

Comparison of the thermal behavior of sewage sludge, herbaceous crops and wood samples

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Abstract

The thermal behavior of a sewage sludge sample, woody (black locust, poplar and willow) and herbaceous (energy grass, wheat straw) biomass as well as mixed (sewage sludge and black locust in ratio 1:1 and 1:3) samples was compared under inert and oxidative atmosphere. The thermogravimetric experiments of each sample demonstrate that the beginning temperature of decomposition is similar in inert and oxidative atmospheres, i.e. the primary bond scissions are not affected by the atmosphere. Nevertheless, oxygen increases the decomposition rate and the volatile evolution of all samples at higher temperatures. Thermogravimetry/mass spectrometry (TG/MS) experiments have been performed in order to determine the mass loss of the samples and the formation of volatile products as a function of temperature in inert atmosphere. Wood and herbaceous biomass samples evolved various organic products (aldehydes, ketones, acids, furan derivatives etc.) beside water and gaseous products. Sewage sludge released mainly water, carbon oxides, methane, hydrogen, hydrocarbons, ketones, acids as well as sulphur- and nitrogen-containing products. High heating value and low heating value of the samples have been determined by a bomb calorimeter. Principal component analysis (PCA) has been used to find statistical correlation between the data. The results unambiguously support the correlation between the thermogravimetric parameters (e.g., DTG_{max}) and the heating values of the samples.

Keywords

Herbaceous biomass, Wood, Sewage sludge, Thermogravimetry, Mass spectrometry, Bomb calorimetry, Principal component analysis

Abbreviations

DTG_{max} : maximum value of the $-dm/dt$ curves

T_{peak} : temperature belonging to the maximum of the $-dm/dt$ curves

$T_{1\%}$: temperature belonging to the 1 % mass loss of the dried samples

T_{start} : onset temperature extrapolated from the DTG curves

T_{end} : extrapolated offset temperature

Char: char residue at 600 °C temperature

Introduction

The countries depending on foreign energy supply try to find economically feasible ways to substitute the fossil energy. Part of the fossil fuels can be replaced by renewable energy resources.

An increasing number of studies are focused on the utilization of the energy from biomass [1-4], sunlight [5, 6], wind [7, 8] and thermal power [9, 10]. Other researches try to enhance the effectiveness of hydroelectricity production from falling water [11] and tidal energy [12, 13]. Sewage sludge is a solid residue originating from industrial and communal wastewater processes. The annual sewage sludge production is about 10 million tons [14] in Europe. The European Union's target to reduce final waste disposal by 50 % by 2050. To minimize the amount of sewage sludge, thermochemical processes can be applied. Sludge can be converted to combustible liquid, tar and gaseous products by pyrolytic methods. The combustible fraction of the volatile products can be applied as a fuel in internal combustion engines [15]. Thermochemical processes are used for converting biomass and the sewage sludge to valuable bioenergy [14-17]. Non-food crops, agricultural residues and wastes as well as sewage sludge can be suitable energy sources. The energy content of the sample has been utilized during the thermochemical methods and the volume of the solid residues becomes much lower than that of the raw material. The energy content of different materials can be characterized by high heating value and low heating value [18, 19], which are measured by a calorimeter [20, 21]. The energy contents of biomass samples are higher than that of the sewage sludge because the sludge contains substantial amount of inorganic compounds. The traditional power plants are not suitable for burning exclusively sewage sludge due to its high ash content. Therefore the sewage sludge can be used as a mixture with biomass fuel of plant origin. That is why great emphasis has been placed in this work on the comparative study of the decomposition characteristics of sewage sludge and biomass samples. Thermal degradation of biomass samples has been studied extensively [22-30], which is a way to produce combustible volatile materials and char residue from natural products. In this work biomass samples were measured under inert and oxidative atmosphere by thermogravimetry/mass spectrometry. Thermal behavior of woody, non-woody, mixed and sewage sludge samples were measured with the goal to find relationship between the thermal decomposition parameters and the energy content of the samples. Statistical analysis (Principal component analysis) has been applied as a mathematical method to find the correlations between the experimental data.

