A kinetic study of roadside grass pyrolysis and digestate from anaerobic mono-digestion

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Abstract

The aim of this research is to evaluate the thermogravimetric behaviour of roadside grass and its digestate obtained from mesophilic anaerobic mono-digestion by quantifying its impacts on biomass composition and properties. Thermogravimetric measurements were conducted in a laboratory furnace under nitrogen flowrate of 100 mL/min in the temperature range from 35 to 800°C at five different heating rates of 2.5, 5, 10, 15 and 20°C/min. Friedman and Kissinger-Akahira-Sunose differential and integral isoconversional models were applied to determine the distributions of activation energies and modified pre-exponential factors per reacted mass (degree of conversion). The investigation demonstrated that anaerobic digestion of roadside grass can be used to generate biochar-richer material (with significantly greater yield of final residues after pyrolysis) with less energy required for subsequent pyrolysis in comparison with raw roadside grass.

Keywords:

Roadside grass; roadside grass digestate; anaerobic digestion; pyrolysis; kinetic study; thermogravimetric measurements; isoconversional models

1. Introduction

Grass is a sustainable source of lignocellulosic material which can be cultivated on non-arable lands, making it non-competitive with other crops for food production (Rodriguez et al., 2017). The location of the area where grass is collected impacts its chemical composition and further application. Grass collected on non-arable lands has been shown to be an abundant and environment-friendly source of material to produce bioenergy in the form of biogas (Bedoić et al., 2019). Another efficient and environmentally attractive process for converting biomass and different types of waste to energy products is pyrolysis (Campuzano et al., 2019). Besides anaerobic digestion and pyrolysis, biomass can be converted to energy and bioproducts through combustion, gasification and biochemical processing (Akhtar et al., 2018).

Pyrolysis is one of the most thoroughly researched thermochemical conversion processes of biomass into valuable hydrocarbon and alternative fuels (Dhyani and Bhaskar, 2018). Slow pyrolysis producing charcoal has been successfully utilised for waste-to-energy and waste-to-liquid purposes (Rostek and Biernat, 2013). Pyrolysis can be studied under different atmospheric conditions (inert or reactive) that affect the complexity of the thermal behaviour of feedstock (Mikulcic et al., 2019). Gaseous products that appear during pyrolysis contain variable chemical constituents based on the feedstock used (Stančin et al., 2019).

Pyrolysis of biomass and waste is widely examined with thermogravimetric analysis (TGA) together with kinetic studies (Zhang et al., 2017). To evaluate the effects of different waste materials on pyrolysis, various experiments have been performed using the TGA (Oyedun et al., 2014). Thermochemical processes (pyrolysis, gasification and combustion) of different types of lignocellulosic biomass have shown that for describing their kinetics, different approaches/models are suggested (Senneca, 2007). Generally, there are two types of kinetic methods which have been used for the description of biomass and waste pyrolysis kinetics, model-fitting and isoconversional or model-free methods (Jain et al., 2016).

Isoconversional methods are more popular in the analysis of biomass pyrolysis kinetics than model-fitting methods (Burnham and Dinh, 2007). The advantages of isoconversional methods include computation of kinetic parameters without modelling assumptions (Ramajo-Escalera et al., 2006) and better suitability for more complex and multiple step reactions (Sánchez-Jiménez et al., 2013). Isoconversional methods can be divided into differential and integral methods (Wang et al., 2017). The Friedman (FR) differential isoconversional model is among the most widely used (Burnham and Dinh, 2007). It has shown adequacy and high matching to experimental data in the pyrolysis of corn stalk (Cai et al., 2018), and has been used to describe the kinetics of Miscanthus grass pyrolysis (Cortés and Bridgwater, 2015). Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) integral isoconversional models have been applied in the pyrolysis of different grass types, such as Para grass (Al Ayed et al., 2016) and Camel grass (Mehmood et al., 2017).

