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Pine Wood and Sewage Sludge Torrefaction Process for Production Renewable Solid Biofuels and Biochar as Carbon Carrier for Fertilizers

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Abstract: This work presents the results of research on the thermo-chemical conversion of woody biomass–pine wood coming from lodzkie voivodship forests and sewage sludge from the Group Sewage Treatment Plant of the Łódź Urban Agglomeration. Laboratory scale analyses of the carbonization process were carried out, initially using the TGA technique (to assess activation energy (EA)), followed by a flow reactor operating at temperature levels of 280–525 °C. Both the parameters of carbonized solid biofuel and biochar as a carrier for fertilizer (proximate and ultimate analysis) and the quality of the torgas (VOC) were analyzed. Analysis of the pine wood and sewage sludge torrefaction process shows clearly that the optimum process temperature would be around 325–350 °C from a mass loss ratio and economical perspective. This paper shows clearly that woody biomass, such as pine wood and sewage sludge, is a very interesting material both for biofuel production and in further processing for biochar production, used not only as an energy carrier but also as a new type of carbon source in fertilizer mixtures.

Keywords: torrefaction; pine wood; sewage sludge; biochar; kinetics

1. Introduction

As a part of the European Union, Poland is a powerful participant in the new European Green Deal which will be a revolution from the point of view of the Polish energy sector. In the future years, new climatic and environmental legislation will provide new obstacles. The Polish energy sector is now confronted with significant issues. The primary issues confronting this sector include high energy consumption, insufficient infrastructure development, production and transportation of fuels and energy, extraction of external energy natural gas, and rising CO_2 pricing. Amongst renewable energy sources, thermodynamic and numerical modeling aspects of biomass torrefaction are characterized by unflagging interest. As part of the research, a thermogravimetric analysis was performed on the basis of which the kinetics of chemical reactions taking place during the process were determined. Additionally, measurements of the total volatile organic compounds from the process were carried out and the combustion data were determined for the torrefaction products obtained. The research was carried out as part of the BIOCARBON project, which aims to design a torrefaction installation equipped with a rolling-bed dryer operating in continuous air mode and a reactor using superheated steam for the torrefaction process. Poland is at the forefront of Europe when it comes to forest area. Currently, the forest area in Poland is over 9.3 million ha. Pine is the most common species in lowland and upland areas. According to the Large-Area Inventory of the State of Forests, pine grows on 60% of the forest area of the state forests and approximately 54% of private and communal forests [1]. Pine's dominance results from the way in which forest management was conducted in the past [2–4]. The detailed percentage of pine forest area broken down by voivodeships of Poland is presented in Figure 1.

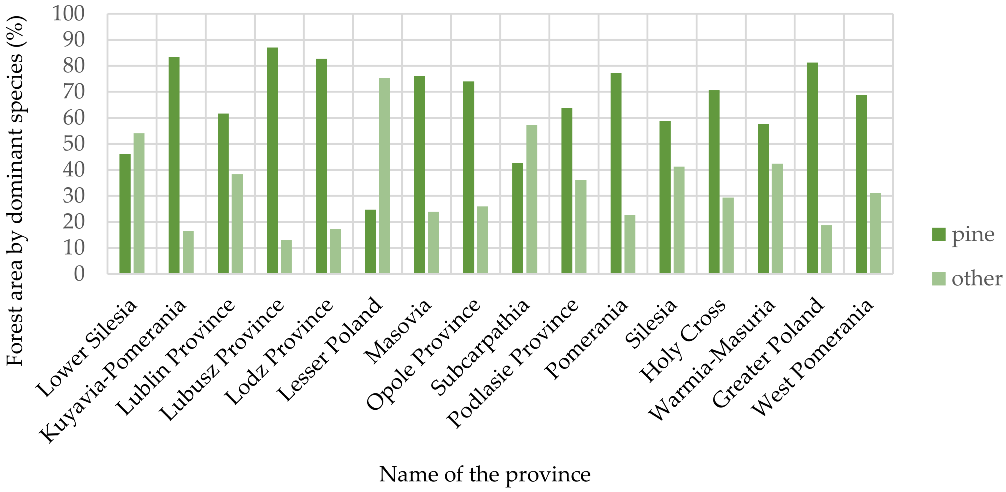

Figure 1. The area of forests on forest land by prevailing species in the voivodship system [1].

During this process, the lignin contained in the biomass heats up under the pressure applied and becomes soft and plastic. In this way, the material can be formed into any shape which allows for easy processing and transportation. As a result of the process, the moisture content of the material decreases, and the calorific value increases. The pelletizing process gives the pine wood fuel properties [5–9]. However, in order to be able to fully use pine wood as fuel, it must be subjected to further technological processes. An important direction of development concerns large-scale processes aimed at the preparation of biomass, where, in addition to drying, briquetting, baling, or pelletization, biomass is also subjected to processes aimed at altering its physical character and changing its moisture content. One such process is torrefaction. It can be said that torrefaction is a process of preliminary thermo-chemical processing of biomass under an inert atmosphere [10–15]. Its main task is to approximate the properties of biomass to the properties of average coals [16]. Sewage sludge is considered to be one of the many harmful substances produced by man. In short, it consists of suspensions of various waste substances in water, discharged from industrial plants and households. Unfortunately, it contains significant amounts of chemical compounds, bacteria, and microorganisms harmful to the environment. Therefore, in order to get rid of harmful substances, it must be treated. As certain technological (biological-chemical) processes are carried out, along with the removal of pollutants, sewage sludge is formed. This includes wastes that need to be treated and managed, and interestingly enough these can be a source of additional fuel due to their properties. Torrefaction is a thermo-chemical treatment of biomass at a temperature range of 200–300 °C; many researchers have done research on woody biomass torrefaction process and its influence on the woody biomass molecular structure [17–23]. It comprises a process that leads to an increase in biomass energy density, mainly as a result of decomposition of the reactive component of biomass, as in hemicellulose under anaerobic conditions [24–30]. During this process, about 30% of the initial weight of the raw material is reduced. This is mainly due to the removal of moisture from the material, but also the release of volatile substances. Due to the carbonization of biomass taking place during torrefaction, the biomass obtains properties that make it similar to coal [31–35]. Torrefied biomass is used not only as a renewable fuel in the energy sector [36–44]. Due to its developed specific surface and microporosity, it can also be used in environmental protection to remove pollutants from water and sewage [45,46]. Another sector of use concerns agriculture. The addition of torrefied biomass to the soil improves its properties and may contribute to reducing the use of fertilizers and plant protection products. It can also increase the effectiveness of using natural fertilizers [47–50]. Due to its very low thermal conductivity and absorption properties, torrefied biomass is also used in construction to produce insulation [51,52].

The sewage sludge used in this study came from the Group Sewage Treatment Plant of the Łódź Urban Agglomeration, which is located on the south-western border of Łódź. The sewage network in Łódź is characterized by a large share of combined sewage, which during heavy rainfalls and snowmelts causes troublesome irregularity in the amount of sewage flowing to the treatment plant. The areas from which wastewater flows into the plant are inhabited by approximately 820,000 people. The facility is a typical mechanical and biological treatment plant with increased removal of biogenic compounds. The biological process is periodically supported by iron coagulant and an external carbon source. The sludge consists of a large amount of organic compounds that affect its calorific value. This is similar to the calorific value of brown coal and can be 10–15 MJ/kg d.m.

One of the many methods of sewage sludge treatment is its thermal conversion. Depending on the technology used, there is a significant reduction in the amount of sludge and a reduction in the onerous impact on the environment. However, each method is fraught with the problem of continuous waste generation, regardless of the time of year or weather conditions. Significant developments in thermal treatment technologies have been observed during the last decade. In addition to legal requirements, technical, economic, and aesthetic considerations have also forced changes in this field. Thermal treatment can also be a source of energy and a source for the recovery of various materials used in road construction and elements such as phosphorus. The mechanism of sewage sludge torrefaction is similar to the torrefaction of plant biomass. The main fractions that are formed during the thermal decomposition of the sludge in an inert atmosphere are as follows: Gaseous fraction; are non-condensing gases (NCG) containing mainly hydrogen, methane, carbon monoxide, carbon dioxide and other gases in smaller concentrations; Solid fraction, mainly consisting of pure carbon with some inert substances. It should be noted that the share of individual fractions depends on the temperature, residence time in the reactor, pressure, turbulence, as well as the properties of sewage sludge (pH, organic matter content, dry matter content). The torrefaction process can be tested by thermogravimetry (TG), differential scanning calorimetry (DSC) and additionally by mass spectrometry (MS) and chromatographic techniques [19,27].

2. Materials and Methods

2.1. Thermogravimetric Analysis

Pinewood and sewage sludge were dried before the thermogravimetric tests. For this purpose, crucibles were calcined for 3 h at 900 °C. Biomass was placed in the prepared crucibles. The drying process was carried out in the Binder 9010-0082 dryer at a temperature of 105 °C for 24 h [53]. Dried samples were transferred to a desiccator to cool down. The next stage of the research was thermogravimetric analysis of biomass, which was aimed at measuring changes in the mass of a given sample depending on the analysis temperature and its time. Measurements were made with a NETZSCH TG 209 F3 Tarsus thermogravimeter. The analysis consisted of heating the biomass sample weighing about 10 mg to the following temperatures; for pine wood 285, 325 and 525 °C and for sewage sludge within the range of 280–520 °C, with a heating rate of 5, 10 and 20 K/min, with a flow of inert gas-nitrogen at a rate of 20 mL/min. The residence time of the sample in the thermogravimeter was set up for 5 to 10 min. The thermogravimetric analysis determines the mass losses as a function of temperature during the biomass torrefaction process. Figure 2 shows a diagram of the installation for the drying process and thermogravimetric analysis of pine wood and sewage sludge.

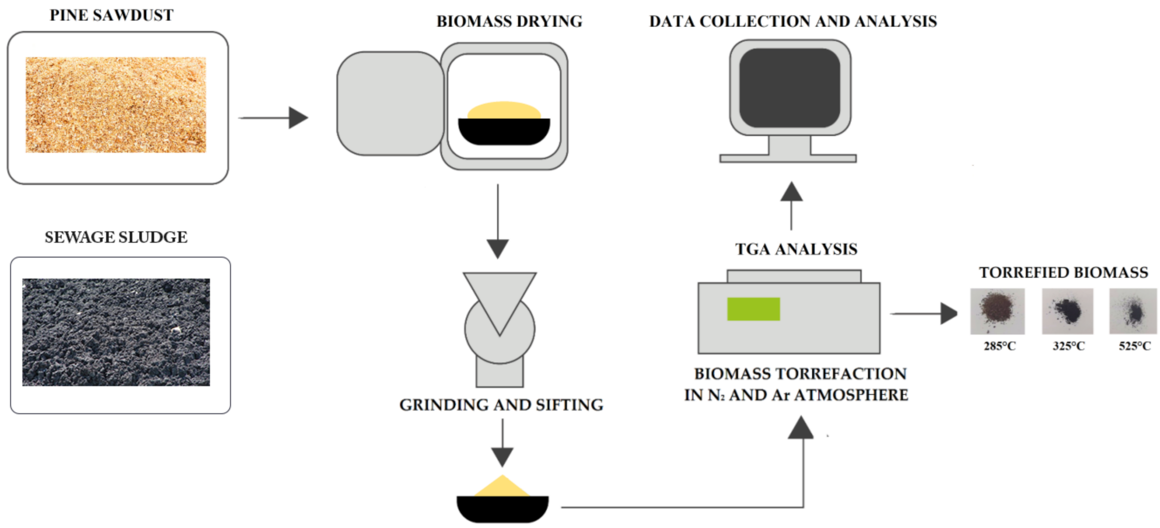

Figure 2. Diagram of an installation for thermogravimetric analysis of pine wood and sewage sludge.

2.2. Kinetic Analysis

Based on the findings obtained from the thermogravimetric analysis with the use of NETZSCH Kinetics 3 software, the reaction kinetics and chemical kinetics for pinewood and sewage sludge were determined. This software is used for thermal measurements of chemical reactions. The analysis allowed for the determination of the speed of chemical processes and the speed of reactions taking place during the torrefaction, and for the determination of the mechanism of individual elementary reactions occurring during the process.

