THERMAL DECOMPOSITION AND OXIDATION OF COAL PROCESSING WASTE

by

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To expand the database of kinetic parameters used for modeling the ignition of coals and their processing waste, promising coal-water slurry and coal-water slurry containing petrochemicals, studies have been performed on an experimental set-up using thermal gravimetric analysis. The research into coals of various ranks (flame, gas, coking, low-caking, and non-baking) and their processing waste (filter cakes) has yielded the decomposition parameters of the organic matter of coal and the formation of volatile substances as well as the oxidation parameters of the coke residue of all the coals and filter cakes under study. The studies cover the temperature range of the burning processes: 450-1300 K (for low-, medium-, and high-temperature burning modes). We have ascertained the dependence of kinetic parameters (pre-exponential factor and activation energy) describing the thermal decomposition of the organic matter of coal on the rank of coals and filter cakes. The findings show that the kinetic parameters describing the thermal decomposition of the organic matter of coal and its processing waste are practically the same. The thermokinetic parameters of coke residue oxidation are close for all the coals under study but they differ significantly for coke residue of filter cakes. The values of thermokinetic parameters obtained in the research are necessary to devise adequate physical and mathematical models and perform numerical studies (for mathematical modeling) of fuel slurry combustion processes in the combustion chambers of power plants.

Key words: coal water slurry containing petrochemicals, coal processing waste, ignition, thermal decomposition, oxidation, thermokinetic constants

Introduction

Greenhouse effect, global warming, global dimming, and their ramifications (rising sea and ocean levels, land devastation, human migration, diseases, excess mortality, *etc.*) have been known to the world since 1824. Almost 200 years have passed. Has humanity found a way to fight this? Have we solved the key problems or is the global threat still present? Unfortunately, we are still in search of answers to these questions. Moreover, the consumption of electric and thermal energy has almost tripled over the last 40 years. At the same time, CO_2 , NO_x , and SO_2 emissions have only gone down 13-15% per ton of fuel equivalent. The current statistics look alarming: on average 4-5 tons of per capita CO_2 emissions. No improvements in the car industry, however, will solve global environmental problems. Almost 80% of CO_2 , NO_x , and SO_2

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emissions fall on power-generating facilities – liquid, solid or gaseous fuel combustion plants. The problem of GHG emissions has to be tackled in heat power engineering [1-3]. The analysis shows that over 40% of heat and power plants as well as other power-generating facilities around the world work on solid fuels (coals of different quality) [4, 5] without any chance of conversion to alternative fuels for a number of objective reasons. At the same time, solid fuels are the most hazardous in terms of consequences for the environment [6, 7].

Over the last 25-30 years, the technologies of coal-water slurries (CWS) have been quite actively developing throughout the world [8-11]. Using these fuels can reduce the emissions of carbon and sulfur oxides *vs.* coal dust and involve low-rank coals (even fire-hazardous brown coals) as raw materials. Alongside CWS, coal water slurry containing petrochemicals (CWSP) is also perceived as a promising slurry fuel [12-14]. The production process of CWSP suspensions also involves a liquid fuel component. The latter makes it possible to significantly expand the range of raw materials for large and small power industries as well as transport industry (diesel fuel can be replaced by CWS) and other sectors. The following materials can be CWSP components [15-17]: low-quality coal dust, oil and coal processing waste, oil sludge, heavy coal-tar products, resins, waste industrial oils, and various combustible liquids. The most important task here is to establish the opportunity to use filter cakes in CWSP, the volumes of such low-quality coal processing residues are estimated in millions of tons in the world [16-19]. The development of a research-backed technology of CWSP production will significantly expand the scope of raw materials used in heat and power industry. As a consequence, there will be an actual alternative to high quality energy fuels based on coal, oil and gas.

One of the deterrents to using CWS and CWSP throughout the world is quite complicated sets of interdependent physical and chemical processes involved in the ignition and combustion of CWS. We need relevant fundamental understanding of these processes and an extensive information base of reliable experimental data. Over the last decades, such data have been obtained in the field of preparation and combustion of CWS [8-10] and CWSP [12-14]. These experiments [8-14], however, were devoted to specific types of coal (matching the coal deposits of a limited number of world regions). These data are difficult to use for a broad-scale development of CWS and CWSP technologies, since the properties of components may vary drastically and, consequently, the ignition and combustion characteristics will be significantly different as well. Therefore, a follow-up on studies [8-14] will be the development of mathematical models simulating the ignition and combustion of CWSP droplets. This stage, however, depends quite considerably on the source data (there are extremely many empirical constants).

