Possibilities of Obtaining Carbon Sorbents on the Basis of a Composition of Wood Waste and Gumlike Products of Coal Processing

G. P. KHOKHLOVA, N. YU. SHISHLYANNIKOVA and YU. F. PATRAKOV

¹Institute of Coal and Coal Chemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Rukavishnikova 21, Kemerovo 650610 (Russia)

E-mail: chem@kemnet.ru

Abstract

For carbonization of binary compositions of pine sawdust with a number of gumlike products of coal processing as an example, it is shown that the use of compositions involving compounds of different nature as the initials for obtaining carbon sorbents allows one to change the mechanism of thermal destruction shifting the temperature ranges and decreasing the rates of intensive decomposition. The yield of carbon residue increases non-additively. Such an approach allows one to broaden the assortment of carbon sorbents, including the materials which cannot be carbonized in the individual form.

INTRODUCTION

Ecologically unfavourable low-energy and off-condition coal, plant and organic industry-related wastes are at the same time essential sources of carbon-containing raw material. However, due to the absence of economically acceptable technologies of their processing into the products in requisition, their useful consumption is still limited. Because of this, investigations connected with the development of new efficient processes of utilization of the wastes of various kinds, including manufacture of carbon sorbents (active carbon) are topical. Carbon sorbents are widely used in various areas of economical activities. The need for these products exceeds the amount of their production. In spite of the accumulation of substantial amount of active coal for various purposes in the world, it is still urgent to broaden the assortment and improve manufacture of carbon sorbents.

Carbon sorbents are known to be obtained by carbonization followed by activation of high-molecular carbon-containing materials (coal, wood, synthetic polymers, *etc.*) [1, 2]. Along with the formation of carbon framework, carbonization involves destruction processes with detachment of heteroatomic and carbon-containing low-molecular compounds. The ratio of structuring to destruction processes determines the yield of carbon residue (CR). It is evident that only those materials during the pyrolysis of which structuring processes are essential can be suitable for obtaining carbon sorbents. Using definite procedures, in particular, adding other components, one may suppress destruction processes and make the equilibrium shift to structuring. On the other hand, the use of compositions consisting of the substances differing from each other in nature allows one to broaden the possibilities of obtaining carbon sorbents and to vary their properties. In this connection, of special interest as a precursor of carbon materials are the compositions in which one of the components helps increasing the yield of carbon during carbonization. For instance, it was discovered in the investigation of thermal transformations in pitch compositions with some polymers (cellulose, polycaproamide) that pitch promotes carbonization of the

polymers providing non-additive increase in the yield of CR; it was assumed that polycyclic aromatic compounds present in pitch act as initiators of carbonization [3, 4]. It may be assumed that other products of coal and oil processing containing polycyclic aromatic compounds would have a positive effect on carbonization of similar polymer materials.

In the present work we investigate the possibility to obtain carbon sorbents on the basis of binary compositions of cellulose-containing material, namely, pine sawdust with the gumlike products of coal processing which contain the compounds with polycyclic aromatic fragments. This choice is especially urgent for the Kuznetsky Basin and similar regions where the resources of coal and wood waste materials are especially large.

EXPERIMENTAL

The initial cellulose-containing material for obtaining carbon sorbents was pine sawdust, which comprises the major part of wood wastes over the territory of the Kuznetsk Basin. By-product coking tar from the West Siberian Metallurgic Plant, light- and heavy-weighed tar from the Leninsk-Kuznetskiy Semicoking Plant, waste products of the Kuznetsk Metallurgic Plant (KMP) from mud collectors were investigated as the second component of the composition. These components are the products of coal processing or contain them in representative amounts (wastes from the KMP) and need broadening of the routes of specialized consumption.