The first method used was the Kissinger method, which determines the linear dependence of the activation energy and the Arrhenius pre-exponential factor on the temperature rise rate as well as the temperature at which the decomposition rate is the highest. It refers to the maximum rate of degradation based on the TG or DTG curves. This method has been standardized to the ASTM E698 method, which is based on the results of differential thermal analysis [54–56]. For the first order reaction, taking place under non-isothermal conditions, at different rates of temperature increase, the rate of decomposition is described by the relationship:

$$ln\, ln \left(\frac{\beta}{T_{max}^2} \right) = -\frac{E_a}{RT_{max}} \tag{1}$$

where: β—sample heating speed (K/min); T_{max}—the temperature at which the sample mass loss rate is greatest (K); A—pre-exponential coefficient; E_a—activation energy (J/mol).

Another method was the Friedman method, which is the most general differential method [57,58] and uses a logarithmic equation:

$$ln\, ln \left(\frac{dx}{dt} \right) = +ln\, ln\, f(x) \tag{2}$$

The last method was the Ozawa–Flynn–Wall method, which, as the Friedman method, allows determination of the activation energy value without the necessity of adopting a specific kinetic model [59,60]. It is based on the integral form of the equation:

$$G(x) = \int \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^{T} exp\left(\frac{-E_a}{RT}\right) dt \quad (3)$$

2.3. Study of the Emission of the Total Volatile Organic Compounds

The next stage of the research was to determine the emission of the total volatile organic compounds from the pine wood and sewage sludge torrefaction process. The dried sample, weighing about 2 g, was placed on a quartz boat, and then the prepared vessel was placed in the PR-45/1350 M electric furnace for 1 h [61]. The tests were carried out at temperatures of 285, 325, and 525 °C. The torrefaction process was carried out in the presence of CO_2, the flow rate of which was 1 L/min. Each trial was repeated 3 times to verify the results provided. The course of the emission of total volatile organic compounds over time was measured continuously during the heating of the sample. A stationary JUM FID 3-500 analyzer was used to determine the emissions. Figure 3 shows a diagram of the installation for conducting VOC total emission tests.

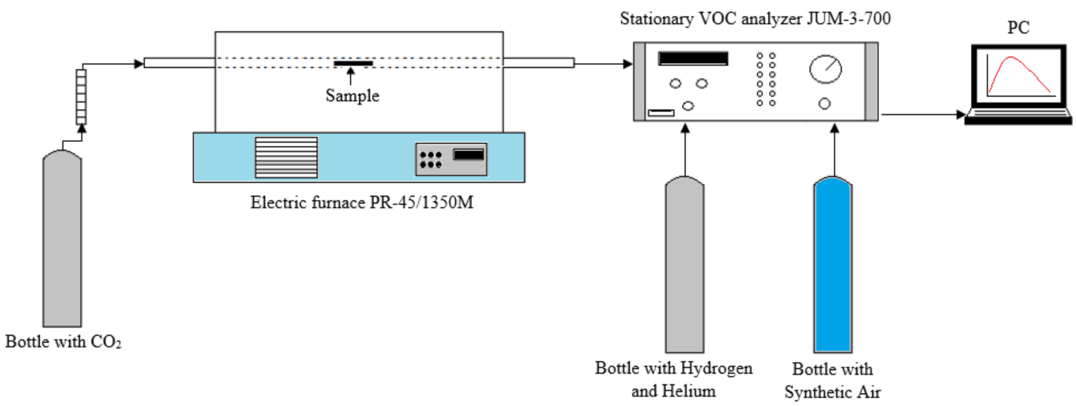

Figure 3. Diagram of an installation for determining the emissions of total volatile organic compounds.

Based on the results of the emission of the sum of VOCs over time and the emission factor was calculated, which defines the amount of pollutants emitted in relation to the amount of fuel undergoing the process.

$$w_{VOC} = \frac{Q_{CO_2} \cdot \frac{1}{\tau_p} \int_0^t c(\tau)dt \cdot \tau_p}{m} \quad (4)$$

where: Q_{CO_2}—carbon dioxide flow rate (m^3/s); τ_p—torrefaction time (s), c—average concentration of volatile organic compounds (mg/m^3); m—sample weight (g).

2.4. Determination of the Heat of Combustion Value of the Obtained Torrefaction

The combustion heat value of the obtained torrefied pine wood and sewage sludge was measured using the Parr 6400 calorimeter. The analysis consisted in burning a given sample in an oxygen atmosphere. From the obtained torrefied material, samples weighing about 1 g were weighed and then placed into a tablet. The prepared samples were placed in crucibles and then in a calorimetric bomb to start the measurement. Figure 4 shows a diagram of the apparatus.

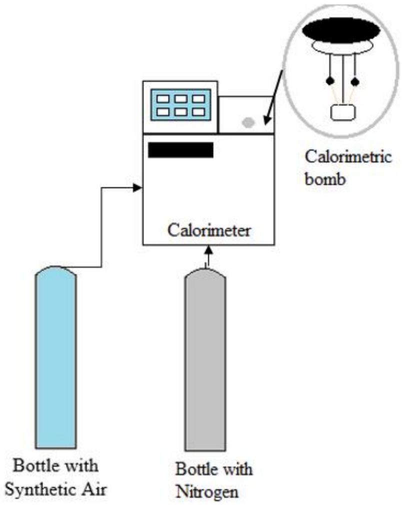

Figure 4. Installation diagram for determining the heat of combustion value.

3. Results

3.1. Thermogravimetric Analysis

An example of a thermogravimetric analysis graph for pine wood was shown at Figure 5. The results presented relate to the process carried out at a temperature of 525 °C, with a heating rate of 20 K/min and a residence time of 8 min. As can be seen in the first stage of the process, drying, the greatest loss of mass was recorded, amounting to approximately 96%. At a later stage of the process, during the torrefaction process, the weight loss was about 28%.

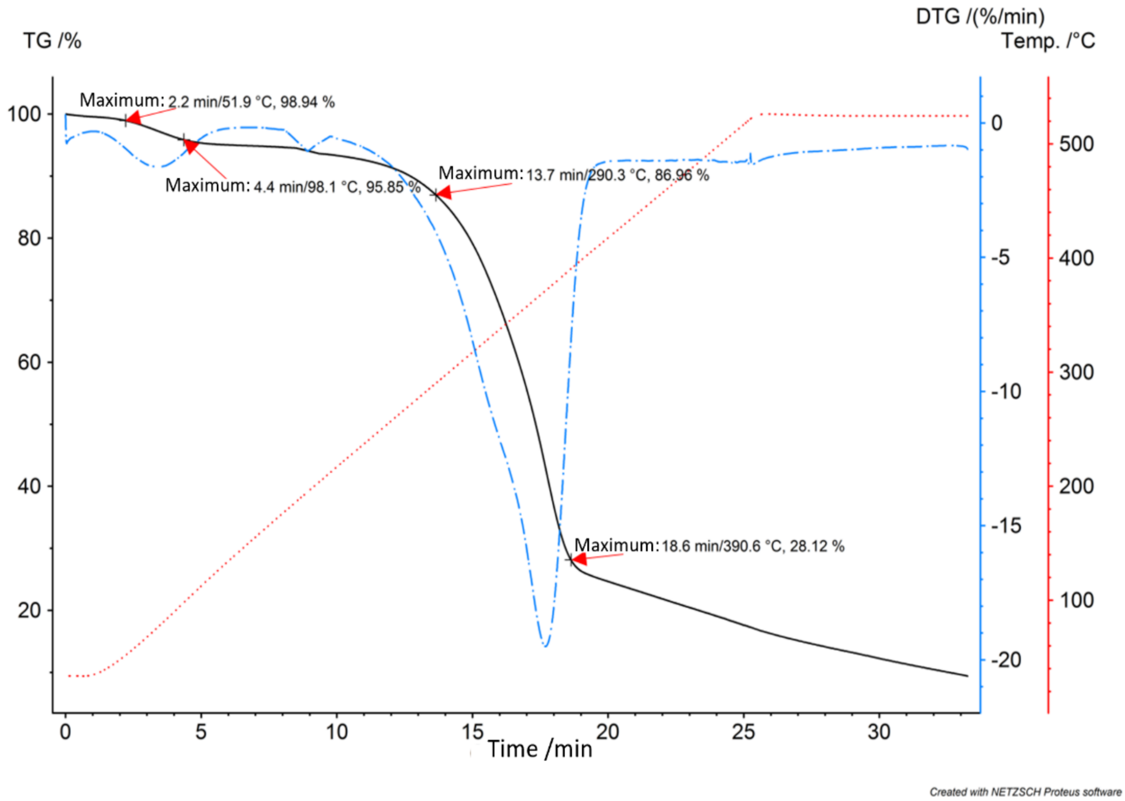

Figure 5. TGA analysis of pine wood and maximum mass loss determination.

Figures 6 and 7 show the changes in the weight of the pine wood and sewage sludge with respect to the temperature and duration of the torrefaction process resulting from changes in the chemical structure, water loss, and degassing of the material. Increases in temperature were linked to significantly higher mass loss in the sewage sludge. In addition to parameters such as combustion temperature and residence time, the heating rate was examined. Figure 6 shows the results of the pine wood weight loss for the thermogravimetric analysis conducted at a heating ratio of 5–10–20 K/min.

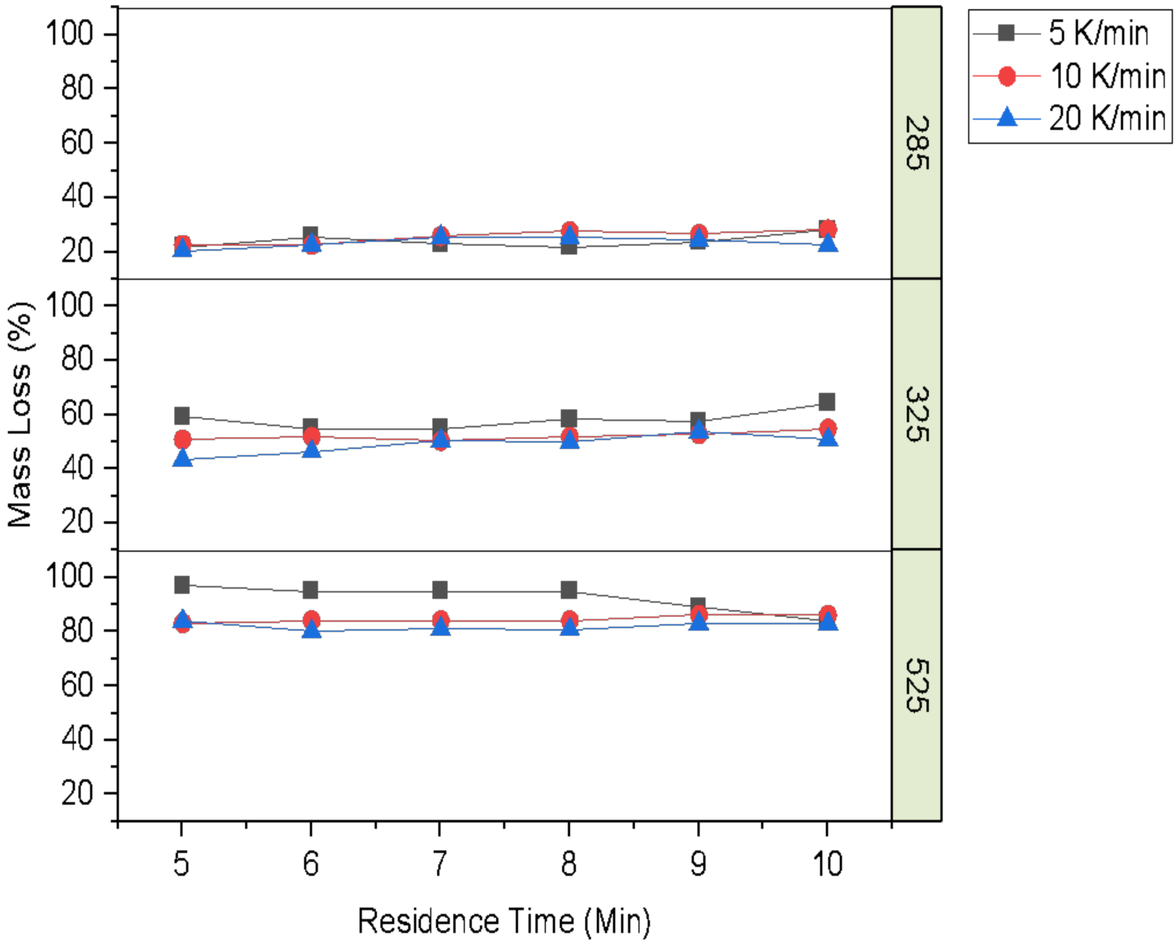

Figure 6. Mass losses during thermogravimetric analysis of pine wood.