A number of approaches have been used for modeling the processes involved in the ignition of CWS and CWPS droplets over the last years: using one's own programming codes [20-22] or mathematical modeling packages [23-25]. However, a comparison of the modeling results with the known experimental data often reveals significant deviations between theoretical and experimental ignition characteristics. These deviations usually stem from the lack of reliable information on the kinetics of thermal decomposition and oxidation of coal fuel components. This stifles the active usage of mathematical modeling software (in particular, ANSYS Fluent, *etc.*) to determine the optimal conditions of CWSP combustion in power engineering.

The aim of this work is to obtain an experimental base of thermokinetic constants by thermal gravimetric analysis for modeling the ignition processes of CWSP based on coal and its processing waste. It is reasonable to study the thermal decomposition of coals and filter cakes as well as the oxidation of coke residue on an experimental set-up.

Experimental set-up and procedures

We studied coals, tab. 1, from Kuznetsk Basin (Kemerovo region, Russia) and their processing waste (filter cakes): F – flame coal (processing plant of the Listvyazhnaya mine), G – gas (processing plant of the Kirov mine), C – coking (Severnaya processing plant), L – low-caking (Chernigovskaya-Koksovaya processing plant), N – non-baking (Kaltanskaya-Energeticheskaya processing plant).

Coal rank	Proximate analysis			Ultimate analysis [% daf]		
Coarrain	A ^d , [%]	V^{daf} , [%]	$Q^{d}_{s,V}$, [MJ/kg]	С	Н	(O+N+S)
Flame coal	13.90	41.59	25.79	77.11	5.77	17.12
Gas coal	17.80	41.36	27.82	79.31	5.34	15.35
Coking coal	14.65	27.03	29.74	87.20	5.09	7.71
Low-caking coal	21.68	27.40	26.21	87.47	5.04	7.49
Non-baking coal	18.07	15.07	27.64	90.13	4.26	5.61
Filter cake of flame coal	36.99	41.47	19.24	73.27	4.90	21.83
Filter cake of gas coal	33.82	43.11	22.16	75.12	4.64	20.24
Filter cake of coking coal	26.46	23.08	24.83	79.79	4.49	15.72
Filter cake of low-caking coal	50.89	30.16	15.23	77.3	4.78	17.92
Filter cake of non-baking coal	21.2	16.09	26.92	87.97	4.1	7.93

Table 1. Results of proximate and element analysis of coals and filter cakes

We performed our measurements on coal analysis samples (air-dry, particle size 150-200 μ m) as well as filter cakes dried at a temperature of 380 K, ground and sieved (particle size 150-200 μ m). These filter cakes were produced during coal flotation, which involves washing coal with a surfactant solution and further screening into separate fractions. Water used for coal washing is fed to special containers for clarification, where coal particles settle. The slurry is pumped out and sent to belt press filters for pressing and filtering through a special membrane. The resulting wet residue of coal particles is known as a filter cake.

Proximate analysis of filter cakes and initial coals measured the humidity of an air-dry analysis sample, W^a , and dry ash level, A^d , and recalculated the VOC concentration in the fuel minus humidity and ash level, V^{daf} , using the corresponding methods [25-27]. Gross heat value of the analysis sample of coals and filter cakes with a constant volume, $Q^d_{s,V}$, was measured by an IKA C 2000 calorimeter according to the method described in [28].

The ultimate analysis of filter cakes and analysis sample, by the method from [29], was carried out using a vario MICRO cube analyzer. We burned the sample in oxygen at a temperature of 1373 K. The resulting gases were separated chromatographically and detected by means of a katharometer. The software pre-installed on the detector measured the mass fractions of C, H, N, and S (oxygen was calculated) and recalculated the VOC concentration in the fuel minus humidity and ash level.

