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Cellulose Thermal Conversion in the Presence of Silicon-Containing Additives

O. S. EFIMOVA and G. P. KHOKHLOVA

Institute of Coal and Coal Chemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Rukavishnikova 21, Kemerovo 650610 (Russia)

E-mail: efimovaos@mail.ru

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Abstract

Using the methods of thermogravimetry, differential thermal analysis, mass spectrometry, IR spectroscopy and electron microscopy it has been demonstrated that on heating cellulose in the presence of SiO_2 and polycarbosilane within the temperature range up to 900 °C the character of cellulose thermal conversion changes and the yield of carbon residue increases. In the case that polycarbosilane was added, silicon is present in the carbon material in the form of organosilicon fragments with Si–C and Si–O–C bonds, as well as in the form of silicon oxycarbide. With adding SiO_2 the main portion of silicon remains in the form of oxide, the amorphous modification in the composition transforming into cristobalite.

Key words: thermal conversion, cellulose, silicon dioxide, polycarbosilane

INTRODUCTION

The employing of biomass resources, in particular, of plant raw material is of an ever increasing researchers' interest all over the world. It is commonly known that the basis of plant raw material is formed by cellulose. Owing to a huge and renewed raw-material base the studies concerning the ways to obtain materials based cellulose is of currently central importance. Moreover, this would allow solving the problem of recycling various kinds of cellulose-containing waste products.

Cellulose, both in the individual form and in the composition of wood is traditionally used for obtaining carbon materials (CM). In order to improve the process of CM obtaining and assortment extending on the base of cellulose, the influence of various organic and inorganic additives is investigated concerning the carbonization process and the properties of CM obtained, such as high-molecular products of carbon and oil processing, P-, B-, N- and halogen-containing compounds, metal salts, *etc.* [1–3].

On the other hand, it is known that thermal conversion of silicon-containing and carbon-forming compounds could result in obtaining of carbon-silicon (Si/C) composites those exhibit good thermo-mechanical parameters as well as high oxidation stability [4]. Due to the properties those composites are considered to be promising for employing in various fields, for example, as catalyst carriers, various filling materials, adsorbents, filters, *etc.* [5]. Elemental silicon, silicon oxide or carbide, tetraethoxy silane as well as various polymers containing carbon and silicon atoms in the molecular structure (for example, polycarbomethylsilane) use to be under investigation as silicon-containing additives for the creation of Si/C composites [6–8]. The source carbon-forming substances employed are presented, as a rule, by coal pitch [6], petroleum and metallurgical coke [9, 10], graphite [11]. However, there are few papers available from the literature de-

voted to the studies on obtaining such materials on the base of cellulose [12–15]. Moreover, there are almost no data in these publications concerning the role of silicon-containing additive modifiers in the process of carbon skeleton formation and transformation at the stages of transition from precursors to the final material. At the same time, the creation of Si/C composites with preset properties requires for profound studying the processes occurring at various stages of the synthesis of such materials.

The aim of the present work consisted in determining the character of silicon-containing additives influence upon thermal conversion of cellulose as well as in determining structural features of Si/C composites obtained.

EXPERIMENTAL

Microcrystalline hydrated cellulose was used as initial cellulose, and Rosil-175 nanodispersed silicon oxide SiO_2 (S_{sp} = = 136 m^2/g) as well as polycarbosilane (PCS) $\{-(CH_3)SiH-CH_2-\}_m\{-Si(CH_3)_2-CH_2-\}_n$, a soluble polymer formed due to heat treatment of silicon carbide were used as silicon-containing additives [16].

