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Characterization of products from pyrolysis of coal with the addition of polyethylene terephthalate

Martina Havelcová^{a,*}, Olga Bičáková^a, Ivana Sýkorová^a, Zuzana Weishauptová^a, Ahmed Melegy^b

^a Ústav struktury a mechaniky hornin AV ČR, v.v.i., V Holešovičkách 41, 182 09 Praha 8, Czech Republic

^b Department of Geological Sciences, National Research Centre, Dokki, Cairo 12622, Egypt

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ABSTRACT

Sub-bituminous coal and admixtures with polyethylene terephthalate were co-processed. The main objective of the study was to produce coke and to determine how ratios of input raw materials affected its structure. All main product yields (coke, tar, gas) were characterized by petrological and chemical methods. The addition of PET to coal in coking blends had impacts on coke yield, its true density, volume contents of fissures and mean reflectance, volume and surface of pores, and the formation of aromatic structures in the coke. However, the properties of coke and gas did not change significantly until 20% of the coal had been replaced with PET bottles in the coal charge.

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1. Introduction

Effective recycling of plastic waste is important for protection of the environment and natural resources, and often has an economic impact. Plastic is one of the most widely used materials in the world. It is advantageous, inter alia, for its multiple recycling options. Although the separation of plastics from general waste, and its recycling, is growing, the amount of unusable plastic waste is still alarming. New ways of processing polyethylene terephthalate (PET) are continually being sought because this plastic is a valuable resource, as demonstrated by its synergism with other materials [1,2].

Recycling processes can be performed in several ways, from material and feedstock recycling to energy and chemical recycling. Methods of disposal of waste beverage PET containers all have disadvantages. Landfilling is problematic due to the low biodegradability of the plastic material. Combustion in incinerators or cement kilns saves fuel, but flue gases may contain toxic substances [3,4]. Chopping of sorted PET products into small flakes requires special equipment since the amorphous PET is flexible and resists crushing and cutting (carried out under water). The quality of PET flakes is particularly affected by the nature of contaminating substances [5]. Flakes have to be washed to remove impurities and then must be dried, which in turn increases energy consumption [1]. Another option is to process PET products into

terephthalic acid and ethylene glycol by chemical depolymerization using microwave energy [6]. These components can then be recycled for the production of pure PET.

Among feedstock recycling are methods based on the combined processing of waste plastics and coal, especially their common pyrolysis [7–11]. It is the least capital intensive process with low operating costs. This is a thermal process, where the absence of air leads to decomposition of the organic material to low molecular weight substances and a solid residue. Products of pyrolysis are coke (char), liquid substances and pyrolysis gases. The quantity and characteristics of the products depend on the conditions under which pyrolysis is carried out, and on the characteristics of the input materials [12–14]. Generally, low temperature processes enhance the development of liquid products, whereas high temperatures promote the formation of gaseous products.

Joint processing of waste plastics with coal, biomass or oil shale, generally co-processing, has been studied extensively [15,16]. Co-processing, on the one hand, offers the possibility of reducing the levels of plastic waste, and on other hand, reveals potential for use in the development of quality products. Liquid products may be further processed e.g. in the petrochemical industry [17]. The solid pyrolytic residue can be activated at high temperature (925 °C), with carbon dioxide, to obtain a low-cost substitute for activated carbon that purifies water polluted with phenols or polycyclic aromatic hydrocarbons (PAHs) [18,19].

Waste plastics have a high calorific value (polyethylene, about 46 MJ/kg; polyethylene terephthalate, about 23 MJ/kg), suggesting their possible use in energy generation, especially by co-processing with lower quality lignite, whose reserves are still adequate. A portion of coal (20%) may be replaced by plastics [20].

* Corresponding author at: Institute of Rock Structure and Mechanics, Geochemistry, V Holešovičkách 41, 18209 Prague, Czech Republic.

E-mail address: havelcova@irms.cas.cz (M. Havelcová).

Çit et al. [7] investigated the effect of varying proportions of polypropylene and polyethylene terephthalate in a mixture with lignite, in the temperature range from 400 to 700 °C. They found that a higher temperature and slower heating of the charge significantly increased the yield of gas and tar at the expense of solid product. A similar conclusion was reached by Mastral et al. [21] and Chunmei et al. [22]. Although other previous findings [23,24] have demonstrated that the addition of plastic wastes, particularly PET, reduced the caking ability of coal, the mechanism of this effect has not been explained.

The quality of coal determines, to a large extent, the quality of the resulting coke. The best coals for coke making are medium-volatile bituminous coals [25], but due to their scarcity and high price, coking coals of this rank are typically used as a base component in blends to achieve the required coke quality and quantity. In practice, coals of differing rank and other supplements of various chemical properties are added, and the usable coal range is broadened. Such blending also leads to the use of coals that would otherwise not be used individually in coke making, because they do not have the desired chemical and coking properties. The blends for coke production must complement each other. PET could be a suitable material. Co-processing also solves the recycling problem of plastic waste by methods other than mechanical, chemical and energy recovery processes for minimizing environmental damage. This alone is grounds for investigating the impact of PET waste on the chemical and physical properties of coke. Besides others, volatile content is used to select coals for coke blending. Volatile constituents of the coal (water, coal-gas, and coal-tar) are released by coking, and the lower the volatile matter in coal, the fewer by-products are produced. The carbon content of coal is also essential in coke making because it forms the mass of the actual coke. Coals with higher carbon content (lower oxygen content) and ordered structures produce cokes with highly ordered and unreactive carbon in graphitic structure.

Within the framework of an international project, pyrolysis of PET with coal from the Maghara area in Egypt was investigated. The main objective was to produce coke and determine how the ratio of initial raw materials affects its structure for further use. Chemical properties of coke are probably of lower significance than physical properties in the efficient operation of a blast furnace but they also have informative value on the quality of the prepared coke. Basic characterization of liquid and gaseous pyrolysis products was also carried out as these are also potentially valuable products with possibilities for future use.

2. Material and methods

2.1. Pyrolysis ingredients

The raw material for pyrolysis was Jurassic sub-bituminous coal from the Safa Formation in the Maghara Area from the northern Sinai in Egypt. The Maghara coals are composed primarily of vitrinite with significant amounts of liptinite macerals: sporinite, cutinite, resinite and liptodetrinite, with low contents of inertinite macerals and mineral matter with traces of quartz, calcite, pyrite, anhydrite and hematite. The high sulphur contents and the relatively high proportion of pyritic sulphur suggests a possible marine transgression after deposition of the precursor peat. The Maghara coals vary from sub-bituminous to highly volatile bituminous coals that appear to be oil prone and are hydrogen rich [26–28]. The basic characteristic of the raw coal is shown in Table 1 and agrees with published data.

