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Evaluation of Wastewater Sludge as a Valuable Resource for Various Energetic Applications and Fuel Production

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Abstract

Thermal conversion offers opportunities for energy recovery from wastewater sludge, but its feasibility depends on feedstock properties. This study evaluates industrial sludges from food processing, refining and coking, alongside municipal sewage sludge, in comparison with coal, biomass and refuse-derived fuel. Proximate and ultimate analysis, ash composition and mercury determination were combined with slagging/fouling indices, preliminary ISO 21640 classification and chemometric analysis. Correlation and cluster analyses revealed marked differences among the sludge streams and showed that their comparison with reference fuels depends on data preprocessing. Elevated chlorine and sulfur contents in selected industrial sludges indicated potential corrosion and operational constraints. None of the samples met the low-tendency criteria of all eight slagging/fouling indices, although these indices require experimental validation for sludge. On a dry basis, eight out of 30 samples (27%; six refinery and two food-processing samples) fell within ISO 21640 classes 1–3 for net calorific value, chlorine and mercury; at measured moisture contents, none reached class 3 or better. The findings indicated that selected industrial sludge streams could serve as alternative fuels or fuel-blend components after appropriate drying, provided that energy requirements, contaminant contents, and process-specific operating risks are considered.

Keywords: industrial wastewater sludge; sewage sludge; thermal utilization; chemometric analysis; energy properties; SRF classification

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1. Introduction

Wastewater sludge is an unavoidable by-product of wastewater treatment plants. Comprehensive data on the global amount of sewage sludge generated are limited [1]. It is estimated that approximately 18 kg of dry sludge is produced per capita per year [2]. Annual sewage sludge production is estimated at about 4.96 million tons of dry matter in the USA and about 11.2 million tons in China [2]. In the European Union, approximately 9–9.5 million tons of dry municipal sewage sludge are produced annually, and this production level has remained relatively stable for several years [3,4]. Sludge production may increase further as wastewater collection and treatment infrastructure expands.

Wastewater sludge is considered a bio-resource (plant nutrients, fertilizers, hydrolytic enzymes, biochar, and biogas produced through anaerobic digestion) due to its considerable

organic matter content and nutrient-rich inorganic fraction [5]. However, its agricultural use is subject to significant restrictions due to organic and inorganic contaminants [6,7]. Improper sludge management can cause secondary pollution of water, soil and the atmosphere, highlighting the need for safe treatment and valorization.

Wastewater sludge can be treated through biochemical conversion, particularly anaerobic digestion for biogas production, and through thermochemical conversion, such as incineration, co-combustion, pyrolysis, gasification and hydrothermal liquefaction/carbonization [8,9]. Anaerobic digestion enables biogas production from wet sludge without prior drying, but the resulting digestate still requires appropriate management. Thermochemical conversion offers additional energy and resource recovery opportunities and may also be applied to digested sludge, although most thermal processes require preliminary drying. Thermochemical conversion enables direct energy recovery through combustion or the production of liquid, solid and gaseous fuels [10–13]. These processes can be a source of valuable products such as bio-oil and biochar, while phosphorus may be concentrated in solid residues and subsequently recovered [14–17]. Assuming the calorific value of sewage sludge at 11–17 MJ/kg, it is estimated that the annually available energy from this waste generated in Poland is at least 6.8 PJ [18]. The energy as well as greenhouse gas (GHG) emission benefits of thermal sewage sludge utilization processes have also been demonstrated [18,19].

Thermal utilization is becoming an important direction of wastewater sludge management in many countries. It accounts for a substantial share of sewage sludge treatment in several European countries, including the Netherlands, Switzerland, Belgium and Germany [20]. In Poland, the amount of thermally utilized wastewater sludge has more than tripled over the past decade, reaching 23% of the total sludge generated [21]. Fluidized-bed combustion (FBC) is the most widely used technology for sewage sludge incineration, while co-combustion is commonly carried out with coal or other waste, e.g., in waste incinerators or rotary kilns (cement plants).

The performance of thermal conversion processes, including incineration, co-combustion, gasification and pyrolysis, depends on physical and chemical properties of wastewater sludge. Key factors include the content of chlorine, sulfur or alkali metals, which, depending on their concentration and chemical form, may contribute to high-temperature corrosion, agglomeration, slagging, fouling, formation of hydrogen chloride, dioxin, sulfur oxides and pollutant emissions [22–24].

Agglomeration is one of the main problems encountered during thermal processes in fluidized bed reactors. The main cause of this phenomenon is in-bed formation of low-melting-point eutectic mixtures, resulting from reactions between alkali compounds present in sludge and silica, mainly originating from bed materials [25]. Sintering of the bed material at high temperatures, together with agglomeration, contributes to the growth of bed particles. This may ultimately lead to bed defluidization and, consequently, costly maintenance operations. Fouling and slagging involve ash deposition on heat exchanger surfaces and on the inner walls of the flue gas duct, reducing the heat transfer rate and increasing the pressure drop [26]. In commercial-scale plants, these processes may lead to complex operational problems and high maintenance and operating costs.

In addition to operational difficulties associated with sludge thermal conversion facilities, emissions of potentially harmful gaseous pollutants, including NO_x, SO_x, HCl, and Cl_2, represent a major concern. Chlorine may serve as a chlorinating agent in the formation of toxic polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) [27,28]. These compounds can be formed in the post-combustion zone through oxy-chlorination reactions catalyzed by metallic species present in fly ash [29]. Chlorine may also enhance the volatilization and subsequent emission of ecotoxic elements (heavy metals), which can

react with chlorine in the gas phase at high temperatures to form volatile chlorides [30–32]. High chlorine contents in the combusted material may also promote corrosion and damage to installation components [26].

The determination of chlorine, sulfur and alkali metal contents in solid fuels and waste subjected to thermal processing provides an important analytical basis for assessing potential operational risks. However, comprehensive data on these properties are still limited, especially for sludges from industrial wastewater treatment plants [33]. Collecting such information is crucial for thermochemical processing of wastewater sludge, particularly because industrial sludge accounts for almost half of the total amount of sludge generated in Poland [21].

In addition to the above-mentioned parameters, which are important from both technical and environmental perspectives, requirements for the use of wastewater sludge as an alternative fuel should also be considered. For this purpose, sludge properties should be assessed with reference to ISO 21640 "Solid recovered fuels—specifications and classes" [34]. This standard defines five classes based on three key parameters: net calorific value (NCV), chlorine content, and mercury content. Therefore, assessing the potential suitability of industrial wastewater sludge for energy recovery and thermochemical conversion requires consideration of its fuel-related properties, slagging/fouling tendencies and other factors that may affect its use in thermochemical processes.

Although wastewater sludge has long been considered as a source of valuable components and an energy carrier, previous studies have mainly focused on municipal sewage sludge or the characterization of individual industrial sludge samples for specific thermochemical conversion processes. For example, Magdziarz et al. [35] investigated ash properties related to the combustion of municipal sewage sludge, while Lin et al. [36] examined the combustion behavior of hydrochar produced from paper sludge by hydrothermal carbonization (HTC). More recently, Wang et al. [37] investigated the catalytic role of mineral constituents in industrial wastewater sludge during co-gasification with textile waste. However, comprehensive assessment of fuel-related properties and their variability within and between different industrial sludge streams, particularly in the context of potential operational risks and alternative fuel classification, remains limited.

The aim of the study was to analyze and evaluate the content of selected problematic components in industrial wastewater sludge, originating from the food industry, refinery and coking wastewater treatment plants, as well as in municipal wastewater sludge. Particular attention was paid to chlorine, sulfur and alkali compounds, as these components may negatively affect the thermal utilization of sludge and cause operational or environmental problems. The study also considered the temporal variability of these parameters over an extended sampling period, an aspect that has received limited attention in the available literature.

