



Combustion behaviour of some biodesulphurized coals assessed by TGA/DTA

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ABSTRACT

Thermal analysis, i.e. TGA/DTA is used to study the changes in the combustion behaviour of microbially treated coals. In view of their high sulphur content and industrial significance three samples are under consideration, i.e. one lignite and two subbituminous from different region in Bulgaria. The differences in burning profiles can be related to structural changes resulted from biological treatments. The overall biological treatment generates these changes probably due to the oxidation process. Concerning organic sulphur biodesulphurization there is no change in any drastic manner of the thermal characteristic parameters. In general, applied biotreatments provoke a complex influence on combustion coal behaviour. From one side a better ignition performance, a minor decrease in higher heating value and diminishing peak temperature of maximum weight loss rate for all biotreated samples are observed. From other side some decrease in the combustibility indicated by an increase in the combustion time and the end of combustion temperature are obvious. Also well determined decrease of self-heating temperature after biotreatments evolves high risk of spontaneous unmanageable coal combustion.

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1. Introduction

Sulphur emission from coal combustion presents many environmental problems, since during burning sulphur is emitted mainly as sulphur oxides. Among various methods of sulphur removal, desulphurization processes before combustion seems to be more promising in view of environmental and economical aspects. Recently, biological approaches, i.e. biodesulphurization, became more popular, as processes were performed under mild conditions with no harmful reaction products and the overall characteristic of coal was slightly affected.

Sulphur is present in coal mainly as inorganic, i.e. pyritic, sulphate, and organic forms. Pyritic sulphur occurs in coal as mineral matter whereas the organic sulphur is presented as an integral part of the coal matrix. Applying different biodesulphurization procedures it is difficult to attain high organic sulphur removal and moderate coal destruction at the same time. The last one reflected in a decrease in coal energy value, which is not recommended for energy production.

The main process covered by coal microbial desulphurization is the removal of inorganic sulphuric minerals (more than 95%). It is

reported that organic sulphur is affected as well and higher than 50% removal is announced [1]. In any case it is of significant importance to achieve high sulphur reductions accompanied by good coal combustion parameters.

Thermal analytical methods such as thermogravimetry (TGA) and differential thermal analyses (DTA) have been shown to be an effective tool to study coal combustion behaviour [2,3]. Various combustion characteristics can be obtained from burning TGA and DTA profiles. Previous TGA studies demonstrated that combustion is influenced by the presence of inorganic material [4], by coal rank [5] and coal macerals [6,7]. Many authors did thermal study of coal but few of them published information concerning the effect of sulphur on coal thermal behaviour [8,9].

The aim of the present study is to evaluate the changes in the combustion behaviour of coals after exposure to the action of bacterial desulphurizing attack. Therefore a comparison is performed between the combustion characteristics of the initial and the biotreated samples.

2. Materials and methods

2.1. Materials

In the present study three high sulphur low rank coal samples from different deposits in Bulgaria are selected. Two of them are

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from “M.Iztok” and “B.Dol” basins, and the last one, in view of its high organic sulphur content is from “Pirin” mine. The “M.Iztok” coal is lignite while “B.Dol” and “Pirin” samples are subbituminous coals. The first two “mean samples” are taken from feet industrial stores while the third one is individually hand picked up from “Pirin” mine. The last coal sample “Pirin” is preliminary demineralized by Radmacher method [10] and treated by diluted nitric acid [11]. The aim of these chemical treatments is to diminish mineral matter and inorganic sulphur influence, mainly pyrite sulphur (S_p), on organic sulphur biodesulphurization efficiency. Before biodesulphurization treatments all coal samples are grounded under 0.06 mm.

