

Article

Production of Low-Mercury Solid Fuel by Mild Pyrolysis Process

Tadeusz Dziok 

Faculty of Energy and Fuels, AGH University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Krakow, Poland; tadeusz.dziok@agh.edu.pl; Tel.: +48-(12)-617-29-06

Abstract: Mercury is considered one of the most harmful ecotoxic elements. A main source of its anthropogenic emissions is fuel combustion. For fuels with a high mercury content, costly methods are required to remove mercury from the flue gases. The solution to this problem is to remove mercury from the fuel before combustion. This can be achieved by a mild pyrolysis process. Solid fuel samples with relatively high mercury content were examined. These included waste (refuse-derived fuel, paper, sewage sludge, and rubber), waste wood biomass (hornbeam leaves, pine and spruce bark), and six coal. The mild pyrolysis process was performed at 300 °C in an argon flow of 500 cm³/min. The residence time was 30 min. Proximate and ultimate analysis (including mercury content) was conducted for raw fuels and chars. The process allowed a significant reduction in mercury content from 36 to 97%. Mercury was most easily removed from biomass and waste with the most difficult being from coal. The effectiveness of mercury removal was determined by the type of fuel and its mercury content. The mercury content in the obtained chars was 0.05–3.4 µg Hg/MJ. The use of such chars will meet current EU emission standards and those to be introduced in the future.

Keywords: waste; biomass; coal; mercury removal; mercury emission



Citation: Dziok, T. Production of Low-Mercury Solid Fuel by Mild Pyrolysis Process. *Energies* **2023**, *16*, 3046. <https://doi.org/10.3390/en16073046>

Academic Editor: Eliseu Monteiro

Received: 9 March 2023

Revised: 21 March 2023

Accepted: 25 March 2023

Published: 27 March 2023



Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Mercury is considered one of the most harmful ecotoxic elements [1]. One of the main sources of its anthropogenic emissions is the fuel combustion process, mainly coal—21% [2]. For example, in Poland, this source accounts for 75% of mercury emissions [3], for nearly 60% of such emissions in North America [2], and for about 37% in China [4]. Mercury emission limits are enforced to reduce mercury emissions. Such limits have been introduced for large combustion facilities in the United States, China [5], and the European Union [6]. To meet these standards for fuels characterized by high mercury content, additional methods are required to remove mercury from flue gases, including SCR (selective catalytic reduction), sorbent injection, as well as the ultraviolet (UV) oxidation of mercury [7].

Mercury emissions from combustion processes can be effectively reduced by using fuels with a very low mercury content. Coal washing processes are commonly used [8], but their effectiveness is limited [9]. A high-quality biomass is a solid fuel characterized by a low mercury content. The mercury content of wood is at the level of only a few µg Hg/kg [10]. There are increasing efforts to protect forests by restricting the use of wood for energy purposes through appropriate regulations [11]. Instead, waste biomass is recommended. However, this type of biomass is characterized by a lower quality including a significantly higher mercury content [12]. For example, the mercury content can be as high as 43 µg Hg/kg in the bark and up to 67 µg Hg/kg in the leaves [12]. The mercury content can be much higher in biomass derived from heavily Hg-polluted areas, up to 803 µg Hg/kg [13]. Furthermore, in order to reduce coal consumption, substitution with alternative fuels produced from waste is being pursued [14]. Waste can be characterized by very high mercury content. For example, the mercury content in RDF (refuse-derived fuel) can reach 1476 µg Hg/kg [15], in sewage sludge up to 2540 µg Hg/kg [16], and in

municipal solid waste up to 46,222 $\mu\text{g Hg/kg}$ [17]. The use of such fuels may result in increased mercury emissions [15]. Therefore, SRF (solid-recovered fuel) standardization was introduced for refuse-derived fuels, where one of the main classification parameters is the mercury content [18].

The solution to this problem is to remove mercury from fuels prior to combustion by a mild pyrolysis process. In the pyrolysis process, the decomposition of organic matter can occur, resulting in a decrease in the chemical enthalpy of the fuel [19]. Therefore, the temperature of the process must be limited. The temperature at which thermal decomposition is acceptable for all solid fuels is 300 °C—mild pyrolysis. For biomass, this is the limiting temperature of the torrefaction process, above which a significant increase in mass loss is observed [20]. For most types of waste, mass loss at 300 °C is acceptable, with mercury releases greater than 80% [21]. For coal, the chemical enthalpy loss at this temperature is relatively low, up to 10% [19].

The various types of solid fuels (waste, biomass, and coal) are characterized by different origins, determining significantly different fuel properties, including mercury content and thermal behavior [12,19,21]. Comparative studies have not yet been conducted for this type of solid fuel. The studies were carried out using different types of equipment and with different process conditions, including temperature, residence time at the final temperature, and purge gas flow rate. The method of determining the effectiveness of mercury content decrease also varied. It has also not been determined whether the mercury content in solid fuels after the mild pyrolysis process will be low enough to meet emission standards during their combustion in power plants without using additional and expensive methods to remove mercury from the flue gas. For this purpose, selected waste, biomass, and coal samples characterized by a relatively high mercury content ($\geq 1.0 \mu\text{g Hg/MJ}$) were treated by a mild pyrolysis process. The process was carried out at 300 °C on a laboratory scale. The mercury removal effectiveness, mercury content in chars, and expected mercury concentration in flue gas were determined. The results obtained were related to the mercury emission limits [6]. Proximate and ultimate analysis of the obtained chars was also performed.

2. Materials and Methods

2.1. Examined Samples

A wide range of solid fuel samples with relatively high mercury content, i.e., $\geq 1.0 \mu\text{g Hg/MJ}$, were selected for the study. These included waste (RDF, paper, sewage sludge, rubber), waste wood biomass (hornbeam leaves, pine and spruce bark), and coal. The RDF sample was obtained from the Polish Regional Municipal Waste Processing Plant (RIPOK). The morphological composition of the RDF sample was as follows: plastic film—29%, plastics—24%, paper waste—21%, textiles—24%, and dust—2%. The sewage sludge sample was obtained from a municipal wastewater treatment plant. Dried sewage sludge was sampled. The car tire chips were used as a rubber sample. The sample was in the form of car tire chips, with a separated steel belt. The paper sample was obtained from a household over a period of one month. These were paper goods, tissues, and cardboard packaging. The coal samples were commercial products—steam coal. All coal was derived from Polish mines located in the Upper Silesian coal basin. Both subbituminous (coal-1, coal-2, coal-3) and bituminous coals (coal-4, coal-5, coal-6) were analyzed. Bituminous coal samples were produced in a washing process and were characterized by relatively high calorific values (above 29.7 MJ/kg). The biomass samples were waste woody biomass. The bark and leaf samples were obtained in October during the preparation of firewood for a household during the fall season. The trees were located in a mountainous area in the south of Poland, in the Małopolska province. The age of the trees was approx. 30–40 years.

