The Release and Reduction of Mercury from Solid Fuels through Thermal Treatment Prior to Combustion

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Abstract: The main source of mercury (Hg) anthropogenic emissions is the combustion of hard and lignite coal in power plants. Reduction of Hg emissions from coal-based power production systems involves Hg removal from the fuel before combustion/gasification by thermal treatment (i.e., low-temperature pyrolysis). Herein, we present the results of laboratory and bench-scale studies on Hg removal from coal via thermal fuel treatment. The influence of the process temperature and coal residence time in the reaction zone on Hg removal efficiency and fuel parameters is studied. The properties of the process products are analyzed as follows: proximate and ultimate analysis for solids as well as H2, N2, CO, CO2, CH4, organic compounds C2–C5, density, and HHV for gaseous. The results show a substantial reduction of Hg in the fuel using a low-temperature pyrolysis process. At moderate pyrolysis temperature provided Hg removal efficiencies of up to 50% for hard coal and over 90% for lignite, with a moderate decrease in the chemical enthalpy of the fuel.

Keywords: coal; pyrolysis; mercury removal

1. Introduction

Mercury (Hg) is a highly toxic element that poses a serious threat to human health. The main source of Hg emissions into the atmosphere is through the combustion of coal for power generation, with the predominant share originating from industrial power plants. Reported technologies currently applied for Hg separation formed during the coal combustion process may be divided into the following two main groups:

- Modifications to the existing flue gas treatment systems (decrease in flue gas temperature, sorbent injection, design modifications);
- New technologies, including pre-combustion Hg removal as well as simultaneous removal of multiple gaseous pollutants.

The method for Hg separation from fuel by thermal treatment (low-temperature pyrolysis) before combustion is an interesting alternative to the methods focusing on Hg removal from flue gases. This is due to higher Hg concentrations and much smaller amounts of purified gas compared to flue gas. The possibility of using low-temperature pyrolysis for simultaneous desulfurization and denitrification of fuel is an additional advantage [1].

Published simulations of systems operating on an industrial scale also indicate that the use of low-temperature pyrolysis is a competitive solution to traditional methods of reducing Hg emissions from the coal combustion process [2].

The majority of publications examine the effect of temperature and residence time on the degree of Hg removal from coal [3–17] and identify the forms of Hg while searching for a relationship between their removal and process temperature [10,12,17–20]. The published data
related to Hg removal by low-temperature pyrolysis implies that, for various sorts of hard coal and different residence times, the average Hg removal was 10–38% at 200 °C, 20–40% at 250 °C, 0–90% at 300 °C, 19–25% at 350 °C, and 20–100% at 400 °C. In most cases, a temperature of 400 °C is sufficient to remove most of the Hg from coal by low-temperature pyrolysis. However, the heterogeneous nature of coal and the lack of research describing the mechanism of Hg removal from coal requires an individual approach for each considered case. The literature concerning Hg removal from coal by low-temperature pyrolysis is listed in Table 1.

Table 1. Published data concerning Hg removal from coal by low-temperature pyrolysis [2,4,5,7–21].

