

MILD PYROLYSIS OF COALS AND ITS IMPACT ON POSSIBLE MERCURY RELEASES FROM PULVERISED COAL-FIRED POWER PLANTS

Maciej CHOLEWIŃSKI*

The Faculty of Mechanical and Power Engineering, Wrocław University of Science and Technology,
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Abstract: The paper concerns the impact of mild pyrolysis of coals on the possible mercury releases from the combustion process. It was proven that while mild pyrolysis may lead to the decrease of mercury content in solid fuel (from 0 do even 80% of dry mass), the resulting increased SO₂/HCl ratio in flue gasses may be disadvantageous in the case of the mercury oxidation as well. However, when optimised, for analysed lignites, this type of thermal pre-combustion technique could satisfy up to 4-26% of mercury decrease requirements while for analysed hard coal it seems to be pointless to adopt it within power plant. Therefore, the environmental benefits of mild pyrolysis will be strongly depend on the type of fuel (i.e. mercury compounds in dry matter) and the conditions (time, temperature) of the process.

Key words: mercury, coal combustion, fuel pre-treatment, limiting the emissions.

1. Introduction

The current transformation of Polish fuel and power sectors, basically focused on the reorganisation of emission-intensive plants (promoting environmental friendly technical layouts) and their progressive substitution by Renewable Energy Sources (RES) and nuclear units, is accompanied by the introduction of several strict new environmental standards (Wierzbowski et al., 2017; Commission Implementing Decision (EU) 2017/1442). Due to the high generation of electricity (81% of total production in Poland in 2015) and heat (approx. 75% of heat generation located in professional heat units) in coal-fired boilers, particular attention – in the case of environmental protection – has been already paid on the evaluation of cost-efficient pollutant control techniques dedicated to both bituminous coal and lignite fuelled power stations (Central Statistical Office, 2016; Hławiczka, 2008). Including current quantities of national emissions and forecasted thresholds, it can be assumed, that in order to adopt future electricity, heat

and cooling supply market to the strict international regulations (i.e. Emissions Trading System (ETS), annual national emission levels, multiple emission standards), several new investments in Polish power sector need to be introduced in the near future – particularly in the case of the heavy metals releases Large Combustion Plants (LCP) (The National Centre For Emissions Management, 2017). Within the next 3-4 years, all professional coal boilers (units with a total rated thermal input of 50 MW and more) will be obligated to meet, among others, strict mercury Best Available Techniques - Associated Emission Levels (BAT-AELs), established 31 July 2017 by the Commission Implementing Decision (EU) 2017/1442 (Table 1). Comparing them to the recorded concentrations of mercury in flue gases in full scale power units (Wang et al., 2010; Burmistrz et al., 2016; Cholewiński, 2017), it can be stated that several of the existing power stations will be forced in the near future to take decisive actions towards the reduction of mercury releases to the atmosphere.

Table 1. BAT-associated emission levels for mercury emissions to air from the combustion of coal and lignite (Commission Implementing Decision 2017/1442 of 31 July 2017).

Total rated thermal input of power plant, MW	BAT-AELs – yearly average or average of samples obtained during one year, µg/m ³ _{ref}			
	New plant		Existing plant	
	Bituminous	Lignite	Bituminous	Lignite
< 300	< 1 – 3	< 1 – 5	< 1 – 9	< 1 – 10
≥ 300	< 1 – 2	< 1 – 4	< 1 – 4	< 1 – 7

Explanations: BAT-AELs refer to concentrations, expressed as mass of emitted substance per volume of flue-gas under the following conditions: dry gas, temperature of 273,15 K, pressure of 101,3 kPa, reference O₂ concentration (6% for combustion of solid fuels).

* Corresponding author, e-mail: maciej.cholewinski@pwr.edu.pl

The mercury control techniques dedicated to solid fuel fired units (Figure 1) covers both pre- and post-combustion technologies. Importantly, the adaptation of each of them need to be preceded by an examination of the working conditions of power system. One of the most vital aspects for the proper introduction of mercury reduction technology is a deep knowledge of the properties of solid fuel used in power unit. When favourable – from mercury emission point of view – coal or biomass is used, it may be possible to meet strict emission standards in a cost-effective way or – in extreme cases – even without additional cost. On the other hand, when the physicochemical properties of solid fuel lead to the disadvantageous composition of flue gases, significantly more expensive and sophisticated technologies will be required to adopt the real-time mercury releases to the thresholds specified in emission standards (Hławiczka, 2008; Cholewiński, 2015). According to many papers, in order to guarantee profitable conditions to mercury capture within power plant, solid fuel should be characterised – much simplified– by low mercury and sulphur content, high chlorine content and high calorific value (Cholewiński, 2017). For instance, to decrease the mercury concentration in flue gas, energy carriers with low mercury content (naturally or after pre-combustion treatment) should be used. However, to guarantee the mercury uptake from the flue gases with reduced mercury quantity, sufficiently low concentration of SO₂ and relatively high of chloride or bromide compounds – in combination with highly efficient precipitators and wet scrubbers (absorbers) – should be provided as well (Rhee, 2016). Only when abovementioned optimisation – using appropriate solid fuel and co-beneficial Hg capture in Electrostatic Precipitator (ESP) or Flue Gas Desulphurisation (FGD)

units – is insufficient to fulfil emission standards, several specific techniques need to be introduced, i.e. sorbent or halogenated additives injection, additional catalysers and absorbers/adsorbers, the reorganisation of combustion process (Hławiczka, 2008; Pan et al., 2013;). This fact has been already confirmed by several independent research – it has been proved that biomass and bituminous coals seem to be more suitable fuels in the case of mercury uptake than lignites (Hławiczka, 2008; Wang et al., 2010; Burmistrz et al., 2016).

