure 11. Effect of ash content on yield of levoglycosan W from the thermal decomposition of: 1) cotton cellulose (ash content 0.20%); 2) cellulose hydrate (0.20%); 3) cotton cellulose (0.05–0.09%); 4) cellulose hydrate (0.05–0.09); 6) cellulose hydrate (< 0.002%).

Investigators who favour a homolytic mechanism of rupture of the glucosidic bond suggest several possible ways in which levoglycosan may be formed, but these can be reduced to two main processes. Cleavage of the polymeric 1,4-bond may be followed by formation of an unsaturated bond at carbon atom (1) (radical I) at the 4-oxygen atom (radical II) (Fig. 10). The radical (I) formed at carbon (1) affects the stability of the 1,4-glucosidic bond of the next unit and causes it to break, after which the hydrogen atom migrates from the 6-hydroxy-group to carbon atom (4) with formation of a 1,6-anhydro-ring [7]. Formation of the alkoxy-radical (II) at carbon (4) of the monomer unit leads to intramolecular detachment of the hydrogen atom from the 6-hydroxyl and the appearance of a new alkoxy-radical [36,38]. The glucosidic link to the next unit is then attacked and broken by the alkoxy-radical, the free-radical centre is transferred to the next unit, and levoglycosan is formed at the same time.

The above sequence of primary steps in the formation of levoglycosan is shown in Fig. 10. One of these steps involves transition from the $C-1$ conformation to $1-C$. The formation of an uncompensated bond (a radical) in an acetal is a necessary precondition for a conformational change in the molecule. We can expect a similar effect if we regard cellulose as a polyacetal.

Kislitsyn [34–36] made a detailed examination of the mechanism of rupture of the glucosidic bond, and our analysis of his published experimental results supports the proposed scheme. However, doubt must be cast on his hypothesis that only one of the two macroradicals—the alkoxy-radical (II)—undergoes thermal depolymerisation with the formation of levoglycosan, while radical (I) undergoes far-reaching decomposition or is stabilised, since the yield of levoglycosan would not then exceed 50%, whereas yields up to 73% have been observed experimentally. Several workers [37,41–44] have given analogous schemes of rupture of a glucosidic bond differing only slightly from those considered above.

IV. EFFECT OF INORGANIC COMPONENTS ON CARBON–CARBON BOND RUPTURE AND DIRECTION OF THERMAL DECOMPOSITION

The influence of inorganic impurities on the yield of levoglycosan from the thermal decomposition of cellulose has been mentioned in a review [2]. Several papers [41,45,46] have referred to a diminished yield when inorganic salts are introduced into cellulose, but these investigations were not systematic. It therefore seems useful to consider here the effect of inorganic components on the rupture of a carbon–carbon bond and on the direction of the thermal decomposition of cellulose.

For a long time after Picter and Sarasin's paper [1] (1918) a high yield of levoglycosan could not be obtained, probably owing to insufficient information on the influence of inorganic components on the mechanism of the thermal decomposition of cellulose, and hence on the yield of levoglycosan. The marked difference in yields observed from cotton cellulose and from cellulose hydrate with ash contents respectively of 0.07% and 0.25% suggested [4,5] that not only the quantity of the mineral elements present but also their composition affected the direction of thermal decomposition. This hypothesis was supported by spectroscopic analysis of ash specimens from the two modifications, which showed that sodium salts changed abruptly the direction of thermal breakdown of cellulose hydrate: in the presence of 0.1–0.02% of sodium salts (reckoned as the mass ratio of sodium cation to cellulose) the process extends to products of far-reaching decomposition at carbon–carbon bonds: with < 0.007% of sodium, breakdown to levoglycosan becomes possible. The same workers then made systematic investigations on cotton cellulose and cellulose hydrate with ash contents of 0.2%, 0.05%, and < 0.002%. Fig. 11 shows that predominant formation of levoglycosan becomes possible with both modifications at an ash content of 0.09%, and is most complete with < 0.002% of ash.

Table 6 summarises the main results obtained [30,31] on the role of salt cations and anions. The average yield of levoglycosan from cellulose with initial spectroscopic contents of 0.03% of ash and 0.0003% of sodium is 48%, while the remaining 52% of products results from far-reaching breakdown. Introduction of chlorides of univalent metals (caesium, sodium, and potassium chlorides) as well as sodium thiocyanate produces a sharp decrease in yield of levoglycosan (to 0–1%) and an increase in the quantity of the latter products to almost 100% (experiments 2–5).

