RAPID PYROLYSIS OF SERBIAN SOFT BROWN COALS

by

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Soft brown coals of the open coal fields of Kolubara and Kostolac are the main domestic energy sources of Serbia. This paper presents the results of investigations on rapid devolatilization of these two coals which have covered kinetics of devolatilization (based on total volatile yield), forms of sulphur and petrographic analysis of coal and char. Experiments of devolatilization were performed in inert gas (N_2) at atmospheric pressure and in batch-type hot-wire screen reactor. The mass-loss values of both coals at selected final reaction temperatures (300-900 °C) and retention times (3-28 s) were obtained. Anthony and Howard's kinetic model was applied over two temperature ranges (300-500 and 700-900 °C). The types of sulphur as monosulphide, sulphate, pyritic, and organic sulphur were determined for chars and original coals. Strong transformation of pyrite was evident even at low temperatures (300 °C). Devolatilization of all types of sulphur has started over 600 and at 900 °C the content of sulphur in char remained only 66% of total sulphur in original coal. Microscopic investigations were carried out on samples prepared for reflected light measurements. The petrographic analysis included: the ratio of unchanged and changed coal, maceral types, the share of cenosferes, isotropic mixed carbonized grains, mixed grains, small fragments, clay, and pyrite. The change of the structure of devolatilized coal was also observed.

Key words: *lignite, rapid devolatilization, sulphur, petrographic analysis*

Introduction

Soft brown coals of the open coal fields of Kolubara (KL) and Kostolac (KS) are main domestic energy sources of Serbia. Coal reserves are big enough to maintain the present mass production of electricity in power stations located near Belgrade. Serious environmental problems which accompany energy production have given more importance to the efforts in the increasing of efficiency of coal utilization. Better understanding of coal conversion behavior in energy production is the part of these efforts.

Devolatilization of organic matter is the first step of coal conversion processes, but very important one for coals with high volatile content, as Serbian brown coals. Bigger part of organic matter of these coals is released during the short period of devolatilization. For Serbian soft coals it is 55-60% (wt, daf) and the chemical energy attached to the volatiles consists 40-50% of total chemical energy of coal [1].

Early studies of devolatilization of pulverized coal were present at the end of sixties (see, *e. g.*, [2]), important progress in understanding of mechanisms and modeling of devolatilization was done in seventies (see, *e. g.*, [3-5]) and further step in conception and mod-

eling of coal structure (see, *e. g.*, [6, 7]) and overall decomposition of organic matter (see, *e. g.*, [8, 9]) was made in eighties. It was shown that the behavior of coal and kinetic parameters of devolatilization largely depend on the type of coal. There are not many experiments where devolatilization of Serbian soft brown coals was studied. Fluidized bed technique was used by Radovanović *et al.* [10], but combustion of larger coal particles was the prime interest of their work.

Entrained flow, 71 mm i. d., reactor for investigation of devolatilization of pulverized coal Kolubara in inert atmosphere (nitrogen) was employed in our previous experiments (see, *e. g.*, [1]). According to these experiments, the influence of particle size and temperature on total volatile yield (V) was shown. Constant maximum value of the volatile yield, V_{max}, for certain temperature depends on particle size. V_{max} was always bigger than volatile content of coal (VM) given by standard proximate analysis (V_{max}/VM was 1.01 for 60-90 µm particles), and 1.5 for 400-500 µm particles. Microscopic investigations of coal char obtained from same experiments have shown significant changes in the structure of coal particle during devolatilization. Round or longitudinal cavities (in accordance to the type of maceral of original coal) were dominant on the microscopic picture of the coal char (see, *e. g.*, [1]).

Pyrolisis experiments of KL and KS coals were performed also using thermogravimetry (TG) and fluidized bed (FB) (see *e. g.*, [11, 12]). The results of experiments were analyzed using the distributed activation energy model. The total volatile yield distribution curve of the activation energies, $f(E)$, and the activation energy frequency factor, $k_o(E)$, for pyrolisis of KL and KS coals were determinated by thermogravimetric experiments [11].

Experiments of devolatilization of KL and KS coals in thermogravimetric (TG) analysis, wire mesh (WM), and pyroprobe reactors were performed by Stojiljković *et al.* [13]. The results of the volatile yields, composition, nitrogen compounds, and the kinetic parameters are presented in their paper. The volatile yields have shown the significant difference for different experimental techniques and reaction temperatures. The overall reaction of devolatilization for two stage regimes (250-500 and 650-950 °C) were presented by the first order reactions and Arrhenius parameters of reaction kinetic were given in the paper. Activation energy (E) for KL coal for these regimes was 89 and 119, respectively.

This paper presents the work on rapid devolatilization of two Serbian soft brown coals KL and KS. Experiments were performed on a hot wire screen reactor in inert atmosphere with final temperatures of reaction 300, 500, 700, and 900 °C. Investigations have covered kinetics of devolatilization (based on total volatile yield), changes of forms of sulphur during devolatilization and petrographic analysis of coal and char.

