MODELING DEVOLATILIZATION PROCESS OF SERBIAN LIGNITES USING CHEMICAL PERCOLATION DEVOLATILIZATION MODEL

by

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Original scientific paper
https://doi.org/10.2298/TSCI180627195Z

Different mathematical models can describe coal devolatilization as the part of combustion process. Some models are simple, while others are more complex and take into account coal's complexity and heterogeneity of structure. A chemical percolation devolatilization model for describing the devolatilization process of two Serbian lignites from Kostolac and Kolubara open coal mines was studied. Results of the model were compared to devolatilization measurements obtained from two experimental methods – a wire mesh reactor and thermogravimetric analysis. Two coal samples with four different granulations were investigated for each lignite under different experimental conditions (different maximum temperatures and heating rates). Total volatile yields obtained from the wire mesh reactor and thermogravimetric analysis together with results predicted by the chemical percolation devolatilization model are presented and compared with literature data. For thermogravimetric analysis simulation, the chemical percolation devolatilization model yielded better results in cases where the kinetic parameters obtained under experimental conditions were used rather than kinetic parameters derived from predefined values in the model itself. For wire mesh reactor, the chemical percolation devolatilization model predictions of devolatilization were mixed and were dependent on temperature.

Key words: *lignite, wire mesh reactor, thermogravimetric analysis, devolatilization, chemical percolation devolatilization model*

Introduction

Although there is increasing use of alternative and clean energy sources, coal as a traditional fossil fuel will remain a reliable source for primary energy production and will continue to serve as one of the main energy resources in the near future [1]. As in many countries, coal is the predominant primary energy source in Serbia. The majority of Serbian primary energy production is based on lignite (70% of assumed 10.66 million tone in 2017) [2]. Pulverized coal combustion is used in thermal power plants located near the biggest open pit coal mines – Kostolac and Kolubara. However, all thermal power plants now face requirements to fulfill high levels of efficiency and low pollutant emissions (especially for SO_x). In this regard, the future development of coal-fired power plants in Serbia is focused on the optimization and improvement of pulverized coal combustion in existing power plants and serious analysis, development and utilization of promising technologies.

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In order to analyze, develop and optimize a coal combustion process, it is important to understand the basic mechanisms of a combustion process (*e.g.* gas-solids reaction kinetics) which requires extensive experimental research. Additionally, optimization and simulation of the combustion process requires development and use of suitable mathematical models. The strong coupling of experimental research, theory, modeling, and optimization provides a powerful approach to understand complex combustion processes, as well as to further develop advanced types of combustors and pollutant control equipment. This is especially important as the coal used in Serbia is mainly lignite with high contents of volatiles, ash and moisture, and with relative low heating value (6700-8000 kJ/kg). The volatiles released process (devolatilization), the early stage of the combustion process, can account for up 70% of total coal (lignite) weight loss and can control ignition, flame characteristics and temperature [3]. Thus, it is important to understand the mechanisms and chemistry of the coal devolatilization process. In addition, the devolatilization process controls softening, swelling, particle agglomeration, char reactivity, and char physical structure; the soot formation (which can dominate radiative energy transport) is controlled by the tar produced during devolatilization [4]. It is clear that significant insights into the complex physicochemical phenomena that occur during devolatilization are crucial for developing the existing coal conversion technologies and implementing new technology.

Several mathematical models have been developed for describing the process of devolatilization – both simple (one-step, two-step or distributed activation energy model) and network (among others, functional group-depolymerization, vaporization, cross-linking, (FG-DVC [5], chemical percolation devolatilization (CPD) model [6], FLASHCHAIN [7], *etc*.). All these models include modeling of the coal network, characterization of the coal structure, depolymerization reactions, cross-linking reactions and formation of tar, char and non-condensable gas [8].

The CPD model was developed and introduced by Grant *et al*. [6]. In CPD model, coal is envisioned as network *i.e*. as collection of fused aromatic rings of various sizes and types, connected with a variety of chemical bridges, some having labile bonds that are easily breakable and *char bridges* that are stable at a given temperature. Model belongs to group of kinetic models. It uses percolation theory which describes the size distribution of discrete coal clusters consisting of molecules that are joined by intact bridges but are isolated from all remaining molecules by broken bridges. Use of this theory avoids use of Monte-Carlo method, with no loss of statistical data. Model uses bathe lattice which gives analytical solutions to statistics of real two and 3-D arrays. Model does not introduce random coefficients like Monte-Carlo, and lattice statistics is implemented with explicit mathematical formulas. It predicts yields of gas, tar and char. Predictions are made for (every) defined time step, until full residence time is reached. Afterwards, the CPD model was compared with other models [8-11] or used for various fuels other than coal [12-15].

Wire mesh reactor (WMR) and thermogravimetric analysis (TGA) methods were used by other authors [16], and good correlation between the CPD model and the WMR for bituminous coals and for lignites has been shown.

The Serbian lignites Kostolac and Kolubara, have previously been investigated using different simple or network models, as well as various different experimental apparatus under different conditions [17-19]. Kolubara lignite was tested previously with the FG-DVC model [18] with good modeling results. In this study, application of a CPD model to Serbian lignites was investigated. Furthermore, the model selected is easy to use without much additional input of experimental data, such as detailed coal characterization data. Verification of the modeling

results was conducted using two different experimental methods – WMR and TGA, under different conditions *i.e.* heating rate, residence time at maximum temperature and heating time.

Materials and methods

Materials

Two different lignites from the Serbian open coal mines Kostolac and Kolubara were studied. Lignite samples (air dried) were crushed, milled and sieved to achieve four target granulations ($x < 0.10$, $0.10 < x < 0.25$, $0.25 < x < 0.50$, $0.50 < x < 1.00$ mm). Proximate and ultimate analyses were conducted according to standards ISO 17246:2010 [20] and ISO 17247:2013 [21]. Additionally, volatile yields of both coals and for every granulation were determined by the standard method for brown coals and lignites (ISO 5071[22]).