However, the direct interpretation of analytical data alone may be insufficient, especially when dealing with heterogeneous materials such as wastewater sludge. Therefore, several multivariate chemometric methods (correlation analysis and hierarchical cluster analysis) were applied to identify relationships between sludge properties [38,39]. In addition, selected fuel-related indices were calculated for the investigated sludge samples and compared with values reported for coal, biomass, and alternative fuels, such as refuse-derived fuel (RDF) [40]. The assessment was further supported by a preliminary comparison of the sludge properties with ISO 21640 class limits [34]. A comparable combination of fuel-property assessment and multivariate data analysis has previously been applied to municipal solid waste (MSW) [41]. By integrating these approaches with the assessment of variability among industrial and municipal sludge streams, the present

study provides a broader basis for evaluating their potential thermochemical utilization and associated operational limitations.

2. Materials and Methods

The methodological approach used in this study was based on linking legal requirements for solid recovered fuels with the physicochemical properties of wastewater sludge and reference solid fuels, including coal, biomass, and RDF. The assessment covered both the parameters required by ISO 21640 [34] for fuel classification and additional indicators relevant to thermal conversion processes.

This approach made it possible to evaluate wastewater sludge not only as a potential energy carrier, but also as a feedstock for thermochemical conversion processes aimed at producing valuable products or secondary raw materials. The analysis was structured from general classification criteria to more specific indicators related to thermal behavior, operational limitations, and potential utilization pathways.

2.1. Research Material

The research was carried out on sludge samples from industrial wastewater treatment plants (WWTPs) associated with animal fat production (AFP), refinery (REF), combined fruit and vegetable processing, milk processing and municipal wastewater (FPM), food production (FP) and coking plant (CP), as well as from a municipal biological wastewater treatment plant (MS) in Poland. Most facilities were located in southern Poland (Silesian and Lesser Poland Voivode-ships), with one in eastern Poland (Masovian Voivodeship). The WWTPs were selected to assess final sludge streams from different wastewater sources, rather than individual treatment effects, and employed broadly similar mechanical-biological treatment schemes with varying reagents, dewatering methods and sludge-handling practices. A series of 3 ÷ 7 sludge samples were taken from each wastewater treatment plant at an interval of at least one month in 2021. Overall, 30 samples of the final product of the wastewater treatment process were examined. In addition, in the case of treatment plants, where sludge dewatering was carried out, samples were also taken before this process (additional 6 samples). A detailed inventory of the number of samples and their sampling period for each considered WWTP is provided in Supplementary Material in Table S1.

2.2. Analytical Methods

The ultimate and proximate analyses were carried out for all sludge samples, which included the determination of: the contents of carbon, hydrogen, chlorine, sulfur, and mercury, and the basic composition of the ash (including the content of alkali metals), as well as the contents of moisture, ash, volatile matter, and net calorific value (NCV). The analyses were carried out in accordance with standards set for solid recovered fuels. A detailed summary of implemented standards is shown in Table 1. Fixed carbon FC (% wt. dry basis) was calculated as the difference between 100 and the sum of the ash and volatile matter content determined on a dry basis. All analyses were performed in at least duplicate, with additional determinations con-ducted when the repeatability limits specified in the relevant standards were exceeded; quality control procedures for chlorine and mercury determinations are described in the Supplementary Material. Detailed analytical data for the examined sludge samples are available in the repository [42].

Table 1. Analytical methods.

Parameter	Unit	Method	Instruments	Standard
Moisture content M_{ar}	%	Drying at 105 °C	TGA Thermostep automated thermogravimetric analyzer (ELTRA GmbH, Haan, Germany)	ISO 21660-3 [43]
Ash content A_d	%	Combustion		ISO 21656 [44]
Volatile matter content *VM*	%	Pyrolysis		ISO 22167 [45]
Net Calorific Value *NCV*	MJ/kg	Calorimeter bomb combustion	C 6000 bomb calorimeter (IKA-Werke GmbH & Co. KG, Staufen, Germany)	ISO 21654 [46]
Carbon content *C*	%	Instrumental	CHS 580 elemental analyzer (ELTRA GmbH, Haan, Germany)	ISO 21663 [47]
Hydrogen content *H*	%			
Sulfur content *S*	%			
Chlorine content *Cl*	%	Instrumental	TitraLab AT1000 automatic titrator (Hach Company, Loveland, CO, USA) C 6000 bomb calorimeter (IKA-Werke GmbH & Co. KG, Staufen, Germany)	EN 15408 [48]
Basic ash composition	%	X-ray fluorescence	Epsilon 3XLE spectrometer (Malvern Panalytical B.V., Almelo, The Netherlands)	ISO 13605:2018 [49]
Mercury content *Hg*	mg/kg	Instrumental	DMA-80 direct mercury analyzer (Milestone S.r.l., Sorisole, Italy)	EN 15411 [50]

As mentioned earlier, the oxide composition of ash from fuels, biomass, and wastewater sludge is important in terms of their combustion and co-combustion. Ash components such as SiO_2, CaO and K_2O cause a shift in ash characteristics toward higher deposition potential and hence increase agglomeration rates. Sodium and potassium are also known to drastically decrease the melting point of ash, and can thus increase ash deposition and fouling of the boiler's heat exchange surface [51]. Experimental studies [52] have also shown that the deposition rate depends on the ratio of chlorine and sulfur. As a result, a number of slagging and fouling indexes have been formulated to determine the risk of sludge formation and ash agglomeration from solid and alternative fuels during combustion. The indexes considered in the paper and the range of values characterizing slagging and/or fouling tendencies are shown in Table S2 in Supplementary Material [53–57].

The ISO 21640 [34] standard was developed to unify the quality of solid fuels produced from different types of waste, where the term solid recovered fuels (SRF) was adopted. This was due to the heterogeneity and instability of the composition of municipal waste, and thus its physicochemical properties, which created challenges for its use in power generation. Similarly, in the case of wastewater sludge, we encounter compositional variability depending on origin, industry, and annual variability. Based on this similarity, this method was used to determine the quality class of sludge as an alternative fuel, which allows us to identify possible directions for its use. The classification is based on the determination of three main parameters: net calorific value (NCV), reflecting the energy potential and economic value of the fuel; chlorine content, associated with technological limitations such as high-temperature corrosion; and mercury content, reflecting environmental concerns related to its toxicity and potential atmospheric emissions (Table 2). The classification was applied to individual samples, which is a simplification: ISO 21640 [34] defines the classes for batches of fuel and uses statistical measures (mean, median, and 80th percentile). Net calorific value and mercury are defined in the as-received state, chlorine on a dry basis. Because the moisture of the sludge was high, the comparison with the reference fuels is presented on a dry basis. The classification is therefore preliminary and comparative; values

below the limit of class 5 are reported as ">5". Net calorific value was additionally assessed at the measured total moisture.

Table 2. RDF classification based on its three key properties (ISO 21640 [34]).

Indicator	Property	Unit (Statistical Measure)	Classes				
			1	2	3	4	5
Economic	Net calorific value (as received, ar)	MJ/kg (mean)	≥25	≥20	≥15	≥10	≥3
Technical	Chlorine content (dry)	% (mean)	≤0.2	≤0.6	≤1.0	≤1.5	≤3.0
Environmental	Mercury content (ar)	Mg/MJ (median)	≤0.02	≤0.03	≤0.05	≤0.10	≤0.15
		Mg/MJ (80th percentile)	≤0.04	≤0.06	≤0.10	≤0.20	≤0.30

2.3. Statistical Analysis

Descriptive statistics and correlation and cluster analyses were carried out in Python 3.12 (NumPy, pandas, SciPy, scikit-learn, statsmodels). Correlations between samples were calculated as Pearson coefficients over 20 variables: ten ash oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3), the sodium and potassium contents of the fuel, and eight slagging and fouling indices (I1, BAI, AI, SI, SR, IC, SA, Fu). Because the variables differ by orders of magnitude, the analysis was performed on the raw values and after $\log_{10}$ transformation and autoscaling (mean-centering and division by the standard deviation of each variable). Correlations between variables are reported as Pearson and Spearman coefficients. Hierarchical cluster analysis of the eight slagging indices used z-scores of each index, Euclidean distance, and Ward's method.

