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SIGNIFICANT WASTE PROPERTIES IN TERMS OF APPLICABILITY IN THE POWER INDUSTRY

The aim of the article is to present the physical and chemical properties of the refuse derived fuel (RDF) substrates, which have a significant impact on the energy recovery process in power plants. The experimental part includes technical (moisture and ash content, net and gross calorific values) and elemental analyses (sulfur, chlorine and mercury content), biomass and non-biomass concentration in the samples. In order to carry out the analysis of reactor slagging and fouling risk, chemical composition of the ash and characteristic ash fusion temperatures were determined. The waste samples are heterogeneous material and their properties are diversified – the moisture content ranges from 1.8 to 29.2 wt. %, the net calorific value from 17.231 to 28.307 MJ/kg, the ash content in the samples from 7.7 to 31.2 wt. %. The S content is in the range from 0.04 to 0.58 wt. %, the Cl content from 0.58 to 2.11 wt. % and the Hg content in the samples from 0.09 to 0.20 mg/kg. It can be observed, that the tested waste is a demanding fuel, because of its unfavorable fouling and slagging properties, which are directly related to the content of oxides with the basic properties.

1. INTRODUCTION

According to the Central Statistical Office [1], almost 12 million tons of municipal wastes were generated in Poland in 2017, which was 311 kg of waste per capita. Over 42% of the generated municipal wastes were landfilled, 27% were recycled, 24% incinerated and 7% designed for composting or fermentation. In order to be properly incinerated, the wastes are subjected to various processes. The most widespread form of processing mixed waste in European countries is mechanical-biological treatment (MBT) [2, 3]. In the MBT facilities, recyclable materials (recovered by mechanical processes such as sieving, pneumatic separation, shredding, magnetic separation), compost and streams of rejects are generated [4, 5]. The rejects, however, can be profitable from the environmental and economic point of view. The stream is deprived of non-combustible

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fraction, the moisture content is reduced and its quality is improved since the organic matter and non-combustible parts are removed [3, 6]. The stream can be a substrate for refuse derived fuel (RDF) [7, 8]. The production of RDF in Poland in 2015-2017 exceeded 2 million Mg [9]. The RDF quality, quantity and composition strongly depends on the waste substrate [10]. The critical parameters of the waste input are moisture content, composition and physical nature [5]. Generally, the waste should be dried, usually the moisture content of RDF is below 25 wt. % [11, 12]. The lowest moisture content is present in plastics and the highest one in organic waste [3, 7, 11]. Paper and cardboard can also have high moisture content [3]. The RDF is commonly composed of paper and cardboard, plastics, textile [11, 12], however wood, rubber and sawdust [7] can also be present. Plastics and paper increase the calorific value of the RDF, because of higher percentage of volatile matter and calorific value [7, 11]. The presence of organic waste lowers the calorific value of RDF [6, 11]. The waste stream is generally characterized by high carbon content and moderate hydrogen content, which indicate a good energy potential [7, 11]. The high amount of nitrogen content in organic waste can cause higher NO_X emissions [11]. The high amount of chloride can cause corrosion in the incineration plants, so the waste components containing high amount of Cl (polyvinylchloride contained in packaging) have to be removed [7, 11].

Production of RDF is one of the waste-to-energy strategies whose goal is to solve both waste and energy problems [13]. The RDF can be utilized for energy recovery in direct combustion or co-combustion systems in cement plants, paper and pulp mills, heat and power plants and incineration plants [6, 14]. Nowadays, most of the RDF produced in Poland are incinerated in cement plants [15]. However, the capacity of RDF production installations is big enough to provide the waste substrates also to the power industry [16].

2. EXPERIMENTAL

The analysis of physical and chemical properties of wastes was conducted in the Laboratory of Fuels and Activated Carbons, which belongs to the Institute for Chemical Processing of Coal.