Product yields by pyrolysis of lignocellulosic biomass can be improved by pretreatment, such as by the application of heat, chemicals or different pretreatment times (Wang et al., 2018) or by integration of aerobic and anaerobic digestion (Juchelková et al., 2015). Pyrolysis is an attractive option for the treatment of digestate due to its seasonal applicability as a fertilizer (Losak et al., 2014), and in cases when digestates contain heavy metals, pathogens and other toxic compounds (Wiśniewski et al., 2015). Pyrolysis of digestate is an interesting option because of the benefits it confers (Li et al., 2017) such as reduction of weight and volume of digestate and elimination of pathogens and odour (Nansubuga et al., 2015). As biochar from digestate can effectively be used for various applications, a combined anaerobic digestion – pyrolysis process might be beneficial because of the low economic value of digestate (Egieya et al., 2019); thus, subsequent pyrolysis of digestate offers an opportunity to improve the profitability of biogas production processes (Egieya et al., 2018).

Digestate has recently attracted significant attention as a potential feedstock for pyrolysis (Wei et al., 2018). Various kinetic studies have been performed on the combined anaerobic digestion - pyrolysis process for biomass/waste material with its digestate, for corn stover and its digestate (Zhang et al., 2017), for food waste and its digestate (Opatokun et al., 2015), and for different organic solid wastes (sewage sludge, food waste, vinasse and cow manure) and their digestates (Li et al., 2017).

This paper presents the continuation of the previous experimental study on anaerobic digestion of two types of roadside residue grass, residue grass from the uncultivated land (next to minor road) and from the highway verge (Bedoić et al., 2019). This research contains two novel scientific contributions, such as the study on pyrolysis of residue roadside grass and its digestate and the study on determination of degraded organic matter during anaerobic process based on the analysis of thermogravimetric curves. Estimation of the organic matter degradation is studied in relation to biochemical biogas potential of grasses, which was determined previously (Bedoić et al., 2019). Two isoconversional models, differential FR model and integral KAS model are used to quantify the impacts of anaerobic digestion of two types of roadside residue grass on parameters of pyrolysis kinetics. Verification of the applied models based on the experimental data and estimated kinetic parameters is finally conducted with the aim to reconstruct the kinetic behaviour of studied feedstocks in the pyrolysis. The study determines the share of compounds in two types of roadside grass and in its digestates without using any chemical solvents and performs the research on the energy recovery of residue grass.

2. Materials and methods

In this section, we present an overview of the methods applied, along with a brief description of TGA; two further linear isoconversional models used in the study are introduced. Our research is linked with a previous investigation on anaerobic digestion of different types of residue grass (Bedoić et al., 2019). Regarding residue grass sampling, preparation and characterisation, and laboratory results from anaerobic digestion, readers are referred to Bedoić et al. (2019).

2.1. Substrates used in the study

We focused on the use of two roadside grass types. The first was collected on the verge next to a minor road (RG-MR), while the second was collected on the verge next to a highway (RG-H). In our previous study (Bedoić et al., 2019) they were marked as RG1 (now RG-MR) and RG3 (now RG-H). Both grasslands are located near Zagreb, the capital city of Croatia, on locations not suitable for food and/or feed purposes. Nine samples were collected on each of the grasslands examined, which were then stored in plastic bags in a vacuum in a freezer at −15°C (Bedoić et al., 2019).

The proximate and ultimate analysis and analysis of heavy metals presence of residue grasses have been performed. The results, including results from field measurements, are presented in Bedoić et al. (2019). Both types of grass (see RG1 and RG3 in Table 1 by Bedoić et al., 2019) showed similar chemical composition; RG-H exhibited higher yield on both a fresh and dry basis, longer stem length, lower moisture and ash contents, higher heating values and higher carbon content, compared to RG-MR. Significant differences were obtained in terms of heavy metal concentrations, where RG-H showed much higher values than RG-MR. On dry basis, RG-H sample contains 93.60 mg/kg of iron, 11.20 mg/kg of zinc, 8.57 mg/kg of manganese and 4.55 mg/kg of copper. On the other side, RG-MR sample contains on dry basis 54.40 mg/kg of iron, 5.86 mg/kg of zinc, 7.64 mg/kg of manganese and 3.72 mg/kg of copper. Other elements like lead, cadmium, mercury and nickel have shown lower concentrations, below 1 mg/kg of dry grass. As expected, higher concentrations of metals were detected for the grass collected in the intense traffic area (highway verge).

