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Investigation of Combustion Characteristics of Mixed Fuel of Biomass and Coal Sludge

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Investigation of co-firing of carbon-containing waste with a high content of ash and biomass was carried out using methods of thermogravimetric analysis. As raw materials coal sludge, characterized by high ash content, and straw, which has a high content of volatile products, were chosen. Combustion characteristics, namely, characteristic temperatures and weight loss rates for raw materials and for their blends of various compositions were measured. It is shown that despite the fact that intense combustion of the selected raw materials occurs in different temperature ranges, the additive principle cannot be used to evaluate the combustion characteristics of their mixtures. The presence of coal sludge in blend leads to a decrease in weight loss rate both in the temperature range typical for the emission and oxidation of volatile products of straw pyrolysis and in the temperature range at which its solid residue is oxidized. The cause of an increase in combustion reactivity of coal sludge, when straw is added, is the catalytic effect of straw ash.

1. Introduction

The accumulation of coal sludge of coal enrichment plants and ash-slag wastes of thermal and electric power plants is a serious environmental problem demanding development of effective technologies of their utilization. At the same time, this type of waste has significant energy potential: according to estimations only in Russia it is about $7.5 \cdot 10^{11}$ MJ. However, there are a number of problems associated with the involvement of coal-containing waste in the economic turnover, in particular, in the energy sector, which are primarily associated with high humidity and high ash content of coal-containing waste. Ways to use renewable carbon-containing waste, including various types of biomass, for energy purposes have been developed to a greater extent today. Biomass can be used directly as solid fuel, and can be processed into gaseous and liquid fuels (Basu, 2013). Improvement of consumer properties of biomass as a solid fuel can be achieved by low-temperature pyrolysis known as torrefaction (Kosov et al, 2014). Torrefaction allows to product solid biofuels with characteristics similar to lignite, which makes it possible to co-firing it with coal (Bergman, 2005). Torrefaction can be used for a wide variety of biomass types: from wood (Kuzmina et al, 2016) to sewage sludge (Isemin et al, 2018). When searching for ways of energy potential usage of high-ash coal-containing wastes, the direction associated with the production of granular mixed fuel of biomass and coal sludge seems feasible and promising. On the one hand, the addition of low ash biomass will reduce the total ash content of mixed fuel. On the other hand, the presence of lignin, which is part of plant biomass and has binding properties, will facilitate the process of pelletisation. In the present work straw was selected as biomass. Considerable interest in this type of biomass is associated with its wide distribution. According to the data presented in (AEBIOM, 2011), energy potential of straw accounts for 7% of the total energy potential of all types of biomass used in energy. In addition, full-scale measurements carried out at a pulverized coal fired unit shown that an addition of straw allows reduce emissions of nitrogen and sulfur oxides (Pedersen et al., 1996).
By using the methods of thermogravimetric analysis the behavior of blends of straw with high ash coal-containing wastes in inert and oxidizing environments was studied. Dependence of the basic combustion characteristics of these blends on the ratio between components of blend was investigated. Based on the obtained experimental data, the mutual influence of the blend components on each other during co-firing was revealed.

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2. Experimental study

Coal sludge and straw, whose properties are very different from each other, were chosen as the initial raw materials for the researches. Proximate analysis of the raw materials was fulfilled by thermal analyser SDT Q600. For ultimate analysis elemental analyser Elementar vario MACRO Cube was used. Lower heating value (LHV) was calculated based on elemental analysis data. To prepare samples, the feedstock with a moisture content of less than 1% was ground and sieved through a sieve with a mesh size of 0.4 mm. In the experiments blends with three different ratios between components straw/coal sludge of 75/25, 50/50 and 25/75 wt.% were used. Thermogravimetric analysis was performed in flow of nitrogen and air at heating rate of 20 °C per minute in the temperature range from room to ~ 950 °C. Based on the thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained in air flow the combustion characteristics of raw materials and their blends were determined. First of all, this is a series of characteristic temperatures (Yuzbasi et al, 2011): ignition temperature (T_{ig}), peak temperature (T_{max}), burnout temperature (T_b). Ignition temperature is the temperature at which TG curves measured in nitrogen and in air diverge and the difference is equal to 1%. Ignition temperature characterizes the beginning of the intense oxidation process, i.e. burning. Peak temperature is the temperature at which the maximum of weight loss rate is observed. Burnout temperature determines the termination moment of oxidation process and is taken equal to the temperature at which weight loss rate in the oxidizing medium decreases to 1% per minute. Another indicator characterizing reactivity of fuel with respect to the oxidation process is the maximum value of the weight loss rate DTG_{max} corresponding to the peak temperature and determined by DTG curves. In a number of papers (Park et al, 2012) to characterize the combustion potential of fuel an indicator representing a combination of two parameters ${DTG_{max}}/{T_{max}}$ is used.