Thermokinetic parameters (pre-exponential factor and activation energy) of the decomposition of the organic matter and oxidation of the coke residue were determined in several stages:

- Stage 1. Inert-atmosphere thermal gravimetric analysis of a coal sample or filter cake.
- Stage 2. Oxidizing-atmosphere thermal gravimetric analysis of coke residue.
- Stage 3. Calculation of thermokinetic parameters from the thermogravimetric data.

Thermal analysis of coals was performed on an STA 449F3 synchronous thermoanalyzer (NETZSCH Company) under the following conditions: a 25-mg sample was placed in a corundum crucible and heated up to 1273 K in argon at a gas-flow rate of 100 ml/min and in argon-air mixture (10 and 50 ml/min, respectively).

Thermogravimetric analysis (TGA) was carried out for the flame coal in the inert atmosphere at the three different rates of heating, namely 10, 20, and 30 K/min. The thermokinetic decomposition parameters of the organic matter of coal have the similar values for all the studied rates of heating, *i. e.* there are almost no differences between values for the three heating rates. Thus, we neglect these differences between values during the mathematical simulation of CWSP combustion. For this reason, thermokinetic parameters of a decomposition of the organic matter of coal and a coke residue oxidation for all the samples of coals and filter cakes were determined at a heating rate that equals to 10 K/min.

Kinetic decomposition parameters (activation energy and pre-exponential factor) were calculated, similar to the methodology used in [30]. We assumed that the initial product A decomposes to form intermediate product B and volatile P_1 . Product B then reacts to form the intermediate product C and liberates the volatile product P_2 , etc.:

$$A \xrightarrow{k_1} B + P_1 \uparrow \xrightarrow{k_2} C + P_2 \uparrow \xrightarrow{k_3} \dots$$
(1)

The liberation rate of volatile substances at each stage can usually be described by a first-order chemical equation with the subsequent calculation of rate constants of the corre-



Figure 1. Typical emission curve of volatile substances during thermal destruction of a sample

sponding stages. The process of chemical destruction will overall correspond to the scheme of first-order consecutive reactions. The rate of the process is derived from the overall accumulation of volatile substances, *i. e.*, their mass is measured over a certain period, with two destruction stages, fig. 1. The mass of the volatile substances liberated is equal to the loss of mass of the solid sample.

As can be seen from fig. 1, the kinetic curve of volatile substance liberation consists of two-stages, each represented by an S-shaped line. They have this shape, because the reaction rate first goes up because the rate constant in-

creases according to the Arrhenius equation and then the destruction rate goes down due to the reagent decomposition.

The mass of volatile substances liberated at each stage is different, and the number of moles participating in the reaction is unknown. Therefore, we can consider by convention that at each stage, the same number of reagent moles decompose, which is equal to the mole rate of the initial substance $n_{A,0}$. The maximum mole rate of volatiles that can be liberated at each stage will also equal $n_{A,0}$:

$$n_{A,0} = n_{P1\max} = n_{P2\max}$$
(2)

The rate of volatile emissions at each decomposition stage will be determined by the mole number of the initial or intermediate solid substance. Then the system of equations describing the two-stage thermal decomposition of the solid phase may look like this:

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$$\frac{\mathrm{d}n_A}{\mathrm{d}\tau} = -k_1 n_A, \quad \frac{\mathrm{d}n_B}{\mathrm{d}\tau} = k_1 n_A - k_2 n_B, \quad \frac{\mathrm{d}n_C}{\mathrm{d}\tau} = k_2 n_B \tag{3}$$

Volatile emission rates:

$$\frac{\mathrm{d}n_{P_1}}{\mathrm{d}\tau} = k_1 n_A, \quad \frac{\mathrm{d}n_{P_2}}{\mathrm{d}\tau} = k_2 n_B \tag{4}$$

Material balance relation:

$$n_{A,0} = n_A + n_B + n_C$$
 or $n_{A,0} = n_A + n_{P1}$, $n_C = n_{P2}$ (5)

