

Article

Evaluation of Waste Blends with Sewage Sludge as a Potential Material Input for Pyrolysis

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Abstract: In line with the requirements of the circular economy, the European Union's waste management legislative changes also concern the treatment of sewage sludge. Although sewage sludge production cannot be prevented, its quantities may be reduced by the synergetic effect of energy recovery via choosing a proper technology. Sewage sludge is difficult to apply as fuel alone, because of its high moisture and ash content. However, its energy use will be increased by adding suitable waste materials (different types of plastics, waste tires and paper rejects). Most recently, the thermal utilization of sewage sludge via incineration or pyrolysis has grown in importance. This article describes the fuel parameters of particular waste materials and of their blends with sewage sludge in connection with laboratory-scale thermal decomposition in an inert atmosphere, for their potential use in a semi-pilot plant pyrolysis unit. For pyrolytic application, the results of thermogravimetric analysis are needed in order to know the maximal temperature of thermal decomposition in an inert atmosphere, maximal mass losses, and weight loss rates. The samples of different thermoplastics mixed with sewage sludge, and low-density polyethylene blends with sewage sludge, had the lowest residual masses (70–74%) and the highest weight loss rates (11–19%/min). On the other hand, the blend of polyester rejects from tire processing, paper rejects and sewage sludge had the second highest residual mass (60%) and the lowest weight loss rate (3%/min).

Keywords: sewage sludge; plastics; waste blends; thermogravimetric analysis; pyrolysis



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1. Introduction

The large quantities of waste and waste packaging produced by consumer society are a risk factor for both human health and ecosystems. During waste production and its disposal, secondary substances may escape into the environment, the constituents of which may be contaminated. The substances contained in waste and packaging can enter the human body through the food chain, and thus negatively affect human health [1,2].

In the Czech Republic (an EU country with 10 million inhabitants), the annual production of corporate waste has been around 22 million tons. In terms of the origin of this waste, a constant trend can be observed in the increasing production of waste particularly by companies engaged in the treatment, collection, and processing of industrial or municipal waste. This includes waste from municipal waste treatment facilities and wastewater treatment plants (so-called secondary waste). However, these materials are not perceived as waste only, but represent secondary raw materials due to their energy potential. At present, the key waste management trend is to move towards a circular economy [3], product reuse, recycling, and the conversion of waste to energy [4], instead of mining

and the additional landfills that lead to the issue of land scarcity [4,5]. Beside the EU waste policies that restrict landfilling (99/31/EC on the landfill of waste) while promoting waste prevention, minimization, and recycling, legislation also focuses on the treatment of sewage sludge—91/271/EEC on urban waste water treatment, and 86/278/EEC on the use of sewage sludge in agriculture [6–8].

Sewage sludge (SS) is an unavoidable waste arising in connection with wastewater treatment. In the EU, the production of SS dry matter per capita is estimated to be 90 g per day [9], meaning that the current annual production of sewage sludge dry matter exceeds 12 million tons. It can be expected that with a growth in the population, and pressures on the construction of new wastewater treatment plants (WWTPs), the production of SS will soar. The development of SS production in tons of dry matter in the Czech Republic, and a comparison of the development in SS disposal in a percentage ratio, in the years 2009–2018 are shown in Figure 1 below.

While a similar trend has been observed in several other EU countries due to stricter registrations or new regulations, Figure 1 implies that the total production of SS in the Czech Republic is growing. As a counter-measure, most SS has been applied directly, particularly in land reclamation projects. On the other hand, the quantities of composted SS are likely to continue to fall due to the stricter requirement for compost sanitization. Most recently, the “thermal utilization” of SS from WWTPs via incineration or pyrolysis has grown in importance, and this area is expanding due to the currently tightening legislation. Pyrolysis is considered advantageous for the decomposition of organic pollutants, the neutralization of pathogens, the reduction of waste, the application for a wide range of products, and significant energy recovery [10].

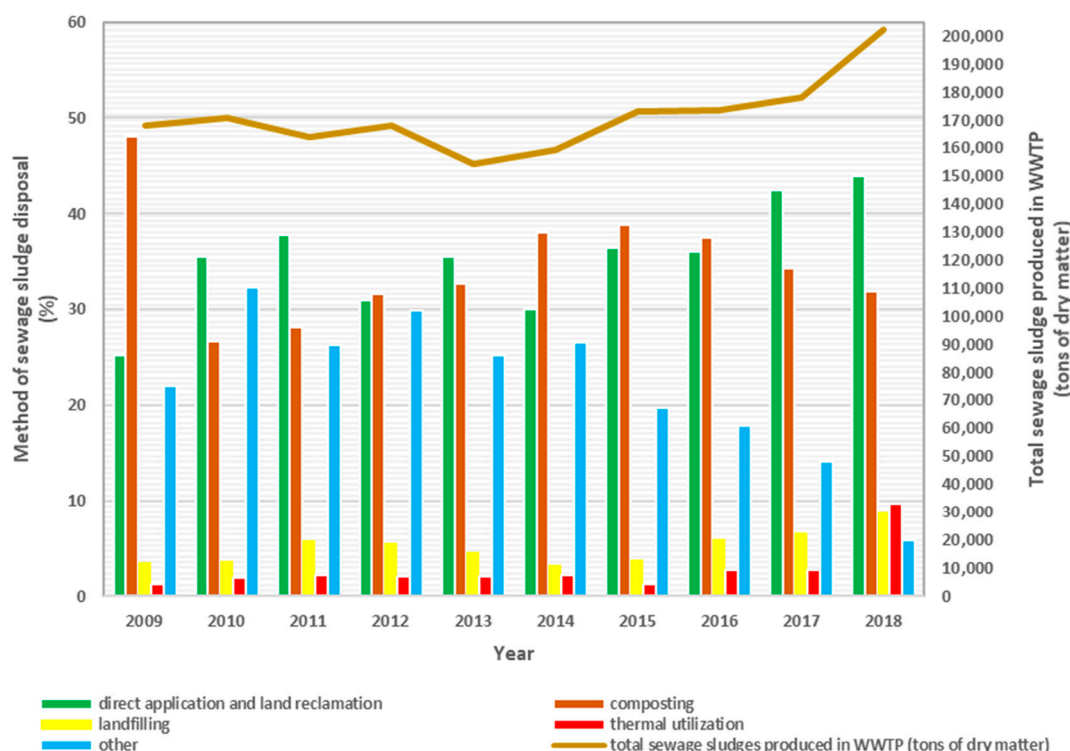


Figure 1. Proportional comparison of sewage sludge disposal in the Czech Republic in the years 2009–2018, modified according to [11].

Referring back to the circular economy principle, and trends for reducing waste, it must be emphasized that the formation of SS cannot be prevented. Besides excess biomass from biological treatment, SS contains heavy metals and drug residues. Research is heading towards solutions regarding the choice of SS disposal technologies to reduce its quantity, while maximizing its energy potential [12]. However, this shows that SS is difficult to use

on its own as fuel, due to its high moisture content [13–15]. After dewatering (depending on the equipment used—filter presses, centrifuges, etc.), the SS dry matter can range from 15 to 32 wt. %. The calorific value of such SS is very low. The calorific value of dried SS is comparable to brown coal or wood biomass in terms of energy content [16–18]. The low heating value of SS dry matter is 17–18 MJ/kg for raw SS, 14–16 MJ/kg for activated SS, and 8–12 MJ/kg for stabilized SS [19].

