

PAHS EMISSION FROM CO-COMBUSTION OF COAL AND GAS FROM SEWAGE SLUDGE GASIFICATION

Sebastian WERLE ^{a*}, Monika MICHCZYŃSKA ^b

^a Dr.; Institute of Thermal Technology, Silesian University of Technology, Konarskiego 22, 44-100 Gliwice, Poland

* E-mail address: *sebastian.werle@polsl.pl*

^b Eng.; Institute of Thermal Technology, Silesian University of Technology, Konarskiego 22, 44-100 Gliwice, Poland

Received: 25.05.2011; Revised: 23.06.2011; Accepted: 28.06.2011

Abstract

The paper presents results of a test study of PAHs (polycyclic aromatic hydrocarbons) from a co-combustion of coal as well as gas from sewage sludge gasification and from the combustion of only coal in low power boiler. During the experiment, exhaust gas samples were taken from combustion of coal with varied addition of gas. Then they were analysed. Total concentration of PAHs was compared with other values for emissions from solid fuels combustion in residential furnaces from literature. The result obtained from the experiment was within the range of values obtained from coal combustion. Also the impact of additional fuel quantity on amount and harmfulness of generated polycyclic aromatic hydrocarbons was compared with data from literature. The concentration of the individual PAHs varied in different ways depending on the amount of co-combusted gas. It was probably caused by the existence of different local conditions. Due to the general nature of the study it was difficult to clearly define exactly what processes take place in the boiler. Only some conjectures could be formulated. Apart from that, it was observed that the carcinogenicity equivalent was higher in the case of co-combustion of additional fuel.

Streszczenie

W pracy przedstawiono wyniki badań emisji WWA (wielopierścieniowych węglowodorów aromatycznych) w procesie współspalania gazu ze zgazowania osadów ściekowych w kotle węglowym małej mocy, a także podczas spalania samego węgla. W trakcie eksperymentu pobierano próbki spalin dla spalania węgla z różnym dodatkiem gazu, a następnie poddano je analizie. Sumaryczne stężenie WWA porównano z innymi wartościami dla emisji z kotłów ciepłowniczych opalanych paliwami stałymi z literatury. Wynik uzyskany z pomiaru mieścił się w zakresie wartości uzyskiwanych ze spalania węgla. Dokonano również porównania wpływu stosowania paliwa dodatkowego na ilość i szkodliwość powstających wielopierścieniowych węglowodorów aromatycznych dla wartości pomierzonych z literaturowymi. Stężenie poszczególnych WWA zmieniało się w różny sposób w zależności od współspalanego gazu. Takie różnorodne zachowanie jest prawdopodobnie spowodowane przez istnienie różnych warunków lokalnych. Jednak ze względu na ogólny charakter badania trudno jest jednoznacznie określić, jakie dokładnie procesy przebiegały w kotle. Można jedynie formułować pewne przypuszczenia. Poza tym zaobserwowano, że równoważnik kancerogenności był większy w przypadku współspalania paliwa dodatkowego.

Keywords: Polycyclic aromatic hydrocarbons; Emissions; Co-combustion; Coal; Gas from sewage sludge gasification.

1. INTRODUCTION

Nowadays, it is important to decrease the amount of pollutants emitted during combustion, such as NO_x. One of the methods of reducing their quantity is co-combustion, realized by inserting additional fuel into furnace [1]. However, attention should also be paid to what impact such actions have on emission of other

substances, such as polycyclic aromatic hydrocarbons. Despite their low concentrations in flue gases, these compounds deserve special attention due to their high harmfulness (i.a. carcinogenicity).

The aim of this study is to determine the emissions of polycyclic aromatic hydrocarbons from the combustion of coal, as well as co-firing coal with gas from

sewage sludge gasification in coal-fired low power boiler. During experiment quantities of 16 individual PAHs were measured for combustion of coal with varied addition of gas. Then the results obtained were analyzed and compared with literature data.