2.2. Biodesulphurization

Active microorganisms and microbial systems are selected bearing in mind results from the previous investigations [12]. Pure cultures of microorganisms are obtained from microbial bank ATCC (American Type Culture Collection) and natural isolates. The isolation and identification of microorganisms as well as the condition for cultivation are carried out by methods described elsewhere [13–16]. Coal samples are mixed with microorganisms in the ratio 3 g coal to 100 ml microorganism medium. Microbial strains are as follow:

- *Phanerochaeta Chrysosporium* (ME464) – (PC), white rot fungi, pH 4.7, temperature 30 °C, 6 days duration;
- *Sulfolobus solfataricus* (35091) – (SS), pH 4.0, temperature 70 °C, 14 days duration;
- *Acidithiobacillus ferrooxidans* – (R, F). Differences between the strains *Acidithiobacillus ferrooxidans* R and F are in oxidation rates to Fe and S.
“B.Dol” and “M.Iztok” samples are treated with microbial strains *Acidithiobacillus ferrooxidans* R and F at the follow conditions:
“B.Dol”-R and “B.Dol”-F at pH 5.0, temperature 28 °C, 21 days duration;
“M.Iztok”-R at pH 2.0, temperature 28 °C, 21 days duration;
- *Pseudomonas putida* – (B), pH 6.0, temperature 28 °C, 21 days duration; microbial strains are assigned in the article for convenience as PC, SS, R, F and B.

The losses of coal matter after applied biotreatments are less than 10% (including deashing), due to the performed technical procedures and no to microbial action.

2.3. TGA and DTA analyses

Coal combustion TGA/DTA analyses are performed on a *Universal V3.0A TA Instruments*. The samples (20–25 mg, particle size below 0.06 mm) are heated to 800 °C at the rate 10 °C/min, individually in the atmosphere of dry air and nitrogen flow rate of 50 cm³/min.

The coal combustion experiments are carried out in an atmosphere of air flow. In order to measure the ignition temperature of coals, the TGA experiments are performed under air and nitrogen atmosphere. Various characteristic parameters from combustion profiles can be obtained. They are defined as follow [17–19]:

- T_{ign} (°C): ignition temperature at which the weight loss curve of the coal combustion is separated from the curve of the coal pyrolysis;
 T_{max} (°C): peak temperature of maximum weight loss rate;
 T_{ec} (°C): end of combustion temperature at which the rate of heat flow is zero;
 $(T_{ec} - T_{ign})$ (°C): temperature interval between T_{ec} and T_{ign} ;

Table 1
Proximate analysis (wt.%) and HHV.

Sample	Moisture ^a	Ash ^a	VM ^a	Fix C ^a	HHV (MJ/kg)	ΔHHV (%) ^b
M.Iztok	5.53	34.30	31.76	28.41	17.45	0
M.Iztok-R	3.65	34.24	34.80	27.31	16.50	5.4
M.Iztok-B	5.44	33.77	31.79	29.00	17.30	0.8
B.Dol	9.15	53.74	13.63	23.48	12.91	0
B.Dol-R	6.92	49.70	16.66	26.72	12.80	0.8
B.Dol-F	6.65	50.77	16.00	26.58	12.30	4.7
Pirin	6.45	10.36	30.97	52.22	23.25	0
Pirin-APF	6.16	0.01	39.66	54.17	23.00	1.1
Pirin-APF-PC	6.62	0.53	39.80	53.05	23.10	0.6
Pirin-APF-SS	5.34	1.69	36.12	56.85	23.20	0.2

SS: *Sulfolobus solfataricus*; PC: *Phanerochaeta Chrysosporium*; R, F: *Acidithiobacillus ferrooxidans* (R and F are differences between the strains *Acidithiobacillus ferrooxidans* in oxidation rates to Fe and S); B: *Pseudomonas putida*; HHV: higher heating value; VM: volatile matter.

^a As received basis.

^b ΔHHV relatively decreasing obtained by a bomb calorimeter, in %.

T_{sh} (°C): self-heating temperature at which the rate of heat flow, in DTA curve, begins to be exothermic;

R_{max} (%/min): maximum combustion rate;

t_q (min): time interval relates to combustion temperature interval between T_{ec} and T_{ign} temperatures.