Then

$$n_B = n_{A,0} - n_A - n_C$$
 or $n_B = n_{P1} - n_{P2}$ (6)

and the system of equations will take the following form:

$$\frac{\mathrm{d}n_{P_1}}{\mathrm{d}\tau} = k_1(n_{A,0} - n_{P_1}), \quad \frac{\mathrm{d}n_{P_2}}{\mathrm{d}\tau} = k_2(n_{P_1} - n_{P_2}) \tag{7}$$

The current mass of volatile substances, m_i , emitted at this stage is proportional to the current number of moles, n_{P_i} , (where *i* is the number of the stage of the kinetic volatile emission curve):

$$\frac{m_i}{m_{i\max}} = \frac{m_{P_i}}{m_{P_i\max}} = \frac{n_{P_i}}{n_{A,0}}$$
(8)

whence it follows that:

$$n_{P_i} = m_i \frac{n_{A,0}}{m_{i\max}} \tag{9}$$

If we use this expression in the system of equations describing the volatile emission rates, we obtain:

$$\frac{d\left(m_{1}\frac{n_{A,0}}{m_{1\max}}\right)}{d\tau} = k_{1}\left(n_{A,0} - m_{1}\frac{n_{A,0}}{m_{1\max}}\right) \Longrightarrow \frac{dm_{1}}{d\tau} = k_{1}m_{1\max}\left(1 - \frac{m_{1}}{m_{1\max}}\right) = k_{1}(m_{1\max} - m_{1}) \quad (10)$$

$$\frac{d\left(m_{2}\frac{n_{A,0}}{m_{2\max}}\right)}{d\tau} = k_{2}\left(m_{1}\frac{n_{A,0}}{m_{1\max}} - m_{2}\frac{n_{A,0}}{m_{2\max}}\right) \Longrightarrow \frac{dm_{2}}{d\tau} = k_{2}m_{2\max}\left(\frac{m_{1}}{m_{1\max}} - \frac{m_{2}}{m_{2\max}}\right)$$
(11)

In the case of coals and filter cakes, quite a long time passes between the decomposition stages. Therefore, by the beginning of the second-stage, the emission of volatile substances as per the first equation has stopped and $m_1 = m_{1\text{max}}$. The resulting system of equations then simplifies to:

$$\frac{\mathrm{d}m_{\mathrm{l}}}{\mathrm{d}\tau} = k_{\mathrm{l}}(m_{\mathrm{lmax}} - m_{\mathrm{l}}) \tag{12}$$

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$$\frac{\mathrm{d}m_2}{\mathrm{d}\tau} = k_2(m_{2\mathrm{max}} - m_2) \tag{13}$$

Here, eq. (10) remains unchanged, whereas the eq. (11) is derived:

$$\frac{\mathrm{d}m_2}{\mathrm{d}\tau} = k_2 m_{2\max} \left(\frac{m_{1\max}}{m_{1\max}} - \frac{m_2}{m_{2\max}} \right) = k_2 \left(m_{2\max} - m_{2\max} \frac{m_2}{m_{2\max}} \right) \tag{14}$$

The total loss of mass of the initial substance and the rate of volatile emission:

$$m = \sum_{i} m_{i}, \quad \frac{\mathrm{d}m}{\mathrm{d}\tau} = \sum_{i} \frac{m_{i}}{\mathrm{d}\tau}$$
(15)

in particular, for two-stages of destruction:

$$m = m_1 + m_2, \quad \frac{\mathrm{d}m}{\mathrm{d}\tau} = \frac{\mathrm{d}m_1}{\mathrm{d}\tau} + \frac{\mathrm{d}m_2}{\mathrm{d}\tau} \tag{16}$$

The process under study runs under non-isothermal conditions. Therefore, the rate constants k_1 and k_2 change according to the Arrhenius equation in the course of the experiment. As a rule, the process is carried out so that the temperature of the sample linearly depends on the reaction time without varying with the volume of the sample:

$$T = T_0 + \beta \tau \tag{17}$$

where T_0 [K] is the initial temperature and β [Kmin⁻¹] – the rate of temperature increase.