The samples of KMP wastes were collected in five different regions of mud collector, mixed thoroughly and filtered through a net with the mesh size of 1 ´ 1 mm to remove foreign particulates (stones, branchlets, *etc.*). A fraction with the particle size 1−2 mm was collected by sieving the sawdust and dried at a temperature of 100 ⁰C for 2 h. The amount of residual water was determined on the basis of thermogravimetric data and taken into account in subsequent calculation. The characteristics of sawdust and gumlike components are presented in Table 1. In the waste products from the KMP, the fraction of the substances insoluble in or-

ganic solvents and composed mainly of fine carbon and metal oxide particles was 19 %. Binary composition mixtures were prepared by mechanical mixing of the corresponding amounts of individual components. Carbonization of the samples (in a quartz trough; weighed portion of about 10 g) was carried out in a pipe muffle furnace in the flow of argon supplied at a rate of 10 cm^3/min; heating of the furnace was carried out at a rate of 5 ⁰C/min to the final temperature of 900 ⁰C. Activation of the obtained CR (a weighed portion of about 2 g) was carried out in the same furnace at a temperature of 900 ⁰C with water vapour supplied at a rate of 0.07 g/min (~0.035 g/g min) till the H$_2$O/CR ratio equal to 0.5−1.0 g/g. Sorption characteristics of the obtained carbon materials were estimated by measuring sorption of benzene vapour under static conditions with the help of desiccator method [5], and by means of iodine sorption (GOST 6217−74). Specific surface S_{sp} was determined by means of thermal desorption of argon (BET procedure) with the analyzer of specific surface Sorbtomer (manufactured by the JSC Katakon, Institute of Catalysis, SB RAS). Thermogravimetric examination was carried out with STA 409 PG/PC instrument of NETZSCH company by heating the sample in He flow supplied at a rate of 10 cm^3/s, with the heating rate of 10 K/min to the final temperature of 900 ⁰C.

RESULTS AND DISCUSSION

The yield of CR from carbonization of the initial substances and their compositions is presented in Fig. 1. One can see that the yields of CR at the mass fraction of components 0 and 100 % correspond to the yields of CR from individual substances. Under the conditions of our experiments, the yield of CR from sawdust is 21 mass %. Coke tar and wastes from the KMP in the individual state give CR with close yields which are 23 and 21 %, respectively. Carbonization of the light and heavy semicoking tar almost does not give CR (the yield is less than 5 %). The yield of CR in carbonization of binary compositions depends on the nature of tar and on its fraction. The highest CR yield is achieved with the compositions involving coke
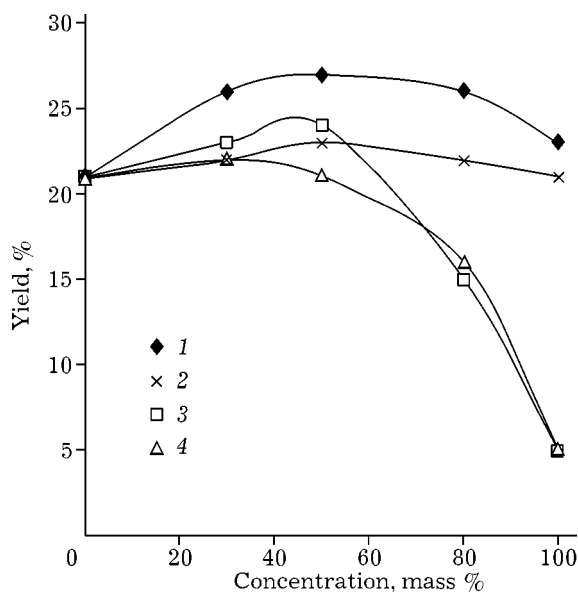
Fig. 1. Yields of carbon residues from the compositions of pine sawdust with coking tar (1), wastes from the KMP (2), light (3) and heavy (4) semicoking tar for different components ratio. $T = 900\ ^\circ$C.

tar, somewhat smaller is CR yield from the waste products of the KMP. This is true within the whole concentration range; however, maximal values are observed when the components are taken at close relative content. In the case of compositions with semi-coking tar, high CR yield is conserved till the tar content of 50 mass %.