In addition to coal, waste PET was used to prepare the coke. Plastic bottles of packaged water were the source of PET, whose production is still high. The elemental composition of PET was 4.25 wt.% hydrogen, 61.27 wt.% carbon and 34.48 wt.% oxygen. PET bottles do not contain sulphur or nitrogen. The bottles were first manually cut into smaller pieces, and then crushed to the desired particle size of <3 mm by knife mill. The coal was ground in a jaw crusher, and was then sieved

Table 1
Parameters of the coal.

Parameter		Maghara
W ^a	[wt.%]	1.8
A ^d	[wt.%]	15.4
C ^{daf}	[wt.%]	75.6
H ^{daf}	[wt.%]	6.6
N ^{daf}	[wt.%]	1.3
S ^{daf}	[wt.%]	4.1
O ^{daf}	[wt.%]	12.4
V ^{daf}	[wt.%]	57.9
FC ^{daf}	[wt.%]	42.1
Q _s ^d	[MJ/kg]	26.7
R _r	[%]	0.43
Vitrinite	[vol.%]	61.6
Liptinite	[vol.%]	26.6
Inertinite	[vol.%]	2.1
Minerals	[vol.%]	10.1

a—as received, d—dry basis, daf—dry and ash-free basis; W, A—moisture and ash content; C, H, N, S, O—element content (oxygen content by difference); V—volatile matter; FC—fixed carbon; Q_s—gross calorific value; R—reflectance.

to a fractional size of 0.5–3 mm. Mixed cokes were prepared from blends of coal with PET in proportions of 5, 10, and 20% (designated as 95/5, 90/10 and 80/20).

2.2. Pyrolysis unit

The samples of Maghara coal alone and their PET admixtures, in ratios indicated above, were heated in a laboratory pyrolysis unit. The weights of input charge were constant at 100 g. The prepared charge mixtures were pyrolysed inside a quartz reactor (about 60 mm inner diameter and 500 mm in length) on a stationary bed. The quartz reactor was placed in a vertical electric resistance furnace. Heating of the furnace was controlled by a programmable furnace heating APOSYS 10 with the desired temperature regime. The input mixtures were heated at a heating rate of 5 °C/min up to a final temperature of 900 °C with a 30-minute dwell time at this temperature. The process was conducted under own atmosphere without access of air under a slight vacuum (from 95,325 to 98,792 Pa). The ambient temperature was between 18 and 20 °C. Both parameters were recorded throughout the experiment. Volatile products were released during thermal decomposition. The volatile products were carried from the reactor through a vertical cooler filled with ethanol as the cooling agent, and cooled to a temperature of –6 °C. Liquid products were captured in a flask. The pyrolysis gases were collected in a gas holder with a capacity of 130 dm³. The gas holder was equipped with a circulation loop and a continuously operating infrared gas analyzer (Teledyne Analytical Instruments, Model 7500), through which changes in the concentration of the generated gaseous components CO, CO₂, and CH₄ were monitored. The concentrations of gaseous components, all temperatures and gas volumes were continuously recorded on a PC every 3 s. Some losses, (5–6 wt.%), incurred during pyrolysis, were caused by leakage of the system, especially during gas collection. Increasing proportions of PET (Fig. 1) in the sub-bituminous coal admixtures did not influence significantly the total amount of gas produced.

Pyrolysis of PET bottles alone gave different results compared with pyrolysis of coal alone and coal-PET admixtures with up to 20 wt.% PET bottles. The majority of volatiles from the PET, almost 100 wt.%, were released during pyrolysis in the temperature range from 350 to 470 °C, with a maximum at 425 °C (Fig. 1a). The decomposition of the mixture of coal with PET bottles (80/20) occurred more slowly, as can be seen from the TG curve (Fig. 1b), and although decomposition began at a similar temperature (340 °C) as the decomposition of PET alone, it was complete at a temperature of 544 °C with a main peak at 406 °C and a small second peak at 435 °C.