3. Results and discussion

3.1. Characteristics of coal samples

The data from proximate analysis are included in Table 1, as well as the data for higher heating value (HHV), determined by a bomb calorimeter [20]. After biotreatment procedures, the reduction of the ash content reaches a maximum of 8%. An exception is at “Pirin”-APF sample, where preliminary treatment with strong mineral acids is applied [10,11].

Elemental analysis data are gathered in Table 2 including the data for types of sulphur species determined by ISO standards [21]. It is demonstrated that the highest biodesulphurization effect towards total sulphur (S_t) is achieved for “M.Iztok-B”, 44%. Concerning inorganic sulphur (S_{inorg}) the highest biodesulphurization is 84% again for “M.Iztok-B” and 77% for “Pirin-APF” where there is a chemical desulphurization. Organic sulphur (S_{org}) is calculated by the difference from S_t and the sum of pyritic (S_p) and sulphate (S_s) sulphur. In this calculation the content of insoluble sulphate sulphur, produced during microbial treatment is not considered [22]. This fact can explain the increased value for S_{org} after biotreatments of “M.Iztok” and B.Dol” coal samples (Table 2).

Concerning biotreatments of coal sample “Pirin” ash pyrite free (APF), the applied microorganisms demonstrate mixed influence on S_{org} and S_{inorg} presence. The diminishing of S_{org} attains 24% by *Phanerochaeta Chrysosporium* (PC) fungi.

There are some oxygen and nitrogen increasing amounts registered in treated samples (Table 2). All performed biotreatments produce moderate oxygen increase while preliminary treatment with diluted nitric acid instead of applying mild conditions attains 4.59 wt.% oxygen increase. So the utilization of diluted nitric acid as coal desulphurizing agent to pyrite removal has an action as oxidation agent, which is in accordance with other study [23].

3.2. TGA and DTA burning profiles

The DTG curves of coal samples are presented in Fig. 1A–D. In these profiles the mass loss up to 100 °C is due to water evaporation. One sharp peak is observed in the range (250–300 °C) before the major degradation for the biotreated “M.Iztok” and “Pirin” coal samples (Fig. 1A and C). This could be assigned to the release of addi-

Table 2
Elemental analysis and sulphur types (wt.%).

Sample	C ^{daf}	H ^{daf}	N ^{daf}	S _{org} ^{daf}	O _{diff} ^{daf}	Types of sulphur species						
						S _t ^{db}	^a ΔS _t	S _s ^{db}	S _p ^{db}	^b ΔS _{inorg}	ΔS _{org}	S _{org} ^{db}
M.Iztok	61.33	6.25	1.23	2.79	28.40	4.77	0	0.44	2.55	0	0	1.78
M.Iztok-R	59.81	5.41	2.47	3.54	28.77	3.37	29	0.25	0.84	64	–	2.28
M.Iztok-B	60.58	5.04	2.28	3.42	28.68	2.68	44	0.13	0.35	84	–	2.20
B.Dol	74.94	6.33	2.01	0.62	16.10	1.39	0	0.22	0.92	0	0	0.25
B.Dol-R	68.88	6.26	3.33	1.11	20.42	1.25	10	0.22	0.51	36	–	0.52
B.Dol-F	70.36	6.02	3.37	1.20	19.05	1.20	14	0.19	0.46	43	–	0.55
Pirin	63.37	5.18	1.54	4.37	25.54	4.88	0	0.48	0.51	0	0	3.89
Pirin-APF	59.29	4.06	2.65	3.87	30.13	4.10	16	0	0.23	77	0	3.87
Pirin-APF-PC	59.40	4.10	2.70	2.95	30.85	3.09	25 ^c	0	0.16	30 ^c	24 ^c	2.93
Pirin-APF-SS	58.60	4.01	3.09	3.32	30.98	3.47	15 ^c	0	0.20	13 ^c	16 ^c	3.27

daf: dry ash free; db: dry basis; S_t: total sulphur; S_s: sulphate sulphur; S_p: pyritic sulphur; S_{org} and S_{inorg}: organic and inorganic sulphur.