Therefore, we assume that with mixing SS with other waste materials (various types of plastics, waste tires, and paper rejects), the energy use of SS will increase. When preparing alternative fuels via the synergetic disposal of waste, it is advisable to concentrate on the disposal of waste occurring in large quantities, as well as to select waste materials originating close to the source, so as to eliminate transportation, storage, and handling costs. Further, indicative calorific values of the original waste products are summarized.

Plastic waste can be converted into valuable fuels [20,21]. Plastics meet the requirement of widely used packaging materials. These materials are also suitable for handling and transport, and their material properties allow for easy molding. Plastics are polymeric substances that can be divided into two main types. First, those that soften when heated are called thermoplastics, which account for 80% of plastics currently in production, e.g., high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP). The second type of plastics that harden when heated are called thermosets [22]. In terms of energy potential, the high heating value of plastics is 46.5 and 44 MJ/kg for PE and PP respectively, and 22.8 MJ/kg for polyester (PES) fibers [23,24].

The remaining waste materials used for the experiments were used tires and paper rejects. Used tires account for a significant share of all rubber waste. The high heating value of tires is similar to that of black coal (30 MJ/kg) [25]. The paper and pulp industries create large amounts of solid waste and wastewater that have to be treated. The methods for converting paper mill waste into energy are discussed [26]. As for the energy potential of paper, its low heating value is 14.11 MJ/kg [27].

It is necessary to find technical solutions that will enable the efficient management of the described waste in order to reduce environmental pollution and meet the requirements of the circular economy [28]. One of the technologies available to deal with these types of waste is pyrolysis. A number of articles have focused on the co-pyrolysis of sewage sludge with other types of feedstocks, such as agricultural waste [29,30], wood waste [31] or lignite [32]. The aim of this article is to describe the energy parameters and simulate the thermal decomposition at the laboratory scale of individual waste materials and novel blends (i.e., different types of waste plastics, paper rejects and polyester waste from tire processing) with SS in an inert atmosphere. This research is important for learning about the discrete processes taking place during pyrolysis, and how the composition of different waste blends changes. Appropriately selected waste blends will be further tested in a semi-pilot plant pyrolysis unit for their energy recovery.

2. Materials and Methods

2.1. Description and Physical Appearance of Input Waste

The photographs of all samples, i.e., raw sewage sludge and input waste, are shown in Figure 2. The description and physical appearance of the input waste are as follows:

- 1, 2—SS—sewage sludge from the municipal wastewater treatment plant, which is anaerobically stabilized, blackish-brown in color, lumpy, with an earthy odor, and very wet. The projected WWTP capacity is 207,000 PT (population total), and HRT (hydraulic retention time) is in the range of 26–32 days depending on temperature;
- 3—LDPE—recycled LDPE from separated collection and sorting lines. This material was wet during processing. It is a flexible (even soft) material, but it is also tough and hard to grind;
- 4—TP—a mixture of crushed sorted hard thermoplastics. Colored materials (mixture of PP and PE) have a low weight, are tenacious and strong, and are easy to grind;

- 5—RDF—polyethylene foils, bags and sorted municipal solid waste (MSW) without PET and hardened plastics. This material was rather wet, contained impurities (clay etc.) and was hard to grind due to its consistency;
- 6—PES—polyester waste (PES) from tire processing contains crushed pieces of tire (styrene–butadiene rubber) and PES textile fiber in the form of small fluffy clumps up to 20 mm in size. It is a loose, non-sticky material that is easy to handle and has a grey color;
- 7—PR—paper rejects with a composition of paper and plastic in the ratio of 50:50. It consists of small plastic particles and paper pulp (cellulose). These fibers are simply bonded under pressure to form solid shapes, and have medium humidity and a light brown color.

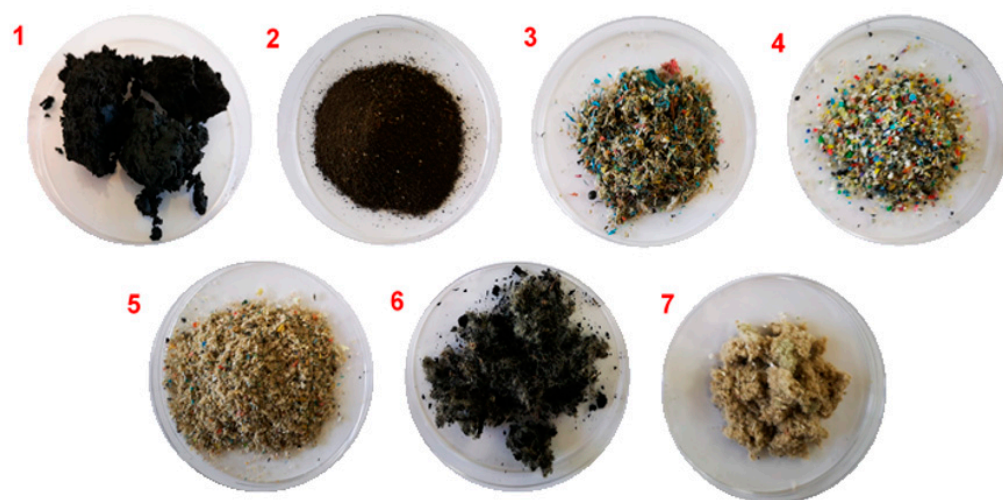


Figure 2. Consistency of 1—raw SS (moisture 72 wt. %) and visualization of waste inputs: 2—dry SS (sewage sludge), 3—LDPE (low-density polyethylene), 4—TP (thermoplastics (non-specified)), 5—RDF (residual derived fuel), 6—PES (polyester), 7—PR (paper rejects).

2.2. Waste Blends Preparation

Six waste materials were selected for experimental tests. The high and low heating values were measured for each waste blend (55 in total). These values were key parameters for the selection of suitable waste blends for the further study of thermochemical conversion processes. Information on the average dry matter or moisture and bulk density of selected waste materials is summarized in Table S1. Specifically, these were sewage sludge from a public wastewater treatment plant (SS), low-density polyethylene rejects (LDPE), non-specified thermoplastics (TP), solid residual fuel (RDF), polyester rejects from tire processing (PES), and paper rejects (PR). All the above parameters were measured according to the standards [33–35]. Except for SS, all materials were ground to a fraction <2 mm on a laboratory mill IKA MF 10 basic (IKA®-Werke GmbH & Co. KG, Staufen, Germany). From each of the individual materials, two and three mixtures were formed together with SS. In total, 55 waste blends in various volume ratios were prepared.

Because SS has an average moisture content of about 72 wt. %, this moisture level was an advantage for mixing with other types of waste. SS served as a binder for individual components. The first “binder tests” were aimed at forming granular mixtures being prepared in volume and weight ratios, respectively. After weighing the individual components of the mixtures, the waste blends were then mixed on a laboratory mixer HOBART—HSM 10 (HOBART GmbH, Offenburg, Germany). The blends were then spread on the surface and freely dried in the laboratory at room temperature for 1 week.