As abovementioned, when the composition of raw (natural) solid fuel does not promote the adaptation of co-beneficial mercury uptake methods as a sufficient combination to meet emission standards, it may be beneficial to introduce one of the pre-combustion treatment technologies (when economically and environmentally justified). Apart from washing and mechanical preparation, an interesting technique, that may lead to the reduction of mercury content in raw fuel and to the transformation of dry matter towards more advantageous physicochemical properties, are thermal methods, i.e. mild pyrolysis. Basically, mild pyrolysis consists on thermal (<500-600°C) treatment of solid fuel in the absence of oxygen or in oxidising atmosphere (only when the temperature of the process is kept below ignition temperatures of the fuel). These conditions – if selected precisely (among others temperature, time of resistance, atmosphere, speed of heating medium) to the specification of a solid fuel (including its form and the type of mercury compounds) – should promote the significant mercury releases from solid material to pyrolytic gas and low degradation of final energy product (Liu et al., 2010). However, to cover an integrated protection of atmosphere, all mercury released during the mild pyrolysis should be captured as it should take place in power plant.

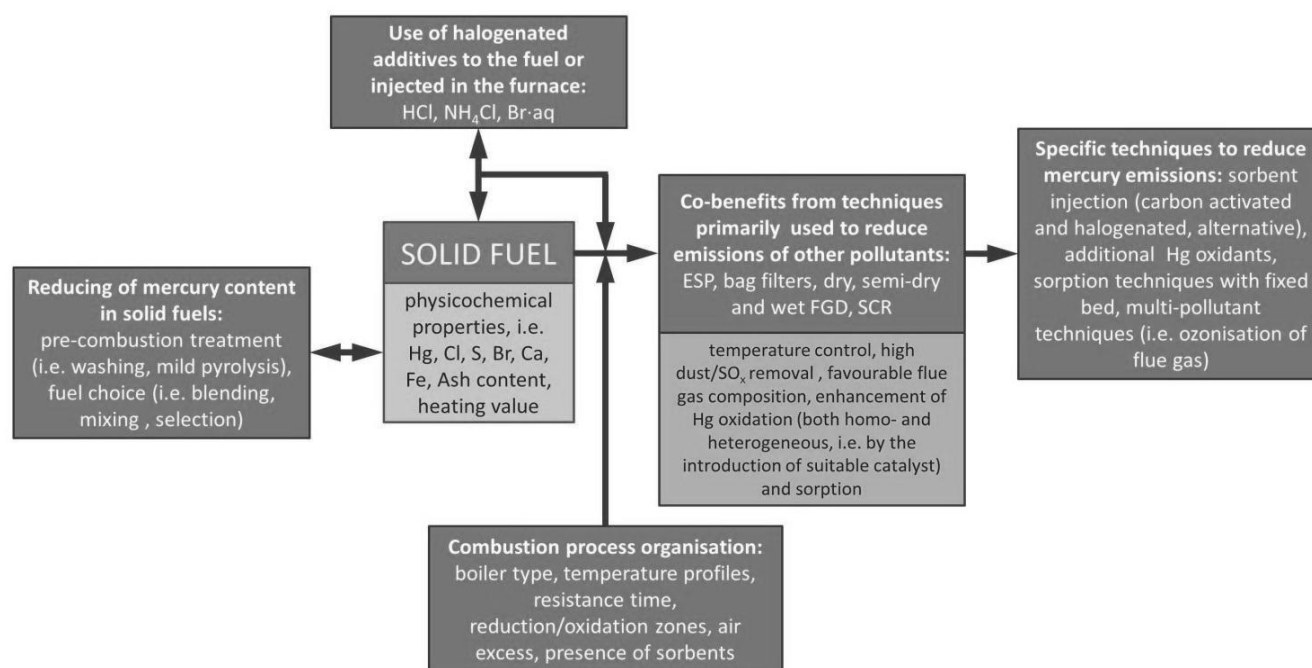


Figure 1. The overview of mercury control techniques and the places of application in power unit in solid fuel fired power plant.

Fortunately, due to the higher concentration of mercury in pyrolytic gases – in comparison to flue gas released from power boiler, its uptake using i.e. adsorption techniques (with fixed bed or impregnated plates) may be performed at lower total costs. As a result, when mild pyrolysis process is cost-optimised (regarding thermal insulation of a reactor, source of heat, own consumption), controlling mercury emissions by its introduction within power plant may lower the investment and running costs in comparison to post-combustion mercury control devices (sorbents or halogenated additives injection).

Importantly, according to Liu et al. (2010) suggested, that during mild pyrolysis, a main form of mercury in pyrolytic gases is elemental one (Hg^0). Therefore, to increase the economy of its uptake from pyrolytic gases, some oxidising techniques seem to be necessary to be implemented.

Depending on the types of mercury components in raw materials, the influence of mild pyrolysis in selected temperature should vary from 0 to nearly 80-90% – according to Luo et al. (2013), mercury accumulated in coals can be released below 150°C (elemental form), between 150-250°C (HgCl_2 , organic-bound compounds), between 250-400°C (HgS , silicate-bounded forms) or only when the temperature is raised to 400-600°C (pyrite-bounded mercury compounds). Therefore, the higher concentration of mercury compounds with low release temperatures, the lower mild pyrolysis temperature is required to get accepted mercury reduction rate or the higher possible reduction of total mercury concentration in final energy product can be obtained for given temperature of the process.

To examine all these aspects, lab-scale tests concerning thermal processing of different coals were conducted. In this article the impact of low temperature (<300°C) mild pyrolysis in air atmosphere in muffle furnace on the mercury content for 4 Polish coals (2 lignites and 2 hard coals) was analysed. Lab tests represented the atmospheric reactor combined with a conveyor belt as a feeding system dedicated to the

pulverised materials.

