

Thermal Decomposition and Combustion of Coals, Fuel Wood, and Hydrolytic Lignin, as Studied by Thermal Analysis

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Abstract—Different biofuel woods (spruce, pine, and spruce and pine bark), hydrolytic lignin, and coals from different deposits [D coal from Inta, Zh coal from Vorkuta, and D coal from Khakassia] were studied on a synchronous thermal analyzer at heating rates of 5, 10, and 20 K/min in inert and air atmospheres. Classical thermogravimetric and differential thermogravimetric curves were obtained to describe the thermal decomposition of hemicellulose, cellulose, and lignin and the combustion of a carbon residue as the main components of the biofuel woods. The decomposition of the coal fuels from different deposits was studied, and the temperature ranges of drying, the release of volatile substances, and the combustion of carbon residues were obtained. The results of thermal analyses were processed with the use of an isoconversional method based on the Friedman and Ozawa–Flynn–Wall models and with the aid of an extended independent parallel reaction (EIPR) model. A satisfactory repeatability of the results was obtained to indicate the applicability of both of these methods. The subsequent study of wood, hydrolytic lignin and, coals from different deposits was carried out with the aid of the EIPR model. The activation energies of biofuel woods varied in a range from 62 to 93 kJ/mol, which are much lower than those of coals (104–116 kJ/mol).

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Biofuel wood is a renewable energy source, which occupies the fourth position in the energy balance after coal, oil-refining products (petroleum residue), and natural gas. As compared with fossil fuels, it possesses an essential advantage in terms of carbon dioxide emissions, which are considered zero rated because plants absorbed the same quantity of carbon dioxide in the course of growth and released oxygen. Furthermore, the sulfur and nitrogen content of biofuel wood is low [1].

A large body of published data on the studies of fossil fuels, especially, on the kinetics of coal combustion, the formation and release of volatile substances, and the combustion of a carbon residue, are currently available [2–5]. Despite the fact that biofuel wood is one of the most ancient forms of fuel, its effective use for power generation purposes remains a problem of considerable current interest for the majority of countries.

Biofuel is widely used in the processes of gasification and pyrolysis. Pyrolysis is a thermal decomposition process and the first stage of gasification and combustion. The process conditions of pyrolysis strongly influence the reactivity of a carbon residue on the subsequent combustion and gasification. Fuel

wood contains 70–85 wt % volatile substances on a combustible basis, and its thermal decomposition comes into play in a temperature range from 160 to 250°C. Because volatile substances play an important role in the heat balance of fuel wood combustion, a study of the processes that occur on the heating and

Table 1. Elemental composition (on an analytical basis) of the samples of spruce, pine, spruce and pine bark, lignin, and coals

Sample	C ^a , %	H ^a , %	N ^a , %	S ^a , %	O ^a , %
Hydrolytic lignin	52.56	5.84	0.2	–	29.78
Spruce (stem)	47.87	6.98	0.33	–	36.94
Spruce (bark)	49.22	7.20	0.87	–	28.87
Pine (stem)	47.73	6.99	0.43	–	37.13
Pine (bark)	47.98	7.00	0.58	–	32.41
Inta coal	40.73	2.67	1.38	2.30	7.92
Vorkuta coal	52.60	3.30	1.50	1.0	4.20
Khakassia coal	58.08	3.98	1.70	0.30	9.65

Table 2. Thermotechnical analysis of the samples of spruce, pine, spruce and pine bark, lignin, and coals

Sample	Analytical moisture content W^a , %	Analytical ash content A^a , %	Yield of volatile substances on an analytical basis V^a , %	Low heat value on an analytical basis Q^a , MJ/kg
Hydrolytic lignin	8.60	3.02	57.83	19.31
Spruce (stem)	6.89	0.99	79.12	17.03
Spruce (bark)	11.63	2.21	65.51	16.98
Pine (stem)	7.38	0.34	79.06	17.31
Pine (bark)	9.50	2.53	68.64	17.29
Inta coal	9.50	35.49	21.99	15.57
Vorkuta coal	8.00	23.63	27.02	21.96
Khakassia coal	9.50	16.8	31.77	21.68

thermal decomposition of biomass forms a basis for the development of methods for increasing the efficiency of the power-generating use of biofuel.