The composition of K_1 (cellulose with SiO_2) was prepared by simple mixing the initial substances, the composition of K_2 (cellulose with PCS) was prepared *via* cellulose impregnation by PCS solution in chloroform. After chloroform evaporating (upon continuous stirring) the samples were grinded in a mortar. The mass fraction of the additive amounted to 5 %. Carbon materials (CM_C material based on cellulose, CM_1 material based on K_1 composition, CM_2 material based on K_2 composition) and solid residue resulted from PCS (SR_{PCS}) were obtained on heating either an individual component or a composition within a tube muffle furnace in nitrogen flow preliminary purified from oxygen and water traces, supplied with a flow rate of 10 cm^3/min; the temperature growth rate in the furnace amounted to 5 °C/min the final temperature value was equal to 900 °C. Samples were held at the final temperature during 20 min, then the furnace was switched off and the samples were cooled in an inert gas flow.

The elemental microsampling analysis was carried out employing the technique described in [17]. The thermogravimetry, differential thermal analysis and mass spectrometry analysis were performed using a STA 409 PG/PC derivatograph with a MS 403 Аполos® mass spectrometer attachment (NETZSCH) on heating a sample in helium atmosphere with the rate of 20 °C/min up to final temperature of 900 °C. Photomicrogfaphy pictuers and surface elemental analysis data were obtained employing a JEOL-6390LA scanning electron microscope with the use of an energy dispersion detector. IR spectra were registered by means of a Tensor 27 FT-IR spectrometer (Bruker) within the wave number range of 4000–400 cm^{-1} with the use of a diffusion reflectance unit.

RESULTS AND DISCUSSION

The process of cellulose conversion into carbon is characterized by a great variety of reactions proceeding in parallel, mainly the reactions of dehydration, depolymerization and aromatization those are accompanied by the evolution of various gaseous products. According to presently accepted concepts [1], the first stage of cellulose thermal destruction results in dehydration (25–240 °C). At a higher temperature (240–400 °C) C–C, C–O bonds are observed to brake and volatile products (CO, CO_2, H_2O, *etc.*), levoglucosan as well as high-molecular carbon-containing compounds are formed. At this stage there is a main mass loss of cellulose observed. With the further heating (400–900 °C) the reactions of aromatization and condensation result in the formation of a graphite-like carbon structure.

The results of thermogravimetric analysis of cellulose, PCS and their compositions are demonstrated in Fig. 1.

The presence of SiO_2 added results in extending the region of intense mass loss, in shifting the temperature corresponding to the maximum destruction rate towards a high-temperature region (from 367 up to 382 °C) and in reducing the rate of decomposition (see Fig. 1, *a*). As a consequence, an endothermic peak on DTA curve is displaced, and its intensity is decreased to a considerable extent (see Fig. 1, *b*), which indicates that there is a decrease in the contribution destructive processes and an increase in the role of polycondensation reactions and the formation of more energetically favourable structures. The yield of the carbon

