

Co-pyrolysis of waste tire/coal mixtures for smokeless fuel, maltenes and hydrogen-rich gas production



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ABSTRACT

The processing of waste tires with two different types of bituminous coal was studied through the slow co-pyrolysis of 1 kg of waste tire/coal mixtures with 15, 30 and 60 wt% waste tires on a laboratory scale. The waste tire/coal mixtures were pyrolysed using a quartz reactor in a stationary bed. The mixtures were heated at a rate 5 °C/min up to the final temperature of 900 °C with a soaking time of 30 min at the required temperature. The mass balance of the process and the properties of the coke and tar obtained were evaluated, further, the influence of the admixture in the charge on the amount and composition of the obtained coke and tar was determined. It was found that the smokeless fuel/carbonaceous sorbent and a high yield of tar for further use can be obtained through the slow co-pyrolysis. The obtained tars contained mostly maltenes (80–85 wt%). FTIR analysis showed that the maltenes from the co-pyrolysis of coal/waste tires exhibited significantly lower aromaticity as compared with that from coal alone. The gas obtained from pyrolysis or co-pyrolysis of waste tire/coal mixtures contained a high amount of hydrogen (above 60 vol%) and methane (above 20 vol%).

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1. Introduction

A major global economic and environmental burden is caused by the disposal of waste tires – they are non-biodegradable and their amount continuously increases with the growing production of the automobile industry [1]. Waste-tire production in Europe is estimated to be around 3.3 million tons per year [2,3], with some states, such as e.g. Bulgaria or Cyprus, only depositing them at landfills. The Czech Republic annually produces approximately 60–70 thousand tons of waste tires, and this number continues to increase [4]; about 30% of this waste is landfilled. Therefore, it is important to deal with its use, e.g. in the construction industry [5], or with its effective chemical treatment. Since waste tires usually contain 45–48% of elastomer, 21–22% of soot, 15–25% of steel reinforcement, 0–5% of textile, 1–2% of ZnO, 1% of sulfur and 6–8% other chemicals (accelerators and activators, fillers, pigments, plasticizers, antioxidants, etc.), they are a valuable source of products with a high utility value.

An effective industrial treatment process is pyrolysis, which is used to transform waste tires and industrial plastic wastes into fuel oil (40–45%), carbon black (30–35%), steel wires (10–15%) and gas (10–12%) [6]. The main product obtained through waste-tire pyrolysis is oils, which have broad application. High oil yields from the

pyrolysis of waste tires alone were achieved by e.g. Fernández et al. [7], who studied the influence of temperature on product yield. Other than classic pyrolysis, it is possible to use co-pyrolysis either with coal [8] or with waste of vegetable origin [9,10]. Acevedo et al. [11] pyrolyzed 6 g of a mixture of coal and scrap tires in the ratio 1:1 at a temperature of 850 °C and a heating rate of 5 °C/min, obtaining up to 37 wt% of tar. Co-carbonization for blast furnace coke production was also studied as a possible route for the recycling of waste tires [12]. The possibilities of using waste tires for the production of hydrogen at low manufacturing costs [13] and co-gasification of waste tires with lignite [14] were investigated as well. Waste plastics can be treated in the same way [15,16].

The literature insufficiently stresses the importance of the preparation of waste tires prior to processing. Because this waste contains steel components, they must be separated by a suitable method [17]; furthermore, it is necessary to select a proper grain size corresponding to the method of thermal treatment and scale of processing. If the feedstock is well prepared, co-utilization of coal with waste tires offers a number of advantages. It is possible to obtain a hydrogen-rich gas [8]; the current study showed a synergetic effect that result in improving the quality as well as quantity of tar [18]; therefore, alternative fuels can be obtained in order to reduce the consumption of fossil fuels. Another advantage is that the co-pyrolysis and co-gasification of waste tires can be successfully carried out on a commercial scale [14].

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This paper studies the co-pyrolysis of waste tires with two different types of bituminous coal on a laboratory scale and examines the properties and composition of the coke as a smokeless fuel or carbonaceous sorbent, the tar and gas obtained as well as their possible uses.

2. Experimental

2.1. Materials

Waste tires with a grain size of 1–5 mm containing less than 50% of natural rubber were used for the co-pyrolysis of model mixtures. Steel parts were removed from the waste tires by magnetic separation [17]. The tires were subjected to thermal decomposition with two types of bituminous coal from the Upper Silesian Basin. One of them was Polish gas coal (A) from the Rydułtowy-Anna Coal Mine (36.4% of volatile matter), the other was Czech coking coal (B) from the ČSM Mine, Ostrava-Karviná District (29.2% of volatile matter). The grain size of the coal was 0.5–4 mm (close to grain size of waste tires). Table 1 shows the results of the proximate and ultimate analyses of input bituminous coals and waste tires.

Proximate and ultimate analyses were carried out according to ISO standards (687:2010, 562:2010, 1171:2010, 333:1996, 334:2013, 625:1996, 157:1996). For all the samples below, the oxygen content was determined by recalculation to 100%. For the samples of coal, waste tires and coke, the higher heating value was determined calorimetrically and the lower heating value was calculated according to the ISO 1928:2009 standard.

2.2. Methods

The slow pyrolysis and comparative analyses of coal alone and their mixtures with 15, 30 and 60 wt% waste tires were performed on a laboratory unit with a fixed bed and a quartz reactor (outer diameter 100 mm, inner diameter 95 mm, length 500 mm) placed horizontally in an electric resistance furnace. Mixtures of coals A or B with 15, 30 and 60 wt% of waste tires were co-pyrolyzed. The weight of the charge was always 1 kg. Based on previous experience [8,15], the charges were heated at a heating rate of 5 °C/min up to the final temperature of 900 °C with a soaking time of 30 min at the required temperature. Volatile products from slow pyrolysis/co-pyrolysis were released during thermal decomposition. (The gas products released from about 200 °C, the tar formed at about 300–400 °C [8], therefore, the main pyrolysis reactions started at about 300 °C (waste tires, see below) and 400 °C (coal, see below).) The volatile products were led from the reactor into a water cooled flask (Fig. 1, position 3) and further in a vertical cooler (Fig. 1, position 4) with cooling water (Fig. 1, position 5). The temperature of cooling water ranged from 8 °C to 12 °C. The liquid portion (water and tar) formed during the experiment was captured and collected in a water-cooled flask after its separation from the stream of raw gas (Fig. 1, position 3). The generated gas was continuously analyzed and subsequently burned in an auxiliary burner (Fig. 1, position 6). For analysis of a gas, a 350 dm³ gasholder (Fig. 1, position 6a) was incorporated in the apparatus

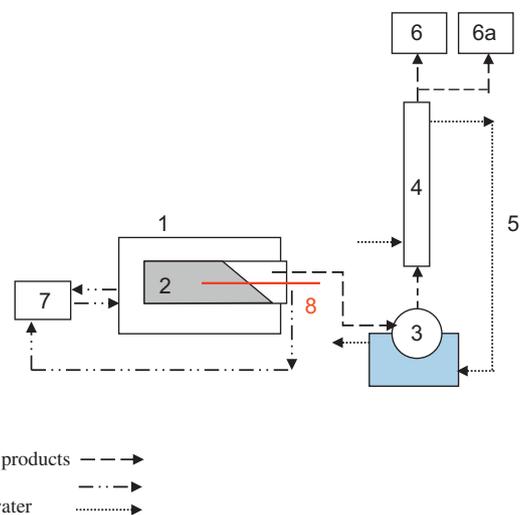


Fig. 1. A functional schema of the laboratory unit with a horizontal bed. 1 – electric furnace, 2 – quartz reactor with a charge, 3 – cooled flask for liquid products, 4 – cooler, 5 – cooling water, 6 – burner, 6a – gasholder, 7 – programmable furnace heating, and 8 – thermocouple.

for a total gas analysis (the auxiliary burner was replaced with gasholder). The gas from pyrolysis of coals A and B and their mixtures with waste tires (T) was analyzed. Water from the resulting liquid portion was separated by azeotropic distillation with n-hexane. The coke obtained was characterized, in addition to common parameters, also by its true and apparent density, porosity and resistivity. This solid product was characterized by the aforementioned analysis and can be considered as smokeless coke. A functional schema of the co-pyrolysis laboratory unit is shown in Fig. 1.