Methods

Wire mesh reactor experimental procedure

Devolatilization studies were performed in a WMR under a nitrogen atmosphere at atmospheric pressure. The configuration of the WMR used is presented in fig. 1 and has already been described in detail in the literature[19-23].

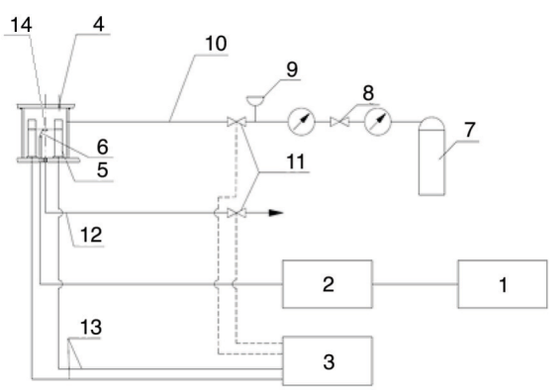

Figure 1. Wire Mesh Reactor; *1 – data logger, 2 – data acquisition, 3 – power supply and control system hardware, 4 – opening for gas chromatograph, 5 – Cl-Al thermocouple, 6 – brass electrode, 7 – nitrogen supply, 8 – regulation valve, 9 – volume flow meter, 10 – rubber supply pipe, 11 – solenoid valves for opening /closing, 12 – bleed rubber pipe, 13 – electric supply lines, 14 – mesh*

A coal sample (approximately 75-95 mg) was spread thinly between the mesh layers – 14. After connecting thermocouples – 5, the reactor was closed and prior to the experiment was washed free of residual gases with nitrogen. The coal sample was heated with the predetermined heating program to the defined temperature, *i.e.* 500, 700 or 900°C. On completion of the heating process, the sample was cooled by radiation to the cold walls of the reactor. The volatile yield was obtained by measuring the difference in coal sample weight before and after heating. Six repetitions were measured for each of the temperatures and granulations, and average value (of six) is used further in study.

Measurements obtained from the WMR (volatile yields) were used to calculate kinetic parameters by solving the Arrhenius equation, eq. (1), and the equation for constant rate, eq. (2).

$$\frac{\mathrm{d}V}{\mathrm{d}t} = k(VM - V) \tag{1}$$

$$k = k_0 \exp\left(-\frac{Ea}{\mathrm{R}T}\right) \tag{2}$$

where V [%] is the volatile yield, VM [%] – the volatile matter, t [s] – the time, k [s^{-1}] – the constant rate, E_a [$Jmol^{-1}$] – the activation energy, k_0 [s^{-1}] – the pre-exponential factor, T [K] – the temperature, R [$Jmol^{-1}K^{-1}$] – the gas constant.

The TGA experimental procedure

The TGA were performed on NETZSCH STA 445 F5 Jupiter thermal analyzer. High purity nitrogen (Class 4.6) was used as a carrier gas in order to provide inert atmosphere. At the same time, nitrogen was used as a protective gas in order to maintain the highly sensitive internal balance (±0.1 μg). Both carrier and protective gas-flows were set to 50 mL per minute. The weight measurements were carried out using the internal balance which provided the following results: Kolubara – 15.45 ±0.10 mg and Kostolac – 13.70 ±0.50 mg, respectively. Test crucibles were made of alumina and were lidded so optimum heat transfer could be realized. Each coal sample was tested using three different heating rates (10, 15, and 20 K per minute). Using these heating rates, the coal samples were heated from room temperature up to 900 °C. During all measurements, the sample temperature controller was turned off, so the set temperature (900 °C) referred to the furnace (not sample) temperature. Kinetic parameters were calculated using the integral isoconversional Kissinger method [24], *i.e.* directly from experimental measurements by varying the heating rate. For further comparison, average measurement results from three different heating rates was used.

Experimental conditions for WMR and TGA are given in tab. 1.

Table 1. Input parameters for the WMR and TGA

Apparatus	Parameter			
	Temperature	Heating rate	Residence time	Heating time
WMR	500, 700, 900 °C	6000 K/s	5000 ms	–
TGA	900 °C	10, 15, 20 K/min	–	88.00, 58.67, 44.00 min

Coal devolatilization modeling

The CPD model was used for modeling the devolatilization process of Kostolac and Kolubara lignites, and the predictions were compared with the measured/calculated results of WMR and TGA. Input parameters for the CPD model corresponded to the operating experimental parameters (heating rate, maximum temperature and residence time) for WMR and TGA (tab. 1). Heating rate and residence time was equal for all experiments done on WMR. Model Coal 29_PSOC_1520 (BYU), with parameters of carbon content and C/H ratio closest to the Serbian lignites, was selected from the CPD model database. The composition of the selected Model Coal was used as the input parameters for the CPD model.

Based on coal proximate and ultimate analysis, the CPD model calculates the following parameters: initial fraction of intact bridges, p_o, initial amount of coke bridges, c_0, co-ordination number, $\sigma + 1$, cluster molecular weight, M_{clust}, and side chain molecular weight, m_δ.

Additionally, Kolubara and Kostolac lignite kinetic parameters were obtained experimentally and implemented in the CPD model. Implementation was done by substation of model's activation energy and pre-exponential factor with the same obtained from researched lignites. This enabled compering of the two cases for evaluation of model's reliability to calculate devolatilization yields of the two Serbian lignites: first used kinetic parameters from the CPD database, second used actual measured kinetic parameters of the researched lignites.