Two values of the times of pyrolysis process (30 min and 90 min) and 5 temperatures (100, 150, 200, 250, 300°C) were taken into account in order to detect the influence of mild pyrolysis parameters on possible mercury removal. Moreover, for 2 selected coals (1 lignite and 1 hard coal), additional assessments were conducted to predict the impact of mild pyrolysis on the mercury concentration in solid products (chars) and to assess the composition of flue gases released from the combustion process. To determine the changes within flue gas composition, stoichiometric mathematical model of combustion process was harnessed.

2. Materials and Methods

2.1. Proximate and ultimate analysis

To characterise the coals, proximate and ultimate analysis were conducted (according to PN/EN standards). All gravimetric tests – total moisture content in solid fuel (W), free moisture content in solid fuel (W_{ex}), ash content in solid fuel (A), volatile matter content in solid fuel (V) – were implemented using CARBOLITE CWF 1300 muffle furnace and laboratory scales sensitive to 0,1 mg. To determine C, H, N, S, Hg in solid fuels, dedicated atomic absorption spectrometers (AAS; LECO TruSpec CHN and S, LECO AMA 254) were harnessed. The higher heating value of solid fuel (HHV) were examined using IKA C-2000 Basic calorimeter. To identify the Cl in solid material, ion chromatography unit THERMO Dionex ICS-1100 was combined with the calorimeter bomb (deionised water with absorbed ions was investigated). Finally, fixed carbon content in solid fuel (FC), lower heating value of solid fuel (LHV) and oxygen content in solid fuel were calculated from the mass balance. Test stands used in analyses were presented in Figure 2.



Figure 2. The lab equipment used in presented researches (from the left: muffle furnace; atomic absorption spectrometer – AAS - dedicated to the determination of carbon, hydrogen, nitrogen and sulphur content in solid materials; calorimeter bomb; AAS dedicated to the determination of mercury content in solid materials; ion chromatograph).

In order to analyse the physicochemical composition of the chars (quoted as HC 1 and L 1), selected properties (C, H, N) were evaluated using aforementioned equipment. To calculate the HHV, simplified formulae based on the proximate and ultimate analysis were introduced – according to Ferens (2014), Neavel et al. (1986) formula seems to be the most accurate equation to determine the calorific value of bituminous coals, while Yin (2011) one – to lignites. Due to the negligible releases of selected components of solid fuels during the mild pyrolysis at the temperatures below 300°C, sulphur and ash contents in the chars were calculated using its initial values (in raw material) and observed mass decrease of samples after the thermal process. Finally, it was assumed that chlorine content in chars was the same as in the raw material (there was no significant releases of Cl during the pyrolysis).

All proximate and ultimate analysis of solid fuels were conducted in the Chair of Energy Technologies, Turbines and Modelling of Thermal and Fluid Flow Processes, at Wrocław University of Science and Technology. Some of the properties of raw materials investigated in this paper (HC 1, HC 2, L 2) have been already published i.e. by Moroń (2014) or Czajka et al. (2016).

A more detailed description of the conducted laboratory tests can be found in the papers released by Cholewiński (2015), Czajka et al. (2016) and Moroń et al. (2016).

2.2. Mild pyrolysis

Mild pyrolysis was conducted in the atmosphere of air in a controllable muffle furnace CARBOLITE CWF 1300. 1 g samples of examined coals (in dry state) were placed in a flat ceramic trays (dedicated to the ash content determination according to PN-ISO 1171:2002). Solid fuels at room temperature were inserted into the furnace and maintained at given process temperature (in a closed chamber) for a specified time (30 or 90 min). After the process, the mass reduction rate of each sample was determined. The air and pyrolytic gas circulation were hold by natural draught and small exhaust fan (mainly in order to remove the pyrolytic gases from the furnace).

2.3. Mathematical model of combustion chamber

To simulate the composition of the flue gases released from the combustion chamber, simplified stoichiometric mathematical model (1) dedicated to pulverised boilers and solid fuels was used (Cholewiński 2017):

$$\begin{aligned}
 & 8.33 \cdot 10^{-2} a C + 0.5 b H_2 + 3.57 \cdot 10^{-2} c N_2 + 3.13 \cdot 10^{-2} d S \\
 & + 3.13 \cdot 10^{-2} e O_2 + 5.56 \cdot 10^{-2} f H_2O + 4.98 \cdot 10^{-3} g Hg \\
 & + 3.13 \cdot 10^{-2} h Cl + \lambda M_s (O_2 + 3.76 N_2) = \\
 & = n_1 CO_2 + n_2 H_2O + n_3 O_2 + n_4 N_2 \\
 & + n_5 SO_2 + n_6 HCl + n_7 Hg + n_8 C
 \end{aligned} \quad (1)$$

where: *a-h* – different constituents contents (weigh fraction) in fuel (*a* – carbon, *b* – hydrogen, *c* – nitrogen,

d – sulphur, *e* – oxygen, *f* – moisture, *g* – mercury, *h* – chlorine), *n_i* – calculated number of moles of selected component accumulated in flue gas from combustion process of 1 g of fuel (1 – carbon dioxide, 2 – water vapour, 3 – oxygen, 4 – nitrogen, 5 – sulphur dioxide, 6 – hydrogen chloride, 7 – elemental mercury, 8 – average carbon in fly ash and in slag – fixed at 3.5%), and *M_s* is number of moles of oxygen per 1 mole of fuel in stoichiometric conditions. In all calculations, air-fuel equivalence ratio λ was equal to 1.2.