Because of the multicomponent character of the tars obtained, they were divided into groups of chemically similar compounds, with asphaltenes and maltenes being separated from the tars. The asphaltenes were prepared by precipitation with n-hexane in two stages [19,20]. In the first stage, most substances soluble in n-hexane with a fiftyfold excess were removed from the tars [21,22]. The suspension was filtered for 24 h. The residues on the walls of the container were dissolved in dichloromethane, and asphaltenes were again precipitated from the solution by n-hexane. Afterwards, the dichloromethane was distilled off and the asphaltene floccules were filtered off. The n-hexane was removed from the maltene solution obtained in a vacuum evaporator and its residues additionally in a vacuum drier at 70 °C and a pressure of 4 kPa. Under these conditions, volatiles, i.e. the BTX (benzene, toluene, xylene) fraction and the oxygenates, mainly phenol, were removed as well.

The chromatographic fractionation of the maltenes obtained was performed in a glass column of a length of 700 mm and an inner diameter of 6.9 mm, provided with brass caps at the ends. The bottom half of the column was filled with fully activated alumina (150 mesh, activated for 8 h at 400 °C) and the upper half

Table 1

The properties of the coals and waste tires used. A – Anna coal, B – ČSM coal, T – waste tires. V – volatile matters, HHV – higher heating value.

Sample	Proximate analysis (wt%)				Ultimate analysis (daf, wt%)					HHV (MJ/kg)
	Water ^a	Ash ^d	S _t ^d	V ^{daf}	C	H	N	S _o	O _{dif}	
A	3.23	7.55	0.54	36.38	84.10	5.43	1.53	0.50	8.44	34.16
B	0.76	8.06	0.57	29.15	86.89	5.30	1.45	0.45	5.91	35.01
T	1.04	6.70	1.09	70.20	88.22	8.18	0.47	0.80	2.33	38.21

daf – dry ash free basis; a – analytical; d – dry; t – total; o – organic; dif – by difference.

with fully activated silica gel (Silica gel 60, 70–230 mesh, Merck KGaA, Darmstadt, activated for 24 h at 160 °C). The sample of the maltenes (0.2 g) was dissolved in 1 mL of hexane and pumped to the column. Subsequently, it was eluted with three mobile phases with increasing elution strength – hexane, toluene and methanol. After the collection of the toluene fraction, the direction of the flow of the solvent through the column was reversed to prevent the highly polar substances (remaining on the silica gel) from contact with the alumina, which is a stronger sorbent than the silica gel; this averted the irreversible sorption of these substances on the alumina. All the mobile phases were pumped at a flow rate of 90–100 mL/h and collected into graduated cylinders at the output. From the fractions obtained, the mobile phase was evaporated on a rotary vacuum evaporator, the fractions were dried in a vacuum drier (80 °C, 4.4 kPa, 1 h) and weighed and analyzed after cooling.

The infrared spectra of the maltenes were measured by the Attenuated Total Reflectance (ATR) method using a Nicolet 740 FTIR spectrometer (Nicolet Instrument Inc. Madison, USA), flushed with dried air in a “Baseline Horizontal Attenuated Total Reflectance” (HATR) cell from Spectra Tech Inc., UK, containing a ZnSe crystal. For the spectrum measurement, 512 scans at a resolution of 2 cm⁻¹ were accumulated. The spectra were processed by the OMNIC software (version 4.1a).

The coke porosity was calculated from the measured values of the true and apparent density according to ISO 5072. The coke resistivity as a measure of the quality of coke (see below) was determined using the original method, in which the electrical resistivity of a cylindrical coke column of a height of 16.0 ± 0.5 mm and a diameter of 16 mm was measured. The cylinder was created by compression of a coke sample of a grain size below 0.2 mm at a pressure of 2,942 kPa in a special container. The tests were performed on the Omega III apparatus (CSAV Praha). The specific coke resistivity (ρ) as calculated according to the formula (1):

$$\rho = P * (R - R_0) \quad (1)$$

where ρ the specific electrical resistivity ($\Omega \text{ mm}^2/\text{m}$), R is the measured electric resistance of the coke cylinder (Ω), R_0 the resistance of the apparatus without the sample (Ω), P is the instrument constant: 12560 mm²/m. It is remarked that the high-quality cokes obtained on the operational or pilot-plant scale have the resistivity of e.g. 1400–2800 $\Omega \text{ mm}^2/\text{m}$, which corresponds to the hydrogen content in coke of e.g. 0.20–0.45 wt% [23]; the higher electrical resistivity imply a lower degree of degassing than in high-quality cokes and indicate the possible use of low degassed cokes only for heating. The thermoplastic properties of the coals used were assessed by the Gieseler method on a R.B. Automazione Gieseler plastometer PL2000, following the ASTM D2639-08 standard procedure.

Waste tires and waste tire/coal mixtures were characterized by the thermogravimetric method on a SETARAM Setsys Evolution 18 analyzer. About 23–25 mg of the dry sample was heated at a rate of 10 °C/min in an inert atmosphere (He, 20 cm³/min) in the temperature range of 25–900 °C.

Gases were analyzed by gas chromatography with thermal conductivity (TCD) and flame ionization (FID) detection. The O₂, N₂ and CO were analyzed on a HP-MOLSIV capillary column (40 °C) with helium as the carrier gas (5 cm³/min) using TCD. Methane and other hydrocarbons were determined on a GS-Gaspro capillary column (60 °C) with nitrogen as the carrier gas (20 cm³/min) using FID (air: 400 cm³/min, H₂: 30 cm³/min, N₂: 20 cm³/min); carbon dioxide on the GS-Gaspro column (40 °C) with helium as the carrier gas (5 cm³/min) using TCD; and hydrogen on an HP-5 capillary column (40 °C) with nitrogen as the carrier gas (7 cm³/min) using TCD.

3. Results and discussion

3.1. Process mass balance

Based on the experiments performed, the mass balances of slow co-pyrolyses were carried out and compared with the balance of the slow pyrolysis of coal alone. During the process, gas was burned; the gas yields below thus include losses. The results of the comparison are evident from Figs. 2 and 3. The yield of gas released by the pyrolysis of coal A alone was 16.2 wt% and by the pyrolysis of coal B it was 14.3 wt%; the growing proportion of waste tire in the coal charge led to a decrease of gas yield and losses to 12.0 wt% (12.2 wt% according to additivity rule calculation, further ARC) and 13.2 wt% (11.5 wt% according to ACR) based on the type of coal A or B (resp.), which was caused by an intensive increase of the tar formed during co-pyrolysis. Due to the low oxygen content in the waste tires in both types of coal (Table 1), the content of reaction water was low in all cases (below 10 wt%).