At a heating speed of 5 K/min, the highest weight loss, 84–97%, was recorded at the temperature of 525 °C. The longer the sample remains at this temperature, the smaller the weight loss. At 285 °C, the weight loss was 22–26%. The longer the sample residence time was, the greater the weight loss was recorded. At 325 °C, the weight loss was 55–64%. At the heating speed of 10 K/min at the temperature of 525 °C, the weight losses were significantly lower than in the case of the heating ratio of 5 K/min and amounted to 83–86%. Lower weight losses were also noted at 325 °C, 51–54%. At 285 °C, the lowest weight losses were observed, which amounted to 22–28%. The last heating ratio used during the tests was 20 K/min. At 285 °C, the weight loss was 20–25%. At a temperature of 325 °C, this value increased to 43–54%, and at a temperature of 525 °C from 80–84%.

Figure 7 shows the results of the weight loss of sewage sludge for the thermogravimetric analysis conducted at a heating ratio of 5–10–20 K/min.

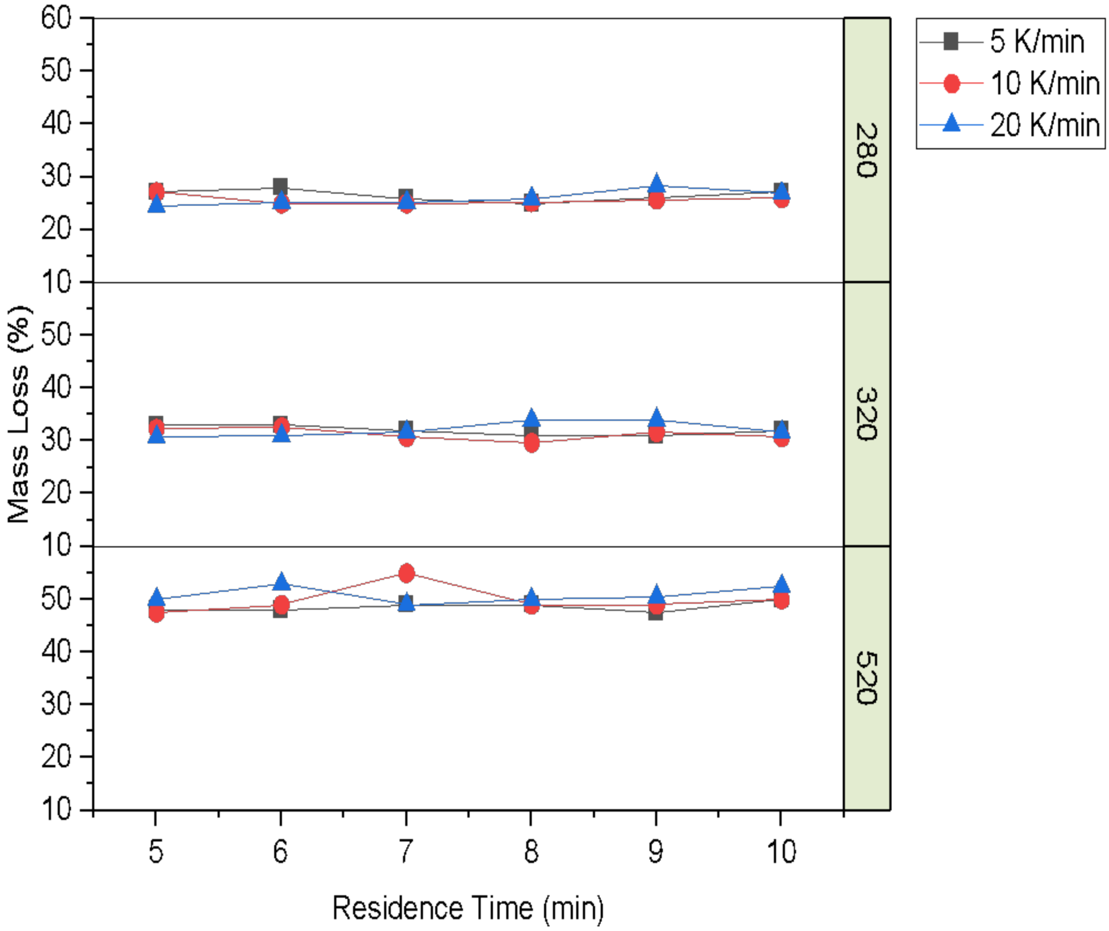

Figure 7. Mass losses during thermogravimetric analysis of sewage sludge at different temperatures.

At the maximum temperature of 520 °C, the mass loss was observed in a range of 47–50% with a heating rate of 5 K/min. Minimum and maximum mass losses were found to be 16 and 55% with respect to the lower and higher working temperatures at a 10 K/min rate. Average mass loss during the 10 K/min heating rate was found to be higher than 5 K/min. Minimum and maximum mass losses were found as 17 and 56% at 20 K/min heating rate. In the case of sewage sludge, the lowest weight loss was achieved during the process at a heating speed of 10 K/min, a residence time of 5 min, and a temperature of 280 °C. Figure 8 indicates the sewage sludge mass loss during thermogravimetric analysis at every 10 °C point in the scale 250–520 °C.

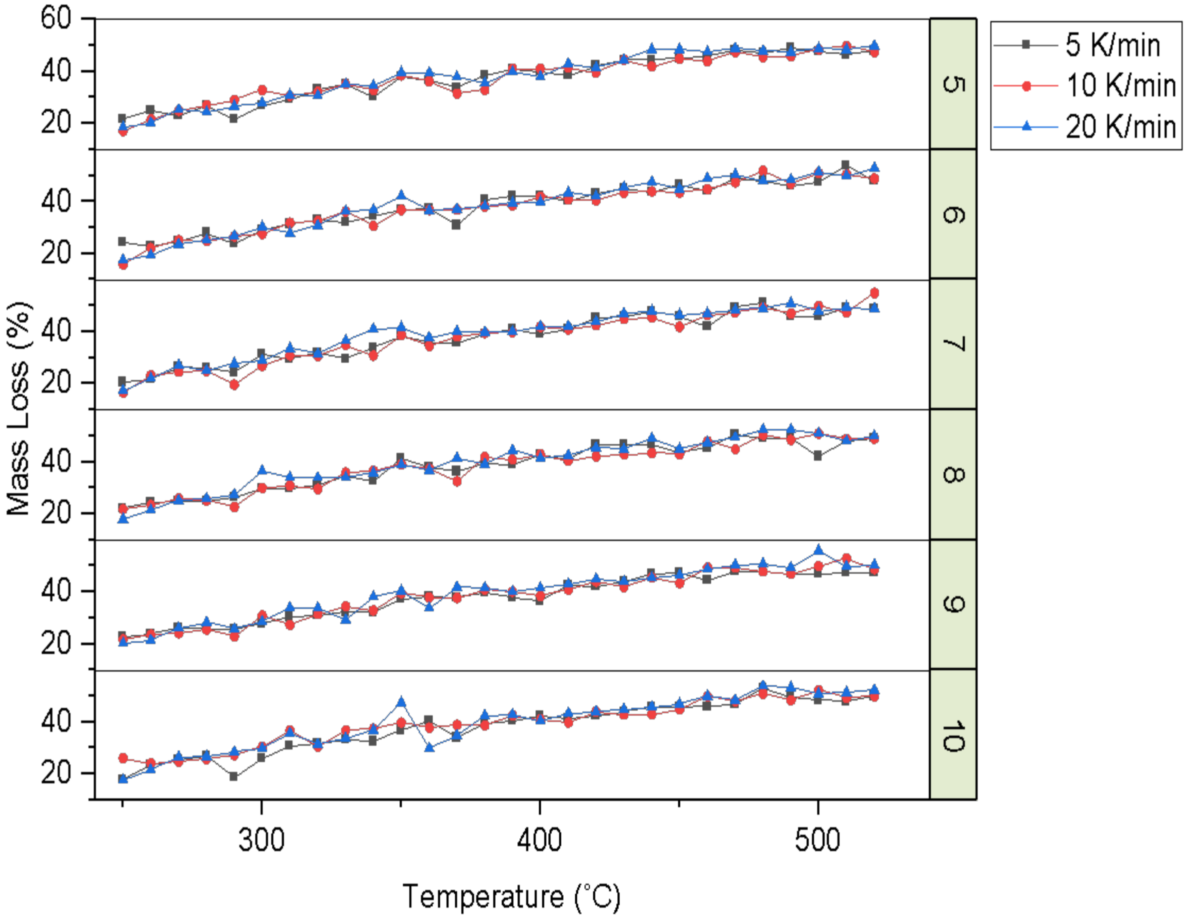

Figure 8. Mass losses of sewage sludge at several temperatures of 250–500 °C, residential time and heating ratios.

A 37–41% mass loss was found at 350 °C and an 18–24% mass loss was observed at 350 °C. The results show the residence time does not have not as much effect on mass loss as temperature. Desired mass loss, 30%, was reached at 300 °C and further. Over 480 °C, 50% mass loss was observed.

3.2. Kinetic Analysis

A kinetic study of the pine wood and sewage sludge torrefaction process was performed based on the findings of thermogravimetric measurements with the use of three different heating rates, 5–10–20 K/min. The sample weighed 10 ± 1 mg where temperatures ranging from 200 to 500 °C were used for the kinetic analysis. Figures 9 and 10 show the TG curves of the sewage sludge torrefaction process for three different rates in a temperature range from 200 to 500 °C.

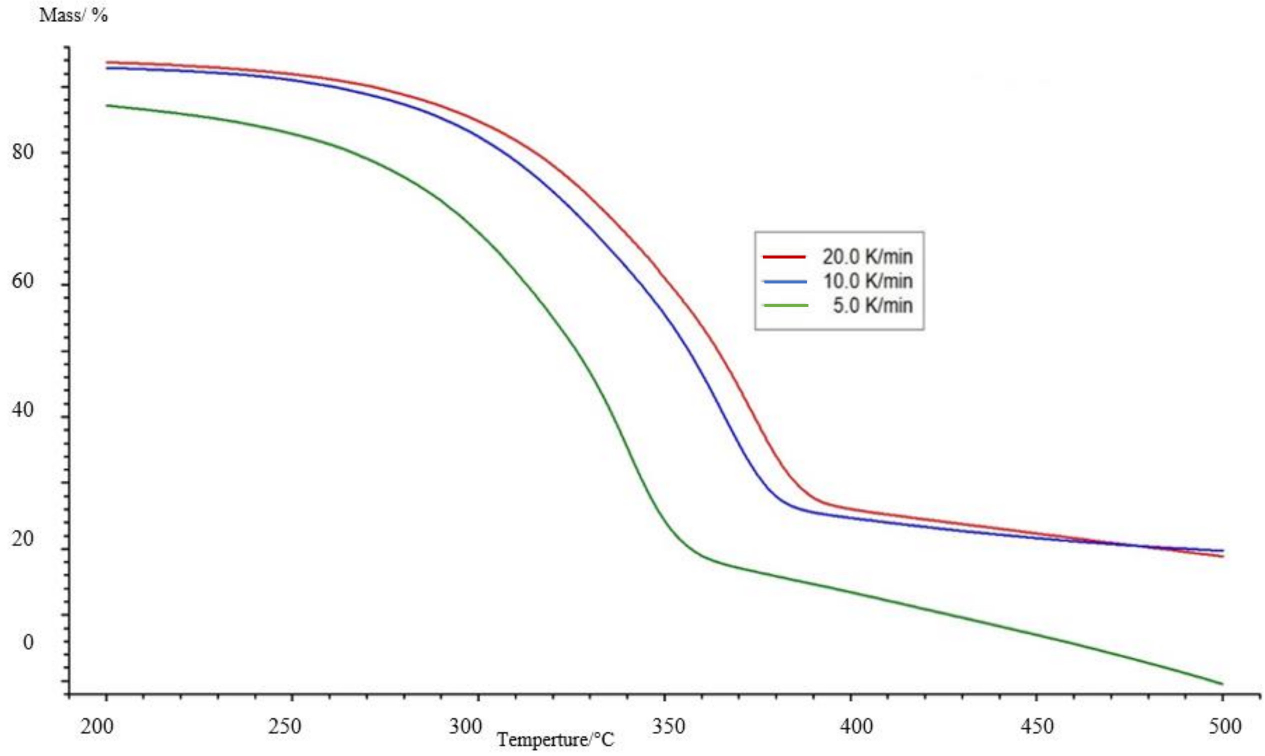

Figure 9. TG curves for three heating rates for pine wood.