Theoretical expected yields of CR, calculated on the basis of the yields of individual components and their fractions, are plotted as a straight line connecting the yields of CR from the individual components. However, one can see in Fig. 1 that the CR yields for all the compositions exceed theoretically expected values within the whole concentration range (the convexity of the curves is upward), which means that the synergetic effect is observed. The largest deviation from additivity is observed for the light and heavy semicoking tar, that is, for those components which almost do not form CR in the individual form. They also contain the largest amount of volatile fractions boiling at a temperature within 200–300 °C (see Table 1), which corresponds to the start of thermal destruction of sawdust (see below). The smallest deviation from additivity is observed in the case of waste products from the KMP, which form CR with rather high yield in the individual form; the amount of boiling fractions within the temperature range 200–300 °C is twice smaller than that in semicoking tar (see Table 1). The deviation from additivity for coking tar occupies an intermediate position; the yield of CR is about the same as that for the KMP wastes, but the content of fractions boiling within 300–400 °C is higher (see Table 1). These facts can prove that the fractions releasing in the temperature range of destruction of the second component (sawdust in the case under consideration) have a decisive influence on the manifestation of synergetic effect. Non-additive increase in the yield of CR from carbonization of the compositions is likely to be a consequence of the fact that the fragments formed during thermal destruction of separate components interact with each other forming a carbon structure. In the case when individual components are carbonized, these fragments are released as volatile products.

TABLE 1

Characteristics of the initial substances

Sample	Concentration, mass %			H/C, at./at.	Yield of volatiles, mass %, within temperature range, °C*		
	C	H	Ash		20–200	200–300	300–400
Coking tar	89.3	5.4	0.5	0.726	17	22	26
Light semicoking tar	78.7	8.7	0	1.327	25	45	26
The same, heavy	78.1	7.3	0	1.122	29	45	21
Wastes from the KMP	65.1	6.8	3.3	1.253	49	22	5
Sawdust**	52.4	7.1	Trace amount (~0.1)	1.636	–	–	–

*According to thermogravimetric data.
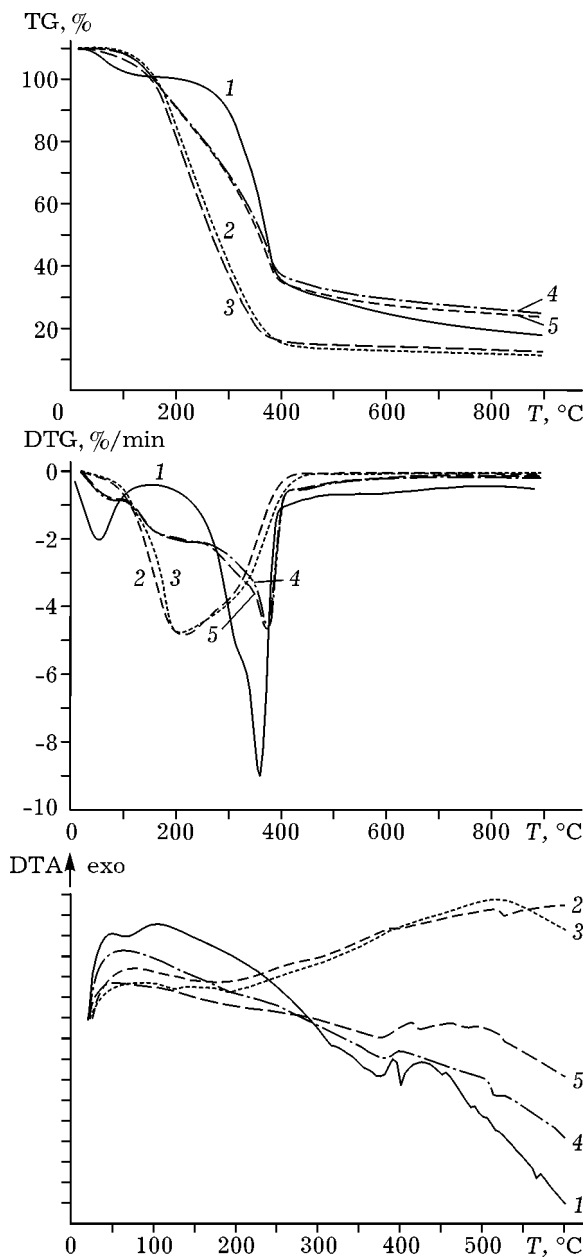
**Calculated for the dry sample.