^a ΔS_t (%) = (S_t initial – S_t exp.) / S_t initial × 100.

^b ΔS_{inorg} (%) = ((S_s + S_p) initial – (S_s + S_p) exp.) / (S_s + S_p) initial × 100.

^c ΔS_t, ΔS_{inorg} and ΔS_{org} are calculated on the basis S_t initial, S_{inorg} initial and S_{org} initial equal to their correspondence S_t, S_{inorg} and S_{org} in APF sample.

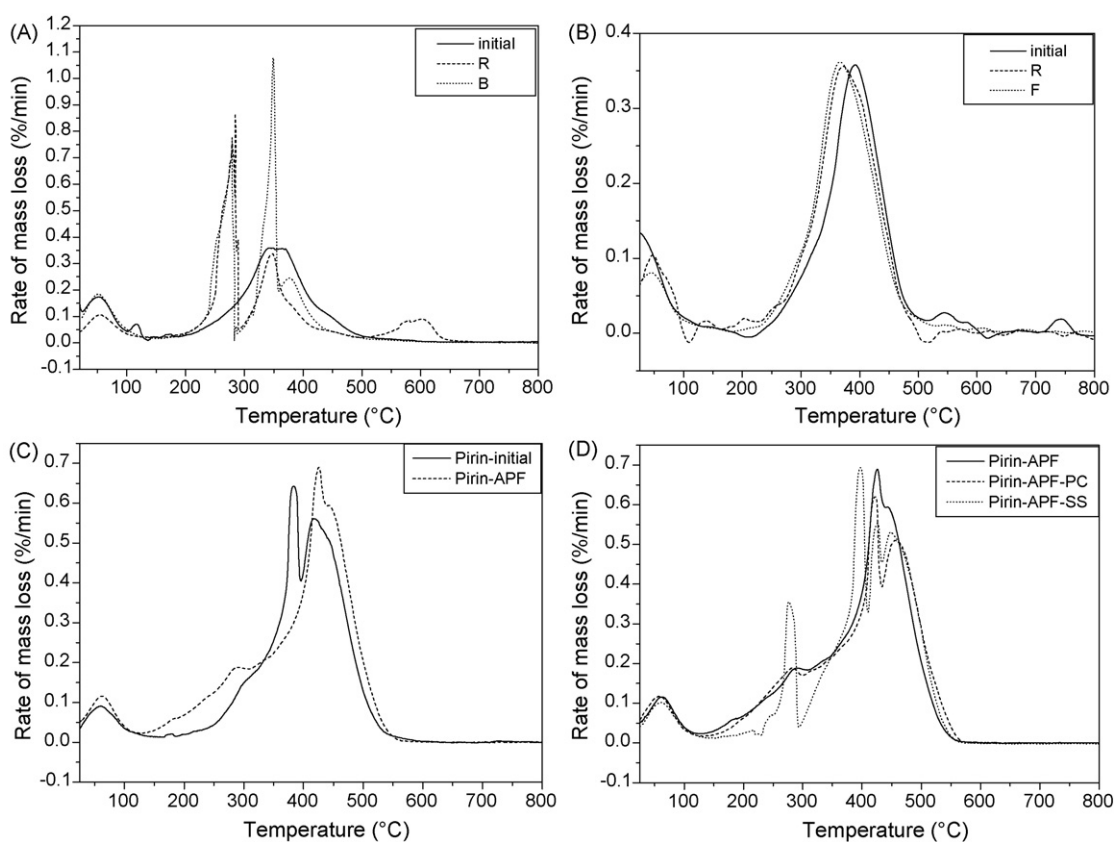


Fig. 1. DTG curves of samples: (A) “M.Iztok”; (B) “B.Dol”; (C) and (D) “Pirin”.

Table 3
Characteristics of combustion.