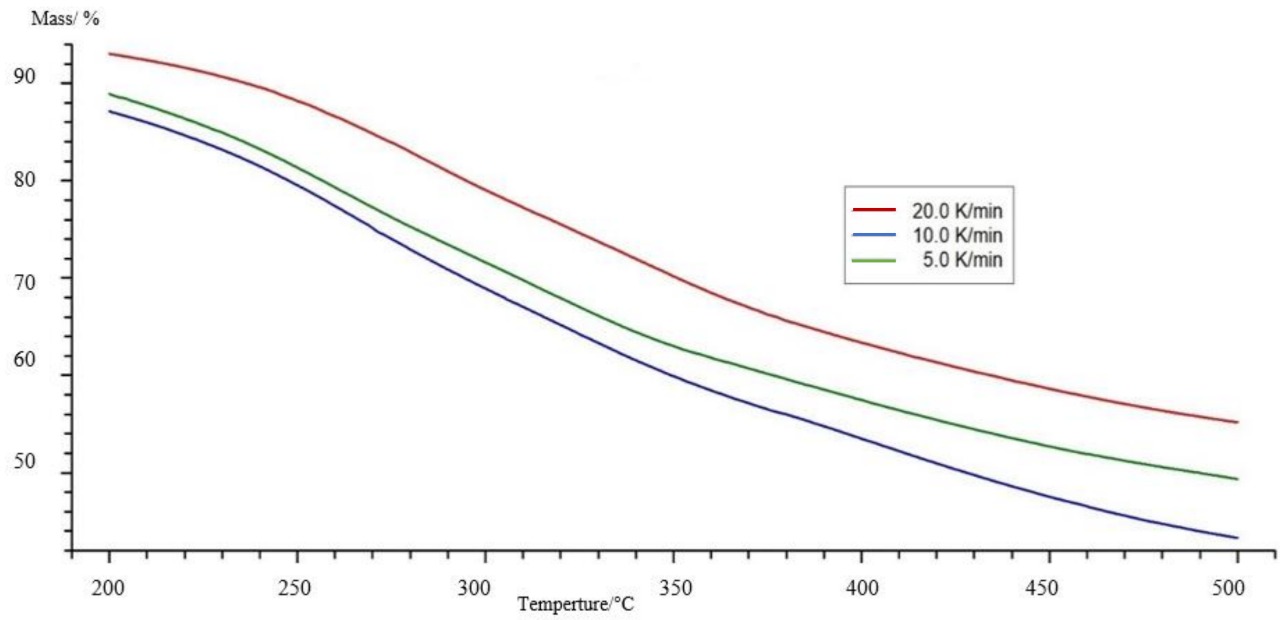

Figure 10. TG curves for three heating rates for sewage sludge.

The determination of the kinetics of the reactions occurring during the torrefaction process began with isoconversion analyses, which allowed the activation energy to be calculated without knowing the reaction model. The first used was the Kissinger analysis method according to ASTM E698, which is based on the assumption that the maximum of a one-step reaction is reached with the same degree of conversion regardless of the heating rate. The activation energy of a solid's thermal decomposition may be estimated using this approach. Its result is a plot of the logarithm of the sample heating speed as a function of the reciprocal of the temperature at the moment when the mass loss rate is the highest. The results are presented in Figures A1 and A2 in Appendix A. Then, the Friedman analysis was performed, which consists of determining the logarithm of the conversion as a function of the reciprocal of temperature. The results of the analysis are presented in Figures A3 and A4. The next method that was used to determine the kinetics of the reaction was the Ozawa-Flynn-Wall method. Thanks to this method, the logarithm dx/dt was plotted as a function of the reciprocal of temperature and, despite the lack of knowledge of the reaction mechanisms at this stage, the activation energy and the pre-exponential coefficient were calculated for each conversion stage. Figures 11 and 12 show the results of the analysis both for pine wood and sewage sludge.

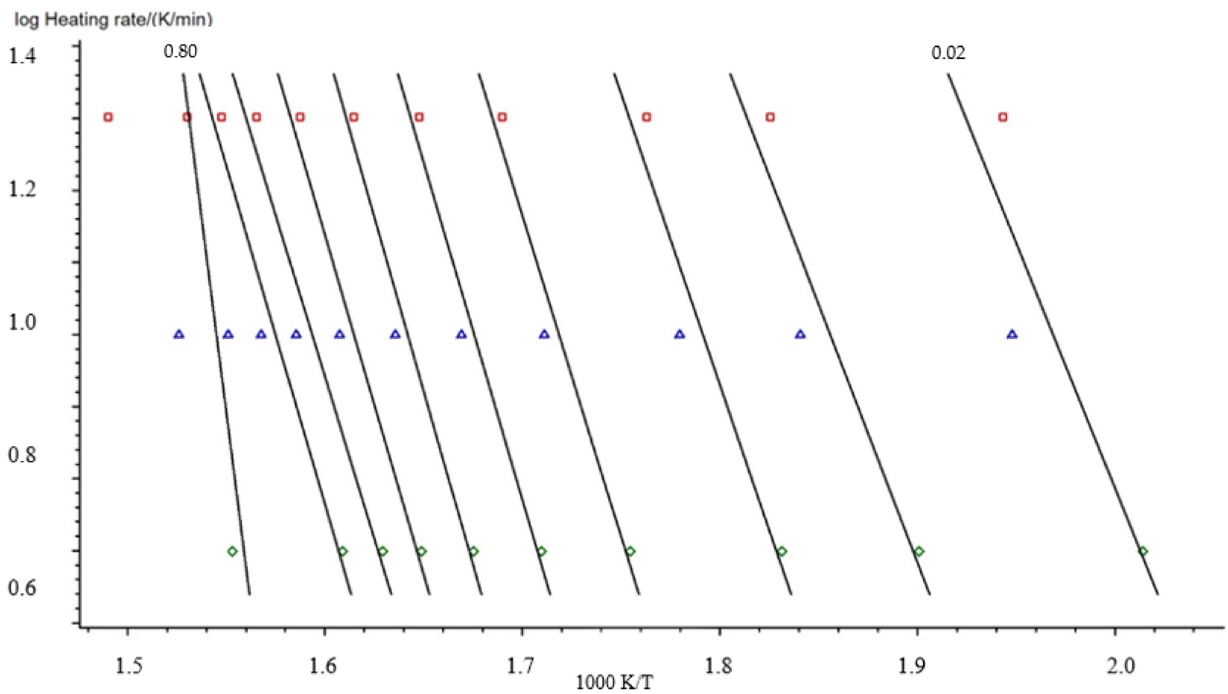

Figure 11. Plot of logarithm dx/dt as a function of the reciprocal of temperature for the Ozawa–Flynn–Wall method for pine wood. Symbols are representing, heating rates, Red: 20K/min, Blue: 10 K/min and Green: 5 K/min.

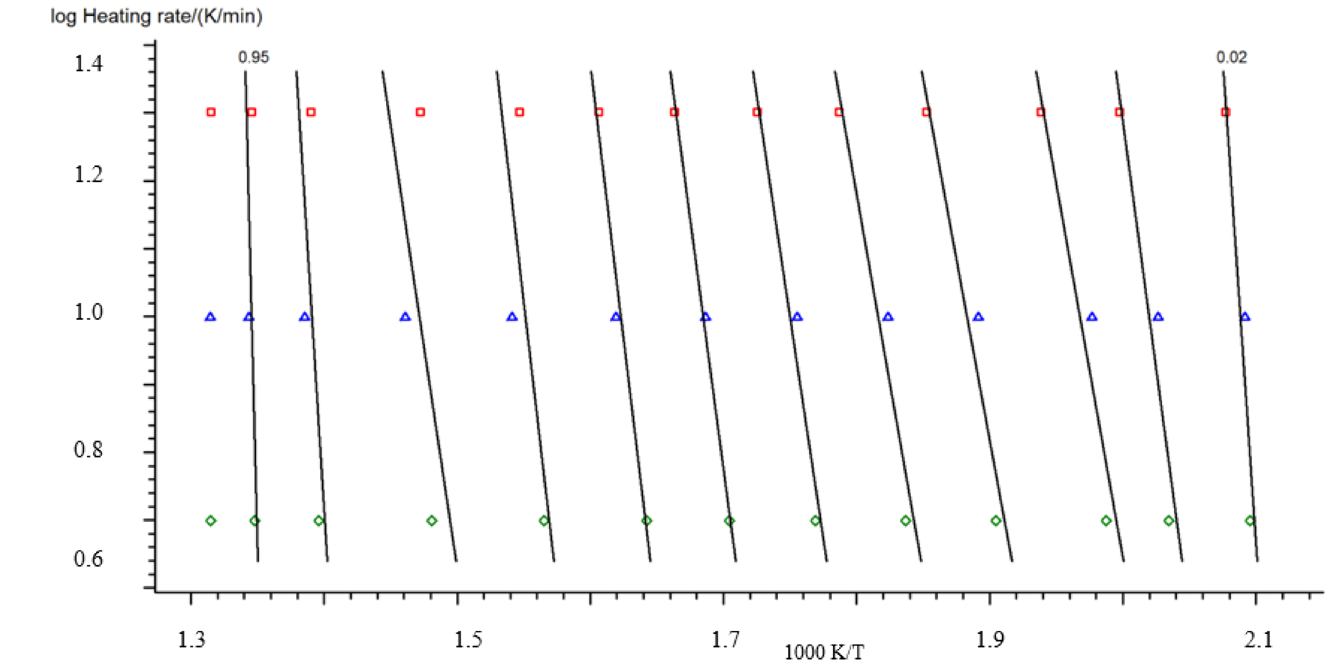

Figure 12. Plot of logarithm dx/dt as a function of the reciprocal of temperature for the Ozawa–Flynn–Wall method for sewage sludge. Red: 20K/min, Blue: 10 K/min and Green: 5 K/min.

The analysis by the Ozawa–Flynn–Wall method allowed the value of the pre-exponential coefficient and the activation energy as a function of the conversion degree to be presented. The results of the analysis are presented in Figures 13 and 14.