2.2. Sample Preparation

The biomass, coal, and RDF samples were dried at room temperature to obtain an air-dried basis. Drying was carried out until the weight of the sample was constant, with an equilibrium between the moisture content in the sample and the humidity of the air in the sample preparation room. The remaining waste samples did not require pre-drying. The sewage sludge sample was taken from the wastewater treatment plant after the drying process. The RDF and rubber samples were ground using a Freezer/Mill 6870D cryogenic mill from SpexSamplePrep (Metuchen, NJ, USA). The biomass and paper samples were ground using an LMN-100 knife mill by Testchem (Pszow, Poland). Samples of coal and sewage sludge (sample provided in caked form) were ground using a LAB-09-200 cylindrical-ring mill from EKO-LAB (Jasien, Poland). Biomass and waste samples were ground to under 1.0 mm (sieve size used in the LMN-100 mill), and coal and sewage sludge samples to under 0.2 mm. The grain size of each sample was determined by its characteristics, the mills used, and the relevant standards. The sample prepared according to the given procedure ensured high precision and reproducibility of the results obtained.

2.3. Sample Characteristics

Proximate and ultimate analysis was performed for the samples analyzed, including moisture (M), ash (A), volatile matter (VM), carbon (C), hydrogen (H), and total sulfur (S_t) content, as well as the calorific value. The moisture content was determined using a Moisture balance MA 110.R by Radwag (Radom, Poland). The ash and volatile matter content were determined using a muffle furnace. The ash content was determined at 550 °C for biomass and waste and at 815 °C for coal. To compare biomass and waste samples with coal, the ash content was also determined for them at 815 °C. The volatile matter content was determined at 850 °C for biomass and coal and at 900 °C for waste. The lower calorific value ($q_{p,net,ad}$) was calculated according to the PN-ISO 1928:2002 standard based on the higher calorific value determined using an IKA C 6000 calorimeter by IKA-Werke GmbH & Co. KG (Staufen im Breisgau, Germany). The content of carbon, hydrogen, and sulfur was determined using a CHS-580 analyzer by Eltra (Haan, Germany). The mercury content (Hg) was determined using the DMA-80 mercury analyzer by Milestone (Soriso, Italy), according to the Milestone procedure. The method of mercury determination was positively verified using certified reference materials: INCT-MPH-2, LECO 502–687, and NIST SRM 1633c standards. The relative expanded uncertainty at the 0.95 confidence level ranged from 1 to 10%.

2.4. Mild Pyrolysis Procedure

The mild pyrolysis process was carried out using the laboratory equipment shown in Figure 1. The fuel sample was placed in a ceramic boat. The mass of the samples was determined by the bulk density and ranged from 0.1 (waste paper, RDF) to 1.0 g (coal). The sample was placed in a tube furnace heated to 300 °C. The temperature of the sample was continuously controlled. The residence time at the final temperature was 30 min. The process was carried out in an argon flow of 500 cm³/min. The sample was then removed from the furnace and cooled. For the chars obtained, analysis was performed as for the raw samples (Section 2.3).

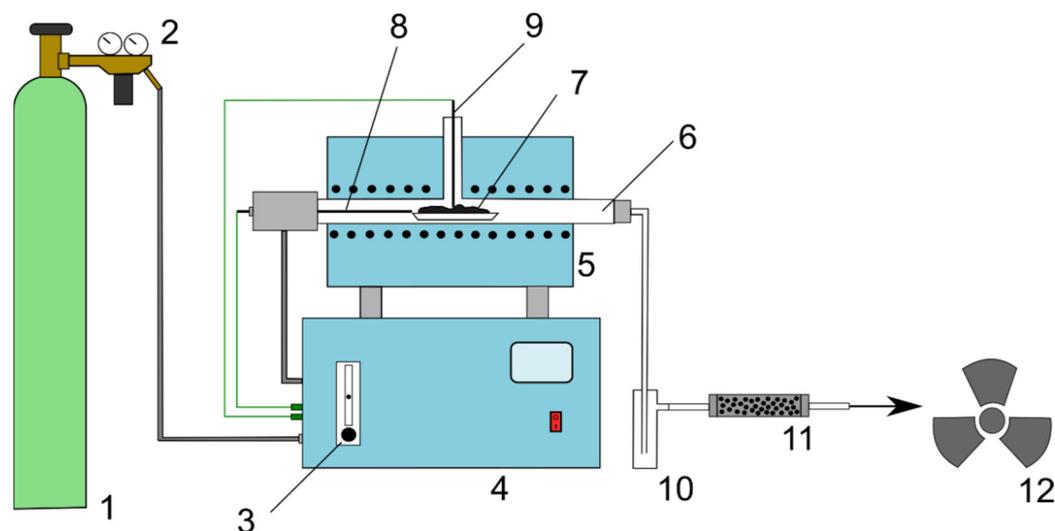


Figure 1. Equipment for the thermal pretreatment of waste: 1—argon cylinder; 2—gas reducer; 3—control valve; 4—furnace heating control system; 5—tube furnace; 6—quartz reactor; 7—boat with sample; 8—thermocouple controlling the temperature of the furnace; 9—thermocouple controlling the temperature of the sample; 10—cooler; 11—activated carbon filter; 12—laboratory exhaust.

3. Results and Discussion

3.1. Mercury Removal Effectiveness from Solid Fuel Samples Analyzed by a Mild Pyrolysis Process

The characteristics of the samples investigated are shown in Table 1. The fuel samples analyzed show significant differences in properties, even within a particular group. This is especially noticeable in the case of waste and coal samples. These differences relate not only to the mercury content but also to the ash and sulfur content.