Experimental

Materials

In this work woody (black locust, poplar and willow) and non-woody (energy grass, wheat straw) biomass samples, sewage sludge as well as mixed black locust and sewage sludge samples were measured. The air dried biomass samples were ground by a cutting mill to <1 mm and further ground to <0.12 mm particle size. The solid sewage sludge sample was pounded in an agate mortar to about <0.1 mm particle size. The mixtures of black locust and sewage sludge samples were prepared after the grounding in ratio 1:1 and 3:1. Before the measurements samples have been dried on 105 °C to weight stability. The methods for solid biofuel sample preparation have been completed using a CEN/TS 14780:2005 EU standard method. The moisture contents of the samples have been measured using standard method MSZ 24000-23:1977. The ash content has been determined at 550 °C in a furnace (MSZ ISO 1171:1993). The carbon, hydrogen, oxygen (MSZ 24000-11/1989), nitrogen (ISO 333:1996), sulphur (MSZ 24000-12:1989), chlorine content (ISO 587:1997) of the samples have been determined based on standard methods.

Methods

Bomb calorimetry

High heating value and low heating value were determined by an automatic IKA C 2000 bomb calorimeter. During the assessment the sample take fire by an electric firing system so the temperature of the inside water is rising. The rise of the temperature of water in the inside vessel was measured during the combustion of about 1-g sample in pure oxygen atmosphere under 30 bar. The heat capacity of the calorimeter system was determined by benzoic acid calibration material.

TG/MS

The TG/MS system consists of a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL quadrupole mass spectrometer. About 4-mg of the biomass samples, 8-mg of the sewage sludge sample were measured in inert (argon) and 0.5-mg biomass and 1.8-mg sewage sludge samples were analysed in oxidative (20 % oxygen and 80 % nitrogen) atmosphere, using flow rates of 140 ml min⁻¹. The samples were heated in a platinum sample pan at a rate of 20 °C min⁻¹ from 25 to 950 °C in inert atmosphere and from 25 to 600 °C using oxidative carrier gas. During the measurements in inert atmosphere, the intensity of the volatile products was monitored by the mass spectrometer. The evolved products were introduced through a glass lined metal capillary heated at 300 °C into the ion source of the mass spectrometer which was operated at 70 eV electron energy. The mass range of 15-100 Da was scanned at every 25 s excluding the main ions of the argon carrier gas. The ion intensities were normalized to the sample mass and to the intensity of the ³⁸Ar isotope of the carrier gas.

Results and discussions

Characterization of the samples

Table 1 shows the proximate analysis data and the energy content of the samples. The volatile content and the char yield were measured by the thermobalance heating up the samples to 900 °C under inert atmosphere. The woody samples (poplar, black locust and willow) have the highest energy contents, while the wheat straw and energy grass have a 3-4 % lower heating values. The sewage sludge can be characterized by the lowest energy content due to the highest inorganic content. The wood samples release the highest yield of volatile matter, whereas the sewage sludge evolves the lowest amount of volatile products. The energy content and composition values of the mixed samples take place between the values of black locust and sewage sludge. The volatile matter of the mixed samples is higher by 1.6-1.7 % than it is expected indicating only slight interactions between the wood and sewage sludge during the decomposition.

The elemental analysis results can be found in Table 2. As expected, the wood samples have the highest carbon content, while sewage sludge has only 22 % carbon. However, sewage sludge has relatively high nitrogen and sulphur contents, which requires thorough flue gas cleaning during its combustion. Wheat straw and energy grass contain perceptible amount of chlorine, which should be taken into account during their combustion.

