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Thermo-Gravimetric Analysis of Solid Fraction of Digestate Obtained by Rumen Fluid-Enhanced Anaerobic Co-Digestion of Sewage Sludge and Cattail

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In this study, thermo-gravimetric analysis (TGA) of the solid fraction of digestate from rumen fluid-enhanced anaerobic co-digestion of sewage sludge and cattail (grass *Typha latifolia*) was performed. TGA analysis was conducted under inert atmospheric conditions (100 mL N_2/min) in the temperature range 25 – 800 °C at three different heating rates: 15, 50 and 100 °C/min. Proximate and ultimate analysis of tested samples was performed and the TG - DTG profiles (thermo-gravimetric profile and the profile of its first derivative) of digestate sample were compared to profiles of undigested sewage sludge and cattail. Kinetic analysis was performed using the Friedman kinetic model.
The results show that anaerobic co-digestion significantly affects the characteristics of feedstock materials, as reflected in the TG and DTG curves. Estimated weight loss during pyrolysis was about 67.8 wt.% for sludge sample and 75.6 wt.% for cattail sample at heating rate of 15 °C/min. Weight loss of digested samples was lower: 55 wt.% on average. Kinetic analysis shows that the digested mixture could be promising feedstock for the pyrolysis.

1. Introduction

Sewage sludge from municipal wastewater treatment plants contains various pollutants, such as micro-organisms, heavy metals, pharmaceuticals, and dioxins, that can cause serious environmental pollution if not treated efficiently (Magdziarz and Werle, 2014). As a result of more stringent requirements for water treatment, sewage sludge production is increasing in all European countries (Bianchini et al., 2016) and pressure to find better treatment and disposal methods for this waste is increasing.
Commonly-used technologies for energy recovery from sewage sludge include anaerobic digestion, incineration, pyrolysis and gasification (Raheem et al., 2018). The considerations of choosing suitable technologies for energy recovery from sewage sludge involves technical and economic feasibility, environmental sustainability, marketing facts and public acceptance (Zaker et al., 2019). Thermochemical processes, like pyrolysis, offer significant volume reduction (Tang et al., 2018), effective pathogen destruction and promising potential for valorization of energy-rich materials (Syed-Hassan et al., 2017). Pyrolysis can generate valuable by-products such as bio-oil, bio-gas and bio-char (Meng et al., 2018).
The key factor for successful implementation of pyrolysis is good knowledge of kinetic and thermodynamic parameters. Various kinetic models can be applied to the description of thermal behavior of biomass. The most popular are iso-conversional kinetic models, such as the integral Kissinger-Akahira-Sunose model, the Ozawa-Flynn-Wall model (Mehmood et al., 2017), and the Friedman model (Cortés and Bridgwater, 2015).
Several studies have been performed regarding sewage sludge pyrolysis (Syed-Hassan et al., 2017), including thermo-gravimetric studies (Magdziarz and Werle, 2014), studies regarding kinetic behavior of sludge (Naqvi et al., 2018), product characterization (Tang et al., 2018), and studies on the integration of pyrolysis with other thermo-chemical processes, such as microwave heating (Zaker et al., 2019) and drying (Ledakowicz et al.,

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2019). Fewer studies have been done on co-pyrolysis of sludge with organic materials (Alvarez et al., 2015) or other waste (Ruiz-Gómez et al., 2017). A literature review shows that studies regarding pyrolysis of digestate from anaerobic co-digestion of sewage sludge with organic materials are lacking.

The aim of this study was to analyse the thermo-gravimetric behavior of a solid fraction of digestate obtained from anaerobic co-digestion of sewage sludge and *Typha latifolia* grass (cattail), that was performed at mesophilic conditions and at sludge/cattail ratio of 1:1 on a dry basis. The novelty of this study is in the use of enhanced anaerobic fermentation by using cattle rumen fluid, which impacts the composition of feedstock materials and consequently its thermo-gravimetric behavior. To the best of the authors' knowledge, no thermo-gravimetric study on this kind of digestate has been performed yet. Thermo-gravimetric analysis was performed together with the kinetic study, where a Friedman kinetic model was applied for the description of pyrolysis kinetics.

2. Materials and methods

In this section, feedstock materials and their characterisation are first described, the procedure for TGA analysis is presented, and finally, an analysis of kinetic parameters is introduced.