Table 1. Characteristics of the samples.

| Fuel Type | Sample | M_{ad} (%) | A_{ad} 550 °C (%) | A_{ad} 815 °C (%) | VM_{ad} (%) | $q_{p.net.ad}$ (kJ/kg) | C_{ad} (%) | H_{ad} (%) | $S_{t.ad}$ (%) | $Hg_{ad}/q_{p.net.ad}$ (µg/MJ) |
|---------------|-----------------|--------------|---------------------|---------------------|---------------|------------------------|--------------|--------------|----------------|--------------------------------|
| Waste | RDF | 2.9 | 16.7 | 14.1 | 70.46 | 23,713 | 56.0 | 8.44 | 0.64 | 32.2 |
| | Waste paper | 6.7 | 15.7 | 13.2 | 71.32 | 14,067 | 39.5 | 6.99 | 0.11 | 1.3 |
| | Sewage sludge | 10.6 | 30.3 | 25.5 | 50.95 | 12,284 | 30.6 | 4.82 | 1.14 | 37.6 |
| | Rubber | 1.4 | 7.5 | 5.6 | 64.24 | 33,338 | 80.0 | 7.83 | 1.70 | 1.9 |
| Woody biomass | Hornbeam leaves | 7.0 | 4.1 | 3.1 | 72.54 | 16,356 | 45.5 | 6.22 | 0.12 | 2.6 |
| | Pine bark | 9.7 | 0.9 | 0.7 | 61.32 | 17,900 | 50.2 | 5.66 | 0.02 | 2.2 |
| | Spruce bark | 8.1 | 1.3 | 1.0 | 66.21 | 17,413 | 47.7 | 6.19 | 0.02 | 1.0 |
| Coal | Coal-1 | 9.1 | ND | 7.1 | 31.94 | 23,179 | 63.4 | 3.79 | 1.02 | 1.8 |
| | Coal-2 | 3.3 | ND | 29.2 | 24.22 | 19,430 | 53.2 | 3.31 | 0.93 | 5.0 |
| | Coal-3 | 2.4 | ND | 35.2 | 21.63 | 18,208 | 49.6 | 3.02 | 0.60 | 11.1 |
| | Coal-4 | 2.0 | ND | 8.1 | 27.83 | 29,716 | 78.4 | 4.80 | 0.68 | 2.2 |
| | Coal-5 | 1.3 | ND | 6.4 | 18.94 | 31,091 | 83.8 | 4.40 | 0.43 | 1.5 |
| | Coal-6 | 1.5 | ND | 10.0 | 21.10 | 29,762 | 79.0 | 4.37 | 0.58 | 6.4 |

$_{ad}$ —air-dried basis; ND—not determined.

The mild pyrolysis process at 300 °C allowed a significant decrease in mercury content regardless of the type of solid fuel analyzed (Figure 2). In terms of mercury content, the obtained chars can be ranked in the following order:

$$\text{biomass chars} \ll \text{waste char} < \text{coal chars}$$

In some cases, it was possible to achieve a mercury content below 0.1 µg Hg/MJ (hornbeam leaves, spruce bark).

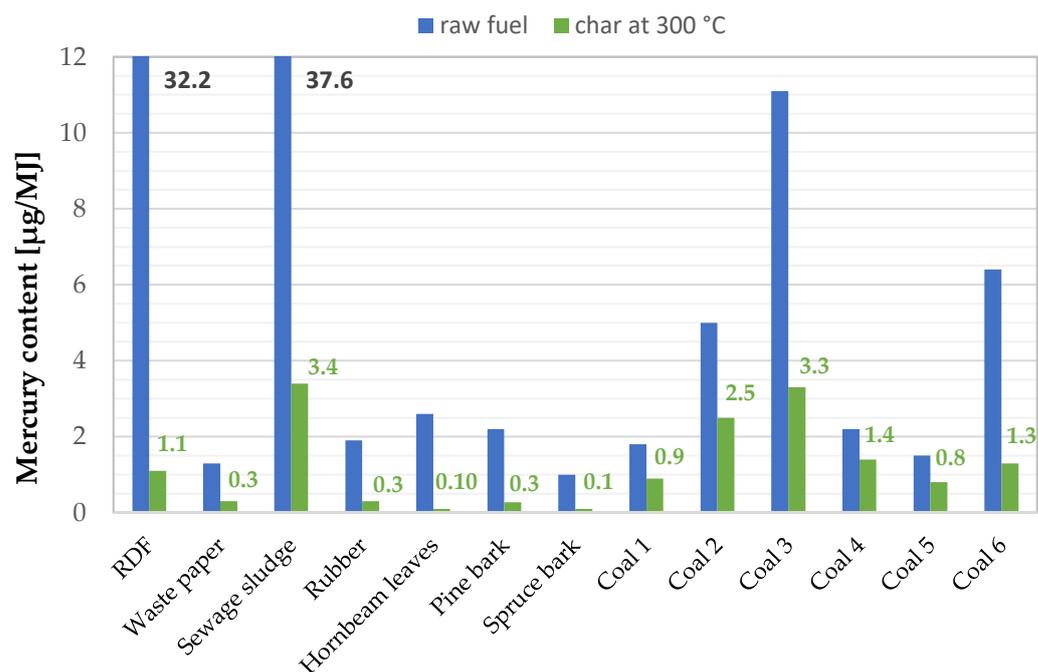


Figure 2. Comparison of the mercury content in raw fuels and chars obtained in the mild pyrolysis process at 300 °C.

The effectiveness of mercury removal from the fuel samples analyzed by mild pyrolysis at 300 °C, determined according to Equation (1), is shown in Figure 3. The estimated effectiveness was high, ranging from 36 to 97%. Mercury was very easily removed from biomass (88–96% with an average of 91%) and waste (84–97% with an average of 87%), with mercury removal from hard coal being the most difficult (36–80%, with an average of 56%).

$$\eta_{Hg} = \frac{\frac{Hg_{raw}}{q_{p,net,ad_raw}} - \frac{Hg_{mp}}{q_{p,net,ad_mp}}}{\frac{Hg_{raw}}{q_{p,net,ad_raw}}} \cdot 100 \quad (1)$$

where

η_{Hg} is the mercury removal effectiveness from analyzed fuel samples in mild pyrolysis process (%);

Hg_{raw} is the mercury content in the sample before mild pyrolysis ($\mu\text{g Hg/kg}$);

Hg_{mp} is the mercury content in the sample after mild pyrolysis ($\mu\text{g Hg/kg}$);

q_{p,net,ad_raw} is the lower heating values of the sample before mild pyrolysis (MJ/kg);

q_{p,net,ad_mp} is the lower heating values of the sample after mild pyrolysis (MJ/kg).

The differences obtained for each group of fuels should be explained by differences in the forms of mercury found in the fuels resulting from their different origins. In biomass, mercury occurs mainly in organic matter bound to sulfur and as inorganic compounds [22]. Mercury can also be found in particles adsorbed from the air on the surface of leaves and bark [12]. Despite significant differences in waste origins, mercury is found in similar forms: biocides [23], printing inks [24], dyes [25], and metal–dye complexes [26]. Mercury compounds are used as a dye in the production of some types of plastics [27]. Mercury in waste can occur as organic mercury, elemental mercury, as well as sulfides [28]. In the case of coals, mercury can be found in both its mineral and organic matter [29]. In mineral matter, mercury is found mainly in pyrite, which can contain up to 0.47% mercury [30]. It should be noted that the share of the individual forms of mercury varies and depends on the origin of the coal and the conditions of coal bed formation [31]. The particular mercury compounds have different behavior under heating; see Table 2. Up to 300 °C, mercury compounds characterized by low and moderate-release temperatures are released from

biomass and waste. In the case of coal, only low-temperature mercury compounds are released up to 300 °C.