Fig. 2. Thermograms of pine sawdust (*1*), heavy (*2*) and light (*3*) semicoking tar and their compositions with sawdust at the mass ratio of 50 : 50 % (*4* and *5*, respectively).

Fig. 3. Thermograms of pine sawdust (*1*), coking tar (*2*), the KMP wastes (*3*) and their compositions with sawdust at the mass ratio of 50 : 50 % (*4* and *5*, respectively).

Thermogravimetric investigation confirms a strong mutual influence of the components on thermal destruction of the composition. Thermograms of the initial substances and their compositions for the 50 : 50 % mass ratio of the components are shown in Figs. 2, 3. One can see that the main processes of thermal destruction of sawdust take place within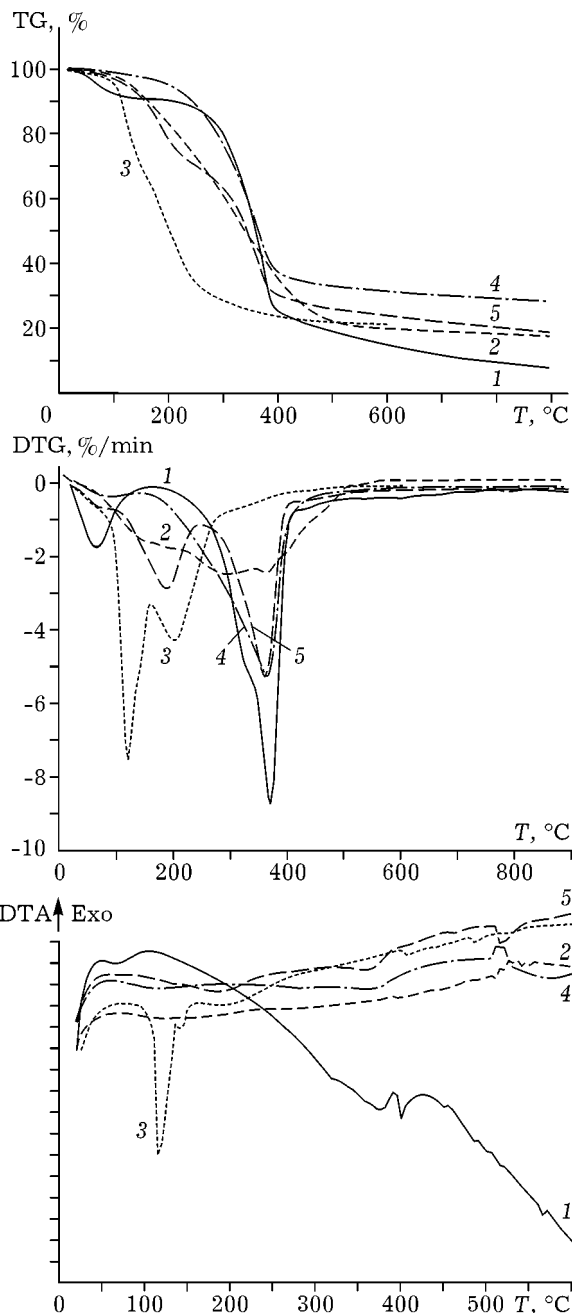 relatively narrow temperature range with a maximum at 371 °C and maximal decomposition rate of 8.7 %/min. The character of decomposition only slightly differs for the light and heavy semicoking tar. Intensive mass loss by these substances proceeds within a broad temperature range and finishes at approximately the same temperature as that for sawdust but is broadened substantially due to the low-temperature region. Maximal decomposition rates are ob-
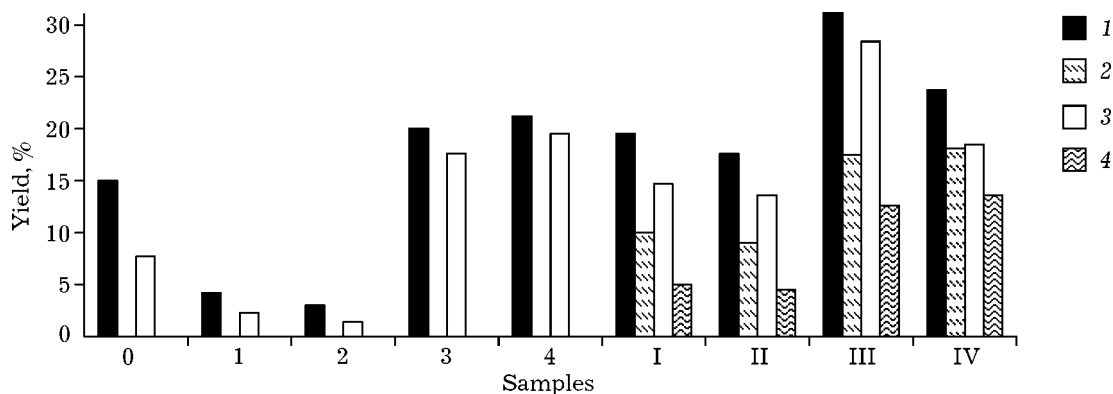
Fig. 4. Yields of carbon residues (CR) at 600 and 900 °C (according to the data of thermogravimetry) from pine sawdust (1), heavy (2) and light (3) semicoking tar, coking tar (4), the KMP wastes (5), their compositions with sawdust with the mass ratio of 50 : 50 % (I − IV, respectively): *1* − CR 600, *2* − T 600, *3* − CR 900. CR 600 and CR 900 were obtained for the compositions, T 600 and T 900 are theoretically expected values for the compositions, basing on the yields of CR from the individual components.