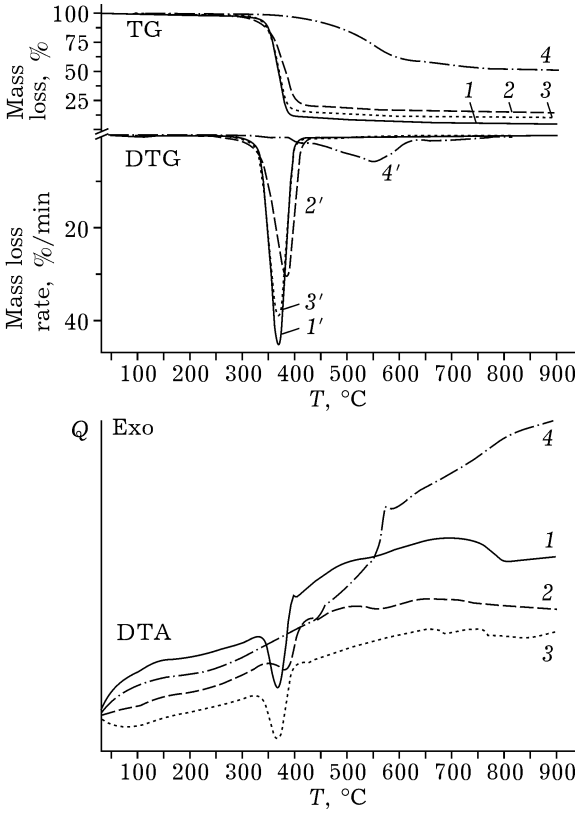

Fig. 1. TG, DTG and DTA curves for the samples under investigation: *1*, *1′* – cellulose; *2*, *2′* – composition with SiO_2; *3*, *3′* – composition with polycarbosilane; *4*, *4′* – polycarbosilane.

residue increases from 5 up to 10 % as calculated for the organic mass of a sample.

With PCS addition the rate of cellulose decomposition and the intensity of corresponding endothermic peak decrease to a lesser extent as compared to those for a sample with SiO_2, whereas the position of peaks does not change. In order to estimate mutual influence of components basing on the yields for individual components we calculated theoretical yield of K_2 solid residue. Polycarbosilane destructed under these conditions forms a residue with the yield of 51 % whose composition includes silicon and carbon. The calculated yield (7 %) appeared lower than that obtained in an experimental way (10 %), which indicates the contribution of structurization and condensation processes to increase in joint cellulose and PCS thermal conversion, just as in the case of K_1. Mutual influence of the components of K_2 mixture during their joint thermal conversion results in the fact that the DTG curve exhibits the only peak within the region of cellulose thermal destruction, whereas an

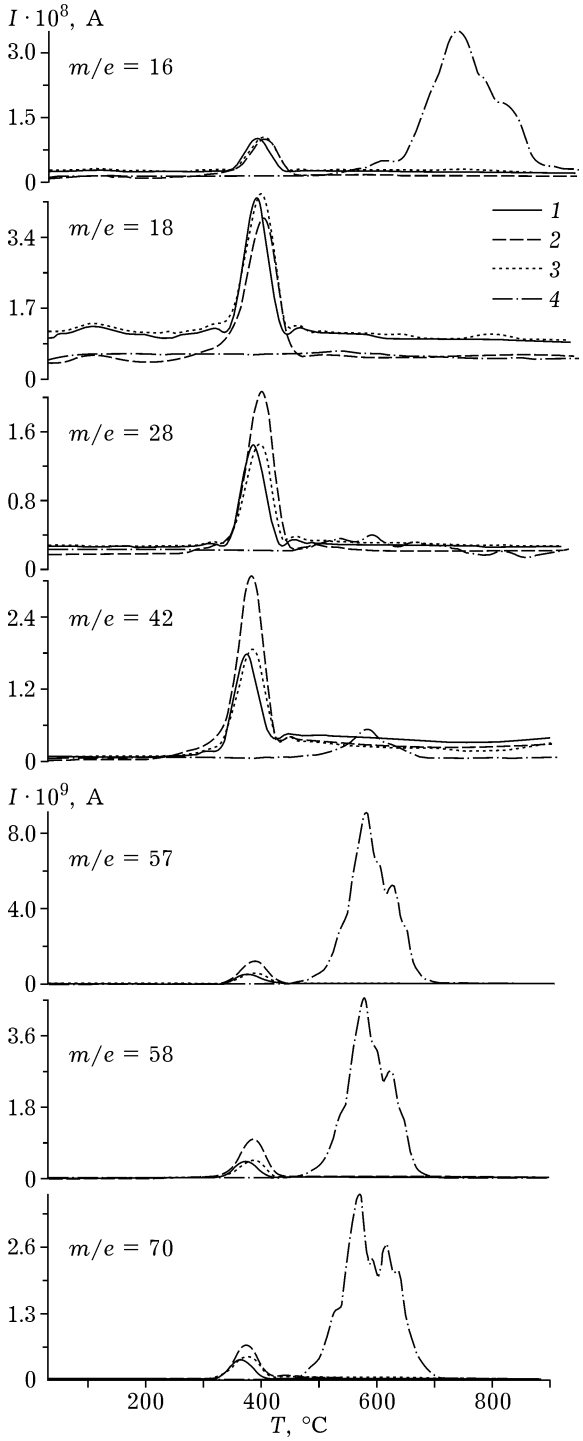

Fig. 2. Evolution curves for main volatile thermal destruction products of cellulose (*1*), cellulose composition with SiO_2 (*2*), cellulose composition with polycarbosilane (*3*), and polycarbosilane (*4*).