Experimental

Coal samples

Bulk samples of coal used in experiments originated from the main coal seam of the KL and KS coal basins.

Characteristics of coal samples (fraction used in experiments) are presented in tabs. 1, 2, and 3. All results reported in this paper are for the fraction in the particle size range 80-100 µm.

The proximate and ultimate analysis, as well as micropetrographic analysis were shown in tab. 1. The ash analysis and size distribution of partially dried and grinded original samples are shown in tabs. 2 and 3.

High contents of volatiles, ash, and oxygen and low heating value are typical for both samples. Content of moisture in as received coal (initial samples) is also very high, 55 wt.% for KL

and 42 wt.% for KS. Coals differ in total sulphur content (0.71 wt.% for KL, 3.11 wt.% for KS) and in forms of sulphur. Dominant form of sulphur is organic sulphur for KL (66.2% of total sulphur) and piritic sulphur for KS (60.8% of total sulphur). The major constituents of ash are presented in tab. 2 and it shows acid character of both ash samples. Results of micropetrographic analysis of coal samples are presented in tab. 1. Both samples are similar in contents of mineral matter and main maceral groups (huminite, liptinite, and inertinite). The high concentration of deinsinite and gelinite with grain sizes less than 0.03 mm are typical. Results show the middle stage of humification and gelification of coal substance (1.35 for KL and 1.68 for KS). In the sample KL the proportion of gelified macerals was 42.0 vol.% and non-gelified macerals 28.0 vol.%; these values were 48.0 vol.% and 20.5 vol.% for the sample KS. According to the huminite reflectance, Rr (0.27 + 0.06% for KL and 0.28 + 0.04% for KS), the coal substance belongs to soft brown coals, designated as M2 (see, $e.\ g.$, [14]), with 39 wt.% and 32 wt.% of xylite.

Apparatus and procedure

Experiments of devolatilization were performed in inert gas (N_2) at the atmospheric pressure and in a batch-type reactor with electrically heated screen. Temperatures of reactions were determined to be 300, 500, 700, and 900 °C, with reaction times 3, 5, 12 (or 15), 20, and 28 s for each reaction temperature.

The reactor and procedure are similar to these widely described in literature (see, $e.\ g.$, [5, 15]). Main reactor characteristics are high heating rate (100-10000 °C/s) and easy control of sample final holding time and temperature (300-1000 °C for up to 60 s), performed using fine thiristor-based pro-

Table 1. Characteristics of KL and KS coals samples

Results of analysis	Samples	
	KL	KS
Proximate analysis		
Ash [wt.%, dry basis)]	35.12	37.12
Sulphur, total [wt.%, dry basis]	0.72	3.06
High heating value [kJkg^{-1}]	15880	14585
Low heating value [kJkg^{-1}]	15030	13625
Ultimate analysis [wt.%, daf]		
– Carbon	54.81	52.70
– Hydrogen	5.47	4.82
– Nitrogen	0.80	0.79
Sulphur + oxygen (by differences)	38.92	41.69
Microscopic analysis of macerals and minerals [vol.%]		
Huminites	79,0	81.0
– Textinite	23.0	15.0
– Ulminite	17.0	17.0
– Atrinite	5.0	9.5
– Densinite	10.0	14.0
– Gelinite	15.0	13.0
Liptinite	6.0	4.5
Inertinite	3.0	8.0
Minerals	21.0	19.0
– Clay	18.0	14.0
– Pyrite	2.0	3.0
– Carbonates	1.0	2.0
Gelification index	1.35	1.68
Huminite reflectance, Rr [%]	0.27	0.28
Xylite [wt.%]	39.00	32.00

Table 2. The ash analysis [m wt.%]

Components	Sample	
	KL	KS
SiO_2	55.8	45.9
Al_2O_3	22.4	20.9
Fe_2O_3	11.3	16.4
CaO	4.7	9.2
MgO	2.0	2.8
K_2O	0.4	0.4
Na_2O	0.5	0.3
SO_3	2.9	4.1
Total	100.0	100.0

Table 3. Size distribution of partially dried and grinded coal samples

| Fraction	Sample			
[mm]	KL [kg]	KL[%]	KS [kg]	KS [%]
–0.08 + 0.00	0.149	2.9	0.133	2.7
–0.1 + 0.08	1.542	30.9	1.856	37.1
–0.125 + 0.1	0.498	10.0	0.531	10.6
–0.25 + 0.125	0.995	19.9	0.986	19.7
–0.315 + 0.25	0.672	13.4	0.685	13.7
–0.5 + 0.315	0.646	12.9	0.603	12.1
–0.8 + 0.5	0.472	9.5	0.175	3.5
–1 + 0.8	0.026	0.5	0.031	0.6
Total	5.00	100	5.00	100

cess control. Reactor is made of 71 mm i. d., 115 mm long stainless steel (SS 316L) pipe. The purge gas inlet and thermocouple connectors are placed on the bottom and the gas outlet and the pressure gage on the upper cover of the reactor. The 325 mesh, 10×50 mm, stainless steel screen is fixed between two massive brass electrodes. A chromel-alumel thermocouple (40 μm wire diameter) is welded on the screen and the reaction temperature is recorded by a fast-response milivoltmeter connected to a personal computer.