2.1 Feedstock materials and thermo-gravimetric analysis

Thermo-gravimetric (TG) studies were performed on dried samples of a solid fraction of digestate obtained from anaerobic co-digestion of municipal sewage sludge and cattail (ratio 1:1 on a dry basis), which was enhanced by using cattle rumen fluid. Sewage sludge was gathered from a local municipal wastewater treatment plant and cattle rumen fluid was collected from a nearby slaughterhouse. Cattail was collected from the bank of the Dravinja river and cut into pieces size of around 0.5 cm x 0.5 cm.

First, anaerobic digestion experiments were performed in 1 L batch reactors at mesophilic conditions (42 °C, 55 d), where the ratio between substrates (sewage sludge + grass) and inoculum was 1:1 on a dry basis. For enhanced fermentation, 50 mL of rumen fluid was added to the mixture. The mixture was further diluted with a buffer solution (Angelidaki et al., 2009) to obtain 6 wt.% dry matter content in each reactor (wet digestion). After anaerobic digestion, the obtained digestate was separated into liquid and solid fractions by centrifugation.

The solid fraction of the digestate was further used in the thermo-gravimetric study (sample marked as "D"). For a comparison of results, undigested samples of sewage sludge (sample marked as "S") and cattail (sample marked as "C") were also analyzed. All the samples were dried at 105 °C in a laboratory dryer until constant weight before being used in the pyrolysis experiments. The basic characteristics of the feedstock materials were determined using relevant analytical methods for waste: total solids (TS) and volatile solids, moisture and ash content. An Elemental Analyser PerkinElmer Series II 2400 was used to determine carbon, hydrogen, nitrogen and sulphur contents. The oxygen content was calculated as the difference of O = 100 – C – H – N – S – Ash (all in wt.%). A higher heating value (HHV) was determined by a bomb calorimeter using the standard method (SIST-TS CEN/TS 16023:2014, 2014).

TGA studies were then performed using a TGA/SDTA851e thermo-gravimetric analyzer (Mettler Toledo) in the temperature range from 25 to 800 °C under an inert atmosphere (ensured by constant nitrogen flow at 100 mL/min). The measurements were conducted with samples weighing approximately 25 ± 1 mg at three different heating rates: 15, 50 and 100 °C/min. From the obtained TGA analyses, TG curves (mass weights vs. temperatures) and DTG (derivative) curves were constructed by means of MS Excel software tool.

2.2 Kinetic analysis by Friedman iso-conversional model

For the kinetic analysis, a Friedman linear kinetic model was used, because it exhibited good agreement with experimental data when applied to the description of the kinetic behavior of sewage sludge (Naqvi et al., 2018) or lignocellulosic biomass (Cortés and Bridgwater, 2015). The Friedman method assumes that the chemistry of the decomposition process depends only on the rate of mass loss and is independent of the temperature. The kinetic parameters, activation energy E_α and modified pre-exponential factor $ln[A_\alpha f(\alpha)]$ can be determined from the slope and intercept of the line obtained by plotting curve $ln\left[\beta_i (d\alpha/dT)_{\alpha,i}\right]$ versus $(-1/RT_{\alpha,i})$ as described by Eq(1) (Cortés and Bridgwater, 2015):

$$ln\left[\beta_i \left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (1)$$

where β_i represents the heating rate (°C/min), T is the temperature (°C or K), R is the gas constant (8.314 J/(mol·K)), and $(d\alpha/dT)_{\alpha,i}$ is the conversion derivative per temperature. The parameter α represents the degree of conversion (/ or wt.%), which is determined by Eq(2):

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_f} \quad (2)$$

where m_0 is the initial mass, $m(T)$ is the mass at temperature T, and m_f is the mass at the final temperature T_f. Before applying the Friedman kinetic model, the derivative conversion curve $(d\alpha/dT)_{\alpha,i}$ should be constructed. To smooth the data obtained in this study and to reduce the impact of the experimental noise, the Moving Average function in MS Excel was utilized (Hogarth, 2012). After the determination of degree of conversion (Eq(2)), the kinetic parameters could be finally calculated from the slope and intercept of the plot given by Eq(1) (Bedoić et al., 2019). In addition, the enthalpy ΔH was calculated according to the following equation (Ahmad et al., 2017a):

$$\Delta H = E_\alpha - RT \quad (3)$$

3. Results and Discussion

This section presents proximate and ultimate analysis of feedstock materials, results from TGA analysis (TG and DTG profiles of analysed samples), and kinetic analysis of experimental data by applying the Friedman model.