Results and discussion

Results of WMR and TGA experiments

The average results of ultimate and proximate analysis for the investigated Serbian coal samples used in described experiments are given in tab. 2.

Table 2. Ultimate and proximate analysis for Kostolac and Kolubara lignites of differing granulations

Coal	Kostolac				Kolubara			
Granulation, [mm]	$x < 0.10$	$0.10 < x < 0.25$	$0.25 < x < 0.50$	$0.50 < x < 1.00$	$x < 0.10$	$0.10 < x < 0.25$	$0.25 < x < 0.50$	$0.50 < x < 1.00$
M [%][ad]	7.63	8.32	8.07	7.69	7.06	7.19	7.72	7.43
A [%][ad]	35.57	33.59	30.81	31.12	27.48	28.73	23.79	28.38
VM [%][daf]	63.03	59.55	60.95	61.42	61.76	62.33	61.50	64.95
C [%][daf]	61.81	67.69	67.67	67.11	63.44	67.18	65.13	60.55
H [%][daf]	5.70	6.05	6.34	6.10	6.08	6.29	6.13	6.07
O* [%][daf]	27.2	21.99	22.11	23.24	28.19	24.51	26.48	30.85
N [%][daf]	41.11	1.14	1.06	1.15	0.82	0.88	0.85	0.95
S [%][daf]	4.15	3.13	2.81	2.39	1.46	1.13	1.40	1.59

M – moisture content, *A* – ash content, *VM* – volatile matter, C, H, O, N and S – carbon, hydrogen, oxygen, nitrogen and sulfur content; * calculated as the difference from 100%

Volatile yields obtained from WMR experiments are given in fig. 2. All granulations showed increasing volatile yields with increasing temperature. This could be explained due to the process of primary devolatilization being dominant at lower temperatures, while at higher temperatures, the process is more intensive and secondary devolatilization reactions occur. With the increase of granulation size, the thermal response of the particles decreases, leading to volatile yield decreases [25]. Generally, with increase of particle size, a temperature gradient occurs from the coal particle surface to its center. The products of decomposition generated near the center of the coal during its migration to the surface can crack, condense, or polymerize, with deposition of some carbon. The amount of carbon deposition increases with the increase in particle size, and hence the volatile yield decreases [26].

The WMR results for Kolubara lignite at 500 °C show decreasing volatile yields as granulation increased. This is expected, as described above. At 700 °C, there was no specific observable trend in volatile yields between different granulations. This could be the result of process intensification at this temperature – a variety of parameters influence devolatilization processes *i.e*. existing mechanisms of primary devolatilization (bond breaking, evolution of tar and gases, formation of char) that occur alongside of secondary devolatilization (evolution of secondary gases from char – CO and H_2O, tars form soot, coke and gases, and gases form lighter gases and soot) [3]. At 900 °C, for Kolubara lignite, volatile yields tended to decrease with increasing granulation size, except for the largest granulations where volatile yield increased. The decreases were smaller than those occurring at 500 °C, showing that at 900 °C, the process was the most intensive and granulation had minimal effect on volatile yields. The largest granulations had an unusual volatile yield increase at 900 °C, which correlated with proximate analysis, tab. 2, and could be explained with granulation enrichment with certain macerals.

For Kostolac lignite, at temperature 500 °C the trend observed is that disregarding the smallest granulation, the difference in volatile yields (daf) between granulations was minimal (standard deviation 0.60). Origin of this phenomena is unclear. It is speculated that hydrogen in smallest granulation is mainly in aliphatic groups, while in other granulations is mainly in aromatic rings. Higher oxygen content found in smallest granulation, if in form of ether, may contribute to higher level of H_2O and CO_2 release. At 700 °C, there was no specific observable

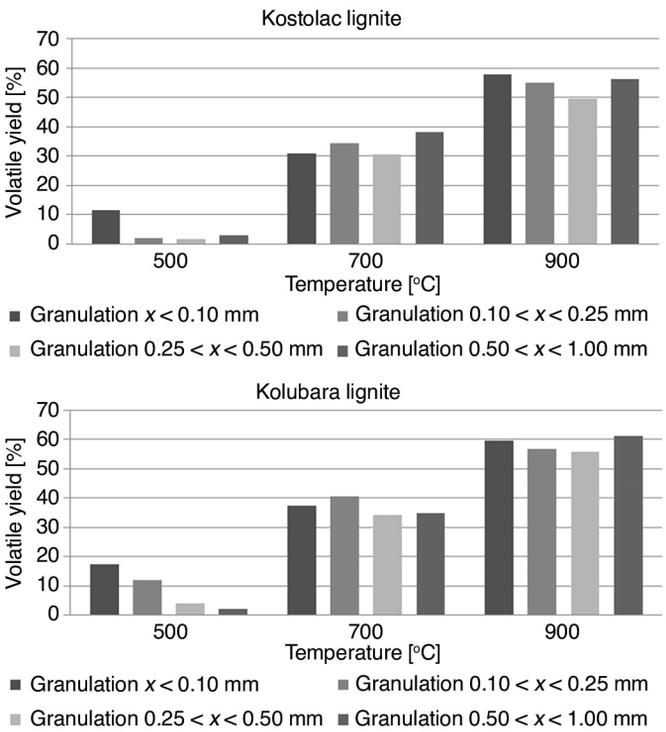

Figure 2. Average volatile yields of the Serbian lignites from the WMR experiment