2. GENERAL INFORMATION ABOUT POLYCYCLIC AROMATIC HYDROCARBONS

2.1. Characteristic and harmfulness of polycyclic aromatic hydrocarbons

The term polycyclic aromatic hydrocarbons (PAHs) means organic compounds made up of carbon and hydrogen atoms, containing at least two fused benzene rings (having one or two carbon atoms in common) [1-4].

In general, the health effects associated with exposure to polycyclic aromatic hydrocarbons can be divided into two groups: acute or short-term and chronic or long-term. The first ones depend mainly on the concentration and the toxicity of individual PAHs, the time and the route of the exposure. Some other factor – such as health conditions and age – are also important. For example, it was reported that short-term exposure to a mixture of these compounds caused impairment of lung function in asthmatics or thrombotic effects in people with ischemic heart disease. It is also known that exposure to high concentrations of PAHs causes symptoms such as eye irritation, irritation and inflammation of the skin, nausea, vomiting, diarrhea [2].

Long-lasting exposition increases the risk of cancer (especially the skin, lung, bladder, gastrointestinal as well as kidney, liver, larynx, etc.) [2, 5]. PAHs can also cause DNA damage, cataracts, kidney and liver damage, and hepatitis, as well as adversely affect the reproductive and endocrine effects and immune system. Long-term exposure to these compounds also enlarges the risk of cell damage caused by gene mutation and death associated with respiratory- circulatory disorders [2].

PAHs easily penetrate cell membranes and the placenta due to their lipophilic nature. In the organism, under the influence of certain enzymes (mainly these in liver) they may be transformed into compounds, which can form bonds with DNA and RNA. Such adducts can be the cause of disorders, and even of initiation and development of cancer [2, 6]. PAHs are regarded as carcinogenic and mutagenic [2, 5-7]. Seven of them are classified as probable human car-

cinogens: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(ah)anthracene, and indeno(1,2,3-cd)pyrene [2].

Also teratogenicity of these compounds has been documented [2, 8]. It was observed that, exposure to them is related with adverse effects, such as fetal growth reduction, low birth weight or premature birth. Exposure to high concentrations of PAHs in the fetal period may also be associated with subsequent impaired cognitive development, reduced IQ and behavioral disorders, childhood asthma or epigenetic changes [2, 8].

2.2. Transformations of polycyclic aromatic hydrocarbons in environment

Polycyclic aromatic hydrocarbons in air can exist in vapor phase or be adsorbed on particulate matter. The form of their occurrence depends on weather conditions, the origin of pollutants and the properties of the individual compound. Generally, heavier aromatic hydrocarbons (with a higher number of rings) exist mainly as adsorbed on dust particles (due to their low vapor pressure). With the deposition of these particulate they get to the earth, plants, or into the water.

In contrast, the lighter PAHs are more volatile and occur mainly in gaseous form. These compounds in the majority are considered to be less toxic. However, they are more reactive and can react with other pollutants, such as ozone, nitrogen oxides and sulfur dioxide to form compounds, which may be more toxic than the original ones [2, 3, 6].

3. EXPERIMENTAL METHODS

3.1. Test stand

The test stand was a retort coal-fired boiler with a capacity of 25 kW, equipped with an automatic feeder, made by company Urzoń. To make testing of co-combustion of coal and gas from sewage sludge gasification possible, some modifications were made – the gas supply nozzle was mounted and a door of the boiler was exchanged for other – with the part of the nozzle. Samples of exhaust gases, which were then sent for analysis, were taken in outlet pipe (Fig. 1).

3.2. Fuel composition

Characteristics of coal and gas from sewage sludge gasification is shown in Tables 1 and 2.