The dry matter or moisture of the blends were always measured after their preparation and after a week of drying. Then, gross and net calorific values and other parameters were determined. From 55 experimental blends, 8 blends were selected on the basis of the highest measured values of gross and net calorific values. In addition, 4 were double

blends and 4 were triple blends. The individual ratios, the combinations of waste materials, the moisture and dry matter, and the gross and net calorific values of selected mixtures are shown in Table S2.

The description and physical appearance of waste blends are shown in Figure 3.

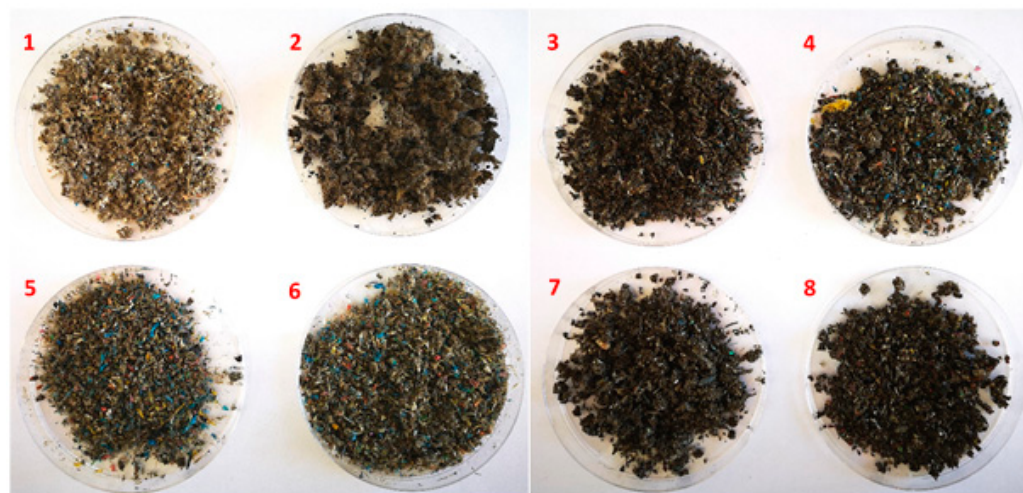


Figure 3. Visualization of 8 selected experimental waste blends (1—3RDF:SS:PR, 2—3PES:SS:PR, 3—4LDPE:SS, 4—4LDPE:2SS:PR, 5—6LDPE:SS, 6—3LDPE:SS:PR, 7—RDF:SS, 8—3TP:SS).

1. The 3RDF:SS:PR blend was light brown in color with a slight odor. The material was light.
2. The 3PES:SS:PR blend was grey with a slight odor. The material was not compact. It consisted of separate pieces of rubber and fluffy PES fibers mixed with sludge.
3. The 4LDPE:SS blend had a good structure. It was slightly damp. LDPE formed a compact mass with sewage sludge.
4. The 4LDPE:2SS:PR blend was well workable and was light black in color. It was slightly damp. Small pieces of LDPE can be seen in the mixture. LDPE formed a compact mass with sewage sludge.
5. The 6LDPE:SS blend was rather dry and did not form a compact mass. Due to the large proportion of LDPE, small colored pieces were visible in the mixture. The mixture was blackish brown in color with a musty smell.
6. The 3LDPE:SS:PR blend was rather dry and did not form a compact mass. The mixture was dark brown in color with a slight odor.
7. The RDF:SS blend was very moist with a strong odor. The mixture was hard to mix together. The individual grains stuck together and formed a lumpy structure.
8. The 3TP:SS blend was very moist with a slight specific odor. The discrete grains stuck together and formed a lumpy structure.

2.3. Analyses of Physical Properties

2.3.1. Proximate Analysis

The moisture, ash, fixed carbon and volatile matter were analyzed.

Total moisture: Raw samples (approximately 50 g) were dried at 105 °C in a laboratory dryer and weighed, and the moisture content was calculated [36].

Moisture of analytical samples: Analytical samples (2×1 g) were dried in glass weighing bottles in a laboratory dryer at 105 °C, then weighed, and moisture content was calculated [37].

Determination of ash content: Analytical samples (2×1 g) were annealed in ceramic dishes in a laboratory oven at 550 °C and weighed, and ash content was calculated. The content of combustible matter in the sample was calculated [38].

Determination of volatile combustible matter content: Analytical samples (2×1 g) were annealed in a crucible with a lid in a laboratory oven at $900\text{ }^{\circ}\text{C}$, then weighed, and volatile combustible matter content was calculated [39].

2.3.2. Ultimate Analysis

The carbon, hydrogen, nitrogen and sulfur in the samples were determined using an analyzer LECO CHN628 (LECO Corporation, St. Joseph, MI, USA) with the additional module 628 S (LECO Corporation, St. Joseph, MI, USA). The principle of C, H, and N determination is based on the combustion of the sample in an oxygen atmosphere at $950\text{ }^{\circ}\text{C}$, and then measuring the concentration of CO_2 and H_2O in the burned gases using the IR detector, and of N_2 using the thermal conductivity (TC) detector [40]. The sulfur is determined by burning the sample in an oxygen atmosphere at $1350\text{ }^{\circ}\text{C}$ and measuring the SO_2 concentration in the burned gases using an IR detector [41]. The oxygen content in fuel was calculated, $\text{O}^{\text{d}} = 100 - \text{ash}^{\text{d}} - \text{C}^{\text{d}} - \text{H}^{\text{d}} - \text{N}^{\text{d}} - \text{S}^{\text{d}}$ (in percentage, ^d means in dry matter) [42].

2.3.3. High and Low Heating Values (HHV, LHV)

The gross calorific value (high heating value; HHV) of the fuels was determined by setting the calorimetry with the calorimeter LECO AC600 (LECO Corporation, St. Joseph, MI, USA) [43]. The principle of the method is based on the combustion of the sample in the form of a bomb of calorimeter, and measuring the increase in the temperature of the water bath with a calorimeter. The net calorific value (low heating value LHV) of the fuels was calculated.

2.4. Thermogravimetric Analysis

Thermogravimetric (TG) analysis was performed with the analyzer STA 449 F1 Jupiter (Netzsch-Gerätebau GmbH, Selb, Germany). The TG conditions were $30\text{--}1000\text{ }^{\circ}\text{C}$, $10\text{ }^{\circ}\text{C}/\text{min}$, $100\text{ mL}/\text{min}$ N_2 ($50\text{ mL}/\text{min}$ purge + $50\text{ mL}/\text{min}$ protective), and isotherm at $1000\text{ }^{\circ}\text{C}$ for 15 min ($20\text{ mL}/\text{min}$ O_2 + $50\text{ mL}/\text{min}$ N_2 protective). An Al_2O_3 crucible was used for a sample mass of 20–21 mg. TG analysis was used to determine the maximum temperature before constant weight loss, and to determine the maximum weight loss as information for the further pyrolysis treatment of waste blends.

2.5. Statistical Analysis

Statistical analysis was carried out using the *MATLAB*® software. Kruskal–Wallis tests, Dunn's test, Shapiro–Wilk test and Levene's test were performed.