The screen is weighed and fixed between the electrodes and the coal sample (app. 10 mg) is spread in the few particle thin layer over it. After connecting of the thermocouple wires, the reactor is closed, evacuated and purged with nitrogen (using three to four times of a reactor volume for each experiment). The sample is heated with the predetermined heating rate to the desired reaction temperature. The control device set-up values for desired heating rates, reaction time, and temperatures had to be determined in several trials (using the same coal quantity) before the experiment. Typical time – temperature curves for KL and KS are shown in fig. 1 and fig. 2, respectively. As the coal sample was small, experiments were repeated 15 to 20 times for each set of experimental conditions in order to provide enough material for chemical and micropetrografic analysis.

The mass loss of every coal sample, *i. e*. the volatile yield, is determined gravimetrically. The weight of coal, screen before and screen together with char after each experiment was determined to within +0.01 mg.

Types of sulphur and sulphur transformations during devolatilization were of the special interest in this work. The proportions of various forms of sulphur (sulphate, monosulphide, pyrite and organic-containing compound) are determined by successive treatment of samples with perchloric solutions of different concentrations, *i. e*. of different boiling points, as selective oxidizing agents. Tests were carried out in inert atmosphere (N_2) in a somewhat modified Bethge's apparatus (see, *e. g*., [16]).

To determine the monosulphide and sulphate forms of sulphur, coal or char sample was treated with 40% $HClO_4$ at 115 °C for 40 minutes. Hydrogen sulphide originating from monosulphides was introduced into 30% of H_2O_2, thus oxidized and determined as sulphate. The sulphate sulphur was determined from a filtrate obtained by filtering and rinsing the remainder of sample at the end of reaction.
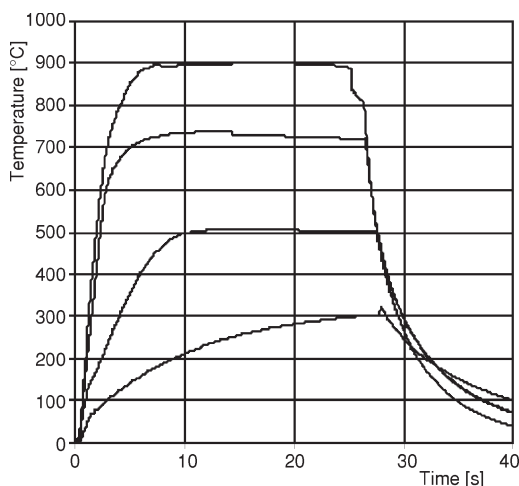
Figure 1. Time-temperature curves for coal Kolubara
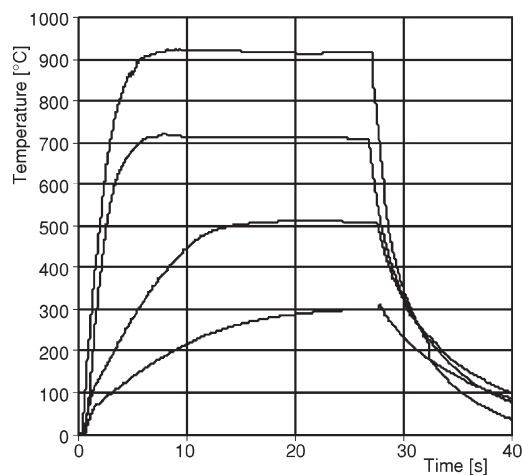
Figure 2. Time-temperature curves for coal Kostolac

The pyritic sulphur was determined in the sample residue. The oxidation was carried out by 55% $HClO_4$ at 145 °C for 90 minutes. The sulphur containing gases produced during the reaction were introduced into 30% of H_2O_2. After the termination of the reaction the sample was filtered, rinsed, and dried. The filtrate was added to the H_2O_2 solution and the sulphate content was determined in the combined liquid mixture.

Finally, the organic sulphur was determined by oxidation of sample residue by a mixture of 75% $HClO_4$ and concentrated H_3PO_4 (9:1) at 200 °C for 60 minutes. At the end of reaction the content of the flask was filtered and filtrate was added to the 30% solution of H_2O_2.

In all cases the concentration of sulphate was determined turbidimetrically and calculated as a content of sulphur in dry sample.

Microscopic investigations were carried out on samples prepared for reflected light measurements. Two polished blocs were investigated from each sample, involving 500 measuring points, according to I.C.C.P. standards [17].

The maceral analysis and determination of the coal rank were carried out according to I.C.C.P. standards and ISO 7404, or JUS BHB 393 standards, respectively. The gelification index was determined from the ratio of gelified to non-gelified macerals.