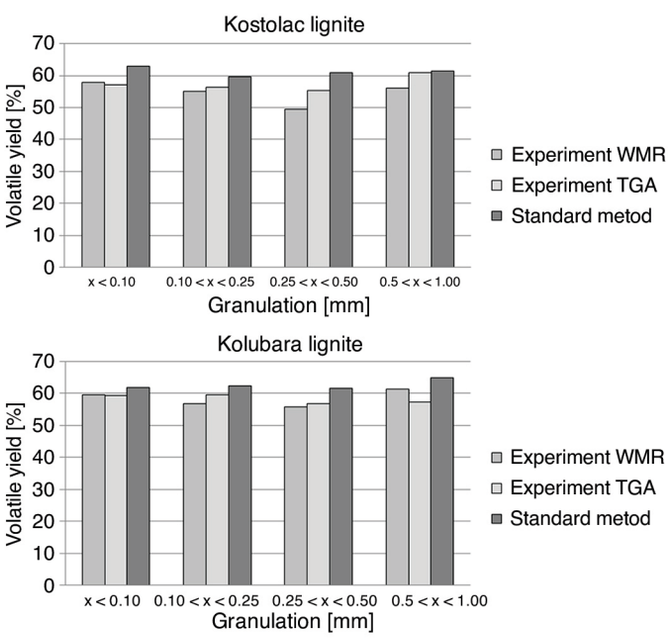

Figure 3. Comparison of Serbian lignite volatile yields at 900 °C obtained with different methods

trend in volatile yields between different granulations. At 900 °C, volatile yields tended to decrease with increasing granulation size, except for the largest granulations where volatile yield increased. Explanations given for Kolubara lignite for temperatures 700 °C and 900 °C could be also applied for coal Kostolac.

Figure 3 shows volatiles yields for both lignites at 900 °C determined by WMR and TGA, and for comparison, volatile yields determined by the standard method.

Volatile yields obtained by TGA decreased with granulation size increase, except for the largest granulations where volatile yields increased. The same trend was observed for volatile yields obtained by WMR. The difference in volatile yields measured by WMR and TGA was the least for the smallest granulation, which can be explained by the minimal secondary reactions which likely occurred during TGA for this particle size.

Volatiles yields determined by the standard method were higher than those measured by WMR or TGA. This was expected due to the different time for devolatilization in the standard method (during the residence time of seven minutes at 900 °C [22], the process of devolatilization could be completed and all the volatiles leave the particles).

Kinetic parameters obtained from the WMR and TGA studies are shown in tab. 3.

Table 3. Kinetic parameters for Kostolac and Kolubara lignites, from WMR and TGA

Coal	Apparatus	Granulation, x [mm]	Activation energy, E_a [J/kmol]	Pre-exponential factor, k_0 [s^{-1}]
Kostolac	WMR	$x < 0.10$	46336	50.65
		$0.10 < x < 0.25$	83198	3340.25
		$0.25 < x < 0.50$	79914	1637.95
		$0.50 < x < 1.00$	76505	1622.30
	TGA	$x < 0.10$	35180	$3.06 \cdot 10^{4}$
		$0.10 < x < 0.25$	41290	$2.31 \cdot 10^{5}$
		$0.25 < x < 0.50$	88380	$7.81 \cdot 10^{12}$
		$0.50 < x < 1.00$	141810	$7.22 \cdot 10^{19}$
Kolubara	WMR	$x < 0.10$	42608	46.07
		$0.10 < x < 0.25$	45700	55.09
		$0.25 < x < 0.50$	68341	603.35
		$0.50 < x < 1.00$	84129	3832.60
	TGA	$x < 0.10$	38360	$8.45 \cdot 10^{4}$
		$0.10 < x < 0.25$	65180	$8.27 \cdot 10^{8}$
		$0.25 < x < 0.50$	82910	$2.20 \cdot 10^{11}$
		$0.50 < x < 1.00$	108950	$1.27 \cdot 10^{15}$

The kinetic parameters differ one from another, and from the results of other authors [19, 23]. Differences between the activation energies obtained could be due to the different methods of determination and also different experimental conditions, namely heating rate, residence time at maximum temperature and different granulation.

For Kolubara lignite, for both experimental techniques, it is clear that activation energy rose as granulation increases. This is a consequence of the greater energy needed for the volatiles to leave particles as their diameters increase. For Kostolac lignite, the same observation was noted for TGA. For Kostolac lignite studied in the WMR, deviation was noticed – larger granulations had substantially higher activation energies than the smallest granulation, and there was no consistent increase in activation energy with increased granulation size. This is in line with volatile yields shown in fig. 2. By comparing the granulations in tab. 2, it can be observed that the contents of some chemical elements differed between the smallest granulation and the others. These differences in levels of chemical elements could be a consequence of different maceral content and/or mode of occurrence of some of the chemical elements in the coal. Overall, these differences in levels of chemical elements could account for the different behavior of the smallest granulation of Kostolac lignite.

The CPD model results

Proximate and ultimate analyses for Model Coal 29_PSOC_1520 (BYU) are given in tab. 4 [27]. The input parameters for Model Coal 29_PSOC_1520 (BYU) are shown in tab. 5, as well as the calculated values of input parameters for the investigated lignites, Kolubara and Kostolac.

Table 4. Characteristics for Model Coal 29_PSOC_1520 (BYU) [27]

Carbon, C [%]$^{[daf]}$	67.40
Hydrogen, H [%]$^{[daf]}$	5.37
Oxygen, O [%]$^{[daf]}$	24.39
Nitrogen, N [%]$^{[daf]}$	1.00
Sulfur, S [%]$^{[daf]}$	1.84
Volatile Matter, VM [%]$^{[daf]}$	53.40

Results of the volatile yields for Kolubara and Kostolac lignites obtained by WMR and TGA (WMREXP,

TGAESP), the CPD model used with Model Coal kinetic parameters, CPD (WMR/TGA) - MC, MCKP, as well as a CPD variant with Kolubara and Kostolac lignites' kinetic parameters, CPD (WMR/TGA) - MC, RKP, are given in figs. 4 and 5. Abbreviations used are in tab. 6.

