

ASSESSMENT OF SYNERGISTIC EFFECT ON PERFORMING THE CO-PYROLYSIS PROCESS OF COAL AND WASTE BLENDS BASED ON THERMAL ANALYSIS

by

**Zagorka M. BRAT^{a*}, Bojan Ž. JANKOVIĆ^b, Dragoslava D. STOJILJKOVIĆ^c,
Miloš B. RADOJEVIĆ^c, and Nebojša G. MANIĆ^c**

^a NIS a.d. Novi Sad, Novi Sad, Serbia

^b Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia,
University of Belgrade, Belgrade, Serbia

^c Fuel and Combustion Laboratory, Faculty of Mechanical Engineering,
University of Belgrade, Belgrade, Serbia

Original scientific paper

<https://doi.org/10.2298/TSCI210516310B>

The preliminary thermogravimetric studies of co-pyrolyzed low rank coals (lignites Kostolac and Kolubara) with waste materials (spent coffee ground and waste rubber granulate) in a form of blends have been performed. Thermal analysis measurements of blend samples were carried out in a nitrogen, atmosphere at three different heating rates of 10, 15, and 20 K per minute. The coal-waste blends were prepared in the percentage ratios of 90:10, 80:20, and 70:30. This work analyzed the synergy analysis for considered blends shown via descriptive parameters during co-pyrolysis process. According to the performed analysis, the presence of synergistic effect was identified, where strong interactions were also observed. For lignite-spent coffee ground blends, it was found that two factors which affect the synergy effect with coal are concentration of added biomass material and the heating rate. For lignite-tire rubber granulate blends, the blending ratio take on a decisive role for positive consequences of a synergistic effect (ratios below 30% of tire rubber granulate in coals are desirable). Also, in this work the influence of micro-scale condition parameters such as heating rate (as the experimental regulatory factor) was analyzed on the magnitude response of synergism during co-pyrolysis.

Key words: low rank coals, waste, blend ratio, synergy effect, heating rate

Introduction

The most important coal deposits in the Republic of Serbia are lignite which geological reserves in relation geological reserves of all other types of coal make up to 97% [1]. Based on official country data the exploitable reserves of coal with a high degree of exploration, which are divided according to profitability into the class of balance reserves of coal profitable for exploitation and the class balance reserves of coal that are currently not profitable for exploitation, for the Serbian lignite are in the ratio 8:1. Also, it should be noted that the presented quantities of lignite about 4 billionns are in the central part of the Republic of Serbia, *i.e.* the Kolubara and Kostolac basins [1]. Furthermore, the total exploitable coal reserves are significant and

* Corresponding author, e-mail: zagorka.brat@gmail.com

represent a realistic basis for the further long-term development of energy in general, and for electricity production in existing power plants [2].

However, the trend of energy transition reflects through decreasing dependency on primary fossil fuels and reduction of the GHG effect due to CO₂ emission control, highlight the introduction of available waste into the co-combustion process with primary fuel in power plant boilers [3]. In that sense, the blending of coal and different types of urban waste residues and industrial solid wastes have been researched as being clean and economic energy alternatives allowing the substitution of traditional fossil fuel, thereby mitigating both the environmental impact brought by its use and partially resolving waste management [4].

According to the literature, Tokmurzin *et al.* [5] investigated the pyrolysis process of the organic fraction of municipal solid waste blended with high volatile coal in different weight proportions. The thermal degradation of these mixtures was investigated in a thermogravimetric analyzer (TGA) and a horizontal tube furnace under a nitrogen environment. Based on obtained results it could be concluded that comparable results between the TGA and fixed bed tests on the residual char fraction can be established as well as the important data necessary for a co-firing technology for solid waste residuals and coal for energy production were presented. Also, according to Khan *et al.* [6], the direct co-pyrolysis of blends comprising lignite coal and waste tires were researched and the effects of various parameters that include coal to waste tires ratio, temperature, pressure, hydrogen donor concentration, and retention time were investigated. The hydrocarbon fractions from C₁₆ to C₃₆ were found in liquid oil through gas chromatograph-mass spectroscopic analysis and the presented results of the study could be applied to the commercial production of pyrolysis oil. Kanca [7] investigated the synergy between lignite and cotton waste by comparing calculated and experimental findings of characteristic temperatures and gas evolution profiles. Based on the presented results, no synergy was found between considered fuels under the pyrolysis conditions. However, the best synergistic interaction was observed in a 50% mixing ratio during combustion.

In order to analyze possibilities for application of blends of lignite and waste material, in this work, the spent coffee ground (SCG) and waste rubber granulate (WRG) were considered. The aim of performed research is to define the influence (effect) of SCG and WRG concentrations (by percentage contributions) in blends with lignites Kostolac (KSL) and Kolubara (KLB) on blend thermal characteristics and synergistic interactions during co-pyrolysis process. This influence was analyzed from the point of view of the existence or absence of the synergistic effect. Also, the influence of micro-scale condition parameters (such as the heating rate) on performing the co-pyrolysis processes was analyzed in this work. The proximate and ultimate analysis of lignite coals, waste materials and their blends were performed, while the co-pyrolysis process characterization was conducted using the TGA experiments.

Materials and methods

Materials

Characteristics of KSL and KLB, classified in the rank of soft brown coals, differs themselves regarding to the chemical composition and shows an increase trend in volatile yield with an increase in temperature [8]. In order to replace a part of lignite amount used as a primary fuel for power generation, two different waste types are chosen: SCG and WRG. All considered samples were collected and prepared according to the standard procedures for sampling and sample preparation in order to consider the variation of characteristics as well as to obtain the representative sample for the blending and further for performing the experimental campaign. The analysis of waste concentration in the blends with KSL and KLB, compared to

the pure lignite samples, SCG and WRG, was performed for the twelve different blend samples, with weight of 10 g, and granulation of $x < 0.25$ mm. The blends percentage composition properties are listed in tab. 1.