For this study, raw grass samples were reduced into smaller pieces of approx. 3–6 cm in length and were dried in a laboratory oven at 105°C until constant weight before use.

Besides the two types of roadside residue grass, their digestates obtained by mono-digestion were used as substrates for the analysis. For anaerobic digestion, substrates were chopped into smaller pieces of approx. 3–6 cm in length. They were placed in 250 mL batch reactors in triplicate together with inoculum, where the ratio between inoculum and grass for anaerobic digestion was 1:1 on a dry basis. In total, 9 g of total solids (TS) were added to each reactor, and the dry matter in each reactor was 6%. Anaerobic digestion was performed for 42 days at 39°C. During the process of anaerobic mono-digestion no inhibition could be observed, despite relatively high concentration of heavy metals in the studied grass samples.

The digestates, RGD-MR - digestate of roadside grass collected on the verge next to the minor road (marked as MRG1 in Bedoić et al., 2019), and RGD-H – digestate of roadside grass collected on the verge next to the highway (marked as MRG3 in Bedoić et al., 2019) were used for this investigation. Before performing TGA analysis, digestates were dried in a laboratory oven at 105°C until constant weight.

More details regarding the residue grass substrates and anaerobic digestion process can be found in Bedoić et al. (2019).

2.2. Thermogravimetric analysis

Thermogravimetric measurements of dried samples (RG-MR, RG-H, RGD-MR and RGD-H) were conducted using a TA Instruments Q500 at the heating rates β_i of 2.5, 5, 10, 15 and 20°C/min at a temperature range from 35 to 800°C under a steady flow of nitrogen (100 mL/min) to maintain an inert atmosphere. Samples weighing approximately 10 mg were used for the analysis. Three replicates were run for each sample, and the average value is reported. TGA data (mass weights and derivative mass weights) were recorded with respect to temperature and time for the five heating rates considered.

2.3. Analysis of hemicellulose and cellulose degradation

To calculate the degradation of hemicellulose (*hc*) and cellulose (*c*) in residue grass samples – $X_{\mathrm{RG}}(hc+c)$ (%) based on the analysis of thermogravimetric curves of grass and digestate, the following relation was used:

$$X_{\mathrm{RG}}(hc+c)=\frac{\bar{x}_{\mathrm{RG}}(hc+c)-\bar{x}_{\mathrm{RGD}}(hc+c)\cdot\dfrac{\bar{x}_{\mathrm{RG}}(l)}{\bar{x}_{\mathrm{RGD}}(l)}}{\bar{x}_{\mathrm{RG}}(hc+c)}\times 100 \tag{1}$$

where $\bar{x}_{\mathrm{RG}}(hc+c)$ is the average share of hemicellulose and cellulose in residue grass sample (before anaerobic digestion), $\bar{x}_{\mathrm{RGD}}(hc+c)$ is the average share of hemicellulose and cellulose in digestate sample (after anaerobic digestion), $\bar{x}_{\mathrm{RG}}(l)$ is the average share of lignin in residue grass sample (before anaerobic digestion) and $\bar{x}_{\mathrm{RGD}}(l)$ is the average share of lignin in digestate sample (after anaerobic digestion). The term “average share of components” is related to the arithmetic mean of a component’s share determined at the selected heating rates. Factor $\dfrac{\bar{x}_{\mathrm{RG}}(l)}{\bar{x}_{\mathrm{RGD}}(l)}$ is introduced in the calculation since the relative share of components during anaerobic digestion changes.