Table 6. Dependence of yields of levoglycosan W_l and of products W_s of the far-reaching decomposition of cotton cellulose on the salt content S (where R is the ionic radius, C the content of cations, and n the number of gram-atoms of cation per mole of cellulose unit).

Expt. No.	Salt	S, %	C, g-atom	n	R, Å	W_l, %*	W_f, %*
1	He added	0.03	—	—	—	48	52
2	CsCl	0.87	$4.6\cdot10^{-4}$	1.5	1.65	0	100
3	KCl	0.30	$3.6\cdot10^{-4}$	1.2	1.33	1–2	98–99
4	NaCl	0.30	$4.6\cdot10^{-4}$	1.5	0.98	1–2	98–98
5	NaCNS	0.42	$4.6\cdot10^{-4}$	1.5	0.98	1–2	98–89
6	LiCl	0.30	$6.2\cdot10^{-4}$	2.0	0.78	6.0	94
7	$BaCl_2$	1.07	$4.6\cdot10^{-4}$	1.5	1.43	9.0	91
8	$CaCl_2$	0.77	$4.6\cdot10^{-4}$	1.5	1.06	15.0	85
9	$ZnCl_2$	0.66	$4.4\cdot10^{-4}$	1.5	0.83	39.0	61
10	Cs_2SO_4	0.93	$4.7\cdot10^{-4}$	1.5	1.65	4.0	96
11	Na_2SO_4	0.30	$3.8\cdot10^{-4}$	1.3	0.98	12.0	88
12	$FeSO_4$	0.74	$4.2\cdot10^{-4}$	1.4	0.83	22.0	78
13	$ZnSO_4$	0.78	$4.2\cdot10^{-4}$	1.4	0.83	16.0	84
14	NaCl	0.04	$6.4\cdot10^{-5}$	0.2	0.98	10.0	90
15	NaCl	0.30	$4.6\cdot10^{-3}$	1.5	0.98	1.2	98–99
16	Na_2SO_4	0.05	$6.4\cdot10^{-5}$	0.2	0.98	22.0	78
17	Na_2SO_4	0.10	$1.3\cdot10^{-4}$	0.4	0.98	19.0	81
18	Na_2SO_4	0.30	$3.8\cdot10^{-4}$	1.3	0.98	12.0	88
19	Na_2SO_4	3.00	$3.7\cdot10^{-3}$	13.4	0.98	12.0	88
20	$ZnSO_4$	0.30	$1.6\cdot10^{-4}$	0.5	0.83	27.0	73
21	$ZnSO_4$	0.78	$4.2\cdot10^{-4}$	1.4	0.98	16.0	84
22	$(CH_3COO)_3Cr$	0.10	$3.3\cdot10^{-5}$	0.1	0.52	43.0	57
23	$(CH_3COO)_3Cr$	2.60	$1.0\cdot10^{-3}$	3.4	0.52	19.0	81

*Mean values from several parallel experiments.

These workers [30] then compared the influence of inorganic salts on the thermal decomposition of cellulose with the physical properties of the cation and the anion of the salt. They tried to establish whether the process was directly dependent on the stoichiometric proportions of salt cation and cellulose hydroxyls or whether it was catalytic. Calculation for the extreme salt contents of 0.05% and 3% showed that one cation corresponded to 2780 and 46.4 hydroxy-groups. Hence only a small proportion of the hydroxyls can be in direct contact with a salt cation; monomer units free from a cation should have decomposed with the formation of levoglycosan, which in fact does not occur. It was therefore assumed that the action of the salt was catalytic. Furthermore, calculation [30] of the ratio of the specific surfaces of salt and cellulose showed that the cellulose surface occupied by the salt was only around 2% of the total cellulose surface [30], which supports the hypothesis of a catalytic effect.

Thus the researches lead to the conclusions that inorganic salts contained in or introduced into cellulose promote thermal cleavage at carbon–carbon bonds with the formation of products of far-reaching decomposition. The nature of both cation and anion influences the direction of the thermal breakdown of cellulose.