Table 1. Proximate analysis data and energy content of the samples

Sample	Moisture/%	Char/% db	Volatiles/% db	Ash /% ar	High heating value/kJ kg ⁻¹	Low heating value/kJ kg ⁻¹
Black locust	11.8	16.7	83.3	2.7	17085	15657
Poplar	13.4	17.2	82.8	1.6	17181	15653
Willow	14.4	16.8	83.2	1.2	16816	15253
Wheat straw	12.8	20.6	79.4	4.1	16449	14942
Energy grass	12.5	24.1	75.9	5.9	16319	14933
Sewage sludge	15.4	49.4	50.6	38.8	9841	8760
50% Black locust and 50% Sewage sludge	13.6	31.3	68.7	20.8	13463	12209
75% Black locust and 25% Sewage sludge	12.7	23.1	76.9	11.7	15274	13933

db: dry basis; ar: as received

Table 2. Ultimate analysis of the samples (as received)

Sample	Carbon/ m/m %	Hydrogen/ m/m %	Oxygen/ m/m %	Nitrogen/ m/m %	Sulphur/ m/m %	Chlorine/ m/m %
Black locust	42.3	5.2	37.2	0.7	0.04	0.05
Poplar	42.5	5.4	36.6	0.5	0.09	0.01
Willow	42.1	5.4	36.4	0.4	0.09	0.01
Wheat straw	40.9	5.3	35.8	0.7	0.10	0.33
Energy grass	40.1	5.0	35.4	0.8	0.10	0.24
Sewage sludge	22.0	3.2	16.7	2.9	0.89	0.09
50% Black locust and 50% Sewage sludge	32.2	4.2	27.0	1.8	0.47	0.07
75% Black locust and 25% Sewage sludge	37.2	4.7	32.1	1.2	0.25	0.06

TG results in inert and oxidative atmosphere

Fig. 1 a-c show the TG and DTG curves of a non-woody (a), a woody (b) and the sewage sludge samples (c) in inert and oxidative atmosphere.

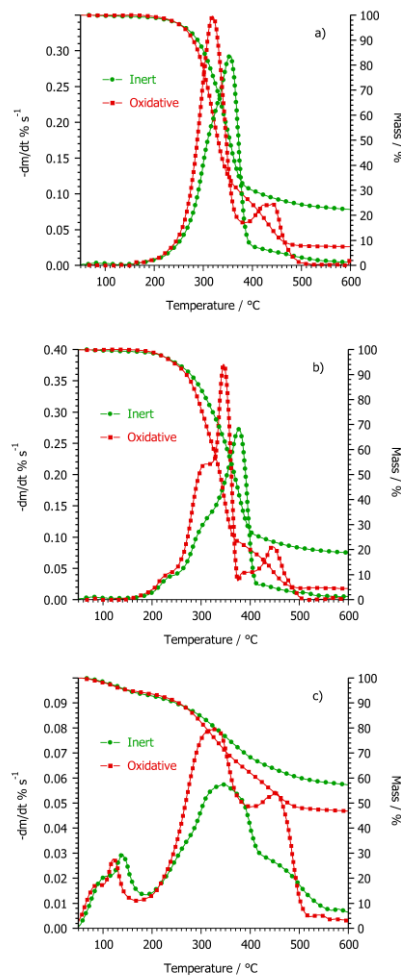


Fig. 1 TG and DTG curves of a-wheat straw, b-willow and c-sewage sludge at 20 °C min⁻¹ heating rate in argon and oxidative (20 % O₂ + 80 % N₂) atmosphere

The mass loss curves can be divided into three parts. The first smallest DTG peak between 50 °C and 170 °C can be attributed to the evaporation of the moisture content. This peak is very small in the plant samples because we studied air-dried samples. In addition, a few per cent moisture was lost before the experiment when the thermobalance is flushed by the carrier gas. The second major peak (between 180 °C and 400 °C) is due to the thermal decomposition of the main components of the biomass samples. The devolatilization phase is very similar in inert and oxidative atmospheres, although oxygen increases the decomposition rate and the volatile evolution is shifted to lower temperatures. However, the thermal decomposition of this stage starts at the same temperature in both atmospheres indicating that oxygen does not take part in the primary bond scissions. Above 400 °C, a slow charring process takes place in inert atmosphere. In oxidative atmosphere, a third peak appears on the DTG curves between 400 °C and 500 °C that can be attributed to the burning of the char. The ash residue at 600 °C is only a few per cent from the willow and wheat straw (4 and 8 %, respectively), while it is rather high (47 %) from the sewage sludge. Therefore the sludge should be mixed with wood samples in the power plants. The measured DTG curves of the mixed sewage sludge and black locust samples are very similar to the curves calculated from the component curves (not shown here) in spite of the 1.6-1.7 % difference in the measured and calculated total volatile content (Table 1).