Table 1. Blends samples designation and their composition

Sample designation	Composition	Sample designation	Composition
KSL9-SCG1	90% KSL – 10% SCG	KLB9-SCG1	90% KLB – 10% SCG
KSL8-SCG2	80% KSL – 20% SCG	KLB8-SCG2	80% KLB – 20% SCG
KSL7-SCG3	70% KSL – 30% SCG	KLB7-SCG3	70% KLB – 30% SCG
KSL9-WRG1	90% KSL – 10% WRG	KLB9-WRG1	90% KLB – 10% WRG
KSL8-WRG2	80% KSL – 20% WRG	KLB8-WRG2	80% KLB – 20% WRG
KSL7-WRG3	70% KSL – 30 % WRG	KLB7-WRG3	70% KLB – 30% WRG

Single samples of appropriate weighing of 1 g for the proximate and 20 mg for TGA measurements were separated from aforementioned basic sample. Available studies showed that the granulation size affects the amount of energy necessary for the process conduction, process duration and volatile yields, hence the optimization is necessary to use waste in the real conditions [9]. The proximate and ultimate analysis of pure lignites and waste samples were also performed in this study. The composition and characteristics of all studied samples were defined by the proximate and ultimate analysis results. For prepared samples, weighing of 1 g, the proximate analysis were conducted according to the appropriate standards [10-16] intended for different types of fuel.

Thermogravimetry measurements

In order to define waste contribution influence on the co-pyrolysis process behavior (reactivity), the TGA of blends has been performed in an N (high purity 99.995 % N₂) atmosphere, using NETZSCH STA 449 Jupiter F5 simultaneous thermal analysis device. A flow rate of carrier gas, N₂, was $\varphi = 50$ mL per minute during the performance of all experiments. The experimental tests with blend sample mass about 20 mg were performed at each used heating rate. The measurements were carried out at three different heating rates as $\beta = 10, 15,$ and 20 K per minute. The samples were heated from the room temperature up to 800 °C. Recording of TGA curves for each tested sample is displayed through the NETZSCH Proteus® software runs, under the WINDOWS® user-friendly interface. User-friendly menus combined with automated routines, make this software very easy to use still providing sophisticated analysis of established experimental data.

Evaluation of synergistic effects during co-pyrolysis

In order to investigate the synergistic effects during the co-pyrolysis, a series of theoretical TGA curves of coal-SCG and coal-WRG blends at different blends percentage composition, tab. 1, were calculated based on the experimental results of each individual coal and each SCG and WRG sample. The detailed theoretical calculation procedure is given by Han *et al.* [17], and the calculated values were compared with obtained experimental TGA curves. The calculation of theoretical TGA curves at any given temperature are expressed:

$$TG_{\text{blend}} = xTG_{\text{waste}} + (1-x)TG_{\text{coal}} \quad (1)$$

where x and $(1 - x)$ are weight percentage of waste material and coal in the blends, respectively, TG_{blend} , TG_{waste} , and TG_{coal} are the mass loss for the blend, waste material (SCG, WRG), and coal (KSL, KLB), respectively.

The difference between the calculated and experimental TGA curves are defined:

$$\Delta TG = TG_{\text{exp}} - TG_{\text{calc}} \quad (2)$$

where ΔTG is the difference between the calculated and experimental values, which can be taken as an indicator of the interaction. The TG_{exp} and TG_{calc} are the experimental and calculated mass losses, respectively. In general, the percentage of increase or decrease of the experimental values with respect to the theoretical values is called synergetic effects. Obviously, ΔTG describes the *extent* of the synergetic effect during the process of co-pyrolysis between additive material and corresponding coal samples [17].

Results and discussion

Results of proximate/ultimate analysis

Table 2 shows the results of proximate and ultimate analysis of studied lignite and waste samples.

Table 2. Results of proximate and ultimate analysis of lignite and analyzed waste samples

Sample		KSL	KLB	SCG	WRG
Proximate analysis [wt.%]	Moisture, M^a	8.32	7.19	10.33	0.64
	Volatile matter, VM^a	59.55	62.33	70.30	56.98
	Ash, A^a	30.65	28.73	3.02	16.28
	Fixed carbon, FC	1.48	1.75	16.35	26.10
	Fuel ratio (FC/VM)	0.025	0.028	0.233	0.458
Lower heating value [MJkg ⁻¹]	LHV^b	15.50	14.39	17.30	32.05
Ultimate analysis ^c [wt.%]	C	67.69	67.18	52.75	76.26
	H	6.05	6.29	6.95	2.01
	O ^d	21.99	24.51	35.03	2.61
	N	1.14	0.88	2.25	0.66
	S	3.13	1.13	-	1.54
	H/C	1.065	1.116	1.570	0.314
	O/C	0.244	0.274	0.498	0.026

^a The analytical mass, ^b defined on ISO 1928:2015 [16], ^c dry basis, and ^d calculated by the difference

Lignite KLB compared to the lignite KSL has lower moisture and ash content, lower heating value, as well as a higher volatile content. Among these coal samples, from the elemental chemical analysis, KLB shows better fuel characteristics than ones related to KSL. Regarding to lignite samples characteristics, the considered waste samples show significantly better properties concerning a higher volatile content and a higher heating value, that is, a lower ash content, which make it potentially applicable for substitution of lignites in the combustion

process. The moisture content in the SCG is higher than moisture content in the analyzed lignite samples. Obtained results of the proximate and ultimate analyses for the SCG comply with the data available in the literature [18].

Considering the results provided for SCG, moisture, and volatile matter contents, as well as a LHV of SCG is higher, and ash content is lower than the same parameters determined for lignites, tab. 2. Excepting the moisture content, which higher quantity is the characteristic item for biomass, SCG shows better fuel properties than lignites, which makes it appropriate for the analysis of possible use in the power generation for co-combustion processes with primary fossil fuels.