Table 1

Demonster	Cen	nent plants	Power plant			
Parameter	Calciner Process burner		1	2	3	
Moisture content, wt. %	<30	<30	45	10-30	10-30	
Net calorific value, MJ/kg	<30 <15		15	10-25	12-18	
Ash content, wt. %	<15	<15	20	10-20	10-20	
Chlorine content, wt. %	< 0.7	<0.7	<1.0	< 0.8	0.1-0.8	
Sulfur content, wt. %	<1.0	<1.0	< 0.5	0.1-1.0	0.1-1.0	

Quality requirements for alternative fuels used in cement plants and power plants [17]

Table 2

Classification parameter	Statistics1	Classes						
	Statistical measure	1	2	3	4	5		
Net calorific value, MJ/kg	mean	≥25	≥20	≥15	≥10	≥3		
Chlorine, wt. %	mean	≤0.2	≤0.6	≤1.0	≤1.5	≤3		
Mercury, mg/MJ	median	≤0.02	≤0.03	≤0.08	≤0.15	≤0.50		
	80th percentile	≤0.04	≤0.06	≤0.16	≤0.30	≤1.00		

Classification parameters for solid recovered fuels (SRF) [18]

The analysis involved parameters significant in terms of applicability in power industry [17] and included the classification in European Standard EN 15357:2011 [18]. Cement plants and power plants use alternative fuels (with 19 12 10 code [19]), including solid recovered fuels SRF for energy generation and have specified requirements for this fuels (Table 1). Table 2 shows the classification parameters for solid recovered fuels.

Materials. The tested material is waste classified with 19 12 12 code – other wastes (including mixtures of materials) from mechanical treatment of wastes other than those mentioned in 19 12 11 [19]. The results of the analysis of >80 mm fraction (14 samples weighing 40–700 g) have been presented, since this fraction is generally used for alternative fuel production [3–8]. The wastes were obtained from the Regional Municipal Waste Processing Installations in Tarnów, Tarnobrzeg, Włoszczowa and Kraków.

Proximate analysis. The proximate analyses involved determination of total moisture content, as received by the weight method, according to CEN/TS 15414-1:2010) (i), ash content, as received by the weight method, according to CEN/TS 15403:2011 (ii), gross calorific value, air-dried basis by the calorimetric method, according to CEN/TS 15400:2011 (iii), and net calorific value, as received by computational method, according to CEN/TS 15400:2011.

Chemical and elemental analyses. The elemental analyses involved the determination of total sulfur content, as received by the high-temperature combustion method with IR detection, according to PN-EN 15408:2011 (i), chlorine content, air-dried basis by the potentiometric titration method, according to Q/LP/24/A:2011 procedure) (ii), mercury content, dry state by the cold vapor atomic absorption spectrometry CVAAS, according to procedure Q/LP/54/A:2011 (iii). The biomass and non-biomass concentrations (in the dry state) were determined by the weight method, according to PN-EN 15440:2011 point A6. The chemical composition of ash (SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, P₂O₅, SO₃, Mn₃O₄, TiO₂, BaO, SrO, Na₂O, K₂O) was determined by the ICP-OES technique using emission spectrometry with inductively coupled plasma, according to Q/LP/65/A:2014 procedure. The characteristic ash fusion temperatures were determined in a high-temperature oven, in oxidizing and semi-reducing atmospheres, according to Q/LP/35/B:2011 procedure.

Fouling and slagging risk. The most popular indices (parameters) which describe the slagging and fouling risk of the reactor are [20–22]:

• the ratio of concentratuons of basic compounds (B) to acid compounds (A) in the ash:

$$B/A = \frac{[Fe_2O_3] + [CaO] + [MgO] + [Na_2O]}{[SiO_2] + [Al_2O_3] + [TiO_2]}$$
(1)