As expected, a heating coke (smokeless fuel) was the majority product in the evaluated series of experiments, which was obtained from the pyrolysis or co-pyrolysis of 1 kg of waste tire/coal mixtures. The pyrolysis of coal A alone produced 72.0 wt% of coke and 7.3 wt% of tar; the yield of coke from the pyrolysis of coal B alone was higher, 77.8 wt%, and of tar lower, 5.0 wt%. Analogously, the coke yields were higher when coal B was used in comparison with coal A in the co-pyrolysis of coal with waste tires. The reason is that coal B has a higher degree of coalification (C^{daf} 86.9 wt%) than coal A (C^{daf} 84.1 wt%) (Table 1).

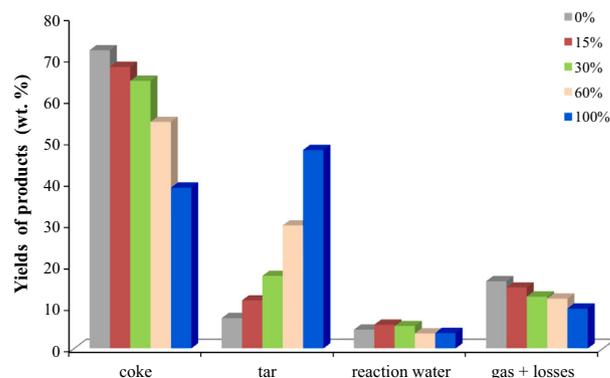


Fig. 2. The yields of products from the slow pyrolysis of coal A (gray columns), the slow co-pyrolysis of coal A with waste tires (colored columns) and waste tires alone (blue columns) (wt%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

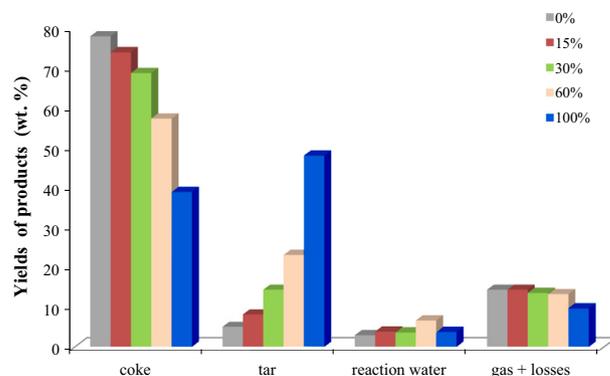


Fig. 3. The yields of products from the slow pyrolysis of coal B (gray columns), the slow co-pyrolysis of coal B with waste tires (colored columns) and waste tires alone (blue columns) (wt%). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The addition of 30 wt% and mainly 60 wt% of waste tires to the charge significantly enhanced the production of the liquid products (including both tar and water). In the case of waste tires/coal A, the yield of tar was 17.5 wt% (19.5 wt% according to ACR) and 29.7 wt% (31.7 wt% according to ACR), respectively. Already the addition of 15 wt% of waste tires increased the production of tar to 11.6 wt% (in the case of coal A) (13.4 wt% according to ACR) and 8.1 wt% (with coal B) (11.4 wt% according to ACR). Similar tar yields (14.2 wt%) were achieved by conducting the process in a vertical bed [8]. It arises from Figs. 2 and 3 that the growing addition of waste tires led to an increase of tar at the expense of coke to 29.7 wt% (in the case of coal A) and 23.0 wt% (in the case of coal B); the organic compounds contained in waste tires increased the yield of tar by 307% and 360%, respectively.

On the contrary, the addition of 30 wt% and 60 wt% of waste tires decreased the production of coke. In the case of waste tires/coal A, the yield of coke was 64.6 wt% (62.0 wt% according to ACR) and 54.7 wt% (52.1 wt% according to ACR), respectively. It was similar in the case of coal B. For a summary of the pyrolysis/co-pyrolysis process, the last column (in blue) shows the pyrolysis of 1 kg of waste tires alone. It is clear that waste tires pyrolysis can produce almost 50 wt% of tar, whereas the yield of the solid product from waste tires is reduced to nearly a half in comparison with coke from coal alone.

3.2. Coke characteristics

The proximate and ultimate analyses of the cokes obtained are shown in Tables 2 and 3. All types of coke were acceptably degassed (H^{daf} 0.73–0.90%). For their low total sulfur content (below 1.2 wt%), they are a suitable potential smokeless fuel. The higher sulfur content in the cokes obtained through co-pyrolysis than in those from the pyrolysis of coal alone is a consequence of the presence of sulfur in waste tires.

The physical and physico-chemical properties of the cokes obtained are shown in Table 4. It arises from the table that the cokes had higher electrical resistivity values than is usual for operational or pilot-plant cokes, high porosity and very similar higher

and lower heating values. As mentioned, the higher electrical resistivity means a lower degree of degassing than in high-quality operational cokes and indicates the possible use of cokes obtained from co-pyrolysis mainly for heating as a smokeless fuel [23]. Because of their high porosity values, they may also be used as sorbents of various pollutants [24]. The addition of 60 wt% of waste tires to coal A led to the generation of fine grained coke, whose porosity could not be determined. The obtained cokes from the co-pyrolysis of both coal types studied, A and B, exhibited a very similar lower heating value (LHV) to the coke obtained through the pyrolysis of coal alone and confirm the possibility of using them for heating.

3.3. Thermogravimetric analysis of waste tires and their mixtures with coal

Waste tires alone began to decompose already at 300 °C in two stages, with the decomposition being completed at ca 485 °C (Fig. 4). On the other hand, the decomposition of both coking- and gas coal did not start until about 400 °C, reaching its maximum at about 450 °C and ending at about 550 °C (Fig. 5). The organic sulfur from waste tires was partly transferred to the raw gas and subsequently to the tar, but preferably to the semi-coke [14], and then to the coke, in amounts depending on the type of the coal used. Since more sulfur was transferred to the coke during the co-pyrolysis of gas coal A (S_o^{daf} 0.66–0.98 wt%, Table 2) than during the co-pyrolysis of coking coal B (S_o^{daf} 0.38–0.59 wt%, Table 3), the tar resulting from the co-pyrolysis of coal A contained less sulfur than that from the co-pyrolysis of coal B (Table 6). Although the additions of the waste tires were the same, they influenced the quality of coke and tar in various ways.

Figs. 4 and 5 demonstrate that the feedstock is nearly decomposed at 600–800 °C, therefore, the final temperature could be chosen in this range. The reason the final temperature of 900 °C was used is that the smokeless fuel was intended as the product. Generally, smokeless fuel has to have a sulfur content less than 2 wt%, preferably less than 1 wt% (dry basis) [25]. In the case of coal or a feedback with coal, the temperature of 900 °C is recommended to reduce the sulfur content in resulting coke significantly [26]. To meet the mentioned requirement for smokeless fuel, the temperature of 900 °C was therefore chosen as the definitive one.

During the process, the interactions between intermediates from co-pyrolysis occur. From Figs. 4 and 5 it is evident that the temperature range of waste tires pyrolysis includes that of coal, which is beneficial to interactions between coal and rubber radicals [27]. These radicals arise from the cleavage of the double bonds and sulfur bridges in the rubber structure and cracking of the alicyclic-aromatic structures in coal. Due to this, the new cross-link and other sp³ bonds are formed. The number of sp³ bonds thus increases during heating and new rigid structures are created, whose sp³ bonds are manifested in the Raman spectra with a relatively large area of the band at 1100–1270 cm⁻¹ [28]. Simultaneously, a synergism in the asphaltene formation was observed which can be explained by the waste tire-coal interactions [27].