intensive peak inherent in individual PCS (within the range of 450–800 °C) is absent.

Figure 2 and Table 1 demonstrate the mass spectrometric analysis data concerning the evolution of the most abundant products for the

TABLE 1

Composition of main volatile thermal destruction products (according to mass spectrometric data)

m/e	Possible structure of a fragment	Content, %				
		Cellulose	K_1	K_2	PCS	
		at *T*, °C				
		376	379	378	571	647
16	CH_4	10.6	8.9	10.2	12.2	85.9
18	H_2O	45.9	34.1	43.2	4.1	1.8
28	CO, $H_2C{=}CH_2$	16.5	18.5	17.1	6.1	1.8
42	$CH_2{=}CO$, $H_2C{=}CH{-}CH_3$	20.0	31.9	21.6	16.3	0
57	$H_3C{-}CO{-}CH_2^{\bullet}$, $H_3C{-}CH_2{-}CO^{\bullet}$, $Si(CH_3){-}CH_2^{\bullet}$	2.4	2.2	3.4	30.6	3.2
58	$H_3C{-}CO{-}CH_3$, $H_3C{-}CH_2{-}COH$, $Si(CH_3)_2^{\bullet}$	2.4	2.2	2.3	16.3	3.2
70	C_4H_6O, $Si(CH_3)_2{-}C^{\bullet}$	2.4	2.2	2.3	14.3	3.5

destruction of individual components and compositions.

Mass spectra of compounds evolved during PCS destruction are characterized by several peaks within the two basic temperature ranges such as 450–600 and 600–800 °C. The main product of PCS decomposition is presented by methane (the fragment mass-to-charge ratio *m/e* 16) which is observed to evolve mainly within a more high-temperature region. Within the low-temperature region the compounds with *m/e* 57 are prevailing, whereas the compounds with *m/e* 16, 42, 58, and 70 are less abundant in the composition of volatile destruction products. The products with *m/e* 57, 58, and 70 could represent, to all appearance, monomeric fragments of PCS.

The main volatile products of cellulose and compositions destruction represent the compounds with *m/e* values equal to 16, 18, and 28 and 42. A lower (approximately an order of magnitude) intensity is exhibited by the products evolved with *m/e* 26 (C_2H_2), 40 (C_3H_4), 44 (CO_2), 68 (C_4H_4O), 78 (C_6H_6)), 57, 58, and 70. In this case the fragments with *m/e* 57, 58 and 70, to all appearance, represent propionic aldehyde, acetone and, for example, a partly hydrogenated furan derivative. The evolution of volatile products within the region of PCS destruction (450–800 °C) in the case of K_2 was almost not observed, except for methane, which supports the hypothesis that the joint thermal conversion of the components occurs mainly in the region of cellulose destruction. The absence of compounds with *m/e* 57, 58, 70 within the temperature range of 450–800 °C and their constant amount in the region of cellulose destruction indicates the latter prevents PCS macromolecules from monomeric defragmentation.

The temperature maxima of the evolution of cellulose destruction products in the presence of additives demonstrate an approximately 10 °C shift towards a high-temperature region, whereas the evolution range exhibits a certain extension. The ratio between the main volatile destruction products in the presence of additives changes: the fraction of unsaturated and oxygen-containing carbon compounds increases whereas the fraction of water decreases. These changes are more considerable in the case of mixture K_1.