The process conditions of pyrolysis (heating rate, temperature, and sample size) play an important role in the structural evolution of a carbon residue. It was established that the rate of heating of a sample affects the total yield of volatile substances, their chemical composition, and the structure of the resulting carbon residue [6–8]. At a high heating rate, a larger quantity of volatile substances is formed than that at a low heating rate, and these volatile substances mainly consist of heavy components with high C/H ratios. A rapid increase in pressure in the wood sample and an explosive release of volatile substances also occur at a high heating rate. On the other hand, the low-rate heating makes it possible to carry out the slow release of volatile substances after studying in detail the polymerization of volatile components in the carbon residue. Secondary reactions, which accompany the process of polymerization, occur on the surface of a carbon residue to increase its quantity. The presence of oxygen-containing functional groups and subgroups in the carbon residue is indicative of its typical amorphous structure and higher reactivity [9–11].

According to the Energy Strategy of Russia for a Period to 2020, which was affirmed by the Government of the Russian Federation (order no. 1234-r of August 28, 2003), coal serves as the largest raw-material base for the RF power engineering. Therefore, the efficient and economic use of coal is also a problem of considerable current interest. Currently, it is impossible to completely replace fossil fuels by renewable biofuel both in the Russian Federation and around the world; however, the partial replacement of coal by fuel wood, for example, in a proportion of 70% coal and 30% fuel wood (in terms of heat release) can be carried out in the boiler units of thermal power plants [12, 13].

In order to convert a boiler unit to the joint combustion of coal and fuel wood, it is necessary to study in detail the thermal properties of coals and biofuel and to apply advanced technologies to the organization of a burning process.

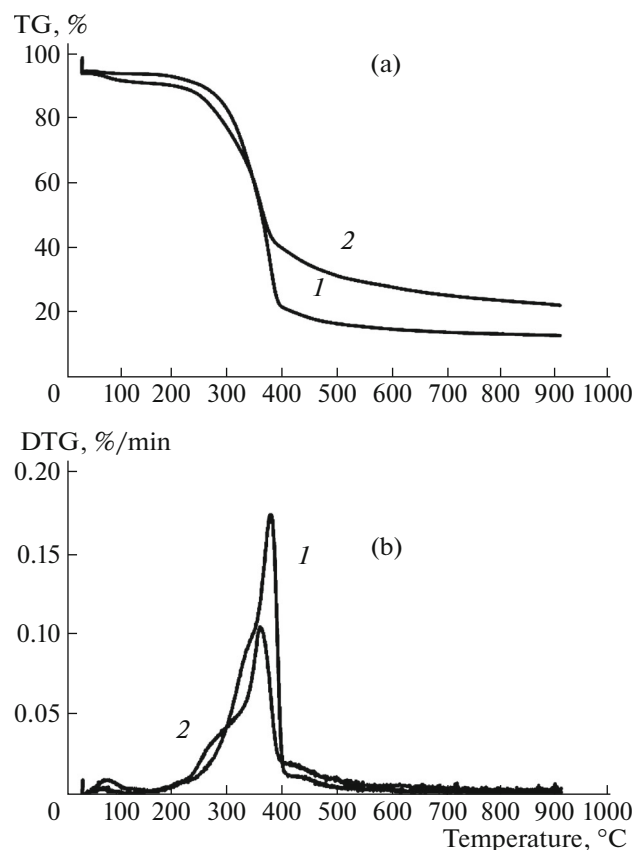


Fig. 1. Results of the (a) TG and (b) DTG analysis of the stem woods of (1) pine and (2) spruce in an inert atmosphere.

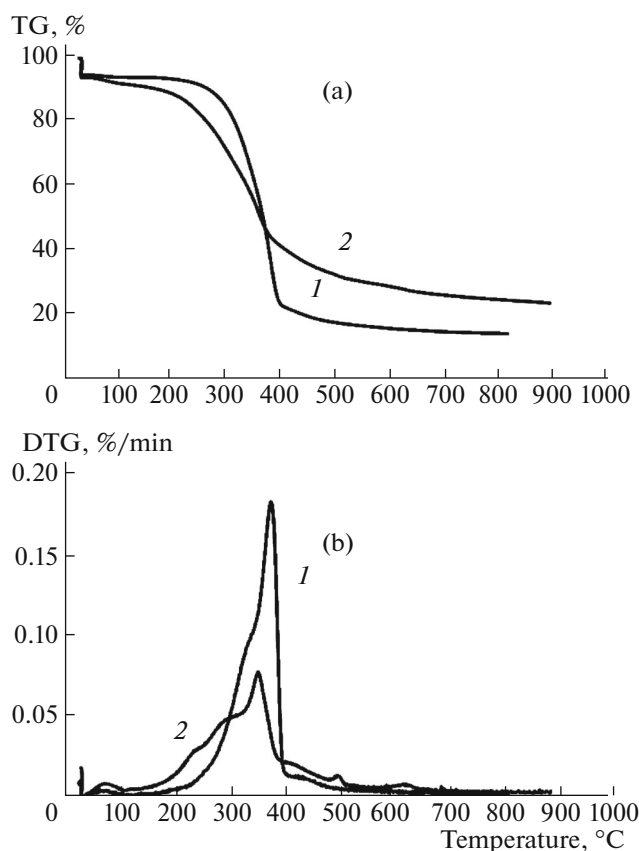


Fig. 2. Results of the (a) TG and (b) DTG analysis of (1) the stem wood of spruce and (2) spruce bark in an inert atmosphere.