In our case, an increasing amount of sp³ bonds with an increase of waste tires content in the initial mixture was reflected in a decrease in the ratio $(C/H)^{at}$ of resulting maltenes (Section 3.5, Table 8, see below), both in the case of coal A and B coal, and in an increase of the alkanes content in these maltenes (Section 3.5, Table 10, see below). Conversely, with asphaltenes, an increase in the $(C/H)^{at}$ ratio (i.e. an increase in aromaticity) with waste tires adding was observed in asphaltenes formed in the case of coking coal B, but not in the case of gas coal A (Section 3.5, Table 9, see below). The reason is that in the case of coal B, the $(C/H)^{at}$ of asphaltene from waste tires alone (0.89) is higher than that of

Table 2
The characteristics of the cokes from the co-pyrolysis of coal A with waste tires (T).

	Proximate analysis (wt%)				Ultimate analysis (daf, wt%)				
	Water ^a	Ash ^d	S _t ^d	V ^{daf}	C	H	N	S _o	O _{dif}
Coke from A	2.91	11.43	0.44	1.13	96.77	0.76	1.26	0.37	0.84
+ 15% T	1.00	13.76	1.01	0.92	96.58	0.79	1.25	0.90	0.48
+ 30% T	0.81	11.94	0.85	0.92	97.12	0.73	1.03	0.66	0.46
+ 60% T	0.68	12.07	1.19	0.64	96.41	0.73	1.00	0.98	0.88
100% T	0.49	13.26	2.14	0.91	93.33	0.52	0.38	1.58	4.19

daf – dry ash free basis; a – analytical; d – dry; t – total; o – organic; dif – by difference; V – volatile matter.

Table 3
The characteristics of the cokes from the co-pyrolysis of coal B with waste tires (T).

	Proximate analysis (wt%)				Ultimate analysis (daf, wt%)				
	Water ^a	Ash ^d	S _t ^d	V ^{daf}	C	H	N	S _o	O _{dif}
Coke from B	0.94	11.84	0.52	0.51	96.80	0.80	1.24	0.48	0.68
+ 15% T	0.68	10.50	0.62	0.81	96.85	0.87	1.25	0.38	0.65
+ 30% T	0.80	10.73	0.84	0.77	96.24	0.90	1.13	0.52	1.21
+ 60% T	0.76	10.34	1.10	0.51	96.69	0.75	0.95	0.59	1.02
100% T	0.49	13.26	2.14	0.91	93.33	0.52	0.38	1.58	4.19

daf – dry ash free basis; a – analytical; d – dry; t – total; o – organic; dif – by difference; V – volatile matter.

Table 4

The properties of the cokes from the co-pyrolysis of coals A and B with waste tires (T). HHV – higher heating value and LHV – lower heating value.

	Specific electric resistivity ($\Omega \text{ mm}^2/\text{m}$)	Density		Porosity (%)	HHV (MJ/kg)	LHV (MJ/kg)
		Apparent (g/cm^3)	True (g/cm^3)			
Coke from A	7200	0.849	1.851	54.2	33.65	33.48
+ 15% T	6600	0.755	1.864	59.5	34.02	33.85
+ 30% T	4550	0.702	1.864	62.4	33.81	33.65
+ 60% T	5550	–	1.870	–	33.59	33.44
Coke from B	4750	0.896	1.856	51.7	33.72	33.54
+ 15% T	4300	0.870	1.862	53.3	33.53	33.34
+ 30% T	4000	0.721	1.861	61.3	33.71	33.52
+ 60% T	5300	0.575	1.860	69.1	33.89	33.73
100% T	4000	–	1.889	–	33.76	33.61

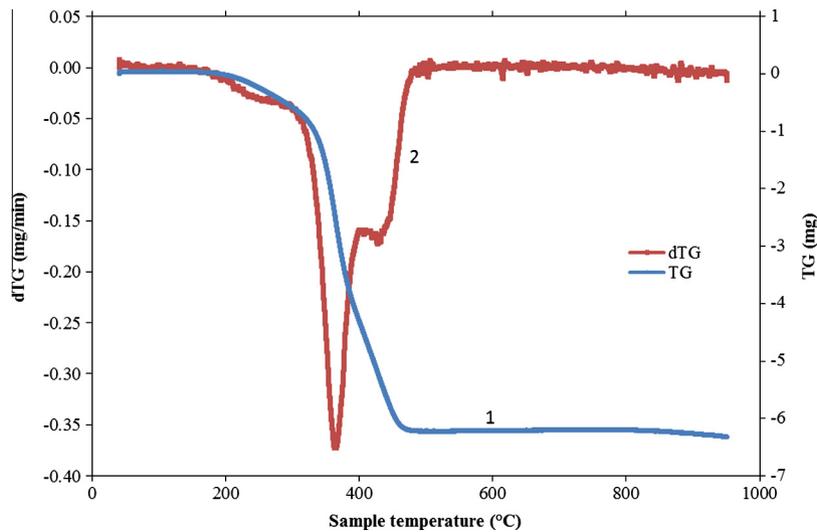


Fig. 4. Thermal decomposition of waste tires. 1 – TG curve (blue), 2 – DTG curve (red). The decomposition in the first stage begins already at 300 °C and reaches the maximum at 365 °C. The second stage of the decomposition takes place from ca 400 to 485 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

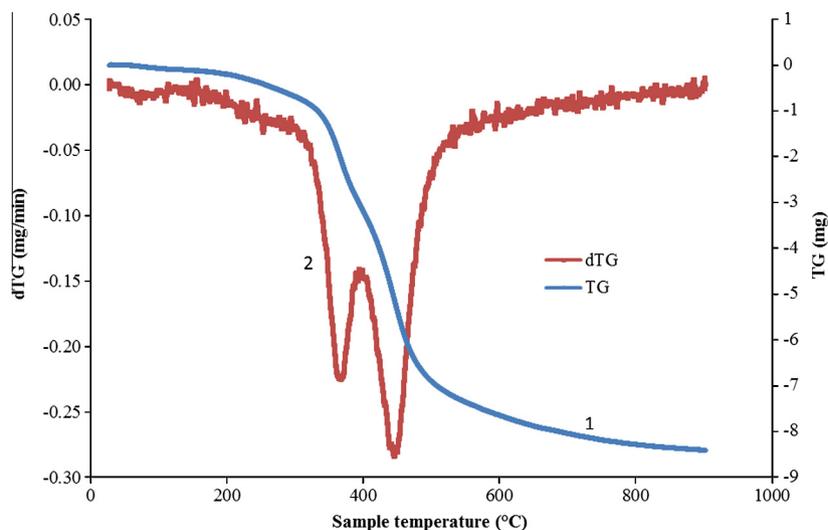


Fig. 5. The thermal decomposition of the mixture of waste tires with coking coal B (ratio: 30/70). 1 – TG curve (blue), 2 – DTG curve (red). Waste-tire decomposition already begins at a temperature of 300 °C, coal decomposition at a higher temperature of ca 400 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

asphaltene from coal B alone (0.83). The addition of waste tires thus supports the aromaticity of the asphaltenes from waste tire/coal B mixtures and their $(C/H)^{at}$ ratio increases with increasing content of waste tires in the mixture. In the case of coal A, $(C/H)^{at}$ of asphaltene from coal A alone is 0.95 and the mentioned ratio of asphaltene from waste tires alone is therefore lower. The addition of waste tires thus does not support the aromaticity of the asphaltenes from waste tire/coal A mixtures and their $(C/H)^{at}$ ratio decreases with increasing content of waste tires in the mixture.