3. Results and Discussion

3.1. Analysis of Input Waste

The analytical results of input waste are summarized in Table S1. Bulk density was an important parameter in waste blend preparation. The plastics, paper rejects and tire waste ash yields were much lower than that of the sewage sludge (49 wt. %). Typical raw sewage sludge has a high moisture content, in our case 72 wt. %, but the samples were analyzed after drying. The SS had a low carbon content (approximately 28 wt. % in dry matter), and a high oxygen content. There were relatively high values for nitrogen and sulfur in SS. The nitrogen in SS has its origin in the microorganisms used for water purification. The sewage sludge is characterized by a much lower HHV than other waste inputs, because of the higher inorganic content and because of the high oxygen content. The composition of SS differs within the literature; however, the authors of Refs. [44,45], for instance, showed comparable values for the chemical composition of sewage sludge.

A higher ash content and lower HHV means less efficient fuel [46]. In Figure 4, the highest ash content and the lowest HHV were determined for SS; on the other hand, RDF has the lowest ash content and the second highest HHV. Mixing the plastics with SS may improve the characteristics of oil and char derived from pyrolytic treatment [10].

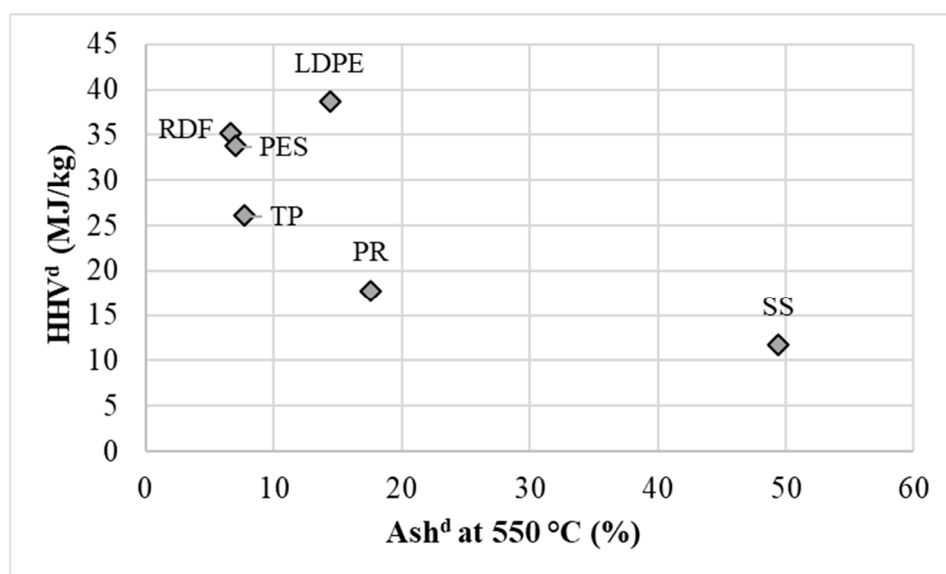


Figure 4. The HHV^d (MJ/kg) and ash^d at 550 °C (%), ^d means in dry matter.

Certain studied plastics, such as RDF, TP and LDPE, have higher volatile matter and weight loss than PR, PES and SS, so there is more chance of the decomposition of volatile matter, and in turn high oil and gas yields (Figure 5) [10].

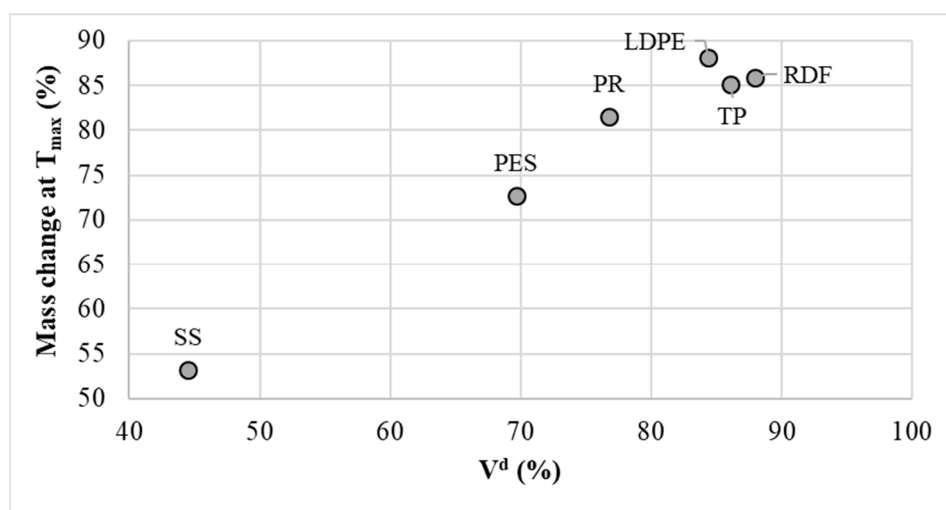


Figure 5. Mass change at T_{max} (%) from TGA and volatile matter V^d (%).

It is apparent from Figure 6 that the combustible matter of SS is the lowest in quantity, while the highest amount of combustible matter with the highest C/H ratio is in TP and PES. The C/H ratio in biomass affects the yields of char, tar, and gas [47]. A higher C/H content means a higher production of char and a lower production of tar, and the opposite holds for lower C/H content. A comparison with pyrolytic products is the aim of future investigations.

3.2. Composition of Waste Blends and Results of Physical Properties of Waste Blends

The compositions of the selected and further-tested waste blends are summarized in Table S2. The results of the proximate and ultimate analyses, and high and low heating values, are shown herein. The International Solid Waste Association set a guideline that specifies that the average LHV of waste should be at least 7 MJ/kg, so that it can be used as an energy source in the pyrolysis process [48]. For all waste blends, the LHV was above this level, and was higher than the LHV of SS (Figure 7).

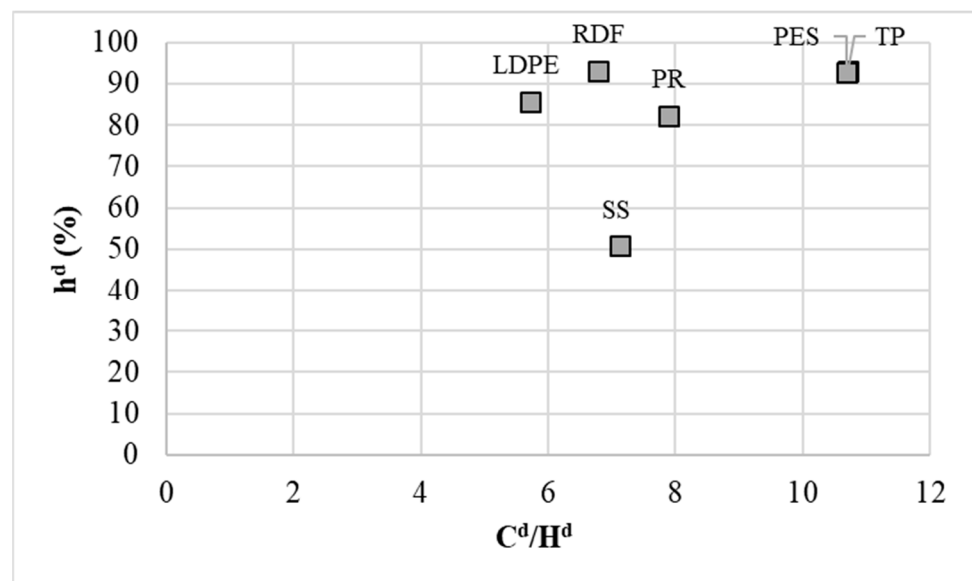


Figure 6. Combustible matter h^d (%) and the ratio C^d/H^d , d means in dry matter.