The aim of this work was to study different fuel woods, hydrolytic lignin, and black coals by thermal analysis and the chromatography of gas mixtures. The thermal decomposition of the samples of spruce and pine stem wood, spruce and pine bark, hydrolytic lignin, and coals from the Inta, Vorkuta, and Khakassia deposits was performed in air and inert atmospheres. The pine and spruce wood samples were chosen for more detailed analysis, and not only kinetic analysis but also the chromatography of gas mixtures were performed for these samples.

EXPERIMENTAL

The fuel woods of different tree species (spruce, birch, and spruce and birch bark) were collected in the territory of Arkhangelsk oblast in the North Western region of the Russian Federation. The samples of coals (D coal from Inta, Zh coal from Vorkuta, and D coal from Khakassia) were provided by Severodvinsk TETs-1 (Heat Station), at which they are used. The samples were preliminarily ground in a Retsch PM 200 mill and sifted on a Retsch AS 200 Control sieve shaker to a granulometric composition from 63 to 125 μm .

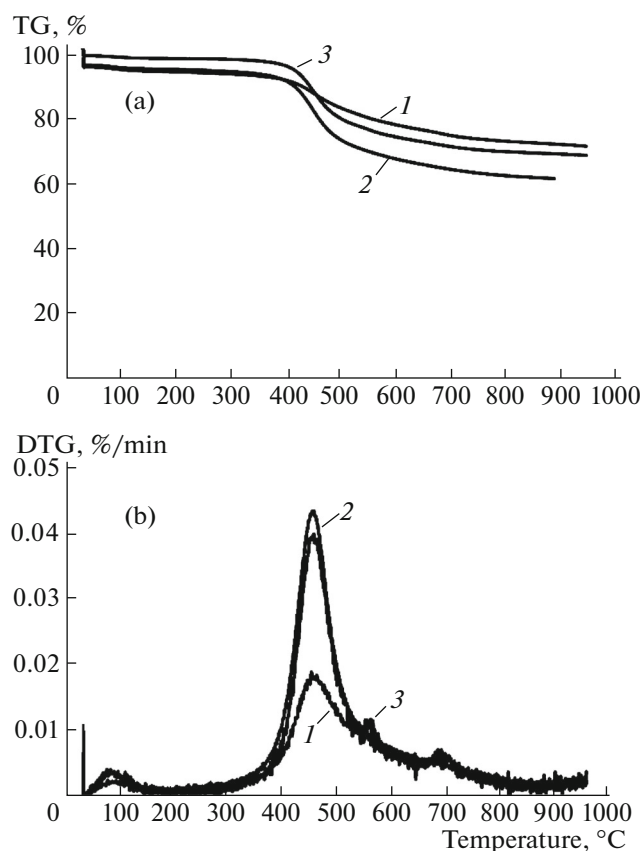


Fig. 3. Results of the (a) TG and (b) DTG analysis of coals from the (1) Inta, (2) Khakassia, and (3) Vorkuta deposits in an inert atmosphere.

The samples of different wood species, hydrolytic lignin, and coals were studied under laboratory conditions; therefore, the results of elemental and thermo-technical analysis are given on an analytical basis.

The carbon, hydrogen, nitrogen, and sulfur contents were determined with the aid of an EuroVector EA-3000 analyzer, and the oxygen content was calculated based on a mass balance (Table 1). The moisture, ash, and volatile matter contents of the test samples were determined in accordance with standard procedures. An IKA C 2000 Basic version 2 calorimeter was used for determining the specific heats of combustion of the fuels. Table 2 summarizes the results of the thermo-technical analysis. Thermogravimetric analysis was performed on a TA Instruments Q500 analyzer.

RESULTS AND DISCUSSION

The results of thermogravimetric (TG) and differential thermogravimetric (DTG) analysis performed in inert and air atmospheres are shown in Figs. 1–4 and 5–8, respectively.