served at 211 and 221 °C for light and heavy tar, respectively, and are equal to 4.8 %/min. For the coking tar, intensive destructive processes take place in a broader temperature range embracing both the lower- and higher-temperature regions in comparison with sawdust. The maximal decomposition rate is achieved at 310 °C and is equal to 2.6 %/min. The mass loss by the KMP wastes proceeds almost entirely within the low-temperature range below the start of intensive thermal decomposition of sawdust; two clear maxima are observed in the DTG curves: at 120 and 202 °C with the decomposition rates of 7.5 and 4.3 %/min, respectively.

Thermograms of compositions (see Figs. 2, 3) are substantially different from those for the individual components. Intensive mass loss by the compositions of sawdust with semicoking tar occurs within the temperature range embracing the regions of mass loss of the individual components. Maxima corresponding to thermal destruction of individual components are observed at a complicated peak in the DTG; however, decomposition rates are lower for the case of compositions. Intensive thermal destruction of the compositions of sawdust with coking tar occurs within much more narrow temperature range than that for the case of individual tar; in its character, it is similar to thermal destruction of sawdust, but the start of intensive decomposition is shifted towards lower temperature and maximal decomposition rate

is lower (5.3 %/min). Thermal destruction of the compositions of sawdust with the KMP wastes is characterized by two regions of intensive mass loss; the positions of these regions are close to those of thermal transformations of the individual components; however, substantial changes are observed. Instead of two peaks on the DTG curve, which is characteristic of the KMP wastes, in the case of the composition we observe one peak at a temperature higher than that of the first peak but lower than that of the second one; maximal decomposition rate is 2.9 %/min at 189 °C. At the same time, the peak which is characteristic of thermal destruction of individual sawdust component shifts to lower temperature; maximal decomposition rate in this region is 5.3 %/min.