| Lp. | Sample Characteristics | Characteristics of the Process | Hg Removal Efficiency | Ref. |
|-----|------------------------|-------------------------------|-----------------------|------|
| 1   | Hard coal; m = 0.5 g, Particle size: <115 μm Dried at 85 °C | Temp. 275–600 °C (LF #6A a), 325–450 °C (PT#8) | Residence Time 10–60 min | LF #6A: 5.3–74% PT#8: 36–80% [7,8] |
| 2   | Hard coal, m = 1 g, Particle size: <200 μm Dried at 105 °C | Temp. 400–1000 °C | Residence Time 15 min | Hard coal 1 b 83–95% Hard coal 2 c 45–85% [8] |
| 3   | Hard coal; m = 0.5 g Particle size: 106–149 μm | Temp. 200–400 °C | Residence Time 0–60 min | SS coals: 9–90% SARM coal d 0–67% [10] |
| 4   | Hard coal and lignite; M = 6 g, Particle size: <74 μm Dried at 105 °C | Temp. 100–300 °C | Residence Time 0–12 min | PRB e coal: 26–70% Lignite f 0–70% [2] |
| 5   | Hard coal and lignite; m = 0.2 g Particle size: 150–250 μm Dried at 105 °C | Temp. 200–900 °C | Residence Time 5–120 min | Ptolemais lignite: 29–80% Bulgarian lignite: 23–95% Australian hard coal: 32–87% [10] |
| 6   | Hard coal and lignite; m = 0.2 g Particle size: 150–250 μm Dried at 105 °C | Temp. 200–900 °C | Residence Time 5–120 min | Ptolemais lignite: 29–80% Ptolemais lignite (D) f 23–95% Megalopolis lignite: 10–70% Australian hard coal: 32–87% [11] |
| 7   | Hard coal, m = 0.5 g Particle size: <149 μm; | Temp. 150–300 °C | Residence Time 60 min | SS coals b 24–80% UF 1: ~60% IL #6: ~20% PT#8 k: ~60% [12] |
| 8   | Hard coal and lignite; m = 45 kg/h (Continuous operation; pilot) | Temp. 150–300 °C | Residence Time 8, 12, 16 min | Gulf Coast Lignite: 63% Canada Lignite: 90% ND Lignite-C: 55% ND Lignite-A: 44% Southern PRB: 71% Eastern PRB: 80% Northern PRB: 36% Colorado Bituminus: 34% [3] |
| 9   | Hard coal, m = 6 g Particle size: <115 μm Dried at 65 °C Hard coal and brown coal m = 200 g | Temp. 200–800 °C | Residence Time 0–60 min | Datong coal: 34–95% (800 °C) Baorixile coal: 29–93% (800 °C) [18] |
| 10  | Particle size: <200–500 μm m = 19 g Particle size: <200 μm dried at 105 °C | Temp. 220–520 °C 200–500 °C | Residence Time 0–60 min 10–85 min | Hard coal: 0–85% Brown coal: 12–99% Hard coal: 0–85% Brown coal: 12–99% [4,5] |
Table 1. Cont.

| Lp. | Sample Characteristics | Characteristics of the Process | Hg Removal Efficiency | Ref. |
|-----|------------------------|--------------------------------|-----------------------|------|
| 11  | Hard coal. m = 100 mg  |                                |                       | [19] |
|     | Particle size: <200 µm |                                |                       |      |
|     | Dried at 105 °C       |                                |                       |      |
|     |                       | 20–660 °C                      |                       |      |
|     |                       | Residence Time                 |                       |      |
|     |                       | Coal C1: 0–55% (600 °C)        |                       |      |
|     |                       | Coal C2: 0–70% (650 °C)        |                       |      |
| 12  | Lignite                |                                |                       | [20] |
|     | Bituminous coals      |                                |                       |      |
|     | Particle size: <200 µm|                                |                       |      |
|     | Dried                 |                                |                       |      |
|     | m = 100 mg            |                                |                       |      |
|     |                       | 40–660 °C                      |                       |      |
|     |                       | Continuous heating process     |                       |      |
|     |                       | 1 °C/min                       |                       |      |
|     |                       | Lignite: 82.4% (400 °C)        |                       |      |
|     |                       | Bit. coals: 45.5–59.1% (400 °C)|                       |      |
|     |                       | The temp. range for            |                       |      |
|     |                       | releasing various Hg species   |                       |      |
|     |                       | was shown to be <150 °C for    |                       |      |
|     |                       | Hg0, 150–250 °C for HgCl<sub>2</sub>/org.-bound Hg|      |      |
|     |                       | 250–400 °C for HgS/silicate-bound Hg and |      |      |
|     |                       | 400–600 °C for pyrite-bound Hg.|                       |      |
| 13  | Lignite                |                                |                       | [14] |
|     | Hard coals: A and B   | 170–410 °C                     |                       |      |
|     | Particle size: 500–1000 µm|                          |                       |      |
|     | Dried                 | online                        |                       |      |
|     | m = 500 mg            | measurement                    | Hard coals: 80% (380 °C) |      |
|     |                       |                               | Lignite: >80% (290 °C)  |      |
| 14  | Bituminous coals      | 100–800 °C                     |                       | [15] |
|     | Size: <200 µm         | 60 min                        | Coal A, Maximal efficiencies: |      |
|     | m = 0.5 g             | 0.1, 0.5, 1.0 atm              | 83% at 650 °C (coal A) |      |
|     |                       |                                | 89% at 500 °C (coal B) |      |
|     |                       |                                | 87% at 400 °C (coal C) |      |
| 15  | Bituminous coals      | 0–1200 °C                      |                       | [16] |
|     | Size: 160–270 µm      | Continuous heating process     | 150–400 °C; 38.9–80.1% m |      |
|     | Dried                 | 20 K/min                       | 500–600 °C; 2.9–29.4% |      |
|     | m = 1 g               |                                | t > 750 °C; 8.9–16.2%, |      |
| 16  | Lignite                | 200–900 °C                     |                       | [17] |
|     | Greek: Ptolemais,     | 5–120 min                      |                       |      |
|     | Megalopolis,          | 0.25, 0.5, 1.0 atm             | 200–300 °C; 32–44% Lmn |      |
|     | Bulgarian, Elhovo,    |                                | 300–600 °C; 36–46% |      |
|     | Australian, Latrobe Valley. |                            | 600–900 °C; 19–31% |      |
|     | Size: 150–250 µm, dried|                             |                       |      |