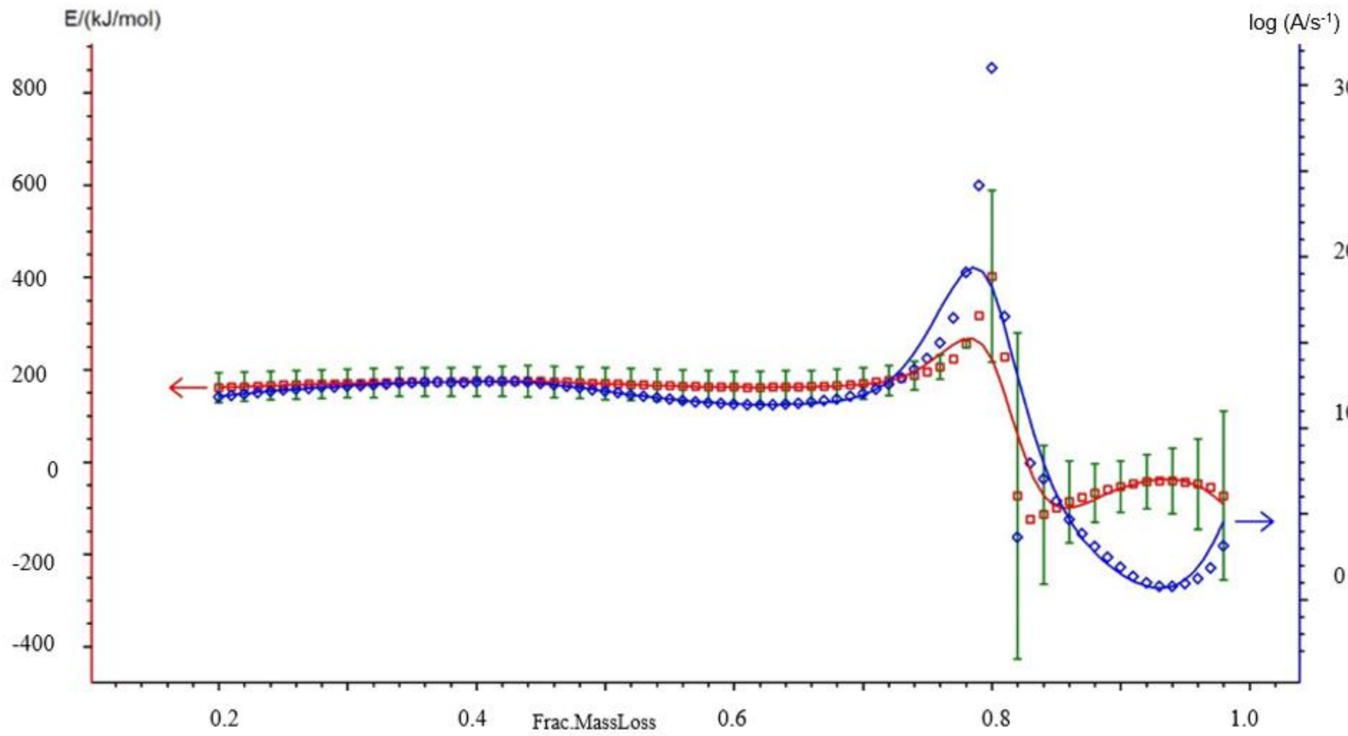

Figure 13. Activation energy (Red color) and pre-exponential coefficient (Blue color) as a function of the degree of conversion determined by the Ozawa—Flynn–Wall method for pine wood. Green color represents the statistical error.

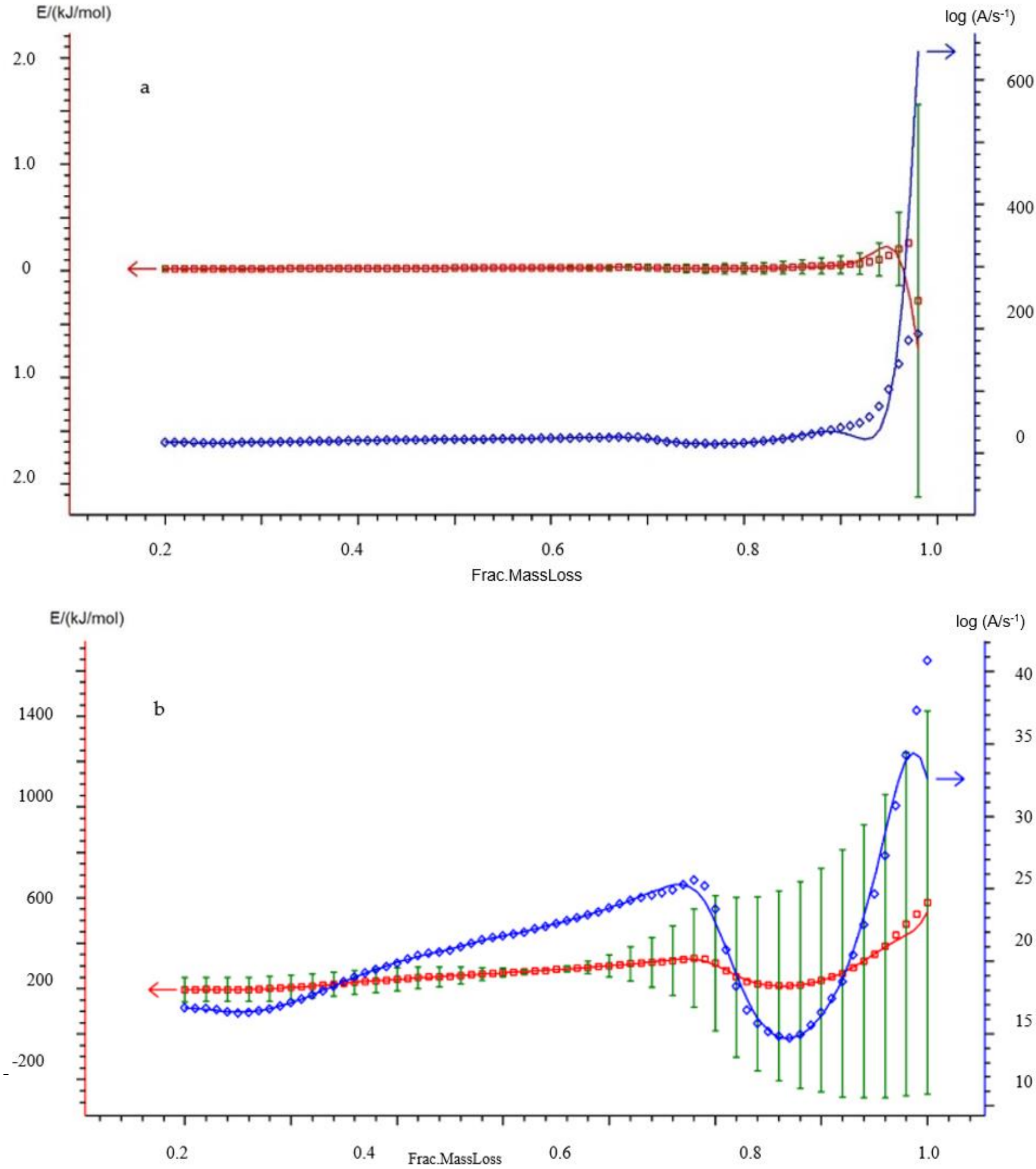

Figure 14. Activation energy (Red color) and pre-exponential coefficient (Blue color) as a function of the conversion degree: (**a**) X = 0.20–0.98, (**b**) X = 0.20–0.90 determined by the Ozawa–Flynn–Wall method for sewage sludge. Green color represents the statistical error.

To better illustrate the results, the above data are presented below in Tables 1 and 2 for both biomasses.

Table 1. Activation energy and pre-exponential coefficient as a function of the degree of reaction determined by the Ozawa–Flynn–Wall method for pine wood.

Fract. Mass Loss	Activation Energy (kJ/mol)	Log (A/s^{-1})
0.020	121.96 ± 61.15	8.85
0.050	128.18 ± 44.82	9.11
0.100	145.76 ± 42.65	10.66
0.200	161.46 ± 32.56	11.85
0.300	170.33 ± 31.30	12.46
0.400	174.80 ± 31.49	12.70
0.500	170.09 ± 34.58	12.16
0.600	162.39 ± 35.23	11.42
0.700	170.42 ± 34.12	12.05
0.800	402.87 ± 186.36	31.02

Table 2. Activation energy and pre-exponential coefficient as a function of the degree of reaction determined by the Ozawa–Flynn–Wall method for sewage sludge.

Fract. Mass Loss	Activation Energy (kJ/mol)	Log (A/s^{-1})
0.020	542.50 ± 172.09	56.16
0.050	270.33 ± 88.04	25.58
0.100	203.17 ± 64.57	18.12
0.200	195.84 ± 53.70	16.77
0.300	205.04 ± 53.72	17.15
0.400	240.66 ± 50.48	19.89
0.500	269.49 ± 19.16	21.76
0.600	300.83 ± 48.94	23.68
0.700	312.47 ± 297.92	23.59
0.800	237.36 ± 492.84	16.48

Similarly to the Friedman method, the activation energy value shows a significant variability from about 120 to 400 kJ/mol. This confirms that the pyrolysis of pine wood samples consists of a series of overlapping reactions. For the case of pine wood analyzed, it is assumed that the pyrolysis process is carried out in one stage. The kinetic equation transforms into a thermo-kinetic equation in dynamic circumstances. Using the Kinetics 3 program, an attempt has been made to mathematically adjust one of the models of the thermal breakdown reaction based on the TG curves acquired as a function of temperature. After taking into account the assumed reaction model, the kinetic parameters of the reaction were determined, meaning the constant pre-exponential coefficient, as well as the activation energy and the matching coefficient. The most accurate fit against the experimental data for the pine wood sample was obtained for the n-order reaction model for n = 2.9. For such a match, the value of the correlation coefficient was 0.9945, the activation energy was 158.65 kJ/mol and the pre-exponential coefficient was 11.61. The results of the model fit are presented in Figure 15 for pine wood. As in the case of kinetic parameters determined by the Friedman method, their great variability is noticeable. We observe an increase in the values of parameters determined for both low and high conversion rates. It should be noted that for the degree of conversion above 0.9, the activation energy values and errors in its estimation assume absurd values. This may indicate the imperfection of the computational methodology as we approach the boundary conditions and the complexity of changes taking place in the sewage sludge in the considered temperature range. The best fit to the experimental data for the sewage sludge sample was obtained for the n^{th} order reaction model for n = 4.98. The correlation coefficient R^2 was 0.9885, the activation energy was 122.74 kJ/mol, and the pre-exponential coefficient (ln A) was 9.42. Figure 16 shows the adjustment of the equation with the calculated coefficients to the experimental data for sewage sludge.

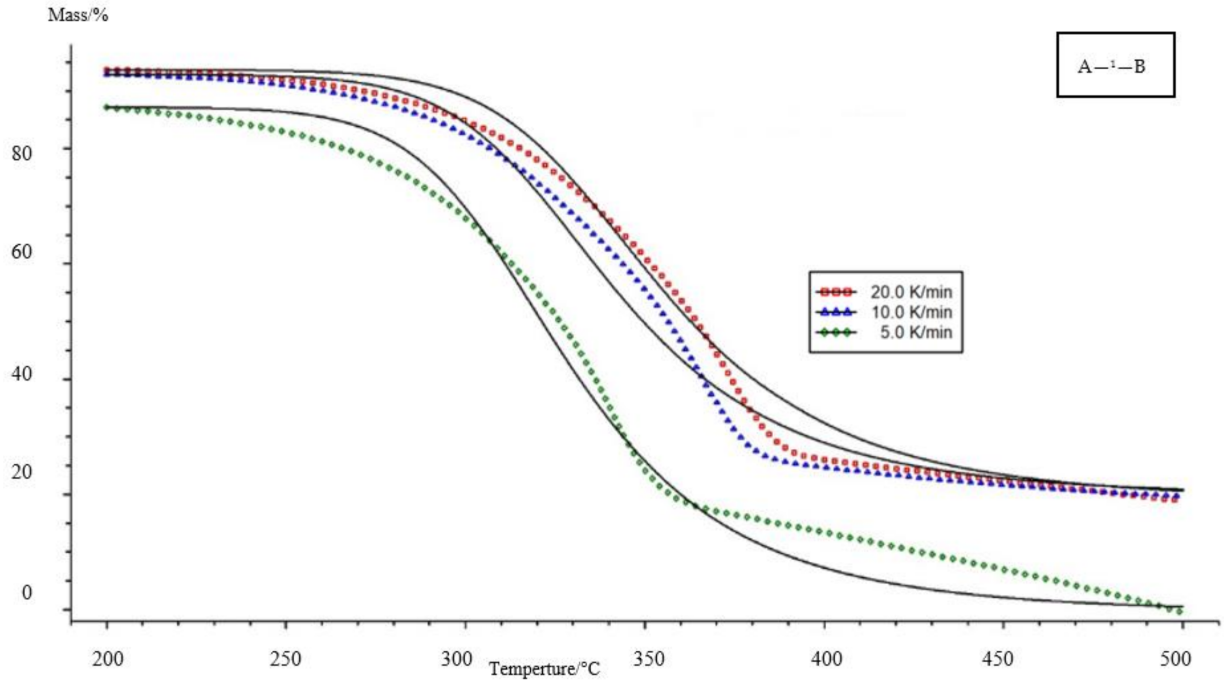

Figure 15. Fitting the calculated kinetic model for pine wood to the experimental data.