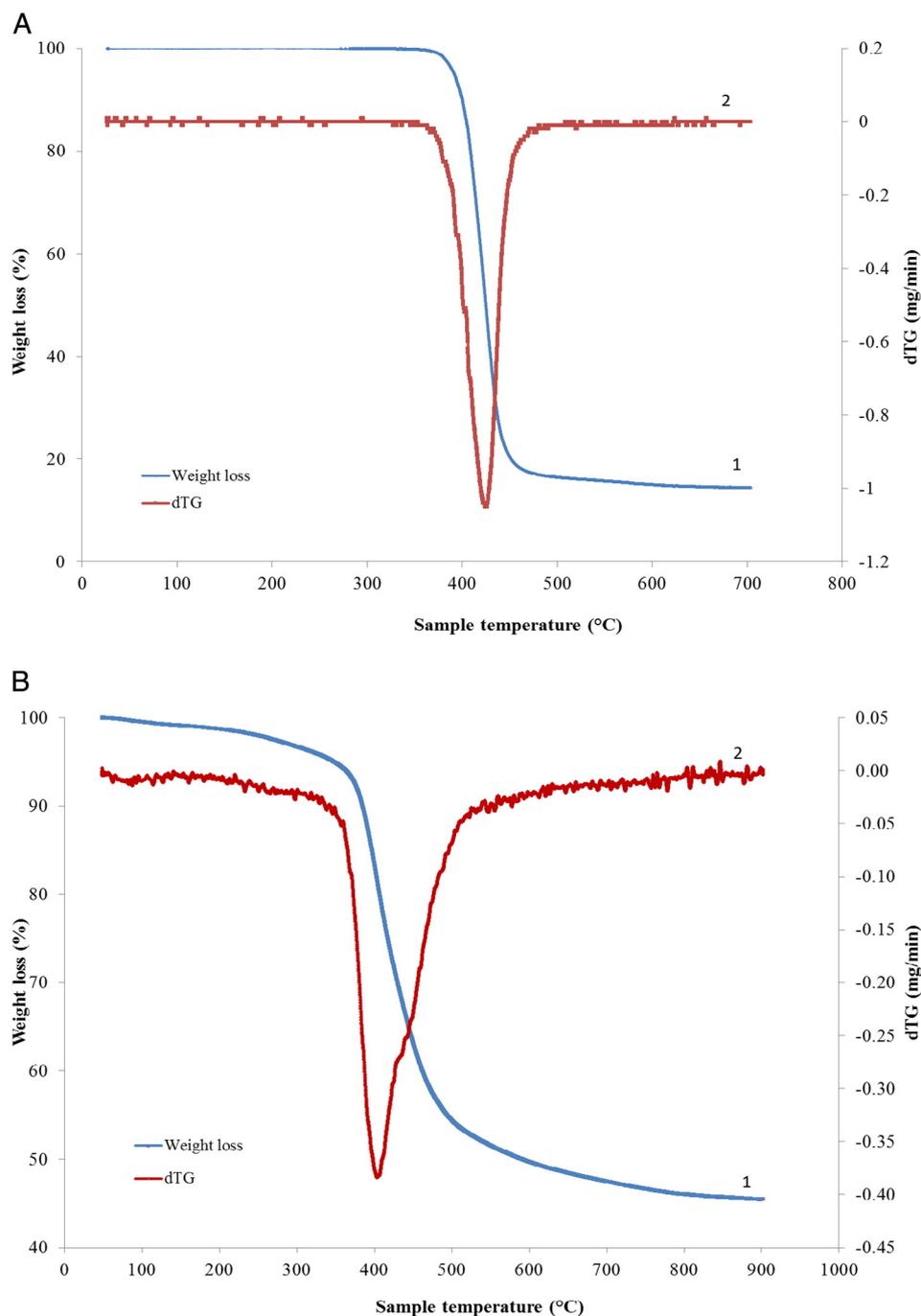


Fig. 1. Thermal decomposition of PET bottles (a), and the admixture with 20 wt.% of PET bottles (b). 1 – Weight loss (%) (blue), 2 – dTG curve (red).

2.3. Product analysis

Samples (raw coal, prepared cokes) were crushed, dried and powdered before chemical analysis. Proximate and ultimate analyses were carried out using standard procedures: moisture by ISO 5069-2:1983, ash by ISO, 1171:2010, and total carbon by ISO 609:1996. The elemental organic composition was determined using a carbon, hydrogen, nitrogen, sulphur/oxygen micro-analyzer CHNS/O (Thermo Finnigan Flash FA 1112). The oxygen content was calculated differentially to 100%.

Polished sections were prepared from the coal and coke samples. Petrographic analysis included determination of rank expressed by vitrinite reflectance, and maceral composition on polished coal grain sections using a NIKON optical microscope with a LUCIA (Laboratory

Imaging) image analysis system for determination of vitrinite reflectance with immersion objective, 40× magnification and oil immersion with refractive index $n = 1.518$ according to ISO 7404:2009. Maceral composition of vitrinite, liptinite and inertinite macerals in the sub-bituminous coal from the Maghara basin (ISO 7404, 2009), and morphology and optical properties of coke walls and pores [29] were determined using an Olympus microscope with the Craig system of immersion objectives with 40× and 100× magnification and PELCON point counter.

The specific surface areas of solid samples were determined by applying the Brunauer, Emmet and Teller (BET) isotherm to data acquired by N_2 adsorption at -197 °C [30]. The distribution of mesopores was determined according to Barrett, Joyner, Halenda [31]. Microporous structural parameters were calculated from the CO_2 isotherm measured at a temperature of 25 °C up to a relative pressure of 0.015 by applying

the Dubinin and Medek equations [32,33]. N₂ adsorption isotherms were measured using Surfer (Thermo Scientific) and CO₂ adsorption isotherms were measured using IGA 100 (Hiden Isochema). Real helium density was estimated by means of a Multipycnometer (Quantachrom).

Pyrolytic gases were analyzed using a GC-analyser (Agilent 6890 N) equipped with thermal conductivity (TCD) and flame ionization (FID) detectors. Carbon oxides were separated at a temperature of 40 °C on an HP-MOLSIV molecular sieve capillary column for CO, and a GS-Gaspro column for CO₂, O₂, N₂, and were analyzed on an HP-MOLSIV capillary column (40 °C) with helium as carrier gas (5 cm³/min) and TCD. The content of O₂, N₂, and controlled determination of CH₄ were also performed on a capillary column with a molecular sieve. Methane and others hydrocarbons (C₂–C₄) were assessed on a GS-Gaspro capillary column (60 °C) using FID detection. Hydrogen content was evaluated on an HP-5 capillary column (40 °C) with TCD detection.

Powdered cokes were Soxhlet extracted with dichloromethane, and solutes were analyzed by gas chromatography using a Thermo DSQ II–Trace Ultra GC equipped with a CP5 capillary column (30 m × 0.25 mm × 25 μm). After splitless injection, a temperature program was started from 40 to 300 °C at 5 °C min⁻¹, with helium as the carrier gas. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analyses were performed using a CDS Pyroprobe 5150 directly connected to a Thermo DSQ II–Trace Ultra GC. Approximately 5 mg of a coke sample were pyrolysed at a temperature of 750 °C for 20 s. The Py-GC interface was kept at 300 °C. The CP5 capillary column was used for separation of pyrolysis products. The temperature program was set from 40 to 300 °C at 10 °C min⁻¹, with helium as the carrier gas. Mass spectra were recorded in the electron impact mode (70 eV) in the range 40–500 *m/z*. Pyrolysis was performed on samples without any pretreatment. Identification of compounds was based on a comparison of spectra from the National Institute of Standards and Technology mass spectral library.

2.4. Quality assurance

All experimental series were repeated three times and the precision of analytical results was assessed by undertaking replicate measurements of the same sample.

The calibration curves for pyrolytic gases were constructed with gas concentrations covering 0–100 μL and using 20 μL syringe. Three replicates were conducted. Gas cylinders of C_xH_x mixtures, CO, CO₂, N₂ and H₂ were obtained with manufacturer claimed purities of >99.5% (Linde). Once a linear calibration curve was obtained, the data was then extrapolated to calculate the concentration of gas in samples. The content of an individual compound in GC/MS and Py-GC/MS was expressed as the relative abundance in percentage of the total area: the area of the individual peak was divided by the total area of the integrated total ion current. Assessment of chromatographic peaks was done according to their retention times, mass spectral data and peak areas. The GC/MS method was validated by using a standard reference material (NIST SRM 1597). The Py-GC/MS system was tested with three reference materials (Kraton 1107, Nylon, and Polyethylene).

Uncertainty of analytical measurement can comprise, in general, many components. In this study the sources of uncertainty taken into consideration were: sample preparation (pyrolysis, extraction, dissolution), the preparation of standard solutions (dissolution), and analytical procedures (instrument, calibration). The corresponding expanded uncertainty was calculated using a coverage factor *k* = 2, equal to Student's distribution at the 95% confidence level when *n* < 30 and it was <0.7% for calorific values and at maximum 9% for the other measurements (moisture and ash content, element content, volatile matter). Relative standard deviations (RSD) was used as parameter associated with analytical uncertainty that characterises the dispersion of the values from repeated determinations of analytes (*n* = 3) that could reasonably be attributed to the measurand (parameters of coke porosity, chemical composition, composition of gases). The results of

the light reflectance measured at 500 points were expressed as the mean values of the reflectance and standard deviation. Standard deviation of the mean vitrinite reflectance *R_r* = 0.43% of the raw coal was σ = 0.05. Standard deviation of the mean reflectance values of the coke walls ranged between 0.48 and 0.65. The maceral composition of coal and coke was expressed as a percentage of the individual component based on 1000 identified points in each sample.