The corresponding changes are observed on the DTA curves (see Figs. 2, 3). Thermograms of the compositions exhibit disappearance of endothermic effects in the lower-temperature region which are observed in the case of individual heavy and light semicoking tar and the KMP wastes. The endothermic peak at 375 °C which characterizes thermal destruction of sawdust is present (with some temperature shifts) also in the DTA curves of all the compositions under investigation; however, its intensity decreases substantially. The endothermic peak at 399 °C disappears while passing from sawdust to compositions; it is overlapped by a more intensive exothermal peak.
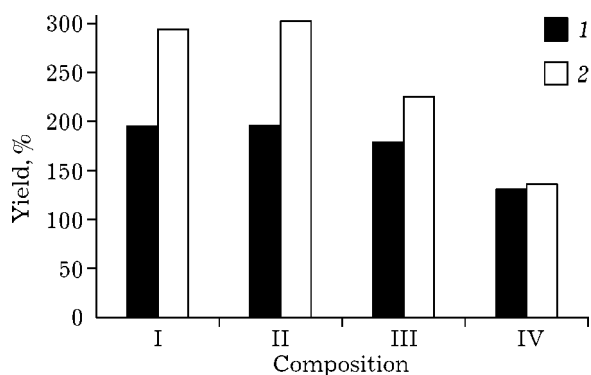
Fig. 5. Yields of carbon residues with respect to theoretically expected yield for the compositions 50 : 50 mass % : pine sawdust with heavy (I) and light (II) semicoking tar, coking tar (III), wastes from the KMP (IV) at 600 (*1*) and 900 °C (*2*).

The CR yields determined according to the data of thermogravimetry[1] (Fig. 4) confirm the occurrence of synergetic effect observed earlier when investigating carbonization in a furnace (see Fig. 1).

Deviation from additivity reaches 200–300 % for the compositions with light and heavy semicoking tar, 230 % for the coking tar and 140 % for the KMP wastes (Fig. 5). Comparing the yields at 600 and 900 °C one may note that the synergetic effect at 900 °C is much higher than that at 600 °C almost for all the compositions under investigation (in the case of the KMP wastes these two values are approximately equal) (see Figs. 4, 5). Therefore, for carbonization of compositions, even at 600 °C carbon structure is formed which exhibits higher thermal stability and therefore is more profitable from the energy viewpoint and more perfect than that in the case of carbonization of individual components; in the latter case, heating from 600 to 900 °C is accompanied by a more substantial mass loss.

So, the use of compositions allows one to affect thermal decomposition processes increasing the contribution from structuring and thus increasing the yield of CR, which provides the possibility to broaden the range of substances suitable for obtaining carbon materials. In this case all the components under investigation (including those which practically do not form CR in the individual form) in compositions with sawdust allow obtaining the carbon material with rather a high yield.

The mutual effect of components, taking place in carbonization of compositions, defines also the features of further activation of the obtained CR, which is exhibited as differences in the ability to interact with the activating agent and in sorption properties of the resulting materials. Some characteristics of activated carbon materials (ACM) are listed in Table 2. For comparison, the corresponding characteristics for the industrial carbon sorbents based on coal (AG-3) and on wood (BAU-A) are shown; these sorbents are known to have high activity; they are widely used to purify water and air [2]. One can see in Table 2 that the highest sorption capacity (taking scorching into account) is achieved for the case of sawdust. The carbon residue obtained on the basis of coking tar is very poorly amenable to activation: under the conditions providing very easy scorching of other substances, the CR based on this tar does not interact with the activating agent; hence, the sorption capacity of the resulting material is very low. Among all the kinds of tar under investigation, only the KMP wastes in the individual form provide high CR yield (see Figs. 1, 3) and can easily be activated; the resulting carbon material possesses high sorption activity with respect to benzene. At the same time, when included into compositions with sawdust, all the kinds of tar under investigation form rather easily activated CR and allow obtaining sorbents with a relatively high yield and good sorption characteristics (the sorption capacity with respect to benzene and iodine), which are in some cases quite comparable with the similar parameters for AG-3 and BAU-A and correspond in these parameters to the requirements for some other grades of industrial active carbon substances [2]. Insufficiently high specific surface (S_{sp}) and sorption capacity of some ACR samples can be increased by increasing the degree of their activation (scorching) (see Table 2) and perhaps by varying the components ratio of the initial composition.