Notes: a—Lower Freeport #6A; b—coal blend used in a coking plant (gascooking coal type 34.1: 70% and orthocoking coal type 35.1: 30%); c—orthocoking coal (floation concentrate) type 35.2; d—standard coal, Republic of South Africa; e—Freedom Mine, US, NDk—orthocoking coal (floation concentrate) type 35.2; f—demineralized Ptolemais; g—Japanese standard coals (SS001, SS004, SS006, SS020); h—Upper Freeport; i—Illinois #6; j—Pittsburgh #8; l—removal efficiency within a given temp. range; m—depend on the coal processed.

Only a few publications describe the effect of the pyrolysis process, including process temperature, on the properties of the purified fuel, which is critical in terms of practical pyrolysis applications. Similarly, the distribution and characterization of other products generated by the pyrolysis process are of interest for future applications. Merdes et al. [7] investigated the change of volatile parts in purified coal and emphasized the importance of maintaining the calorific value of the fuel in addition to achieving high degrees of Hg separation. Wichlinski [15] did not determine the loss of calorific value of fuel when analyzing the loss of carbon (C) element emitted during the pyrolysis process. Skodras [12] showed the reactivity of the resulting carbonates and co-correlated Hg removal with the removal rate of sulfur, nitrogen, C, and volatile parts. However, their composition or the chemical enthalpy loss of the fuel was not provided. Sotiropoulou [21] examined the correlations between Hg removal and C conversion expressed as the loss of volatile fuel components. Only the WRI report [2] on the implementation of pilot studies for the
process temperatures of 300 °C contained data related to parameters for specific US coals (550–600 °F).

The effects of temperature and time of the pyrolysis process on the degree of Hg removal and the characteristics of the fuel obtained were studied in this paper. The study was carried out using Polish reference coals used in the power industry. The goal of the study was to determine the pyrolysis process temperatures that allow for efficient Hg removal while reducing the fuel’s degradation rate by measuring the change in the chemical enthalpy flux. Furthermore, we determined the properties of the obtained fuels as a function of process temperature, as well as the distribution of pyrolysis products and the parameters of gaseous products produced by the process.

2. Materials and Methods

2.1. Samples

The presented study was conducted using lignite BC1, BC2 (from the “Belchatów” coal mine, Bełchatów, Poland), hard coals HC1, HC2 (from the “Janina” coal mine, Libiąż, Poland), and hard coal HC3 (from the “Wieczorek” coal mine, Katowice, Poland). The fuels’ characteristics are provided in Table 2. The samples from the pyrolysis tests were prepared in accordance with PN-90/G-04502 (air-dried basis, ground, and sieved < 0.2 mm).

Table 2. Characteristics of hard coals (HC1, HC2, HC3) and lignite (BC1, BC2).

| Parameter | Unit | W^{ar} | W^{ad} | A^{d} | V^{d} | HHV^{d} | C^{d} | H^{d} | N^{d} | S_{t,^{d}} | O^{d} | Hg^{d} | ppb |
|-----------|------|--------|--------|-------|-------|---------|-------|-------|-------|-----------|-------|--------|-----|
| HC1       | %    | 12.10  | 12.10  | 34.86 | 27.3  | 68.9    | 3.95  | 1.07  | 1.39  | 12.53     | 81    |        |     |
| HC2       | %    | 15.07  | 12.10  | 31.68 | 25.6  | 65.4    | 4.06  | 0.99  | 2.06  | 12.18     | 116   |        |     |
| HC3       | %    | 8.86   | 15.07  | 30.39 | 30.5  | 77.8    | 4.47  | 1.27  | 0.44  | 6.89      | 27    |        |     |
| BC1       | %    | 7.8    | 11.06  | 48.07 | 23.5  | 60.7    | 4.39  | 0.74  | 0.90  | 22.17     | 414   |        |     |
| BC2       | %    | 9.76   | 9.76   | 50.77 | 23.8  | 60.5    | 4.77  | 0.63  | 0.70  | 23.56     | 392   |        |     |
| Uncertainty| %    | 0.2    | 0.2    | 0.19  | 0.16  | 0.5     | 0.1   | 0.03  | 0.05  | -         | 0.01  |        |     |

W—moisture content, A—ash content, V—volatile matter, HHV—higher heating value, C—carbon, H—hydrogen, N—nitrogen, S—sulphur, O—oxygen, Hg—mercury, analytical state: \(^{ad}\)—air dried basis; \(^{ar}\)—as received basis; \(^{d}\)—dry basis; \(^{t}\)—total, \(^{O}\)—from differences. BCT1-BCT11 are symbols of pyrolysis process in different temp. and different residence time for lignite BC1 and BC2. HCT1–HCT15 are symbols of pyrolysis process in different temp. and different residence time for hard coals HC1, HC2 and HC3.