3. Results and discussion

3.1. Mass balance

The influence of PET on the distribution of pyrolysis products was evaluated within the whole process (Fig. 2). As the reference experiment, pyrolysis of the original coal from Maghara without any addition of PET was carried out (100/0).

The yield of coke, when PET was added to the coking blend, decreased from 55.0 to 51.0 wt.%. As expected, the increasing addition of PET to the coal charge increased the formation of liquid and gaseous products; however the liquid fraction increased by only 5%. The results are different from other published results [34], where a coking mixture of Maghara coal with 20 wt.% of mixed plastics (multi-component plastic waste with polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinylchloride) with a high content of carbon and hydrogen increased tar production by 30% with a simultaneous 16% decrease in the yield of coke.

The organic and aqueous phases were separated from the liquid fraction by azeotropic distillation with *n*-hexane at 80 °C (Fig. 2). Then *n*-hexane was distilled off at 105 °C. The water content ranged from 3 to 10 wt.%. The tar increment was observed after water separation when 5 and 10 wt.% of PET was added to the coal charge, while a higher proportion of PET (20 wt.%) caused a decrease in the tar obtained. This was caused by the high oxygen content in coal as well as in PET (34.48 wt.%), which resulted in its transformation into water and oxygen gas compounds.

3.2. Basic cokes characteristics

Generally, coke is comprised predominantly of elemental carbon, organized in a micro-porous polycrystalline matrix consisting of non-graphitic structures in which possible mineral impurities are incorporated [35]. The coke matrix is made up of interconnected polyaromatic units which, during carbonization, are oriented in parallel. In an imperfect state, the matrix pores are filled firstly by mineral substances, and secondly, by hydrocarbon residues that are trapped inside the coke structure, thus forming a non-porous portion of the final coke [36]. Pyrolysis conditions of coking as well as starting materials have an impact on the quantity and nature of these residues. The better the carbonization process, the greater is the aromaticity of the resulting coke. An ideal coke would actually have a perfectly ordered structure [37].

The prepared cokes have high carbon contents but this content decreased with increasing addition of PET to the coking blend (Table 2).

Changes in nitrogen and sulphur were negligible. An increase in oxygen content in the cokes prepared from blends compared to that prepared from raw coal alone was observed. This suggests that addition of PET promoted the inclusion of oxygen functional groups in the coke matrix and therefore had little effect on the content of sulphur and nitrogen heteroatoms. This effect however was not true for the highest PET addition of 20 wt.%. This can be attributed to a stronger effect on the development of fluidity and on the physical processes of softening and resolidification during carbonization [13]. Yields of volatile matter from the cokes increased a little with the addition of PET to the coking blend.

The H/C atomic ratios of cokes are generally very low (Table 2) as compared with raw coal (1.13) and the PET (0.8) H/C ratio is considered to reflect the degree of aromaticity of the coke [38]. It is <1 for polycyclic

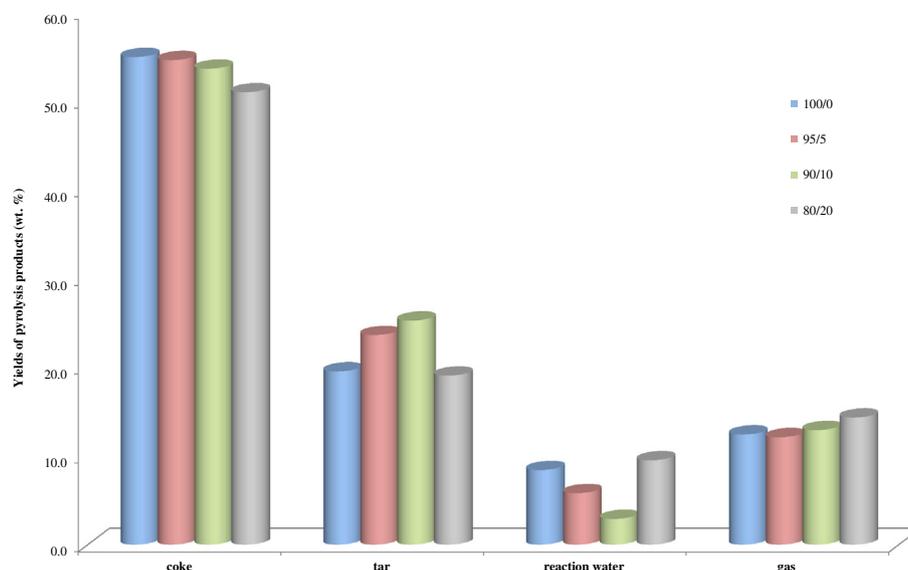


Fig. 2. Evolution of pyrolysis and co-pyrolysis products from coal with PET.

aromatic hydrocarbons and decreases with an increasing number of condensed aromatic rings. The low H/C ratios for prepared cokes suggest that the cokes constitute bulky molecules with a high proportion of polycrystalline carbon matrix. The H/C ratios of all cokes were almost the same; the lowest H/C ratio was from coke prepared from the blend of 90% coal and 10% PET. This means that coking of coal blends results in a decreasing H/C ratio of the coke because large amounts of hydrogen enter the gas phase during preparation (Fig. 2, Table 5).

3.3. Petrographic structure of cokes

Laboratory-prepared cokes represent isotropic and dense-to-porous materials whose resistance and optical properties decrease with increasing levels of plastic wastes. The isotropic character is influenced by a low ranking of the feed coal that has very weak caking properties and by the addition of PET plastic waste. According to Díez et al. [23], addition of PET plastic waste of up to 10 wt.% decreased the fluidity of coal, the anisotropic texture of coke, and produced mainly isotropic carbon material.

Results of microscopic textural analyses of laboratory-prepared coals are summarized in Table 3. Average reflectance values (R %), measured on homogenous coke matter with respect to coke walls, decreased from

5.81% in coke 100/0 to 5.44% in sample 80/20. Coke walls formed more than half of the coke matrix volume, and thickness, composition and properties varied. They are formed by a small portion of completely fused vitrinite (Fig. 3A) with the disappearance of grain boundaries. The discontinuous phase consisted mainly of infusible (Fig. 3B) and degassed (Fig. 3C) coal matter, including a low proportion of inertinite macerals and minerals with distinct boundaries and contacts between individual grains (Fig. 3C). It was found that increasing addition of PET decreased the fraction of fused and partly fused matter (Fig. 3A), and increased the content of degassed (Fig. 3B) and unfused matter (Fig. 3C). The remnants of inertinite structures, quartz and thermally altered clay minerals, pyrite, and carbonates (Fig. 3C, D) were relatively consistent in all prepared cokes.