Devolatilization apparatus was constructed and devolatilization experiments were completed at the Faculty of Mechanical Engineering, Department for Process Engineering and Thermomechanics, University of Belgrade. All analysis of coal and char samples were made in laboratories of IHTM, Institute of Chemistry, Belgrade, but micropetrografic characterization of samples was done by Faculty of Mining, University of Belgrade. Ash analysis was performed by the Mining Institute, Belgrade.

Results and discussion

Devolatilization

Heating conditions for devolatilization of coal samples KL and KS are shown in figs. 1 and 2. The period of rapid heating with linear change of temperature followed by the period of constant reaction temperature is evident for all temperature curves. The average heating veloci-

ties which could be achieved in this set of devolatilization experiments for reaction temperatures 300, 500, 700, and 900 °C were 120, 160, 220, and 270 °C/s, respectively.

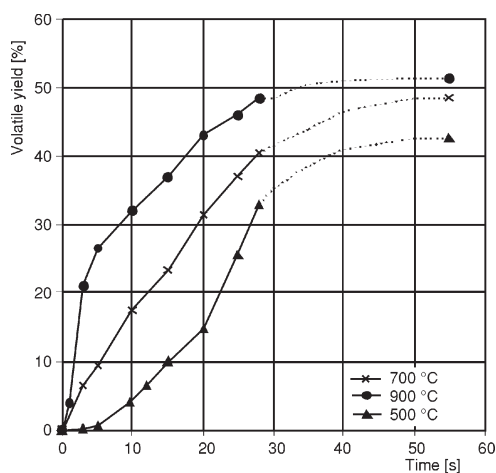*Results of devolatilization tests* are presented in figs. 3 to 6.

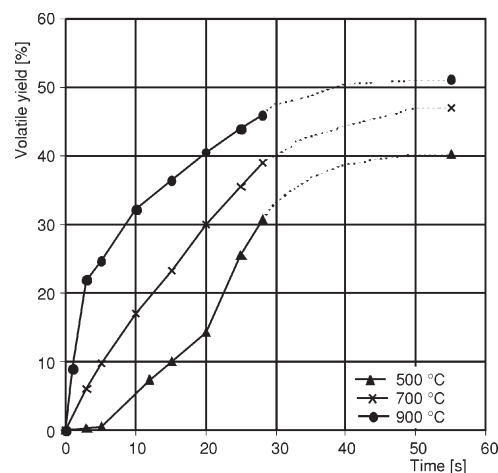**Figure 3. Volatile yield for coal Kolubara**

Figure 4. Volatile yield for coal Kostolac

Reaction time dependence of the mass loss (Δm), *i. e.*, the volatile yield, is shown for coal KL in fig. 3 and for KS in fig. 4. It can be seen that the process of devolatilization was not completed for the maximum reaction time of 28 s used in this set of devolatilization experiments. Extrapolations have shown (doted parts of curves in figs. 3 and 4) that devolatilization could be completed for all reaction temperatures in 45 to 55 s. The maximum volatile yield for each temperature is also bigger than the measured value for Δm at 28 s and it was obtained by the curve fitting of time dependence of Δm and temperature dependence of maximum volatile yield.

The reaction temperature dependence of maximum volatile yield is given in figs. 5 and 6. The highest reaction temperature for this set of devolatilization experiments was 900 °C and
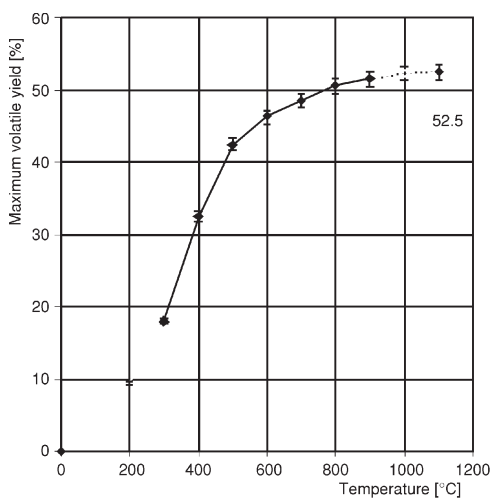

Figure 5. Dependence of maximum volatile yield on temperature for coal Kolubara
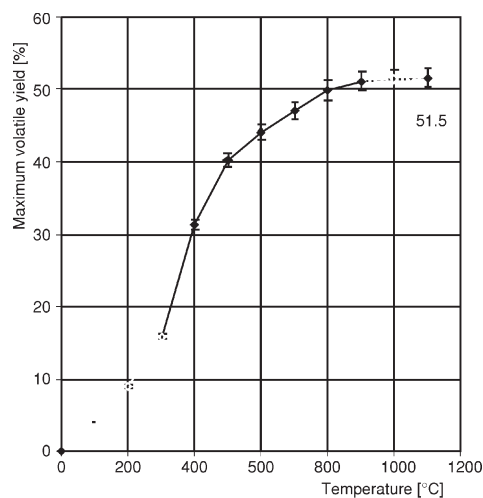

Figure 6. Dependence of maximum volatile yield on temperature for coal Kostolac

correspondent values for the maximum volatile yield for KL and KS were 51.0 and 51.4%, respectively. The character of curves presented in fig. 5 and 6 show that devolatilization started after 200 °C but before 300 °C. The both curves have their maximum at 1100 °C and the values for the maximum volatile yield at this temperature for KL and KS were 52.0 and 51.5%, respectively. These values present total amount of volatiles that can be achieved for both coals in hot wire screen reactor devolatilization experiments (see, *e. g.*, [18]).