Cluster analysis (CA) is one of the most widely used methods for chemometric analysis. Researchers use this method to analyze both chemical and environmental data. Cluster analysis allows the grouping of objects (e.g., test samples) based on significant similarity (e.g., chemical similarity), as well as the identification of outliers [58]. Cluster analysis involves categorizing a set of objects into groups, also known as clusters, so that objects in one group are as distinct as possible from those in other groups [59]. It is a particularly valuable technique in chemical and environmental research, where the aim is to identify and compare the patterns present or indicate possible anomalies. Both chemistry and environmental and energy research use this method.

The goal of cluster analysis is to group the studied objects or analyzed variables into clusters that identify their mutual similarities and differences. In the current study, we employed hierarchical cluster analysis, an unsupervised method that creates clusters based on the distance between objects (here, samples) in a multidimensional space. Samples were clustered using the eight slagging and fouling indices as variables. Because the indices are expressed on different scales (SR in percent, AI in kg/GJ, the remaining indices as dimensionless ratios), each index was standardized to a z-score so that all indices contributed with equal weight to the Euclidean distance. As z-scores are sensitive to extreme values, the clustering was repeated after $\log_{10}$ transformation, and only the agreement of both clusterings with the fuel type is reported (Section 4). Clusters were merged with Ward's method, and the results are shown as a clustergram.

3. Results

3.1. General Characteristics of the Samples

The results of the proximate analysis of the investigated wastewater sludges and selected reference solid fuels are presented in Figure 1a,c. Moisture content was reported both on an as-received basis (total moisture) and on an air-dried basis (ad; residual moisture),

whereas volatile matter, ash content, fixed carbon (FC), and net calorific value (NCV) were expressed on a dry basis to facilitate comparison between sludge streams and reference fuels. However, the actual moisture content reduces the energy available from sludge and may necessitate energy-intensive drying before thermal conversion.

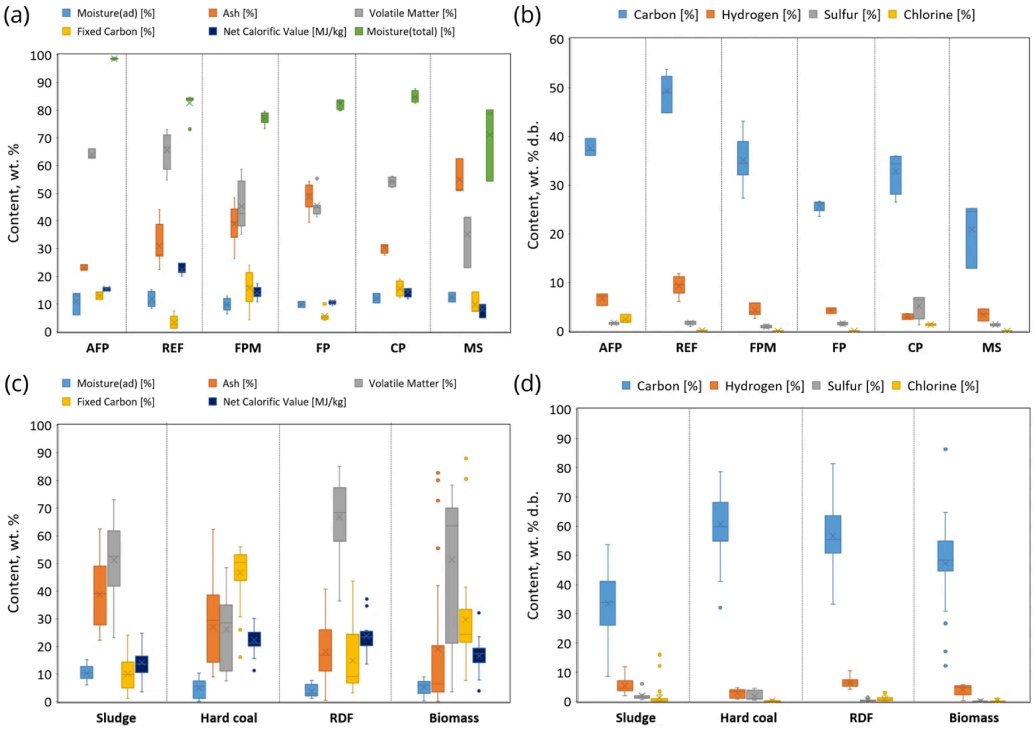

Figure 1. Proximate and ultimate analysis of the analyzed wastewater sludges and selected reference fuels: (**a**) proximate analysis of individual sludge samples; (**b**) ultimate analysis of individual sludge samples; (**c**) proximate analysis of wastewater sludges compared with hard coal, RDF and biomass; (**d**) ultimate analysis of wastewater sludges compared with hard coal, RDF and biomass. $M_{(total)}$—total moisture content; $M_{(ad)}$—moisture content in the air-dried state; V—volatile matter; A—ash content; FC—fixed carbon; NCV—net calorific value; C, H, S and Cl—carbon, hydrogen, sulfur and chlorine, respectively; db—dry basis. Except for $M_{(total)}$ and $M_{(ad)}$, all parameters are expressed on a dry basis.

Considerable differences were observed among the sludge samples, particularly in terms of total moisture content, ash content, volatile matter, and fixed carbon. These parameters are important for assessing the suitability of sludge for thermal conversion, because they directly affect fuel handling, drying requirements, calorific value, and the amount of solid residue formed during processing.

The total moisture content varied markedly among the investigated sludge samples. AFP sludge showed the highest average moisture content, reaching 98.8%, which resulted from the absence of mechanical dewatering in the wastewater treatment plant process line. In contrast, the other investigated sludges had average total moisture content in the range of 71 ÷ 85%, which is typical of mechanically dewatered sludges. However, even these values are high from the perspective of thermal utilization and indicate the need for preliminary drying. According to the literature [25], the moisture content of sludge intended for thermal processing should usually be reduced to approximately 35–59%. Nevertheless, some thermochemical processes, such as hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC), can process feedstocks with high water contents [10].

The analyzed sludges also differed significantly in ash content, with average values ranging from 23 up to 55% db. The highest ash content was observed for municipal sludge (MS), reaching 62.5% db. Such high ash contents are unfavorable for energy recovery,

because ash acts as ballast and, together with the moisture, reduces the calorific value of the sludge. Moreover, ash may contain compounds responsible for operational and environmental problems during thermal conversion, including alkali compounds, sulfur and ecotoxic elements. Therefore, wastewater sludge should be regarded as a specific type of waste-derived biomass/waste, characterized by both high moisture and high mineral matter contents.

The investigated sludges were characterized by relatively high volatile matter (VM) contents, with average values ranging from 35.2 to 65.6% db. The highest VM content was found for REF and AFP sludges, while the lowest was observed for MS sludge. The fixed carbon (FC) content of the investigated sludges was relatively low, with average values ranging from 5.7 (for FP sludge) to 15.8% (for FPM sludge). Similar trends were observed for the considered RDF and biomass samples. This indicates the high reactivity of sludge organic matter during thermal treatment. Under high-temperature conditions, the organic matter present in sludge can be rapidly decomposed, resulting in the formation of gaseous and condensable products, leaving only a small amount of char. This is particularly important in pyrolysis, where low fixed carbon content may lead to a limited char yield at higher temperatures. Consequently, the solid pyrolysis products may be dominated by the mineral fraction, i.e., ash, rather than by carbonaceous matter [60]. From the perspective of gasification and combustion, the high volatile matter content may favor rapid devolatilization, easier ignition and faster initial conversion of the organic fraction. However, the overall process efficiency also depends on char reactivity, ash content, mineral matter composition and operating conditions [61].

The results of the ultimate analysis of the investigated wastewater sludges, grouped by sludge type, are presented in Figure 1b. The highest average contents of C and H were determined for REF sludge, reaching 49.4% db and 9.3% db, respectively. The average C contents in AFP, FPM, FP, CP, and MS sludges were 37.6, 35.1, 25.6, 32.8 and 20.9% db, respectively. The corresponding H contents were 6.74, 4.33, 4.25, 2.95 and 3.42% db. The relatively high C and H contents in REF sludge may be associated with the characteristics of refinery wastewater and the possible presence of residual organic compounds originating from liquid fuel processing. Similarly, the elevated H content in AFP sludge may reflect the nature of the treated wastewater and the possible presence of animal-fat residues.