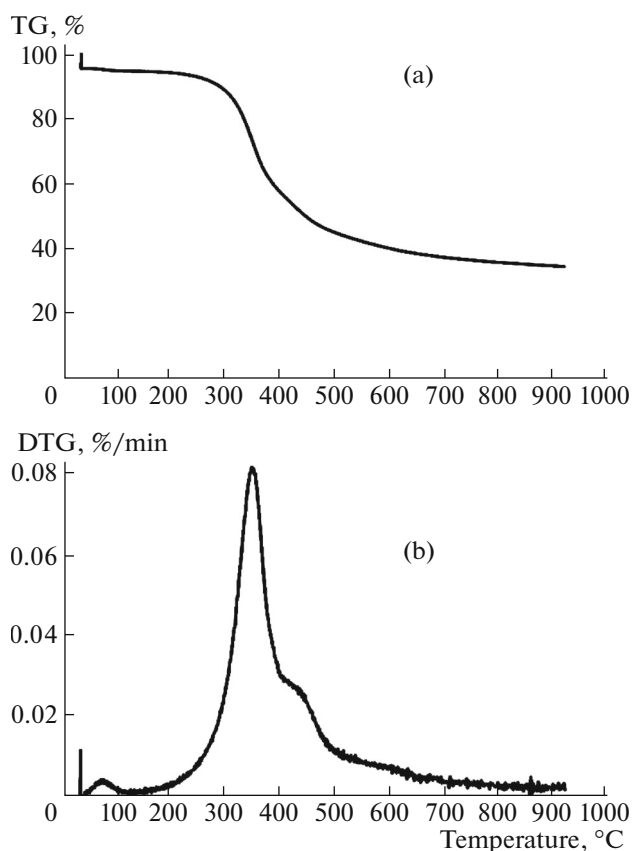
Table 3. Thermogravimetric analysis of the samples of spruce, pine, spruce and pine bark, lignin, and coals

Sample	Inert atmosphere	
	temperature ranges, °C	
	drying	yield of volatiles
Pine	20–100	251–395 (375)*
Pine bark	20–121	215–381 (361)
Spruce	20–90	286–400 (381)
Spruce bark	20–106	230–365 (349)
Inta coal	20–148	357–481 (439)
Vorkuta coal	20–153	381–495 (452)
Khakassia coal	20–161	402–489 (443)
Hydrolytic lignin	20–126	279–471 (347)
Sample	Air atmosphere	
	temperature ranges, °C	
	drying	yield of volatiles
Pine	20–95	261–369 (349)*
Pine bark	20–110	237–355 (320)
Spruce	20–96	273–367 (350)
Spruce bark	20–103	211–348 (326)
Inta coal	20–126	392–537 (481)
Vorkuta coal	20–131	376–550 (452)
Khakassia coal	20–138	398–598 (547)
Hydrolytic lignin	20–82	281–401 (306)

* The temperature corresponding to a maximum rate of the release of volatile substances is given in parentheses.

The TG and DTG data were compared for spruce stem wood and bark, pine stem wood and bark, coals from different deposits, and hydrolytic lignin.

The classical TG and DTG curves in Figs. 1–4 describe the evaporation of moisture and the release of volatile substances. Considering biofuel wood (Figs. 1, 2) and hydrolytic lignin (Fig. 4), we can recognize three main zones. The first zone in a temperature range from 20 to 140°C with a weight loss of about 10% (depending on fuel) was characterized by the evaporation of moisture. On further heating, the degradation of organic compounds came into play; it was accompanied by the release of volatile substances over a wide range of temperatures, and a maximum weight loss was noted at 300–400°C. Thus, the temperature of a maximum rate of the release of volatile substances was 375°C for pine stem wood; this temperature for pine bark was somewhat lower: 361°C (Table 3). The above

**Fig. 4.** Results of the (a) TG and (b) DTG analysis of hydrolytic lignin in an inert atmosphere.

values for spruce were approximately the same; this fact can be explained by the similarity of their properties as coniferous wood species. The temperature of a maximum rate of the release of volatile substances from hydrolytic lignin was 347°C (Table 3), which is somewhat lower than that for spruce and pine woods; this can be explained by the action of a hydrolytic process on the structure of wood raw material (Table 2). The temperature range of 250–400°C corresponds to the second zone of active pyrolysis. The main weight loss (from 45 to 60% depending on the type of fuel) and the thermal decomposition of hemicellulose and cellulose as the components of biofuel woods occurred in this zone. The third zone is located in a temperature range from 400 to 800°C, and it characterizes the process of passive pyrolysis, when the prolonged thermal decomposition of matter, predominantly, lignin occurred. The weight loss in this range varied from 10 to 15% depending on the sample.