3.1 Characterisation of feedstock materials

The results of ultimate and proximate analyses of the feedstock materials used in the TGA study are shown in Table 1. The smallest amount of volatile solids among all the samples was determined in the digestate (62.42 wt.%), although this value was still relatively high. The calorific value (HHV) of digestate was 11.66 MJ/kg, which is approximately half of the HHV for sewage sludge. The calorific value of cattail was 15.75 MJ/kg, which is close to value stated in the literature (18.32 MJ/kg) (Ahmad et al., 2017b), and comparable to other energy crops, such as miscanthus (18.73 MJ/kg), switchgrass (19.60 MJ/kg), wheat straw (16.00 MJ/kg) (Syed-Hassan et al., 2017), and camel grass (15.00 MJ/kg) (Mehmood et al., 2017). Sewage sludge has likewise shown similar calorific values as reported previously (Syed-Hassan et al., 2017). The ash content was highest in digestate (37.58 wt.%), lower in the sludge (19.94 wt.%) and lowest in the grass sample (9.26 wt.%).
Regarding elemental analysis, it can be seen that the raw sewage sludge and cattail have higher carbon content (42.6 and 45.8 wt.%) than digestate (26.3 wt.%). The nitrogen content in the case of undigested sewage sludge was 8.1 wt.%, while the other two samples contained about half of that value. It is interesting to note that in the digestate, a considerable amount of sulphur (8.7 wt.%) was determined in comparison with the other two substrates (1.2 wt.% in sample S and 0.5 wt.% in sample C). This is most likely due to the destruction of organic material during the anaerobic digestion process (Dewil et al., 2009). Relatively high carbon content and relatively high content of volatiles measured in digestate suggests that the solid fraction of digestate is, despite slightly lower calorific value, a promising substrate for pyrolysis process.

Table 1: Proximate and ultimate analysis of feedstock materials

Parameter	Digestate (D)	Sewage sludge (S)	Cattail (C)
Total dry solids (wt.%)	≈6.00	18.47	11.11
Moisture content (wt.%)	≈94.00	81.53	88.89
Volatile solids (wt.%)	62.42	80.06	90.74
Ash (wt.%)	37.58	19.94	9.26
Higher heating value, HHV (MJ/kg)	11.66	20.10	15.75
C (wt.%)	26.28	42.60	45.82
H (wt.%)	4.01	6.73	7.06
N (wt.%)	4.37	8.06	3.65
S (wt.%)	8.72	1.18	0.51
O (wt.%)	19.04	21.49	33.7

3.2 Thermo-gravimetric analysis

Thermo-gravimetric analyses show the weight loss in materials (biomass and waste) under increasing temperature, and indicate the conversion of material into products including solids, liquids and gases. Figure 1 shows a) TG curves and b) DTG curves for analysed materials. Curves for digestate are shown at three different heating rates (15, 50 and 100 °C/min), while for clarity, for grass and sludge samples only at 15°C/min.

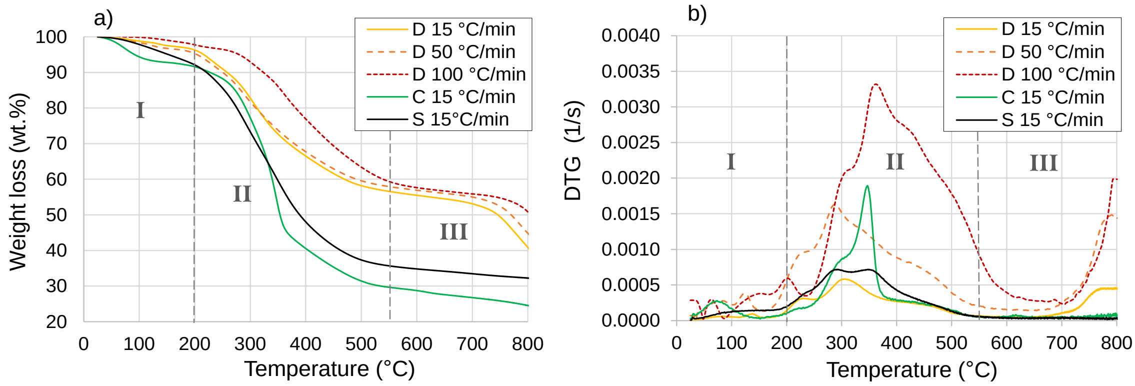

Figure 1: a) TG curves and b) DTG curves for digestate (D), sewage sludge (S) and cattail (C) samples