The NCV of the investigated wastewater sludge varied substantially, with average values ranging from 8.1 to 22.4 MJ/kg. The lowest average NCV was determined for MS sludge, mainly due to its high ash content. In contrast, refinery sludge was characterized by generally having the highest NCV; among these samples, the maximum value reached 24.8 MJ/kg, which was associated with relatively high volatile matter and hydrogen content, as well as moderate ash content.

Compared with reference fuels (Figure 1c), wastewater sludges were generally characterized by higher moisture and ash contents than hard coal, biomass and RDF. RDF, especially when rich in polymer-derived materials, showed a higher combustible fraction than hard coal, whereas biomass exhibited the widest variability in proximate composition due to differences in origin and type. In terms of ash content, selected RDF samples may resemble wastewater sludge more closely than biomass. Among all considered fuel samples, wastewater sludge has the lowest NCV due to ballast of moisture and ash, with the exception of the refinery sludge (REF). The highest NCVs were noted for RDF and hard coal samples. This parameter not only varies strongly with the ballast content but also with the elemental composition—content of C, H, S and Cl (Figure 1d). The lowest C content was determined in the sludge samples, and the highest in the hard coal samples. The highest S content was found in samples of coals, while the highest chlorine content was found in both RDF and sewage sludge samples.

3.2. Chlorine Content

The chlorine content, considered here as an important parameter of technological classification, varied widely in the investigated wastewater sludge samples, from 0.05 to 3.46% db. This variability was mainly related to the different origins of the samples. Differences in the average chlorine content among sludges from each wastewater treatment plant were statistically significant, as confirmed by one-way analysis of variance ANOVA on ranks, i.e., the Kruskal–Wallis test ($p = 0.0005$). The highest chlorine contents were observed for AFP and CP sludges, reaching 1.80–3.46% and 1.16–1.60% db, respectively, which were markedly higher than those in the other investigated sludges. Therefore, these sludges may pose an increased risk of high-temperature corrosion during thermal utilization, depending on the operating conditions and chlorine speciation. In contrast, the chlorine content in the other sludges (REF, FPM, FP and MS) did not exceed 0.2% db, indicating a low risk of corrosion. Nevertheless, both sludge and RDF samples showed higher content of this corrosive element than coal and biomass samples (Figure 1d).

When sludge is considered as waste for thermal utilization, the required process temperature depends partly on its chlorine content. This should also be taken into account when sludge is co-combusted in waste incineration plants or cement plants. According to the Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions [62], hazardous wastes containing more than 1% halogenated organic substances, expressed as chlorine, require a combustion temperature of at least 1100 °C. Therefore, this requirement may apply to AFP and CP sludges, although only total chlorine content was determined in this study, whereas the other tested sludges, with Cl content below 1%, could be thermally treated at a lower temperature, but not below 850 °C.

The highest chlorine content in AFP samples was most likely related to the fact that this sludge had not been mechanically dewatered at the wastewater treatment plant. Since chlorine in wet wastewater sludge may occur partly as dissolved chloride ions [63], the effect of dewatering on chlorine concentration was assessed. For this purpose, chlorine contents were compared in samples collected at the same time before and after dewatering. Mechanical dewatering of analyzed sludge was carried out using centrifuges for FPM, FP, CP, MS, and filter presses for REF. As expected, chlorine content on a dry basis decreased markedly after dewatering (Table 3). The relative decrease in chlorine concentration was calculated as the ratio of the difference between chlorine content before and after dewatering to the initial chlorine content of the sludge, all expressed on a dry basis. The relative decrease in chlorine concentration was higher in sludges with higher initial chlorine contents. Therefore, the relative decrease was low for municipal sludge, amounting to only 7%, whereas in high-chlorine sludge (CP) it reached 92%.

Table 3. Chlorine content in analyzed sewage sludges before and after dewatering. The relative decrease in chlorine concentration was calculated using mean values expressed to three decimal places, whereas the chlorine concentrations presented in the table were rounded to two decimal places in accordance with the analytical standard.

	REF	FPM	FP	CP_1	CP_2	MS
Cl content before dewatering [%db]	0.44	0.21	0.25	16.07	12.19	0.09
Cl content after dewatering [%db]	0.18	0.09	0.09	1.29	1.44	0.08
Cl content relative decrease [%]	60	58	64	92	88	7

3.3. Sulfur Content

The total sulfur content of the analyzed wastewater sludge samples also varied from 0.62 to 6.72% db. The average S content differed significantly among the tested sludges

depending on their origin, as confirmed by the Kruskal–Wallis test ($p = 0.0097$). Particularly high sulfur contents were observed in CP sludges originating from the treatment of coke oven wastewater, ranging from 5.96 to 6.72% db. This may be related to the specific composition of coke oven wastewater and to the use of iron sulphate coagulants during wastewater treatment. In the remaining sludge samples, the total sulfur content remained at a moderate level, with average values ranging from 0.94 to 1.71% db, while individual values did not exceed 2.06% db. The S contents in MS sludge and FPM sludge (where part of the stream was also municipal wastewater) were similar to the values previously reported in the literature [64]. The other presented fuel samples are also characterized by varying S content, with the highest concentrations typical of hard coals (Figure 1d).

Sulphur in fuel may promote high-temperature corrosion. However, increasing the proportion of sulfur oxides in the flue gas can also prevent the formation of alkali chloride deposits through sulphation reactions. Therefore, a sufficiently high [S]/[Cl] molar ratio is generally considered beneficial for reducing the risk of high-temperature corrosion [65]. A [S]/[Cl] molar ratio above 2.0 indicates a low potential for chloride corrosion, whereas values above 4.0 may result in a negligible concentration of chlorine in boiler deposits and thus substantially reduce corrosion risk. Among the analyzed final sludge samples, only sludge AFP had a [S]/[Cl] molar ratio below 2.0, indicating a high corrosion potential. For the other final sludge samples, this ratio exceeded 4.0. However, it was observed [66] that the presence of chlorine in deposits did not always correlate with the [S]/[Cl] ratio. It also depended on the content of aluminum and silicon, with lower Al and Si contents favoring higher Cl contents in deposits, as well as on alkali concentrations, where higher alkali contents promoted Cl enrichment in deposits.

High sulfur content in sewage sludge can cause not only harmful SO_x emissions during incineration and co-combustion processes but may also lead to the formation of H_2S and COS in syngas produced during sludge gasification. These compounds may cause deactivation of synthesis catalysts; therefore, their removal from the gas stream or the use of suitable additives in the bed material may be necessary [67].

3.4. Mercury Content

Mercury content was analyzed because of its environmental significance and its role as one of the key parameters used in the classification of solid recovered fuels according to ISO 21640 [34]. Wastewater sludge was generally characterized by higher Hg contents than the reference fuels. RDF samples had slightly lower Hg levels, whereas biomass samples showed minimal mercury contents (Figure S1 in Supplementary Materials).

Particularly high Hg contents were determined in sludge samples from the coking industry, ranging from 12.7 to 22.6 mg/kg db. In the remaining final sludge samples, Hg content did not exceed 1.5 mg/kg db and averaged 0.29 mg/kg db. Such a large difference indicates that the industrial origin of sludge is a key factor controlling Hg content and should be considered when assessing its suitability for thermal utilization or use as a solid recovered fuel.

3.5. Alkali Content and Ash Composition

Differences among wastewater sludge samples from different WWTPs were also reflected in their highly variable ash composition (Figure S2 in the Supplementary Materials). The ash obtained from combustion of the analyzed sludge samples at 550 °C differed mainly in the content of iron, aluminum and silicon oxides. The high iron oxide content in CP sludge ash was most likely associated with the use of ferrous sulphate as a coagulant during wastewater treatment, which is consistent with elevated S content in this sludge. In hydrothermal liquefaction of sewage sludge, $FeSO_4$ may improve bio-oil yield, but at the same

time it may also introduce additional sulfur contamination [68]. Comparing the particular oxides content of different fuels/waste, the SiO_2 content is at a similar level of variation. CaO content is observed in the highest shares for biomass, and iron oxide is highest in the sludge samples.