Figure 5. Input parameters for the four granulation sizes of Serbian lignites, Kostolac and Kolubara, and Model Coal

	$0.1 < x$		$0.1 < x < 0.25$		$0.25 < x < 0.50$		$0.50 < x < 1.00$		Model Coal 29_PSO C_1520 (BYU) [18]
	Kostolac	Kolubara	Kostolac	Kolubara	Kostolac	Kolubara	Kostolac	Kolubara	
m_{δ}	63.1	59.7	55.5	55.3	57.0	57.6	55.8	63.4	51.9
M_{clust}	428.6	474.1	478.2	502.8	528.4	481.2	479.9	468.1	386.1
p_0	0.545	0.522	0.444	0.452	0.405	0.494	0.455	0.563	0.564
$\sigma + 1$	2.86	3.34	4.07	4.01	4.04	3.67	3.97	2.66	4.19
c_0	0.150	0.150	0.133	0.150	0.135	0.150	0.150	0.150	0.150

Table 6. Abbreviations used for comparing experimental and model results

WMREXP / TGAEXP[daf]	WMR / TGA
CPD (WMR/TGA) - MC, MCKP	CPD model used with: WMR/TGA experimental conditions, Model Coal characteristics and model coal kinetic parameters
CPD (WMR/TGA) - MC, RKP	CPD model used with: WMR/TGA experimental conditions, Model Coal characteristics and real kinetic parameters (from Kolubara and Kostolac lignites)

For devolatilization at 900 °C, the volatile yield of Kolubara coal was higher after both the WMR and TGA studies than it was when the CPD model used Model Coal kinetic parameters (for all granulations). Differences were in the range of 1.8-10.7% (WMREXP) and 13.1-17.0% (TGAEXP). The difference between carbon content of Kolubara lignite and the selected Model Coal from the CPD model database was minimal – Kolubara lignite has a carbon content of 60.55-67.18% (daf) depending on granulation, while the Model Coal contains 67.4% (daf) carbon. However, the ratio of carbon to hydrogen was higher for the Kolubara coal (C/H 9.98-10.68) than for the Model Coal (C/H 12.55), which shows that Kolubara lignite has a higher hydrogen content. As hydrogen is released from the particles at higher temperatures (this starts at ~700 °C [28]), total volatile yield starts to rise at this temperature, which could be reason the yields from the practical study exceeded yields predicted by the CPD model.

For devolatilization at 900 °C, in the WMR study, the volatile yield of Kostolac lignite was higher than was predicted by the CPD model when Model Coal kinetic parameters were used, for all granulations except granulation size $0.25 < x < 0.50$ mm. Differences were below 5.1% (WMREXP), except for a single outlier granulation that differed from the model predictions by 10.8%. Differences for TGAEXP ranged between 10.7-18.9%.

The difference between the carbon content of Kostolac and Model Coal was minimal – Kostolac lignite had a carbon content of 61.81-67.69% (daf) for all granulations, while the Model Coal contained 67.4% carbon. However, the carbon to hydrogen ratio was somewhat greater for Kostolac lignite (C/H was 10.66-11.19 for the Kostolac coal, and 12.55 for the Model Coal),