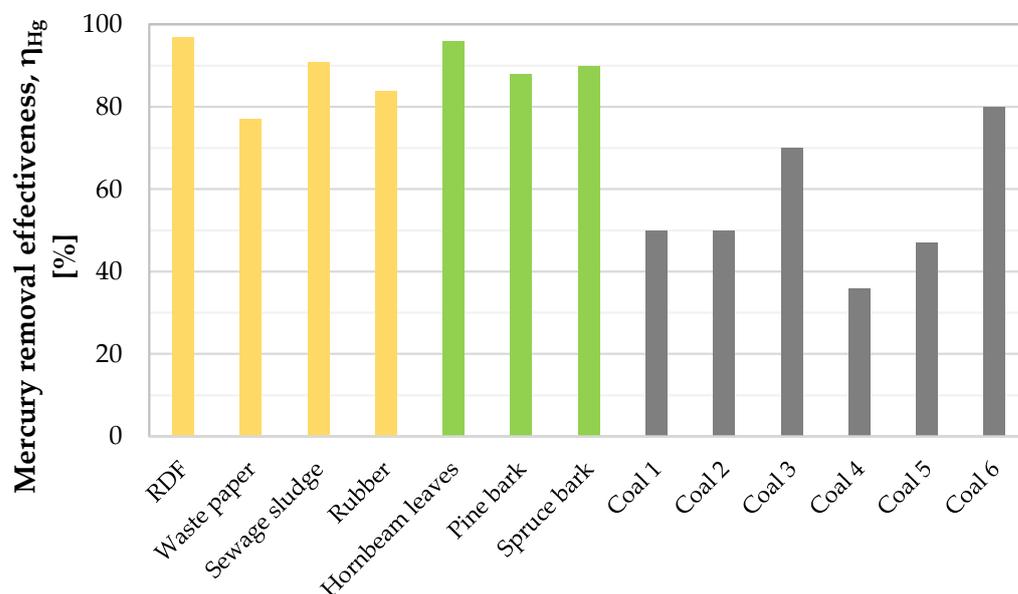


Figure 3. Effectiveness of mercury removal from analyzed fuel samples by mild pyrolysis at 300 °C (orange color—waste samples; green color—wood biomass samples; gray color—coal samples).

Table 2. Groups of mercury compounds found in solid fuels characterized by different thermal behavior.

| Group of Mercury Compounds | Temperature Range for Mercury Compound Release | | |
|----------------------------------|--|--------------|--------------|
| | Biomass [32] | Waste [21] | Coal [33] |
| Low release temperature (LRT) | up to 250 °C | up to 200 °C | up to 300 °C |
| Medium release temperature (MRT) | 200–350 °C | 200–300 °C | 300–600 °C |
| High release temperature (HRT) | above 350 °C | above 300 °C | above 600 °C |

3.2. Influence of Mercury Content in Fuel Samples Analyzed on Its Removal Effectiveness in the Mild Pyrolysis Process

According to data from the literature, the main parameter that determines the effectiveness of mercury removal in the pyrolysis process is temperature [19]. With the increase in pyrolysis temperature, the effectiveness increases. On the basis of the obtained results, the second important parameter was found to be the mercury content in the fuel sample. For the relationship between the effectiveness of mercury removal in mild pyrolysis and the mercury content in the fuel, a significant coefficient of determination at the 0.95 confidence level ($R^2 = 0.339$) was obtained. Higher coefficients of determination were obtained for the waste and coal subpopulations analyzed separately; see Figure 4 (for the biomass samples analyzed, no such relationship was obtained, as very high mercury removal effectiveness was recorded in each case). This can be explained by a similar mechanism of mercury release within the fuels in the given group. For both waste [21,34] and coals [33,35], a linear relationship between the activation energy for the mercury release process and the pre-exponential coefficient from the Arrhenius equation was recorded—a compensation effect. This means that the course of mercury release within a given fuel group is similar. The different slopes of the trend line (Figure 4) and the increase in the coefficient of determination for the analyzed fuel groups separately suggest that the differences in mercury occurrence between fuel types are significant.

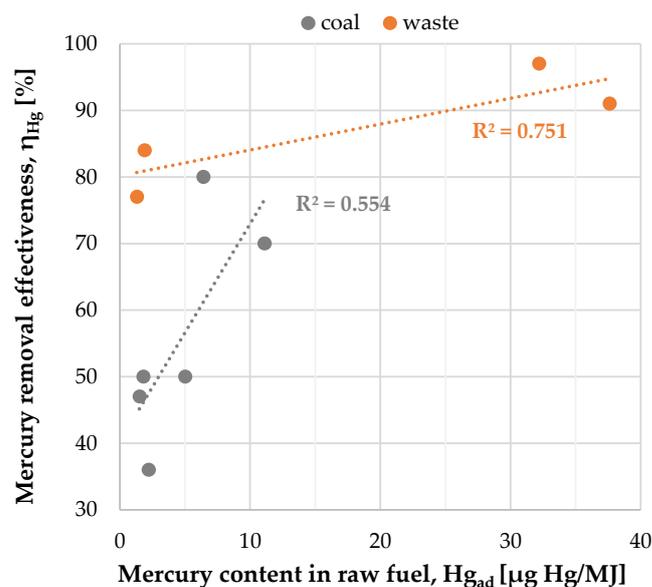


Figure 4. Relationship between the effectiveness of mercury removal in the mild pyrolysis process and the mercury content in raw fuel.

3.3. Possibility of Reducing Mercury Emissions through the Use of Chars Obtained from the Mild Pyrolysis Process

The low mercury content in chars will result in relatively low mercury concentrations in the flue gases. Figure 5 shows the calculated mercury concentration in the raw (untreated) flue gases, assuming that all the mercury in the fuel is released into the flue gases. The calculated concentration of mercury in the raw flue gases ranged from 0.1 to 9.2 $\mu\text{g Hg/Nm}^3$. In most cases, mercury concentrations would meet emission levels established in the EU. For sewage sludge char only, the mercury concentration in the flue gases is higher, but it would still be within acceptable levels for a power plant fueled with lignite (<10 $\mu\text{g Hg/Nm}^3$ [6]). For comparison, calculated mercury concentrations in the flue gases for raw fuel combustion ranged from 2.6 to 106.8 $\mu\text{g Hg/Nm}^3$ (dry, 6% O_2) for spruce bark and sewage sludge, respectively. The use of chars will also significantly reduce mercury emissions from the cement production process, where waste-derived fuels are mainly used [36].