The TG and DTG curves for digestate show similar characteristics at all three tested heating rates, although at the highest heating rate the curve slightly differs. Comparison of TG and DTG curves at a heating rate of 15 °C/min between untreated and digestate (D) samples shows significant differences in their shape. Also, weight loss for both untreated samples is much faster, especially at temperatures between 300 and 400 °C. The curve of cattail exhibited similar thermal degradation patterns as other lignocellulosic materials, such as camel grass (Mehmood et al., 2017) or pinewood sawdust (Alvarez et al., 2015). The TG curve for sewage sludge is in accordance with those reported in the literature (Magdziarz and Werle, 2014).
Characteristics of DTG curves, peak temperature (T_p) and maximum value of DTG for the analysed samples at a heating rate of 15 °C/min are shown in Table 2. As it could be seen, the peak temperature of cattail (346.82 °C) was higher than the other two peak temperatures (302.66 °C and 291.83 °C for D and S samples). From the DTG curves of digestate sample a shift in the pyrolysis peak temperature could be observed (see Figure 1b), since the maximum rate of weight loss for digestate sample at a heating rate of 15 °C/min was measured at 302.66 °C, while at a heating rate of 100 °C/min at 362.14 °C.

Table 2: Weight loss during different stages of pyrolysis and characteristics of DTG curves for the samples pyrolysed at a heating rate of 15 °C/min

Sample	T_p (°C)	DTG_{max} (1/s)	Weight loss (wt.%) Dehydration (Stage I)	Active pyrolysis (Stage II)	Passive pyrolysis (Stage III)	Total weight loss (wt.%)	Final residue (wt.%)
Sewage sludge (S)	291.83	$7.17 \cdot 10^{-4}$	7.05	56.79	3.96	67.80	32.20
Cattail (C)	346.82	$1.89 \cdot 10^{-3}$	7.22	54.96	13.37	75.55	24.45
Digestate (D)	302.66	$5.84 \cdot 10^{-4}$	3.06	39.13	12.76	54.95	45.05

Analysis of TG and DTG curves shows that the weight loss of tested samples during the pyrolysis took place in three major stages (see Figure 1 and Table 2): the dehydration stage (stage I), active pyrolysis stage (stage II) and passive pyrolysis stage (stage III).
The first stage (stage I) is attributed to the mass loss due to dehydration of low boiling fractions, mainly the loss of intracellular water (Mehmood et al., 2017). In the case of digestate (D), this happened in a temperature range between room temperature and ≈159 °C, where weight loss was about 3 wt.%. The digestate samples show lower weight loss than the other two undigested samples (both about 7 wt.%). In the temperature range between 200 and 550 °C (stage II), the main devolatilization step (active pyrolysis) occurred. Major weight loss was observed during this stage in all tested samples, which may be related to the degradation of hemicellulose and cellulose (Ahmad et al., 2017a). The percent of weight loss in digestate was about 39 wt.%. The shape of DTG curves for grass and digestate suggests that the decomposition of biomass during the active pyrolysis stage incorporates more than one reaction (Naqvi et al., 2018). In the last stage (stage III), so-called passive pyrolysis was observed in the temperature range between 550 and 800 °C, where the degradation of high-temperature thermally stable components occurred. In contrast to the untreated sludge, the TG curves of digestate and grass in this stage show considerable weight loss (≈13 wt.%), which could be related to the degradation of lignin (Ahmad et al., 2017b). The overall weight loss for undigested samples was 67.80 wt.% for sewage sludge and 75.55 wt.% for cattail, while weight loss of digestate was lower, about 55 wt.% on average. The increase of heating rate from 15 to 100 °C/min caused a decrease of weight loss for digestate sample for around 10 wt.%

(from 59.85 to 49.54 wt.%). These findings associated with the degradation of substrates are in agreement with the findings of similar studies for sewage sludge (Alvarez et al., 2015), and grass and digestate from mono-digestion of grass samples (Bedoić et al., 2019).