3.4. Tar characteristics

The tars obtained were liquid at room temperature. The highest yield (30 wt%) was achieved during the co-pyrolysis of coal with 60 wt% of waste tires (Fig. 2). The content of the waste tires added altered the tar viscosity, which was accompanied by a decrease of density below 1 g/cm^3 (by 10–12%). In all of the cases, the addition of waste tires reduced the amount of ashes contained in the tars in comparison with tars from the pyrolysis of coals A and B alone (Table 5), with the maximum decrease being achieved in the 60 wt% addition to coal A (by 93%). In the case of the co-pyrolysis 60 wt% waste tires with coal B, a decrease by 65–70% was observed. The basic characteristics of tars obtained, namely

Table 5

The basic characteristics of the tars. A – tar from coal A, B – tar from coal B, and LHV – lower heating value.

Sample	Yield (wt%)	Ash ^a (wt%)	Density (g/cm^3)	LHV (MJ/kg)
A	7.3	1.22	1.03	36.59
+ 15% T	11.6	0.16	1.01	38.17
+ 30% T	17.5	0.09	0.97	39.22
+ 60% T	29.7	0.08	0.93	40.54
B	5.0	0.20	1.08	37.42
+ 15% T	8.1	0.07	0.99	39.27
+ 30% T	14.3	0.06	0.94	38.87
+ 60% T	23.0	0.07	0.95	40.42
100% T	47.9	0.03	0.88	–

^a Analytical.

Table 6

Elemental analysis of the tars (dry ash free basis, wt%). A – tar from coal A and B – tar from coal B.

Sample	C	H	N	S	O_{dif}
A	81.11	7.95	1.08	0.79	9.07
+ 15% T	82.97	8.64	0.59	0.55	7.25
+ 30% T	83.98	9.15	0.44	0.49	5.94
+ 60% T	84.69	9.97	0.37	0.47	4.50
B	84.72	7.39	0.91	0.51	6.47
+ 15% T	84.81	8.71	0.60	1.44	4.44
+ 30% T	83.25	9.06	0.45	0.85	6.39
+ 60% T	84.68	9.76	0.53	1.05	3.98
100% T	81.80	10.69	0.42	0.19	6.90

dif – by difference.

Table 7

The mass balance of the solvent separation of the tars from pyrolysis of coals A and B and the co-pyrolysis of coals A and B with 15, 30 and 60 of waste tires (T) (wt%). A – tar from coal A and B – tar from coal B.

Sample	A	+15% T	+30% T	+60% T	B	+15% T	+30% T	+60% T	100% T
Maltenes	76.6	80.1	80.3	81.9	81.8	83.4	84.7	83.3	85.2
Asphaltenes	8.8	7.6	7.2	6.4	7.2	6.6	5.9	5.9	4.8
Preasfaltenes	14.6	12.3	12.5	11.7	11.0	10.0	9.4	10.8	10.0

their lower heating value (36–41 MJ/kg), shown that they can be used for heating [14,29].

Because the use of tars as a source of chemicals was also considered, their composition was investigated. The elemental analysis of the tars is evident from Table 6. As expected, the addition of the waste tires affected their elemental composition – a higher waste-tire content in the initial mixture led to an increase in the carbon and hydrogen content at the expense of nitrogen and oxygen. Concerning sulfur, on the other hand, the addition of waste tires led to an increase in its content only in the case of the co-pyrolysis with coal B (from 0.51 up to 1.44 wt%); on the contrary, its content decreased in the co-pyrolysis with coal A (from 0.79 down to 0.47 wt%). These changes are a consequence of the different behavior of organically bound sulfur in waste tires during the co-pyrolysis with coking- and gas coal, as follows from thermogravimetric analysis.

3.5. Maltene characteristics

The results of the solvent separation of the tars are listed in Table 7. The mass balance shows that the tars obtained contained mostly maltenes (77–85 wt%) and many fewer asphaltenes (6–9 wt%). The content of the maltenes was always increased with the addition of waste tires in comparison with their content in the tar from coal alone, specifically at the expense of the asphaltenes, whose content decreased with the growing addition of an additive. The extraction residue (preasphaltenes) was mostly 10–12 wt%. Therefore, attention was paid to maltenes, which were

Table 8

The elemental analysis of the maltenes (dry ash free basis, wt%).

Sample	C	H	N	S	O_{dif}	$(C/H)^{at}$
A	85.39	8.91	0.90	0.38	4.42	0.80
+ 15% T	84.41	9.02	0.63	0.42	5.52	0.79
+ 30% T	86.34	9.51	0.49	0.28	3.38	0.76
+ 60% T	86.72	9.59	0.50	0.30	2.89	0.75
B	86.14	8.57	0.68	0.34	4.27	0.84
+ 15% T	86.70	9.29	0.41	0.88	2.72	0.78
+ 30% T	86.14	10.11	0.23	0.41	3.11	0.72
+ 60% T	87.43	9.88	0.36	0.49	1.84	0.74
100% T	88.01	10.60	0.13	0.36	0.90	0.70

at – atomic.

Table 9

The elemental analysis of the asphaltenes (dry ash free basis, wt%).

Sample	C	H	N	S	O_{dif}	$(C/H)^{at}$
A	74.40	6.51	1.80	1.39	15.90	0.95
+ 15% T	79.68	7.18	1.92	1.79	9.43	0.92
+ 30% T	80.20	7.93	1.18	1.81	8.88	0.84
+ 60% T	80.38	8.01	0.97	1.91	8.73	0.83
B	78.52	7.89	0.96	0.92	11.71	0.83
+ 15% T	80.51	7.15	1.03	1.77	9.54	0.94
+ 30% T	80.62	7.23	0.95	1.82	9.38	0.93
+ 60% T	79.35	6.92	1.57	2.40	9.76	0.96
100% T	82.54	7.75	1.07	1.96	6.68	0.89

at – atomic.

Table 10

The mass balance of the maltenes fractions (wt%). AM – maltene from tar A and BM – maltene from tar B.

Sample	AM	+15% T	+30% T	+60% T	BM	+15% T	+30% T	+60% T	100% T
Alkanes	11.4	19.7	35.7	31.6	15.3	17.0	24.3	25.6	42.1
Aromates	38.2	37.2	26.4	25.0	43.1	39.2	34.4	25.2	13.6
Polar compounds	45.2	33.6	37.9	43.4	40.3	41.1	38.1	42.3	41.9
Losses	5.2	9.5	0	0	1.3	2.7	3.2	6.9	2.4

thus a dominant component in all the cases. The elemental analyses of the maltenes and asphaltenes obtained are shown in Tables 8 and 9.

The atomic ratios of the maltenes (C/H)^{at} (Table 8) were significantly lower than those of the asphaltenes (Table 9), which indicates that the maltenes, as expected, had lower aromaticity than the asphaltenes. From Table 7 is evident that maltenes represent a quantitatively significant part of obtained tars which is a favorable feature of waste tires/coal co-pyrolysis, because the addition of maltenes rejuvenates old asphalt, improves its binding properties and restores its elasticity [30].

The maltenes obtained were subjected to chromatographic fractionation on a column. The results are shown in Table 10. With acceptable losses (most frequently below 5%), it may be said that the addition of waste tires significantly affected the composition of the maltenes, because, with the addition of T to coal A, the content of alkanes increased from 11 to 36 wt% and the content of aromates decreased from 38 to 25 wt%; the addition of T to coal B caused an increase in the content of alkanes from 15 to 26 wt% and a decrease in the content of aromates from 43 to 25 wt%. The content of polar compounds in the maltenes was high, but no trend associated with the addition of waste tires was observed.