It should be noted that the results presented refer to the amount of mercury completely released into the raw, untreated flue gases. Under industrial conditions, from 0.1 to 0.9% of the mercury remains in the bottom ash/slag [37]. Additionally, a significant amount of mercury is effectively removed from the flue gases during the cleaning process [7]. The particulate removal devices themselves allow mercury removal from 2 to 84%, which is adsorbed by fly ash [37,38]. Therefore, the real concentrations of mercury in the flue gases will be much lower. This will allow power plants to meet the mercury emission regulations without the need to implement additional methods of mercury removal from flue gases, including the use of the sorbent injection method [39], which is costly [40].

As mentioned in Section 3.1, mercury can occur in solid fuels in various forms: mineral constituents, organic compounds, or as elemental mercury. Depending on the mercury compound, evaporation, decomposition, or sublimation may occur during heating [41]. All of these forms are harmful [1] and must be removed from process gases. This requires the use of sorbents. However, it is less costly than removing mercury from flue gases, because its concentration in process gases is significantly higher [42]. This solution allows the use of a fixed bed of sorbent [43], as well as the regenerable sorbents [44], which will also reduce costs.

The use of sorbents to remove mercury from process gases results in the generation of mercury-containing waste (spent sorbent). A widely used method of their management is disposal. Mercury sorbents must be characterized by the high stability of the captured mercury. Commonly used activated carbons allow mercury to bind highly stably and re-

main immobilized during disposal [45]. Therefore, the use of mercury sorbents ensures the effective removal of mercury from the environment. To reduce the amount of waste sorbent generated, activated carbons can be regenerated [46]. Mercury released in the regeneration process can be effectively stabilized and solidified by amalgamation or complexation with sulfur in the form of cinnabar [47].

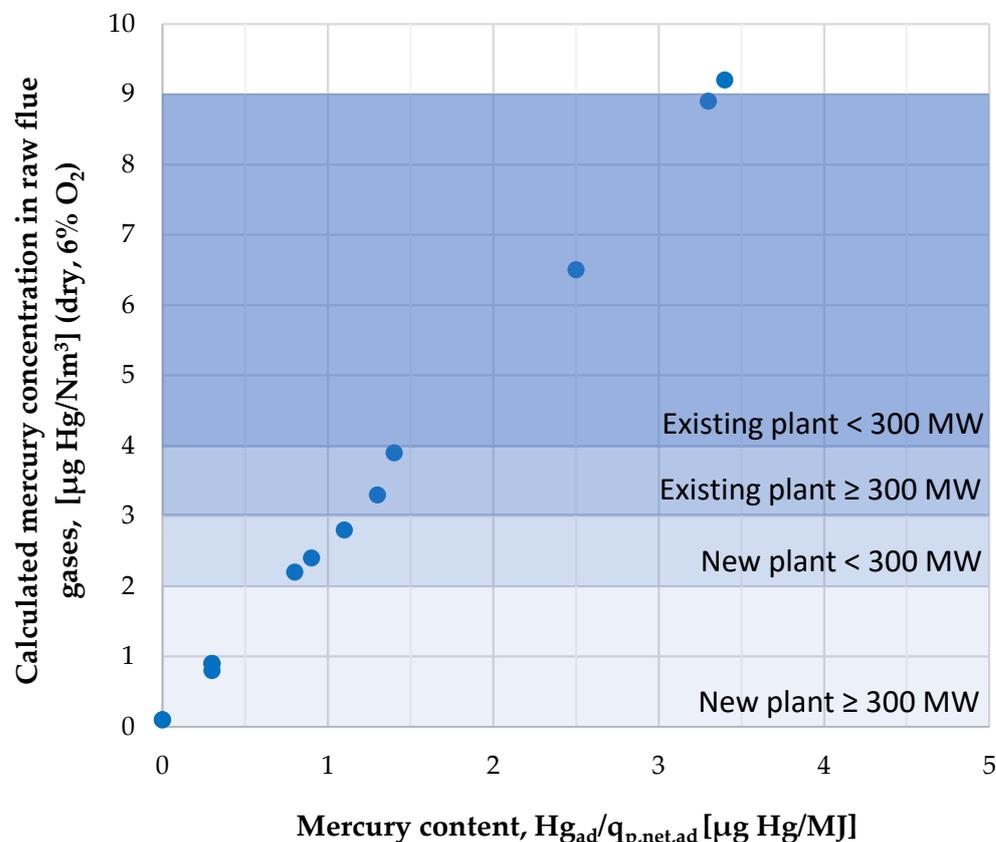


Figure 5. Relationship between mercury content in analyzed samples after mild pyrolysis process and calculated mercury concentration in raw flue gases (different shades of blue background represent the emission levels of mercury emissions to air from the coal combustion applicable in the European Union according to BAT-LCP [6]).

3.4. Additional Benefits of the Mild Pyrolysis Process

The use of the mild pyrolysis process of solid fuels has the additional benefits of increasing the calorific value and reducing the content of sulfur, moisture, and volatile matter; see Table 3. The moisture content obtained in the chars was up to 2.5% for waste, up to 1.1% for coals, and 0.5% for biomass. In most cases, the mild pyrolysis process resulted in a decrease in the sulfur dioxide emission factor (Figure 6). The decrease in the emission factor should be explained by both the decrease in the sulfur content and the increase in the calorific value of the chars. Only for pine and spruce bark and coal-3 chars, did the factor not decrease. In the case of the biomass samples, the sulfur content was at a very low level (0.02%), and in the case of the coal-3 sample, sulfur could be found in significant amounts in the mineral matter, mainly in pyrite. Pyrite decomposition occurs above 600 °C [48]. As a result of the partial decomposition of the organic matter, the mineral matter was concentrated, as was noted, by an increase in the ash content. The highest increase in the ash content was recorded for RDF, which was 22 pp (dry basis). Significant increases were also observed for waste paper and sewage sludge, 13 and 11 pp, respectively (dry basis). For other fuels, the increase was less than 1.3 pp (dry basis). Except for RDF and rubber samples, where there was an increase in the calorific value. The highest increase was recorded for the pine bark sample, which reached 4.5 MJ/kg. For the rubber sample,

a slight decrease in calorific value was noticed, but it was within the repeatability limit. In the case of RDF, there was a decrease in the calorific value due to a significant increase in the ash content. Such a phenomenon is well known [49]. At 400 °C and above, the calorific value of RDF decreases significantly to a level of a few MJ/kg [50]. This should be explained by the rapid decomposition of paper, textiles, and plastics [21], which are the main fractions of RDF. Significant mass loss of RDF results in an increase in ash content up to 80% [50]. A higher calorific value was obtained for rubber char than for industrial chars obtained from pyrolysis of used car tires at 500–550 °C, which is 26–28 MJ/kg [51]. In the case of using the chars from the mild pyrolysis process in the gasification process, it is necessary to perform relevant kinetic studies, because the pyrolysis process affects the reactivity of the obtained chars [52]. This is especially relevant for biomass and waste chars, for which a significant reduction in volatile matter content was recorded: from 4 to 27 pp (dry basis). For the coal samples analyzed, the decrease in the volatile matter content was negligible, below 2 pp (dry basis).