For the test black coals, the process of drying occurred in a range of 20–161°C (Fig. 3). On the subsequent heating, a latent period of the thermal degradation of the organic matter of coal preceded the emission of gas. At 340–380°C, the release volatile sub-

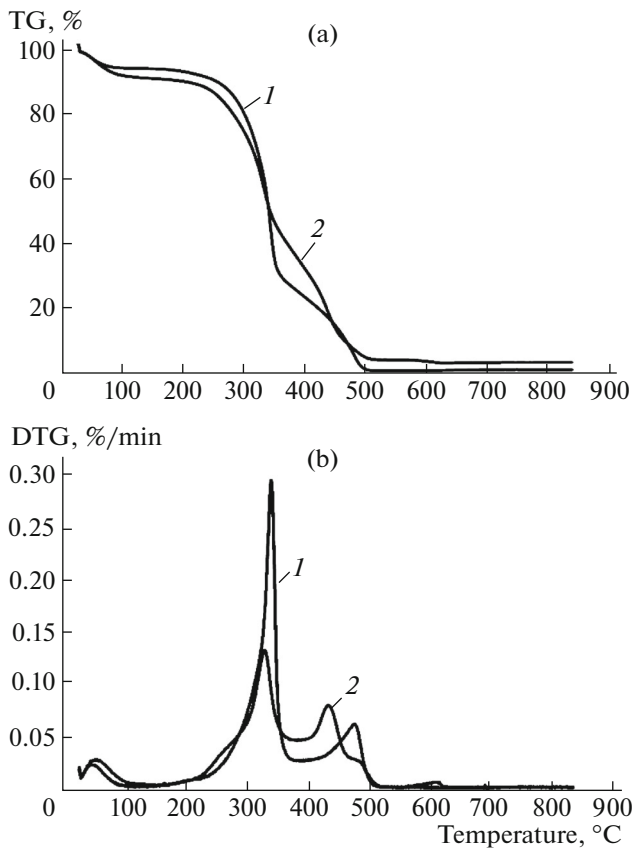


Fig. 5. Results of the (a) TG and (b) DTG analysis of (1) the stem wood of pine and (2) pine bark in an atmosphere of air.

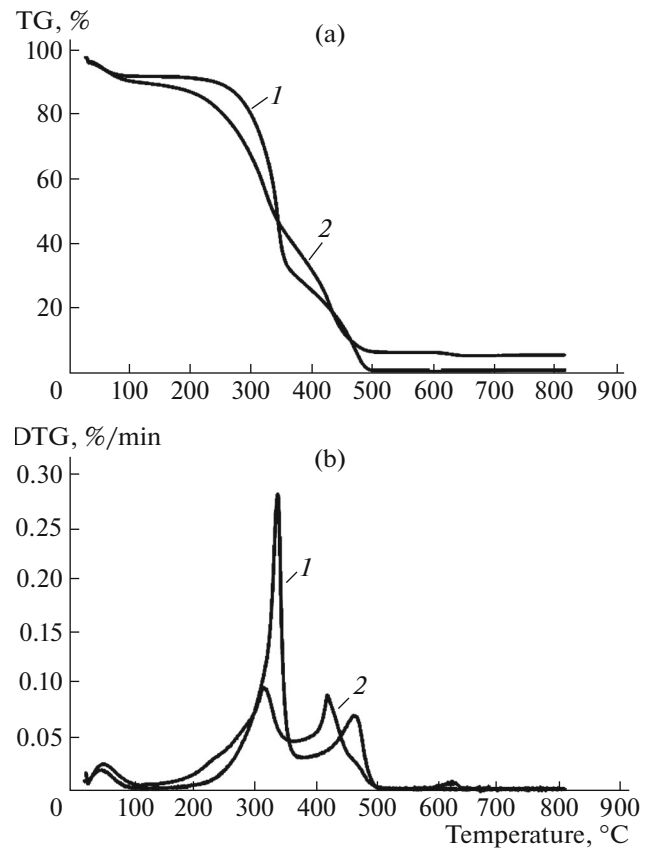


Fig. 6. Results of the (a) TG and (b) DTG analysis of (1) the stem wood of spruce and (2) spruce bark in an atmosphere of air.

stances came into play to reach a maximum rate at 440–452°C (Table 3). Thus, for the test black coals, a temperature range of 400–570°C corresponded to the zone of active pyrolysis. The process of passive pyrolysis occurred at 570–900°C, and it was characterized by the prolonged thermal decomposition of organic matter.