3.5.1. Maltenes FTIR characteristics

Fig. 6 shows the FTIR spectra of the maltenes from tars B, B + 30% T and B + 60% T. The acquired spectra differed only slightly. Therefore, after a qualitative description, they were subjected to semi-quantitative evaluation to reveal the differences between them. The spectra of the analyzed maltenes comprise bands of aromatic and aliphatic structures in addition to the oxygenous functional groups and, for a more detailed description, the bands in the areas of 3100–2750 cm⁻¹ and 1830–1530 cm⁻¹ were separated

using the Gauss-Lorentz mixed function (Figs. 7 and 8, respectively). The bands found in the spectra and their assignments according to [31,32] are included in Table 11.

Briefly, the bands 3100–2750 cm⁻¹ are the aromatic and aliphatic C–H bonds; those at 3054 and 3014 cm⁻¹ are aromatic C–H stretching; at 2959 and 2874 cm⁻¹ methyl groups, at 2925 and 2854 cm⁻¹ methylene groups, and the band at 2897 cm⁻¹ methine groups (Fig. 7, Table 11). The bands at 1460, 1379 and 1317 cm⁻¹ include bending vibrations of CH₃ and CH₂, other bands of bending vibrations are in the area of 900–700 cm⁻¹ (out-of-plane bending). The individual bands correspond to the neighboring aromatic hydrogens on the aromatic ring: 875 cm⁻¹ (1H), 815 cm⁻¹ (2H), 786 cm⁻¹ (2H and 3H), 747 cm⁻¹ (4H).

The bands in the spectrum area of 1830–1530 cm⁻¹ are stretching vibrations of C=C bonds in aromatic rings; these vibrations correspond to the bands at 1637, 1616, 1596, 1584, 1521 and 1500 cm⁻¹ (Fig. 8, Table 11). Phenols and alcohols have a broad band at 3372 cm⁻¹ in their spectrum (Fig. 6) which are the stretching vibrations of hydrogen-bonded O–H bonds. The band at 3538 cm⁻¹ is O–H groups bound by a weaker hydrogen bond. The spectra of the analyzed maltenes contain further aliphatic and aromatic esters (1739 and 1724 cm⁻¹, resp.), carboxylic acids (1701 cm⁻¹), and quinones (1680 and 1654 cm⁻¹) (Fig. 8, Table 11) [31,32].

The increase in the content of the alkanes with the addition of waste tires is illustrated by the difference of the FTIR spectra of maltenes from tars B + 30% T and B + 60% T, obtained by subtracting the spectrum of the tar B maltene from the spectra of the tar B + 30% T maltene and the B + 60% T maltene (Fig. 9). The increase of the bands of the aliphatic C–H bonds in the subtracted spectra arises from the growth of the intensities of the bands between 3000 and 2750 cm⁻¹. The band intensities of the maltene from

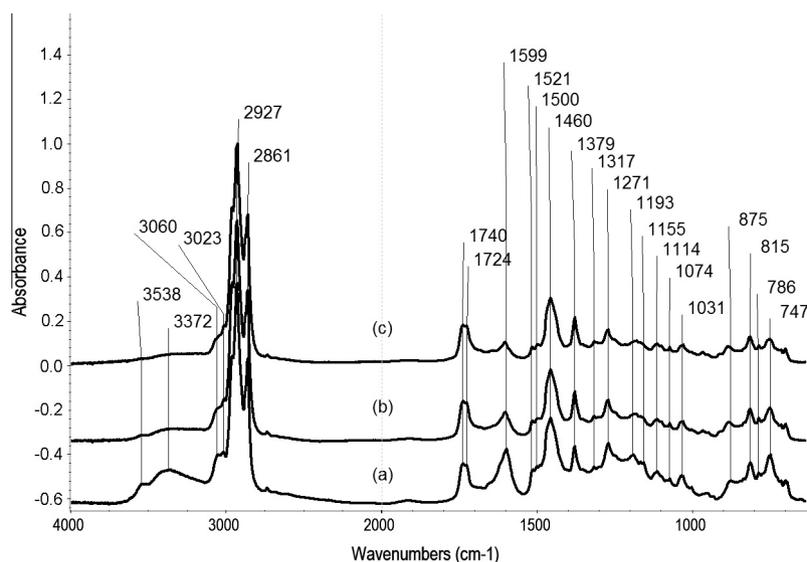


Fig. 6. The FTIR spectra of the maltene from tar B (a), the maltene from tar B + 30% T (b), and the maltene from tar B + 60% T (c).

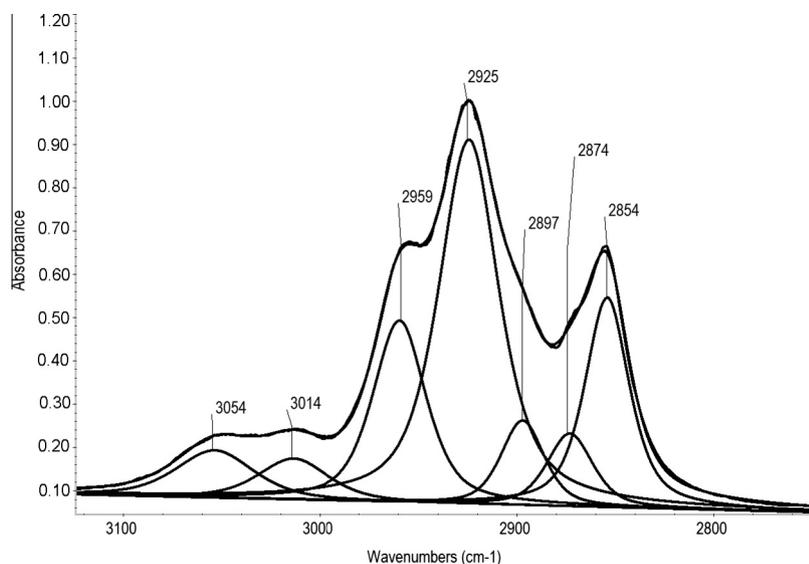


Fig. 7. The separation of the bands in the area 3100–2750 cm^{-1} of FTIR spectra of the maltene from tar B + 60% T. The FTIR spectra of the maltenes from tars B and B + 30% T were similar.

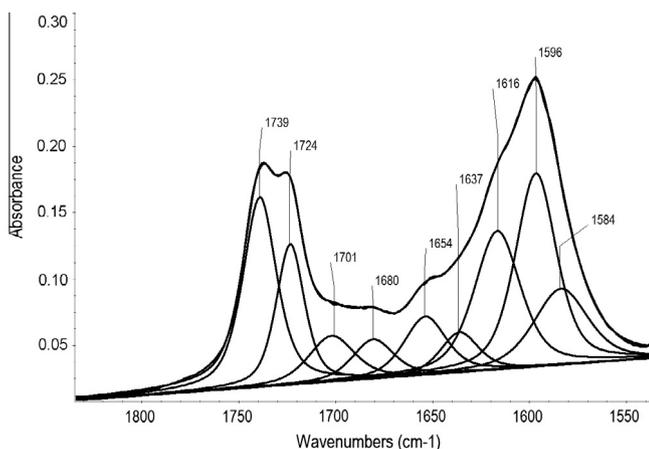


Fig. 8. The separation of the bands in the area 1830–1530 cm^{-1} of FTIR spectra of the maltene from tar B + 60% T. The FTIR spectra of the maltenes from tars B and B + 30% T were similar.

tar B + 60% T (Fig. 9, (b), bottom spectrum) are significantly higher as compared with those of the maltene from tar B + 30% T (Fig. 9, (a), upper spectrum). The content of aromatic structures in the maltene from tar B + 60% T (b) is approximately twice as low in comparison with the maltene from tar B + 30% T (a), as implied by the decrease of the intensities of the bands at 3056, 1597 and 900–700 cm^{-1} (namely at 748 cm^{-1}). The decrease in the hydroxyl groups content in the case (b) is evident from the decrease of the intensities of the bending O–H vibrations in the area 1300–1000 cm^{-1} as compared with (a).