Then the Arrhenius dependence of the constants at the i^{th} stage will take the following form:

$$k_i = k_{0i} \exp\left[-\frac{E_i}{\mathbf{R}(T_0 + \beta\tau)}\right]$$
(18)

and the rate equation of the i^{th} stage of the first order reaction:

$$r_i = \frac{\mathrm{d}m_i}{\mathrm{d}\tau} = \exp\left(a_i - \frac{b_i}{T_0 + \beta\tau}\right)(m_{i\max} - m_i) \tag{19}$$

where

$$a_i = \ln k_{0i}$$
 and $b_i = \frac{E_i}{R}$ (20)

The rates of changes in the sample mass are derived from the diagram determined experimentally. The parameters $a_i = \ln k_{0i}$ and $b_i = E_i/R$ are selected by linearizing the rate equation of the corresponding stage:

$$\ln \frac{r_i}{m_{i\max} - m_i} = a - \frac{b_i}{T_0 + \beta\tau}$$
(21)

The last expression is an equation of a straight line in axes:

$$\ln \frac{r_i}{m_{i\max} - m_i} - \frac{1}{T}$$

where a_i is the intercept and b_i is the slope.

Results and discussion

Table 2 presents the thermokinetic parameters of the flame coal. The ranges of variation of the investigated parameters are shown at different heating rates and temperature ranges. In general, we can note a good correlation of the obtained data for different heating rates of the sample.

 Table 2. Thermokinetic parameters of a thermal decomposition of the flame coal in the inert atmosphere

 Temperature range, [K]
 473-938
 939

 Heating rate [Kmin-]]
 E [Istracl-]]
 E [Istracl-]]

Temperature range, [K]	473-938		939-1169		
Heating rate, [Kmin ⁻¹]	E, [kJmol ⁻¹]	$k, [S^{-1}]$	E, [kJmol ⁻¹]	$k, [S^{-1}]$	
10	49.47	2.33·10 ²	86.43	3.35·10 ³	
20	47.81	3.24·10 ²	58.37	$1.50 \cdot 10^{2}$	
30	50.51	6.74·10 ²	61.84	3.33·10 ²	

Figure 2 presents typical thermal gravimetric curves in an inert atmosphere for three ranks of the coals under study. There are two loss peaks on the curves of the mass loss rate: the main low-temperature loss peak resulting from the decomposition of the organic matter of coal and formation of volatile substances and the high-temperature loss peak most likely stemming from the decomposition of mineral carbonates in coal [31]. As we have established, the higher the coal rank (from flame to non-baking one), the higher the peak decomposition temperature of the organic matter.



Figure 2. Thermogravimetric curves of mass loss (a) and rate of mass loss (b) of the coal samples under study; 1 - rank G, 2 - rank L, 3 - rank N

The thermogravimetric data are linearized in axes:

$$\ln \frac{\frac{\mathrm{d}m_i}{\mathrm{d}\tau}}{m_{i\mathrm{max}} - m_i} - \frac{1000}{T}$$

The equation of the straight line defines the activation energy and pre-exponential factor for the first and the second decomposition stages, fig. 3. The thermokinetic decomposition parameters of the organic matter of coal and the formation of volatile substances for all the coals and filter cakes under study are presented in tab. 3.



Figure 3. Linearization of the temperature dependence of the L-rank coal thermal destruction rate

As reflected by tab. 3, with a growing coal rank comes a linear increase in the activation energy at the first stage and an exponential increase in the pre-exponential factor, fig. 4. The parameters of the second decomposition stage are independent of coal rank. Apparently, the thermokinetic parameters of the second decomposition stage depend on the chemical composition of the mineral matter. In addition, the thermokinetic decomposition parameters of coals and their processing waste (filter cakes) are virtually equal.

 Table 3. Thermokinetic parameters of thermal decomposition (in an inert atmosphere)