The volatile matter content of coals was much lower than that of fuel woods; therefore, the combustion of a carbon residue was the main exothermic process in the thermal analysis in an atmosphere of air (Fig. 7). The DTG curves of the thermal analysis of black coals in an atmosphere of air exhibited only one characteristic peak related to the release and combustion of volatile components and the burning-out of carbon. For biofuels with high volatile matter contents, the DTG curves (Figs. 5, 6, and 8) exhibited two characteristic peaks, which corresponded to the stages of the release and combustion of volatile substances and the burning-out of a carbon residue. In this case, the peaks corresponding to a maximum rate of the release of volatile substances were shifted to the region

of lower temperatures, as compared with those in an inert atmosphere.

The results of the TG analyses of the test fuels are consistent with the data of thermotechnical analyses in terms of moisture, ash, volatile matter, and carbon residue contents. The release of volatile substances from fuel wood and hydrolytic lignin came into play well before, and it occurred at lower temperatures, in comparison with coals; this fact indicates that the reactivity of biofuel is higher than that of coals.

The kinetic studies were carried out both with the aid of differential and integral isoconversional methods based on the Friedman and Ozawa–Flynn–Wall models and with the use of an extended independent parallel reaction (EIPR) model [14], which separately described the kinetics of the thermal decomposition of lignin, cellulose, and hemicellulose (xylan). The kinetic parameters (activation energies and reaction rate constants based on the Friedman and Ozawa–Flynn–Wall models) were determined at different degrees of decomposition in the course of sample pyrolysis or combustion at three different rates of heating based on the results of TG analysis. The EIPR

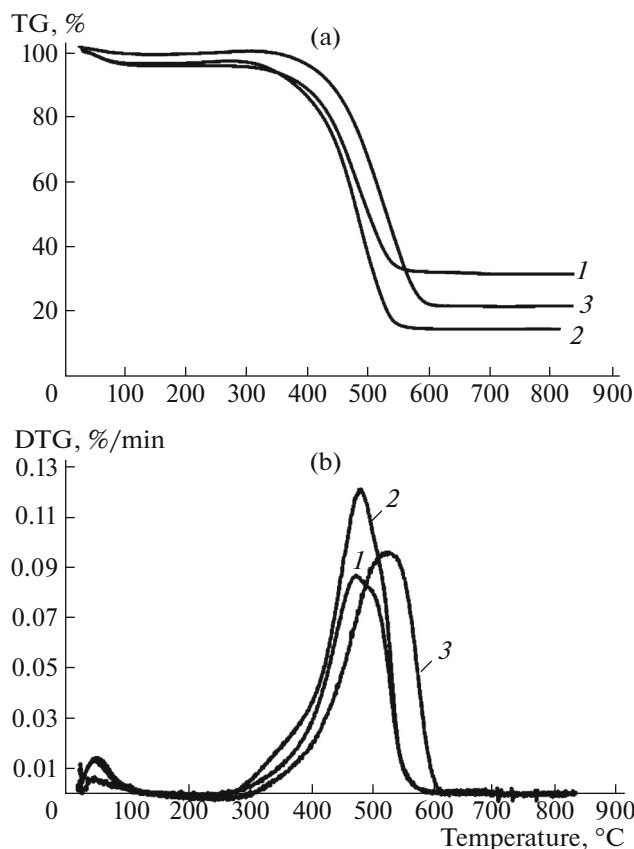


Fig. 7. Results of the (a) TG and (b) DTG analysis of coals from the (1) Inta, (2) Khakassia, and (3) Vorkuta deposits in an atmosphere of air.

model makes it possible to separately determine kinetic parameters for the thermal decomposition of each particular sample component: lignin, cellulose, and hemicellulose for biofuel woods (Tables 4, 5).

Comparing the data in Tables 4 and 5, we can make a conclusion on the consistency of the average values of activation energies and reaction rate constants of the combustion of pine and spruce samples in an atmosphere of air. The average values of the activation energies found with the aid of isoconversional methods were 117.7 and 117.2 kJ/mol for pine and spruce, respectively, whereas those found with the aid of the EIPR model were 99.6 and 147.06 kJ/mol, respectively. A disagreement between the data can be related to an inaccuracy in the determination of the percent concentrations of the components of wood—hemicellulose, cellulose, and lignin, which were taken in accordance with published data [15]. The data [15] on wood were generalized, whereas the concentrations of hemicellulose, cellulose, and lignin were represented individually for each species.

Table 6 summarizes data on the kinetic characteristics of the stem wood and bark of pine and spruce,

hydrolytic lignin, and coals from different deposits in inert and air atmospheres based on the EIPR model.

As noted above, the kinetic characteristics of fuel woods (pine and spruce stem wood and bark and hydrolytic lignin) were determined for each particular component of the biofuel. The average value was calculated based on the percentage of a component in wood. The kinetic parameters of hydrolytic lignin as a by-product of wood conversion were also found based on the components of this product.