V. USE OF RESULTS FOR PRACTICAL PURPOSES

Investigation of the directed thermal degradation of cellulose indicates [4–8,26] a low yield of levoglycosan at the first stage with both modifications, i.e. easily hydrolysable polysaccharides and monosaccharides.

The results made possible the development of a new combined method for processing plant material (instead of the hydrolytic process adopted at present) with the aim of obtaining monosaccharides as substrates for growing yeast and for other purposes. Industrially, a single, fairly narrow régime of hydrolysis (high temperature and pressure) is used to convert both readily and difficultly hydrolysable polysaccharides into monoses. Under the conditions adopted the monosaccharides break down, which leads to a loss of 30–40% of the carbohydrate components of the plant material.

At present there are no industrial methods for the combined processing of plant materials that, by organically coupling hydrolytic and pyrolytic processes, would permit the successive conversion of readily and difficultly hydrolysable polysaccharides and lignin of vegetable tissues into valuable chemical products. Study of the thermal degradation of cellulose in a high vacuum with external heating [7,23] yielded laws governing the direction of the process and a suggested mechanism for its thermal depolymerisation with the formation of levoglycosan. A high vacuum was necessary because of the low vapour pressure of levoglycosan, and a satisfactory yield could then be obtained by conducting the decomposition at a sufficiently low pressure; the same conditions also ensure maximum suppression of oxidising processes.

Comparison of results obtained by several workers showed [47] that increasing the residual pressure to 2–5 mmHg in reaction vessels with external heating produced a sharp drop in the yield of levoglycosan. This fact, together with the difficulty of ensuring uniform heating of large quantities of cellulose in the evacuated apparatus, made this method impracticable. For the first time, therefore, the directed thermal decomposition of cellulose was attempted [47] in a stream of superheated steam or an inert gas at a low pressure and preheated to a temperature below that required for the decomposition. This enabled (i) air to be displaced from the reaction vessel independently of the residual pressure, thereby preventing oxidising processes; (ii) direct contact to be established between the heat-transfer agent and any quantity of material, so that heating was more uniform; and (iii) the heat-transfer agent to be used to accelerate exhaustion of the decomposition products from the high-temperature zone. This method has since been applied successfully on laboratory and pilot-plant scales.

Researches undertaken by a group of workers [48–50] laid the foundations of a new technology for the combined processing of vegetable materials in which hydrolytic processes are used only to convert readily hydrolysable polysaccharides into monosaccharides or furaldehyde, while difficultly hydrolysable polysaccharides and lignin are converted into several valuable products by the thermal decomposition of cellulose and lignin in a single technical cycle. The total yield of products is 78% in the combined method, instead of 30–40% in the modern hydrolytic industry. Results of this work were shown at the VDNKh "Science 1967" Exhibition and at the "Chemistry 70" International Exhibition.

Thus the coupling of hydrolytic and thermal processes enables vegetable material to be processed with more efficient utilisation of its components and also yields

products that can be exploited in various branches of the national economy. This method achieves degradation of cellulose to a monomer (levoglycosan) and the thermolysis of lignin in a single industrial cycle. A carbonaceous residue remains (10–15%).

The furaldehyde and the monosaccharide formed in the combined method are used on existing lines. The tar from the vacuum thermolysis (the water-insoluble part) can be employed for the preparation of tanning agents, foundry binding agents, etc. The carbonaceous residue (Karbost) has been tested as a substitute for difficultly available materials—Megrozin, sawdust, lampblack.

Since levoglycosan might become a commercial product for the first time, and experience of its application is lacking, both abroad and in the Soviet Union, research was undertaken on possible uses for it and its derivatives, and on developing methods for preparing some of them. Research on the application of levoglycosan is the subject of a separate paper. Only certain possibilities will be mentioned below. It may find application as a monomer for synthesising the polymer dextran[51,52]. Copolymers of the methacrylic ester of levoglycosan have been claimed[53] in the production of artificial membranes with carbohydrate residues in medicine. Levoglycosan can yield pigments used in the manufacture of daylight-fluorescent paints and enamels[54]. Chemically pure levoglycosan can be employed as a substitute for pharmacopoeial glucose in the tableting of medicinal preparations.

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