2.4. Analysis of kinetic parameters

Two linear isoconversional models (Li et al., 2017) were used for the determination of kinetic parameters of roadside grass and roadside grass digestate pyrolysis, as shown in Table 1. In Table 1 β_{i} is the heating rate (°C/min), α is the degree of conversion (/ or %), T is the temperature as a general parameter of process (°C or K), $(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,\mathrm{i}}$ is the conversion derivative per temperature at the given degree of conversion and heating rate, $A_\alpha f(\alpha)$ is a modified pre-exponential factor in the Friedmann isoconversional model (1/s), $A_\alpha/g(\alpha)$ is the modified pre-exponential factor in the Kissinger-Akahira-Sunose isoconversional model (1/s), E_α is the activation energy (J/mol), $T_{\alpha,\mathrm{i}}$ is the temperature at the given degree of conversion and heating rate required for model application (K), and R is the universal gas constant (8.314 J/(mol·K)).

Table 1: Linear isoconversional kinetic models applied on the pyrolysis of roadside grass and roadside grass digestate

To conduct a kinetic analysis using the models in Table 1, it is necessary to determine the degree of conversion at a certain temperature $\alpha(T)$, as:

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

where m_0 is the mass at temperature T_0, $m(T)$ is the mass at temperature T, and m_f is the mass at the final temperature T_f. Since biomass sample contains retained water and could also contain light volatile compounds, the first stage is a dehydration stage. Pyrolysis occurs in the second and third stages, which are called active and passive pyrolysis. Both pyrolysis stages correspond to the decomposition of cellulose, hemicellulose and lignin. It has been reported that the dehydration stage ends at about 150°C, and pyrolysis of lignocellulosic biomass starts (Chen et al., 2013).

When applying the Friedman isoconversional model in the kinetic study of pyrolysis, it is necessary to determine the derivative conversion curve $(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}$. Since the curve has been reported to have many fluctuations, it is recommended to apply some smoothing tool to reduce the impact of the noisy data (Vyazovkin et al., 2011). In this study, the Moving Average of data in Excel was applied (Hogarth, 2014) to smooth the experimental derivative conversion curves.

After the degree of conversion has been determined, the calculations of parameters based on the thermogravimetric measurements follows. For the Friedman isoconversional model, at the given α, E_α and $\ln[A_\alpha f(\alpha)]$ are obtained from the slope and intercept of the plot of $\ln[\beta_\mathrm{i}(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,\mathrm{i}}]$ versus $(-1/RT_{\alpha,\mathrm{i}})$. For the Kissinger-Akahira-Sunose isoconversional model, at the given α, E_α and $\ln[A_\alpha/g(\alpha)]$ are obtained from the slope and intercept of the plot of $\ln[\beta_\mathrm{i}/T^2_{\alpha,\mathrm{i}}]$ versus $(-1/RT_{\alpha,\mathrm{i}})$.

To represent the deviations of activation energy and modified pre-exponential factor (based on linear regression) at the given degree of conversion, the confidence interval has been used (Cai et al., 2018). The specific level of confidence was set at 95% to present a range of values of activation energy and modified pre-exponential factor within the selected probability (Bartocci et al., 2019).

To reconstruct the kinetic behaviour of pyrolysis of the selected feedstocks, the average values of kinetic parameters at the given degree of conversion are used.

3. Results and discussion

In this section, the results of our experiments of biomass pyrolysis and modelling of pyrolysis kinetics are presented.

3.1. Thermogravimetric analysis

The results of thermogravimetric analysis of roadside grass (RG) and roadside grass digestate (RGD) in terms of thermogravimetric (TG) and derivative TG (DTG) curves are presented in Figure 1 for five different heating rates (β_i of 2.5, 5, 10, 15 and 20°C/min), where the temperature range is from 35 to 800°C. TG shows the loss of weight during heating, while DTG shows the first derivative of TG which indicates the main devolatilization stages more clearly (Ceylan and Kazan, 2015). TG curves for analysed samples (RG-MR, RG-H, RGD-MR and RGD-H) show steady or decreasing trends with increased temperature, while the changes in TG curves (weight loss) are shown as peaks in DTG curves.