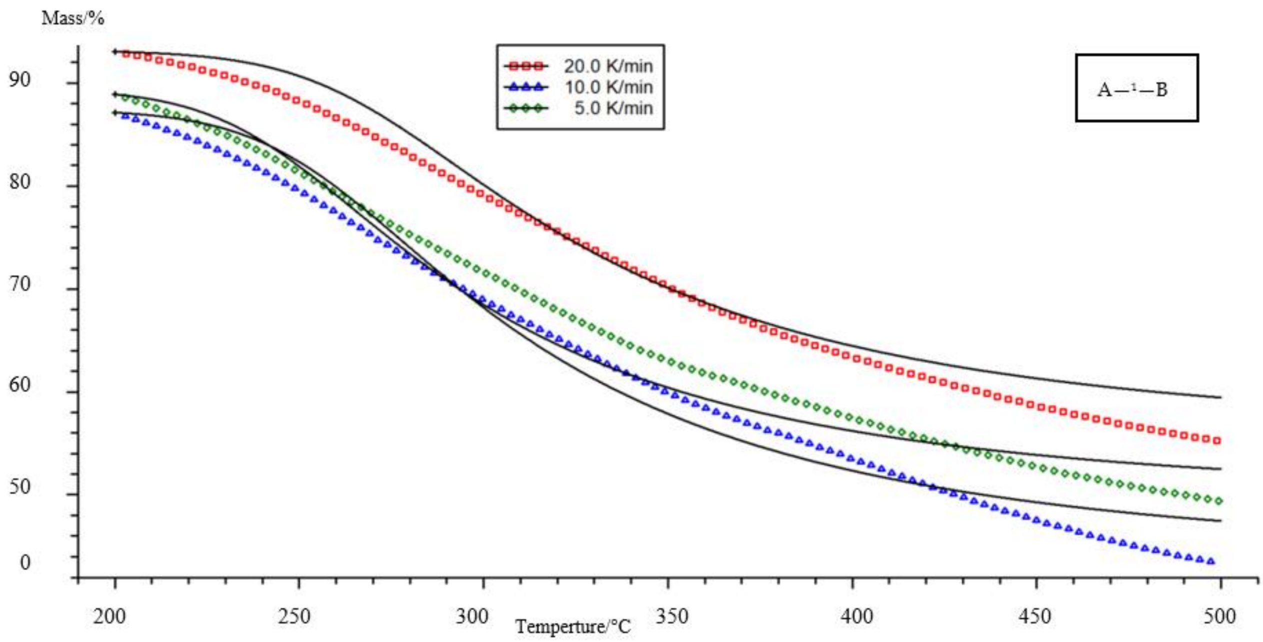

Figure 16. Fitting the calculated kinetic model for sewage sludge to the experimental data.

It should be noted that the calculated triplet (n, E_a, ln A) represents just the optimal mathematical fit of the equation to the experimental data, and in this case it has no strict physical meaning (reaction order). This method of calculating activation energy is obvious: it merely serves to correlate the model with experimental data and has no relevance as a definition. The research results presented refer only to research biomass pine wood and sewage sludge.

3.3. Study of the Emission of the Sum of Volatile Organic Compounds

The next stage of the research was to determine the emission of the total volatile organic compounds from the process. The analysis conducted provided data on the course of emission of the total VOC over time, thanks to which the pollutant emission index from the process was calculated. Figure 17 shows the course of emissions of the total VOC over time at 285 °C.

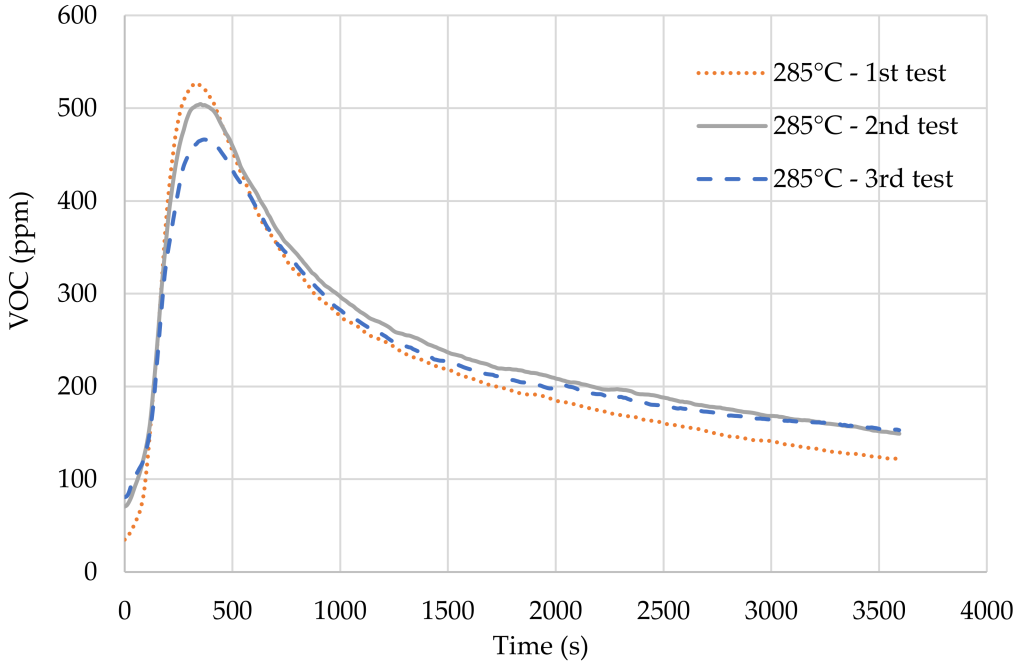

Figure 17. Time course of VOC total emission at 285 °C.

During the process at 285 °C, the maximum emission was reached in 342 s and was about 525 ppm. At the temperature of 325 °C, this value increased to about 1100 ppm, and at the temperature of 525 °C to 8200 ppm. Based on these results, the emission factor was calculated in accordance with formula (4). The results are shown in Figure 18.

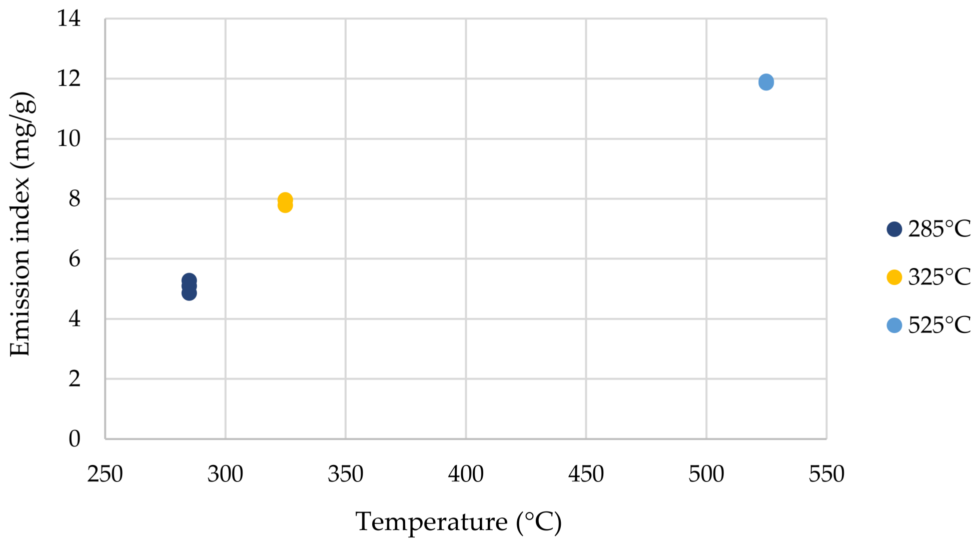

Figure 18. Values of the determined VOC total emission factor.

The highest value of the emission index was achieved at the highest temperature of the process, and it was about 12 mg/g. For a temperature of 285 °C the value was about 5 mg/g and for 325 °C it was about 8 mg/g.

3.4. Determination of the Heat of Combustion Value of the Obtained Torrefaction Products

The combustion heat of the pine wood torrefacts obtained was measured using a Parr model 6400 calorimeter. Table 3 shows the results obtained.

Table 3. Determined values of the heat of combustion of the obtained torrefaction products.

Biomass Type	Moisture, [%]	C^{ad}, [%]	N^{ad}, [%]	H^{ad}, [%]	S^{ad}, [%]	Cl, [%]	$Volatile^{ad}$ [%]	Ash [%]	Heat of Combustion, [MJ/kg]
Pine wood	7.7	42.3	0.63	5.61	0.07	0.115	82.4	4.2	18.19
Torrefied Pine Wood									
(285 °C, 10 min)	6.42	51.15	0.67	6.14	0.03	0.014	72.36	4.64	21.72
(325 °C, 7 min)	2.83	53.24	0.23	5.62	0.03	0.013	70.13	6.97	27.48
(525 °C, 5 min)	1.39	57.29	0.15	3.47	0.04	0.012	37.23	10.12	31.48
Sewage Sludge	7.8	31.10	4.46	5.87	0.09	0.01	59.8	40.5	13.24
Torrefied Sewage Sludge:									
(280 °C, 9 min)	3.8	31.4	4.47	5.23	0.01	0.009	27.4	72.5	3.68
(320 °C, 6 min)	2.2	32.60	4.29	4.61	0.01	0.01	25.25	74.32	3.44
(520 °C, 5 min)	2.0	26.35	3.25	2.42	0.01	0.01	23.43	77.65	3.29

The Higher Heating Value (HHV) of the raw biomass was found to be 18.1898 MJ/kg at the ambient temperature. When heat of 525 °C was applied, the calorific value of the sawdust increased by 73% compared to raw biomass. Even though there was no actual difference in calorific value between 20 and 285 °C, there was an obvious increase between 285 and 325 °C. One possible reason may be due to the high content of essential oils in the pine wood sample, which decomposes at temperatures above 300 °C.

4. Discussion

This work is based on an attempt to optimize the most effective parameters for solid biofuels production and biochar as a carrier for fertilizers in the torrefaction process. Different residence time and heating rate results show that there are no significant changes in mass loss for both pine wood and sewage sludge, unlike temperature. At the lowest temperature, the mass loss of sewage sludge was found higher from pinewood. The reason may be that lignocellulosic structure of pine wood is more thermally stable than non-lignocellulosic biomass. When the temperature was increased to 325 °C, the differences reached 20% and for 525 °C, the mass loss of PW reached 97%, whereas for SS it was only 55%. This can be explained by the fact that the ash content of sewage sludge is much higher than pine wood. Nguyen et al. (2020) also mention that non-fibrous structures such as sewage sludge have less thermal resistance, while the fibrous structure of lignocellulosic biomass degradation requires a much longer time to reach the same percentages of mass loss [57]. The volatile substance of PW was much higher than that of SS, while the ash content of SS was much higher than that of PW. Nwabunwanne et al. (2021) found that sewage sludge torrefaction temperatures should not exceed 300 °C because of the unwanted high ash amount. In addition, they have proved that a thermally pretreated sewage sludge torrefaction process leads to the achievement of more stable solid biofuel with less ash amount [62]. While pine wood has 65–72% volatile matter, sewage sludge has around 50% wt [63,64]. Huang et al. (2016) found very similar results in their work with leucaena and the sewage sludge torrefaction process [65,66]. Summarizing the above results, it can be noted that the torrefaction process is complex. The process conditions, such as temperature, residence time, and heating speed, should be selected in such a way as to obtain the lowest possible loss of mass in the shortest possible time. In both cases of pine wood and sewage sludge, the lowest weight losses were achieved during the process at a heating speed of 20 K/min, a residence time of 5 min, and a temperature of 285 °C.

The Effect of the Torrefaction Residence Time

The TGA analysis of pine wood and sewage sludges revealed that torrefaction process temperatures over 320 °C resulted in lower mass yields and energy. Effects of the torrefaction process residence time were investigated for temperatures under 525 °C. In Figures 6–8 we can see correlation between the effects of the woody biomass and sewage sludge torrefaction residential time on the physico-chemical characteristics of pine wood and sewage sludge torrefaction. It can be observed that the effect of torrefaction residence time on volatile matter and ash content was not as significant as the influence of biomass torrefaction process temperature. In Figures 6–8 we can observe that when the residence time of torrefaction increases, the mass yield decreases. Above observations can be described by the effect of reduction in the water and volatile content of the woody biomass and sewage sludges. In addition, at the beginning there was a significant mass loss of the sewage sludge torrefaction process, while the change in mass yield was not as significant with a longer torrefaction residence time. The results can be explained by the fact that more reactive components decompose at the beginning of the torrefaction. It was also observed that the mass yield decreases with the torrefaction residence time. It can be concluded from Figure 8 that the mass loss increases with a longer torrefaction time. Nevertheless, in all previous investigations, the pine wood and sewage sludges torrefaction residential time has been presented to be less meaningful than the temperature.