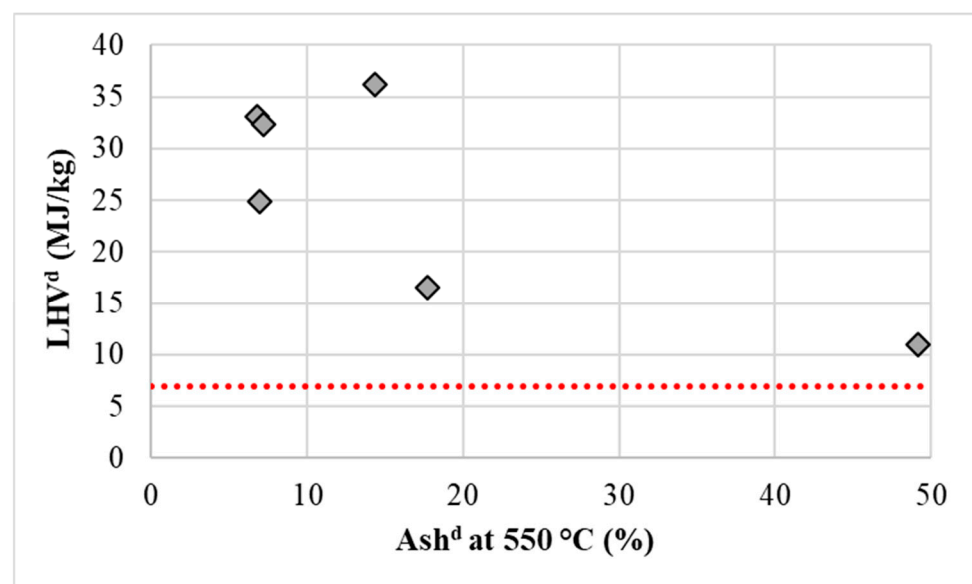


Figure 7. The LHV^d (MJ/kg) and ash^d at 550 °C (%).

3.3. Thermogravimetric Analysis of Wastes and Their Blends

TG analysis was performed for the determination of the minimal temperature for the maximal yield of pyrolysis products, and the maximal mass losses of wastes and their blends.

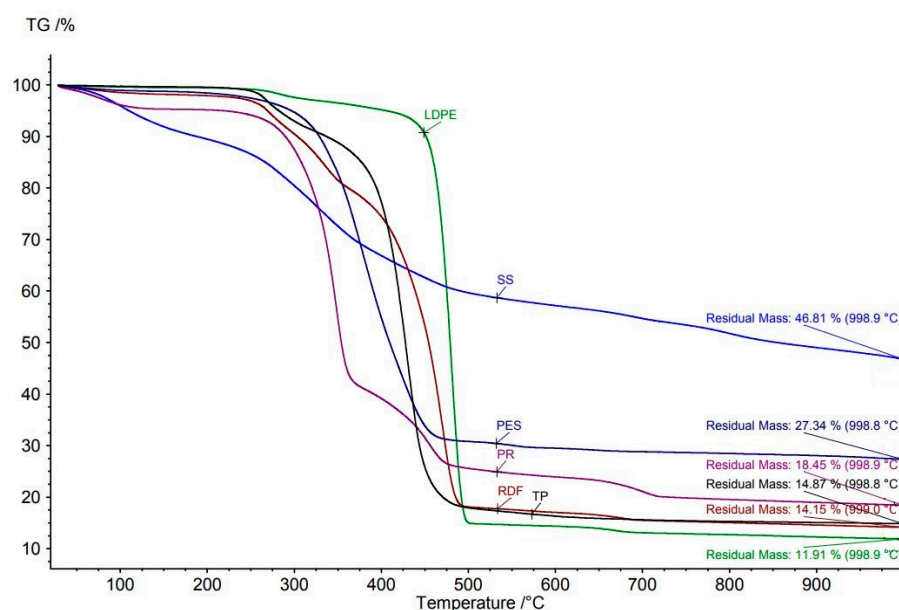
3.3.1. Input Materials

For all samples, a typical weight loss up to approx. 100 °C is associated with the removal of water from the sample during its pyrolysis decomposition. The highest decrease is seen for the sample of sewage sludge and paper rejects, which is related to the high moisture content (Table S1). The results for the TGA/DTG of the input waste materials are shown in Table 1, and the TG curves of the input waste materials are shown in Figure 8. The temperatures of maximum weight loss in the TGA experiments for the input waste materials are shown in Figure S1.

Table 1. Results of TGA/DTG for the input waste materials.

Inlet Material	Tmax	Mass Change at Tmax	T1	Weight Loss Rate at T1
	°C	%	°C	%/min
LDPE	998.9	88.09	479.9	26.98
RDF	999.0	85.85	469.1	11.73
TP	998.8	85.13	429.3	13.77
PR	998.9	81.55	348.1	11.85
PES	998.8	72.66	378.6	6.16
SS	998.9	53.19	325.2	1.62

Note: T1 is the temperature of highest mass loss determined from the DTG curves.

**Figure 8.** TG curves of input waste materials.

Sewage Sludge

For the sample of SS, (1) the first interval of decomposition was between 100 and 200 °C, which is related to the decomposition of sewage sludge components (biodegradable organic material and bacterial matter); (2) the second interval was between 200 and 520 °C, which related to the decomposition of organic matter (hydrocarbons between 200 and 390 °C, proteins, sugars, aliphatic compounds of SS between 390 and 520 °C); (3) at temperatures above 520 °C, the volatile matter evaporates from the carbon residue (secondary pyrolysis), and weight loss associated with organic matter may continue up to 600 °C; (4) at temperatures above 600 °C, inorganic material (e.g., CaCO₃, ash in SS) decomposes [10,49]. As described in a recent review [10], there is a difference in the pyrolysis product (tar and char) yields under fast and slow pyrolysis. Slow pyrolysis generally leads to higher char yield and lower tar yield than fast pyrolysis.

Plastics

For all samples containing plastics, a weight loss of up to 500 °C is typical, which is associated with the pyrolysis decomposition of a particular plastic. The thermal degradation of plastics takes place via a chain mechanism—fission reactions involving serial and parallel reactions (individual reactions overlap) [50]. The thermal decomposition of plastics takes place in several steps: chain radical mechanism → initiation → H-abstraction → beta-scission → radical recombination [51].

Thermal decomposition is related to the chemical structure and complexity of the substance. PP decomposes at lower temperatures than HDPE due to tertiary carbons in the polymer structure, as described by [52]. In our experiments, the plastics decomposed in the

order PES > TP > LDPE, from lower to higher temperatures. LDPE and TP decomposed in a narrow temperature range. For pure plastics, there should be no carbon residue [53], which is not the case for our plastic materials.