The kinetic constants of black coals were calculated by a somewhat other method. The DTG curve of the thermal decomposition of coal in an atmosphere of nitrogen has three peaks (without taking into account a peak due to the process of drying, Fig. 3). One clearly pronounced peak characterizes the temperature of a maximum rate of the release of volatile substances, and two small peaks occur in the region of higher temperatures. The kinetic parameters were calculated for each of the peaks. In an atmosphere of air, the DTG curve of the thermal decomposition of coal takes another form (Fig. 7). It has a single peak (without taking into account a peak that corresponds to the pro-

Table 4. Kinetic study of the thermal processes in spruce and pine samples in an air atmosphere with the use of the Friedman and Ozawa–Flynn–Wall models

Degree of conversion, %	Friedman model		Ozawa–Flynn–Wall model	
	E , kJ/mol	$\log A/s^{-1}$	E , kJ/mol	$\log A/s^{-1}$
	pine			
0.02	5.66	4.54	0.05	4.90
0.05	0.02	3.62	0.01	4.53
0.10	3.96	3.10	1.76	3.86
0.20	98.16	6.21	13.69	2.20
0.30	226.62	17.95	146.28	10.92
0.40	240.38	18.98	245.27	19.82
0.50	213.57	16.45	232.99	18.51
0.60	201.25	15.19	210.25	16.36
0.70	38.37	5.96	60.33	2.74
0.80	91.40	4.25	48.66	1.40
0.90	184.40	11.13	166.90	10.36
0.95	179.05	10.80	245.81	16.04
0.98	44.55	4.96	4.63	2.43
Average value	117.49	9.47	105.9	8.77
Degree of conversion, %	Friedman model		Ozawa–Flynn–Wall model	
	E , kJ/mol	$\log A/s^{-1}$	E , kJ/mol	$\log A/s^{-1}$
	spruce			
0.02	13.47	1.43	33.44	1.77
0.05	7.77	2.67	8.87	2.66
0.10	68.94	3.51	34.47	0.16
0.20	208.69	16.57	160.95	12.54
0.30	232.96	18.44	196.21	15.50
0.40	216.55	16.78	210.51	16.56
0.50	201.97	15.36	204.41	15.88
0.60	194.23	14.47	193.65	14.82
0.70	49.45	1.22	88.62	5.17
0.80	120.85	6.53	105.71	6.03
0.90	115.91	6.21	121.73	6.95
0.95	73.37	3.23	162.29	9.92
0.98	36.27	4.47	2.00	2.73
Average value	118.49	8.53	117.14	8.51

Table 5. Kinetic study based on the EIPR model

Sample constituent	Kinetic parameters		Component concentration, %
	E , kJ/mol	$\log A/s^{-1}$	
	pine		
Hemicellulose	78	4.89	20
Cellulose	108	6.79	65
Lignin	92	4	15
Average value	99.6	5.99	—
Sample constituent	Kinetic parameters		Component concentration, %
	E , kJ/mol	$\log A/s^{-1}$	
	spruce		
Hemicellulose	111	7.65	19
Cellulose	193.17	14.27	48
Lignin	101	4.56	33
Average value	147.06	9.81	—

cess of drying). The kinetic constants were calculated for this peak.

The greatest values of activation energies and reaction rate constants were noted for coal fuel. The average value of the activation energy of coal lies in a range from 104 to 116 kJ/mol, whereas the average value of the activation energy of biofuel woods, including hydrolytic lignin, lies in a range of 62–93 kJ/mol. This can be explained by the fact that molecular bonds in coal are stronger than those in the fuel woods. The activation energy of hydrolytic lignin is lower than that of the fuel woods due to the weakening of molecular bonds in the process of wood hydrolysis.

In an inert atmosphere, the kinetic model of the process of pyrolysis was described with the aid of a multicomponent mechanism, which considered the process of pyrolysis as the sum of three independent and simultaneous reactions related to the yield of volatile substances from the hemicellulose, cellulose, and lignin. The data obtained show that, generally, the activation energy is lower in an inert atmosphere than that in air.