Considering the results provided for the WRG sample, moisture, volatile matter, and ash contents are lower, and the LHV is higher than the same parameters determined for lignites. Considering these results, except its sulfur content determined in the ultimate analysis, make the WRG appropriate for the analysis for its possible use in the power generation for the co-combustion processes with primary fossil fuels as previously suggested. Considering H/C and O/C values, KSL and KLB belongs to the lignite coal samples, SCG sample belongs to biomass feedstock sample, while WRG sample complies with the anthracite zone, in accordance to the Van Krevelen diagram analysis.

The SCG has the highest H/C (= 1.570) ratio, tab. 2, compared to other fuels, which means that SCG owns the higher energy efficiency and tendency to lowered CO₂ emission, during its thermo-chemical conversion (*e.g.* the combustion process). The H/C ratio values are conducted by the H content of studied fuels, so based on the H content values of these fuels, the appropriate distribution of H/C ratios has been realized, tab. 2. The WRG sample shows the lowest values of both, H/C and O/C ratios, closely related to very poor content of H and O, tab. 2. As can be seen, the biomass sample (SCG) present higher concentrations of C, H, and O as compared to lignite coals, which also results in higher LHV value (except for WRG), tab. 2. However, the KSL is characterized with a higher S (= 3.13) and N (= 1.14) contents, tab. 2, which indicate that SO_x and NO_x emissions can be seriously concern during its thermo-chemical conversion. On the other hand, the SCG with the highest content of O, tab. 2, may indicates the higher thermal reactivity than other fuel samples. Compared proximate analysis results of blend samples, tab. 3, with samples of lignites and SCG, tab. 2, it could be noticed that with an introduction of SCG into blends with both lignites, the total volatile yield is decreased compared to lignite coals.

The decrease in volatile yield could be proved by an existence of secondary reactions, that is, synergistic interactions between released gases from lignites and SCG [19]. Volatile composition depends on the SCG concentration contribution in blends, and it increases with an increase in SCG contribution extents. Also, with an increase in waste SCG concentration, the ash content in the blends decreased, which corresponds to a tendention approach by biomasses properties.

By an introduction of the SCG into the blends, compared to the lignite samples, the total moisture content decreased for blends with lignite KSL, so that is, increased for blends with lignite KLB. Also, with an increase in the waste concentration, further increase in moisture content could be noticed for both blend types. With an increase in waste concentration in blends with lignite KSL, the heating value increased, while blends with lignite KLB show further decrease in the heating value with an increase in the waste concentration. This could be consequence of the increasing of the moisture [20] and lignin content in the SCG [21]. With an increase in SCG concentration in blends with KLS, the LHV value increases, but it decreases for blends with the lignite KLB, which can be attributed to the increase in the moisture content of the blends with lignite KLB.

Table 3. Lignites and SCG/WRG blends proximate analysis results

Analysis	Sample	KSL9-SCG1	KSL8-SCG2	KSL7-SCG3	KLB9-SCG1	KLB8-SCG2	KLB7-SCG3
Proximate analysis [wt.%]	M	8.10	8.16	8.05	7.58	7.80	8.14
	Volatiles	38.53	42.72	47.20	45.75	47.13	50.22
	FC	21.99	21.46	18.76	22.03	23.46	21.73
	A	31.38	27.66	25.99	24.64	21.61	19.91
	Fuel ratio (FC/VM) ^a	0.571	0.502	0.397	0.481	0.498	0.433
LHV [MJkg ⁻¹]		14.23	14.66	15.41	16.35	16.14	15.99
Analysis	Sample	KSL9-WRG1	KSL8-WRG2	KSL7-WRG3	KLB9-WRG1	KLB8-WRG2	KLB7-WRG3
Proximate analysis [wt.%]	M	7.04	6.31	5.65	7.06	6.45	5.58
	Volatiles	38.28	40.41	42.67	43.11	45.39	45.71
	FC	18.61	22.02	26.85	24.30	23.54	24.68
	A	36.07	31.26	30.48	25.53	24.62	24.03
	Fuel ratio (FC/VM) ^a	0.486	0.545	0.629	0.564	0.519	0.540
LHV [MJkg ⁻¹]		16.84	17.05	19.33	18.00	20.08	21.05

^aFC: Fixed carbon, VM: volatile matter (volatiles)

Synergy effect analysis KSL-SCG and KLB-SCG blend cases

For evaluating the extent of synergistic effects from KCL and KLB coals and SCG biomass, the comparison between experimental data and calculated data based on the mass loss assessments of mixture samples are illustrated in figs. 1 and 2.

The trends of TG_{exp} and TG_{calc} plotted against the SCG percentage ratio in the KSL sample under various heating rates (10, 15, and 20 K per minute) are shown in figs. 1(a)-1(c). In a similar manner, the trends of TG_{exp} and TG_{calc} plotted against SCG percentage ratio in the KLB sample, under various heating rates (10, 15, and 20 K per minute) are shown in figs. 2(a)-(c).

From comparison of the experimental TG curves (full lines) and calculated ones (dashed lines) for various KSL-SCG, fig. 1, and KLB-SCG, fig. 2, blends, there is a strong interaction between the components in studied blends, and therefore, the synergistic effect is noticeably pronounced for all observed cases. As a consequence of this phenomenon, the experimental TG curves are not well described by the calculated curves, which means that the additive rule is not acceptable for the present coal-biomass blends. More details related to the appearance of the synergistic effect in observed mixtures are given in tab. 4. From the results presented in tab. 4, regardless of the amount of biomass added to the coal samples (both KSL and KLB coals), in most of the cases considered the negative effect is obtained, which could indicate that the SCG causes negative synergy during the co-pyrolysis process. However, in a certain cases, there are deviations and they are strongly conditioned by the heating rate and the influence of additives on specific processes that take place in certain temperature intervals.