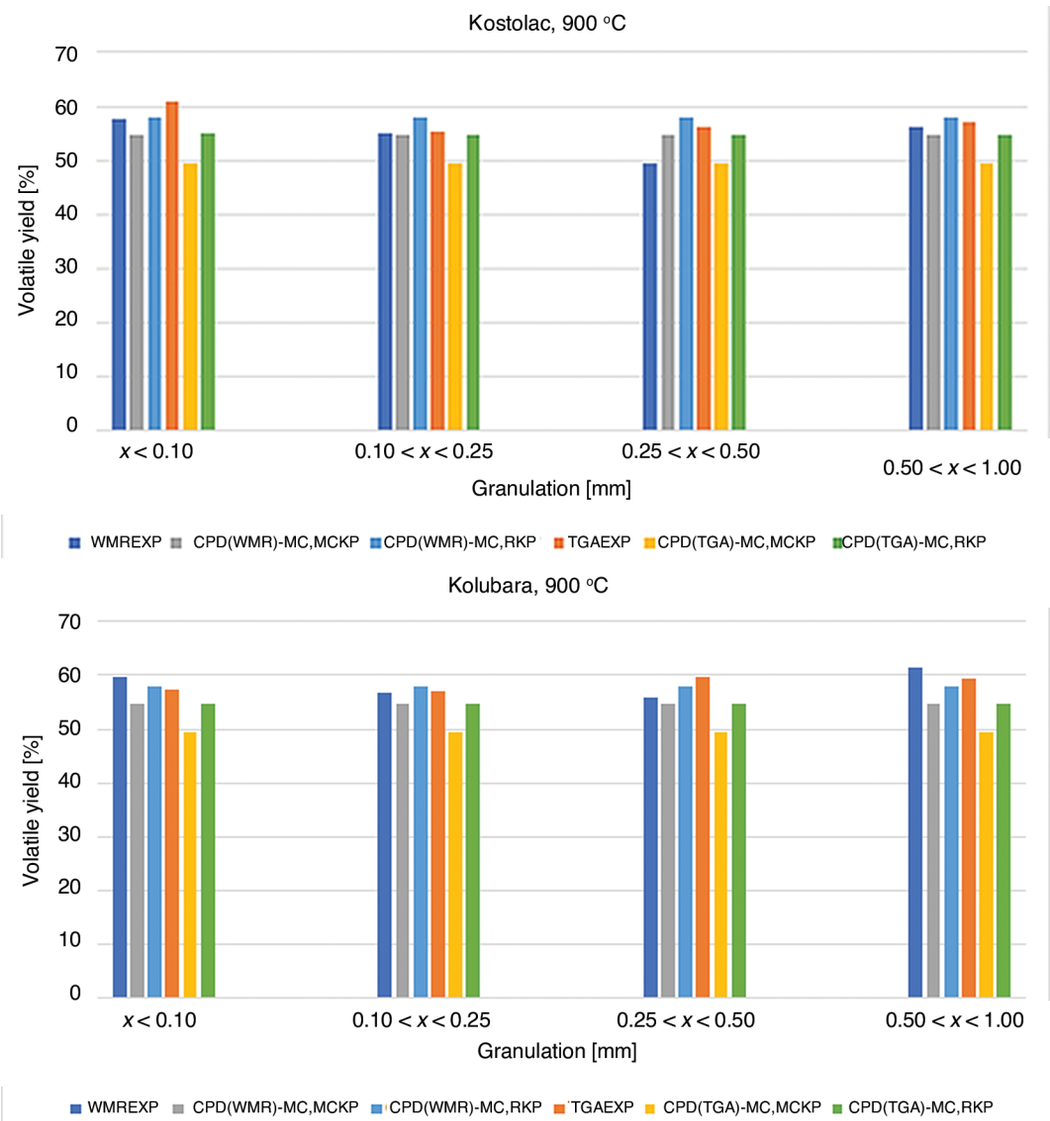

Figure 4. Comparison of volatile yields from WMR and TGA and the CPD model at 900 °C

showing that Kostolac lignite has a higher hydrogen content than the Model Coal. The same explanation as given for Kolubara lignite likely applies to Kostolac lignite.

Comparing our experimental results and results predicted by the CPD model with Model Coal or with Kostolac/Kolubara coal's kinetic parameters, some distinctive trends can be observed fig. 4. CPD (WMR/TGA) – MC, RKP predicted higher volatile yield than did CPD (WMR/TGA) – MC , MCKP, for both WMR and TGA. The difference between these two variants was between 2.2-11.2% for Kostolac and 1.6-11.5% for Kolubara coal. As a result of higher predicted levels of volatile yields compared to CPD (WMR/TGA) – MC, MCKP, CPD (WMR/TGA) – MC, RKP predicted, in term of accuracy, mixed results for WMR. However, using the actual kinetic data for Kostolac/Kolubara in the CPD model improved the accuracy of

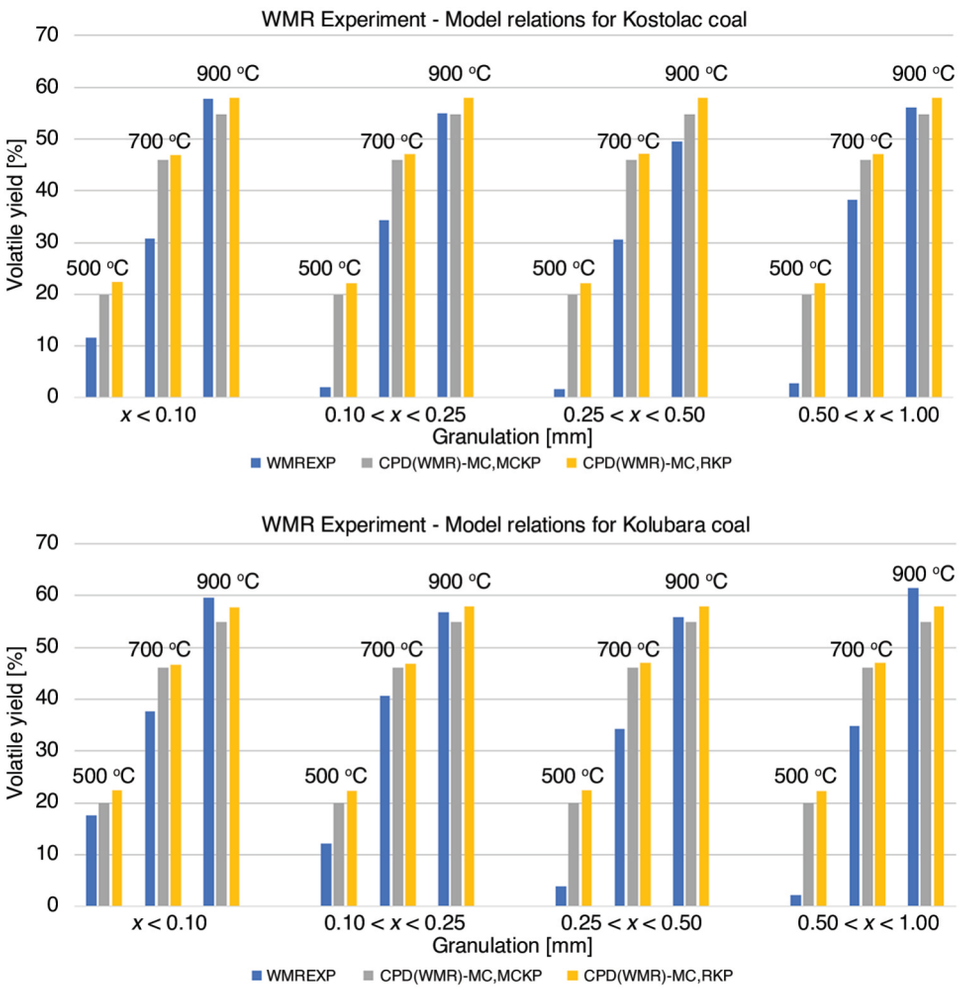

Figure 5. Comparison of volatile yields from WMR and the CPD model, different temperatures

predicted devolatilization for both Serbian lignites for TGA. Differences for WMR, for Kolubara were between 1.9-5.6%. For Kostolac, differences were between 0.3-5.3%, except for a single before mentioned outlier granulation - 17.3%. For TGA, deviations were up to 9.9% (granulation 0.1 < x, Kostolac coal), indicating the potential of using such kinetic parameters in predicting volatile yields with greater accuracy.