TG/MS results in inert atmosphere

Fig. 2 presents the evolution of the most significant products measured by the mass spectrometer during the thermal decomposition of wheat straw (Fig. 2a-b) and willow (Fig. 2c-d) in inert atmosphere. The intensities have been scaled to obtain comparable peak heights.

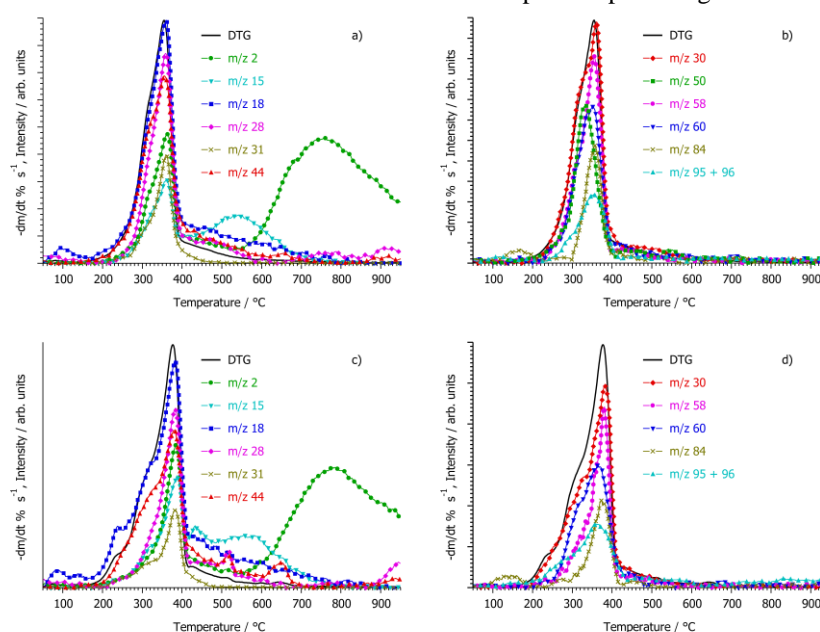


Fig. 2 The DTG curves and the evolution profiles of some products from - a, b - wheat straw and - c, d - willow in argon atmosphere (m/z 2, hydrogen; m/z 15, methane; m/z 18, water; m/z 28, carbon monoxide; m/z 30, formaldehyde; m/z 31, CH_3O^+ ; m/z 44, carbon dioxide; m/z 50, methyl chloride; m/z 58, acetone; m/z 60, acetic acid and hydroxy acetaldehyde; m/z 84, furanone; m/z 95+96, furfural)

The scaling factors for the individual species evolved from wheat straw and willow are the same. After the release of moisture content, the decomposition of the woody and non-woody samples alike starts with the thermolysis of the extractives and lignin side groups at about 180 °C. As the mass spectrometric evolution curves reveal, low molecular mass products (e.g., water, formaldehyde) can be detected at low temperatures. The shoulder on the DTG curves at about 230 °C can be attributed to the decomposition of the extractives [23]. The thermal degradation of the lignin starts at about 200 °C and ends at about 600 °C [24]. However, the decomposition of lignin can not be separated from the other parts of the DTG curves because it has a significantly lower decomposition rate than the carbohydrates.

The second shoulder on the DTG curves at about 310 °C can be attributed to the degradation of hemicellulose components. This can be clearly seen on the DTG curve of willow (Fig. 2c-d). The