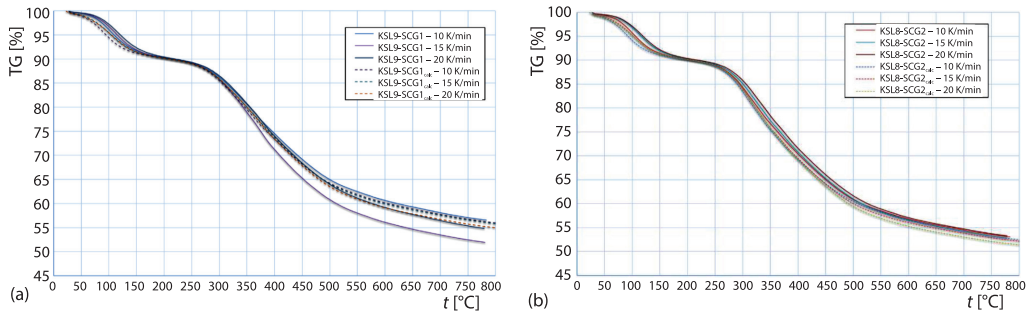


Figure 1. The TG profiles comparison between the experimental and calculated value from the mixtures under various heating rates (10, 15, and 20 K per minute); (a) KSL9-SCG1, (b) KSL8-SCG2, and (c) KSL7-SCG3 (for color image see journal web site)

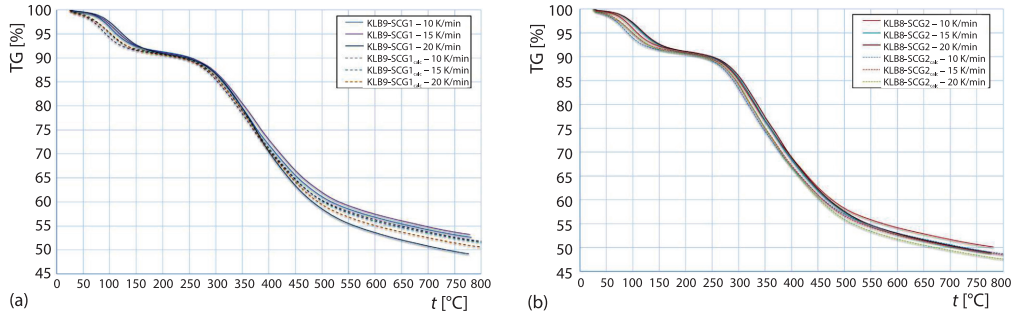


Figure 2. The TG profiles comparison between the experimental and calculated value from the mixtures under various heating rates (10, 15, and 20 K per minute); (a) KLB9-SCG1, (b) KLB8-SCG2, and (c) KLB7-SCG3 (for color image see journal web site)

For KSL-SCG blends, the two factors which affect the positive synergy effect for KSL lignite are concentration of added biomass (SCG in %) and heating rate (as strong regulatory factor). Namely, for the low concentration of the SCG in the blend, KSL9-SCG1 (90% KSL-10% SCG), the higher heating rate (as 20 K per minute) primarily favors the formation of the char, while the lower heating rate (for 15 K per minute) extends the temperature interval, that besides the promotion of the char formation, the enhance in the yields of volatiles and tars is

Table 4. Synergy analysis for KSL-SCG and KLB-SCG blends shown via descriptive parameters during co-pyrolysis process

Sample	Heating rate, β [Kmin ⁻¹]	Synergistic analysis		
		Temperature interval, ΔT [°C]	Interaction	Effect
KSL9-SCG1	10	25-200	Exp. higher than calc.	Negative
KSL9-SCG1	15	25-200	Exp. higher than calc.	Negative
KSL9-SCG1	20	25-200	Exp. higher than calc.	Negative
KSL9-SCG1	10, 15, 20	200-250	Overlap – no interaction	No effect
KSL9-SCG1	10	250-800	Exp. higher than calc.	Negative
KSL9-SCG1^a	15	250-800	Exp. lower than calc.	Positive
KSL9-SCG1	20	250-625	Exp. higher than calc.	Negative
KSL9-SCG1	20	625-800	Exp. lower than calc.	Positive
KSL8-SCG2	10	25-800	Exp. higher than calc.	Negative
KSL8-SCG2	15	25-800	Exp. higher than calc.	Negative
KSL8-SCG2	20	25-800	Exp. higher than calc.	Negative
KSL7-SCG3	10	25-250	Exp. higher than calc.	Negative
KSL7-SCG3	15	25-250	Exp. higher than calc.	Negative
KSL7-SCG3	20	25-250	Exp. higher than calc.	Negative
KSL7-SCG3	10	250-375	Exp. higher than calc.	Negative
KSL7-SCG3	10	375-800	Exp. lower than calc.	Positive
KSL7-SCG3	15	250-325	Exp. higher than calc.	Negative
KSL7-SCG3	15	325-800	Exp. lower than calc.	Positive
KSL7-SCG3	20	25-800	Exp. higher than calc.	Negative
Sample	Heating rate, β [Kmin ⁻¹]	Synergistic analysis		
		Temperature interval, ΔT [°C]	Interaction	Effect
KLB9-SCG1	10	25-375	Exp. higher than calc.	Negative
KLB9-SCG1	15	25-375	Exp. higher than calc.	Negative
KLB9-SCG1	20	25-375	Exp. higher than calc.	Negative
KLB9-SCG1	10	375-800	Exp. higher than calc.	Negative
KLB9-SCG1	15	375-800	Exp. higher than calc.	Negative
KLB9-SCG1	20	375-800	Exp. lower than calc.	Positive
KLB8-SCG2	10	25-550	exp. higher than calc.	Negative
KLB8-SCG2	15	25-550	Exp. higher than calc.	Negative
KLB8-SCG2	20	25-550	Exp. higher than calc.	Negative
KLB8-SCG2	10	550-800	Exp. higher than calc.	Negative
KLB8-SCG2	15	550-800	Overlap – no interaction	No effect
KLB8-SCG2	20	550-800	Exp. higher than calc.	Negative
KLB7-SCG3	10	25-500	Exp. higher than calc.	Negative
KLB7-SCG3	15	25-500	Exp. higher than calc.	Negative
KLB7-SCG3	20	25-500	Exp. higher than calc.	Negative
KLB7-SCG3	10	500-800	Exp. lower than calc.	Positive
KLB7-SCG3	15	500-800	Exp. higher than calc.	Negative
KLB7-SCG3	20	500-800	Exp. higher than calc.	Negative