2.2. Pyrolysis

2.2.1. Pyrolysis–Scale 1–19 g

The laboratory studies concerning the impact of coal temperature and residence time on the degree of Hg removal from lignite and hard coals were conducted using a thermogravimetric analyzer TGA 701 (LECO Corporation, St. Joseph, MI, USA). The weight of the sample was approx. 1 g and 19 specimens were analyzed simultaneously in nitrogen. The tests were conducted over a temperature range of 200–500 °C with residence times of 0–10 min for lignite and 0–8 min for hard coals. The process conditions of the performed studies are detailed in Table 3. For analysis, coal specimens with a grain size below 0.2 mm were employed. A coal specimen was weighed separately into 19 open ceramic crucibles (coal sample per crucible: \(1 \pm 0.5 \) g) and introduced into the analyzer. The samples were heated to a specific temperature at the rate of approx. 36 K/min under a nitrogen atmosphere (with nitrogen flow rate of 3.5 L/min). After the pyrolysis process was completed, the analyzer remained closed, and the samples were cooled under a nitrogen atmosphere to room temperature. Then, the charred specimens were collected into one vessel, and Hg content and other relevant physical and chemical properties were measured using procedure Q/LCA/32/A: 2021 of the Institute of Energy and Fuel Processing Technology, based on International Standard ISO 15237:2016 [22].
Table 3. Experimental temperature ranges for testing and residence time impact on Hg removal content from lignite (BC1, BC2) and hard coals (HC1, HC2, HC3).

| Temp. of Pyrolysis Process | BC     | HC     |
|----------------------------|--------|--------|
|                            | Residence Time of Lignites in the Required Temp. during the Pyrolysis Process (min) | Residence Time of Hard Coals in the Required Temperature during the Pyrolysis Process (min) |
|                            | 0      | 4      | 8      | 10     | 0      | 4      | 8      |
| 200 °C                     | BCT1   | BCT2   | BCT3   | BCT4   | HCT1   | HCT2   | HCT3   |
| 250 °C                     | BCT5   | BCT6   | BCT7   | BCT8   | HCT4   | HCT5   | HCT6   |
| 300 °C                     | BCT9   | BCT10  | BCT11  |        | HCT7   | HCT8   | HCT9   |
| 350 °C                     | BCT12  | BCT13  |        |        | HCT10  | HCT11  | HCT12  |
| 400 °C                     | BCT14  |        |        |        | HCT13  |        |        |
| 450 °C                     |        |        |        |        | HCT14  |        |        |
| 500 °C                     | BCT15  |        |        |        |        |        |        |

2.2.2. Pyrolysis–Scale ~ 100 g

The obtained carried out on lab-scale (~1 g) were verified on the workstation of low-temperature pyrolysis in the fixed-bed (the weight of the sample was approx. ~100 g). The presented research setup was created in cooperation with Joint Research Center, Institute for Energy Petten (The Netherlands). The test setup included an electric furnace, a steel retort (where the tested materials were converted), and a system for collecting the liquid and gaseous fractions. The instrument’s specification required the use of particle size samples in the range of 0.5–3.14 mm. The retort with fuel was introduced into the furnace and heated at a rate of 10 °C/min to 250 °C and 300 °C for lignite, and a temperature range of 350–550 °C for hard coals (temperature was selected based on TGA results and the current lab-scale results). In the case of lignite after reaching the required final temperature of the pyrolysis process, heating of the retort was stopped and the residence time of the coal at the final temperature of the process was 0 min. At this time the retort was immediately removed from the heating zone without opening and cooled down to room temperature under a nitrogen atmosphere. In the case of hard coal, tests were carried out for the following two residence times:

- When the test temperature reached the set temperature, heating was immediately stopped by removing the retort from the furnace heating zone and allowed to cool to room temperature under an inert atmosphere by continuously purging it with nitrogen. The residence period of the sample at the given temperature was assumed to be 0 min in the test;
- Once the test temperature reached the set temperature, the sample was maintained in the furnace’s heating zone for another 20 min before being removed and cooled to room temperature under a nitrogen atmosphere. The residence period of the sample at the given temperature was supposed to be 20 min in this test. (see Table 4).