Figure 1: TG-DTG curves of RG and RGD samples at different heating rates: a) 2.5 °C/min, b) 5 °C/min, c) 10 °C/min, d) 15 °C/min, e) 20 °C/min

All the samples underwent three main stages of weight loss, which indicate the processes of dehydration, active and passive pyrolysis (Slopiecka et al., 2012). The stages are the drying, devolatilization and char formation stages (Chandrasekaran et al., 2017). In the dehydration stage, evaporation of water and light volatile compounds occurs; in the active pyrolysis stage, the degradation of hemicellulose and cellulose takes place, and in the final stage, decomposition of lignin occurs (Chandrasekaran et al., 2017). Hemicellulose and cellulose degrade at a similar temperature range (simultaneously) and thus only one peak is typically obtained in the DTG curve (Parthasarathy and Narayanan, 2014). The last stage typically shows slow continued loss of weight, as solid residue is slowly decomposed (Peng et al., 2001). The final residue at 800°C consists of biochar and ash (Peng et al., 2001).

In Figure 1 it can be seen that RG-H shows the highest peak of the DTG curve at the highest temperature at each of the applied heating rates, and exhibits a more intense peak shoulder compared to

RG-MR. Unlike the RG samples, peak shoulder in the DTG curves in the case of RGDs is not clearly visible. We assume that this is because both cellulose and hemicellulose from RG are partly degraded under anaerobic conditions, which impact the DTG curves of RGD by fading the peak shoulder. Similar observations have been reported in the analysis of food waste and its digestate pyrolysis (Opatokun et al., 2015).

According to the TG curves, all the RGDs show higher amounts of residues or lower weight loss during pyrolysis due to lower cellulose and hemicellulose content in the samples. In terms of grass samples, RG-MR shows a slightly higher yield of the final residue compared to RG-H. This result can be explained through the higher share of ash and carbon in the RG-MR sample (10.4% of ash and 47.1% of carbon, on dry basis) than in the RG-H sample (8.4% of ash and 46.2% of carbon, on dry basis) (Bedoić et al., 2019).

More detailed information regarding the mass loss intervals and characteristic temperature zones (Ye et al., 2010) of all samples is shown in Tables 2 and 3. Table 2 shows five characteristic temperature zones during different stages of decomposition of RG and RGD samples at five different heating rates. *T1* in Table 2 represents the end of the dehydration stage or the start of the biomass pyrolysis process. The active pyrolysis stage occurs at temperatures between *T1* and *T5*. This stage (stage II) can be divided into zones I and II, where zone I occurs at temperatures *T1* – *T3*, and zone II at temperatures *T3* – *T5*, with maximum weight loss at *T2* and *T4*. For more details regarding characteristic temperature zones, see (Ye et al., 2010). As mentioned previously, the upper limit of the temperature range, 800°C, is applied.

Table 2: Characteristic temperature zones during different stages of decomposition of RG and RGD samples

Table 3: Weight loss (in wt.%) during different stages of decomposition of RG and RGD samples

Results show that the dehydration stage occurs from the starting temperature to about 136 to 191°C for RG samples, and to about 137 to 189°C for RGD samples. The active pyrolysis stage is observed to be in the following temperature ranges:

- RG-MR: start from ca. 136°C (2.5 °C/min) to ca. 191°C (20°C/min), end from ca. 343°C (2.5°C/min) to ca. 396°C (20°C/min),
- RG-H: start from ca. 139°C (2.5°C/min) to ca. 191°C (20°C/min), end from ca. 356°C (2.5°C/min) until ca. 418°C (20°C/min),
- RGD-H: start from ca. 137°C (2.5°C/min) to ca. 187.5°C (20 °C/min), end from ca. 332°C (2.5°C/min) until ca. 394°C (20°C/min),

- RGD-H: start from ca. 141°C (2.5°C/min) to ca. 189°C (20°C/min), end from ca. 364°C (2.5°C/min) until ca. 415°C (20°C/min),