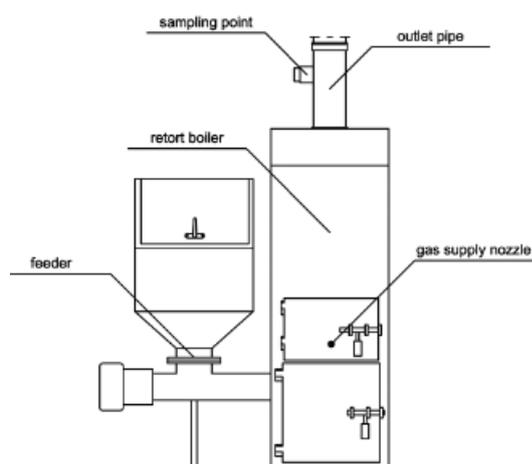


Figure 1.
Test stand scheme

It may be noted that the used gas significantly differs from the typical reburning fuel, which is natural gas. Natural E-class gas consists almost entirely of methane (96-98%) and its calorific value is at least 31.0 MJ/m³ [9]. In contrast, the gas obtained from the gasification of sewage sludge contains mainly of N₂ and also CO and CO₂ and has much lower calorific value.

Table 1.
Ultimate and proximate analysis of coal

Proximate analysis, % (as received)	
Moisture	9.30
Volatile matter	30.60
Ash	4.30
Ultimate analysis, % (dry basis)	
C	72.36
H	4.34
N	1.35
O	21.59
S	0.36
Lower heating value (dry basis)	
LHV, MJ/kg	29.20

Table 2.
Analysis of gas from sewage sludge gasification gas

Composition of gas, % vol	
CO	28.5
H ₂	5.0
CH ₄	1.0
CO ₂	15.0
N ₂	50.5
Lower heating value	
LHV, MJ/m _n ³	4.49

3.3. Sample collection and analysis

Before the measurements of the emissions, the boiler was in operation for approximately two hours, to ensure that steady-state was achieved at the beginning of emission measurements. The exhaust gas containing polycyclic aromatic hydrocarbons was collected using a probe and passed through the glass fiber filter. Then it flows through the cooling tube, where low-weight PAHs were condensed. Other PAHs were captured using the adsorption tube packed with adsorbent containing 5 g of XAD-2 resin, and the absorption bottle filled up with dichloromethane. All samples containing PAHs have been cooled to 4°C before extraction. After extraction and purification the samples have been analyzed using high-performance liquid chromatography system (HPLC) Simadzu. Calibration was performed using diluted standard solution of 16 PAHs recommended by the U.S. EPA (Environmental Protection Agency). The analysis was made by *ICHPW* in Zabrze (Poland).

4. RESULTS AND DISCUSSION

4.1. The concentrations of polycyclic aromatic hydrocarbons in relation to the amount of co-combusted gas

The concentration of PAHs (µg/m_n³) changed in different ways for different compounds during varying the amount of co-combusted gas. However generally studied PAHs were divided into 3 groups:

- 1) First group included: naphthalene, acenaphthalene, fluorene, phenanthrene, fluoranthene, benzo(b+k)fluoranthene, dibenzo(a, h)anthracene + ideno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene. Their emission from the combustion of only coal was greater than from co-combustion of gas.
- 2) Second group included: acenaphthene, anthracene, pyrene, benzo(a)anthracene, benzo(a)pyrene and perylene. Emission of these compounds from the combustion of only coal was smaller than from co-combustion of gas.
- 3) Third group included: chrysene and benzo(e)pyrene. Their emission approximately did not change.

Such diverse behavior was probably caused by the existence of different local conditions. However, due to the general nature of the study it is difficult to determine exactly what kind of processes take place in the boiler. Due to the large excess of air ratio ($\lambda = 2.01-2.29$) there was the highly oxidizing atmosphere in the boiler, and the addition of gas most like-

ly caused the formation of PAHs secondary combustion zone and it could cause a decline of the 8 measured compounds.