Table 3. Proximate or ultimate analysis of chars obtained by mild pyrolysis of analyzed fuel samples at 300 °C.

| Sample | M _{ad} (%) | A _{ad} 550 °C (%) | A _{ad} 815 °C (%) | VM _{ad} (%) | q _{p.net.ad} (kJ/kg) | C _{ad} (%) | H _{ad} (%) | S _{t.ad} (%) |
|----------------------|---------------------|----------------------------|----------------------------|----------------------|-------------------------------|---------------------|---------------------|-----------------------|
| RDF char | 1.1 | 38.6 | 32.5 | 53.33 | 21,238 | 51.7 | 6.42 | 0.49 |
| Waste paper char | 2.5 | 29.1 | 24.5 | 54.47 | 15,697 | 44.4 | 3.97 | 0.07 |
| Sewage sludge char | 2.5 | 44.0 | 37.1 | 37.82 | 13,516 | 35.0 | 3.37 | 0.96 |
| Rubber char | 0.7 | 8.6 | 6.4 | 60.88 | 33,261 | 79.0 | 7.91 | 1.50 |
| Hornbeam leaves char | 0.5 | 5.4 | 4.0 | 65.48 | 20,341 | 53.4 | 6.15 | 0.13 |
| Pine bark char | 0.5 | 1.1 | 0.8 | 61.19 | 22,396 | 58.3 | 5.71 | 0.02 |
| Spruce bark char | 0.5 | 1.9 | 1.4 | 64.17 | 21,292 | 57.1 | 6.23 | 0.02 |
| Coal-1 char | 1.1 | ND | 7.4 | 32.70 | 26,189 | 71.2 | 4.08 | 0.82 |
| Coal-2 char | 0.6 | ND | 29.3 | 23.38 | 20,338 | 56.0 | 3.27 | 0.95 |
| Coal-3 char | 1.1 | ND | 37.0 | 20.86 | 18,378 | 50.7 | 2.96 | 0.61 |
| Coal-4 char | 0.4 | ND | 6.9 | 28.10 | 30,494 | 80.3 | 4.73 | 0.68 |
| Coal-5 char | 0.6 | ND | 6.6 | 18.88 | 31,771 | 83.9 | 4.17 | 0.42 |
| Coal-6 char | 0.4 | ND | 10.0 | 21.18 | 30,113 | 82.8 | 4.49 | 0.51 |

_{ad}—air-dried basis; ND—not determined.

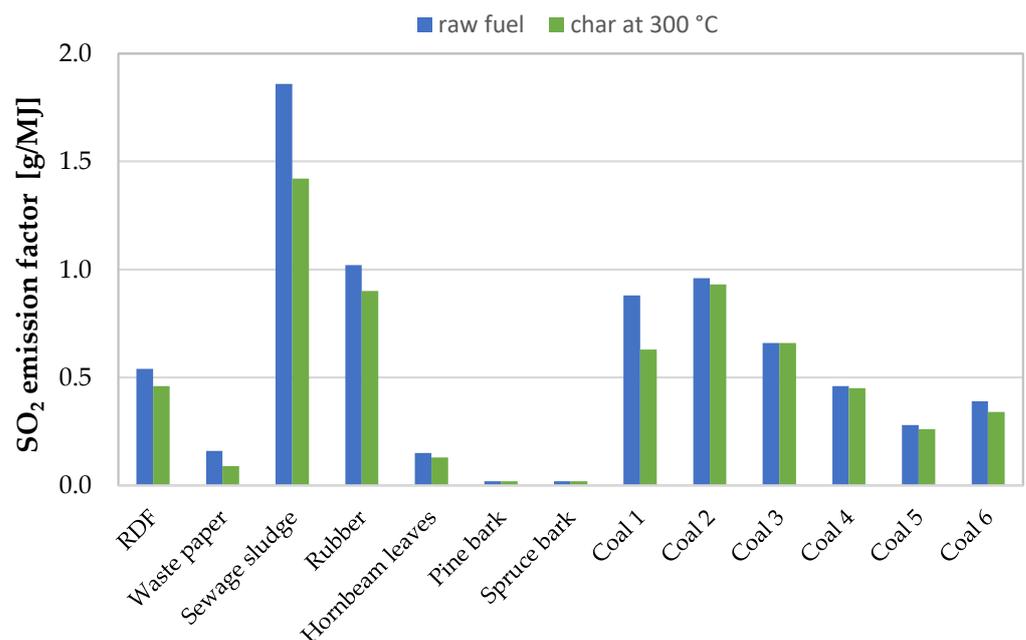


Figure 6. Comparison of the sulfur emission factor for raw fuels and chars obtained in the mild pyrolysis process at 300 °C.

4. Conclusions

The mild pyrolysis process leads to a significant decrease in mercury content. Its removal effectiveness ranged from 36 to 97%. Mercury was easiest to remove from biomass, slightly more difficult to remove from waste, and most difficult to remove from coal. The average effectiveness was 91, 87, and 56%, respectively. The mercury content in the chars ranged from 0.05 to 3.4 $\mu\text{g Hg/MJ}$. The effectiveness of mercury removal from the samples analyzed was determined by the type of fuel (biomass, waste, and coal) and the mercury content. As the mercury content in the fuel increased, its removal effectiveness increased. This was particularly noticeable within a particular fuel group. This should be explained by differences in the mode of mercury occurrence in the fuels of a given group and differences in their thermal behavior. The use of chars obtained in the mild pyrolysis process will meet EU emission standards (BAT-LCP). The use of chars derived from the mild pyrolysis process of solid fuels will allow power plants to meet the emission standards for large combustion plants adopted in the European Union, which will contribute to a significant reduction in mercury emissions. The calculated concentration of mercury in the raw flue gases ranged from 0.1 to 9.2 $\mu\text{g Hg/Nm}^3$. It is therefore possible to meet the standards without the adoption of additional methods of removing mercury from flue gases, such as sorbent injection. This is a promising solution to meet the more stringent limits that may be enforced in the future.