The PES sample is characterized by the TG decomposition curve of tires [54], which decomposes at two temperatures (361 and 410 °C). The first step is attributed to the presence of natural rubber, while the second step to a blend of butadiene rubber with styrene-butadiene rubber [55].

Paper Rejects

For all samples containing paper waste, a typical weight loss appeared at a temperature of approx. 250–350 °C, which is not typical for pure plastics. This proportion is greater than the proportion of the thermal decomposition of plastics (approx. 350–470 °C) [56].

The residual mass was recorded in the order, from highest to lowest: SS > PES > PR > TP > RDF > LDPE. The weight loss rate (%/min) was recorded in the following order, from highest to lowest: LDPE > TP > PR > RDF > PES > SS. The mixing of sewage sludge with other waste is desirable, as the mass loss should increase, as well as the weight loss rate of the prepared waste blends.

The temperature and weight reproducibility of LDPE are shown in Figure S2.

3.3.2. Waste Blends

The results of the thermogravimetric analysis of waste blends are not comparable with those in the literature because they are unique and have not been reported. According to the authors' knowledge, the study of Zaker et al. [57] published the results of the co-pyrolysis of sewage sludge with LDPE. Therein, the samples containing 25%, 50% and 75% mass percentage of LDPE were tested. As is apparent, greater amounts of LDPE in the blend mean that the TG curve is similar to the pyrolysis behavior of LDPE, which was seen in our case. In the study of Hu et al. [58], the isothermal pyrolysis of polyethylene, paper towel and textiles, and their mixture in a ratio of 4:1:1, was carried out in a fixed bed reactor between 475 °C and 550 °C.

The TGA/DTG results of waste blends are summarized in Table 2. The temperatures of maximum weight losses in the thermal TGA experiments for waste blends are shown in Figure S3.

For all samples, a typical weight loss up to approx. 100 °C was associated with the removal of water from the samples during their pyrolysis decomposition.

Sewage Sludge

For all samples containing sewage sludge, a gradual weight loss is typical, with the greatest weight distribution up to 500 °C, and further thermal decomposition is visible at a temperature of 660–670 °C [54].

Plastics

For all samples containing plastics, a weight loss of up to 500 °C is typical and is associated with the pyrolysis decomposition of a particular plastic.

For the LDPE:SS samples (4:1 and 6:1), a TG curve of LDPE decomposition is typical [50,53] due to the higher content of LDPE in the samples; see Figure 9.

The shape of the TG curve is similar for RDF:SS and 3TP:SS samples (Figure 10). The pyrolysis decomposition of the plastic waste mixture prevails. For hardened plastics, pyrolysis decomposition occurs at lower temperatures (419 °C) than PE without hardened plastics (462 °C). The sample containing hard plastics (TP) shows a sharp drop in weight in a narrower temperature range than for the sample containing PE + RDF.

Paper Rejects

For all samples containing paper rejects, there is a typical weight loss in the temperature range of approx. 250–350 °C [56].

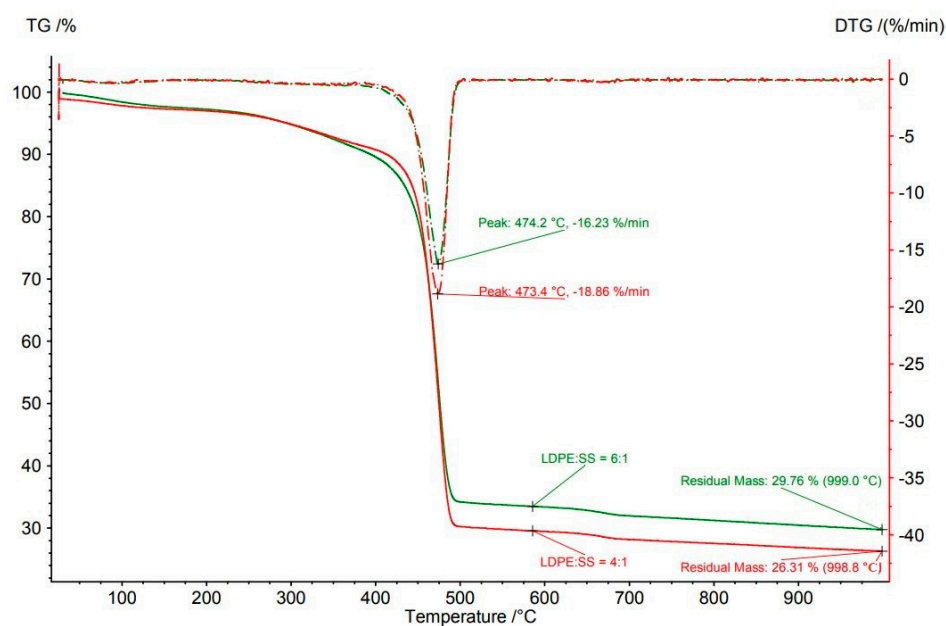


Figure 9. TG/DTG curves of LDPE:SS in 2 different volume ratios.

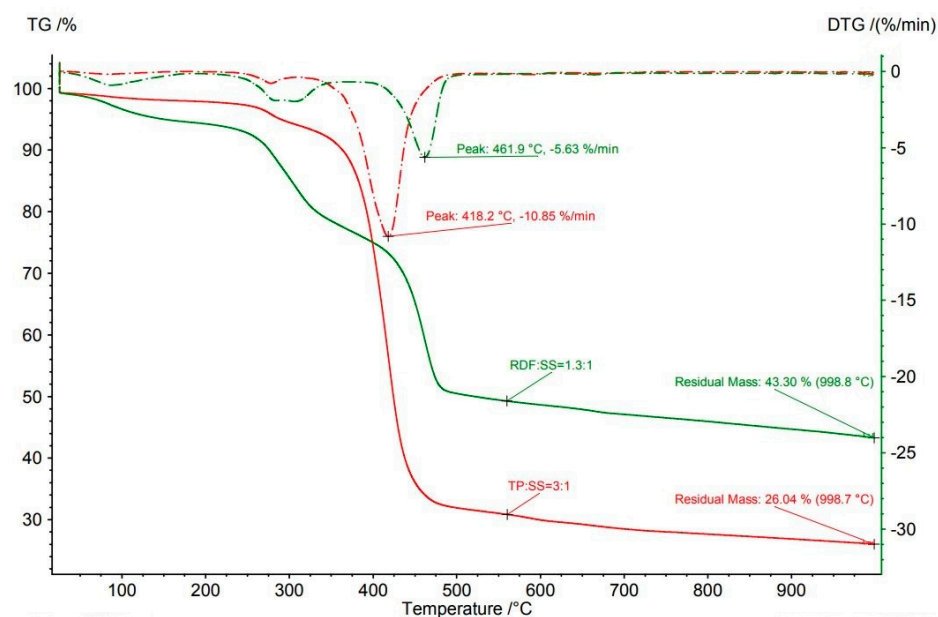


Figure 10. TG/DTG curves of RDF:SS and TP:SS in 2 different volume ratios.