Presumably, a reduction zone was generated, where the gas was injected, which should favor the formation of PAHs, but it was relatively small, because there is little space between the deflector and the place of the gas injection. This could explain the increase in concentration in the exhaust gas of 6 different compounds. Perhaps more PAHs could be produced in this area, but they were mostly oxidized before reaching the flue. It is also possible that as a result of the formation of additional flame in the chamber (at the place of gas injection) flow in the combustion chamber can be changed due to the

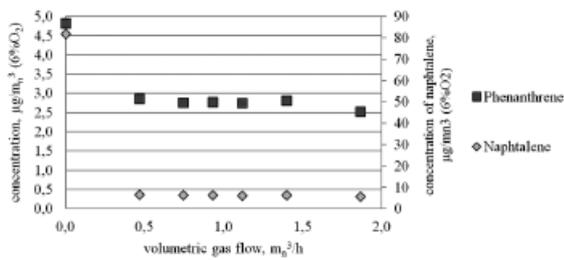


Figure 2a.
The concentration of naphthalene and phenanthrene (group 1) versus syngas addition to co-combustion process

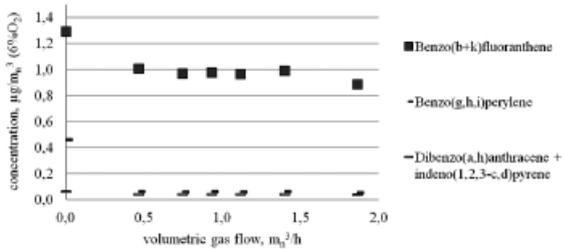


Figure 2b.
The concentration of benzo(b+k)fluoranthene, and benzo(g,h,i)perylene and dibenzo(a,h)anthracene + indeno(1,2,3-c,d)pyrene (group 1) versus syngas addition to co-combustion process

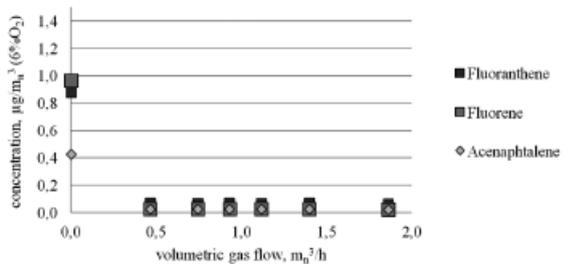


Figure 2c.
The concentration of fluoranthene, fluorene and acenaphthalene (group 1) versus syngas addition to co-combustion process

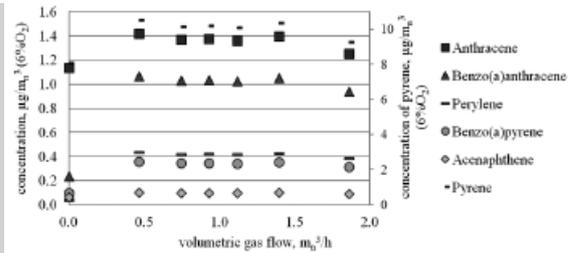


Figure 3.
The concentration of acenaphthene, anthracene, pyrene, benzo(a)anthracene, benzo(a)pyrene and perylene (group 2) versus syngas addition to co-combustion process

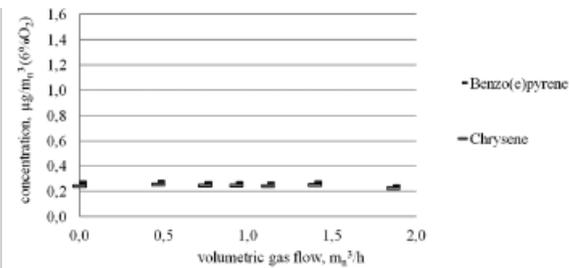


Figure 4.
The concentration of benzo(e)pyrene and chrysene (group 3) versus syngas addition to co-combustion process

change of temperature and flow resistance, which could e.g. “strangle” air flow through the bed of coal. Total concentrations of PAHs from the co-combustion of gas from the sewage sludge gasification remained approximately constant – did not change depending on the amount of gas. These relationships are shown in Figures 2-4.

The total concentration of PAHs ($\mu\text{g}/\text{m}_n^3$, 6% O_2) during the co-combustion of gas was maintained approximately at a constant level – about $24 \mu\text{g}/\text{m}_n^3$ irrespective of the amount of gas (Fig. 5). Only for the last measurement a slight decrease to $22 \mu\text{g}/\text{m}_n^3$ was observed. It is difficult to decide if this difference was caused by a real reduction in the amount of PAHs for higher amount of gas, or perhaps it was connected with uncertainty, which has influence on measurements, especially in a dynamically changing conditions. Perhaps this reduction could be associated with a lower excess of air ratio, which was obtained during this measurement – according to the literature too high excess air ratio also increases the amount of PAHs [1, 10-11]. A smaller amount of air probably caused that the exhaust gas stream is smaller for this measurement than for the others, and therefore flue gas could be longer resident in the reaction zone, what might favor reducing the amount of PAHs [1, 10-11].