hemicellulose shoulder is less pronounced on the DTG curve of wheat straw because it is merged with the cellulose peak. This can be explained by the well-known observation [22, 26, 27] that the decomposition of cellulose is shifted to lower temperatures in the presence of alkali ions. Wheat straw has relatively high inorganic content (Table 1) including potassium therefore its cellulose content decomposes at lower temperatures than that of willow. During the decomposition of hemicellulose, significant amount of low molecular mass products are released (e.g., water, carbon dioxide, formaldehyde) indicating the fragmentation of the sugar moieties. The evolution of acetic acid confirms the presence of acetyl groups in hemicellulose. Furanaldehyde represents a typical product of both hemicelluloses and cellulose showing that it can be formed from pentoses and hexoses, too. The pyrolysis of cellulose results in the formation of significant amount of levoglucosan, which can not be detected by TG/MS due to condensation in the transfer line. Nevertheless, other major products like furfural, furanone, hydroxyacetaldehyde, and acetone can be monitored from both wheat straw and willow. However, the major products of cellulose decomposition are the low molecular mass fragmentation products, such as water, carbon monoxide, carbon dioxide, formaldehyde, and methanol. Wheat straw releases measurable amount of methyl chloride (m/z 50 in Fig. 2b), which is the reaction product of the inorganic chlorine of relatively high amount (see Table 2) with methyl groups evolved from cellulose or lignin. Willow produces a small sharp carbon monoxide peak at about 510 °C and a carbon dioxide peak at about 650 °C (Fig. 2c), which are the decomposition products of calcium oxalate present in the axial parenchyma cells of the bark of wood. Methane and hydrogen represent other high-temperature products, which are formed during the charring process of the organic matter. Methane has a separated small peak at about 450 °C from the willow, which is originating from lignin. Hardwood lignin has the highest methoxyl group content, which is split during thermal decomposition leading to methane formation [24].

The thermal decomposition of sewage sludge occurs in a very broad temperature interval as shown in Fig. 3.

The evaporation of water starts at the beginning of the measurement and ends at about 170 °C. The high amount of adsorbed water and the crystallization water of the inorganic components of sewage sludge results in a double water peak as seen on the DTG and mass spectrometric curve (m/z 18) in Fig. 3a. The center peak of the DTG curve originates mainly from the thermal decomposition of organic components, which can be monitored by the fragments of methane (m/z 15), water (m/z 18), carbon dioxide (m/z 44) and CH_3O^+ ion (m/z 31) corresponding to the main fragments of hydroxyacetaldehyde and methanol. The evolution of hydroxyacetaldehyde and acetic acid (m/z 60) as well as acetone (m/z 58) indicates the presence of carbohydrates in the sewage sludge (Fig. 3b). The shoulder on the DTG curve at about 480 °C can be attributed to the release of aliphatic fragments as it is illustrated by the formation of ethenyl (m/z 27) and propenyl (m/z 41) fragments. The aliphatic products in this temperature range can be derived from the decomposition of fatty acid esters. This assumption is supported by the release of carbon dioxide at the same temperature indicated by the shoulder on the evolution curve of m/z 44. Fatty acid esters present in the extracts of wood decompose also at this temperature range [23]. At high temperatures, slow charring reactions of the organic matter of sewage sludge take place with the release of methane at about 500 °C and evolution of hydrogen at about 700 °C producing very broad peaks. The carbon dioxide evolution continues up to 900 °C with two peaks at about 660 °C and 840 °C, which can be attributed to the decomposition of inorganic carbonates, probably calcium and sodium carbonates. The last carbon dioxide peak coincides with a high carbon monoxide peak, which can be explained by the secondary reaction of the evolved carbon dioxide with the carbonaceous residue leading to carbon monoxide formation (Boudouard reaction).