Results obtained from the CPD model, with Model Coal or with Kostolac/Kolubara coal's kinetic parameters, showed very little difference between Kolubara and Kostolac coals, for both experimental apparatuses, indicating the elemental composition of coal is more relevant than kinetic parameters. Consequently, if the existence of granulation in the modeling is related only to the kinetic parameters, and the CPD model cannot recognize it in any other way, then granulation is of little or no importance to the model usage. Indeed, this can be observed in figs. 4 and 5, by comparing CPD (WMR/TGA) – MC, MCKP and CPD (WMR/TGA) – MC, RKP: the differences between the granulations, for the same temperature, are almost constant.

The smallest granulation has the smallest resistance as a consequence of the smallest path needed for volatiles to be transported from the coal particle's interior to the surface. If the smallest granulation is taken as relevant for the comparison between our experimental data and the CPD model, then the difference between the achieved and predicted yields for Kolubara coal was 4.75%, fig. 5. Fletcher *et al*. [29] explained that the model predicts generation of a certain amount of tar, which is not equal to zero, at the lower temperatures. This quantity of tar is accounted for by the existence of certain mobile materials in the coal grid, which can be released even during lower temperatures regimes (500-600 K) or lower heating rates (100 K/s). For the analyzed coal, Pittsburg No. 8 [29], Fletcher *et al*. obtained initial tar quantity to be approximately 5%, which is near percentage difference between Kolubara's lowest granulation and the Model Coal in the current study.

In favor of this explanation is Fletcher's consideration of mass transport for the CPD model [16]. While literature on mass transport outside the coal particle formulates tar release as a function of light gas release, the CPD model treats mass transport of tar and light gas separately. Mass release of our Model Coal's light gas and tar are given in tab. 7. The tar yield is not much lower than the light gas yield, and at the lower temperature, they are almost equal.

Generally, tar yields are higher with increased devolatilization temperatures up to a maximum value, usually 450 °C to 600 °C, depending on experimental conditions. Above this temperature, secondary reactions causing tar cracking and depolymerization become more dominant, leading to gas yield increase. Higher temperatures promote scission of side chains and bridges.

Table 7. Mass yields of tar and light gas for Model Coal

Temperature [°C]	f_{tar} [%]	f_{gas} [%]
500	10.68	11.62
700	18.77	27.22
900	19.32	35.48

As granulation size increases, there was increasing difference in the volatile yields obtained experimentally and the predicted CPD model volatile yields. This is due to the model's inability to distinguish different kinetic parameters and granulation effects on volatile yield, as previously discussed.

For devolatilization at 700 °C, the predicted volatile yield was higher for the Model Coal than we obtained experimentally (for all granulations) (the model predicted up to ~26% greater yields). However, the difference between predicted and experimental volatile yields was lower at 700 °C than it was at 500 °C (up to ~89% greater yields). This shows the effect of initial tar yield diminishes as the devolatilization temperature increases.

Also, volatile yields are dependent on particle porosity. Li *et al*. [30] established the connection between porosity and CPD model parameters. Particle porosity increases or decreases as a function of the parameters m_{δ}, M_{clust}, p_0, $\sigma+1$, c_0, tab. 5 [30].

The parameter p_0 shows the initial amount of bridges and side chains. Increased p_0 denotes an increased quantity of bridges and a reduced quantity of side chains, which results in an increase in the light gas yield made from reaction of formation of stable char bridge. Reaction of side chains cracking creates light gas. This reaction is reduced due to smaller number of side chains. Reaction of light gas creation from stable char bridge formation is faster than the reaction of light gas creation from cracking of side chains, and consequently, the increase in p_0 causes an increase in porosity (and external mass transport). Individually, the trend (function) of the p_0 change between the granulations' obtained volatile yields is not perceived.

The parameter c_0 represents the initial amount of coke bridges. Increasing c_0 reduces the yield of tar, which results in an increased quantity of side chains, which leads to an increased

amount of light gas. Since the increase in the yield of light gas is less than decrease in the yield of tar, with increasing c_0 there is decreasing of porosity and consequent decrease in volatile yield. The parameter c_0 was the same for all granulations of Kolubara lignite and model coal, tab. 5, so would not affect the differences in volatile yields seen between our experimental data and the CDP model.

The co-ordination number ($\sigma + 1$) denotes the number of bridges and side chains on each cluster (group of molecules), and denotes interconnection of bridges. Increasing co-ordination number leads to an increased yield of light gas, and consequently to increase of porosity (on the other hand, increasing the yield of tar does not mean a direct increase in porosity). The tar yield is reduced when co-ordination number increases, because the number of bridges and side chains has increased, and tar separation is reduced. The increase in the light gas yield is higher than the decrease of tar yield, and by increasing co-ordination number, the porosity and yield of the volatiles increase. All granulations of Kolubara lignite had a smaller co-ordination number than Model Coal, tab. 5, which indicates the tar yield of Kolubara lignite should be greater and total volatile yield lower than those of Model Coal. This is generally in line with the explanation of volatile yields at 500 °C and 700 °C, for all granulations, previously discussed.