CONCLUSIONS

The results of DTG analyses showed that the decomposition of wood and hydrolytic lignin in an inert atmosphere exhibits one peak (without taking into account the peak of drying); this can be explained by the fact that the decomposition of the three main components of fuel wood (hemicellulose, cellulose,

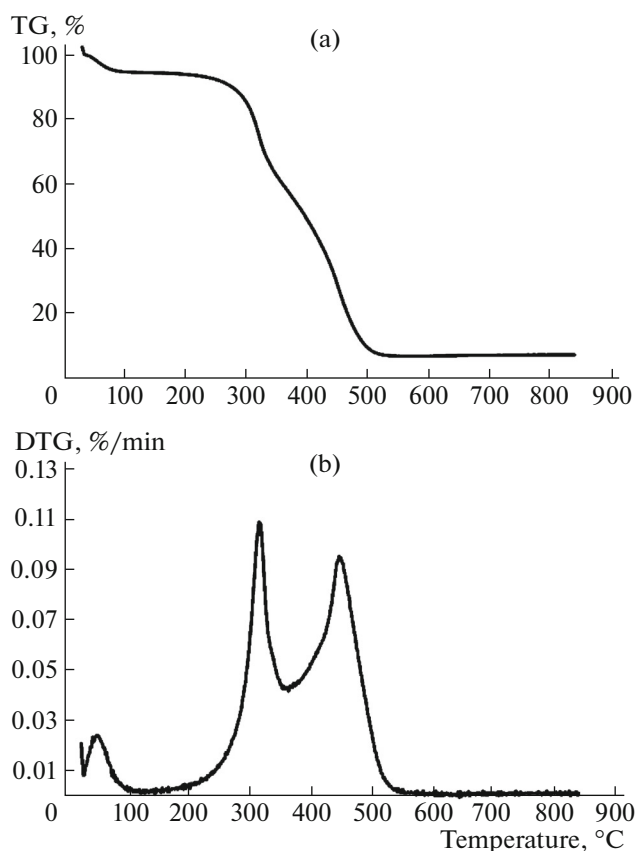


Fig. 8. Results of the (a) TG and (b) DTG analysis of hydrolytic lignin in an atmosphere of air.

and lignin) occurs simultaneously but with different rates over a wide range of temperatures. Hydrolytic lignin (in contrast to the fuel wood) is characterized by a broader temperature range of the release of volatile substances. In an atmosphere of air, two peaks are observed: the first peak is similar to that in an inert atmosphere, and the second corresponds to the combustion of a carbon residue. Coal fuel has one characteristic peak in the DTG curve because the volatile matter content of the initial fuel is small and the processes of the release of volatile substances and the combustion of a carbon residue interfere with each other.

The thermal analysis data were processed with the use of both isoconversional methods based on the Friedman and Ozawa–Flynn–Wall models and with the aid of the EIPR model. The good repeatability of the results was obtained to indicate the applicability of both methods; therefore, further studies of fuel woods and black coals from different deposits were performed with the aid of the EIPR model. The values of the activation energies of the fuel woods lie in a range from 62 to 93 kJ/mol, which is much lower than that for coal (104–116 kJ/mol).

Table 6. Results of a kinetic study of different wood samples of based on the EIPR model in inert and air atmospheres

Sample constituent	Kinetic parameters				Component concentration, %
	inert atmosphere (nitrogen)		air atmosphere		
	E , kJ/mol	$\log A/s^{-1}$	E , kJ/mol	$\log A/s^{-1}$	
pine					
Hemicellulose	75.9	5.09	78	4.89	20
Cellulose	100	6.05	108	6.79	65
Lignin	84	3.14	92	4	15
Average value	92.78	5.42	99.6	5.99	
spruce					
Hemicellulose	123.63	7.65	110.63	7.65	19
Cellulose	200.17	14.27	193.17	14.27	48
Lignin	120.98	8.56	100.98	4.56	33
Average value	159.49	11.13	147.06	9.81	
pine bark					
Hemicellulose	73.9	4.89	78	4.89	20
Cellulose	100	6.05	108	6.79	65
Lignin	83	3.01	92	4	15
Average value	92.23	5.36	99.6	5.99	
spruce bark					
Hemicellulose	72	1.27	70	4.58	19
Cellulose	72	3.17	83	4.85	48
Lignin	42.9	0.64	95	4.85	33
Average value	62.39	1.97	84.49	4.79	
hydrolytic lignin					
Hemicellulose	78	4.26	77	4.26	60
Cellulose	87	4.02	92	4.02	20
Lignin	60	1.01	50	1.01	20
Average value	76.2	3.56	74.6	3.56	
Inta coal					
Peak 1	135	7.51	106	5.03	24
Peak 2	180	7.28			20
Peak 3	64	1.55			56
Average value	104.24	4.13	106	5.03	
Khakassia coal					
Peak 1	135	7.49	106	5.03	55
Peak 2	110	4.7			25
Peak 3	75	1.16			20
Average value	116.75	5.53	106	5.03	
Vorkuta coal					
Peak 1	135	7.46	107	4.54	55
Peak 2	110	4.63			25
Peak 3	70	0.97			20
Average value	115.75	5.45	107	4.54	

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