The ash from analyzed wastewater sludge samples also differed in the contents of alkali and alkaline earth elements. In general, all sludge samples had a high content of sodium and potassium (determined as the sum of their oxides $Na_2O + K_2O$) compared to solid fossil fuels and similar to RDF [69]. Biomass samples have the highest content and range of variability for K_2O content. The range of TiO_2 and P_2O_5 content is the widest for sludge samples among the presented fuels/wastes.

High contents of alkali and alkaline earth compounds may contribute to fouling, agglomeration and slagging during thermal conversion. However, these processes are complex and are affected not only by alkali content, but also by ash composition, mineral transformations, temperature and process conditions. Therefore, several indices are commonly used to assess the tendency of fuels and wastes to cause agglomeration, slagging or fouling during combustion [25,26].

3.6. The Selected Slagging Indices

The obtained values of the SR ratio for wastewater sludge in the range from 17 to 65 suggest a potential tendency to slagging according to this index (Figure 2a). The SR (silica ratio) values below 65 indicate a high possibility of slagging, while values in the 65–72 range indicate a medium tendency [57]. The range of these values is found for most of the examined sludge samples. Similarly, the majority of the studied RDF and biomass samples show a tendency to slagging, based on the obtained SR index (Figure 2c). Only the group of hard coal samples is dominated by samples with a low and medium tendency.

A Bed Agglomeration Index, BAI, below 0.15 corresponds with agglomeration [70]. Due to the high content of iron oxides in the ash of the tested sludge, this indicator is high (Figure 2a). However, it should be mentioned at this point that the content of iron compounds can also be of major concern, because under conditions with insufficient oxidant, iron compounds can form relatively low-melting ferrous metasilicate or ferrous orthosilicate, resulting in bed agglomeration [71]. Nevertheless, when analyzing the ranges of the BAI index, the largest values are obtained for the presented samples of hard coals (Figure 2c).

The IC Contamination Index in the range of 0.3–3.0 signals high agglomeration of pollutants, while values below 0.3 and above 3.0 indicate a low tendency to agglomerate [72]. This indicator for the examined sludges has very wide variability and the highest values among the considered fuels (Figure 2c). Nearly all samples of hard coals and RDF are characterized by a high tendency to agglomeration, while almost all samples of biomass have IC index values in the range indicating a low tendency to agglomeration.

Alkali Index AI values in the range of 0.17–0.34 indicate the possibility of agglomeration, while AI > 0.34 is associated with a very high agglomeration tendency according to the original index criteria. The calculated AI values for the examined sludge samples (Figure 2b) were very high, suggesting a potential elevated risk of agglomeration and slagging. Almost all presented fuel/waste samples had very high AI values, indicating a high tendency to agglomeration and slagging based on this index (Figure 2d).

Another indicator often used to predict agglomeration is base-to-acid ratio SI (also known as Rb/a). With increasing SI values, the tendency of fuel/waste ash for fouling is greater. In many cases, it was applied to fuels with a low phosphorus content, which in the case of biomass and wastewater sludge occurs in significant amounts. Therefore, a modified version of this indicator has been proposed [70,72] considering phosphorus oxide as well. SI values less than 0.75 and greater than 2.0 are associated with low tendency to

deposition; values between 0.75 and 2.0 correspond with a high tendency to deposition [72]. Based on this indicator, the examined sludges may exhibit a medium to high tendency for agglomeration and fouling (Figure 2b).

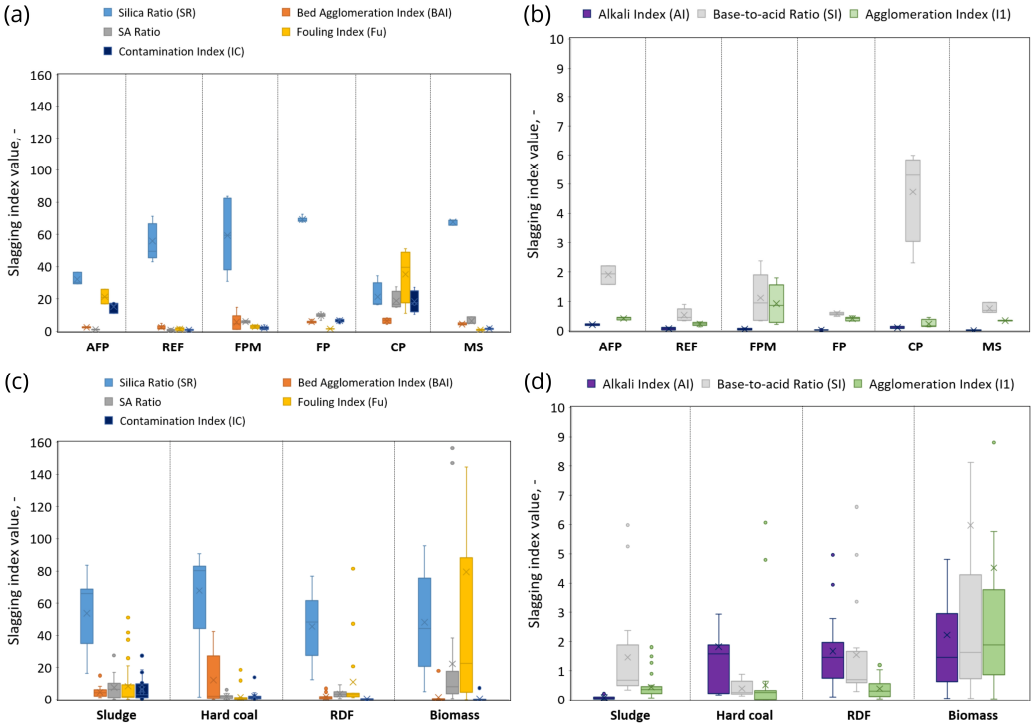

Figure 2. The selected slagging indices of analyzed wastewater sludges, and selected fuels: (**a**) SR (silica ratio), BAI (Bed Agglomeration Index), SA ratio, Fu (fouling index), and IC (Contamination Index) for investigated wastewater sludges; (**b**) AI (Alkali Index), SI (base-to-acid ratio) and I1 (Agglomeration Index) for investigated wastewater sludges; (**c**) SR, BAI, SA, Fu, IC for wastewater sludges compared with hard coal, RDF and biomass; (**d**) AI, SI, and I1 for wastewater sludges compared with hard coal, RDF and biomass. Scattered points in panels (**c**,**d**) indicate outlying observations outside the box-plot whiskers.

Agglomeration Index I1 takes into account also the chlorine and sulfur content. This indicator is based on the general observation that the presence of S and Cl, which at high temperatures promote gas-phase release and binding in volatile compounds, affects the initial concentration of alkali in the gas phase [73]. If the value exceeds 1 then the examined material has a high agglomeration potential. The I1 values for the tested sludge samples in most cases did not exceed 1 (Figure 2b). Only for three samples of FPM sludge I1 was above 1 with a maximum of 1.8. Both RDF and hard coal samples are characterized by I1 values below 1, while for biomass samples the value of the I1 index exceeded this value severely, and reached a maximum of up to 8.8 (Figure 2d).

The ability to form deposits is described by the SA ratio, and if its value is below 1.87 then the fuel used has a low potential to form deposits. If the SA value is in the range from 1.87 to 2.65, then the fuel is characterized by medium deposition potential. If the SA value is above 2.65, the applied fuel has a high ability to form deposits. All the presented samples have a wide range of the SA values, which allows them to be classified into the medium and high ranges (Figure 2c). The highest values of this ratio were recorded for biomass samples.

The last considered index is the Fu fouling index. A low degree of fouling is expected for Fu < 0.6, high for Fu values up to 40, and very high for values above 40. For all the

considered fuel/waste samples, the value of the index varied greatly, and reached the highest values in the case of biomass (Figure 2c).