^aQuantities which were bolded are to express a easy eye-guiding throughout the discussion in the text

also included, tab. 4. It should be noted that the coal particles could be considered as a nearly inert carbonaceous substrate with a little participation in volatile evolution of biomass. It indicated the effect of free radical donation from biomass did not play an important role which was assumed to stabilize the atomic groups from coal pyrolysis and enhance the yields of tar and char under low heating rate in TG features, tab. 4.

On the other hand, for high concentration of SCG in the blend, KSL7-SCG3 (70% KSL-30% SCG), the lower heating rates (such as 10 and 15 K per minute) promotes enhanced yields of tar and char, tab. 4. In the case of KLB-SCG blends, there are two clear events that are strictly related to extreme limits, the lowest and highest additive contribution the coal mixture, and the influence of the lowest and highest heating rate. For KLB9-SCG1 case (90% KLB-10% SCG), the high heating rate (20 K per minute) promotes both tar and char yields, while for KLB7-SCG3 (70% KLB-30% SCG), the low heating rate (10 K per minute) primarily favors formation of the char, tab. 4. In all considered cases, the positive indicator shows that synergistic effects which exist between lignite coals and SCG indicate the higher tar and char yields than calculated ones during co-pyrolysis. Furthermore, in other cases, the large quantity of released volatiles from the SCG may hinder the release of volatiles from the coals, which explains the negative synergistic effects, tab. 4. From these results, it is obvious that the heating rate in the case of lignite-SCG blends plays a very important role on the synergistic effect (negative and/or positive) during co-pyrolysis. Therefore, the heating rate has an important role as control parameter for distribution of co-pyrolysis products by changing the temperature, tab. 4. Considering all the facts generally, more gas and liquid products would be obtained at low temperature ($<500\text{ }^{\circ}\text{C}$), and high temperature was more beneficial to the formation of solid products. The reasons for this phenomenon were the distinct chemical reactions between SCG and lignite coals at the different temperature range. Chemical decomposition and depolymerization reaction played a dominant role in the co-pyrolysis process at low temperature range, and high hydrogen content in SCG, tab. 2, stopped the free radicals recombining with chars, thus generating a large number of pyrolysis tar and gas. In the high temperature zone, thermal poly-condensation reaction of chars to generate coke was the primary reaction. However, in the current cases, the addition of SCG to studied coals mixtures (especially for 20% of SCG at all heating rates, tab. 4) has a *negative effect* on the *release of volatiles* (gases) during co-pyrolysis. So, in the considered cases, the negative effect on blends decomposition resulting in a lower volatile yield than expected. Since the addition of SCG to lignite samples has a predominantly negative synergistic effect in the co-pyrolysis.

Based on established results, the co-pyrolysis behavior of lignite-SCG blends can be summarized:

- There is a specific relationship between the synergy effect and heating rate. Considering previous results, in most cases, the lower heating rate can be beneficial to synergistic effect. When the heating rate is low, the response time of lignocellulosic material in SCG (especially the cellulose) and coal particles reaches the same temperature which will be prolonged, and can be conducive to the full contact reaction of the two reactants.
- The lower heating rate could reduce the temperature difference between the surface and the inside of SCG and lignite particles, accelerate the heat transfer, and then affect the pyrolysis process. The active material formed from deforming and softening of fibres material (*i.e.* cellulose) was adsorbed on the surface of coal particles, blocked the pore structure of coal molecules, and prevented the overflow of volatile products until the pyrolysis temperature rose to a certain level [22].

- The volatile expanded due to the heat to generate sufficient internal pressure to overcome the resistance before it started to be released. Therefore, there was a certain lag in the volatile products at this time, which made the experimental TG_{exp} in considered pyrolysis stage was higher than the calculated TG_{calc} (theoretical) value, tab. 4. The synergy effect related to interactions that occurred during co-pyrolysis lead to different behaviors compared to simply addition of coal and biomass. In TGA measurements, this was caused by longer reaction time between particles and volatile products produced in the primary pyrolysis process.

The KSL-WRG and KLB-WRG blend cases

For evaluating the extent of synergistic effects from lignite (KCL, KLB) coals and WRG waste material, the comparison between experimental data and calculated data based on the mass loss assessments of mixture samples are illustrated in figs. 3 and 4. The trends of TG_{exp} and TG_{calc} plotted against WRG percentage ratio in KSL sample under various heating rates (10, 15, and 20 K per minute) are shown in figs. 3(a)-3(c). Also, trends of TG_{exp} and TG_{calc} plotted against WRG percentage ratio in KLB sample under various heating rates (10, 15, and 20 K per minute) are shown in figs. 4(a)-4(c).