The structural differences between the maltenes analyzed were studied based on the semi-quantitative parameters listed in Table 12. The parameter $H_{\text{ar}} = A_{\text{ar}} / (A_{\text{ar}} + A_{\text{al}}) * 100$ expresses maltene aromaticity, i.e. the relative representation of aromatic C–H bonds (A_{ar} – the area above the baseline of 3103–2998 cm^{-1} (aromatic vibrations), A_{al} – the area above the baseline of 2998–2770 cm^{-1} (aliphatic vibrations)). It arises from the data shown that the maltenes from tars B, B + 30% T and B + 60% T have a much higher content of aromatic substances than the maltenes from tars A, A + 30% T and A + 60% T. Maltene aromaticity decreases in both

Table 11

The assignment of bands in the infrared spectra of the maltenes from tars B, B + 30% T and B + 60% T (according to [31,32]).

Band position (cm^{-1})	Assignment
3538	$\nu(\text{O}-\text{H})$
3372	$\nu(\text{O}-\text{H})$ H-bonded
3054	$\nu(\text{C}-\text{H})_{\text{ar}}$
3014	$\nu(\text{C}-\text{H})_{\text{ar}}$
2959	$\nu^{\text{as}}(\text{CH}_3)$
2925	$\nu^{\text{as}}(\text{CH}_2)$
2897	$\nu(\text{CH})$
2874	$\nu^{\text{s}}(\text{CH}_3)$
2854	$\nu^{\text{s}}(\text{CH}_2)$
1739	$\nu(\text{C}=\text{O})$ in aliphatic esters
1724	$\nu(\text{C}=\text{O})$ in aromatic esters
1701	$\nu(\text{C}=\text{O})$ in COOH
1680, 1654	$\nu(\text{C}=\text{O})$ in quinones
1637, 1616, 1596, 1584, 1521, 1500	$\nu(\text{C}=\text{C})$ in aromatics
1460	$\delta_{\text{s}}(\text{CH}_2, \text{CH}_3)$, strong band
1379, 1317	$\delta(\text{CH}_3)$
1271, 1193, 1155, 1114, 1074, 1031	$\nu(\text{C}-\text{C})_{\text{ar}}$, $\nu(\text{C}-\text{O})$, $\delta(\text{O}-\text{H})$ in esters, phenols, ethers, alcohols
875	$\gamma(\text{C}-\text{H})_{\text{ar}}$ 1H adjacent
815	$\gamma(\text{C}-\text{H})_{\text{ar}}$ 2H adjacent
786	$\gamma(\text{C}-\text{H})_{\text{ar}}$ 2H and 3H adjacent
747	$\gamma(\text{C}-\text{H})_{\text{ar}}$ 4H adjacent

ν^{as} and ν^{s} – antisymmetric and symmetric stretching vibrations, δ – bending vibrations, γ – out-of-plane vibrations, ar – aromatic.

series A and B with the growing content of waste tires in the feedstock. It means that maltene aromaticity depends on the structure of the coal used, and, further, an addition of waste tires to coal significantly decreases the aromaticity of the maltenes obtained. Using the parameter I_{2925}/I_{2959} , which gives the ratio between the methylene- and methyl-band intensities, it is possible to compare the length/branching of the aliphatic chains or substituents. It is evident from the results that the length/branching are the highest in the case of the maltenes from tars from the pyrolysis of coals alone. The waste tires addition reduces the degree of substitution/branching of the maltenes obtained.

The relative representation of the hydroxyl groups was compared using the intensity of the I_{3351} band, which was related to the intensity of the significant band of the bending vibrations of the aliphatic C–H bonds at 1460 cm^{-1} (Table 11). From the data

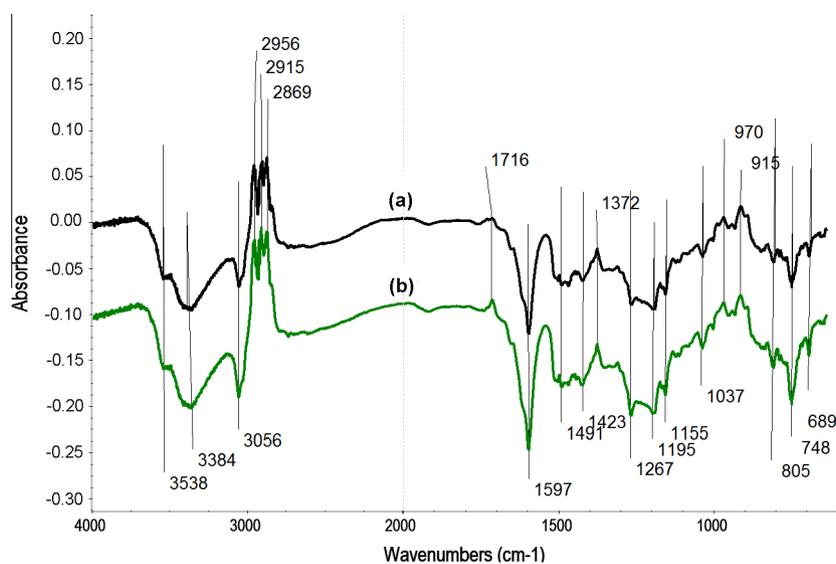


Fig. 9. The difference of the spectra obtained by subtracting the spectrum of the maltene from tar *B* from the spectrum of the maltene from tar *B* + 30% T (a) (upper spectrum) and of the maltene from tar *B* + 60% T (b) (bottom spectrum).

Table 12

Semi-quantitative ATR-FTIR parameters of the maltenes from tars A, A + 30% T and A + 60% T and from the tars B, B + 30% T and B + 60% T.

Sample	H_{ar}	I_{2925}/I_{2959}	I_{3351}/I_{1456}	$I_{C=O}/I_{1456}$	I_{1739}/I_{1456}	I_{1724}/I_{1456}	I_{1701}/I_{1456}	I_{1680}/I_{1456}
A	2.12	1.60	0.477	1.688	0.633	0.612	0.233	0.210
+ 30% T	1.07	1.46	0.264	1.573	0.613	0.585	0.200	0.176
+ 60% T	0.86	1.41	0.147	1.554	0.624	0.591	0.186	0.153
B	4.90	1.56	0.507	1.421	0.554	0.525	0.178	0.164
+ 30% T	1.87	1.41	0.186	1.615	0.633	0.604	0.205	0.174
+ 60% T	0.95	1.42	0.116	1.650	0.643	0.626	0.214	0.167

A_{ar} – the area above the baseline of 3103–2998 cm^{-1} (aromatic vibrations).

A_{al} – the area above the baseline of 2998–2770 cm^{-1} (aliphatic vibrations).

$H_{ar} = A_{ar}/(A_{ar} + A_{al}) * 100$.