Sample	Temperature	Pre-exponential	Activation energy F [k Imole ⁻¹]	
	Talige, [K]		energy <i>E</i> , [kJmole ·]	
Filter cake of	483-913	4.79.102	53.24	
flame coal	913-1183	$5.05 \cdot 10^2$	70.87	
Flame coal	473-938	$2.33 \cdot 10^{2}$	49.47	
	939-1169	3.35·10 ³	86.43	
Filter cake of	475-920	$7.85 \cdot 10^2$	56.91	
gas coal	921-1156	3.53·10 ²	67.29	
Gas coal	473-938	$7.06 \cdot 10^2$	56.73	
	939-1161	6.46·10 ³	92.06	
Filter cake of	473-920	$1.03 \cdot 10^{3}$	59.66	
coking coal	920-1170	8.09·10 ³	94.15	
Coking coal	483-973	3.95·10 ²	55.44	
	973-1200	3.08·10 ³	88.36	
Filter cake of	523-900	$1.02 \cdot 10^4$	73.78	
low-caking coal	900-1120	1.45.105	114.50	
Low-caking coal	523-900	$1.12 \cdot 10^4$	73.96	
	900-1120	$4.01 \cdot 10^4$	104.10	
Filter cake of	573-888	3.6.104	82.82	
non-baking coal	888-1220	2.69·10 ²	67.04	
Non-baking coal	573-900	5.97·10 ⁴	87.06	
	900-1220	3·10 ²	67.33	

In low-rank coals, a macromolecule of coal has the largest pendant groups. An increased content of oxygen in pendant groups results in the thermal instability of the organic matter. Such bulky side groups quite easily break away from the nucleus of a large molecule during coal pyrolysis. Therefore, the thermokinetic parameters of low-rank coals have the lowest values. The higher the coal rank, the shorter the side groups. The content of oxygen also drops in functional groups, and the polyaromatic nucleus of a macromolecule expands. These changes raise the thermal stability of the organic matter of coal, which, in turn, increases the values of thermokinetic parameters. The thermokinetic decomposition parameters of the organic matter of coal and the formation of volatile substances are close to those of coal decomposition from other deposits of the world, *e. g.*, for Australian coals [32] of similar ranks, the activation energy also ranges from 50 to 90 kJ/mole (and similarly depends on the rank). Turkish and Pakistani coals [33] as well as coals from deposits in other countries, *e. g.*, [31], have comparable values. It is, therefore, quite likely that same-rank coals (flame, gas, coking, low-caking, non-baking) from other deposits will have the values of the said thermokinetic param



Figure 4. Dependence of activation energy and pre-exponential factor on carbon content

the values of the said thermokinetic parameters similar to those established in tab. 3. The thermokinetic parameters of more oxidized coals are likely to be somewhat lower than those of less oxidized coals of the corresponding ranks.

The thermogravimetric data of the coke residue in an oxidizing environment were processed in a similar way. Oxidation was supposed to run in an excess of oxygen as a pseudo-first-order reaction. The thermokinetic parameters of the heterogeneous coke residue combustion for all the coals and filter cakes under study are presented in tab. 4.

In the case of coke residue oxidation, the thermokinetic parameters are close for all the coals under study, whereas these parameters differ significantly for coke residue of filter cakes, tab. 4. This must be because the mineral part of the coke residue affects the oxidation process. For coals with moderate ash level, the share of the mineral part in the coke residue is negligible and does not seem to have any considerable impact on the oxidation process. When it comes to filter cakes, though, which have high ash level in the first place, the share of mineral part in the coke residue seems significant as does its impact on the coke residue oxidation process.

In this research, we obtained the thermokinetic parameters of thermal

Table 4. Thermokinetic parametersof coke residue oxidation

Sample	Pre-exponential factor k , $[s^{-1}]$	Activation energy E, [kJmole ⁻¹]
Filter cake of flame coal	5.71.1011	224.79
Flame coal	2.29·10 ⁹	182.51
Filter cake of gas coal	9.25.107	153.52
Gas coal	$1.72 \cdot 10^9$	180.19
Filter cake of coking coal	2.06·10 ⁸	162.97
Coking coal	$1.18 \cdot 10^{9}$	179.58
Filter cake of low-caking coal	$2.01 \cdot 10^{10}$	194.24
Low-caking coal	3.17·10 ⁹	181.67
Filter cake of non-baking coal	$4.68 \cdot 10^{10}$	206.12
Non-baking coal	6.43·10 ⁹	185.31

decomposition and oxidation of coke residue for the coals of various ranks from Kuznetsk Basin, Russia. The data obtained allowed us to determine how thermokinetic parameters of the thermal decomposition of the organic matter depend on the coal rank, which makes it possible to forecast the values of thermokinetic parameters of coals from other deposits of this basin. We also established that the thermokinetic parameters of the thermal decomposition of coal processing waste agree with the said values of initial coals, which in turn enables us to forecast the values of thermokinetic parameters. If the coke residue of coal processing waste is oxidized, it

does not seem possible to forecast the values of thermokinetic parameters at this research stage. Thermokinetic parameters of the initial coal coke residue are close for all the coals irrespective of their rank.