Sample	T _{ign} (°C)	T _{max} (°C)	T _{ec} – T _{ign} (°C)	R _{max} (%/min)	t _q [min (') s (")]	T _{sh} (°C)	T _{ec} (°C)
M.Iztok	262	351	224	0.36	35' 6"	222	486
M.Iztok-R	200	283	249	0.84	34' 36"	213	449
M.Iztok-B	215	349	274	1.07	35' 30"	185	489
B.Dol	275	393	208	0.36	34' 24"	235	483
B.Dol-R	250	373	232	0.36	34' 54"	219	482
B.Dol-F	250	366	249	0.37	34' 48"	220	499
Pirin	258	384	262	0.64	22' 36"	256	520
Pirin-APF	250	424	294	0.69	26' 12"	220	544
Pirin-APF-PC	242	423	318	0.62	30' 42"	194	560
Pirin-APF-SS	250	395	300	0.69	26' 12"	199	550

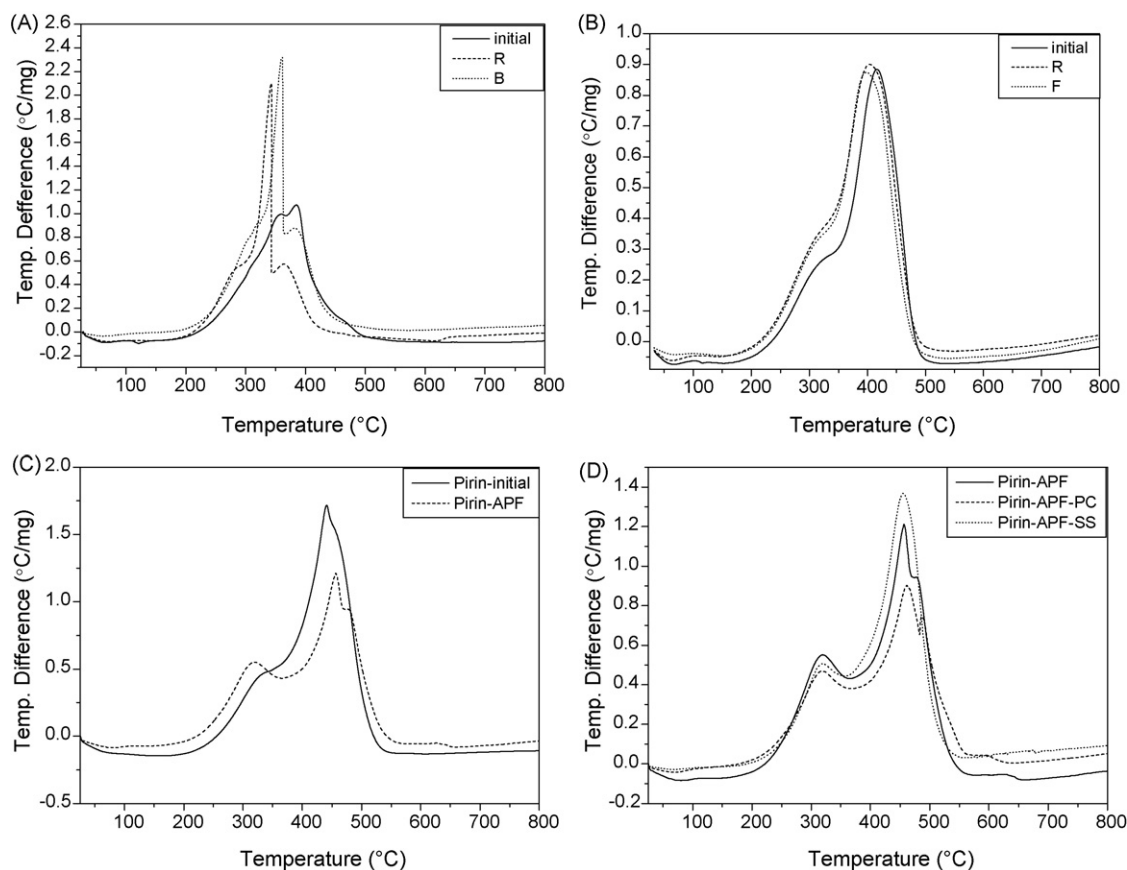


Fig. 2. DTA curves of samples: (A) "M.Iztok"; (B) "B.Dol"; (C) and (D) "Pirin".