• slagging index *R*_s, wt. %:

$$R_s = S^d (B/A) \tag{2}$$

where S^d is the per cent content of sulfur in a dry material,

• clogging index F_u :

$$F_{u} = R_{s} = \frac{\left[\operatorname{Na}_{2}\operatorname{O}\right] + \left[\operatorname{K}_{2}\operatorname{O}\right]}{S^{d}} = (B/A) \times \left(\left[\operatorname{Na}_{2}\operatorname{O}\right] + \left[\operatorname{K}_{2}\operatorname{O}\right]\right)$$
(3)

• slag viscosity index *S_R*:

$$S_{R} = \frac{\left[\operatorname{SiO}_{2}\right]}{\left[\operatorname{SiO}_{2}\right] + \left[\operatorname{Fe}_{2}\operatorname{O}_{3}\right] + \left[\operatorname{CaO}\right] + \left[\operatorname{MgO}\right]}$$
(4)

• the ratio of concentrations of iron oxide to calcium oxide:

$$Fe/Ca = \frac{[Fe_2O_3]}{[CaO]}$$
(5)

• the sum of concentrations of iron oxide and calcium oxide in the ash, wt. %:

$$Fe + Ca = [Fe_2O_3] + [CaO]$$
(6)

The limit values of fouling and slagging indices for ash from solid fuels applied for energy purposes are shown in Table 3. The results of the analyses of the chemical composition of ash generated from the tested waste samples are given in Table 5.

Table 3

Donomoton	Fouling ability							
Parameter	Low Mediu		ium	High		Very high		
B/A	<0.4 or > 0.7			0.4–0.7				
Rs	<0.6 0.6-		2.0	2.0-2.6		2.6>		
Fe/Ca	< 0.3	.0		0.3-3.0				
Total Fe + Ca	<	10%				_		
F_u	≤0.0	6	0.6-40			>40		
S_R	>72		72-	72–65		≤65		

Limit values of fouling indexes [20-22]

3. RESULTS AND DISCUSSION

3.1. TECHNICAL AND ELEMENTAL ANALYSES

Figure 1 shows the results of the technical and elemental analyses of the samples of tested wastes. The total moisture content varies from 1.8 to 29.2 wt. %, and the average value for all samples is 12.6 wt. %. The net calorific value is in the range 17.231–28.307 MJ/kg and the average value is 20.036 MJ/kg. The ash content in the samples varies from 7.7 to 31.2 wt. % and the average value is 18.3 wt. %. Some relationships can be found between the moisture content, ash content and net calorific value. The samples (7, 8, 11) with high moisture content have relatively low net calorific value. Also the high content of ash has a negative impact on the net calorific value (it can be seen in samples 3, 13, 14). In sample 1, low ash (7.7 wt. %) and moisture (1.8 wt. %) content result in high net calorific value (28.307 MJ/kg).

Figure 2 shows the dependences of the gross calorific value, biomass and non-biomass concentration in the tested material on the ash content. The concentration of biomass (biodegradable fraction) is more or less at the same level – around 38–45 wt. %, except the material where the amount of ash reaches 70 wt. %. In this case, the concentration of biomass is at around 25 wt. %. Comparing these results with high heating values of the tested materials, we can see how significant the concentration of non-biomass fraction (plastic such as thermoplastic) changes depending on the ash content in the studied materials. This fraction also brings a significant amount of energy, that reaches up to 42 000 J/kg [23] multiplied by the mass of this fraction present in the tested material. Due to the presence of the plastic fraction, the tested materials are characterized by such high gross calorific values.

The elemental analyses include sulfur, chlorine and mercury content (Fig. 1). The sulfur content varies from 0.04 to 0.58 wt. % and the average value for all samples is 0.27 wt. %. The chlorine content is in the range 0.58-2.11 wt. % and the average value is 1.17 wt. %. The mercury content in the samples ranges from 0.09 to 0.20 mg/kg and