Pores and fissures are an integral part of the coke. Their formation is associated with release of volatiles during carbonization phases of coal and PET waste. The volume of pores larger than 100 μm , formed as bubble-like structures generated by gas evolved in the molten coal during carbonization (Fig. 3A), decreased with increasing addition of PET. Conversely, the volume of pores after degassing of cell structures composed of liptinite macerals (sporinite, resinite, and liptodetrinite), increased (Fig. 3B). Fissures that are expressions of shrinkage occurring during and after solidification of the semicoke (Fig. 3D) also increased. The microscopic studies showed that to maintain the quality of coke prepared from sub-bituminous coal from the Maghara deposit, the addition of 5 wt.% PET waste was optimal because reflectance values and volumes of pores were only slightly decreased.

Table 2

Composition of the prepared cokes.

Coke		100/0	95/5	90/10	80/20
SOM	[wt.%]	1.3	1.1	0.9	0.9
W ^a	[wt.%]	2.2	2.5	1.9	2.1
A ^d	[wt.%]	27.8	28.2	26.4	26.4
C ^{daf}	[wt.%]	90.9	88.0	78.2	86.3
H ^{daf}	[wt.%]	0.9	0.7	0.6	0.8
N ^{daf}	[wt.%]	1.4	1.7	1.2	1.3
S ^{daf}	[wt.%]	0.8	0.7	0.5	0.4
O ^{daf}	[wt.%]	5.9	8.9	19.4	11.2
V ^{daf}	[wt.%]	2.7	2.8	2.7	3.9
FC ^{daf}	[wt.%]	97.3	97.2	97.3	96.2
Q _g ^d	[MJ/kg]	23.2	23.5	24.4	24.3
H/C		0.12	0.10	0.09	0.11
Yield	[wt.%]	55.0	54.6	53.6	51.0

a—as received, d—dry basis, daf—dry and ash-free basis; SOM—soluble organic matter; W, A,—moisture and ash content (oxygen content by difference); C, H, N, S, O—element content; V—volatile matter; FC—fixed carbon; Q_g—gross calorific value.

Table 3

Microscopic textural characteristics of the cokes.

Parameter	100/0	95/5	90/10	80/20
Reflectance R (%)	5.81	5.69	5.54	5.44
Σ Walls (vol.%)	53.7	55.2	59.8	65.0
Fused matrix (vol.%)	19.4	5.4	4.4	3.9
Degassed matrix (vol.%)	14.1	17.3	20.1	19.8
Unfused matrix (vol.%)	7.8	18.0	21.4	27.4
Inertinite (vol.%)	0.6	0.5	0.7	0.8
Minerals (vol.%)	13.8	14.0	13.2	13.1
Fissures (vol.%)	3.4	3.9	5.8	8.3
Σ Pores (vol.%)	42.9	40.9	34.4	26.7
Pores after melting of coal mass (vol.%)	21.7	19.4	14.1	8.4
Pores after degassing of coal mass (vol.%)	21.2	21.5	20.3	18.3

The values in bolds indicate the proportion of the total values.

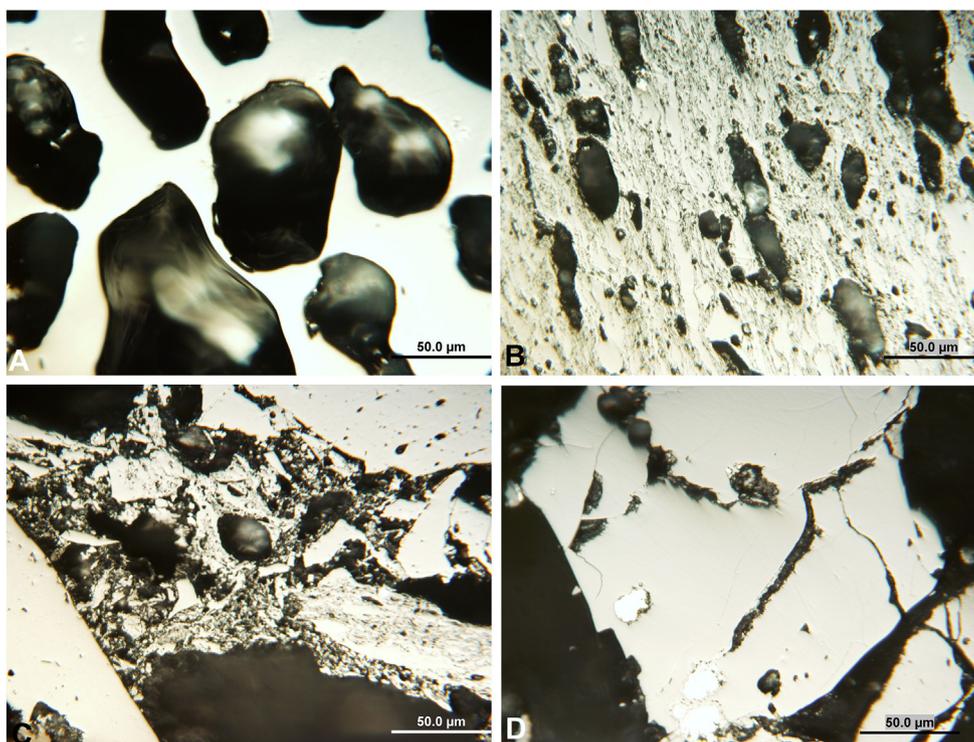


Fig. 3. Photomicrographs of the basic structures of coke from co-pyrolysis of sub-bituminous coal and PET plastic waste. (A) Pores and isotropic coke walls from fused vitrinite (telovitrinite) mass in coke sample 100/0. (B) Pores and isotropic coke walls from degassed mixture of vitrinite (detrovitrinite) and liptinite mass in coke sample 95/5. (C) Discontinuous isotropic coke wall (coke sample 95/5) with distinct boundaries between unfused, slightly degassed vitrinite grains and porous detrital matter composed of remnants from detrovitrinite, inertodetrinite, macrinite and clay minerals. (D) Fissures in isotropic unfused vitrinite mass with light inclusions of altered pyrite.

3.4. Characterization of porous structures in coke

The porous structure of prepared cokes, which has considerable importance for mechanical strength and reactivity to CO_2 , was influenced firstly by the level of volatiles releasing during plastic and post-plastic stages of carbonization, and secondly by the amount of the resulting char [36]. Analytical results of coke porosity are presented in (Table 4).