To simulate one of the existing power plants, 200 MW class power unit with pulverised fuel boiler, total average net efficiency of 40% and 300 working days (annual capacity ratio 82% – 7,200 hr) per year were adopted. To calculate the dust concentration in raw flue gas *S_{dust}* (in reference gas conditions), empirical equation (2) were implemented (Cholewiński 2017):

$$S_{dust} = \left(100 A^f L_{dry} a_u + \frac{C_{fa}}{L_{dry} B} \right) \frac{21 - O_2^{ref}}{21 - O_2} \quad (1)$$

where: *S_{dust}* is fly ash concentration in g/m³ref, *L_{dry}* is the quantity of dry flue gas per 1 kg of fuel, *a_u* is the ratio of the quantity of mineral matter accumulated in fly ash to total mineral matter in received fuel, *C_{fa}* is the stream of carbon accumulated in fly ash, in kg/s, *B* is fuel consumption in kg/s, *O₂* is oxygen concentration in raw flue gas, and *O₂^{ref}* is reference oxygen concentration in flue gas.

To simulate pulverised fuel combustion chamber, the value of *a_u* was fixed at 0.9, *C_{fa}* – at 4%, *O₂^{ref}* – at 6%. Furthermore, in all further calculations concerning combustion of chars, moisture content of 1% was established. For the coals the values for received (upper index "r") state were used.

3. Results

The results reported in Tables 2-6 and Figures 3-5 represent the average values of selected properties of the solid materials. Due to high homogenisation of air-dried samples, the diversity of results obtained during the laboratory tests was relatively low (Standard Deviation < 4-5%). As a result, the uncertainty analysis was not included in this paper.

3.1. Properties of the coals

In Table 2 and Table 3, the results of proximate and ultimate analysis were presented. It was shown, that from mercury emission point of view, hard coals and lignites may differ significantly. For instance, lower concentrations of Hg (almost 10-times) and significantly higher of chlorine (10-15 times) in two selected hard coals will promote both lower Hg concentrations in flue gas and higher oxidation rate of gaseous Hg (represents i.e. by SO₂/HCl or HCl/Hg_(tot) ratios in flue gas) in comparison to two selected lignites. Moreover, the values of Hg, S and Cl may differ even within the same

group of solid fuels as well.

The increased moisture and ash contents may be treated as significant disadvantage – high moisture content leads to the decrease of LHV of the fuel, uncontrollable saturation of water from flue gas and increased quantity of flue gas (resulting in increased energy consumption of fans), while ash content – to higher stream of solid wastes (that need to be finally utilized or stored) and increased efficiency of precipitators. However, for gaseous mercury, in some specified conditions – i.e. higher Hg^{2+} presence, fly ash can be a valuable natural

sorbent, therefore its presence must be conducted in two areas (including among others the composition of fly ash).

In Figure 3 the graphical comparison of 4 analysed fuels was highlighted. More aspects concerning the impact of each of the property of solid fuel on combustion process and emission issues have been sufficiently presented by Kordylewski (2008) and Rybak (2006). To compare the obtained values with another coals, publications of Hławiczka (2008), Cholewiński (2015) or Burmistrz et al. (2016) can be taken into account.

Table 2. Ultimate analysis of selected fuels (air-dried samples).

Fuel	C	H	N	S	O	Hg	Cl
	wt%					ppb	wt%
hard coal 1	75.7	4.3	1.2	1.2	5.6	66	0.31
hard coal 2	62.5	4.0	1.1	0.9	5.1	166	0.20
lignite 1	51.9	3.7	0.5	1.1	18.3	513	0.02
lignite 2	59.0	4.8	0.5	1.3	14.9	306	0.02

Table 3. Proximate analysis and calorific values of selected fuels (air-dried samples).

Fuel	W	W _{ex}	A	V	FC	HHV	LHV
	wt%					MJ/kg	
hard coal 1	3.1	3.7	8.6	32.7	55.6	25.7	24.7
hard coal 2	0.8	12.1	25.4	25.7	48.1	25.2	24.3
lignite 1	8.1	44.6	16.4	41.8	33.7	19.9	18.9
lignite 2	2.0	36.3	17.5	46.6	33.9	22.8	21.7

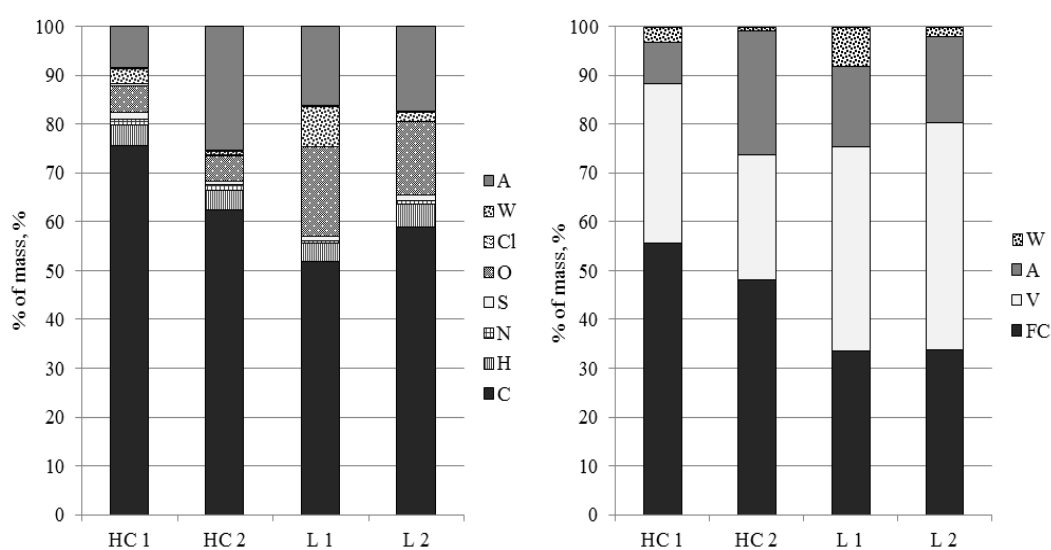


Figure 3. Proximate and ultimate analysis of analysed coals.