5. Conclusions

This work was focused on two different biomass torrefaction processes. The first one (which is the most common in Polish forests) concerns pine wood from the lodzkie voivodship forests and the second sewage sludge from the Group Sewage Treatment Plant of the Łódź Urban Agglomeration. In this article, the authors mainly investigated the impact on the biomass of torrefaction temperature, mass loss, moisture content, HHV, and VOC emission during the torrefaction process. In addition, the authors quantified various parameters of the pine wood torrefaction process and sewage sludge to be used as carbonized solid biofuels and as an additive for fertilizers. A kinetic analysis was conducted, and the proper temperature for the carbonization process and residence time for specific mass loss ratios were determined.

As a result of this research, it was found that from a mass loss ratio and economical perspective, the most optimal torrefaction temperatures for pine wood and sewage sludge to produce biochar, which can be a carrier for biofertilizers, lie between 325 and 350 °C. However, the temperatures can be changeable in practice based on the type of raw material, amount of heating ratio, and also the chemical structure of the untreated material. In a further investigation, torgas can be utilized as a heat source for the carbonization process due to the high quantities of volatile organic compounds in the tracks. The variability of the activation energy value depending on the degree of conversion probably indicates that the reactions of pine wood pyrolysis are not homogeneous but rather consist of many overlapping and parallel thermo-chemical processes. This can also have an influence on the bio-economy since an appropriate mass loss ratio to energy loss for diverse woody biomass during the carbonization process has a substantial impact on the pricing of torrefied solid biofuel and biochar as fertilizer price carriers (the use of under or over heat throughout the process has a major influence on the final product pricing).

In the near future, further work will be concentrated on the pine wood and sewage sludge torrefaction process. This first phase of research work shows which temperatures for pine wood and for sewage sludges are the best to obtain mass loss in a range of 50% compared to untreated substrates and kinetics which were necessary for apparatus design (biomass counter-flow torrefaction reactor). From our previous studies and from economical calculations (costs of bicarbon production at industrial scale for C additives production for fertilizers) we know that 50% is the most reasonable mass loss to produce still relatively cheap bio-product which can be use by companies which are producing biofertilizers. From biomass torrefaction temperature limitations and again from our previous collaboration with agro-engineers, and from their conducted toxicity test we know that biomass should be thermally treated in the temperature range close to 320–350 °C to neutralize toxic substances.

The major task will comprise the design and construction of an installation for a continuous drying and superheated steam torrefaction process using kinetics data from this article. Which includes the design of a biomass dryer run on hot air as well as a torrefaction reactor run on dry steam (superheated steam). As the novelty of this work in the winter of 2021, a new installation will be built including a counter-flow torrefaction reactor with superheated steam torrefaction, and experimental research will be carried out on the conditions of the torrefaction process of woody and agricultural biomass mix with digested solid residues DGS to produce carbonized solid biofuels such as biocarbon as a carrier for organic fertilizers, with data from this study [67–69].

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds of dry and torrefied pine wood and sewage sludges are available from the authors.

Appendix A

Figures A1 and A2 present data analysis for the Kissinger method (ASTM E698).

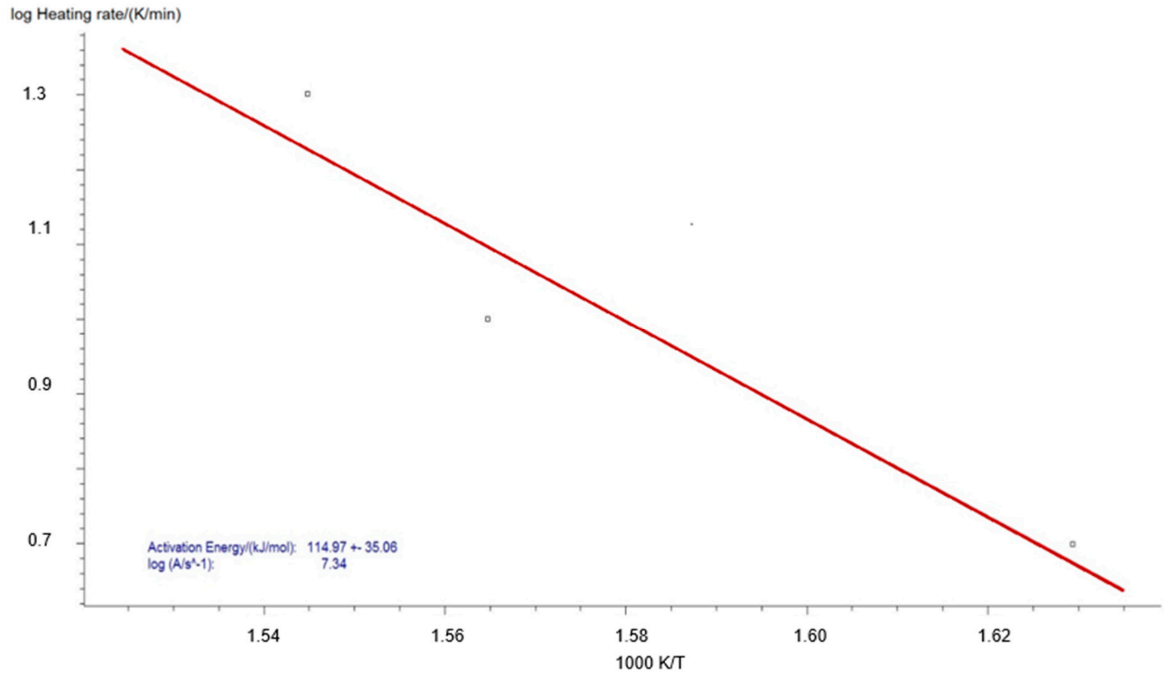


Figure A1. Kissinger analysis (ASTM E698) for pine wood.

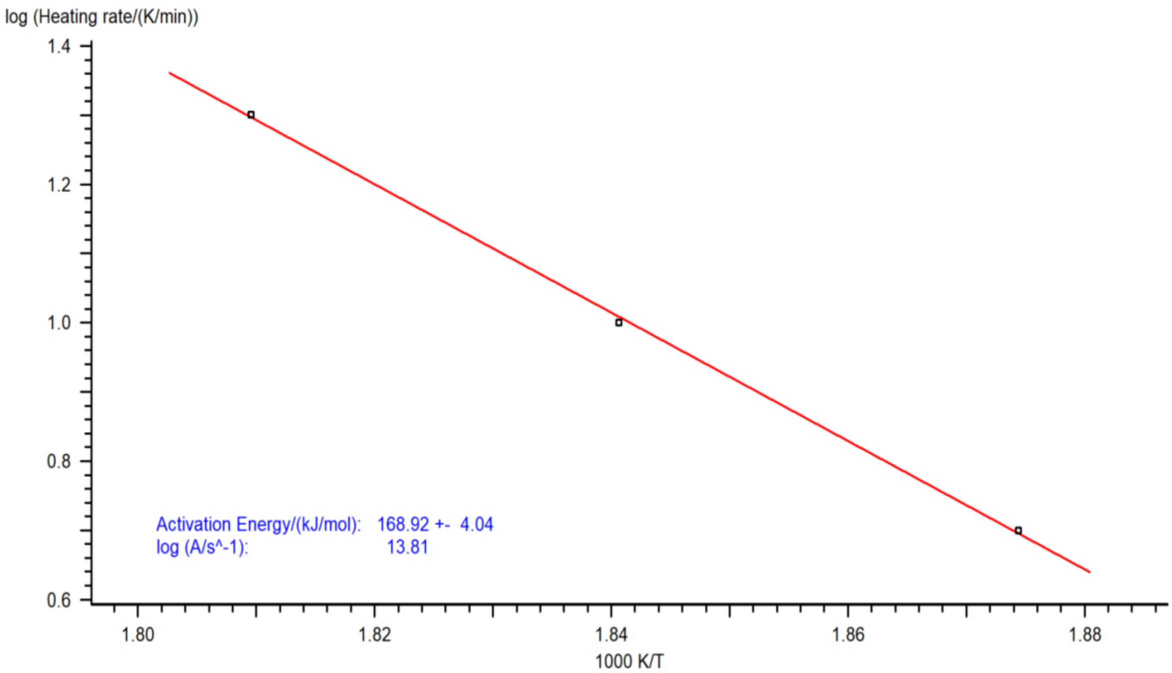


Figure A2. Kissinger analysis (ASTM E698) for sewage sludge.

Thanks to the use of the above-mentioned method, the activation energy value of the pine wood pyrolysis process was obtained, which was 115 kJ/mol. However, attention should be paid to the very high relative error of this method, which is about 35 kJ/mol, about 30% of the activation energy value. The obtained value of the activation energy of the sewage sludge torrefaction process was approximately 169 kJ/mol with an error of

4.04 kJ/mol. Figure A3 and A4 represents Friedman method for both biomass pine wood and sewage sludge for 3 different heating rate. Red line represents 20 K/min, blue line is 10 K/min and green line is 5 K/min.

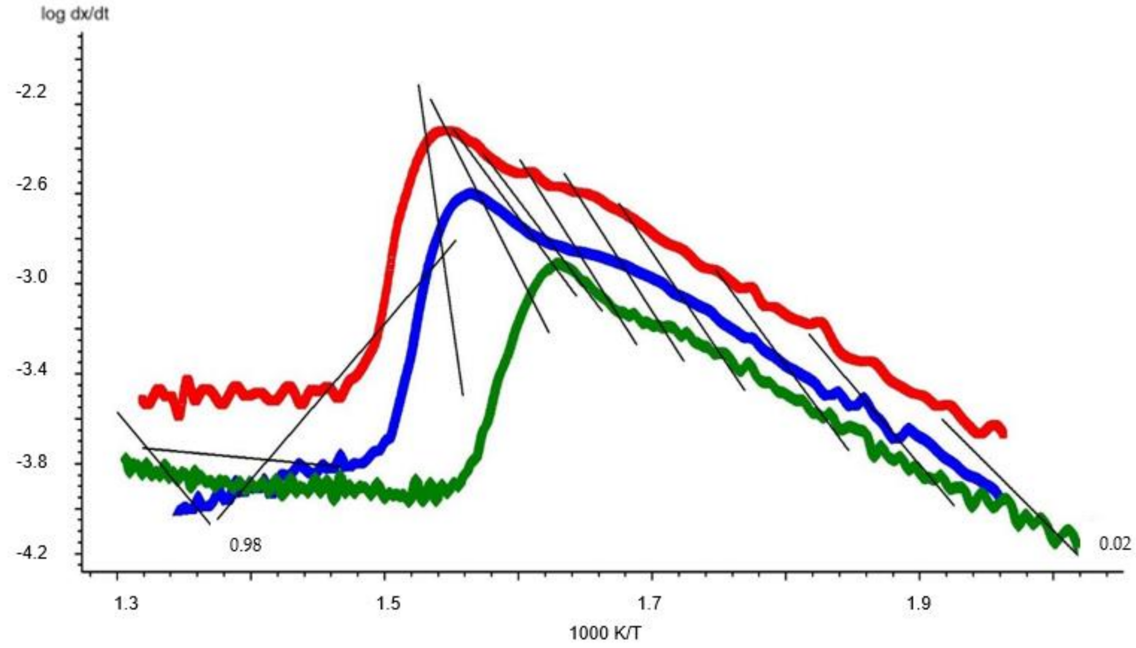


Figure A3. Plot of logarithm dx/dt as a function of reciprocal of temperature by Friedman method for pine wood. Red line represents 20 K/min, blue line is 10 K/min and green line is 5 K/min.