The M_{clust} and m_δ denote the weights of clusters and side chains, respectively, within the coal lattice. Increasing the mass of the clusters leads to a reduction in the mass of the side chains - there is an increase in the mass that remains within the coke residue, and a decrease in porosity. In contrast, by increasing the mass of the side chains, there is an increase in porosity. For Kolubara lignite, for all granulations, both M_{clust} and m_δ were higher than those of Model Coal, tab. 5. The high M_{clust} in Kolubara lignite (it was higher than the M_{clust} of Model Coal by about 30%) means the volatile yield of Kolubara coal should be lower than that of Model Coal. The m_δ of Kolubara lignite was also higher than that of Model Coal, which should lead to higher volatile yield than that predicted for Model Coal. Consequently, at lower temperatures, M_{clust} is dominant, and since it was higher for Kolubara lignite, the total volatile yield we measured from this lignite was lower than that predicted by the CPD for Model Coal. At higher temperatures, weights of both clusters and side chains have an effect (there is also a breakdown of clusters), which is in line with our results (higher volatile yields for Kolubara lignite).

Some differences were observed between Kostolac and Kolubara lignites. For devolatilization at 500 °C or 700 °C, volatile yields were predicted to be higher for the Model Coal than the yields we obtained from the Serbian lignites during our experimental procedures (for all granulations). The difference between volatile yield for smallest granulation of Kostolac lignite and Model Coal at 500 °C was approximately 92%, fig. 5. This difference is larger than the difference between the Kolubara lignite and Model Coal, and cannot be explained as generation of tar at lower temperatures. However, by comparing the volatile yields and m_δ for the granulations of Kostolac lignite, tab. 5, a trend is recognizable – the high volatile yield for the lowest granulation corresponds to the high values of side chain mass, which in turn means higher porosity and yields.

Regarding the mass of clusters and the yields at 900 °C, the Kostolac granulation of $0.25 < x < 0.50$ mm had a lower volatile yield than that predicted for Model Coal. The M_{clust} was higher than that predicted for Model Coal, but this was also the case for all other Kostolac granulations and for Kolubara coal. A possible explanation is that M_{clust} was so high it hindered the effect of m_δ and significantly lowered the particle porosity. In favor of this argument is the fact that for the Kostolac granulation of $0.25 < x < 0.50$ mm, M_{clust} was the highest among the calculated in this study, while p_0 was the lowest, tab 5.

Comparing CPD (WMR) – MC, MCKP and CPD (WMR) – MC, RKP, the second model (using the real kinetic parameters from Serbian lignite) predicted higher volatile yields at 500 °C and 700 °C, resulting in pushing the results further away from values obtained experimentally. Both model usages were inadequate, as the differences for CPD (WMR) – MC, MCKP (the CPD model with Model Coal parameters as inputs) were between 71-1142% for Kostolac and 14-781% for Kolubara lignite; and for CPD (WMR) – MC, RKP (the CPD model with our measured parameters as inputs), differences were between 93-1292% for Kostolac and 28-888% for Kolubara lignite.

At 700 °C, the difference between results of the two main model variants was coherent between granulations and minimal. For example, for the largest granulation of Kolubara lignite, implementing CPD (WMR) – MC, MCKP predicted higher volatile yields from our WMREXP measurements by 31.7%, while implementing CPD (WMR) – MC, RKP predicted higher yields by 34.8%. Similarly, for the largest granulation of Kostolac, the model predicted higher volatile yields in range by 20.4 and 23.1% in volatile yields from our measurements, respectively. These heighten yields were not as high as those predicted at lower temperatures, but they were still significant compared to the results of our modeling at 900 °C. Altogether, this made the model unsuitable for investigating the Serbian lignites studied at 500 °C and 700 °C.

Conclusions

Based on practical devolatilization experiments with WMR and TGA, and devolatilization modeling using a CPD model, for Serbian Kostolac and Kolubara lignites, the following can be concluded:

- Measured volatile yields of Kolubara and Kostolac lignites (WMR and TGA) show general trends of increasing with temperature increase and decreasing with granulation size increase. Activation energy generally increases as granulation increases, as more energy is needed for volatiles to leave the particles. Deviations from these trends could be due to granulation enrichment with certain macerals, which can be inferred from elemental and proximate analyses of the studied coals.
- Volatile yields obtained by standard method ISO 5071 were, as expected and due to the longer time during which devolatilization can occur when this method is followed, higher than those measured by the WMR or TGA experimental methods.
- For the presented apparatuses and experimental procedures, kinetic parameters differed from the results of other authors who examined the subject lignites. This is likely a consequence of different equipment, temperature, residence time, *etc*., as well as differences in the coal over time as the excavation of the mine progresses.
- The CPD model was used to compare predictions of volatile yields using: kinetic parameters from Kolubara and Kostolac coals, CPD (WMR/TGA) – MC, RKP and data from a similar coal from the database, CPD (WMR/TGA) – MC, MCKP, but produced mixed results. For the WMR apparatus, the accuracy of model prediction depended on the temperature of volatilization, while for TGA, the predicted volatile yields were closer to actual yields when our subject coal's kinetic parameters were employed (for the investigated temperature of 900 °C).
- The CPD model proved unsuitable for predicting volatile yields of the two studied Serbian lignites at 500 °C or 700 °C.

Nomenclature

c_0 – initial amount of coke bridges (CPD)
E_a – activation energy, [Jmol^{-1}]
f_{gas} – mass yield of gas in total yield, [%]
f_{tar} – mass yield of tar in total yields, [%]
k – constant rate, [s^{-1}]
k_0 – pre-exponential factor, [s^{-1}]

M_{clust} – cluster molecular weight (CPD)
m_δ – side chain molecular weight (CPD)
p_0 – initial fraction of intact bridged (CPD)
R – gas constant, [Jmol^{-1} K^{-1}]
T – temperature, [K]
t – time, [s]
V – volatile yield, [%]
VM – volatile mater, [%]
x – granulation size, [mm]

Greek symbol

σ +1 – co-ordination number (CPD)

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Paper submitted: June 27, 2018
Paper revised: June 28, 2018
Paper accepted: June 30, 2018