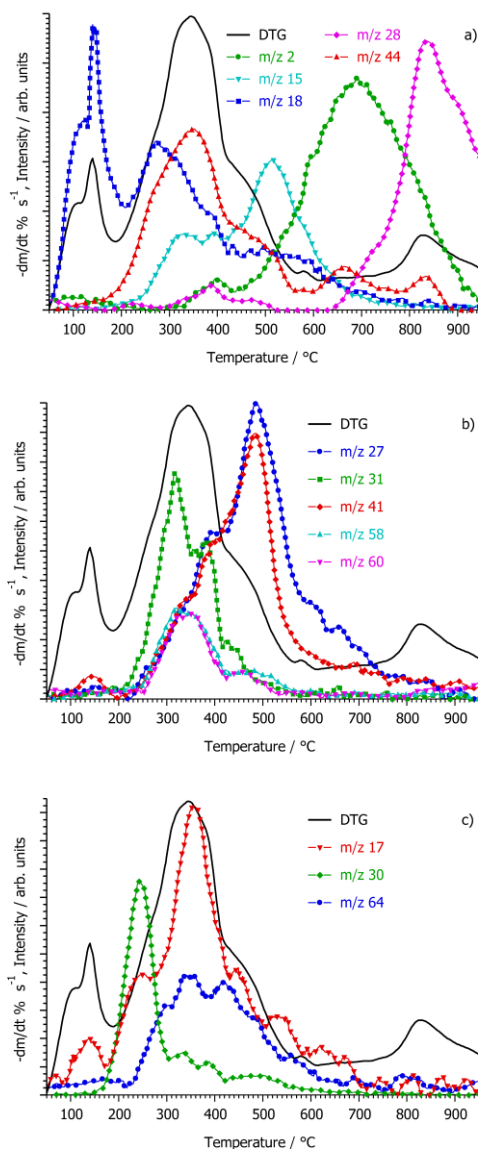


Fig. 3 The DTG curve and the evolution profiles of some products from sewage sludge in argon atmosphere: a - main products (m/z 2, hydrogen; m/z 15, methane; m/z 18, water; m/z 28, carbon monoxide; m/z 44, carbon dioxide), b - other organic compounds (m/z 27, $C_2H_3^+$; m/z 31, CH_3O^+ ; m/z 41, $C_3H_5^+$; m/z 58, acetone; m/z 60, acetic acid and hydroxy acetaldehyde), c - nitrogen- and sulphur-containing products (m/z 17, ammonia; m/z 30, NO_x ; m/z 64, sulphur dioxide)

The sewage sludge contains almost 3 % nitrogen and 0.9 % sulphur (Table 2). The curves of nitrogen- and sulphur-containing MS ions can be seen in Figure 3c. Signal at m/z 17 represents exclusively ammonia since the fragment ion of water has been subtracted from the total intensity of m/z 17. Small amount of adsorbed ammonia is released together with the moisture content above 100 °C. The maximum of ammonia evolution is at about 350 °C, where the devolatilization of the organic matter occurs. Various nitrogen-containing compounds (e.g., carbamide) are present in the sewage sludge, which may release ammonia during heating. There is a shoulder on the ammonia curve at lower temperature (at about 240 °C). This shoulder probably originates from ammonium salts. Nitrite or nitrate compounds must be present in the sludge because a significant amount of nitrogen oxides is formed as evidenced by the m/z 30 ion (NO^+) at about 230 °C temperature. A much broader peak is formed from the sulphur-containing moieties. Sulphur dioxide (m/z 64) evolution occurs from 200 °C to 700 °C indicating the presence of various sulfonates or sulfates in the sewage sludge.

PCA calculations

Principal component analysis has been applied to find correlations between the TG-parameters and the energy data of the samples [25, 27]. In the calculation, the most important TG parameters (T_{peak} , DTG_{max} , $T_{1\%}$, T_{start} , T_{end} , Char yield) and the low and high heating values of the samples have been used. PCA gives the linear combinations (Factors) of the original parameters in order to present the differences and similarities between the samples [31, 32]. As Fig. 4 shows Factor 1 describes 75.15 % and Factor 2 describes 19.87 % of the total variance, i.e., two factors are sufficient to characterize the major differences between the samples. The score plot (Fig. 4a) shows that the woody, non-woody, and the sewage sludge samples are found in the different part of the figure. The first principal component separates the woody and non-woody samples from the sewage sludge sample. The difference between the thermal decomposition of the herbaceous crops (energy grass and wheat straw) and the woody samples is described by the second principal component. The thermogravimetric and calorific characteristics of the mixed samples are found between those of the woody samples and the sewage sludge, because they have been mixed from these two constituents.