It should be highlighted that these indices are based mainly on fuel/waste composition and do not account for interactions with bed materials or specific operating conditions. Therefore, they can only indicate potential problems during the thermal conversion of wastewater sludge. Moreover, these indices have been developed and evaluated mainly for fossil fuels and biomass. Considering the specific ash composition of the analyzed sludge and the differences between the results obtained from individual indices, further laboratory-scale investigations or in situ monitoring of slagging, fouling and agglomeration would be necessary to verify their predictive applicability to wastewater sludge.

In addition to the negative aspects of the presence of large amounts of mineral matter in wastewater sludge and its chemical composition, there are also positive ones such as the catalytic effect in gasification processes [74].

4. Classification and Discussion

To verify the feasibility of using the examined sludges as energy carriers or substrates for thermal conversion processes, the collected data set was first subjected to correlation analysis (Figure S3 in Supplementary Material). Coking-plant sludge (CP; four final samples and two samples taken before dewatering, six in total) was excluded from the analyses of ash composition and slagging indices. The exclusion follows from the distinct fuel properties of this sludge (mercury 12.7–22.6 mg/kg, sulfur up to 6.72% and chlorine 1.16–1.60% on a dry basis), not from its position in the correlation analysis.

Due to the purpose of the conducted research, the correlation analysis was limited to the content of individual oxides in ash, the sodium and potassium contents of the fuel and the values of the slagging indices. The correlation between samples was first calculated on raw values (Figure S3). The mean Pearson coefficient between sludge and coal was 0.81, between sludge and RDF 0.69, and between sludge and biomass 0.48. These coefficients are dominated by variables with a large numerical range (such as SR and SiO_2) and therefore mainly reflect scale. After $\log_{10}$ transformation and autoscaling, which give each variable the same weight, the corresponding coefficients were −0.04 for coal, −0.25 for RDF and −0.24 for biomass, while the mean coefficient within the sludge group was 0.49 (Figure 3). The similarity of sludge to coal and RDF seen in the raw data was not supported after scaling.

It has already been mentioned that the examined sludges differ from each other significantly. Therefore, the next step was to assess to what extent they differ from each other in terms of ash chemical composition and ability for slagging and fouling. For this determination, the data set was reduced to sludge samples only, and we checked which samples correlate most strongly, and which analyzed variables are responsible for such correlation (Figure 4).

On raw values, the sludge from the animal-fat plant (AFP) was the most distinct (mean coefficient with the other plants 0.61–0.67), and the sludge from the food-processing plants (FPM, FP) and municipal sewage sludge (MS) formed a group with mean coefficients of 0.92–0.96 between plants. After $\log_{10}$ transformation and autoscaling the mean coefficients between these sludges fell to the range from −0.17 to 0.04 (from −0.49 to 0.04 for all pairs of plants; Figure 5), so the apparent homogeneity of this group depends on the scaling. The FPM samples were also dissimilar to one another after scaling (mean coefficient within the plant 0.06).

The strongest correlations between variables are listed in Table S3. Because the distributions are skewed, some strong Pearson correlations were not supported by Spearman rank correlation, for example IC–Fu ($r = 0.81$, $\rho = 0.19$, $q = 0.53$; $n = 30$), and should be

regarded as driven by a few samples. These correlations refer to the sludge samples only and may differ for the other fuels.

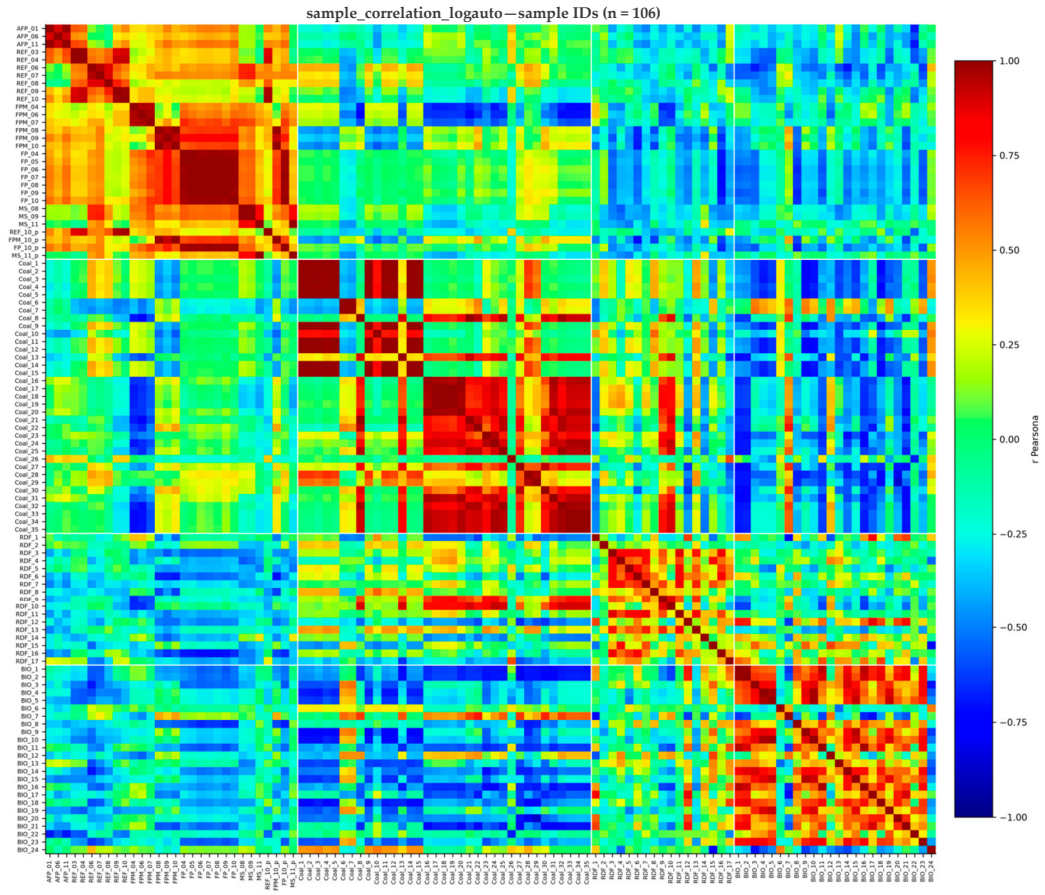

Figure 3. Correlation between samples (Pearson coefficient) calculated over ash oxides, fuel alkali contents and slagging indices, after $\log_{10}$ transformation and autoscaling; coking-plant sludge excluded.

The next step in analyzing the collected data was to identify a common group for samples from different sources. For this purpose, cluster analysis (CA) was used, and the results of this analysis in the form of a dendrogram are shown in Figure 5. Hierarchical cluster analysis of the eight slagging indices (z-scores, Ward's method, three clusters) did not separate the fuel types: two of the three clusters consisted of three biomass samples each, characterized by extreme values of Fu, SA or BAI, and the remaining 100 samples formed one cluster. The agreement between the clusters and the fuel type was negligible (adjusted Rand index, ARI = 0.02; n = 106); after $\log_{10}$ transformation it was 0.27, and the agreement between the two clusterings was 0.07. The dendrogram was therefore not used as a criterion of similarity between the fuels.

The comparison of slagging indices was performed on a subset of 70 samples selected in the earlier version of the analysis on the basis of the original dendrogram: seven biomass samples, 23 coal samples, 26 wastewater sludge samples (22 final and four pre-dewatering samples; AFP, CP and FPM_04 not included) and 14 RDF samples. The slagging and fouling indices were classified with the limits in Table S2 [53–57]. None of the samples simultaneously met the lowest limits of all eight indices; the sludge samples met at most six of the eight. As a summary measure, the mean share of indices in the low class was calculated for each fuel: 58% for sludge, 57% for coal, 43% for RDF and 38% for biomass (Figure S4).