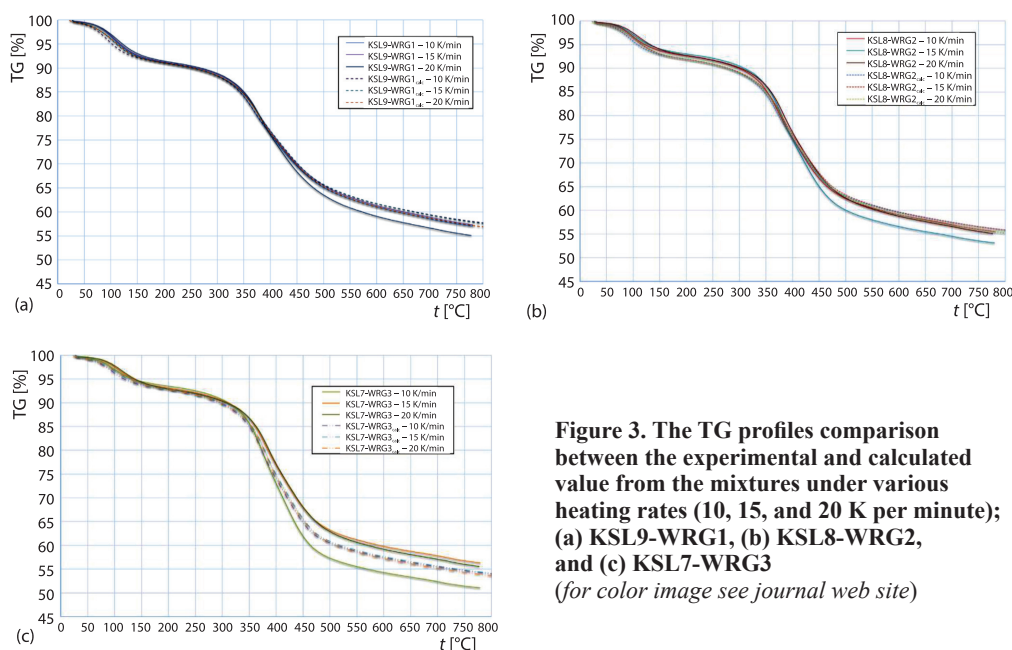


Figure 3. The TG profiles comparison between the experimental and calculated value from the mixtures under various heating rates (10, 15, and 20 K per minute); (a) KSL9-WRG1, (b) KSL8-WRG2, and (c) KSL7-WRG3 (for color image see journal web site)

Considering TG_{exp} and TG_{calc} curves of KSL-WRG and KLB-WRG mixtures with those related to lignite-SCG mixtures, certain differences can be noticed where the presence of synergistic effect in this case can affect differently than in the previous consideration. More details related to synergistic effect for KSL-WRG and KLB-WRG blends co-pyrolysis are given in tab 5.

It can be observed from results presented in tab. 5 that the synergism between lignites (KSL and KLB) and WRG has a much more positive effect than the addition of SCG into lignite samples on the co-pyrolysis. The addition of 10% of WRG into the KSL lignite at all heating rates (10, 15, and 20 K per minute) causes that difference between the experimental co-processed value and the *hypothetical mean* is positive, tab. 5, then it can be concluded that adding

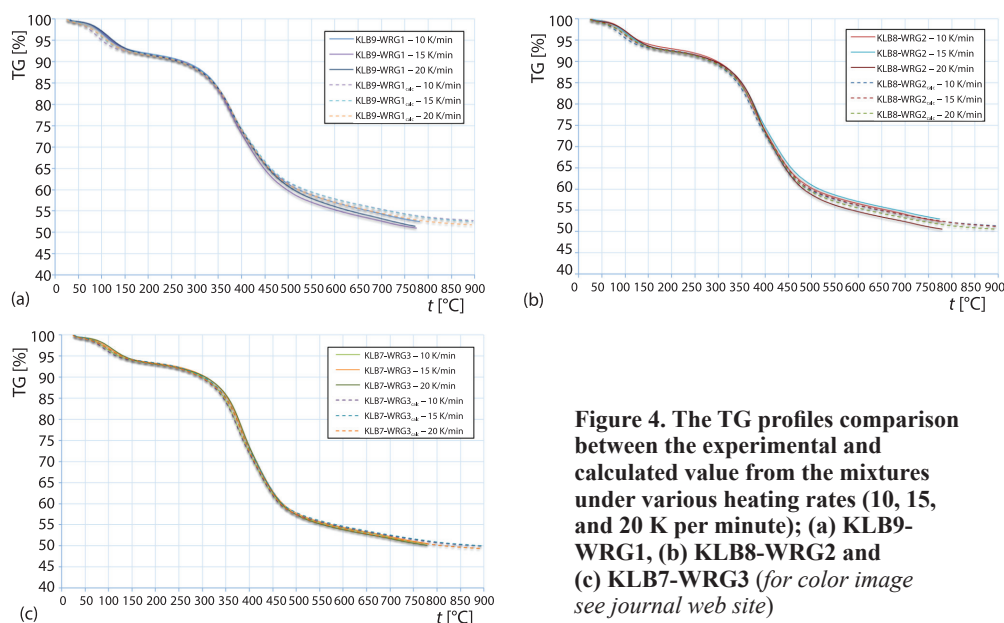


Figure 4. The TG profiles comparison between the experimental and calculated value from the mixtures under various heating rates (10, 15, and 20 K per minute); (a) KLB9-WRG1, (b) KLB8-WRG2 and (c) KLB7-WRG3 (for color image see journal web site)