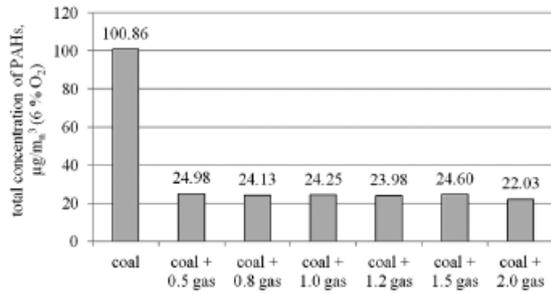


Figure 5.
Dependence of total concentrations of PAHs on amount of co-combusted gas
Note: 0.5 gas means the gas flow was 0.5 m³/h etc.

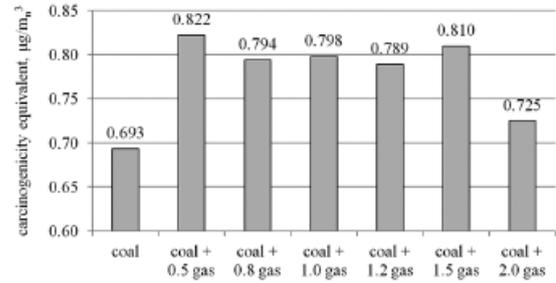


Figure 6.
Dependence of carcinogenicity equivalent on amount of co-combusted gas

4.2. Assessment of carcinogenicity equivalent

Carcinogenicity equivalent, that is total concentration of PAHs converted into concentration of benzo(a)pyrene (BaP) was calculated for each measurement using the equation:

$$A = \sum k_i C_i \quad (1)$$

A – carcinogenicity equivalent, µg/m³

k_i – toxic equivalency factor for cancer potency relative to BaP of i-th PAH

C_i – concentration of i-th PAH, µg/m³

The following values of quivalency factors were taken from the literature [7, 13] dibenzo(a,h)anthracene+indeno(1,2,3-c,d)pyrene – 5; benzo(a)pyrene – 1; benzo(a)anthracene and benzo(b+k)fluoranthene – 0.1; anthracene, chrysene, benzo(e)pyrene and benzo(g,h,i)perylene – 0.01; for the other measured PAHs – 0.001.

The results of calculations are shown in Figure 6. It may be pointed out that, carcinogenicity equivalent is lower for combustion of only coal, despite the fact that the total concentration of PAHs is then higher. Co-combustion caused the reduction of total concentration of PAHs, however, only concentrations of three more carcinogenic PAHs slightly decreased – benzo(g,h,i)perylene by 87% (taking into consideration the results for the additive gas 0.5 m³/h [0.47 m_n³/h]), dibenzo(a,h)anthracene+indeno(1,2,3-c,d)perylene – 33%, and benzo(b+k)fluoranthene – 22%, while the concentration of benzo(a)anthracene increased by approximately 346%, benzo(a)pyrene – 260%, and concentrations of chrysene and benzo(e)pyrene remained approximately unchanged.

4.3. Comparison of the obtained results with literature data

Total concentration of PAHs from coal combustion was compared with other values of emission from heating boilers fired by solid fuels [14]. The results are shown in Figure 7. It can be seen that the result obtained from the measurements is in the range of literature values from combustion of coal.