Specific surface area, micropore volume ($r = 0.4\text{--}1.5\text{ nm}$), surface of micropores, and mesopore volumes ($r = 1.5\text{--}30\text{ nm}$) are the main textural parameters that were determined. The pore radii ranges of micro- and meso-pores were in agreement with IUPAC classification [39]. The result of addition of PET to the coking blends was the reduction of true density, which fell by 4.6% in 80/20 coke. The addition of PET increased the specific BET surface area, moving in a very narrow range between $2.3\text{ m}^2/\text{g}$ and $3.4\text{ m}^2/\text{g}$; this, however, did not reflect the quantity of PET. The distribution of mesopores, according to [31], showed that with increasing PET in coking blends, the total volume of mesopores increased while shifting towards lower radii, especially in sample 80/20 (Fig. 4). This sample also showed the lowest volume and surface of micropores. The addition of 20% PET to the coking blend caused a

narrowing of larger mesopores and a restriction of access to micropores. The microporosity of the cokes corresponded with the continuity of the microporous structure of the original coal that was not destroyed by temperature or pressure [40]. All prepared cokes could be used directly, or after activation as sorbents, particularly of gases.

3.5. Chemical composition of cokes using GC/MS and Py-GC/MS

To determine the composition of the soluble part of the cokes, dissolved fractions were analyzed. Solubility of the cokes in dichloromethane (SOM) was low (Table 2) confirming their aromatic structure.

Alkanes (51–21%), fatty acids and their esters (45–36%) were identified in the extracts together with polycyclic aromatic hydrocarbons (PAH), which formed 6–27% of the total content. The relative contents of alkanes, fatty acids and their esters decreased with increasing proportions of PET in the coking blends. Conversely, the relative contents of

Table 4
Parameters of coke porosity with and without PET.

Sample	ρ_{He} (g/cm^3)	S_{BET} (m^2/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	S_{micro} (m^2/g)	E (kJ/mol)	r_{mode} (nm)
100/0	2.0862	1.5	–	0.1281	346	9.6902	0.67
95/5	2.0339	2.3	0.0040	0.1258	345	10.1930	0.66
90/10	2.0208	3.4	0.0042	0.1218	338	10.5350	0.65
80/20	1.9898	2.7	0.0060	0.1070	299	10.7129	0.65

ρ_{He} – helium density (RSD < 0.1), S_{BET} – specific surface area (RSD < 10), V_{meso} – volume of mesopores (RSD < 10), V_{micro} – volume of micropores (RSD < 1), S_{micro} – surface area of micropores (RSD < 1), E – characteristic energy (RSD < 1), r_{mode} – modus of micropores radii (RSD < 1), RSD – relative standard deviation in %.

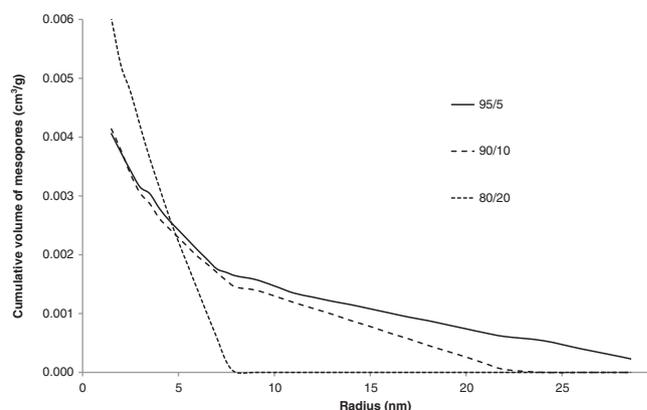


Fig. 4. Cumulative curves of mesopore volume distribution.

PAHs in coking blends increased with increasing PET (Fig. 5a). Phenanthrene (compound with 3 aromatic rings) was dominant in all extracts except sample 80/20 (Fig. 5b). A large difference was evident because in the 80/20 extract, compounds containing four, five and six aromatic rings (pyrene, benz(a)anthracene, chrysene, perylene, benzo(a)pyrene, benzo(e)pyrene, benzo(ghi)perylene), and particularly higher levels of benzofluoranthenes were identified. The RSDs of the relative abundances were in a range of 0.7–2.1%, which meets the requirements for repeatability.

The type and level of identified PAHs in samples of coke extracts is a reflection of the composition of the solid coke. From a less compact coke with an imperfectly organized matrix, PAHs with higher levels of condensed aromatic rings were not rigidly integrated into the polycrystalline matrix during the pyrolysis coking process [34].

Generally, the heating of coke during Py-GC/MS analysis leads to cleavage of chemical bonds within the macromolecular structure and the development of a mixture of compounds, indicating specificity in the macromolecule. The simpler hydrocarbons are identified by analytical pyrolysis the lower the content of nonporous structures and the more perfect the polycrystalline carbon matrix is. The ideal coke would therefore not have any identifiable products detectable by Py-GC/MS under the given conditions.

Compounds identified in pyrograms of the cokes were alkanes, alkenes, benzene, alkyl benzenes, polycyclic aromatic compounds and their substituents, and a few heterocompounds (Fig. 6). The increasing contribution of PET in coking blends had an impact on the proportion and level of hydrocarbons; simple pyrograms of cokes from samples 80/20 and 90/10 had no alkylnaphthalenes, naphthalene or heterocyclic compounds among the resulting compounds. Conversely, polycyclic aromatic hydrocarbons were enriched, but their representation was different among coke samples. Sample 80/20 had PAHs with a higher

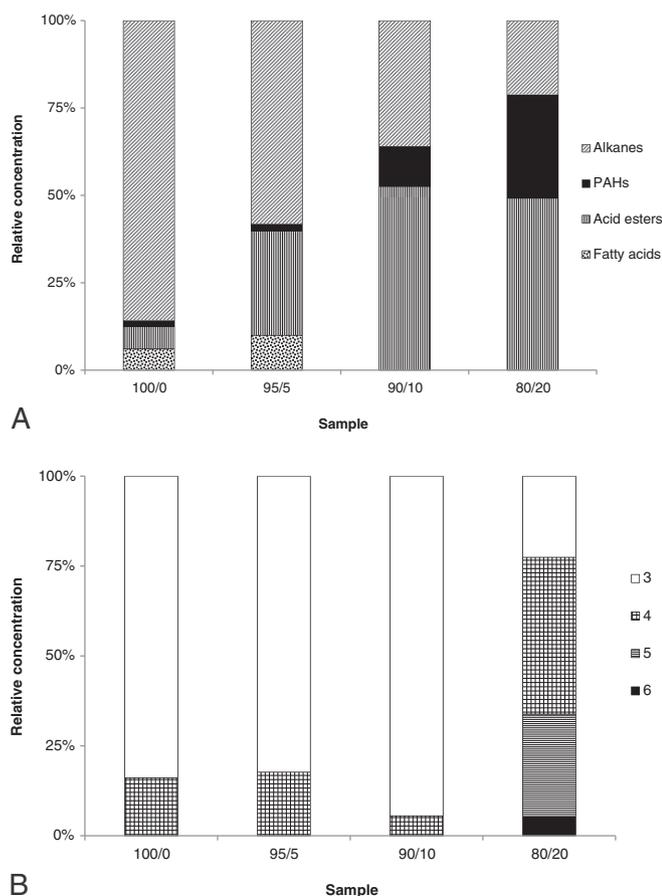


Fig. 5. Distribution of compound groups (a), and PAHs (b) in cokes extracts.