3. Results and discussion

Results of proximate and ultimate analysis of raw materials together with values of its lower heating value are summarized in Table 1. The carbon content in the studied raw materials is almost the same. The share of fixed carbon in coal sludge significantly exceeds the corresponding indicator for straw. At the same time, straw is characterized by a high content of volatile products. The consequence of the high ash content of coal sludge is the relatively low value of its heating value, which is close to the heating value of straw.

Table 1: Characteristics of straw and coal sludge

	Straw	Coal sludge
Proximate analysis (%, dry basis):		
Ash	8.19	47.18
Volatile products	71.7	17.7
Fixed carbon	20.11	35.12
Ultimate analysis (%, dry basis):		
Carbon	43.32	45.3
Hydrogen	5.65	2.83
Oxygen (by difference)	42.28	1.8
Nitrogen	0.54	0.92
Sulphur	0.02	1.97
Ash	8.19	47.18
Lower heating value (dry basis):		
LHV, MJ/kg	17.2	18.9

The above differences in the properties of coal sludge and straw, following from proximate analysis data, lead to a significant difference in the DTG curves for the studied raw materials, measured both in inert (Figure 1a) and in oxidizing (Figure 1b) environment. As can be seen from Figure 1b on the DTG curve for straw, measured in air, two maximums are observed: the first is associated with release and subsequent oxidation of volatile products, the second – with solid residue burning. The low content of volatiles in the coal sludge leads to the fact that similar processes for this type of raw material regardless of environment begin much later and proceed smoothly without a pronounced maximum on the DTG curve. As can be seen from Figure 1, release of volatiles for coal sludge begins at a temperature corresponding to the temperature at which the release and oxidation of the volatile pyrolysis products of straw practically ends. Moreover, the complete burnout of the solid residue of straw comes to the end (T_b = 477.9 °C), when the burning rate of the solid residue from coal sludge is still far from its maximum (T_{max} = 553.8 °C). Thus, during researches in combustion of mixtures of straw and coal sludge three characteristic temperature ranges can be distinguished, namely: 200-350, 350-500 and 500-700 °C.

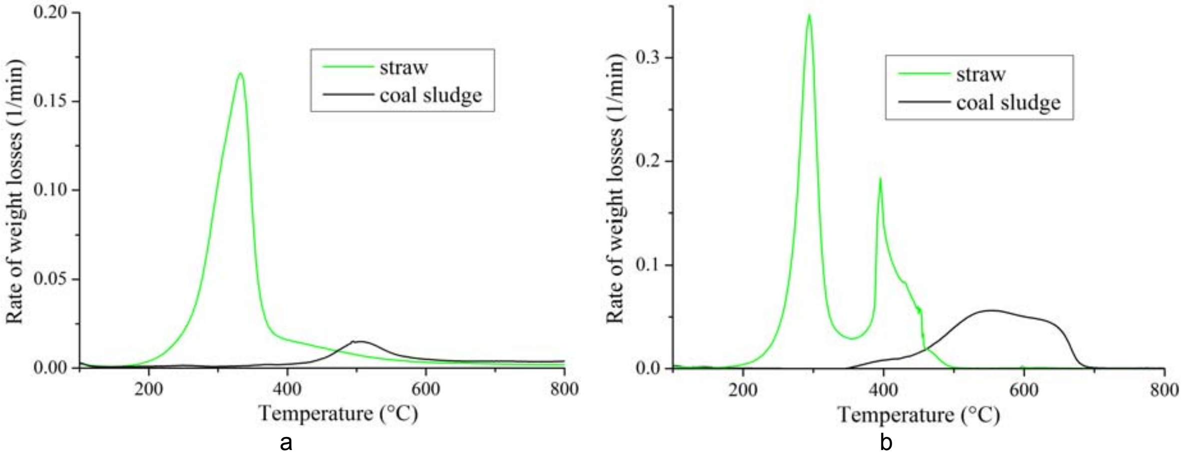


Figure 1: Experimental DTG curves for straw and coal sludge in flow of nitrogen – (a) and air – (b)