The TG curves of the LDPE:SS:PR samples (3:1:1 and 4:2:1) are shown in Figure 11. The TG degradation of LDPE is dominant for these samples [50,53]. The course of the TG curves is similar, and the residual mass is very similar. Higher humidity was observed in the sample LDPE:SS:PR = 3:1:1 (greater mass loss up to 100 °C).

The TG curves for the PES:SS:PR and RDF:SS:PR samples are similar up to a temperature of approx. 300 °C (Figure 12). The sample containing PES decomposes at two temperatures for a temperature range of approx. 300–500 °C, while the RDF sample decomposes in a narrow temperature range of 400–500 °C.

The shape of the TG curve of 3RDF:SS:PR is similar to the 3LDPE:SS:PR sample (Figure 13). They also have similar weight losses at similar decomposition temperatures.

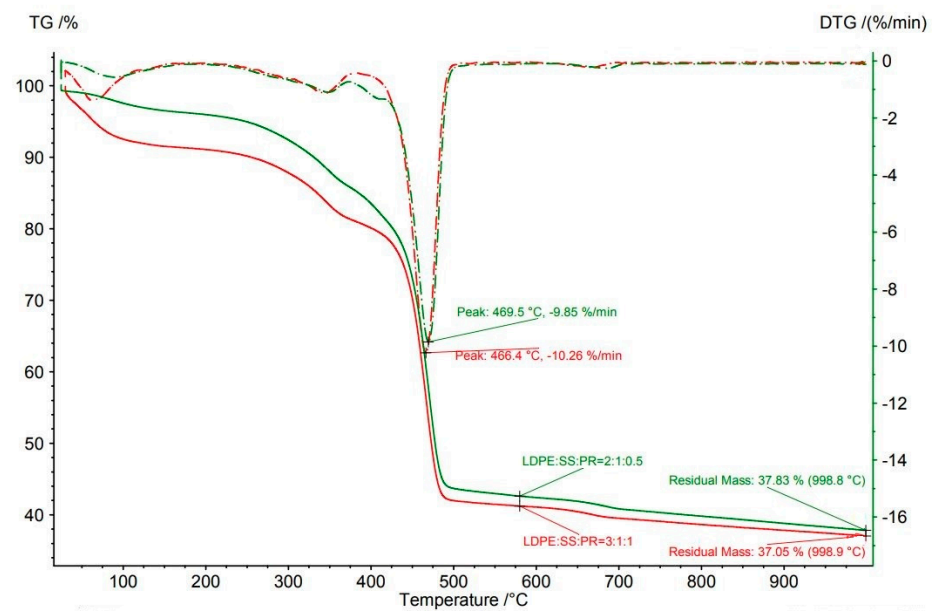


Figure 11. TG/DTG curves of LDPE:SS:PR in 2 different volume ratios.

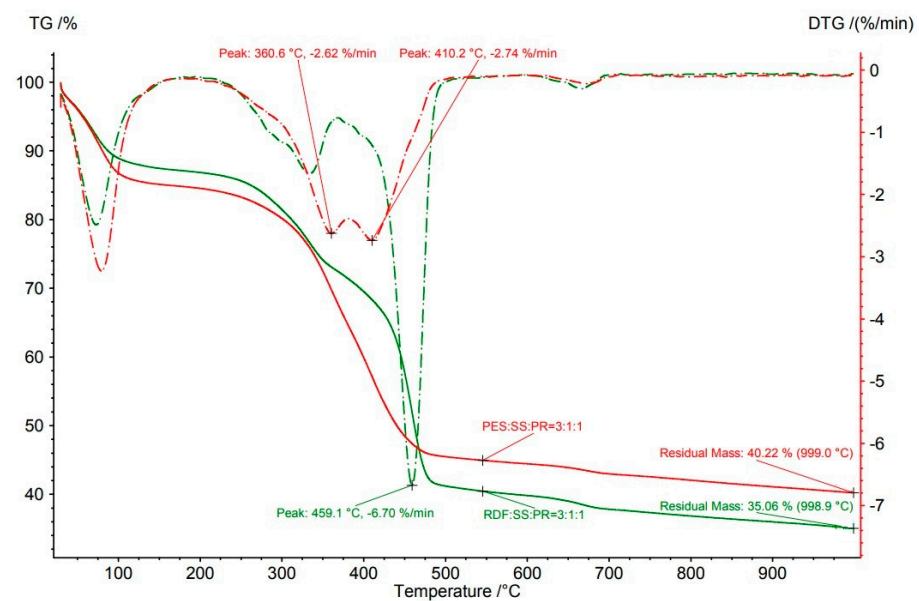


Figure 12. TG/DTG curves of PES:SS:PR and RDF:SS:PR in the same volume ratio.

Table 2. TGA/DTG results of waste blends.

Waste Blend	Volume Ratio	Tmax	Mass Change at Tmax	T1	Mass Change at T1	Weight Loss Rate at T1
		°C	%	°C	%	%/min
TP:SS	3:1	998.7	74.0	418.2	67.0	10.9
LDPE:SS	4:1	998.8	73.7	473.4	72.7	18.9
LDPE:SS	6:1	998.9	70.2	474.2	67.8	16.2
RDF:SS:PR	3:1:1	998.9	64.9	459.1	32.6	6.7
LDPE:SS:PR	3:1:1	998.9	63.0	466.4	39.4	10.3
LDPE:SS:PR	4:2:1	998.8	62.2	469.5	48.1	9.9
PES:SS:PR	3:1:1	999.0	59.8	360.6 *		2.6
PES:SS:PR	3:1:1	999.0	59.8	410.2 *	39.7	2.7
RDF:SS	1.3:1	998.8	56.7	461.9	31.7	5.6

Note: * Thermal decomposition within the range 250–500 °C occurred at two temperatures (Figure 13)

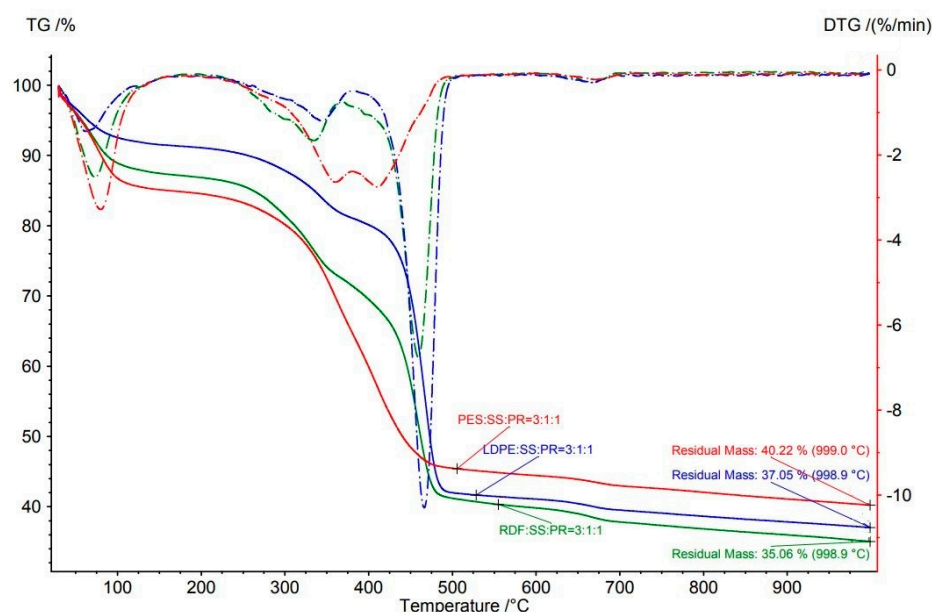


Figure 13. TG/DTG curves of RDF:SS:PR, LDPE:SS:PR and PES:SS:PR in the same volume ratios (3:1:1).