Table 3 shows the weight loss during different stages of decomposition for all the analysed samples for the five heating rates considered. From Table 3 it can be seen that the first dehydration stage shows slightly higher weight loss for RGD samples (ca. 6 to 8%) than for RG samples (ca. 4 to 5.5%). RG-H samples on average contain slightly more cellulose and hemicellulose, $\bar{x}_{\text{RG-H}}(hc+c)$=60%, compared to RG-MR samples, $\bar{x}_{\text{RG-MR}}(hc+c)$=56%. Since temperatures *T2* and *T3* could not be determined for the RGD samples due to the shoulder fading in DTG curves, the share of cellulose and hemicellulose is calculated by subtracting the share of moisture, lignin and final residue from the total amount (100 wt.%). Therefore, the amount of hemicellulose and cellulose in digestate samples is estimated on average, $\bar{x}_{\text{RGD-MR}}(hc+c)$=37% and $\bar{x}_{\text{RGD-H}}(hc+c)$=42%.

The degradation of lignin at the observed heating rates started at ca. 340 to 400°C in the RG-MR sample, at ca. 360 to 420°C for the RG-H sample, at ca. 330 to 390°C for the RGD-MR sample and at ca. 360 to 415°C for the RGD-H sample. The mass loss caused by lignin degradation and charring is as follows: $\bar{x}_{\text{RGD-MR}}(l)$=17%, $\bar{x}_{\text{RG-MR}}(l)$=13%, $\bar{x}_{\text{RGD-H}}(l)$=15%, and $\bar{x}_{\text{RG-H}}(l)$=12%. The differences in mass loss during the lignin degradation and biochar formation stage between RGD samples and raw RG samples are 3 and 4%, on average. Since the relative share of components during anaerobic digestion changes, this could be the reason for the measured deviations. However, estimation of the amount of lignin in samples should be taken with caution, since it was obtained by using experimental data and theoretical background related to pyrolysis of lignocellulosic biomass (Carrier et al., 2016). It has been reported that partial degradation of lignin under inert atmosphere starts at 200°C, while at 400°C it starts to be intensified (Carrier et al., 2011).

When Eq. (1) is applied, the results show that during monodigestion of RG-MR, ca. 50% of cellulose and hemicellulose was converted to biogas ($X_{\text{RG-MR}}(hc+c)$=49.5%), and in the case of RG-H, degradation of cellulose and hemicellulose is estimated at $X_{\text{RG-H}}(hc+c)$=44.0%). Degradation is similar for both grass types, which is also supported by the fact that for both, similar biochemical biogas potential values (BGP) were obtained, 0.436 Nm^3/kgTS for RG-MR and 0.413 Nm^3/kgTS for RG-H (Bedoić et al., 2019).

The results show that mono-digestion has been incomplete (49.5 and 44 % conversion of cellulose and hemicellulose). To further increase the degradability of biomass and enhance biogas production, co-digestion and addition of additives such as bio-based carbon materials (Yun et al., 2018) and accelerants such as for example urea, plant ash (Zhang et al., 2018) or steel slag (Han et al., 2019) to substrates have been recognised to be more efficient than mono-digestion (Wang et al., 2019). Similar conclusions have been obtained by thermogravimetric analysis of digested residue from aloe peel waste and dairy manure (Huang et al., 2016).

At 800°C, the average final residue yields for RG-MR and RG-H are ca. 25% and 23%. However, RGD samples have shown a higher yield of final residue at 800°C; for RGD-MR, the yield was ca. 38%, and for RGD-H, ca. 37%. Both RGD-MR and RGD-H have shown much higher yields of the final residues at 800°C than the RG feedstocks. Similar conclusions were obtained when using food waste as feedstock (Opatokun et al., 2015).

This study has shown that significant quantities of final residue (mainly biochar) are obtained from pyrolysis of roadside grass and its digestate. Biochar could have various applications, such as it could be used as an additive material for improving stability of anaerobic digestion, as an approach to carbon sequestration, in animal husbandry, as a soil conditioner, in the building sector, in treatment of drinking and waste waters and in many other applications (Schmidt, 2012). Combined anaerobic digestion – pyrolysis process from roadside grass might also improve the profitability of biogas production processes (Egieya et al., 2018).