Table 4. Experimental temperature ranges for testing and residence time impact on Hg content removal from lignite (BC1, BC2) and hard coals (HC1, HC2, HC3). The experiment scale was 100 g.

| Temp. of Pyrolysis Process | BC1 | BC2 | HC1 | HC2 | HC3 |
|---------------------------|-----|-----|-----|-----|-----|
|                            | Residence Time of Lignites in the Required Temp. during the Pyrolysis Process (min) | Residence Time of Hard Coals in the Required Temp. during the Pyrolysis Process (min) | |
|                            | 0   | 20  | 0   | 20  | 0   | 20  | 0   | 20  |
| 250 °C                     | x   |     |     |     |     | x   |     |     |
| 300 °C                     | x   |     |     |     |     | x   |     |     |
| 350 °C                     |     | x   |     |     |     | x   |     |     |
| 400 °C                     |     |     |     |     |     |     |     |     |
| 450 °C                     | x   |     |     |     |     |     |     | x   |
| 500 °C                     |     |     |     |     |     |     | x   |     |
| 550 °C                     |     |     |     |     |     |     | x   | x   |
In the process, continuously liquid and gaseous products were collected for detailed qualitative and quantitative analysis. Analysis of the gaseous products (i.e., to determine gaseous products composition, organic compounds content, high-heat value, and density) was carried out using a gas chromatograph with FID (Flame Ionization Detector), TCD (thermal conductivity detector), PFPD (Pulsed Flame Photometric Detector) detector (model CP3800, Varian, Palo Alto, CA, USA). Determination of Hg content in the pyrolytic gas consists of transmission definite volume of research gas by activated carbon sorbents where mercury was adsorbed.

2.3. Mercury Determination

Determination of Hg content was achieved using an MA-2 analyzer (Nippon Instrument Corporation, Osaka, Japan).

The measuring method consisted of the amalgamation of mercury vapors after thermal decomposition of the sample in the analyzer. Detection was performed using a non-dispersive double-beam Cold Vapor-Atomic Absorption (CVAAS) Spectrophotometer. Determination of the total Hg content was performed in accordance with reference [23] procedure Q/LCA/32/A: 2021 of Institute of Energy and Fuel Processing Technology, based on International Standard ISO 15237:2016. For calibration, NIST Certified Reference Materials were used. The effectiveness of Hg removal from the fuel was established based on the measurements of Hg content in coal and char received in pyrolysis process.

3. Results and Discussion

3.1. Studies of the Impact of Coal Temperature and Residence Time on the Degree of Hg Removal from Fuel

The results of the impact of coal temperature and residence time on the degree of Hg removal from fuel are presented in Figures 1 and 2. In the case of lignite (BC1, BC2), the average Hg content decreased during the pyrolysis process at 200 °C (the degree of Hg removal depending on the residence time of the fuel in the reaction zone was 9.6–26%; Figure 1). When the temperature was increased to 250 °C, the Hg content in the fuel showed a significant decrease and the Hg removal efficiency was 69–84%. A further increase in temperature to 300 °C increased the degree of Hg removal to 90%. The average Hg removal efficiency ratio obtained for hard coals (HC1, HC2, HC3) was far lower. At 200 °C, the decrease in Hg content was insignificant, and, depending on the residence time, the degree of Hg removal varied between 1.2% and 16% (Figure 2).

Figure 1. The average percentage efficiency of Hg removal from coal under low-temperature pyrolysis for lignite (BC1, BC2); dependence on process temperature at different residence times (0, 4, 8, 10 min).
Hg content showed a considerable reduction in the fuel and 50% removal efficiency was attained at 350 °C. Compared to the results presented in Figure 1, Figure 2 shows that a further increase in the process temperature to 400 °C did not affect Hg removal efficiency, and only at 450–500 °C was an increase up to 56% and 75% observed, respectively. A temperature increase in the range of 200–500 °C led to an 8–39% loss in the coal weight for lignite (BC1, BC2) and 11–27% for hard coals (HC1, HC2, HC3). The highest decrease occurred within the range of 300–500 °C (27%) and 400–500 °C (12%) for lignite (BC1, BC2) and hard coals (HC1, HC2, HC3), respectively. The residence time of the fuel remaining in the reaction system affected Hg removal efficiency, with the largest impact exerted at low temperatures (200, 250, and 300 °C, Figures 1 and 2) and within the residence time range of 0–4 min.