From the above and a comparison of the DTG curves presented in Figure 1b, one would expect that in the co-firing the influence of the two raw materials under consideration on each other can manifest itself only in the temperature range of 350-500 °C, and in other temperature ranges the additivity principle must be fulfilled. The experimental DTG curves for three coal sludge-straw blends with different weight ratios between the components are presented in Figure 2.

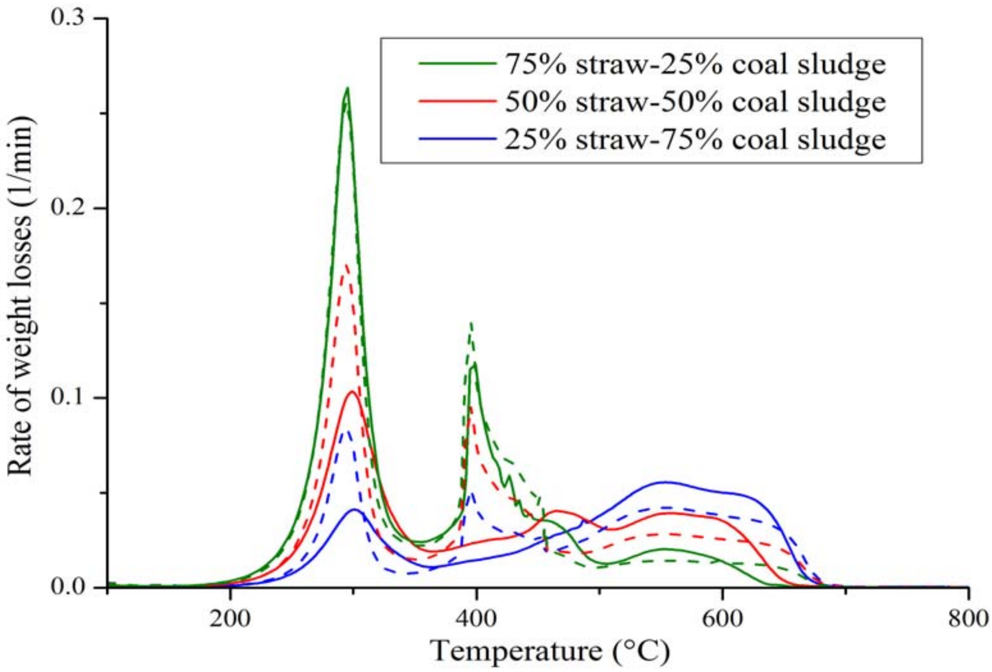


Figure 2: DTG curves for blends of straw with coal sludge: solid lines – experiment, dash lines – calculation assuming additivity

Under the additivity principle, the differential thermogravimetric dependence for blend DTG_{bl} can be calculated as:

$$DTG_{bl} = \alpha_{st}\, DTG_{st} + \alpha_{cs}\, DTG_{cs} \tag{1}$$

where DTG_{st} and DTG_{cs} – the differential thermogravimetric dependences for straw and coal sludge, α_{st} and α_{cs} – weight fraction of straw and coal sludge in initial blend, respectively. Note that all experimental DTG curves are normalized to the initial weight of the sample. The calculated according to the above formula (1) DTG curves for three coal sludge-straw blends with different weight ratios between the components are also presented in Figure 2. Combustion characteristics, including the characteristic temperatures T_{ig}, T^{i}_{max}, T_b and the maximum values of the weight loss rate DTG^{i}_{max} for straw and coal sludge, as well as for their blends are given in Tables 2 and 3.

From comparison of the experimental and calculated DTG dependences, presented in Figure 2, and data, given in Tables 2 and 3, one can see that the additivity principle is violated in all three temperature ranges and the degree of deviation from it depends on the ratio between the components of the blend.