WRG into KSL lignite enhanced tar and char (400-800 °C) generation. When the difference is *negative*, it can be assumed that *gas yields* are *higher* in the *individual* pyrolysis of lignite and WRG [23]. Also, the addition of 20% of WRG into KSL lignite leads to the same effect, *i.e.* the positive impact on the production of tars and chars, tab. 5. However, in the case of KSL7-WRG3 mixture, only the low heating rate (10 K per minute) affects the movement in the positive direction of the enhancing the tar and char formation, and to some extent of elevating the gas yields (but apparently to a much lesser extent), tab. 5. Generally, adding waste tire to the lignite coal leads to a decrease of the gas yields [24]. The reason for the increase of tar yields by adding WRG into lignite might be possible *via* transferring hydrogen from tire to the lignite as a result of the radical stabilization [25]. The similar situation can be observed in the case of KLB-WRG blends, tab. 5). The main difference lies in the behavior of KLB8-WRG2 blend at high heating rate (20 K per minute) and for the blends with the highest concentration of WRG in the lignite coal (KLB) for all heating rates, tab. 5. In these cases, an increase in the WRG content of the mixture and the high heating rate leads to the increased *positive synergetic effect* in the production of *tar* and *char* products. This synergetic effect can be explained by hydrogen radicals released from the tire at all temperatures, while the radicals can terminate the decomposition of the tire, and the volatile liquid products are leaving the reaction medium *prior* to their cracking to gases further in the presence of WRG. On the other hand, considering synergetic effect that occurs at higher temperatures (>500 °C) for both mixture systems (lignite + SCG and lignite + WRG mixtures, tabs. 4 and 5), it can be assumed that the solid products – *chars* are different in their morphology properties, where it can be expected that lignites – waste rubber granulates chars are characterized by a more porous surface structure. Since on the positive effect identified at high temperatures where the char formation takes place and where the experimental value is lower than calculated one, tab. 5, the addition of the WRG will not lead to the inhibition of thermal decomposition process. In the latter case, when co-pyrolysis of lignite-WRG mixtures is examined, the participation of concentration ratio of WRG in coal blends has a greater impact than the heating rate, and the opposite is true in the case of lignite-biomass (SCG) mixtures.

Table 5. Synergy analysis for KSL-WRG and KLB-WRG blends shown via descriptive parameters during co-pyrolysis process

Sample	Heating rate, β [Kmin ⁻¹]	Synergistic analysis		
		Temperature interval, ΔT [°C]	Interaction	Effect
KSL9-WRG1	10	25-200	Exp. higher than calc.	Negative
KSL9-WRG1	15	25-200	Exp. higher than calc.	Negative
KSL9-WRG1	20	25-200	Exp. higher than calc.	Negative
KSL9-WRG1	10, 15, 20	200-400	Overlap – no interaction	No effect
KSL9-WRG1^a	10	400-800	Exp. lower than calc.	Positive
KSL9-WRG1	15	400-800	Exp. lower than calc.	Positive
KSL9-WRG1	20	400-800	Exp. lower than calc.	Positive
KSL8-WRG2	10	25-400	Exp. higher than calc.	Negative
KSL8-WRG2	15	25-400	Exp. higher than calc.	Negative
KSL8-WRG2	20	25-400	Exp. higher than calc.	Negative
KSL8-WRG2	10	400-800	Exp. lower than calc.	Positive
KSL8-WRG2	15	400-800	Exp. lower than calc.	Positive
KSL8-WRG2	20	400-800	Exp. lower than calc.	Positive
KSL7-WRG3	10	25-350	Exp. higher than calc.	Negative
KSL7-WRG3	15	25-350	Exp. higher than calc.	Negative
KSL7-WRG3	20	25-350	Exp. higher than calc.	Negative
KSL7-WRG3	10	350-800	Exp. lower than calc.	Positive
KSL7-WRG3	15	350-800	Exp. higher than calc.	Negative
KSL7-WRG3	20	350-800	Exp. higher than calc.	Negative
Sample	Heating rate, β [Kmin ⁻¹]	Synergistic analysis		
		Temperature interval, ΔT [°C]	Interaction	Effect
KLB9-WRG1	10	25-200	Exp. higher than calc.	Negative
KLB9-WRG1	15	25-200	Exp. higher than calc.	Negative
KLB9-WRG1	20	25-200	Exp. higher than calc.	Negative
KLB9-WRG1	10, 15, 20	200-375	Overlap – no interaction	No effect
KLB9-WRG1	10	375-800	Exp. lower than calc.	Positive
KLB9-WRG1	15	375-800	Exp. lower than calc.	Positive
KLB9-WRG1	20	375-800	Exp. lower than calc.	Positive
KLB8-WRG2	10	25-375	Exp. higher than calc.	Negative
KLB8-WRG2	15	25-375	Exp. higher than calc.	Negative
KLB8-WRG2	20	25-375	Exp. higher than calc.	Negative
KLB8-WRG2	10	375-425	Exp. higher than calc.	Negative
KLB8-WRG2	15	375-425	Exp. higher than calc.	Negative
KLB8-WRG2	20	375-425	Overlap – no interaction	No effect
KLB8-WRG2	10	425-800	Exp. higher than calc.	Negative
KLB8-WRG2	15	425-800	Exp. higher than calc.	Negative
KLB8-WRG2	20	425-800	Exp. lower than calc.	Positive
KLB7-WRG3	10, 15, 20	25-550	Overlap – no interaction	No effect
KLB7-WRG3	10	550-800	Exp. lower than calc.	Positive
KLB7-WRG3	15	550-800	Exp. lower than calc.	Positive
KLB7-WRG3	20	550-800	Exp. lower than calc.	Positive

^aQuantities which were bolded are to express a easy eye-guiding throughout the discussion in the text

Conclusions

Thermogravimetry measurement tests of lignite coals (KSL and KLB) blends with SCG and WRG with different concentrations are performed, in order to define influence of the waste material and its concentration, the heating rate, the particle size, and mutual differences between lignites on the co-pyrolysis process performing. It was found that studied waste materials (SCG and WRG) are characterized by different pyrolysis products, which were primarily governed by their differences in the basic polymer composition. These differences can influence on the appearance of some divergences which take place during decomposition reaction pathways of studied blends, reflecting on the synergetic effects in the co-pyrolysis processes. It was established that the most intensive interactions occur in the second and third co-pyrolysis zones, due to the heat and mass transfer phenomena. At higher temperatures (>500 °C) favoring higher heating rates, the co-pyrolysis process of lignite-SCG blends was characterized by the higher reaction rates due to the longer contact time between particles and volatiles. It was concluded that strong synergistic interactions affect the characteristics of blends, especially for the blends with SCG. Therefore, it could be recommended to perform additional tests with different installation with much higher heating rates, which would comply to the industrial pyrolysis conditions, as well as to give a recommendation for a type of waste introduction (separate or pre-mixed) to power boilers. Besides, the further investigation should define precise WRG concentration, based on the limits regarding the GHG (greenhouse gas emissions). The results reported in this work can serve in the assessment analysis for the development of future co-firing plants using coal-waste blends, within the power generation industry.