Additionally, thermal coal processing enables sulfur removal from fuel [1]. The studies conducted showed an increase in the process temperature caused a reduction of sulfur content in solid products. The average removal efficiency obtained at 500 °C was 29% and 46% for hard coals (HC1, HC2, HC3) and lignite (BC1, BC2), respectively (Figure 3).

For hard coals (HC1, HC2, HC3), within the temperature of 200–250 °C and 350–400 °C, the observed average changes in Hg removal with temperature was negligible and the removal efficiency curve assumed a characteristic shape. The characteristic shape, including the occurrence of a local maximum at a temperature of approx. 400 °C, was
explained by the transfer of the coal into its plastic state and a change in its porous structure (porosity loss) [21,24]. The temperature at which the maximum removal efficiency occurred depended on the degree of carbonification, heating rate, grain size, and plastic properties of the analyzed fuel. In the case of American bituminous coals with a high content of volatiles, the maximum removal efficiency was 400–500 °C [21,24]. The shape of the efficiency curve (Figure 2) was primarily due to the distribution of Hg forms in the coals because the coals did not reach their plastic state during the temperature range studied. This was evident by analyses conducted according to the PN-G-04565:1994 standard, which could influence the shape of the curve. According to reports, the pyrolysis process, especially the degree of Hg removal, is affected by the type of coal studied. However, the observed discrepancies in the data indicated that the type of Hg contained in the coals tested, rather than the physicochemical features of the coal, affects the efficacy of Hg removal [9,10,18].

Sequential leaching employed (NH$_4$C$_2$H$_5$O$_2$, HCl, HF, and HNO$_3$) for testing of Hg distribution in typical American coals indicated that in the case of bituminous coals, more Hg was associated with supplied minerals (up to 65%), while in sub-bituminous coals, Hg was associated mostly with organic matter (up to 100%) [25].

### 3.2. Influence of Process Parameters on the Properties of Refined Fuel

The properties of the coal used and the chars produced are illustrated in Figures 4 and 5. Increasing the pyrolysis temperature reduced the moisture and volatile content, which increased the percentage loss of chemical enthalpy of the char. We can speak about refined fuel since the low-temperature pyrolysis method, in this case, is utilized to greatly improve the quality of coal by eliminating mercury from it. Both the lignite and hard coals processes initially led to elevated heating values (due to the removal of moisture from the fuel) and subsequently to its decrease. However, for hard coals (HC1, HC2, HC3) and lignite (BC1, BC2), within the analyzed temperature range, the higher heating value was maintained at a level similar to that of raw coal. For the air-dried state, fuel properties for lignite changed more rapidly with temperature changes, and the changes were observed at 250 °C, whereas further process temperature increases exerted a far larger impact on the char properties than for hard coals. Increasing the pyrolysis process temperature to 500 °C led to an average reduction of C, hydrogen (H), and volatiles (V) content in the char by 38%, 66%, and 61%, respectively, compared to the input fuel. A very sudden drop in chemical enthalpy (by 42%) of the char was also observed (Figure 4). For hard coals, noticeable changes in the fuel properties were observed within the temperature range of 300–350 °C, and a further increase in temperature to 500 °C caused a considerable reduction in H, C, and V content (56%, 21%, 49%), as well as a reduced fuel enthalpy of 26% (Figure 5). Comparison of the average changes in the fuel properties and average Hg removal efficiency revealed that the optimum process temperature values for lignite (BC1, BC2) and hard coals (HC1, HC2, HC3) were at 300 °C and 350 °C, respectively (Figures 4 and 5).

Figure 4. The average change of parameters and composition of refined fuel for lignite; percentage loss of C, H, and V, content, fuel chem. enthalpy vs. process temperature.
Results obtained for lignite (BC1, BC2) confirmed high Hg removal efficiency. When the treatment was conducted at 300 °C, an Hg removal efficiency of 86.7% for BC1 and 93.0% for BC2 was achieved. The refined fuel (char) was thought to have a high calorific value and low moisture content. The percentage loss of chemical enthalpy of purified fuel compared to the input fuel. The Hg removal efficiency for particular samples of coal is illustrated in Figure 6.

3.3. Verification of the Results of Bench Scale Experimental Test

The process parameters and refined fuel composition are presented in Table 5. Additionally, Table 5 shows the Hg removal efficiency from tested coal and the loss of chemical enthalpy of purified fuel compared to the input fuel. The Hg removal efficiency for particular samples of coal is illustrated in Figure 6.