TABLE 2

Elemental analysis data for carbon materials

Samples	Content, %				Atomic ratio	
	C	H	O	Ash	H/C	O/C
CM_C	96.5	0.9	2.6	<1	0.11	0.02
CM_1	69.2(92.8)	0.5(0.7)	4.9(6.6)	25.4	0.09	0.05
CM_2	74.5(95.9)	0.6 (0.7)	2.6(3.4)	22.3	0.10	0.03

Notes. 1. The content of oxygen is determined from the difference. 2. Parenthetically is indicated the content as calculated for an ash-free sample

To all appearance, the interaction of cellulose carboxy groups with surface groups of SiO_2 (or the groups of partly oxidized PCS) facilitates their abstraction from the molecule of cellulose and promotes the formation of unsaturated carbon-carbon bonds. On the other hand, the binding of water molecules by SiO_2 surface causes their evolution to be shifted towards a higher temperature range, which results in the formation of an increased amount of oxygen-containing carbon compounds. The same factor determines the broadening of evolution peaks corresponding to volatile products in the mass spectra of compositions.

The elemental composition of CM is presented in Table 2. The organic part of CM_C, CM_1 and CM_2 is characterized by a highly-condensed aromatic structure, which is indicated by a low value of H/C ratio. The aromaticity level for CM based on compositions is somewhat higher as compared to that for CM_C. In CM_1 an increased amount of oxygen-containing groups is observed. The ash of CM_1 represents a white powder (SiO_2). In the case of CM_2 a grey colour of ashes indicates a possible presence of carbon-containing structures, for example, silicon oxycarbide (an intermediate species between SiO_2 and SiC with a structure such as Si (C, O)) in the mixture with SiO_2, which is formed as a result of both due to individual PCS thermal destruction [16], and due to binding with the carbon matrix. The solid residue from PCS thermal destruction represents an almost completely fireproof at 900 °C product such as silicon carbide with silicon oxide impurity [16].

Figure 3 demonstrates photomicrography pictures of CM surface. The elemental composition (without taking into account the content of hydrogen) and a hypothetical structure of the phases isolated are presented in Table 3.

All CM under investigation represent microfibres of various lengths with the diameter