3.2. Kinetic analysis

Thermogravimetry and isoconversional models can provide an estimation of kinetic data (activation energy and pre-exponential factor) from reaction parameters such as temperature and heating rate without estimation of reaction mechanisms (Damartzis et al., 2011). The activation energy and modified pre-exponential factors were obtained using FR and KAS methods. Their distribution for RG and RGD samples has been determined based on the performed thermogravimetric analysis data for conversions between 20 and 70% in step sizes of 5%. Degrees of conversion lower than 20% and higher than 70% are not shown because of significant fluctuations observed (especially for digestate samples), which were probably associated with the thermal behaviour of lignin (Carrier et al., 2016). In addition, verification of the applied models was performed, and average values of kinetic parameters obtained by this study were used to verify models with the experimental data.

3.2.1. Friedman (FR) model

The values of activation energy (E_α) and modified pre-exponential factor in logarithmic expression ($\ln[A_\alpha f(\alpha)]$) for pyrolysis of RG and RGD samples were obtained using the FR isoconversional model, as shown in Figure 2. The error bars in Figure 2 represent confidence intervals with a confidence level of 95%.

Figure 2: Distribution of E_α and $\ln[A_\alpha f(\alpha)]$ per the degree of conversion by means of FR model

Estimated values of E_α in the studied range of conversions vary between 160 and 600 kJ/mol for RG-MR samples, and between 170 and 380 kJ/mol for RG-H samples. Both RG samples show a slight increase in the values of E_α from $\alpha = 0.20$ to 0.30; between $\alpha = 0.30$ to 0.50, a stagnation/slight decline of E_α is shown, and after $\alpha = 0.50$, a significant increase in the E_α can be observed. Such a trend in the distribution of E_α using the FR model was also reported for corn stalk pyrolysis (Cai et al., 2018) and for miscanthus pyrolysis (Cortés and Bridgwater, 2015).

On the other hand, RGD samples have shown much lower values of E_α in the considered ranges of conversions; for RGD-MR it is between 20 and 170 kJ/mol, while for RGD-H it is between 10 and 170 kJ/mol. RGD samples show the highest E_α at the lowest value of α, and with an increase in the degree of conversion, E_α continuously declines in the case of RGD-MR, while RGD-H declines up to $\alpha = 0.45$, and then stagnation appears.

Similar trends as for E_α are observed for the change of $\ln[A_\alpha f(\alpha)]$ with the degree of conversion. The highest value of $\ln[A_\alpha f(\alpha)]$ is for RG-MR, about 110 s^{-1}, while the highest value for RG-H is around 60 s^{-1}. RGD samples show negative values of $\ln[A_\alpha f(\alpha)]$, with the lowest value around -8 s^{-1}.

To reconstruct the kinetic process using the FR model, Eq. (3) is used in the non-logarithmic form. The results of the verification process are presented in Figure 3.

Figure 3: Experimental and FR kinetic model based on E_α and $\ln[A_\alpha f(\alpha)]$ data for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

At all heating rates, the FR model shows high-level matching with the experimental data for RG samples. Higher fluctuations of the model compared to the experimental data are shown for RGD samples. The peaks of the curves for RG samples move to higher temperatures with an increase in heating rate. That observation is not seen for RGD samples. Furthermore, RGD samples show a wider range of temperatures in terms of the $\beta_i(d\alpha/dT)$ distribution. Since the weight loss in the active pyrolysis stage (stage II) is significantly lower for RGD samples, and the residue yield greater than for RG samples, this observation is supported by the analysis of TG curves. The kinetic parameters obtained with the FR model show a better fit for RG samples than for RGD samples. At lower heating rates of 2.5 and 5°C/min, RGD samples show a good model fit to the experimental data.

3.2.2. Kissinger-Akahira-Sunose (KAS) model

Using the KAS isoconversional model, the values of activation energy (E_α) and modified pre-exponential factor in logarithmic expression ($\ln[A_\alpha/g(\alpha)]$) for pyrolysis of RG and RGD samples are obtained, as shown in Figure 4**Error! Reference source not found.**.