Table 5. Refined fuel characteristic.

| Coal | Temp. °C; Residence Time, min | Proximate Analysis, % | HHV d | Ultimate Analysis, % | Hg d | Efficiency Removal Hg | Loss in Entalphy * |
|------|-------------------------------|-----------------------|--------|----------------------|------|-----------------------|-------------------|
|      | W ad | A d | V d | MJ/kg | C d | H d | N d | S d | O d | ppb | % | % |
| HC1  | 350; 0 | 2.2 | 12.47 | 29.79 | 27.2 | 69.5 | 4.00 | 1.19 | 1.31 | 11.5 | 66 | 14.9 | - |
|      | 450; 0 | 0.8 | 13.51 | 30.18 | 27.2 | 68.9 | 4.17 | 1.17 | 1.36 | 11.26 | 51 | 31.6 | - |
| HC2  | 450; 0 | 1.3 | 17.12 | 26.95 | 25.5 | 65.0 | 3.71 | 0.99 | 1.90 | 10.97 | 84 | 28.9 | 2 |
|      | 450; 20 | 1.8 | 18.43 | 15.17 | 26.4 | 68.7 | 2.89 | 1.12 | 2.08 | 6.47 | 107 | 22.3 | 13.4 |
|      | 550; 0 | 0.5 | 16.58 | 22.31 | 26.2 | 67.2 | 3.44 | 1.06 | 1.96 | 9.47 | 89 | 29.1 | 5.2 |
|      | 550; 20 | 1.4 | 19.98 | 8.34 | 27.3 | 72.3 | 2.39 | 1.19 | 1.58 | 2.26 | 33 | 78.6 | 20.0 |
| HC3  | 450; 0 | 0.6 | 8.35 | 15.65 | 30.7 | 80.7 | 3.34 | 1.45 | 0.44 | 5.44 | 15 | 51.3 | 11.8 |
|      | 550; 0 | 0.6 | 10.06 | 8.51 | 30.9 | 82.3 | 2.63 | 1.49 | 0.41 | 2.83 | 9 | 73.7 | 20.1 |
| BC1  | 300; 0 | 1.7 | 9.97 | 42.74 | 24.9 | 65.0 | 4.10 | 0.76 | 0.80 | 19.36 | 29 | 86.7 | - |
| BC2  | 300; 0 | 1.2 | 10.53 | 48.71 | 24.2 | 61.6 | 4.52 | 0.65 | 0.71 | 21.93 | 306 | 26.3 | 3.8 |

Results obtained for lignite (BC1, BC2) confirmed high Hg removal efficiency. When the treatment was conducted at 300 °C, an Hg removal efficiency of 86.7% for BC1 and 93.0% for BC2 was achieved. The refined fuel (char) was thought to have a high calorific value and low moisture content. The percentage loss of chemical enthalpy of purified fuel compared to the input fuel reached 10%.

In the case of tests conducted using hard coal HC1 (from the “Janina” coal mine) at 350 °C, the determined Hg removal efficiency was 14.9% (i.e., 24.1% lower than research conducted on a lab-scale-TGA). It was observed that increased temperature to 450 °C significantly impacted Hg removal efficiency by approx. 16.7% (the current efficiency of Hg removal was 31.6%). Further tests of low-temperature pyrolysis conducted on a lab scale (~100 g) using a new hard coal sample from the “Janina” coal mine (HC2) confirmed the earlier results. At 450 °C, independent of the residence time of the fuel in the reaction zone,
the removal efficiency was determined as 28.9% (Figure 6, Table 5). A significant increase in Hg removal efficiency (78.6%, Figure 6) was obtained at 550 °C with a residence time of 20 min. Unfortunately, this was connected with a significant loss of fuel chem. enthalpy (up to 20%).

![Figure 6. Hg removal efficiency of bench scale experimental test, %](image)

The obtained results from hard coal HC3 (from the “Wieczorek” coal mine) showed that a considerable reduction of Hg content in the fuel using low-temperature pyrolysis was possible. Hg removal efficiency at 550 °C reached 73.7% for HC3 (residence time of 0 min). However, as in the case of HC2, a decrease in chem. enthalpy (by 20%) of char was also observed. Yields of the pyrolysis products are provided in Table 6. Characteristics of the gaseous pyrolysis products are provided in Table 7.