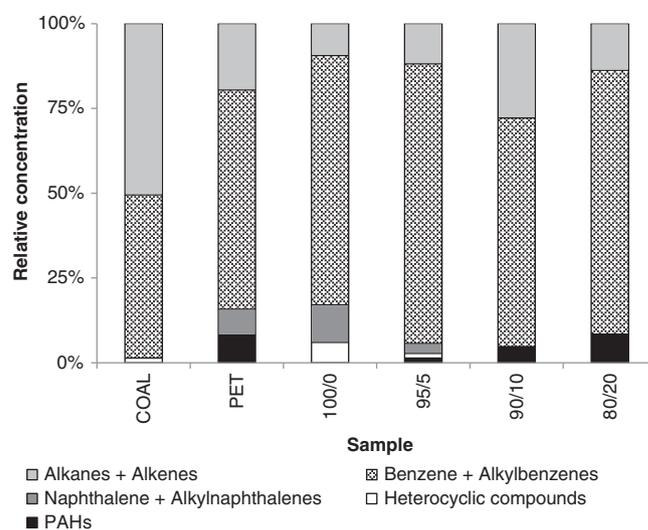


Fig. 6. Compound distribution in the original coal, PET, and in the cokes according Py-GC/MS pyrolysed at 750 °C.

number of aromatic rings (fluoranthene, pyrene, benz(a)anthracene, chrysene), and particularly higher levels of benzofluoranthenes. The RSDs of the relative abundances were in a range of 1.2–5.1%.

The identified compounds were of low molecular weight and represented the remains of original higher molecular weight hydrocarbons that were not incorporated into the microporous structure of the coke. Under the conditions of Py-GC/MS analysis, at a pyrolysis temperature of 750 °C, it was not possible to break the carbon bonds that form the polycrystalline structure of cokes, however, it was possible to fracture the links that are parts of compounds or groups not forming the solid carbonaceous matrix. The simplest representation of hydrocarbons was in the coke that was prepared from the 90/10 blend, in which it can be assumed that the best arranged carbonaceous matrix was closest to the ideal coke state.

3.6. Composition of gases

Pyrolysis gases contained four main components, methane, carbon dioxide, carbon monoxide and hydrogen (Table 5). The lower hydrogen and carbon content in PET bottles resulted in a decrease in total hydrocarbons except ethylene, in the coking blends. Cleavage of hydrocarbons with longer chains occurred during thermal decomposition at the pyrolysis temperature of 900 °C. Although the proportion of PET bottles in the charge was up to 20 wt.%, during thermal decomposition there was no increase in hydrogen production, but conversely, the hydrogen content slightly decreased by 3%. This decrease in hydrogen production

Table 5
Composition of gas from co-pyrolysis of coal with PET bottles (vol.%).

Sample	100/0		95/5		90/10		80/20	
		RSD		RSD		RSD		RSD
CH ₄	28.65	2.1	28.26	3.2	27.54	3.0	24.81	2.5
C ₂ H ₄	1.36	0.4	1.75	0.6	2.20	1.1	2.90	1.3
C ₂ H ₆	3.45	0.3	3.25	0.4	3.31	0.4	2.92	0.4
C ₃ H ₆	1.21	0.4	0.97	0.2	1.03	2.1	0.77	0.7
C ₃ H ₈	1.31	0.9	1.18	2.1	1.18	2.5	0.88	1.2
∑ C ₄	0.32	0.3	0.29	0.1	0.27	1.6	0.23	1.4
N _{2,r}	3.57	0.9	2.68	0.8	2.50	0.6	2.42	0.7
CO	9.55	3.9	10.22	3.6	10.42	2.9	11.73	3.1
CO ₂	7.05	2.5	7.92	2.7	8.94	2.9	11.20	2.7
H ₂	43.52	4.2	43.58	4.3	42.61	4.9	42.13	4.6

N_{2,r} – nitrogen resulting from the reactions, RSD – relative standard deviation in %. The values in bolds indicate the total proportion of the values, the values in romans indicate relative standard deviation in %.

occurred at the expense of higher ethylene production that doubled with the addition of 20 wt.% of PET to the coal charge. Nitrogen ($N_{2,r}$) is ballast matter in the gaseous products and was generated from in-coal chemically bounded nitrogen. The data presented in Table 5 are reliable because the RSDs ($n = 9$) were lower than 5%.

The composition of the gas mix (CO_2 , CO , CH_4) was influenced by the addition of PET to the coal charge (Fig. 7). Increasing PET led to an increased in CO levels, with the main increase occurring at around 500 °