3.2. Properties of the chars

In Table 4 mercury contents in chars generated in different temperatures and times were presented. Importantly, the impact of both temperature and time of pyrolysis on Hg presence in final solid product seems to vary significantly depending on the processed fuel (Figure 4.). The changes of mercury content in the cases of L 2 and HC 2 appear to be less sensitive to time (there is no need to increase the time from 30 min to 90 min, that may be beneficial in increasing of the capacity of the whole reactor) and more sensitive to temperature (higher temperature means higher mercury releases). Significant decrease of mercury content for each of the fuels during the 90 min pyrolysis was noticed for the temperatures above 200°C, that may be explained by the high contents of HgS, silicate- and pyrite-bounded mercury compounds in analysed fuels.

Differences between mercury contents between different temperatures and the same times might be an indicator of the further mercury removal potential (some

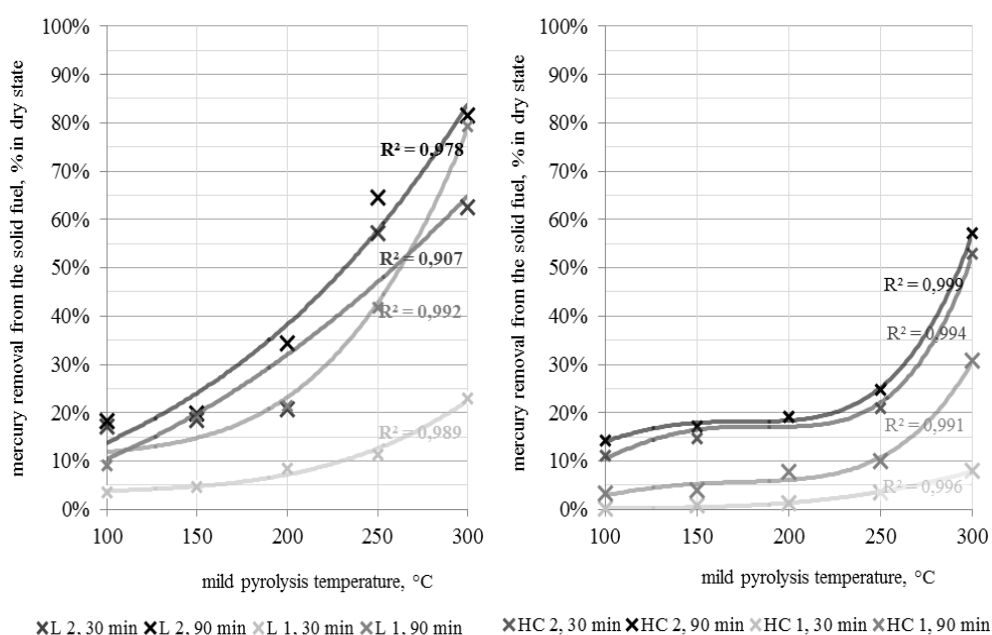
parts of the coal would have not been heated and only a part of the whole sample was processed) at the expense of reduction of production capacity per-unit.

In Figure 5 the loss of dry mass of coals during mild pyrolysis was presented. Significantly higher values were obtained for lignite, that may be identified as a mass of pyrolytic gases released during the whole process and the decrease of solid material before final combustion. As mentioned before, to satisfy easy mercury uptake, high concentrations of Hg and small quantities of pyrolytic gases should be met. However, as indicated, highest mercury releases are take place during increased fuel decomposition (lignite), that may be disadvantageous aspect during the process gas cleaning. Similarly for hard coals, low degradation of dry solid matter is not accompanied by notable mercury releases.

Again, the behaviour of thermal decomposition of solid fuels during mild pyrolysis seems to be specific aspects of the fuel, therefore it should be analysed individually.

Table 4. Mercury content in chars obtained from mild pyrolysis of analysed coals (dry samples – upper index "d").

Fuel	Time of pyrolysis	Temperature, °C				
		100	150	200	250	300
HC 1 Hg ^d = 74 ppb	30 min	74	73	73	71	68
	90 min	71	71	68	66	51
HC 2 Hg ^d = 166 ppb	30 min	147	142	134	131	78
	90 min	142	138	134	125	71
L 1 Hg ^d = 553 ppb	30 min	534	527	506	490	426
	90 min	503	446	434	322	114
L 2 Hg ^d = 336 ppb	30 min	279	274	267	144	126
	90 min	275	269	221	120	62