In the temperature ranges corresponding to the burning of both the volatile pyrolysis products of straw (200-350 °C) and the burning of its solid residue (350-500 °C), the measured values of the weight loss rate are less than the similar values calculated under the additivity assumption (Table 2). In this case, with an increase in the content of coal sludge in the mixture this difference increases. Moreover, as can be seen from Figure 2, when the content of coal sludge in the mixture is equal to and more than 50%, the peak at 400 °C on the corresponding experimental DTG curves (typical for straw) disappears.

Table 2: Combustion characteristics of samples in the range from 200 °C up to 500 °C

Composition of sample	T_{ig}, °C	T^{1}_{max}, °C		DTG^{1}_{max}, min^{-1}		T^{2}_{max}, °C		DTG^{2}_{max}, min^{-1}	
	exp.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
Straw	251.2	294.2	294.2	0 .342	-	395.6	-	0.184	-
75% straw - 25% coal sludge	256.4	295.3	294.2	0.264	0.256	399.2	395.6	0.118	0.140
50% straw - 50% coal sludge	273.6	299.0	294.2	0.104	0.170	-	395.6	0,023*	0.096
25% straw - 75% coal sludge	289.1	301.2	294.2	0.041	0.084	-	395.6	0,014*	0.052
Coal sludge	443.2	-	-	-	-	-	-	-	-

* – since there is no pronounced extremum in the experimental DTG dependences corresponding to the indicated ratio of the components, the experimental values of the weight loss rate at temperature of 395.6 °C were taken as DTG^{2}_{max}.

At temperatures above 450 °C, when the rate of weight loss due to combustion of coal sludge increases markedly, the experimental values of the weight loss rate for all studied mixtures are more than the calculated ones (Table 3). With the growth of the weight fraction of straw in blend this difference increases. Simultaneously a decrease in burnout temperature is observed, the experimental values of T_b are also less than the calculated ones. It should be noted, that an increase in the thermochemical reactivity of poor coal during their co-firing with some types of plant biomass (Vamvuka et al, 2014) and with municipal solid waste (Muthuraman et al, 2010) was mentioned earlier.

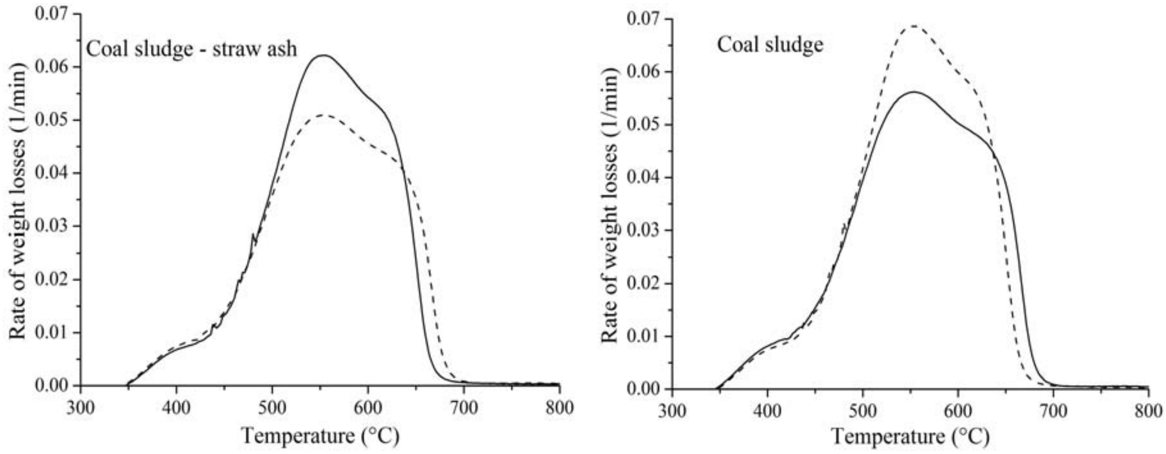
Table 3: Combustion characteristics of samples in the range from 500 °C up to 700 °C

Composition of sample	T^{3}_{max}, °C		DTG^{3}_{max}, min^{-1}		T_b, °C	
	exp.	calc.	exp.	calc.	exp.	calc.
Straw					477.9	
75% straw - 25% coal sludge	554.9	555.5	0.020	0.014	612.1	650.5
50% straw - 50% coal sludge	556.4	553.5	0.039	0.028	639.0	666.8
25% straw - 75% coal sludge	552.7	553.5	0.056	0.042	663.2	671.0
Coal sludge	553.8	-	0.056	-	673.6	-