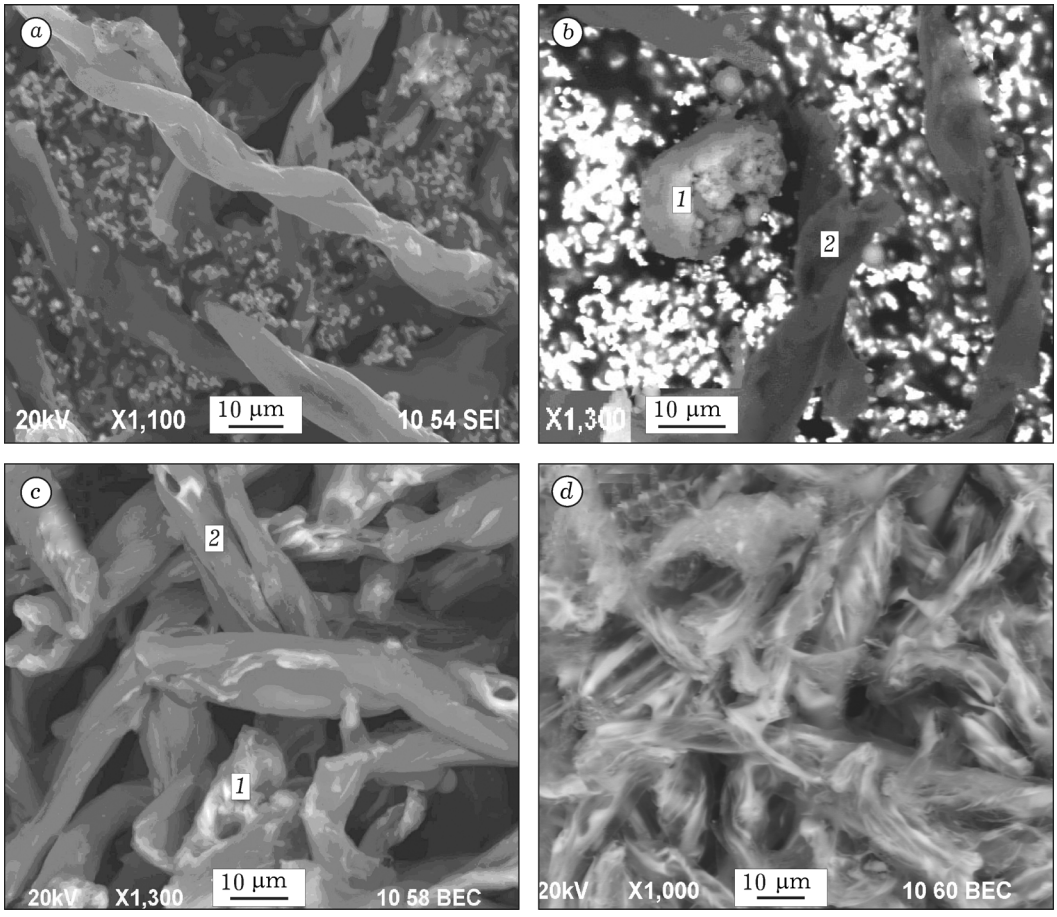

Fig. 3. Photomicrography picture of the carbon materials surface based on cellulose (*a*), its composition with SiO_2 (*b*), the composition with polycarbosilane (*c*) and its residue after heating in air at 900 °C (*d*): *1* – phase 1, *2* – phase 2.

TABLE 3

Elemental composition of separate surface phases of carbon materials

Samples	Phase	Mass fraction, %		
		C	O	Si
CM_C	–	75	25	–
CM_1	1	35	55	10
	2	82	17	1
CM_2	1	77	17	6
	2	72	5	23
SR_{CM_2}	–	7	55	38

of 10–20 μm. The diameter of fibres for CM_1 and CM_C amounts to about 10 μm, and for CM_2 it is about 20 μm. The microstructure of CM based on compositions is characterized by the presence of at least two phases with different elemental compositions.

In CM_1 (see Fig. 3, *b*) the phases distinguished are in a separated state. Phase 1 which was, to all appearance, formed in the course of cellulose thermal destruction on the surface of a particle of SiO_2, is enriched with silicon and oxygen and, alongside with SiO_2, contains a plenty of oxygen-containing carbon-based structures. On the contrary, phase 2 was generated on the base of cellulose which contacted with a small amount of SiO_2 thus it contains a minimum amount of silicon. The bulk of phase 2 consists of carbon, the content of oxygen therein being lower as compared to that for CM_C, which could indicate the dehydrating and structurizing action of SiO_2 in catalytic amounts.

In the case of CM_2 (see Fig. 3, *c*) both phases contain silicon and closely contact each other. In comparison with CM_C the distinguished structures, particularly those with a high content of silicon, are depleted with oxygen. Basing on the data concerning the ratio between the elements one could assume that there are organosilicon structure fragments such as Si–C and Si–O–C present within the carbon skeleton in phase 2. Phase 1, to all appearance, represents a carbon structure with an increased content of siloxane fragments.

After heating CM_2 in air at 900 °C during 2 h there is an unburnt material (SR_{CM_2}), whose structure includes carbon atoms (see Table 3). This material holds the structure of initial fibres (see Fig. 3, *d*) and, to all appearance, represents silicon oxycarbide.