Figure 4: Distribution of E_α and $\ln[A_\alpha/g(\alpha)]$ with the degree of conversion by means of KAS model

E_α estimated by the KAS model for RG samples in the studied range of conversions vary between 150 and 430 kJ/mol for RG-MR, and between 160 and 260 kJ/mol for RG-H samples. Similar results were obtained for the pyrolysis of Para grass (between 180 and 230 kJ/mol, (Al Ayed et al., 2016)) and Camel grass with the KAS model (between 150 and 190 kJ/mol, (Mehmood et al., 2017)). The results obtained in this study and by analyses of specific grass types show a narrower range of activation energies for specific grass types than for unclassified species of grass. On the other hand, RGD samples again show lower values of E_α compared to RG samples; for RGD-MR the range is between 30 and 170 kJ/mol, while for RGD-H it is between 20 and 175 kJ/mol. Again, RGD samples show the highest E_α at the lowest value of α. KAS modeling shows that with an increase of the degree of conversion, E_α continuously declines in the case of both RGD samples.

Similar trends with the degree of conversion as for E_α are obtained for $\ln[A_\alpha/g(\alpha)]$ for both RG and RGD samples. The highest value of $\ln[A_\alpha/g(\alpha)]$ is obtained for RG-MR, about 80 s^{-1}, while the highest value for RG-H is about 45 s^{-1}. It should be noted that modified pre-exponential factors obtained with FR and KAS models cannot be compared directly, since the expressions of functions are slightly different. RGD samples again show both positive and negative values of $\ln[A_\alpha/g(\alpha)]$, where the lowest value is about -5 s^{-1}.

To reconstruct the kinetic process with the KAS model, Eq. (4) is used in the non-logarithmic form. The results of the verification process are shown in Figure 5.

Figure 5: Experimental and KAS kinetic model based on E_α and $\ln[A_\alpha/g(\alpha)]$ for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

The KAS model shows matching with the experimental data for the middle temperature range of 450 to 700 K in the case of RG samples, and between 500 and 1,050 K for RGD samples. At lower temperatures, the KAS model deviates significantly from the experimental data. Again, more intense fluctuations of the model compared to the experimental data are shown for RGD samples. For all the analysed samples, the highest match of KAS model to experimental data is at the lowest heating rate (2.5°C/min). Slowly heating the samples leads to a better and more effective heat transfer to the inner layers of biomass (Mani et al., 2010). Therefore, the model results match the experimental data best at lower heating rates. Kinetic parameters obtained with the KAS model are more effective in the case of RG samples than in the case of its digestate.

4. Conclusions

The analysis of TG and DTG curves of selected feedstocks shows that estimated amount of degraded cellulose and hemicellulose in roadside grass during the AD process is around 44 to 50%. Roadside grass digestate has shown a greater yield of final residues (ca. 38%) than roadside grass samples (ca. 24%). The combined process, anaerobic digestion of roadside grass and pyrolysis of its digestate, contributes to the production of green bioenergy in the form of heat and electricity, while reducing energy requirements (activation energy and pre-exponential factor) for pyrolysis.

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Symbols

$(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}$	Conversion derivative per temperature at the given degree of conversion and heating rate
0	Initial (mass or temperature)
$A_\alpha/g(\alpha)$	Modified pre-exponential factor in KAS isoconversional model (s^{-1})
$A_\alpha f(\alpha)$	Modified pre-exponential factor in FR isoconversional model (s^{-1})
f	Final (mass or temperature)
m	mass (kg)
R	Universal gas constant, 8.314 J/(mol·K)
T	Temperature, general parameter of process (°C or K)
$T_{\alpha,i}$	Temperature at the given degree of conversion and heating rate required for model application (K)
X	degradation of hemicellulose and cellulose during anaerobic digestion of roadside grass

	(/ or %)
$\bar{x}$	average share of a component in a biomass sample (/ or %)
α	Degree of conversion (/or %)
β_i	Heating rate (°C/min)

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