Kinetics of devolatilization was determined using the model proposed by Anthony and Howard (see, *e. g.*, [19]). According to this model, widely accepted in literature, rapid devolatilization of coal consists of the big number of parallel reactions with same reaction rate constant, but with different activation energies. If Gaussian distribution of activation energies is applied, the volatile yield during the process of devolatilization can be calculated using the following equation:

$$\frac{V_{tot} - V}{V_{tot}} = \int_0^{\infty} \exp\left(-k_0 \int_0^t \exp\left(-\frac{E}{RT}\right) dt\right) \frac{(E - E_0)^2}{2\sigma^2} dE \tag{1}$$

$$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right) \tag{2}$$

where E_0 is the mean activation energy, σ – the standard deviation, V – the cumulative volatile yield up to time t, V_{tot} – total amount of volatiles at infinite time, and k_0 – the reaction rate constant.

There are four kinetic parameters, V_{tot}, k_0, E_0, and σ, that have to be determined using the experimental results and eq. (1). Trapezium's rule was applied for the numerical solution of eq. (1). It was not possible to find the parameters k_0, E_0, and σ that could achieve the good fitting of experimental curves at any time and any temperature, because of the difficulties in numerical solution caused by the broad range of reaction temperatures. The method used by Lappas *et al.* (see, *e. g.* [20]) was applied and the temperature range was divided into two parts: low (300-500 °C) and high temperatures (700-900 °C). The application of the model proposed [19] over two temperature ranges gave the good fitting of experimental curves. Kinetic parameters obtained by modeling are shown in tab. 4 (see, *e. g.*, [18]).

The comparison of pairs of k_0 and E values presented in tab. 4 and values for k_0 and E obtained for pyrolysis of KL and KS coals using TG and FB [11, 12] shows very good agreement. The total volatile yield distribution curve of the

Table 4. Kinetics parameters (A – 300-500 °C; B – 700-900 °C)

Coal	V_{tot} [%]	Kinetic parameters					
		E_0 [kJkmol^{-1}]		k_0 [s^{-1}]		σ [kJkmol^{-1}]	
		A	B	A	B	A	B
KL	52.5	182.9	224.4	$7.4 \cdot 10^{11}$	$1.1 \cdot 10^{11}$	5.86	8.37
KS	51.5	203.9	230.3	$9 \cdot 10^{12}$	$5 \cdot 10^{11}$	5.86	16.7

activation energies, $f(E)$, and the activation energy frequency factor, $k_0(E)$, for pyrolysis of KL and KS coals determinated by TG experiments [11] as well as the pairs of k_0 and E values for FB experiments of Oka *et al.* [12] are shown in fig. 7. The values of k_0 for both coals presented in tab. 4 lie at the same k_0 *vs* E curves for low temperature regime (300-550 °C), but show much lower values than those which correspond to the k_0 *vs*. E curves for high temperature regime (700-900 °C). Stojiljković *et al.* [13] have used the first order reaction model in analysis of re-
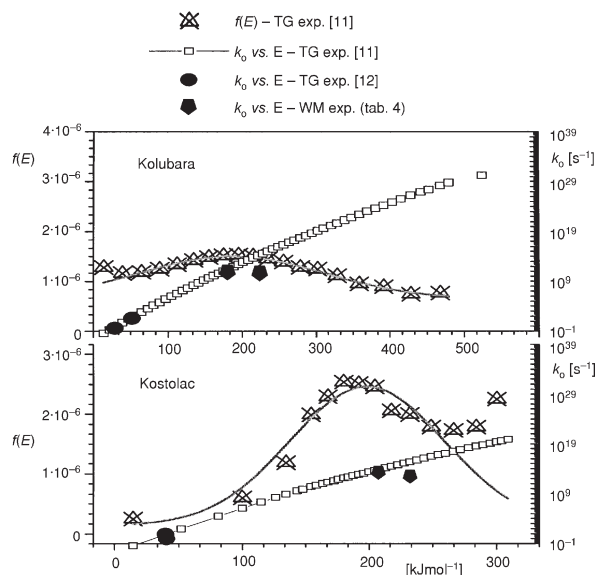
Figure 7. Experimental results for $f(E)$ and k_o obtained by thermogravimetric and fluidized bed and results of wire mesh experiments presented in tab. 4

sults of the pyrolysis of Kolubara coal in their TG experiments. The obtained values of activation energies for temperature regimes, 250-550 °C and 650-900 °C, are 89 and 119 kJ/kmol, respectively.