3.3 Kinetic analysis

Pyrolysis of a biomass is a heterogeneous reaction, whose reaction dynamics and chemical kinetics are influenced by the activation energy and pre-exponential factor. The values of activation energy E_α and pre-exponential factor $ln[A_\alpha f(\alpha)]$ at different conversion degrees obtained by Friedman kinetic model for digestate sample are shown in Table 3. The data at the lowest and the highest conversion degrees were excluded, due to significant fluctuations.

Table 3: Activation energy E_α, pre-exponential factor $\ln[A_\alpha f(\alpha)]$ and enthalpy ΔH for digestate sample with regard to conversion degree

Conversion degree, α	Activation energy, E_α (kJ/mol)	Pre-exponential factor, $ln[A_\alpha f(\alpha)]$ (1/s)	Enthalpy, ΔH (kJ/mol)
0.2	53.08	5.25	48.26
0.3	58.39	5.97	53.58
0.4	76.74	8.83	71.92
0.5	110.55	13.99	105.73
0.6	151.15	19.43	146.33
0.7	64.84	2.75	60.02
0.8	59.26	2.04	55.49

As it could be seen, the activation energy E_α increased up to conversion degree of 0.6, where maximum value of about 151 kJ/mol was calculated, and from that point on the value decreased. The pre-exponential factor $ln[A_\alpha f(\alpha)]$ and enthalpy ΔH showed the same trend. The enthalpy ΔH, which represents the energy consumed by the sludge for its conversion to various products, differed from E_α by around 4.8 kJ/mol at each conversion degree. The range of E_α for digestate was between 53–151 kJ/mol (Table 3), which is comparable to the range calculated by the same model for miscanthus (113–143 kJ/mol), and is lower than that reported for para grass (102–233 kJ/mol) (Ahmad et al., 2017a) or *Typha latifolia* grass (134–204 kJ/mol) (Ahmad et al., 2017b). For the last two cases, other isoconversional models were used, in particular the Flynn-Wall-Ozawa and Kissenger-Akahira-Sunose models, which are also model-free kinetic methods which require measurements for multiple conversions. On the other hand, the Friedman kinetic model for pyrolysis of sewage sludge containing higher amounts of ash provided a wider range of E_α, 10.6–306.2 kJ/mol (Naqvi et al., 2018).
Based on the properties and obtained kinetic data, the digestate could, besides pyrolysis, be potentially used for gasification or combustion and as a solid fuel in the form of pellets. However, sludge digestates are, in practice, rarely used for such a purpose, since they could contain undesirable substances and their use could be limited. Co-digestion and further co-pyrolysis or co-combustion of sludge with other organic biomass present an opportunity to overcome these limitations (Alvarez et al., 2015). The kinetic data obtained in this study accordingly represent valuable information for further investigations regarding thermal treatment and energy recovery of products from enhanced digestion of residues and waste.

4. Conclusions

The results of thermo-gravimetric analysis show that thermal degradation of tested samples occurs mainly at temperatures up to 550 °C, although considerable weight loss was observed in the temperature range 550 – 800 °C. When comparing undigested samples and digestate, significant differences between their TG - DTG profiles were obtained. The weight loss of digestate during pyrolysis was much lower than the weight loss of grass and sludge samples. The reason is that in anaerobic digestion, biomass is to some extent already degraded by microorganisms, which is consequently reflected by thermal degradation. The results of kinetic and thermo-gravimetric analyses show that the solid fraction of digestate obtained from anaerobic digestion of sewage sludge and cattail (enhanced by rumen fluid) could be suitable feedstock for energy recovery by pyrolysis. Digestate shows higher final residue yields and is a promising feedstock in terms of carbon content, volatiles content and calorific value, despite its lower values compared to untreated samples.
Further work could take various directions, such as the further study of kinetics by other models, investigating the impact of different pollutants such as heavy metals on the pyrolysis process, characterization of pyrolysis products and enhancement of their quality, performing the pyrolysis process at a larger scale, and studying the efficiency, operating costs and environmental impact of the pyrolysis process.

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