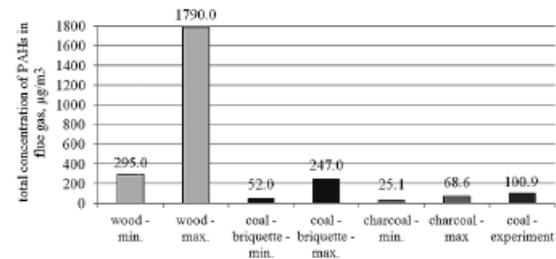


Figure 7.
Comparison of total concentration of PAHs with other results for heating boilers fired by solid fuel

Also the impact of additional fuel quantity on amount and harmfulness of generated polycyclic aromatic hydrocarbons was compared with data from literature. For this purpose, total concentrations of PAHs and carcinogenicity equivalents for combustion of coal (experiment) and oil (data available in the literature) [15]. The calculation results are shown in Figure 8.

In the conducted experiment the total concentration of polycyclic aromatic hydrocarbons is lower for the co-combustion of gas. However, this is primarily due to a considerably higher content of naphthalene detected for combustion of only coal. If naphthalene had not been included in the sum of PAHs, the differences of concentration would not be so large.

It should also be noted that in case of test study, there was strongly oxidizing atmosphere in the boiler

($\lambda > 2$), and moreover the addition of gas probably caused spontaneous formation of secondary combustion zone lowering amount of PAHs. Besides, the used gas was significantly different from a typical reburning fuel and this could cause some differences. Usually gas used in reburning mainly consists of methane, which under certain conditions promote the formation of PAHs. This can be observed in the literature data in substantial increase of these compounds concentration for reburning with natural gas. According to literature the carcinogenicity equivalent is higher for the combustion of additional fuel. So it is in the case of the measurements, although this difference is much smaller. In general, reducing atmosphere (rich mixture) favors processes of PAHs formation and weight growth (so also the formation of the more harmful compounds). Most likely, the reduction zone, which was formatted during experiment, was relatively small (due to the small distance between the place of gas injection and deflector). This could explain the slight increase in the carcinogenicity equivalent. It is also possible that relatively low temperatures in this zone hindered the formation of PAHs. According to [11], the synthesis reactions of these compounds are endothermic and, therefore, bigger amount of them is formed at higher temperatures. Perhaps also the PAH that could be produced in the reducing zone was mostly oxidized before reaching the flue.

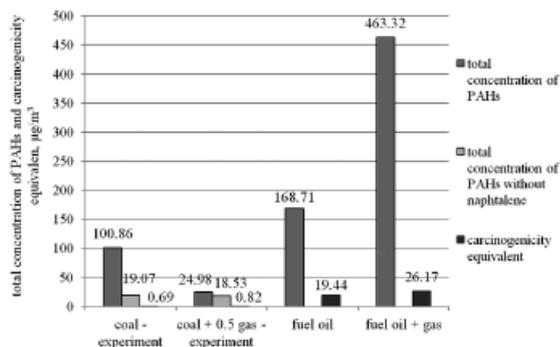


Figure 8. Comparison of the impact of additional fuel quantity on PAHs concentration and carcinogenicity equivalent for measurements and literature data

5. CONCLUSIONS

Due to the general nature of the study it was difficult to clearly define exactly what processes, influencing polycyclic aromatic hydrocarbons, take place in the boiler. Only some conjectures could be formulated.

There was strongly oxidizing atmosphere in the boiler (relatively high excess air ratio: $\lambda > 2$). What is more the injection of gas most likely caused spontaneous formation of a secondary combustion zone. This could explain the lower total concentration of PAHs for combustion with addition of gas from sewage sludge gasification than for the combustion of only coal.

Presumably a small reduction zone, which should favor the formation and mass growth of polycyclic aromatic hydrocarbons, was formatted. It is possible that this was what caused the increase of the content of the 6 analyzed components and the larger carcinogenicity equivalent for gas co-combustion, despite the fact that the compounds which might be created in this zone were probably oxidized before reaching the flue. It is also possible that the relatively small increase of PAHs concentration is connected with a relatively low temperature in that zone, which hindered their formation. The emission of PAHs could also be affected by change in flow conditions in the boiler, caused by formation of additional flame because of gas injection. Besides, an unusual composition of the gas could cause some important differences in behavior in comparison to typical reburning fuel.