Sulphur transformations

In studying devolatilization of coals, it is significant for sulphur transformations studies to examine changes occurring in the various forms of sulphur at the given temperatures. Content of different sulphur forms in chars of KL and KS coals is presented in tab. 5.

This is the reason why various forms of sulphur have been identified in the chars obtained at 300, 500, 700, and 900 °C and in the initial coal samples.

Table 5. Sulphur content in origin coal and chars

Temperature [°C]	Su proximate analysis [%]	Sor proximate analysis [%]	Sm [%]	Ss [%]	Sp [%]	Sk = Sm + Ss + Sp [%]	Sor by difference [%]
Kolubara (KL)							
Origin coal	0.72	0.47	0.01	0.06	0.18	0.25	0.47
Char 300	0.45	0.14	0.01	0.08	0.22	0.31	0.14
Char 500	0.42	0.18	0.01	0.12	0.1	0.23	0.19
Char 700	0.47	0.16	0.01	0.16	0.12	0.29	0.18
Char 900	0.50	0.25	0.03	0.11	0.1	0.25	0.25
Kostolac (KS)							
Origin coal	3.11	0.47	0.06	0.76	1.83	2.65	0.46
Char 300	3.36	0.50	0.07	0.78	2.01	3.17	0.50
Char 500	2.99	0.88	0.09	0.85	1.17	2.11	0.88
Char 700	2.88	0.5	0.1	1.05	1.25	2.4	0.48
Char 900	2.90	0.60	0.09	0.85	1.36	2.3	0.6

The following changes have been noticed at the given temperatures.
−   Devolatilization of both coals at the temperature of 300 °C was accompanied by similar changes in mass loss of samples, but individual sulphur forms in coals were different in

behavior. In the KS chars, contents of all the sulphur forms were slightly increased, meaning that the total sulphur content became also higher. The organic sulphur was most probably part of the stable molecules (thiophenic forms, aromatic sulfides) and that is why it did not undergo any change when the devolatilization process of organic substance started. Opposite to the KS coal, the KL coal, where total sulphur comprises 65.3% of the organic sulphur, demonstrated a considerable change of the organic sulphur content. The organic sulphur was a constituent part (the aliphatic sulphur compounds, thiols, di-sulphides) of the organic matrix that was lost at 300 °C, thus decreasing the total sulphur content.

– At the temperature of 500 °C most of pyrite was decomposed. It has been assumed that a part of the formed H_2S react with the organic matrix, thus causing the increase of organic sulphur, especially in the KS coals.

– At the temperature of 700 °C it was noticed that the organic sulphur content decreased in both coals, although somewhat more in the KS coal. Increase of the pyrite sulphur is, however, most probably a consequence of the reaction of sulphur released from the other forms of sulphur and iron, resulting in the total increase of sulphur.

– At 900 °C, the certain increase of the organic sulphur content was noticed, especially in the KL coal. It is probable that the other forms of sulphur compounds were built in the organic matrix. Decomposition of sulphates occurred only at this temperature.

In order to get a real picture on the devolatilization of the various sulphur forms, data obtained on the content of individual sulphur forms in the char were computed for the initial quantity of coal (g/g of the initial coal). Figures 8 and 9 show the obtained results.

Sulfate sulphur has been noted to change only at the temperatures above 600 °C. Changes occurring in the pyrite sulphur were already noticeable at the temperature over 300 °C. The behavior of organic sulphur depends very much on the structure of organic matrix of coal. It is illustrated by the rapid loss of organic sulphur at low temperatures in KL chars and its stable values in KS for the same temperatures.

In devolatilization at the temperatures above 600 °C all the forms of sulphur were decomposed. The total sulphur remained in char at the temperature of 900 °C was only 66.15% for KS and 59.72% for KL of the total sulphur of initial coal sample.
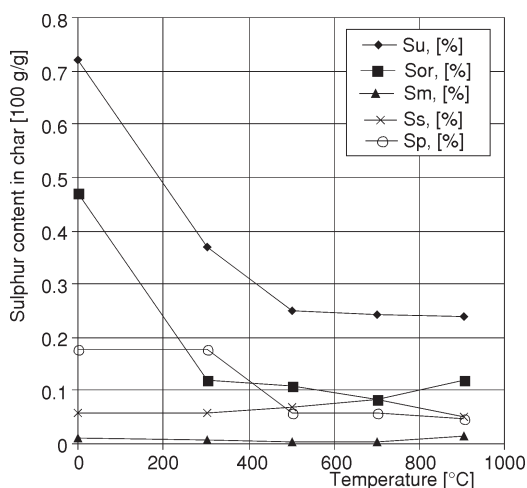