Acknowledgment

Authors would like to acknowledge financial support of Ministry of Education, Science and Technological Development of the Republic of Serbia according to the contract number 451-03-9/2021-14/200105.

References

- [1] ***, Energy Sector Development Strategy of the Republic of Serbia for the period by 2025 with projections by 2030 in, Republic of Serbia, Ministry of Mining and Energy, Department for strategic planning in energy sector, Belgrade, Serbia, 2016, pp. 98
- [2] Jie, D. et al., The Future of Coal Supply in China Based on Non-Fossil Energy Development and Carbon Price Strategies, *Energy*, 220 (2021), 119644
- [3] Neofytou, H., et al., Sustainable Energy Transition Readiness: A Multicriteria Assessment Index, *Renew. Sustain. Energy Rev.*, 131 (2020), 109988
- [4] Merdun, H., et al., Kinetic and Thermodynamic Analyses during Co-Pyrolysis of Greenhouse Wastes and Coal by TGA, *Renewable Energy*, 163 (2021), Jan., pp. 453-464
- [5] Tokmurzin, D. et al., Characterization of Solid Char Produced from Pyrolysis of the Organic Fraction of Municipal Solid Waste, High Volatile Coal and Their Blends, *Energy*, 191 (2020), 116562
- [6] Khan, A., et al., Co-Pyrolysis and Hydrogenation of Waste Tires and Thar Coal Blends, Energy Sources, – Part A: Recovery, Utilization, and Environmental Effects, 39 (2017), 15, pp. 1664-1670
- [7] Kanca, A., Investigation on Pyrolysis and Combustion Characteristics of Low Quality Lignite, Cotton Waste, and Their blends by TGA-FTIR, *Fuel*, 263 (2020), 116517
- [8] Životić, M. M., et al., Modelling Devolatilization Process of Serbian Lignites Using Chemical Percolation Devolatilization Model, *Thermal Science*, 23 (2019), Suppl. 5, pp. S1543-S1557
- [9] Oyedun, A., et al., Optimisation of Particle Size in Waste Tyre Pyrolysis, *Fuel*, 95 (2012), May, pp. 417-424
- [10] ***, ISO 5068-2 Brown Coals and Lignites – Determination of Moisture Content – Part 2: Indirect Gravimetric Method for Moisture in the Analysis Sample, International Organization for Standardization, 2014
- [11] ***, ISO 5071-1 Brown Coals and Lignites – Determination of the Volatile Matter in the Analysis Sample – Part 1: Two Furnace Method, International Organization for Standardization, 2013

- [12] ***, ISO 1171 Solid mineral fuels – Determination of Ash Content, in, International Organization for Standardization, 2010
- [13] ***, SRPS EN ISO 18134-3 Solid Biofuels – Determination of Moisture Content – Oven Dry Method – Part 3: Moisture in General Analysis Sample, 2017
- [14] ***, SRPS EN ISO 18123 Solid biofuels – Determination of the Content of Volatile Matter, 2017
- [15] ***, SRPS EN ISO 18122 Solid biofuels – Determination of Ash Content, 2017
- [16] ***, ISO 1928 Solid Mineral Fuels – Determination of Gross Calorific Value by the Bomb Calorimetric Method, and Calculation of Net Calorific Value, International Organization for Standardization, 2015
- [17] Han, B., *et al.*, Co-Pyrolysis Behaviors and Kinetics of Plastics-Biomass Blends through Thermogravimetric Analysis, *Journal of Thermal Analysis and Calorimetry*, 115 (2014), 1, pp. 227-235
- [18] Vardon, D. R., *et al.*, Complete Utilization of Spent Coffee Grounds to Produce Biodiesel, Biooil, and Biochar, *ACS Sustainable Chemistry & Engineering*, 1 (2013), 10, pp. 1286-1294
- [19] Biagini, F., *et al.*, Devolatilization Rate of Biomasses and Coal-Biomass Blends: An Experimental Investigation, *Fuel*, 81 (2002), 8, pp. 1041-1050
- [20] Demirbas, A., Effects of Moisture and Hydrogen Content on the Heating Value of Fuels, Energy Sources, – Part A: *Recovery, Utilization, and Environmental Effects*, 29 (2007), 7, pp. 649-655
- [21] Demirbas, A., Relationships between Heating Value and Lignin, Moisture, Ash and Extractive Contents of Biomass Fuels, *Energy Exploration & Exploitation*, 20 (2002), 1, pp. 105-111
- [22] Wu, Z., *et al.*, Synergistic Effect on Thermal Behavior during Co-Pyrolysis of Lignocellulosic Biomass Model Components Blend with Bituminous Coal, *Bioresour. Technol.*, 169 (2014), Oct., pp. 220-228
- [23] Suelves, I., *et al.*, Synergetic Effects in the Co-Pyrolysis of Coal and Petroleum Residues: Influences of Coal Mineral Matter and Petroleum Residue Mass Ratio, *Journal Anal. Appl. Pyrolysis*, 55 (2000), 1, pp. 29-41
- [24] Acar, P., *et al.*, The Pyrolysis of Scrap Tire with Lignite, Energy Sources – Part A: *Recovery, Utilization, and Environmental Effects*, 34 (2011), 3, pp. 287-295
- [25] Sinag, A., *et al.*, Characterization of the Liquid Phase Obtained by Copyrolysis of Mustafa Kemal Pasa (MKP) Lignite (Turkey) with Low Density Polyethylene, *Energy Fuels*, 20 (2006), 5, pp. 2093-2098