The experimental data obtained deepen the insight into the kinetics of the processes involved in the thermal decomposition and oxidation of solid fuels. In particular, the database of reliable kinetic constants is expanded, which is based on a set of papers published over the last 20 years, *e. g.* we can underline works [34-38]. The development of laboratory-based measurement equipment will help us take major steps to create a unified database of thermophysical and thermokinetic characteristics of widely used solid and composite fuels [39-41].

Conclusions

- We obtained values of thermokinetic parameters (pre-exponential factor and activation energy) describing the decomposition of the organic matter and oxidation of the coke residue of the coals and their processing waste. This information has been systematized into an experimental database to cater for the needs of the modern computational science in reliable data on the kinetics of the processes involved in fuel ignition. The database containing thermokinetic constants for thermal decomposition and oxidation of coal processing waste will smooth the way for using mathematical modeling to explore the main deterrents to their broad-scale application in power engineering as the primary or secondary component of promising coal-water slurry and coal-water slurry containing petrochemicals.
- We showed the maximum differences of values of thermokinetic parameters (pre-exponential factor and activation energy) describing the decomposition of the organic matter and oxidation of the coke residue of the coals and their processing waste. This result is important for predicting differences of the characteristics of ignition and combustion of CWS and CWSP, prepared from various coal components all over the world. Using the present work, it is possible to predict the differences in the thermokinetic characteristics for slurries, typical for China, India, Japan, the USA, Russia and other countries.
- Expansion of the created database with kinetic parameters of the thermal decomposition and oxidation of the components of CWS and CWSP by involving all promising components (in terms of environmental, economic and energy criteria), in particular, coals of different grades, coal waste, used combustible liquids, refinery waste, wood waste, plant wastes, *etc.* is an important direction of development of this work.

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Nomenclature

A	 initial substance 	т	 total loss of mass (percentage), [%]
A^d	 ash level of dry sample, [%] 	m_i	- current mass (percentage) of volatile
В, С	 intermediate solid product 		substances released at this stage, [%]
C ^{daf}	 fraction of carbon in the sample converted 	m_{imax}	 total mass (percentage) of volatile
	to a dry ash-free state, [%]		substances released at this stage, [%]
Ε	 activation energy, [kJ mol⁻¹] 	N^{daf}	 fraction of nitrogen in the sample
E_i	- activation energy of stage <i>i</i> , $[kJ mol^{-1}]$		converted to a dry ash-free state, [%]
H ^{daf}	 fraction of hydrogen in the sample 	$n_{A,0}$	 number of moles of initial substance
	converted to a dry ash-free state, [%]	n_{Pi}	 current number of moles
k	 pre-exponential factor, [s⁻¹] 	O^{daf}	- fraction of oxygen in the sample converted
k_{0i}	- pre-exponential factor of stage i , $[s^{-1}]$		to a dry ash-free state, [%]
k_i	- reaction rate constant of stage i , $[s^{-1}]$	P_i	 volatile substance

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- $Q^{d}_{s,v}$ enthalpy of combustion of dry sample of coal, [×10⁶Jkg⁻¹]
- rate of mass loss at stage, [%/min]
- S_t^{daf} fraction of sulfur in the sample converted to a dry ash-free state, [%]
- *V*^{daf} yield of volatiles of coal to a dry ash-free state, [%]
- W^a humidity of analytical sample of coal in an air-dry state, [%]
- *T* temperature of the sample, [K]
- T_0 initial temperature of the sample, [K]

Greek symbol

 β – rate of temperature increase, [K/min]

Acronyms

C – coking coal

- CWS coal-water slurries
- CWSP- coal-water slurries containing
- petrochemicals
- F flame coal
- G gas coal L – low-caking
- L low-caking coal
- N nonbanking coal
- VOC volatile organic compounds

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