The weight loss rate (%/min) is highest in the order LDPE:SS > 3TP:SS > LDPE:SS:PR. The lowest weight loss rate is for 3PES:SS:PR. These values are important for comparison with future semi-pilot plant pyrolysis experiments.

3.3.3. Comparison of TG with Weight Loss at 900 °C (Gravimetric Analysis)

TGA showed that volatile matter was generally the most abundant component in the sludge blends. Volatile matter on a dry basis ranged from 54.1 wt. % to 73.8 wt. % for different sludge blends (Table S2). The volatile matter of input sewage sludge was 44.5 wt. %, which is a similar value for sewage sludge samples as was presented by Ref. [59].

The residual weight for the input waste materials at 900 °C from TGA was (from highest to lowest order): SS > PES > PR > TP > RDF > LDPE. The chemically simpler the substance, the lower the residual weight.

The residual weight for waste blends at 900 °C from TGA was (from highest to lowest order): RDF:SS > 3PES:SS:PR > 4LDPE:2SS:PR > 3DLPE:SS:PR > 3RDF:SS:PR > 6LDPE:SS > 4LDPE:SS > 3TP:SS.

The weight loss in the RT–900 °C range measured by TGA fits within the accuracy of the measurement (Section 3.3.1), with the weight drop measured in a muffle furnace for input waste materials (Figure S4). There is a bigger discrepancy for waste blends (especially for RDF:SS and 3LDPE:SS:PR). The reason is due to the inhomogeneity of waste blends (Figure S5).

The co-pyrolysis of SS with tested waste at laboratory scale showed a higher weight loss in the temperature range of 200–600 °C, so there is more chance of the decomposition of volatile matter into high oil and gas yields [10].

3.3.4. Statistical Evaluation

Multivariate testing was used to evaluate whether TG is statistically comparable for various ranges of temperatures. Every input material (LDPE, PES, PR, etc.) was split into ten groups for temperatures, in the following intervals: [0 °C, 100 °C], [100 °C, 200 °C] . . . [900 °C, 1000 °C]. Every measurement was tested separately to decide if there are significant differences in TG for various temperature intervals. Furthermore, the same temperature intervals were compared for different input materials. According to the Shapiro–Wilk test, they are not normally distributed, and the even variances are not equal for all groups (Levene’s test), meaning that the ANOVA test with post hoc Tukey HSD test could not

be realized. Instead, a Kruskal–Wallis with pos hoc Dunn’s test was used. Applying a Kruskal–Wallis test we determined whether the TG for different temperature intervals is the same. The p-value was always close to zero, so we rejected the hypothesis that the medians of all groups are equal. According to Dunn’s test we found that every neighboring group shows no difference in terms of median values.

Moreover, the Kruskal–Wallis test was used to compare the medians for the same temperature interval, which had the same median value between different input materials. Even in this case we always reject the null hypothesis that all medians are equal. Table S3 displays the cases wherein the medians show no statistically significant difference (according to Dunn’s post hoc test).

4. Conclusions

Comprehensive characterization provided concrete data for the optimization and modeling of the pyrolysis treatment of sewage sludge and its blends with various waste samples. Sewage sludge could be classified as a suitable feedstock for thermochemical conversion processes, with 61.2% organic contents (mass loss between 100 and 600 °C) and HHV of 11.8 MJ/kg on a dry basis. However, the HHV of sewage sludge is low, and therefore it is suitable to mix sewage sludge with selected waste for further pyrolytic applications, and thus achieve the synergetic effect of disposing of certain types of waste. Waste materials (different types of plastics, waste tires, and waste paper) were selected based on their availability to eliminate transportation, storage, and handling costs. For pyrolytic applications, the results from thermogravimetric analyses are required in order to know the maximal temperature of thermal decomposition in an inert atmosphere, maximal mass losses, and weight loss rates. The residual mass was in this order, from highest to lowest: SS > PES > PR > TP > RDF > LDPE. Furthermore, 55 waste blends were prepared in various volume ratios. The visual comparison carried out and HHV was measured for each waste blend, and these were key parameters for the selection of suitable waste blends. It is apparent from the thermogravimetric analysis that all waste blends thermally decomposed up to the temperature 500 °C, with the maximal weight loss rate. The residual mass for waste blends at 900 °C from TGA was in the following order, from highest to lowest: RDF:SS > 3PES:SS:PR > 4LDPE:2SS:PR > 3LDPE:SS:PR > 3RDF:SS:PR > 6LDPE:SS > 4LDPE:SS > 3TP:SS. Thermoplastics with sewage sludge (3TP:SS) and LDPE with sewage sludge (LDPE:SS) had the lowest residual masses and the highest weight loss rates. On the other hand, the waste blend of polyester waste with sewage sludge and paper rejects (3PES:SS:PR) had the second highest residual mass and the lowest weight loss rate.

The conversion of input materials into oils and gases is strongly dependent on the pyrolysis temperature, which was also confirmed by TGA/DTG analysis. Higher pyrolysis temperatures have always led to higher gas volume yields, as observed in many previous studies [60–62]. We confirmed that the highest average mass yield was observed during the pyrolysis of plastics. In conclusion, the most suitable combinations of materials and temperature from TGA for the production of pyrolysis oils and gases are the 3TP:SS and 4LDPE:SS waste blends. Further research will focus on applied pyrolysis in a semi-pilot plant unit with analyses of outputs.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2076-3417/11/4/1610/s1>, Figure S1: Temperatures of maximum weight losses in TGA experiments for inlet waste materials, Figure S2: TGA reproducibility of LDPE waste material, Figure S3: Temperatures of maximum weight losses in thermal TGA experiments for waste blends, Figure S4: Comparison of mass change measured by TGA and by the standard method in a muffle oven, Figure S5: Comparison of mass change measured by TGA and by the standard method in a muffle oven, Table S1: Analytical results of input waste materials, Table S2: Analytical results of waste blends, Table S3: Comparable groups.

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review and editing, L.K., S.D., S.H. and M.D.; visualization, P.M.; supervision, S.H., I.J. and L.K.; project administration, S.D.; funding acquisition, S.H., M.D. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

EU	European Union
HHV	high heating value
HRT	hydraulic retention time
LDPE	low density polyethylene
LHV	low heating value
MSW	municipal solid waste
OLR	organic loading rate
PES	polyester
PR	paper rejects
PT	population total
RDF	residual derived fuel (polyethylene foils, bags and sorted municipal solid waste)
SS	sewage sludge
TG	thermogravimetric
TP	thermoplastics (non-specified)

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