Let us consider the possible causes of such behavior of combustion characteristics for mixtures. As follows from Figure 1b, in the temperatures up to 350 °C, coal sludge is a neutral component and its influence can be manifested only through the effect on the diffusion of the volatile pyrolysis products of straw towards the sample surface. With an increase in the proportion of coal sludge in the mixture, the time for the egress of volatile pyrolysis products of straw from the sample increases. An indirect confirmation of the validity of such explanation is not only a decrease in the experimental values of DTG_{max}^{1} in comparison with the calculated ones, but also a shift of the experimental values of T_{max}^{1} to higher temperatures with an increase in the proportion of coal sludge in the mixture (Table 2).

As expected, the most significant deviation from the principle of additivity is observed in the temperature range from 350 °C to 500 °C. In this temperature range, with an increase in the proportion of coal sludge in the mixture, not only a significant diminution of the rate of weight loss is observed in comparison with the expected values, but, as mentioned above, also a change in the shape of the DTG dependences. Such behavior of DTG dependences for blends is apparently associated with release of the volatile pyrolysis products from coal sludge. As seen from Figure 1a the maximum rate of their formation is achieved at a temperature of 500 °C. Oxidation of volatile products begins at a temperature of 350 °C (Figure 1b). This process competes with the process of combustion of the solid residue of the straw and obstructs the access of oxygen necessary for its combustion.

In the temperature range above 500 °C, when the combustion of solid residue of coal sludge occurs, along with it in a sample only ash of straw is present. Since ash fraction is relatively small due to the low ash content in straw, it can hardly affect the diffusion of oxygen towards the solid residue of coal sludge. At the same time, the straw ash can manifest itself as a catalyst for coal sludge combustion. To verify this assumption, a thermogravimetric analysis of a blend of coal sludge and straw ash in an air flow was carried out. The weight fraction of straw ash in the mixture with coal sludge was α_{ash} = 9.4%. The results are presented in Figure 3 and in Table 4.



a b

Figure 3: DTG dependences for mixture of coal sludge with straw ash (a): solid line – experiment, dash line – calculation assuming additivity. DTG dependences for coal sludge (b): solid line – experiment, dash line – experimental dependence measured for the mixture of coal sludge with straw ash in terms of coal sludge

Table 4: Combustion characteristics of sample consisting of coal sludge and straw ash

	T_{max}, ^{o}C	DTG_{max}, min^{-1}	T_{b}, ^{o}C
Experimental value	552.4	0.062	659.3
Calculation assuming additivity	553.8	0.051	672.8
Experimental values measured for mixture of straw ash and coal sludge in terms of coal sludge	552.4	0.069	660.2
Coal sludge	553.8	0.056	673.6

In Figure 3a there are presented the experimental and calculated DTG dependences for the blend of coal sludge with straw ash. The calculation for blend under the assumption of additivity was carried out according to formula (1), which, due to the fact that the mass of straw ash does not change during heating, takes the form:

$$DTG_{bl} = (1-\alpha_{ash})\, DTG_{cs} \quad (2)$$

In turn, to compare the experimental DTG curve measured for coal sludge with the experimental DTG curve for the blend the latter was renormalized taking into account the weight fraction of coal sludge in the blend (Figure 3b). From Figure3 and data, presented in Table 4, it follows that the addition of straw ash to coal sludge leads to an increase in reactivity of coal sludge with respect to the oxidation process at temperature above 500 °C and a decrease in the burnout temperature, which, in its turn, points to catalytic properties of straw ash.

4. Conclusions

As a result of researches based on thermogravimetric analysis, the combustion characteristics of coal sludge and straw, as well as their blends with different ratios of initial components were determined. It is shown that despite the significant difference in the combustion behaviour of the studied raw materials, the additive principle cannot be used in assessing the combustion characteristics of their mixtures. The addition of coal sludge to straw leads to a significant slowdown in the combustion rate of both the volatile pyrolysis products of straw and its solid residue. At the same time, the addition of straw accelerates the combustion of coal sludge and reduces the burnout temperature. It has been experimentally shown that the effect of straw on the burning of coal sludge is due to the catalytic effect of the mineral component of straw, i.e. its ash.

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