| Coal       | Temp., °C | Residence Time, min | Char, % | Liquid Products, % | Gaseous Products, % |
|------------|-----------|---------------------|---------|--------------------|---------------------|
| HC1        | 350       | 0                   | 94.5    | 2.53               | 5.6                 |
|            | 450       | 0                   | 91.0    | -                  | -                   |
|            | 450       | 20                  | 73.0    | 13.7               | 13.3                |
| HC2        | 550       | 0                   | 85.5    | 9.2                | 5.3                 |
|            | 550       | 20                  | 70.0    | 18.1               | 12.0                |
|            | 550       | 20                  | 71.1    | 19.9               | 9.1                 |
| HC3        | 450       | 0                   | 85.5    | 9.2                | 5.3                 |
|            | 550       | 0                   | 77.0    | 14.4               | 8.6                 |
|            | 550       | 0                   | 93.0    | 3.29               | 7.5                 |
| BC1        | 300       | 0                   | 85.0    | 8.0                | 7.0                 |
| BC2        | 250       | 0                   | 85.0    | 12.8               | 2.2                 |
|            | 300       | 0                   | 85.0    | 12.8               | 2.2                 |
| Uncertainty|           |                     | 0.02    | 0.02               | 0.05                |

Table 6. Yields of the pyrolysis products.
Table 7. Characteristics of the gaseous pyrolysis products.

| Coal | Temp., °C | Residence Time, min | Gaseous Compounds Composition, % | Org. Compounds C_2~C_5, % | Density, kg/m^3 | HHV, MJ/m^3 |
|------|-----------|---------------------|---------------------------------|-------------------|----------------|-------------|
|      |           |                     | H_2  | N_2  | CO  | CO_2 | CH_4 |                   |               |             |
| HC1  | 350       | 0                   | 0.13 | 92.95 | 1.10 | 4.84 | 0.10 | 0.12              | 1.28           | -            |
|      | 450       | 0                   | 0.07 | 90.06 | 1.23 | 5.44 | 0.13 | 0.14              | 1.29           | 0.50         |
|      | 450       | 20                  | 0.63 | 81.59 | 2.05 | 11.22 | 0.49 | 0.00              | 0.46           | 0.49         |
| HC2  | 450       | 0                   | 2.70 | 57.32 | 5.41 | 24.40 | 4.40 | 0.15              | 0.46           | 2.17         |
|      | 550       | 20                  | 12.45| 33.93 | 5.11 | 17.78 | 25.71 | 4.34              | 1.11           | 15.91        |
|      | 550       | 20                  | 8.62 | 39.09 | 8.87 | 17.57 | 16.83 | 6.04              | 1.20           | 14.06        |
| HC3  | 450       | 0                   | 3.55 | 62.84 | 2.80 | 9.30 | 16.56 | 4.59              | 1.19           | 10.36        |
|      | 550       | 0                   | 14.38| 29.76 | 3.23 | 10.37 | 33.31 | 7.25              | 1.02           | 17.49        |
| BC1  | 300       | 0                   | 0.10 | 87.84 | 1.43 | 9.16 | 0.10 | 0.05              | 1.32           | 0.30         |
|      | 250       | 0                   | 0.01 | 90.95 | 0.11 | 6.34 | 0.03 | 0.01              | 1.29           | 0.02         |
| BC2  | 300       | 0                   | 0.13 | 74.50 | 1.46 | 0.37 | 0.37 | 16.73             | 1.38           | 0.31         |
|      | Uncertainty|               | 0.43 | 0.57 | 0.13 | 0.03 | 0.10 | 0.02              | 0.49           | 0.49         |

4. Conclusions

The introduction of Hg emission standards in the coal-fired power industry will, in most cases, result in the necessity of implementing additional technologies to clean flue gases. Apart from the best commercially developed technologies related to sorbent injection, other technological solutions are worth considering, including Hg removal from fuel prior to its combustion by means of thermal treatment.

The results of our research with Polish coals confirmed the possibility of obtaining high Hg removal efficiency from coal before the combustion process using the low-temperature pyrolysis process. The implementation of a moderate process temperature provided removal efficiencies of 50% and 90% for hard coal and lignite, respectively. Moreover, such high Hg removal efficiency was obtained with relatively low losses of chem. enthalpy of the fuel, which did not result in loss of its functional properties according to lab-scale tests and was verified for lignite on a large lab-scale using a rotary kiln system. The results indicated that the optimal process temperature for the tested coal was 300 °C, which gave an Hg removal efficiency of over 90% with a 4% decrease in chem. Enthalpy of the fuel. The obtained results may constitute the development, verification, and demonstration of Hg removal technology using the pyrolysis process at a pilot scale.

Unlike traditional gas purification systems used in power plants, which remove Hg from the waste gas stream, our presented approach is low-cost and easier to implement on a larger scale due to the small gas stream leaving the processing system.

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