tional volatile organic matter during biotreatment. The curves of all samples demonstrate the major peaks of weight loss in the range 350–400 °C. There is a general trend that the peak maximum of all biotreated samples is shifted to lower temperatures (Fig. 1A–D, Table 3). After peak temperature of maximum weight loss rate for "Pirin" samples additional peaks are found which are referred to "delayed burnout". This behavior can be associated with a more difficult burning of lower reactivity char combustibles [24].

The most thermal changes in biotreated coals are registered as a result of oxidation by microorganisms *Acidithiobacillus ferrooxidans* and *Pseudomonas putida* on a lignite sample "M.Iztok" from one side and from other, first after action on subbituminous "Pirin" coal by diluted mineral acids and second by microbial treatment with *Sulfolobus solfataricus* strain on ash pyrite free "Pirin" sample. After running microbial and chemical oxidation processes a new peak of devolatilization appears with a maximum round 270 °C. This observation can assign to the new compounds formed and it is in agreement by the investigation of other authors [9].

Concerning the DTG profiles of samples "B.Dol" (initial, R and F) in Fig. 1B it is shown that only the main peak at round 400 °C is shifted at lower temperature region for the biotreated samples and no additional peaks appeared.

Fig. 2A–D of DTA profiles visualize the evolution of heat flow with elevated temperatures. First part of DTA curves corresponds to a global endothermic process, which is a result of water adsorption (endothermic) and oxidation reactions (exothermic). This thermal interval finishes when oxidation reactions predominate and energetic balance begins to be exothermic, at the temperature of self-heating (T_{sh}). After that combustion process follows with two stages of volatile matter releasing and coal char combustion. They comprise first period of increasing rate of heat loss where one or two combined exothermic peaks appear due to the combustion of

the volatile matter and heat releasing. The exothermic maximum is attained when a burning of the residual solid is occurred in the stage of coal char combustion. A rapid diminishing of the rate of heat flow follows (Fig. 2A–D) and temperature differences of DTA curves pass to the last endothermic region of the global combustion process. Different coals under study and their biodesulphurized solid products demonstrate different DTA patterns in the global combustion process.

For lignite "M.Iztok" initial (Fig. 2A) the large shoulder covers the exothermic region to the first exothermic peak near 350 °C corresponds to a volatile matter releasing stage. This shoulder at biotreated samples R and B for the same "M.Iztok" lignite is shifted to lower temperatures. Next combustion stage, namely coal char combustion, includes a sharp exothermic maximum for biotreated lignite shifted also to lower temperatures in comparison to the exothermic maximum of initial lignite.

Concerning the thermal behaviour of subbituminous "B.Dol" initial coal, since the volatile matter is released a smooth increasing in weight loss and released heat of strong exothermic effect are shown in Figs. 1B and 2B. The global shape of two figures is close and after biotreatments the general view of DTG and DTA profiles is retained. Only the T_{max} around 400 °C of both curves for biotreated "B.Dol" samples is shifted to lower temperature region near 370 °C.

Thermal behaviour of "Pirin" samples is visualized separately for samples after preliminary chemical treatment (Figs. 1C and 2C) and the samples after biodesulphurization (Figs. 1D and 2D). On DTA profile (Fig. 2C) an exothermic shoulder on an exothermic peak maximum near 420 °C is found. The first shoulder corresponds to volatile matter releasing stage and the main peak to char combustion stage. After chemical treatment for ash pyrite free coal sample the released heat of the first exothermic shoulder transforms to a well defined exothermic peak near 300 °C. The exothermic maxi-