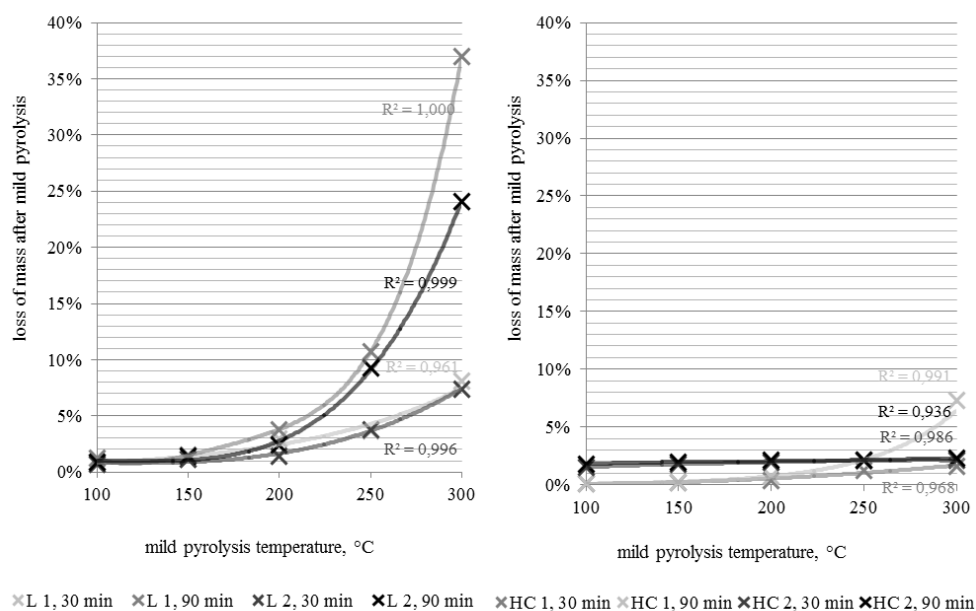


Figure 5. Loss of dry mass of the sample of lignite (left) and hard coals (right) after the mild pyrolysis.

In Table 5 selected proximate analysis and ultimate analysis of the chars from the pyrolysis of hard coal 1 were presented, while in Table 6 – of L 1 chars. In both cases, small changes within fuel composition (C, H, N) was noticed – during low temperature mild pyrolysis, ash and sulphur content slightly rises while carbon, hydrogen and mercury – goes down. HHV seems to stay at the same value, however, if the char is utilised locally, the LHV of char may be higher than LHV of “raw” fuel due to the co-beneficial removal of moisture (first stage of mild pyrolysis covers drying of the sample). Therefore, mild pyrolysis in this case might be considered as a drying process with increased temperature combined with mercury removal.

For higher temperatures (300°C) and pyrolysis times (90 min), all fuels seem to be decomposed more significantly, that results i.e. in lower HHV (drop by 10-20%) and significantly higher ash and sulphur content (by 10-35%, highly dependent on the mass loss during the pyrolysis).

A graphical representation of the changes in mercury contents and mass decrease of the analysed solid materials during the mild pyrolysis were estimated in Figures 4-5 using least-squares function approximation. To identify the accuracy of suggested shapes, coefficients of determination R^2 were highlighted. This calculations may be used in order to predict the transformation rates of the solid materials i.e. in other temperatures of the process.

Table 5. Selected proximate analysis and calorific values of HC 1 chars (dry samples – upper index "d").

Temperature, °C	A*	C	H	N	S*	Hg	Cl**	HHV*
	wt%						ppb	wt%
30 min								
100	9.01	69.9	4.1	1.1	1.30	74		27.27
150	9.02	68.6	4.2	1.0	1.30	73		26.83
200	9.03	68.3	4.1	1.0	1.30	73	0.32	26.57
250	9.11	68.8	3.9	1.0	1.32	71		26.55
300	9.15	68.5	3.7	1.0	1.32	68		26.03
90 min								
100	9.01	69.2	4.2	1.1	1.30	71		27.08
150	9.02	68.5	4.2	1.0	1.30	70		26.76
200	9.06	67.9	3.9	0.9	1.31	68	0.32	26.08
250	9.19	66.8	3.2	1.0	1.33	66		24.62
300	9.71	64.6	2.6	1.0	1.40	51		22.72

* calculated, ** anticipated.

Table 6. Selected proximate analysis and calorific values of L 1 chars (dry samples – upper index "d").

Temperature, °C	A*	C	H	N	S*	Hg	Cl**	HHV*
	wt%					ppb	wt%	MJ/kg
30 min								
100	18.68	54.1	4.2	0.5	1.16	534		19.39
150	18.71	54.2	4.1	0.5	1.16	527		19.37
200	19.07	54.1	4.1	0.5	1.18	506	0.022	19.34
250	19.21	55.6	3.9	0.5	1.19	490		19.64
300	20.14	55.9	3.6	0.5	1.25	426		19.48
90 min								
100	18.72	53.9	4.1	0.5	1.16	503		19.31
150	18.79	52.1	4.3	0.4	1.17	446		18.90
200	19.23	55.4	3.9	0.5	1.20	434	0.022	19.52
250	20.71	53.7	3.2	0.5	1.29	322		18.49
300	29.37	46.8	2.2	0.7	1.82	114		15.59

* calculated, ** anticipated.

Table 7. Simulation of flue gas composition of coals and selected chars.

Fuel	B	S _{Hg(tot)}	S _{SO2}	S _{HCl}	S _{dust}	η _{Hg} (new/exist.)	E _{Hg} (new/exist.)	HCl/SO ₂	HCl/Hg _(tot)
	thous. tonnes	μg/m ³ _{ref}	mg/m ³ _{ref}	mg/m ³ _{ref}	g/m ³ _{ref}	%	kg/yr	mg/g	μg/mg
HC 1 raw state	547	7.3	2,283	303	7.4	36/68-84	5.5-11.1/22.2	132.72	41.67
HC 1 char - 30 min, 200°C	510	8.0	2,853	360	8.9	50/75-88	4.6-9.2/18.5	126.18	45.45
HC 1 char - 90 min, 200°C	519	7.5	2,904	365	9.0	47/73-87	4.6-9.3/18.5	125.69	47.62
HC 1 char - 30 min, 300°C	519	7.5	2,926	364	9.1	47/73-87	4.6-9.3/18.6	124.40	47.62
HC 1 char - 90 min, 300°C	591	6.3	3,476	408	10.8	37/68-84	4.7-9.4/18.9	117.38	66.67
HC 2 raw state	615	19.1	2,070	236	26.3	79/90-95	4.7-9.4/18.8	114.01	12.35
L 1 raw state	1,382	74.9	3,212	30	21.6	91/95-99	5.2-21.0/36.7	9.34	0.40
L 1 char - 30 min, 200°C	711	71.0	3,319	32	24.1	90/94-99	5.0-20.1/35.1	9.64	0.45
L 1 char - 90 min, 200°C	702	59.7	3,290	31	23.8	88/93-98	5.0-20.2/35.3	9.42	0.52
L 1 char - 30 min, 300°C	701	58.3	3,427	31	24.8	88/93-98	5.1-20.3/35.5	9.05	0.53
L 1 char - 90 min, 300°C	867	20.0	6,398	40	46.3	65/80-95	4.9-19.6/34.3	6.25	2.00
L 2 raw state	1,002	54.5	3,176	25	19.2	87/93-98	5.2-20.9/36.6	7.87	0.46