The loading plot (Fig. 4b) shows that the values of T_{end} and char yield correlate negatively with the low and high heating value as well as with DTG_{max} of the samples. Factor 1 is composed mostly of these parameters and mainly differentiates the sewage sludge from the other samples. The high char yield of sewage sludge is due to the high ash content, which results in lower energy content. The lower volatile content of sewage sludge leads to the lower devolatilization rate, i.e., lower DTG_{max} value. T_{peak} , T_{start} and $T_{1\%}$ contribute mainly to Factor 2, which shows the main differences between the wood and herbaceous plant samples. T_{peak} can be attributed to the temperature of the maximum decomposition rate of cellulose component of biomass samples. It is well known that the decomposition of herbaceous crops is shifted to lower temperature than that of wood samples due to the higher inherent potassium ion content. The decomposition of wood samples commences at lower temperature due to their higher extractive content in comparison with the herbaceous plant samples. Therefore T_{start} and $T_{1\%}$ contribute to the differences between these samples, which are described mainly by Factor 2.

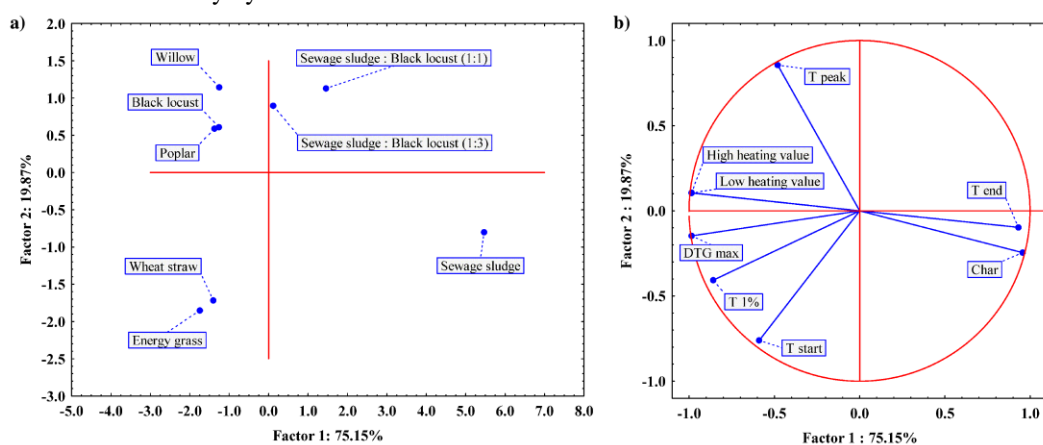


Fig. 4 Results of principal component analysis: score (a) and loading (b) plots based on the calorific values and TG-parameters

Conclusions

During this work thermogravimetric parameters and calorific values of woody and herbaceous biomass samples, sewage sludge and mixed samples were determined and compared. The differences between the samples have been evaluated by the use of principal component analysis. Correlations have been found between the calorific values and the parameters of the thermal decomposition. Woody, herbaceous and sewage sludge samples were clearly separated by the TG parameters in the score plot. The higher inorganic content of sewage sludge explains the main difference in the thermal decomposition of the sewage sludge and the other biomass samples. These differences manifest itself in the calorific values, yield of carbonaceous residue, rate of the thermal decomposition and the ending temperature of the degradation. Woody and herbaceous biomass samples can be discerned mainly by the TG parameters characteristic of the thermal decomposition of cellulose (T_{peak}) and extractives (T_{start}). The mechanism of thermal

decomposition under inert atmosphere can be changed by low amount of inorganic components. The decomposition of cellulose is shifted to lower temperatures in the herbaceous crops since the mechanism of the cellulose decomposition is changed by the higher potassium ion contents of wheat straw and energy grass. Wheat straw and energy grass contain 0.2-0.3 % chloride ions, which can react with methyl fragments deriving from the organic moieties of the samples, thus leading to methyl chloride evolution. During the thermal decomposition of sewage sludge, NH₃, NO_x and SO₂ are released from nitrogen- and sulphur-containing inorganic components. As TG measurements under oxidative atmosphere confirm, sewage sludge starts and ends to burn at similar temperatures like biomass samples. So sewage sludge can be mixed and burned with agricultural by-products if the flue gas is cleaned from NO_x and SO₂.

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