---

[1]The differences in the data on the yield of CR in thermogravimetric studies and those obtained for carbonization in a furnace are explained by the difference in technological parameters of carbonization process which affect the results substantially.

TABLE 2

Some characteristics of carbon sorbents based on individual components and compositions
obtained with different consumption of the activating agent

Sample	Consumption of the activating agent H_2O/CR, g/g	Scorching, mass %	Static activity with respect to benzene, mg/g	Sorption activity with respect to iodine, %	S_{sp}, m^2/g
Carbon sorbent obtained on the basis of individual components:					
pine sawdust	0.5	35	520	125	964
the KMP wastes	1.0	55	429	–	–
coking tar	0.5	3	25	–	–
Carbon sorbent obtained on the basis of composition, 50 : 50 mass % sawdust:					
with the KMP wastes	0.5	35	446	46	311
with coking tar	1.0	47	419	54	700
with light semicoking tar	0.5	27	254	45	491
with heavy semicoking tar	0.5	21	214	30	255
	0.75	35	338	44	299
	1.0	54	669	74	569
AG-3	–	–	311	56	825
BAU-A	–	–	329	47	730

Undoubtedly, the preparation process and the properties of carbon sorbents based on different compositions require a more detailed investigation which would allow one to increase the yield of product and its sorption characteristics, and to recommend the area of the most rational application. Different sorption activity of the samples with approximately equal scorching evidently points to different porous structure of the sorbents, which is determined by the nature of the initial compound. Because of this, the use of the substances of different nature as the initial material for compositions opens inexhaustible possibilities for variations of the porous characteristics of carbon sorbents obtained on this basis.

CONCLUSIONS

Thus, it is demonstrated that carbon sorbents with rather high sorption characteristics can be obtained with a high yield on the basis of the compositions of wood waste and gum-like products of coal processing. Carbonization of these compositions is accompanied by changes in the mechanism of thermal transformations as a result of interactions between the products of thermal destruction of individual components; this is exhibited as the shifts of temperature ranges of intensive decomposition and a decrease in the rate of destruction of the compositions; the yield of CR increases non-additively, that is, synergetic effect is observed. As a result, the use of compositions allows one to increase the yield of the final product and broaden the range of carbon sorbents, including the introduction of materials which hardly carbonize in the individual form.

REFERENCES

1 V. B. Fenelonov, Poristy uglerod, izd. IC SB RAS, Novosibirsk, 1995.

2 V. M. Mukhin, A. V. Tarasov, V. N. Klushin, Aktivnye ugli Rossii, Metallurgiya, Moscow, 2000.

3 S. S. Shchukin, Yu. G. Kryazhev, A. A. Sokolovskiy, *Khim. Volokna*, 4 (1991) 19.

4 T. G. Jashiashvili, Yu. G. Kryazhev, O. Kirret, A. Kogerman, *Izv. AN ESSR*, 34, 2 (1985) 150.

5 L. D. Gluzman, I. I. Edelman, Laboratorny kontrol' kokskohimicheskogo proizvodstva, Gos. nauch.-tekhn. izd-vo lit. po chernoy i tsvetnoy metallurgii, Khar'kov, 1957.

6 I. N. Ermolenko, I. P. Lyubliner, N. V. Gul'ko, Elementosoderzhashchiye ugol'nye voloknistye materialy, Nauka i tekhnika, Minsk, 1982.