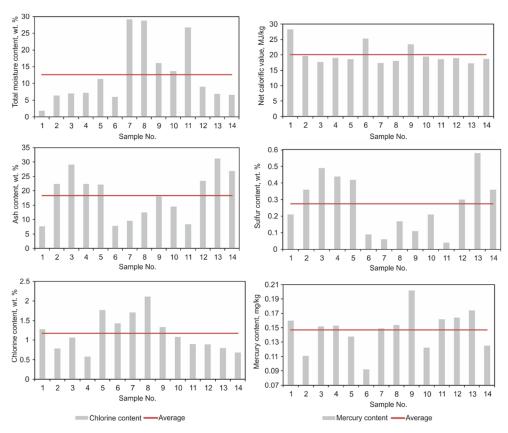


Fig. 1. Results of the technical and elemental analyses of the wastes

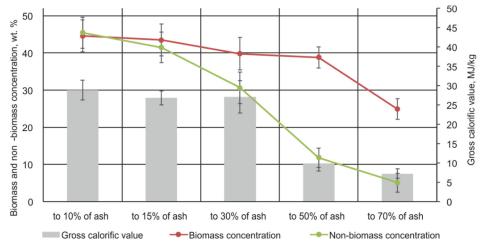


Fig. 2. Dependences of the gross calorific value, biomass and non-biomass concentrations on the ash content

the average value is 0.15 mg/kg. Chlorine compounds may generate technical problems in combustion equipment, such as corrosion [11] or the formation of deposits in the kiln and oxidation on the inner layer of the kiln [3, 5].

Specifically, the HCl produced during combustion is mainly responsible for the corrosion of the heat exchangers of the boilers [5]. The high amount of chlorine in waste is correlated with the amount of plastics, especially PCV [5]. Sulfur is another important element, the amount of which should be known since the presence of sulfur causes the generation of acid gases SO_2 and SO_3 which contribute to air pollution and corrosion [12]. The Hg content is one of the most significant global environmental pollutants because of its medium and long term impacts on health [14]. Mercury compounds have toxicity to organisms in aquatic and terrestrial environment [24].

3.2. FOULING AND SLAGGING RISK

Table 4 shows the characteristic ash fusion temperatures: sintering, softening, melting point and flow temperature for all the waste samples.

Table 4

Atmosphere	Parameter	Minimum	Maximum	Average	Median
Oxidizing	sintering point	990	1160	1102.69	1120
	softening point	620	1340	1040.24	1120
	melting point	1140	1520	1219.51	1190
	flow temperature	1170	1530	1271.46	1210
Semi-reducing	sintering point	900	1080	1017.04	1030
	softening point	640	1310	1017.56	1070
	melting point	1090	1520	1226.59	1170
	flow temperature	1130	1530	1269.51	1210

Characteristic ash fusion temperatures [°C]

The results of characteristic ash fusion temperatures of the ash generated during waste sample incineration show, that all temperatures in majority of the samples are lower than for, e.g., coal [25]. It indicates, that there is a significant risk of the reactor fouling and slagging during the waste incineration process. The surface slagging is caused by presence of ash, which is characterized by significant adhesion properties in relation to the reactor's material and its low softening point. Table 5 shows the chemical composition of ash analysis for 10 randomly selected fractions.

Based on chemical composition of the ash (Table 5) and formulas (1)–(6) presented in point 2.6, calculations of fouling risk factors for 10 selected fractions were carried out. Table 6 presents fouling abilities according to limit values, shown in Table 3.