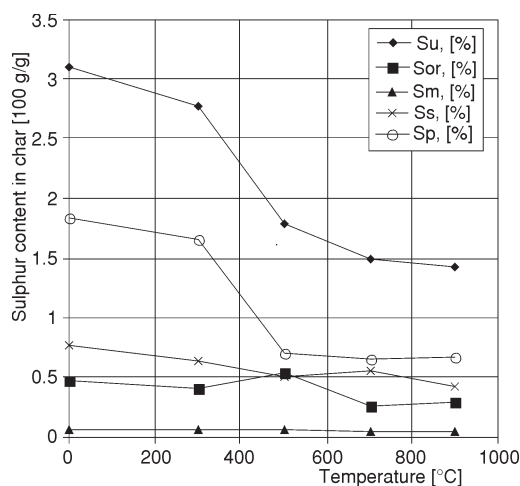**Figure 8. Change of sulphur during devolatiliization for Kolubara coal**

Figure 9. Change of sulphur during devolatiliization for Kostolac coal

Microscopic investigations

Results of petrographic analysis of coal samples and chars after devolatilization at selected temperatures (300, 500, 700, and 900 °C) are shown in tab. 6. In order to determine types of visual changes of coal in different stages of devolatilization, the following classes of coal matter are determined: (1) unchanged coal, (2) changed coal, (3) cenospheres, (4) isotropic mixed carbonized grains, (5) mixed grains, (6) small fragments, (7) clay, and (8) pyrite. The transformation of original coal matter to new products can be described as strongly temperature dependent.

There is a very high content of unchanged coal in samples devolatilized at 300 °C (81.5 vol.% for KL and 82.0 vol.% for KS). Samples maintain their maceral composition, as it is shown in tab. 6. Chars KL and KS differ from original coals only in little higher concentration of the maceral gelinite which remains high also in chars devolatilized at 500 °C. A sharp drop of the gelinite concentration is observed at 700 ° C and it is not present in chars at 900 °C. Characteristics of the grain class (2), changed coal, is higher reflectance in comparison to the un-

Table 6. Petrographic composition of coal and char classification

Different categories of grains [vol.%]		Kolubara coal				Kostolac coal			
		300 [°C]	500 [°C]	700 [°C]	900 [°C]	300 [°C]	500 [°C]	700 [°C]	900 [°C]
1.	Unchanged coal	81.5	33.0	9.5	1.0	82.0	57.0	15.0	3.0
	Humotelinite	38.5	3.0	–	–	25.0	5.0	–	–
	Humodetrinite	14.0	4.0	–	–	20.0	13.0	4.0	–
	Gelinite	18.0	20.0	3.5	–	24.0	29.0	6.0	–
	Liptinite	5.0	1.0	–	–	6.0	2.0	–	–
	Intertinite	6.0	5.0	6.0	1.0	7.0	8.0	5.0	3.0
2.	Changed coal (devolatilized huminite)	7.0	34.0	31.5	14.0	3.0	30.0	38.0	13.0
3.	Cenospheres (isotropic)								
	Thin walled	–	1.0	4.0	8.5	–	0.5	–	7.0
	Thick walled	–	3.5	10.0	5.0	–	1.1	6.0	5.0
4.	Isotropic mixed carbonized grains Homogeneous	–	8.0	6.0	15.0	–	3.0	7.0	9.0
	Porous structure	–	6.0	12.0	29.0	–	–	12.0	24.0
5.	Mixed grains (min. matter and carbonized coaly matter)	–	–	11.0	12.0	–	–	8.0	11.0
6.	Small fragments (<0.010 mm; partly inertinite)	–	–	7.0	8.0	–	–	6.0	12.0
7.	Clay	10.0	11.0	6.5	4.0	12.0	6.5	5.0	10.0
8.	Pyrite, Pyrrhotite	1.5	3.5	2.5	3.0	3.0	2.0	3.0	6.0

changed coal and small changes of coal matter typical for the start of devolatilization. This class appears in small percentages in chars devolatilized at 300 °C (7.0 vol.% for KL and 3.0 vol.% for KS), it is dominant for chars at 500 and 700 °C (over 30 vol.%), but does not exceed 14 vol.% for chars at 900 °C. Classes (3), (4), (5), and (6) are not present in chars at 300 °C.

A high content of unchanged coal for chars at 500 °C (33.0 vol.% for KL and 57 vol.% for KS) can be observed, but typical for this temperature is the appearance of new products. These are the cenospheres with the isotropic walls and carbonized grains which can characterize homogeneous or porous structure (classes 3 and 4 in tab. 6). Some number of grains appear with the gradual change from homogeneous to porous structure. The slight increase of grain sizes with the rise of temperature is also evident.