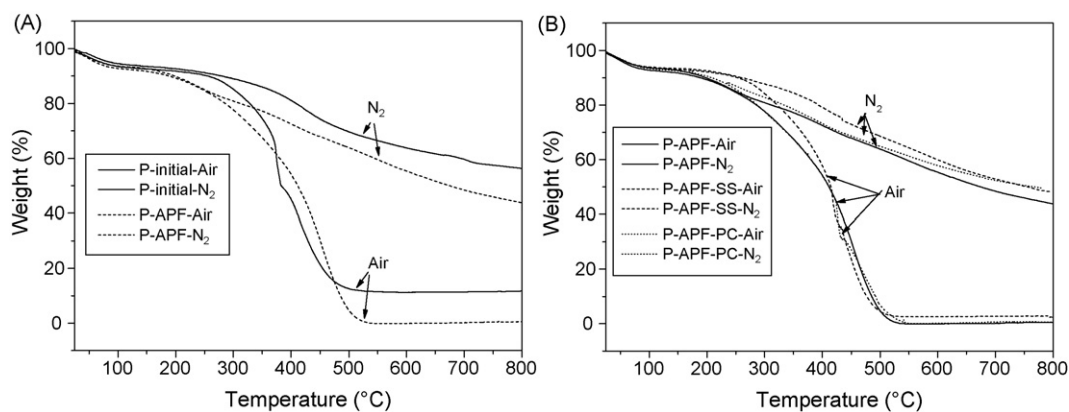


Fig. 3. (A and B) TG curves of "Pirin" coal samples in air and N_2 .

imum is shifted to about 450°C and a new small exothermic peak round 480°C follows. The last exothermic peak can connect with some lower reactivity char combustibles additional produced by biotreatments. In Fig. 2D the thermal heating profiles of biotreated "Pirin" coal are visualized. The peak maxima of these DTA curves are almost on the same position of which it can be concluded that organic sulphur biodesulphurization do not change in any drastic manner the thermal behaviour of biotreated "Pirin" ash pyrite free (APF) samples.

3.3. Characteristic parameters from combustion

The ignition is an important preliminary step in the coal combustion process due to its influence on the formation and emission of pollutants, flame stability and flame extinction. Therefore the ignition behaviour of coal is of considerable importance of controlling the combustion process. Ignition is the substantial burning of coal particles or evolved volatile matter. Hence, an ignition temperature is either the minimum gas temperature or the temperature at which the coal particles ignite. As it is reported [25] the ignition temperature and mechanism are not inherent properties of coal. They depend on the type of test apparatus and the operating conditions employed. Therefore, the ignition temperature of a fuel should be determined under conditions similar to those in which it is used. For comparative investigations of different fuel samples it is not necessary, but the conditions must be the same for all analysis.

To our knowledge there is not a standard method for determining coal ignition temperature. Thermogravimetric ignition measurement is employed often, because it allows a comparison of coal ignition with ignition of treated coals under well-defined conditions. The experiments are usually performed for small, finely milled samples and at slow heating rate.

Tognotti et al. [17] used thermogravimetric (TG) equipment to measure ignition temperature (T_{ign}) of coal particles. The T_{ign} was taken as the temperature at which the mass loss curves in the oxidation and pyrolysis experiments deviate. In our study T_{ign} of "Pirin" samples is demonstrated in Fig. 3A. The T_{ign} data are summarized in Table 3. It is obvious that after biotreatments the values of T_{ign} for all samples are shifted to lower temperatures.

Peak temperature of maximum weight loss rate (T_{max}) is usually considered as the most important feature of DTG profiles. Coals with lower peak maxima temperatures generally can be ignited and burned easier. In our study, the tendency is that T_{max} of all biotreated coal samples are shifted to lower temperature region (Table 3). Concerning T_{max} of chemical desulphurized "Pirin" ash pyrite free coal there is an opposite tendency of increasing T_{max} which is explained with the loss of mineral matter catalytic effect

on coal combustion [26]. T_{max} looks to be a very sensitive factor to the type of treatment as the applied biotreatments resulted in different burning profiles. A reason for shifting the T_{max} to lower temperature range is due to production of more volatile matter during biotreatment. It is highly expressed in the case of "M.Iztok-R" sample (Tables 1 and 3).