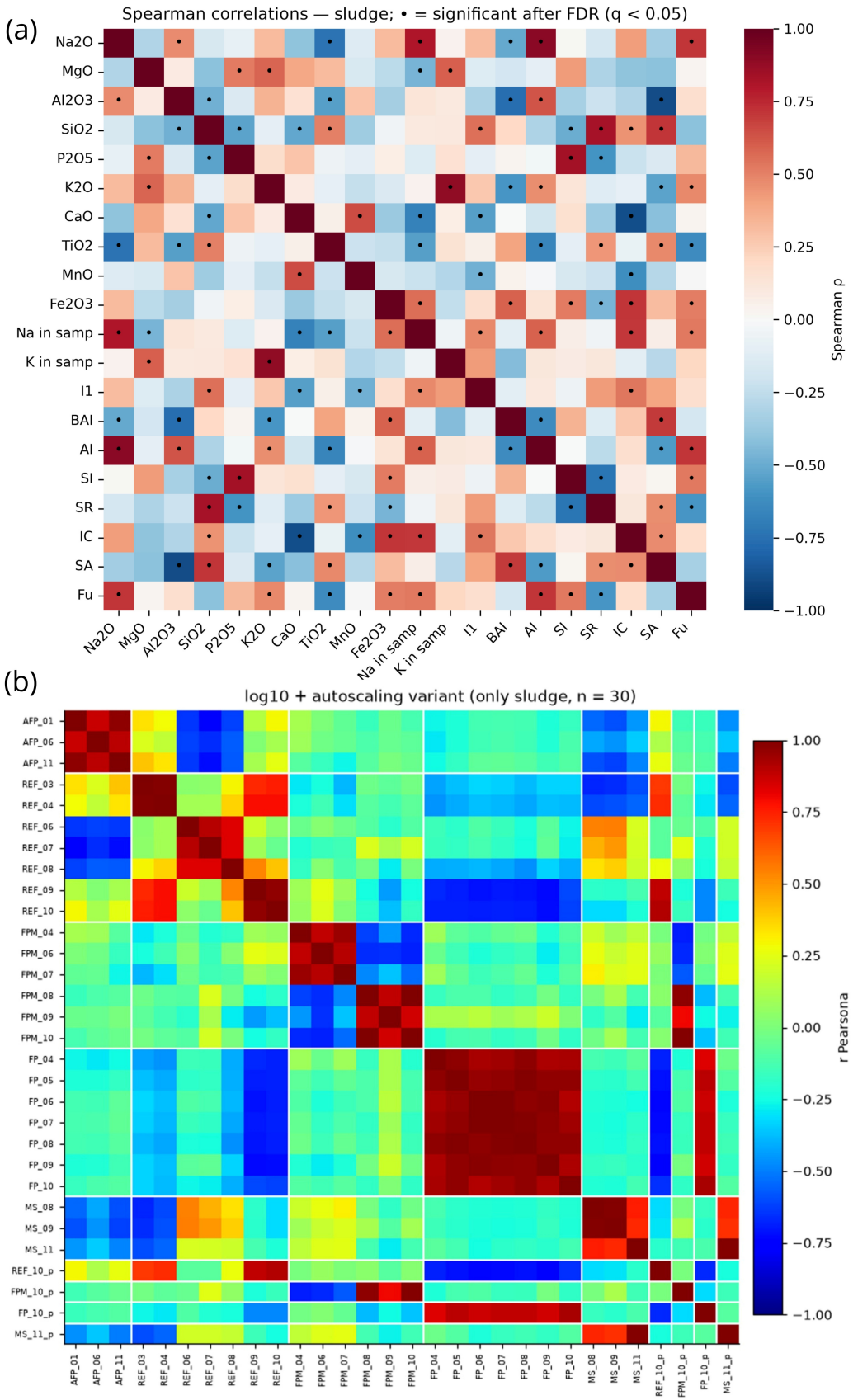

Figure 4. Correlation heat maps for the sludge samples: (**a**) correlations between variables (Spearman correlation, after $\log_{10}$ transformation and autoscaling; coking-plant sludge excluded, ash oxides, fuel alkali contents and slagging indices); (**b**) correlations between individual samples (Pearson coefficient, after $\log_{10}$ transformation and autoscaling).

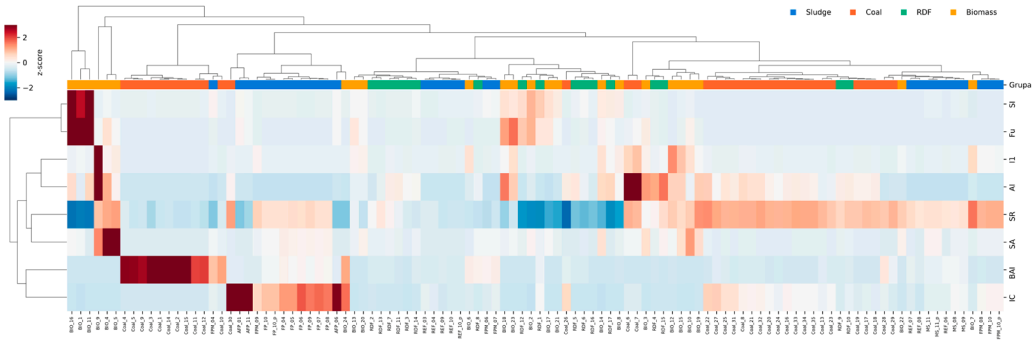

Figure 5. Clustergram of the slagging indices (z-scores, Euclidean distance, Ward's method); the eight indices in rows, samples in columns.

The share of indices in the low class was similar for sludge and coal, but no sample met all limits, and the result depends on the index definitions, which were developed mainly for coal and biomass. It therefore does not by itself indicate that the sludge can be used for combustion; this requires the additional criteria discussed below. However, a suitable oxide composition of the ash is not the only determinant of the energy use of the sludge. To evaluate the feasibility of using wastewater sludge in power generation in terms of energetic, technological and environmental aspects, an SRF classification methodology in accordance with ISO 21640 [34] was used (Table 4).

Table 4. Share of final samples in the ISO 21640 [34] classes for net calorific value, chlorine and mercury, on a dry basis; individual samples; class limits as in Table 2; ">5" denotes values outside class 5.

Parameter	Class	Biomass	Coal	Sludge	RDF
NCV	1	14%	52%	0%	36%
	2	0%	30%	23%	57%
	3	43%	13%	20%	7%
	4	14%	4%	43%	0%
	5	29%	0%	14%	0%
	>5	0%	0%	0%	0%
Cl	1	71%	35%	77%	7%
	2	29%	61%	0%	29%
	3	0%	4%	0%	22%
	4	0%	0%	10%	21%
	5	0%	0%	10%	14%
	>5	0%	0%	3%	7%
Hg	1	100%	100%	70%	72%
	2	0%	0%	0%	14%
	3	0%	0%	4%	7%
	4	0%	0%	10%	0%
	5	0%	0%	3%	7%
	>5	0%	0%	13%	0%

As mentioned earlier, due to the very high moisture content of the wastewater sludge, it is necessary to dry it before further use in thermochemical processes. Because ISO 21640 [34] defines net calorific value in the as-received state, the sludge was first assessed at the measured total moisture. Of the 30 final sludge samples, only one (REF_06, total moisture 73.2%) reached class 5 for net calorific value, and 29 were outside class 5. No sample was in classes 1–3. All parameters were therefore additionally compared on a dry basis, which corresponds to a fully dried fuel and allows comparison with the reference fuels.

On a dry basis, 13 of the 30 final sludge samples (43%) were in classes 1–3 for net calorific value. When chlorine and mercury were also taken into account, eight samples (27%) remained in classes 1–3: six from the refinery plant (REF; five in class 2 and one, REF_06, in class 3) and two from the FPM plant (FPM_06 and FPM_10, class 3). Their chlorine content corresponded to class 1, and the mercury content to class 1 in most cases and class 3 in REF_06. REF_07 fell to class 4 because of its mercury content. Evaluated as a batch, only the REF plant reached class 2 on a dry basis, and none of the six plants reached class 3 or better at the measured moisture. According to an estimate from the NCV-moisture relationship (Figure S5), the mean net calorific value of the REF batch remains in class 3 up to a total moisture of about 30%, and individual REF samples up to 22.7–36.1%, depending on the sample.

The remaining FPM samples and the FP sludge were mostly in class 4 for net calorific value (FP_04 in class 5). The sludge from the municipal plant (MS) was in class 5 for net calorific value and in classes 4–5 for mercury, and class 1 for chlorine. The AFP sludge reached classes 3–4 for net calorific value on a dry basis, but its chlorine content placed it in class 5 or outside class 5; the CP sludge fell outside class 5 because of mercury.