Explanations: S_{Hg(tot)} is total mercury concentration in raw flue gas (defined as the gaseous mercury concentration in raw flue gases at the temperature >700°C), S_{SO2} is sulfur(IV) oxide concentration in flue gas, S_{HCl} is hydrogen chloride concentration in flue gas, η_{Hg} is mercury uptake efficiency, E_{Hg} is mercury emission.

3.3. Predicted mercury concentration in flue gases

To predict the composition of flue gases released from combustion chamber, simplified mathematical model (1) concerning combustion of pulverised solid fuel was used. As mentioned before, calculations were made using 200 MW net power plant. Mercury releases were compared to the BAT-AELs – as a result, necessary mercury uptake efficiencies were assessed as well as annual quantities of heavy metal introduced to the atmosphere. The results were collected in Table 7.

Firstly, significant differences in the concentrations of Hg, SO₂ and HCl for selected raw fuels were obtained. For hard coals, it was, respectively, 7.3 µg/m³_{ref}, 2,283 mg/m³_{ref}, 303 mg/m³_{ref} for HC 1 and 19.1 µg/m³_{ref}, 2,070 mg/m³_{ref}, 236 mg/m³_{ref} for HC 2, while for lignites – 74.9 µg/m³_{ref}, 3,212 mg/m³_{ref}, 30 mg/m³_{ref} (L 1) and 54.5 µg/m³_{ref}, 3,176 mg/m³_{ref}, 25 mg/m³_{ref} (L 2). It was highlighted that hard coals can obtain much more favourable flue gas composition (less mercury and more HCl) – SO₂/HCl and HCl/Hg ratios were 15-150 times higher than lignites. As a result, by the adaptation of mercury uptake within precipitators and wet scrubbers it might be possible to obtain critical 80-95% of total mercury emission control within power unit (annual emission of Hg to the atmosphere between 5-22 kg). On the other hand, in the case of lignites, the situation may be vastly different – high concentration of Hg and SO₂ and marginal HCl presence will lead to low oxidation rate of gaseous mercury and extensive atmospheric releases. Therefore, to adopt existing lignite-fired power plants to the future BAT-AELs (the uptake of mercury 87-99% will be required), several mercury-focused techniques (i.e. halogenated sorbent injection) will be necessary to introduce.

The calculations of the combustion of the chars generated in the mild pyrolysis of HC 1 and L 1 showed the marginally improvements within the composition of flue gases. When chlorine components in the fuel are not released during pyrolysis, after the combustion of chars better HCl/Hg ratio should increase (the possibility to oxidise the Hg⁰ by Cl), however, HCl/SO₂ decreases and promotes SO₂ inhibition effect. Therefore, while the mercury content in solid material and Hg concentration in flue gas after pyrolysis might decrease up to 80%, the increased SO₂ concentration may result in decreased oxidation rate of gaseous mercury and lowered mercury uptake in ESP and wet FGD.

The increased values of SO₂ or dust may be a result of decreased concentration of moisture in energy carrier (first stage of the process is covered by material drying) as well as the transformation of the dry matter during the mild pyrolysis (leading to increased concentration of sulphur and mineral matter). The implementation of chars from mild pyrolysis of selected coals must be combined with the increase of the efficiency of dust collectors as well.

4. Conclusions

In this article the impact of mild pyrolysis of 4 Polish coals on the mercury content and possible Hg, SO₂, HCl and dust concentration was examined. It was proven that the transformation of energy carriers during low-temperature thermal decomposition should be analysed individually – due to the different mercury compounds shares in solid matter, degree of coalification or moisture content. For analysed coals, significant mercury releases (up to 60-80%) were obtained mainly for the temperatures of 300°C and time 90 min. In other investigated cases, the main positive impact of thermal processes is enhanced drying of the material.

After mild pyrolysis, the combustion of char – in comparison to the raw material – should result in both decrease concentration of total mercury in flue gas and the increase of SO₂ concentration. For instance, the application of char L 1 generated in temperature 300°C for 90 min may lead to significant decrease of mercury concentration (by almost 75% in comparison to the raw material), however, due to the increased concentration of SO₂ (almost two times higher) and still relatively low concentration of HCl, the oxidation level of elemental mercury in flue gas may be lowered (more Hg⁰ in flue gas means lower uptake of total Hg in conventional ESP and FGD). As a result, to identify the impact of mild pyrolysis on mercury emission from coal-fired power units, several real-time tests are needed to introduce before final decision concerning the desirability of the implementation of thermal pre-combustion treatment of solid fuel.