Funding: This research project was supported by the program ‘Excellence initiative—research university’ for the AGH University of Science and Technology.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Eisler, R. *Mercury Hazards to Living Organisms*; CRC Press: Boca Raton, FL, USA, 2006; pp. 1–312. [CrossRef]
2. UN Environment. *Global Mercury Assessment—2018*; UN Environment Programme Chemicals and Health Branch: Geneva, Switzerland, 2019.
3. National Centre for Emissions Management (KOBiZE). *Poland’s Informative Inventory Report 2022—Submission under the UNECE CLRTAP and NEC Directive*; Ministry of Climate and Environment: Warsaw, Poland, 2022.
4. Jiang, X.; Wang, F. Mercury emissions in China: A general review. *Waste Dispos. Sustain. Energy* **2019**, *1*, 127–132. [CrossRef]
5. Li, X.; Teng, Y.; Zhang, K.; Peng, H.; Cheng, F.; Yoshikawa, K. Mercury Migration Behavior from Flue Gas to Fly Ashes in a Commercial Coal-Fired CFB Power Plant. *Energies* **2020**, *13*, 1040. [CrossRef]
6. BAT-LCP, 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. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32017D1442> (accessed on 1 March 2023).
7. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **2003**, *82*, 89–165. [CrossRef]
8. Joy, A.; Qureshi, A. Reducing mercury emissions from coal-fired power plants in India: Possibilities and challenges. *Ambio* **2023**, *52*, 242–252. [CrossRef] [PubMed]
9. Zajusz-Zubek, E.; Koniecznyński, J. Coal cleaning versus the reduction of mercury and other trace elements’ emissions from coal combustion processes. *Arch. Environ. Prot.* **2014**, *40*, 115–127. [CrossRef]
10. Yang, Y.; Yanai, R.D.; Driscoll, C.T.; Montesdeoca, M.; Smith, K.T. Concentrations and content of mercury in bark, wood, and leaves in hardwoods and conifers in four forested sites in the northeastern USA. *PLoS ONE* **2018**, *13*, 0196293. [CrossRef]
11. Commission Implementing Regulation (EU) 2022/2448 of 13 December 2022 on Establishing Operational Guidance on the Evidence for Demonstrating Compliance with the Sustainability Criteria for Forest Biomass Laid Down in Article 29 of Directive (EU) 2018/2001 of the European Parliament and of the Council. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32022R2448> (accessed on 1 March 2023).
12. Dziok, T.; Kołodziejka, E.K.; Kołodziejka, E.L. Mercury Content in Woody Biomass and Its Removal in the Torrefaction Process. *Biomass Bioenergy* **2020**, *143*, 105832. [CrossRef]
13. Chiarantini, L.; Rimondi, V.; Benvenuti, M.; Beutel, M.W.; Costagliola, P.; Gonnelli, C.; Lattanzi, P.; Paolieri, M. Black pine (*Pinus nigra*) barks as biomonitors of airborne mercury pollution. *Sci. Total Environ.* **2016**, *569*, 105–113. [CrossRef]
14. Psomopoulos, C.S.; Kiskira, K.; Kalkanis, K.; Leligou, H.C.; Themelis, N.J. The Role of Energy Recovery from Wastes in the Decarbonization Efforts of the EU Power Sector. *IET Renew. Power Gener.* **2022**, *16*, 48–64. [CrossRef]