Table 5

Oxide	1	2	3	4	5	6	7	8	9	10
SiO ₂	35.91	53.94	44.69	50.49	37.66	42.94	56.17	51.53	48.15	56.02
Al ₂ O ₃	16.27	7.76	14.94	10.30	17.29	14.96	8.35	12.18	7.73	7.83
Fe ₂ O ₃	8.79	6.62	6.07	6.37	7.72	9.13	4.98	6.92	10.30	5.86
CaO	23.48	18.51	21.27	19.31	21.93	20.9	18.87	18.59	16.79	17.47
MgO	2.87	1.85	2.96	2.02	2.95	2.86	1.99	1.92	1.69	1.90
P ₂ O ₅	2.10	0.52	0.75	0.77	0.80	0.70	0.64	0.62	0.55	0.55
SO ₃	4.21	3.74	3.11	3.81	3.19	3.02	3.63	4.29	3.55	4.49
Mn ₃ O ₄	0.12	0.12	0.14	0.13	0.17	0.14	0.10	0.12	0.22	0.15
TiO ₂	1.62	1.21	1.53	1.39	1.63	1.47	1.03	1.20	1.03	1.07
BaO	0.48	0.22	0.14	0.34	0.14	0.14	0.21	0.24	0.17	0.20
SrO	0.06	0.05	0.06	0.05	0.05	0.05	0.05	0.06	0.05	0.06
Na ₂ O	2.12	3.14	2.75	2.87	2.49	3.67	3.44	2.89	2.38	2.98
K ₂ O	0.98	1.2	1.11	1.26	0.90	1.08	1.26	1.16	1.09	1.21

Chemical composition of ash for 10 selected fractions [wt. %]

Table 6

Limit values of fouling indexes

Index	1	2	3	4	5	6	7	8	9	10	Fouling ability
B/A	0.69	0.48	0.54	0.49	0.62	0.62	0.45	0.47	0.55	0.43	very high
<i>R</i> _s , wt. %	0.26	0.28	0.21	0.25	0.24	0.31	0.23	0.28	0.29	0.26	low
Fe/Ca	0.37	0.36	0.29	0.33	0.35	0.44	0.26	0.37	0.61	0.34	low
Total Fe + Ca, wt. %	32.27	25.13	27.34	25.68	29.65	30.03	23.85	25.51	27.09	23.33	very high
F_u	2.15	2.08	2.09	2.03	2.10	2.93	2.10	1.89	1.90	1.82	medium
S _R	0.51	0.67	0.60	0.65	0.54	0.57	0.68	0.65	0.63	0.69	very high

It can be observed, that the tested combustible fraction of waste is a demanding fuel, because of its unfavorable fouling and slagging properties which are directly related to the content of oxides with the basic properties. It means that the waste should be enriched or should be co-incinerated with basic (conventional) fuel. Calcium and iron oxides can be added to the waste, in order to improve the slagging properties of the ash. It is also possible to incinerate such materials in specially designed reactors, which specific construction minimize the fouling and slagging phenomena.

4. SUMMARY

The analyses show significant diversity in waste properties. This variety should be taken into account, in order to properly incinerate the waste. It is crucial, to produce a suitable fuel mixture (SRF), which will meet the technical requirements of the installation and have satisfactory energy properties. The presented data show that moisture and ash content have a significant impact on calorific values. In order to ensure the proper energy parameters, the fuel mixture should be dried and the mineral part (e.g., sand, glass, metals) should be removed. Also, the presence of polymers increases the calorific values. In order to keep the environmental requirements and to avoid the devices damage, sulfur, chlorine and mercury contents should be as low as possible. For example, greater recovery of PVC could reduce the Cl content in the wastes [5]. Appropriate separation of hazardous waste and wet scrubbing [10] could reduce the heavy metal content, such as Hg [5].

The waste can also have unfavorable fouling and slagging properties and in order to reduce the risk, they should be enriched (e.g., with calcium or iron oxides) of coincinerated with conventional fuel.

The combustible fraction of waste is a material, which can be applied in the power industry, after proper preparation. Nowadays, the only recipient of the combustible fraction of waste in Poland are cement plants. However, their capacity is not sufficient in relation to national production of combustible fraction of waste abilities. In 2017, the amount of generated RDF was 2.4 million Mg, while almost 1.3 million Mg was incinerated in the cement plants [9]. That is why waste incineration in power industry can be a supplement of Polish waste management. Unfortunately, the branch encounter difficulties connected with formality, technology and economy. The waste incineration plant must meet strict emission and process requirements, which is practically impossible in the existing in power plants WR boilers [26]. The modernization of existing power plants is expensive and technically complicated, that is why a building of new, dedicated installation seems to be the best option.

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