Also it should be not forgotten that in case of concentrations on such a relatively low level, as in the case of the conducted experiment, measuring uncertainty is not negligible.

REFERENCES

- [1] Wilk R. K., Podstawy niskoemisyjnego spalania (Basics of low-emission combustion), Wydawnictwo Gnome, Katowice 2001 (in Polish)
- [2] Kim K.-H., Jahan S. A., Kabir E., Brown R. J. C.; A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects, Environment International, 2013, 60, p.71-80
- [3] Kubica K.; Powstawanie i emisja WWA podczas spalania węgla (Formation and emission of PAHs during coal combustion), conference materials (in Polish) "Spalanie węgla '99", Ustroń-Zawodzie 24-26 of March 1999 (in Polish)

- [4] *Ravindra K., Sokhi R., Van Grieken R.*; Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation, *Atmospheric Environment*, 2008, 42, p.2895-2921
- [5] *Boffetta P., Jourenkova N., Gustavsson P.*; Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons, *Cancer Causes and Control*, 1997, 8, p.444-472
- [6] *Koniecznyński J., Kozielska B., Żeliński J., Staisz J., Pasoń-Koniecznyńska A.*; Skład ziarnowy oraz zawartości i profile wielopierścieniowych węglowodorów aromatycznych w pyłach emitowanych z obiektów energetyki komunalnej i zakładowej (Particle size distribution as well as content and profiles of polycyclic aromatic hydrocarbons in dust emitted from municipal and factory power facilities), Wydawnictwo Politechniki Śląskiej, Gliwice 2003 (in Polish)
- [7] *Chen S.-C., Liao C.-M.*; Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources, *Science of Total Environment*, 2006, 366, p.112-123
- [8] *Perera F., Herbstman J.*; Prenatal environmental exposures, epigenetics, and disease, *Reproductive Toxicology*, 2011, 31, p.363-373
- [9] *Kordylewski W.*; Spalanie i paliwa (Combustion and fuels), Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2008 (in Polish)
- [10] *Wilk R., Zieliński Z., Szłęk A.*; Emisja wielopierścieniowych węglowodorów aromatycznych przy spalaniu oleju opałowego (Emission of polycyclic aromatic hydrocarbons from fuel oil combustion), *Gospodarka Paliwami i Energią*, 1995, 2, p.2-6 (in Polish)
- [11] *Liu K., Han W., Pan W.-P., Riley J. T.*; Polycyclic aromatic hydrocarbon (PAH) emission from coal-fired pilot FBC system, *Journal of Hazardous Materials*, 2001, 84, p.175-188
- [12] *Wilk R., Zieliński Z., Szłęk A.*; An experimental study of formation of polycyclic aromatic hydrocarbons during the combustion of gaseous fuels, *Archivum Combustionis*, 2002, Vol.20 No.1-2, p.25-35
- [13] *Jung K. H., Yan B., Chillrud S. N., Perera F. P., Whyatt R., Camann D., Kinney P. L., Miller R. L.*; Assessment of benzo(a)pyrene-equivalent carcinogenicity and mutagenicity of residential indoor versus outdoor polycyclic aromatic hydrocarbons exposing young children in New York City, *International Journal of Environmental Research and Public Health*, 2010, 7, p.1889-1900 [EPA-United States Environmental Protection Agency]
- [14] *Oanh N. T. K., Reutergardh L. B., Dung N. T.*; Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels, *Environ. Sci. Technol.*, 1999, 30, p.2703-2709
- [15] *Durman-Młynarska A., Gizicki W., Kordylewski W., Miller R.*; Effects of applying of low-NO_x combustion systems for oil burning on the emission of PAHS, *Archivum Combustionis*, 2000, Vol.20 No.3, p.3-7
- [16] *Michczyńska M.*; Badania emisji WWA w procesie współspalania gazu ze zgazowania osadów ściekowych w kotle węglowym małej mocy (Study on PAHs emission from co-combustion of gas from sewage sludge gasification in low power coal boiler) – Bachelor degree project, ITC, Politechnika Śląska, Gliwice 2014 (in Polish)