15. Dziok, T.; Bury, M.; Bytnar, K.; Burmistrz, P. Possibility of Using Alternative Fuels in Polish Power Plants in the Context of Mercury Emissions. *Waste Manag.* **2021**, *126*, 578–584. [[CrossRef](#)]
16. Lee, S.-S.; Wilcox, J. Behavior of mercury emitted from the combustion of coal and dried sewage sludge: The effect of unburned carbon, Cl, Cu and Fe. *Fuel* **2017**, *203*, 749–756. [[CrossRef](#)]
17. Tao, Z.; Dai, S.; Chai, X. Mercury emission to the atmosphere from municipal solid waste landfills: A brief review. *Atmos. Environ.* **2017**, *170*, 303–311. [[CrossRef](#)]
18. ISO 21640:2021; Solid Recovered Fuels—Specifications and Classes. ISO: London, UK, 2021.
19. Misztal, E.; Chmielniak, T.; Mazur, I.; Sajdak, M. The Release and Reduction of Mercury from Solid Fuels through Thermal Treatment Prior to Combustion. *Energies* **2022**, *15*, 7987. [[CrossRef](#)]
20. Tumuluru, J.S.; Sokhansanj, S.; Hess, J.R.; Wright, C.T.; Boardman, R.D. A review on biomass torrefaction process and product properties for energy applications. *Ind. Biotechnol.* **2021**, *7*, 384–401. [[CrossRef](#)]
21. Dziok, T.; Bury, M.; Burmistrz, P. Mercury release from municipal solid waste in the thermal treatment process. *Fuel* **2022**, *329*, 125528. [[CrossRef](#)]
22. Chiarantini, L.; Rimondi, V.; Bardelli, F.; Benvenuti, M.; Cosio, C.; Costagliola, P.; Di Benedetto, F.; Lattanzi, P.; Sarret, G. Mercury speciation in Pinus nigra barks from Monte Amiata (Italy): An X-ray absorption spectroscopy study. *Environ. Pollut.* **2017**, *227*, 83–88. [[CrossRef](#)] [[PubMed](#)]
23. Velusamy, S.; Roy, A.; Sundaram, S.; Kumar Mallick, T. A review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment. *Chem. Rec.* **2021**, *21*, 1570–1610. [[CrossRef](#)]
24. Xue, M.; Wang, S.; Huang, C. Determination of heavy metals (Pb, Cd, Cr and Hg) in printed paper as food packaging materials and analysis of their sources. *CIESC J.* **2010**, *12*, 32.
25. Tian, Z.; Yang, Y.; Wang, L. An improved method for assessing environmental impacts caused by chemical pollutants: A case study in textiles production. *Toxicol. Ind. Health* **2020**, *36*, 228–236. [[CrossRef](#)]
26. Rezić, I. *Historical Textiles and Their Characterization*; Cambridge Scholars Publishing: Cambridge, UK, 2022.
27. Turner, A.; Filella, M. Hazardous Metal Additives in Plastics and Their Environmental Impacts. *Environ. Int.* **2021**, *156*, 106622. [[CrossRef](#)]
28. Cheng, L.; Wang, L.; Geng, Y.; Wang, N.; Mao, Y.; Cai, Y. Occurrence, Speciation and Fate of Mercury in the Sewage Sludge of China. *Ecotoxicol. Environ. Saf.* **2019**, *186*, 109787. [[CrossRef](#)] [[PubMed](#)]
29. Zheng, L.; Liu, G.; Qi, C.; Zhang, Y.; Wong, M. The use of sequential extraction to determine the distribution and modes of occurrence of Mercury in Permian Huaibei coal, Anhui Province, China. *Int. J. Coal Geol.* **2008**, *73*, 139–155. [[CrossRef](#)]
30. Ding, Z.; Zheng, B.; Long, J.; Belkin, H.E.; Finkelman, R.B.; Chen, C.; Zhou, D.; Zhou, Y. Geological and geochemical characteristics of high arsenic coals from endemic arsenosis areas in southwestern Guizhou Province, China. *Appl. Geochem.* **2001**, *16*, 1353–1360. [[CrossRef](#)]
31. Yudovich, Y.E.; Ketris, M.P. Mercury in coal: A review—Part 1. Geochemistry. *Int. J. Coal Geol.* **2005**, *62*, 107–134. [[CrossRef](#)]
32. Dziok, T. Thermal removal of mercury from hard coal and biomass. *Przemysł Chem.* **2019**, *98*, 1757–1759. [[CrossRef](#)]
33. Sotiropoulou, R.E.P.; Serafidou, M.; Skodras, G. Thermal mercury removal from coals: Effect of pyrolysis conditions and kinetic analysis. *Fuel* **2019**, *238*, 44–50. [[CrossRef](#)]
34. Bury, M.; Dziok, T.; Borovec, K.; Burmistrz, P. Influence of RDF Composition on Mercury Release during Thermal Pretreatment. *Energies* **2023**, *16*, 772. [[CrossRef](#)]
35. Merdes, A.C.; Keener, T.C.; Khang, S.-J.; Jenkins, R.G. Investigation into the fate of mercury in bituminous coal during mild pyrolysis. *Fuel* **1998**, *77*, 1783–1792. [[CrossRef](#)]
36. Chatziaras, N.; Psomopoulos, C.S.; Themelis, N.J. Use of Waste Derived Fuels in Cement Industry: A Review. *Manag. Environ. Qual. Int. J.* **2016**, *27*, 178–193. [[CrossRef](#)]
37. Pilar, L.; Borovec, K.; Szeliga, Z.; Górecki, J. Mercury Emission from Three Lignite-Fired Power Plants in the Czech Republic. *Fuel Process. Technol.* **2021**, *212*, 106628. [[CrossRef](#)]
38. Wichliński, M.; Wielgosz, G.; Kobyłecki, R. The effect of circulating fluidized bed boiler load on the emission of mercury. *J. Energy Inst.* **2019**, *92*, 1800–1806. [[CrossRef](#)]
39. Li, H.; Huang, G.; Yang, Q.; Zhao, J.; Liu, Z.; Yang, J. Numerical simulation of sorbent injection for mercury removal within an electrostatic precipitator: In-flight plus wall-bounded mechanism. *Fuel* **2022**, *309*, 122142. [[CrossRef](#)]
40. Shen, A.; Wang, Y.; Wang, R.; Duan, Y.; Tao, J.; Gu, X.; Wang, P.; Xu, Z. Numerical Simulation of Sorbent Injection into Flue Gas for Mercury Removal in Coal-Fired Power Plant. Part 2. Operational Parameters and Optimization. *Fuel* **2022**, *326*, 124990. [[CrossRef](#)]
41. Iwashita, A.; Tanamachi, S.; Nakajima, T.; Takanashi, H.; Ohki, A. Removal of Mercury from Coal by Mild Pyrolysis and Leaching Behavior of Mercury. *Fuel* **2004**, *83*, 631–638. [[CrossRef](#)]
42. Chmielniak, T. Reduction of Mercury Emissions to the Atmosphere from Coal Combustion Processes of Using Low-Temperature Pyrolysis—A Concept of Process Implementation on a Commercial Scale. *Rynek Energii* **2011**, *93*, 176–181.
43. Jastrzab, K.; Mazurek, I. The Study of Thermal Desorption of Mercury Compounds from Spent Active Cokes Used for Exhaust Gas Treatment in Waste Incineration Plants. *Inżynieria I Ochr. Sr.* **2013**, *16*, 273–285.
44. Antuña-Nieto, C.; Rodríguez, E.; Lopez-Anton, M.A.; García, R.; Martínez-Tarazona, M.R. Noble Metal-Based Sorbents: A Way to Avoid New Waste after Mercury Removal. *J. Hazard. Mater.* **2020**, *400*, 123168. [[CrossRef](#)]

45. Graydon, J.W.; Zhang, X.; Kirk, D.W.; Jia, C.Q. Sorption and stability of mercury on activated carbon for emission control. *J. Hazard. Mater.* **2009**, *168*, 978–982. [[CrossRef](#)]
46. Bentley, M.; Fan, M.; Dutcher, B.; Tang, M.; Argyle, M.D.; Russell, A.G.; Zhang, Y.; Sharma, M.P.; Swapp, S.M. Catalytic regeneration of mercury sorbents. *J. Hazard. Mater.* **2013**, *262*, 642–648. [[CrossRef](#)]
47. Chalkidis, A.; Jampaiah, D.; Aryana, A.; Wood, C.D.; Hartley, P.G.; Sabri, Y.M.; Bhargava, S.K. Mercury-bearing wastes: Sources, policies and treatment technologies for mercury recovery and safe disposal. *J. Environ. Manag.* **2020**, *270*, e110945. [[CrossRef](#)]
48. Zhang, X.; Kou, J.; Sun, C. A comparative study of the thermal decomposition of pyrite under microwave and conventional heating with different temperatures. *J. Anal. Appl. Pyrolysis.* **2019**, *138*, 41–53. [[CrossRef](#)]
49. Stepień, P.; Białowiec, A. Kinetic parameters of torrefaction process of alternative fuel produced from municipal solid waste and characteristic of carbonized refuse derived fuel. *Detritus* **2018**, *3*, 75–83. [[CrossRef](#)]
50. Özkan, A.; Banar, M.; Çokaygil, Z.; Tezer, Ö. Characterization of the pyrolysis products of RDF. In Proceedings of the 3rd International Exergy, Life Cycle Assessment, and Sustainability Workshop & Symposium (ELCAS3), Nisyros, Greece, 7–9 July 2013.
51. Czerski, G.; Śpiewak, K.; Grzywacz, P.; Wierońska-Wiśniewska, F. Assessment of the catalytic effect of various biomass ashes on CO₂ gasification of tire char. *J. Energy Inst.* **2021**, *99*, 170–177. [[CrossRef](#)]
52. Grzywacz, P.; Czerski, G.; Gańczarczyk, W. Effect of pyrolysis atmosphere on the gasification of waste tire char. *Energies* **2022**, *15*, 34. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.