Following the approach proposed by the authors in [41] for RDF, sewage sludge belonging to Classes 4 and 5 (not limited to Classes 1–3 as well) may be considered as feedstock in thermal conversion processes for the production of liquid fuels, bio-char and gas (hydrogen production) (Figure 6). Sludges that meet the requirements for classes 1–3 after drying but may carry the risk of slagging, fouling or agglomeration can be co-combusted with another fuel such as coal, provided that the properties of the fuel blend and operating conditions are appropriately assessed.

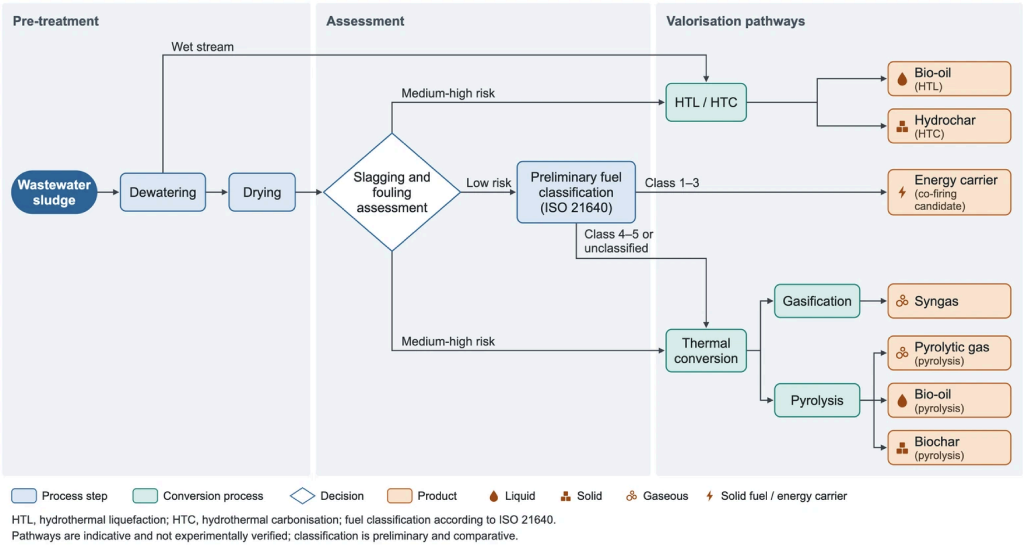

Figure 6. Wastewater sludge main utilization pathways (this study).

However, Figure 6 should be interpreted as showing indicative options rather than as a definitive process-selection algorithm. ISO 21640 [34] classification and slagging/fouling indices alone are insufficient to determine the most appropriate thermochemical route. Technology selection also depends on moisture content, elemental composition, ash content and composition, contaminant levels, reactor configuration, and the desired product. Hydrothermal processes such as HTL and HTC are particularly relevant to high-moisture sludge because they can process wet feedstocks without prior energy-intensive drying. Pyrolysis and gasification generally require lower feedstock moisture, while ash-forming elements and inorganic constituents may influence product yields and quality and, particularly in gasification, may contribute to agglomeration, slagging or deposition depending

on reactor design and operating conditions. Consequently, sludge assigned to classes 4–5 or remaining outside the ISO 21640 [34] classification limits should not automatically be directed to a specific conversion route; its suitability requires process-specific assessment.

5. Conclusions

Wastewater sludge is characterized by a highly variable composition of both the main components (moisture, ash and combustible matter) and mineral components (ash composition). Therefore, the properties of sludge should be systematically studied in order to enlarge the database, allowing sludge classification to be carried out for thermochemical processes or disposal. This would avoid technological problems with the utilization of these wastes.

The content of analyzed impurities varied within a very wide range depending on the origin of the wastewater sludge, and the sludge streams differ markedly from one another. The multivariate comparison also showed the importance of data preprocessing: the similarity to coal and RDF in ash composition suggested by raw values, which are dominated by variables with a large numerical range, was not confirmed after $\log_{10}$ transformation and autoscaling. Therefore, it is not possible to generalize the values of these parameters for all wastewater sludges, and each sludge stream should be assessed individually.

The chlorine, sulfur and ash composition of the tested wastewater sludge could be affected by both the characteristics of the wastewater itself (its source) as well as the wastewater treatment and sludge handling process, such as the use of flocculant additives and dewatering. In the paired samples, the relative decrease in dry-basis chlorine concentration after mechanical dewatering ranged from 7 to 92%.

None of the samples showed a low slagging and fouling tendency for all eight indices; the sludge samples met at most six of the eight limits. On average, sludge met the low-tendency limits for a similar share of indices as coal (58% and 57%), but this result depends on index definitions developed mainly for coal and biomass. The very high content of chlorine, sulfur and alkali in the analyzed sludge, especially sludge from wastewater treatment plants associated with animal fat production and coke-ovens, may cause problems with the proper operation of boilers, thus requiring control of the input composition or the operating parameters of the installation.

In the preliminary comparison with the ISO 21640 [34] class limits, no final sludge sample reached classes 1–3 at the measured total moisture. On a dry basis, eight of 30 samples (27%) were in classes 1–3; these were refinery sludge (class 2–3) and two FPM samples (class 3). Evaluated as batches, only the refinery sludge reached class 2 on a dry basis, and, according to an estimate, class 3 for a total moisture of up to about 30%. The sludge from animal-fat production and from the coking plant was outside class 5 in some or all samples because of chlorine or mercury, and the remaining sludge streams were in classes 4–5.

From a practical perspective, the results indicate that selected industrial wastewater sludges, traditionally considered primarily as wastes requiring thermal disposal, may also represent valuable alternative fuels or components of fuel blends after appropriate drying. This approach could enable energy recovery to become a primary objective of their thermal utilization rather than merely a secondary benefit of waste disposal, provided that fuel quality, operational requirements and the energy demand for drying are taken into account.

The results obtained indicated the need to monitor the properties and the proportion of wastewater sludge used in thermal treatment facilities to assess their potential influence on high-temperature corrosion, agglomeration, fouling, slagging and pollutant emissions. The research also highlights the potential of data analysis methods to identify relationships between sludge properties and support the future development of machine learning

algorithms for assessing their suitability for energy recovery. However, this requires a more comprehensive database accounting for wastewater origin, treatment processes and sludge-handling practices, as well as experimental validation of slagging and fouling indices against actual operational behavior during sludge combustion and co-combustion. Such data could enable the development of predictive models to identify key factors contributing to technological risks and support the early detection of potentially problematic sludge streams. In the future, these algorithms could assist in sludge classification and decisions concerning fuel blending, sludge feed composition and operating conditions, thereby helping to minimize operational problems during thermal utilization.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en19225412/s1. The supplementary material consists of the following sections: 1. Additional to Materials and Methods, including: Table S1. Sewage sludge samples; Table S2. Summary of selected slagging indices; 2. Additional to Results, including: Table S3. Pairwise correlations between the 20 fuel and ash variables for sewage sludge samples: Pearson's r, Spearman's ρ and the Benjamini–Hochberg false discovery rate-adjusted *p*-value (q). Pairs are ordered by decreasing absolute value of Pearson's r; Figure S1. Mercury content of analyzed wastewater sludges (a) and selected fuels (b); db—dry basis; Figure S2. Ash composition of analyzed wastewater sludges (a,b) and selected fuels (c,d): (a, c) content of SiO_2, Al_2O_3, CaO and Fe_2O_3; (b,d) content of Na_2O, K_2O, MgO, P_2O_5, TiO_2 and MnO; 3. Additional to Classification and Discussion, including: Figure S3. Correlation analysis (HeatMap) type of samples on raw values; Table S3. Pearson's correlation coefficients for the analyzed variables; Figure S4. Mean share of the eight slagging and fouling indices classified as low, by fuel (thresholds of Table S2; 70-sample subset with corrected sample labels); Figure S5. The relationship of NCV and the moisture content of REF sludge.

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