I_{2925} and I_{2959} – the intensity of the band at the baseline of 2998–2770 cm^{-1} .

I_{3351} – the intensity of the band at the baseline of 4000–2200 cm^{-1} .

$I_{C=O} = I_{1739} + I_{1724} + I_{1701} + I_{1680}$.

$(I_{1739} + I_{1724} + I_{1701} + I_{1680})$ – the intensity of the bands at the baseline of 1830–1530 cm^{-1} .

presented in Table 12, it follows that the maltene from tar *B* has a higher content of hydroxyl groups than that from tar *A* and the content of hydroxyl groups in phenols and alcohols in maltenes decreases with the increasing addition of waste tires. The smallest amounts of O–H groups were found in the maltenes from the co-pyrolysis with the highest content of waste tires.

The total content of carbonyl groups is expressed by the sum of carbonyl group band intensities: $I_{C=O} = I_{1739} + I_{1724} + I_{1701} + I_{1680}$, which was again related to the intensity of the band of the bending vibrations of the aliphatic C–H bonds at 1460 cm^{-1} . It is evident from its values that the carbonyl content is higher in the maltene from tar *A* than from tar *B*, but the content of carbonyl groups decreases in series A; in series B, on the other hand, carbonyls increase with the growing waste tire content in the feedstock. It is evident from the results that the compounds containing carbonyl groups (esters, acids, quinones) do not exhibit the same trend with waste tire addition and their content depends rather on the structure of the coal used.

3.6. Characteristics of the gas

As already mentioned, a gasholder for the capture and subsequent analysis of the gases produced was incorporated in the apparatus in the series of experiments with coals A and B. The composition and properties of slow pyrolysis gases from 1 kg

of coal alone and waste tires alone as well as from their mixtures (15, 30 and 60 wt% of waste tires) are listed in Table 13.

It arises from Table 13 that the addition of waste tires to coal has increased the production of light hydrocarbons C_2 – C_4 (ethylene, ethane, propylene, propane, butanes). This increase was positively reflected in the physical properties of the gas, mainly in the higher heating value. With the addition of 60 wt% of waste tires, this value increased by about 8%. The content of more than 60 vol% of hydrogen in the gas is significant as well (obtaining of hydrogen-rich gas).

In more details, it further arises from Table 13 that slow co-pyrolysis of waste tires with coal yields a gas with a hydrogen content of 62–65 vol%. Such gas can be considered as hydrogen-rich. This result was achieved without a cracking agent. The reason is that waste tires contain 8 wt% of hydrogen, while coal only 5 wt% (dry ash free basis, Table 1). Therefore, an addition of waste tires to coal can increase the hydrogen content in the resulting gas in co-pyrolysis process without cracking agents, but this assumption is necessary to prove experimentally. We proved that a gas with 62–65 vol% of hydrogen is formed in co-pyrolysis (Table 13). The cause again is clear from Table 13. The pyrolysis of waste tires alone yields a gas with 52 vol% of hydrogen and 16 vol% of hydrocarbons C_2 – C_4 . In the presence of coal, a gas with 62–65 vol% of hydrogen and only 4–7 vol% of hydrocarbons C_2 – C_4 is formed. Therefore, in the presence of coal the cracking of the feedstock

Table 13

The composition and properties of pyrolysis gases from coals A and B and its mixtures with T. HHV – higher heating value, s – gas density, d – relative gas density (related to air).

Sample	Gas component (vol%)						HHV (MJ/m ³)	s (kg/m ³)	d (–)
	CH ₄	∑C ₂ –C ₄	H ₂	CO	CO ₂	N _{2,r}			
A	25.49	3.96	63.52	4.64	1.40	0.99	22.10	0.402	0.311
+ 15% T	23.95	4.65	64.13	4.90	1.56	0.81	22.23	0.408	0.316
+ 30% T	24.37	5.43	62.90	4.78	1.68	0.84	22.82	0.414	0.320
+ 60% T	23.94	7.38	61.07	4.59	2.18	0.84	23.90	0.456	0.353
B	26.29	3.28	63.96	4.31	1.28	0.88	21.86	0.388	0.300
+ 15% T	24.71	3.85	64.74	4.55	1.43	0.72	21.99	0.394	0.305
+ 30% T	25.13	4.50	63.64	4.44	1.54	0.75	22.57	0.400	0.309
+ 60% T	24.69	6.12	62.18	4.26	2.00	0.75	23.63	0.440	0.341
100% T	23.44	15.65	51.98	4.08	3.75	1.10	32.54	0.675	0.522

N_{2,r} – nitrogen resulting from the slow pyrolysis/co-pyrolysis reactions.

proceeds differently in comparison with the waste tires alone and provides more hydrogen and less hydrocarbons C₂–C₄. In our previous work [15], the influence of cracking of tar on hydrogen production was tested. The tar formed in co-pyrolysis in the first stage was cracked in the second stage using a cracking module at a temperature of 1200 °C. The resulting gas contained up to 82 vol% of hydrogen. In the case of waste tires, we tested a technologically simpler one-stage process which simultaneously provided the interesting products: smokeless fuel and maltenes.

Sulfur-containing gas components were below the detection limit. The changes in the sulfur content were observed in the solid and liquid products of slow co-pyrolysis, as previously discussed. From the utility properties presented in Table 13, it follows that the gas obtained using co-pyrolysis can be used for heating the actual pyrolysis unit or for the production of energy or heat.

On the whole, the results obtained indicate that the use of tar and smokeless fuel from co-pyrolysis is very real. The yields of smokeless fuel and tar are quite high; for smokeless fuel (coke), it is up to 57 wt%, for tar up to 30 wt% (Figs. 2 and 3, Table 5). The key features of coke (ash and sulfur contents, resistivity, porosity and LHV, Tables 2–4) clearly show that it can be used as a smokeless fuel or an industrial carbonaceous sorbent. Basic tar characteristics (ash content and LHV, Table 5) prove that it is suitable as a substitute fuel with LHV 36–41 MJ/kg. Alternatively, tar from co-pyrolysis can serve as a source of maltenes for repairing asphalt surfaces [30].

4. Conclusion

The treatment of waste tires through co-pyrolysis with two different types of coal, gas and coking coal, on a laboratory scale was investigated. The slow co-pyrolysis was carried out with mixtures containing 15%, 30% and 60% of waste tires. It was found that even with high additions of waste tires it is possible to obtain further utilizable cokes and tars in a high yield. The characterizations of the products have shown that the cokes (LHV 33–34 MJ/kg) and tars (LHV 36–41 MJ/kg) obtained can be used as heating ones. The gas obtained has an acceptable higher heating value, higher than e.g. the gas from the pyrolysis of lignite, and can be used as a source of heat and energy.

FTIR spectroscopy was used to analyze the maltenes obtained through the co-pyrolysis of coal with waste tires. The results lead to the following conclusions:

- the addition of waste tires to coal significantly decreases the aromaticity of the maltenes obtained;
- maltene aromaticity depends on the structure of the used coal;
- the addition of waste tires to coal reduces the degree of substitution/branching of the maltenes obtained;

- the content of hydroxyl groups in phenols and alcohols in the maltenes decreases with growing waste tire addition;
- the relative representation of carbonyl groups in the maltenes does not exhibit the same trend with waste tire addition and depends on the structure of the coal used.

Coke from co-pyrolysis can be used as a smokeless fuel or an industrial carbonaceous sorbent, tar is suitable as a substitute fuel or it can serve as a source of maltenes for repairing asphalt surfaces.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.enconman.2016.02.069>.

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