A microscopic view of row and changed coal, and different category of chars is shown in fig. 10(a-h).
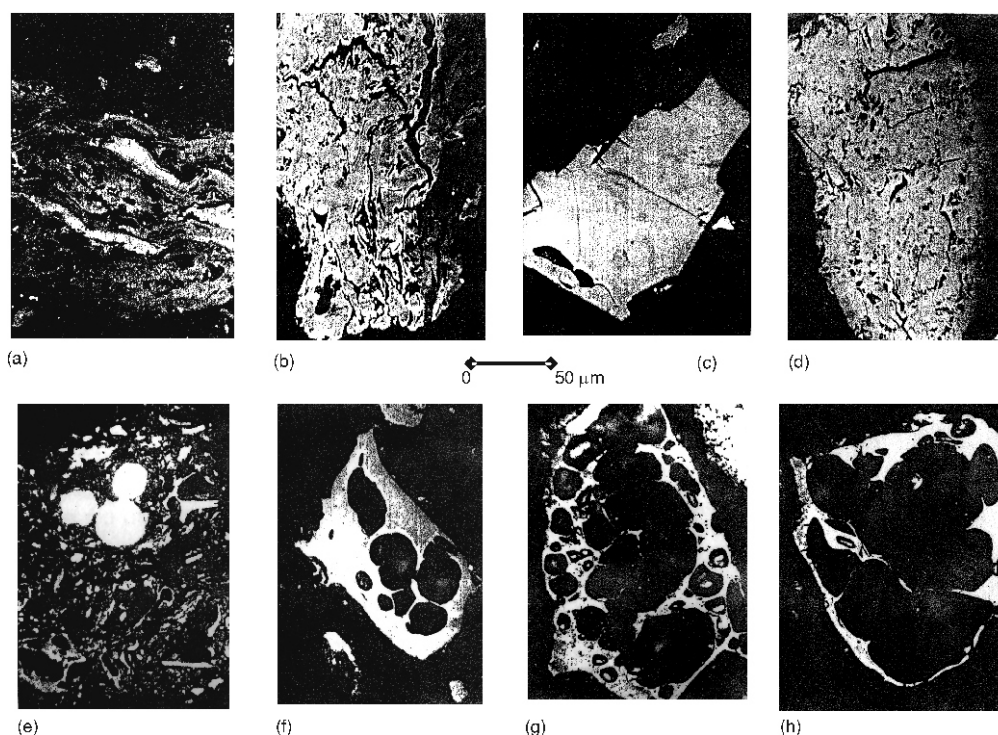
Figure 10. Characteristic view of row and changed coal, and different category of chars (KL and KS mine)
(a) unchanged coal – textinite with changed resinite (300 °C, KL); (b) changed coal – beginning of devolatilization (500 °C, KL); (c) isotropic homogeneous white grain with high reflectance (900 °C, KS); (d) isotropic porous grain with high reflectance (900 °C, KS); (e) agglomerate: small cenospheres, fragments (inertinite), clay, and pyrite (900 °C, KS); (f) isotropic grain with devolatilization vacuoles (900 °C, KS); (g) thick-wallcenospheres (900 °C, KL and 700 °C, KL); (h) thin-wallcenospheres (900 °C, KL and 700 °C, KL); (reflected light, oil,   360)

Conclusions

Rapid devolatilization experiments using hot wire-screen reactor gave the time and temperature dependence of the volatile yield for soft brown coals Kolubara (KL) and Kostolac

(KS). It was shown that maximum volatile yield exceed the values of volatile content given by standard proximate analysis. Obtained values for KL and KS are 52.5 wt.% and 51.5 wt.%, respectively.

The Anthony and Howard model was used for determination of kinetic parameters for total volatile yield. Two sets of parameters were found for two temperature regions and good agreement of model predictions and experimental curves was achieved.

The types of sulphur as monosulphide, sulphate, pyritic, and organic sulphur were determined for chars and original coals. Strong transformation of pyrite was evident even at low temperatures (300 °C) for KS, as well as significant change of organic sulphur for KL. Devolatilization of all types of sulphur has started over 600 °C and at 900 °C the content of sulphur in char remained only 66% of total sulphur in initial coals.

Micropetrografic investigations have shown that coals KS and KL have similar behavior during devolatilization. Heterogeneous structure of initial coal matter caused the formation of different new products typical for the particular stages of devolatilization.

Good knowledge of devolatilization, especially for high volatile coals as Kolubara and Kostolac, is the basis for proper combustion modeling and burner design and that is essential for efficient use of energy and environment protection.

Nomenclature

E – activation energy, [kJkmol^{-1}]
E_o – mean activation energy, [kJkmol^{-1}]
k_0 – reaction rate constant, [s^{-1}]
Δm – mass loss, [mg]
R – universal gas constant, [Jmol^{-1}K^{-1}]
Su – total sulphur content of coal or char, [%]
Sor – content of organic sulphur, [%]
Sm – content of monosulphide sulphur, [%]
Ss – content of sulphate sulphur, [%]
Sp – content of pyrite sulphur, [%]
T – reaction temperature, [°C]
t – time, [s]

VM – volatile content by standard proximate analysis, [%]
V_{tot} – total volatile yield, [%]

Greek letters

σ – standard deviation, [kJkmol^{-1}]

Abbreviations

FB – fluidized bed
KL – Kolubara coal
KS – Kostolac coal
TG – tertmogravimetry

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