Temperature of self-heating (T_{sh}) or spontaneous heating is an important characteristic for the practical use as it concerns the coal safely storage in coal-yards. Self-heating is the process resulting in a temperature increase of a coal mass. This phenomenon is provoked by the heat-generating chemical reactions of the oxidant (oxygen) and the fuel. If the generated heat is not transmitted to the exterior, a self-heating process might take place and spontaneous combustion will eventually occur. From the different techniques monitoring spontaneous combustion of coal [27–29] the DTA approach is broadly used as a method to trace the self-heating [18]. The T_{sh} is evaluated as an indicator of the susceptibility of coals to self-heating and spontaneous ignition. T_{sh} is the temperature at which the rate of heat flow in the DTA curve begins to be exothermic. As can be seen from Table 3 there is a clear diminishing of T_{sh} for all coal samples after biotreatments and chemical treatment for "Pirin-APF" sample also. The lowest T_{sh} value (185°C) is attained for "M.Iztok"-B sample. This means that there is a high risk of autogenously heating in a stock pile of such coal and spontaneous unmanageable combustion even result.

From the DTA curve it is also possible to determine the end of combustion (T_{ec}). This is in correspondence to the temperature when the rate of heat flow is zero [18]. General tendency is observed for increasing T_{ec} values of bio- and chemical treated samples, respectively combustion temperature interval ($T_{\text{ec}} - T_{\text{ign}}$) (Table 3). This is reflected on longer necessary time shown by t_{q} parameter, which value also increase. This observation is due to increasing the amounts of fixed carbon of treated coal samples (Table 1), which involves the necessities of longer combustible time to burn up more amounts of carbonaceous matter.

Concerning applied demineralization and depyritization procedures [10,11] for "Pirin-APF" sample and its relation to coal combustion characteristics, a clear decrease in the combustibility is obtained. It is indicated by the increases in peak temperature T_{max} , the end of combustion temperature T_{ec} and decreases in self-heating temperature T_{sh} (Table 3). This observation can be associated with removed coal mineral mass, which may play some catalytic influence on coal combustion [26].

3.4. Energy values

Higher heating value (HHV) is the most important coal characteristic, as the primary goal of coal use is as an energy source for

thermal power plants and industrial boilers. This technological fuel characteristic is determined experimentally by a bomb calorimeter [20]. It is registered that higher heating values decrease slightly for biotreated coals [Table 1]. This observation can be explained merely by biodesulphurization effects of applied microbial systems, since the ash content decreases for treated coals after cleaning procedures is not so high (max 8%). The highest decrease in calorific value is for the sample of biotreatment procedure R for “M.Iztok” coal (5.4%).

4. Conclusion

Thermal analysis is used as a preliminary evaluation of possible changes in the combustion behaviour of biotreated coal samples. TGA and DTA experiments are carried out in the present study. The burning profiles of the initial and treated coals demonstrate some small differences. The last can be related to structural changes from the biological treatments. These changes are probably due to the oxidation process provoked by the overall biological treatment. Concerning organic sulphur biodesulphurization, determined clearly for biodesulphurized ash pyrite free “Pirin” coal, there is no change in any drastic manner of thermal behaviour of these samples. In general, applied biotreatments provoke a complex influence on combustion coal behaviour. From one side for biotreated samples are observed: (i) a better ignition performance; (ii) a minor decrease in higher heating value; (iii) diminishing of peak temperature of maximum weight loss rate (T_{max}). From the other side some decrease in the combustibility are obvious: (i) an increase in the combustion time (t_q); (ii) an increase in the end of combustion temperature (T_{ec}); (iii) a decrease of self-heating temperature (T_{sh}); Decreasing of T_{sh} parameter after biotreatments evolves high risk of spontaneous unmanageable combustion, especially for “M.Iztok”-B sample. Nevertheless the benefits of reduced sulphur emissions must be taken into account as a serious advantage for general evaluation of the process.

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