IR spectroscopy data (Fig. 4) confirm the formation of new bonds and the mutual influence of the components in the process of their joint thermal conversion. So, IR spectrum of CM_1, alongside with the initial SiO_2 bands inherent in amorphous silica, demonstrates a band with the maximum at the wave number of 624 cm^{-1}, which indicates that there is a conversion of the amorphous SiO_2 modification into cristobalite [18]. On heating of amorphous SiO_2 up to 900 °C in the absence of cellulose there is no transition to the crystalline state observed. The IR spectrum of SR_{PCS} within the range of wave numbers less than 1250 cm^{-1} are exhibits the absorption bands corresponding to amorphous silica with a minor impurity of crystalline SiO_2 modification. A high broadening of the bands could be caused by the presence in the sample of other bonds those exhibit absorbing within the mentioned wave number range (C–H, O–H, C–O, Si–C) [19].

In the IR spectrum of CM_2 there are no intense bands of amorphous SiO_2 observed in the case of SR_{PCS}, whereas there are an absorption band at 1245 cm^{-1} (Si–O–C bonds in organosilicon structures) and a wide band within the range of 1100–700 cm^{-1} observed; the latter could correspond to Si–O bonds in organosilicon structures in silicon oxycarbide as well as to Si–C bonds in silicon carbide. The overlapping of the bands indicates that there is an

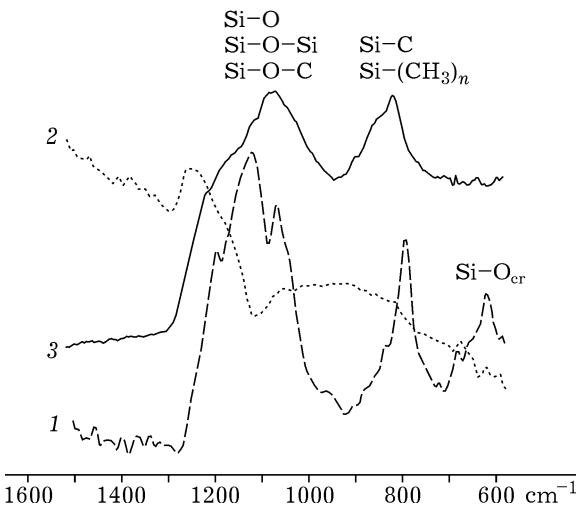

Fig. 4. IR spectra of carbon materials based on cellulose compositions with SiO_2 (*1*), polycarbosilane (*2*) and solid residue of polycarbosilane thermal destruction (*3*).

interaction between Si–C and Si–O bonds right up to the formation of bonds close to oxycarbide ones [16].

CONCLUSION

1. Influence of silicon compounds such as SiO_2 and PCS upon the process of cellulose thermal conversion was investigated within the temperature range up to 900 °C. It has been demonstrated that in the presence of silicon-containing additives the rate of decomposition decreases, the temperature and the evolution character of volatile destruction products and their quantitative composition exhibit changing, as well as the yield of carbon residue exhibits an increase.

2. In the case of silicon oxide added the contribution of oxidation processes increases thereby the fraction of oxygen-containing carbon compounds in volatile destruction products grows, and the amount of oxygen-containing groups in the carbon residue increases.

3. During the process of cellulose thermal destruction together with PCS, joint thermal conversion of the components is observed to occur, mainly, within the region of cellulose destruction; in this case the defragmentation of the PCS molecule and the evolution of volatile Si-containing compounds are inhibited.

4. Silicon in the carbon material based on the composition of cellulose with PCS exists in the form of organosilicon fragments with Si–C and Si–O–C bonds and in the form of silicon oxycarbide Si (C, O). Silicon oxycarbide demonstrates a fibrous microstructure corresponding to the fibres of carbonized cellulose. A great bulk of silicon in the carbon material based on cellulose with silicon dioxide added remains in the form of SiO_2; in this case the amorphous modification of silicon dioxide is transformed into cristobalite, whereas on heating the carbon material without cellulose under similar conditions the amorphous SiO_2 modification remains unchanged.

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