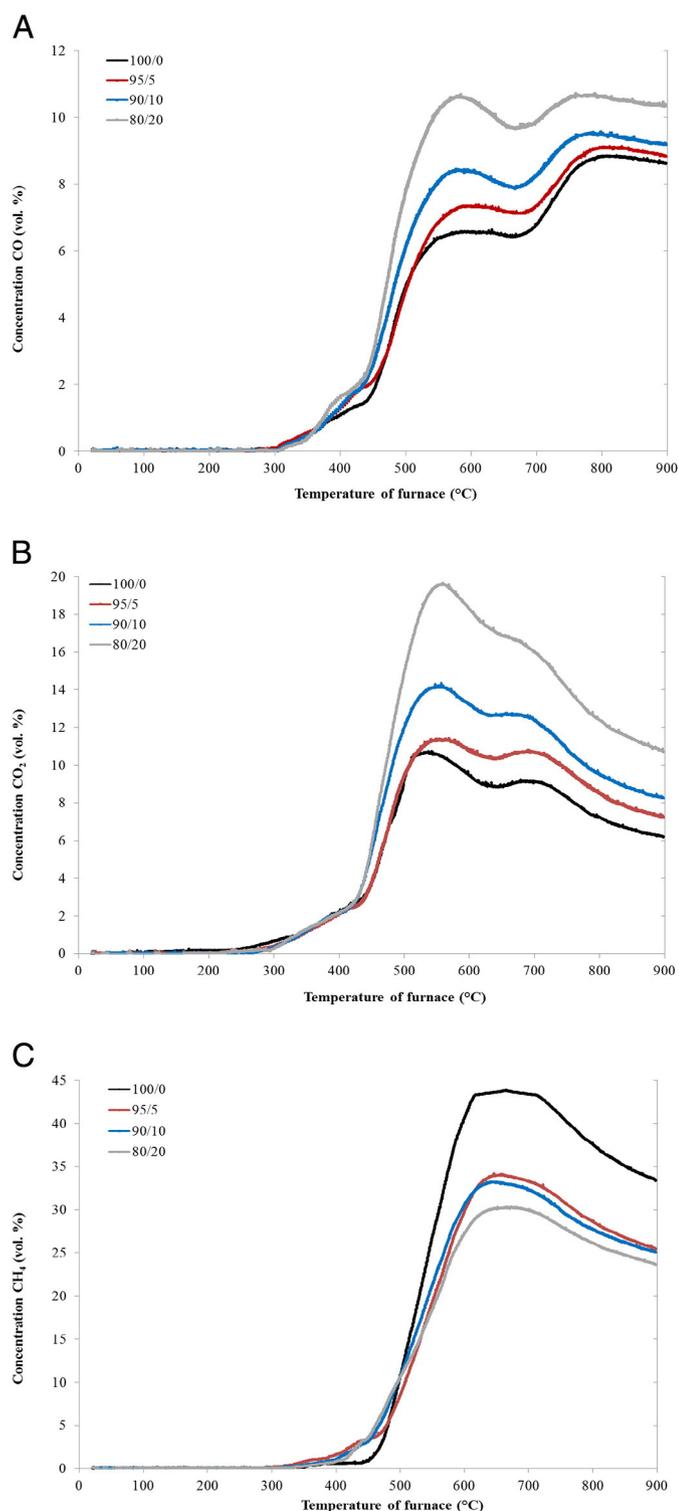


Fig. 7. Evolution of CO (a), CO_2 (b), and CH_4 (c) during pyrolysis of coal alone and with 5% PET, 10% PET and 20% PET.

C with two maxima (10.65 vol.% and 10.71 vol.% CO) at 582.8 °C and 760.6 °C, respectively. From pyrolysis of coal alone, two maxima for CO were at 586.5 °C and 805.7 °C (Fig. 7a). The presence of $-O-C=O-$ bonds in the PET molecule, which starts to decompose at 250 °C, influenced CO_2 release (Fig. 7b) [41]. Decomposition continued until 555 °C and the peak evolution of CO_2 during pyrolysis ended around 530 °C, then CO_2 content decreased [35]. The opposite trend in gas production was observed during evolution of CH_4 (Fig. 7c). During the pyrolysis of coal alone, CH_4 began to be released at a temperature of about 450 °C, however the addition of PET into the charge led to a decrease in CH_4 release at a temperature of 420 °C due to the initial decomposition of benzene rings in the PET molecule. In contrast, with the addition of light mixed waste plastics (density below 1000 kg/m^3) to lignite, the development of CH_4 was not affected [38]. Although the addition of PET accelerated the release of CH_4 , its total quantity, as compared to CH_4 from pyrolysis of raw coal alone, was considerably lower. This decrease was 22%, 24% and 31%, depending on the increasing addition of PET (5, 10, and 20 wt.%).

The overall decrease in CH_4 , H_2 , and other light hydrocarbon compounds were expressed in higher heating values (HHV) of pyrolysis gases (Table 6). However, the maximum decrease in HHV (7%) is not so significant because HHV is still sufficient for use of the gases. Therefore, HHV together with the gas density as important utility property were calculated and compared in order to describe an influence of waste PET bottles these properties. Oxygen, during pyrolysis, crossed mainly into the ballast CO_2 . By the addition of 20 wt.% PET into the charge, CO_2 production increased by 59%, while in the case of CO this increased only by 23%. This was caused by cleavage off these molecules from the molecules of PET. The content of methane decreased but there is a slight increase of ethylene, which was generated by cleavage off the benzene ring to the small stable molecules. The increased CO_2 content is shown in gas density (ρ) and relative density (d) (Table 6).

The energetic values of the released gases were not affected by the addition of PET bottles to the coal charge, even in amounts up 20 wt.%.

4. Conclusion

Increasing additions of PET to the coal charge influenced the production of coke and the development of liquid and gaseous products; however the production of coke was decreased by only 4 wt.%, and liquid fractions were increased by only 5 wt.% for the highest PET contribution.

The sub-bituminous coals from the Maghara basin are not ideal coking coals. Nevertheless, results of coke, tar, and gas production are worth studying for other potential uses. By pyrolysis of coal mixed with PET, 86–89 vol.% of gas was released, consisting of flammable substances, 42–44 vol.% of which was hydrogen. With respect to accepted gross calorific values (22.6 to 24.0 MJ/m^3), hydrogen can be used (without further modification) as an energy gas. The calorific values were reduced mainly due to ballast CO_2 , whose share makes up 11.2 vol.%.

The increasing addition of PET to coal in coking blends caused a lowering in the mean reflectances of the cokes, the volume contents of pores, and an increase in fissure volumes that are integral parts of the cokes. The addition of PET also led to lower coke yields, to a reduction

Table 6
Physical properties of gas from co-pyrolysis of coal with PET bottles.

Sample		100/0	95/5	90/10	80/20
HHV	(MJ/m^3)	24.37	23.97	23.98	22.57
RSD		4.8	2.3	3.9	1.9
ρ	(kg/m^3)	0.670	0.675	0.697	0.729
RSD		0.7	0.8	1.1	1.0
d	(–)	0.519	0.523	0.539	0.564
RSD		0.7	0.7	0.9	1.0

HHV – higher heating values, ρ – gas density, d – relative density, RSD – relative standard deviation in %.

in true density, and to an increase in total mesopore volumes and decreased volume and surface of micropores. PET addition also supported the formation of solid coke aromatic structures as was demonstrated by the low H/C atomic ratios as well as GC/MS and Py-GC/MS results. However, the higher content of PET in the coking blend also led to warping of the structures or to the formation of poorer aromatic structures during carbonization (sample 80/20). This was indicated by the narrowing of larger mesopores, limiting of access to micropores, reduction in the specific BET surface area, and by the presence of PAHs with more aromatic rings in the 80/20 extract, as well as by increased PAHs in the pyrolysate.

The microscopic study revealed that the optimal addition of PET waste to coal from Maghara was 5 wt.% in order to maintain the quality of coke, because reflectance values and volumes of pores were only slightly decreased. From the point of view of chemical structure, coke prepared from the 90/10 blend seemed optimal because the coke carbonaceous matrix was close to the ideal coke state. According to their porous structures, all prepared cokes could be used directly or after activation as sorbents. Even by replacing up to 20% of coal by PET bottles in the coal charge, the properties of coke and gas did not change significantly, and can be further used as fuels.

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