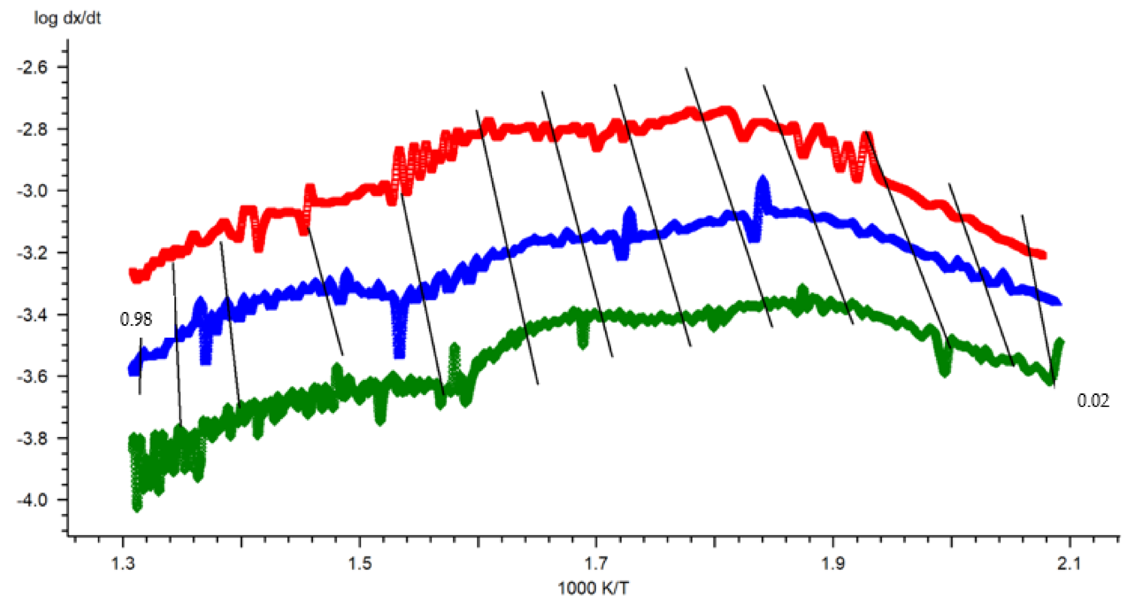


Figure A4. Plot of logarithm dx/dt as a function of reciprocal of temperature by Friedman method for sewage sludge. Red line represents 20 K/min, blue line is 10 K/min and green line is 5 K/min.

Thanks to the Friedman method, it is also possible to present the values of the activation energy and the pre-exponential coefficient as a function of the degree of conversion, as shown in Figures A5 and A6.

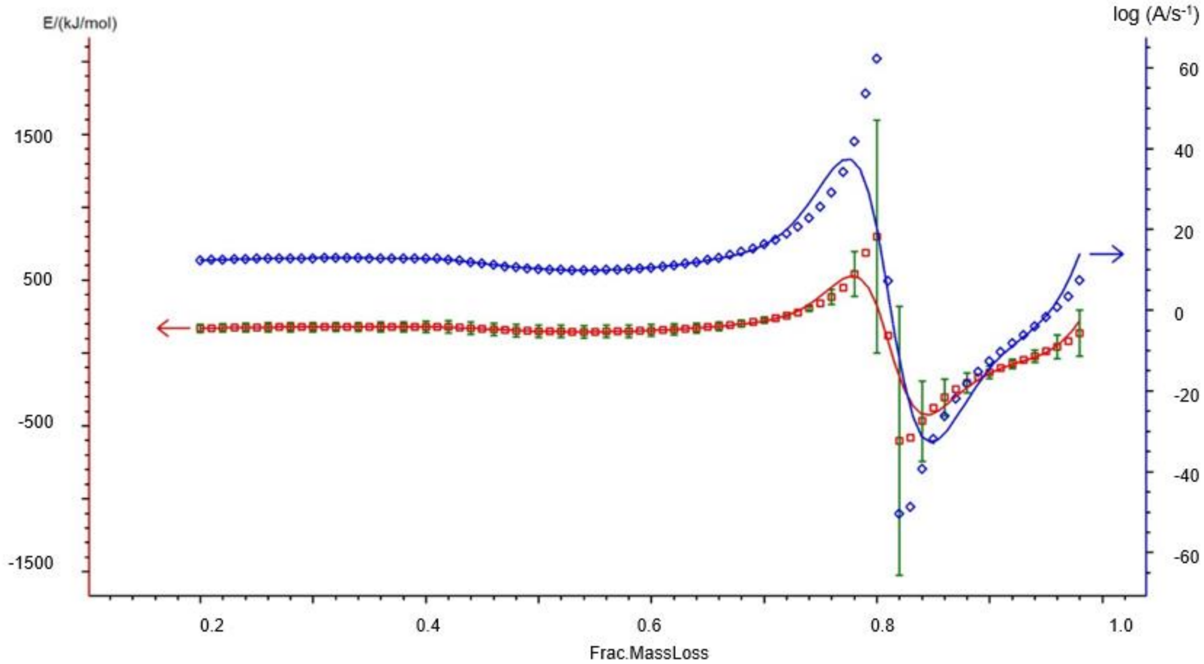
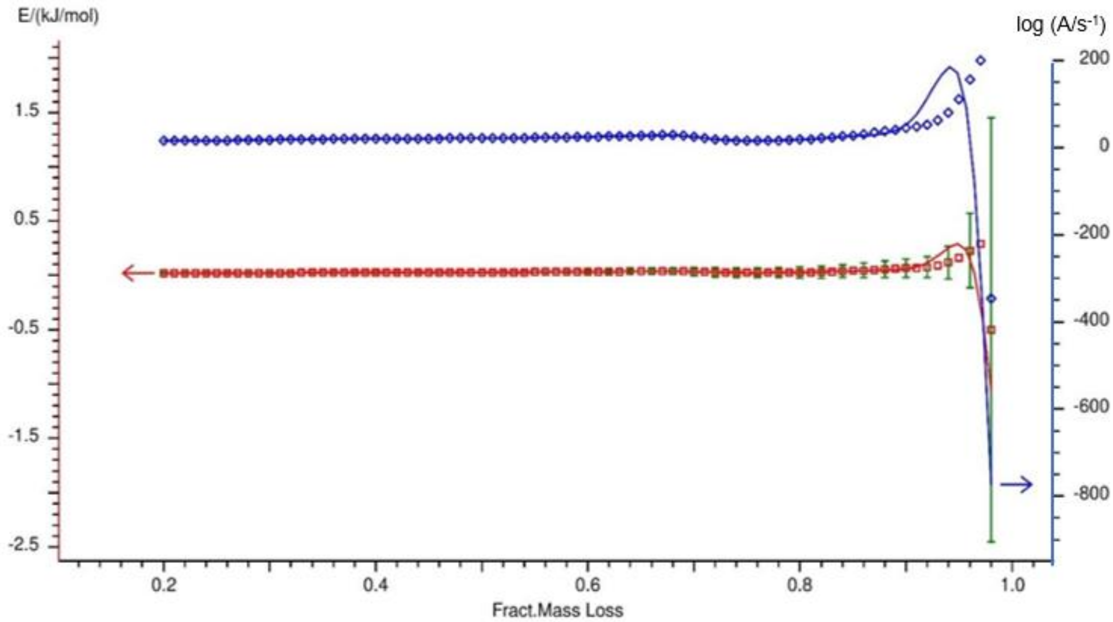
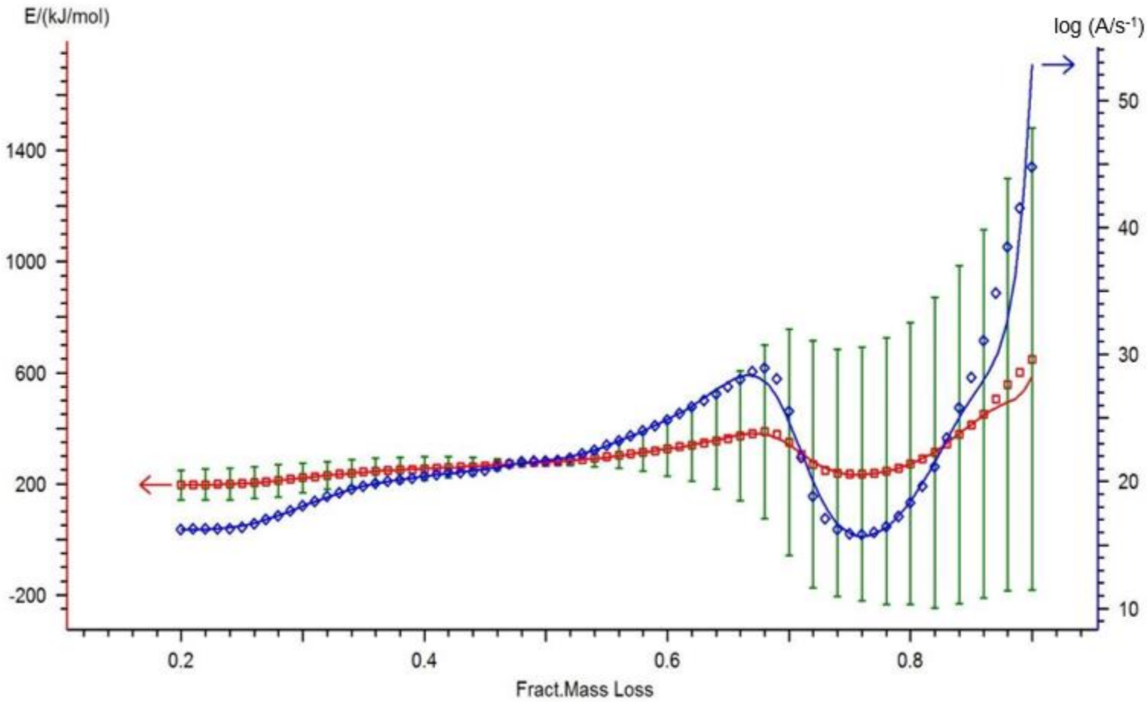


Figure A5. Activation energy (Red color) and pre-exponential coefficient (Blue color) as a function of the degree of reaction determined by the Friedman method for pine wood. Green color represents the statistical error.



(**a**)

Figure A6. *Cont.*



(**b**)

Figure A6. Activation energy (Red color) and pre-exponential coefficient (Blue color) as a function of the conversion degree: (**a**) X = 0.20–0.98, (**b**) X = 0.20–0.90 determined by the Friedman method for sewage sludge. Green color represents the statistical error.

On the basis of Figures A5 and A6, it can be concluded that the activation energy for the pine wood and sewage sludge samples varies depending on the degree of conversion. The variability of the activation energy value as a function of the degree of reaction may indicate the fact that the pyrolysis reaction of pine wood is not homogeneous and consists of many overlapping and parallel processes of thermal decomposition of individual biomass components. The exact values of the determined activation energy are presented in Tables A1 and A2.

Table A1. Activation energy and pre-exponential coefficient as a function of the degree of reaction determined by the Friedman method for pine wood.

Fract. Mass Loss	Activation Energy (kJ/mol)	Log (A/s^{-1})
0.020	113.71 ± 57.16	7.79
0.050	134.47 ± 43.26	9.56
0.100	154.97 ± 36.97	11.25
0.200	169.96 ± 27.86	12.33
0.300	178.59 ± 31.70	12.89
0.400	179.87 ± 39.00	12.82
0.500	150.14 ± 42.32	10.22
0.600	154.05 ± 40.74	10.57
0.700	224.25 ± 15.23	16.32
0.800	799.80 ± 798.45	62.31

Table A2. Activation energy and pre-exponential coefficient as a function of the degree of reaction determined by the Friedman method for sewage sludge.

Fract. Mass Loss	Activation Energy (kJ/mol)	Log (A/s^{-1})
0.020	378.99 ± 216.09	37.70
0.050	208.04 ± 83.17	18.76
0.100	188.15 ± 60.14	16.18
0.200	195.43 ± 53.66	16.23
0.300	221.23 ± 53.10	18.07
0.400	254.79 ± 42.46	20.40
0.500	277.71 ± 4.05	21.62
0.600	325.90 ± 97.57	24.87
0.700	349.52 ± 407.02	25.55
0.800	272.76 ± 507.67	18.33

An analysis of Figure A6 and the data in Table A2 shows that the variability of the determined kinetic parameters (E and A) depending on the degree of reaction is noticeable. Very high variability and accompanying errors are observed when approaching the boundary conditions, that is for low and high values of the conversion degree ($X < 0.1$ and $X > 0.9$). These fluctuations result in part from the methodology of determining kinetic parameters. On the other hand, they are a consequence of the complex course of the torrefaction process for material such as sewage sludge.

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