In the case of hard coals, low temperature (<300°C) mild pyrolysis seems to be an ineffective way to reduce mercury emissions from combustion process (the most likely due to high content of mercury compounds with high release temperatures, i.e. pyrite-bounded or silicate-bounded). For instance, relatively low decrease of mercury content and increased sulphur concentrations may result in reduced oxidation rate of mercury in flue gases. However, in comparison to lignite, low quantities of Hg_(tot) and high of HCl in flue gases should result in satisfactory mercury uptake at the level of 70-90%, therefore implementation of this type of thermal pre-combustion mercury reduction technique seem to be pointless. To obtain profitable HCl/SO₂ and HCl/Hg ratios in flue gases after mild pyrolysis of selected coals, it might be valid to combine thermal process with the additional pre-combustion desulphurisation. From the mercury emission point of view it is crucial to increase Cl and bromine content in solid fuels and to decrease S and Hg – while mild pyrolysis might be useful to reduce mercury content, it is still important to couple it with sulphur removal.

Finally, the application of mild pyrolysis in coal fired power units must be combined with efficient mercury capture technology from pyrolytic gases. While the decrease of mercury content in solid fuel, that is used i.e. in power boiler, might reduce the quantity of mercury introduced to the atmosphere from a power plant, the Integrated Pollution Prevention and Control strategy

(mentioned in EU Directive No. 96/61/WE) will be covered only when mild pyrolysis in full scale unit is integrated with one of a highly efficient atmosphere protection method.

Literature

- Burmistrz, P., Kogut, K., Marczak, M., Zwoździak, J. (2016). Lignites and subbituminous coals combustion in Polish power plants as a source of anthropogenic mercury emission. *Fuel Processing Technology*, Vol. 152, 250-258.
- Central Statistical Office (2016). Production Department, Energy statistics in 2014 and 2015. Statistical Information and Elaboration. *Central Statistical Office*, Warsaw.
- Cholewiński M. (2017). Szacowanie unosu rtęci z procesów spalania paliw stałych. *Zeszyty Energetyczne*, Vol. 4, 73-87. (in Polish)
- Cholewiński M. (2015). Badanie paliw stałych pod kątem ograniczenia emisji rtęci z bloków węglowych. *Zeszyty Energetyczne*, Vol. 2, 65-81. (in Polish)
- Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 establishing best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for large combustion plants.
- Czajka K., Kisiela A., Moroń W., Ferens W., Rybak W. (2016). Pyrolysis of solid fuels: Thermochemical behaviour, kinetics and compensation effect. *Fuel Processing Technology*, Vol. 142, 42-53.
- Ferens W. (2014). Kaloryczność paliw stałych. *Zeszyty Energetyczne*, Vol. 1, 149-158. (in Polish).
- Hławiczka S. (2008). Rtęć w środowisku atmosferycznym. *Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk*, Zabrze. (in Polish)
- Kordylewski W. (2008). Spalanie i paliwa. *Oficyna Wydawnicza Politechniki Wrocławskiej*, Wrocław. (in Polish).
- Liu L., Duan Y-F., Wang Y-J., Wang H., Yin J-J. (2010). Experimental study of mercury release behavior and speciation during pyrolysis of two different coals. *Journal of Fuel Chemistry and Technology*, Vol. 38, No. 2, 134-139.
- Luo G., Ma J., Han J., Yao H., Xu M., Zhang Ch., Chen G., Gupta R., Xu Z. (2013). Hg occurrence in coal and its removal before coal utilization. *Fuel*, Vol. 104, 70-76.
- Moroń W. (2014). Wpływ atmosfery O₂/RFG na zapłon i formowanie się płomienia. *Zeszyty Energetyczne*, Vol. 1, 113-124. (in Polish)
- Moroń W., Ferens W., Czajka K.M. (2016). Explosion of different ranks coal dust in oxy-fuel atmosphere. *Fuel Processing Technology*, Vol. 148, 388-394.
- The National Centre For Emissions Management (2017). Krajowy bilans emisji SO₂, NO_x, CO, NH₃, NMLZO, pyłów, metali ciężkich i TZO za lata 2014-2015 w układzie klasyfikacji SNAP. Raport syntetyczny, Warsaw. (in Polish).
- Neavel R.C., Smith S.E., Hippo E.J., Miller R.J. (1986). Interrelationships between coal compositional parameters. *Fuel*, Vol. 65, No. 3, 312-320.
- Pan WP., Cao Y., Zhang K. (2013) Mercury Emission, Control and Measurement from Coal Combustion. In: Qi H., Zhao B. (eds) *Cleaner Combustion and Sustainable World*. Springer, Berlin, Heidelberg.
- Rhee S-W. (2016). Control of mercury emissions: policies, technologies, and future trends. *Energy and Emission Control Technologies*, Vol. 4, 1-15.
- Rybak W. (2006). Spalanie i współspalanie biopaliw stałych. *Oficyna Wydawnicza Politechniki Wrocławskiej*, Wrocław. (in Polish)
- Wang S.X., Zhang L., Li G.H., Wu Y., Hao J.M., Pirrone N., Sprovieri F., Ancora M.P. (2010). Mercury emission and speciation of coal-fired power plants in China. *Atmospheric Chemistry and Physics*, Vol. 10, 1183-1192.
- Wierzbowski M., Filipiak I., Łyżwa W. (2017). Polish energy policy 2050 – An instrument to develop a diversified and sustainable electricity generation mix in coal-based energy system. *Renewable and Sustainable Energy Reviews*, Vol. 74, 51-70.
- Yin C-Y. (2011). Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel*, Vol. 90, 1128-1132.

Acknowledgments

The author would like to express his sincere appreciation to Dr Wiesław Ferens and Prof. Wiesław Rybak for their valuable comments and suggestions throughout this research. This research was a part of the project No. K0903/0402/0231/16 “Badania procesów cieplno-przepływowych w urządzeniach i systemach energetycznych – zaawansowane czyste techniki kotłowe i użytkowanie paliw” and was financed under the „Dotacja statutowa na prowadzenie badań naukowych dla młodych naukowców oraz uczestników studiów doktoranckich” programme by the Ministry of Science and Higher Education Republic of Poland.