Simultaneous Thermal Analysis of Norway Spruce Wood Pellets with Digestate Additive: A DSC and TGA Study

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Wood pellets represent one of the most important solid biofuels produced from renewable lignocellulosic biomass, yet the thermal behaviour of pellets containing alternative additives such as digestate from biogas plants remains insufficiently characterised. This study provides a dataset from simultaneous differential scanning calorimetry and thermogravimetric analysis for four wood pellet samples: three commercial Norway spruce pellets of different geographical origin and quality classes, and one experimental sample prepared as a one-to-one mass mixture of spruce sawdust and solid digestate from an agricultural biogas plant. Measurements were performed in an oxidative atmosphere from 30 to 700 degrees Celsius at a heating rate of 20 degrees Celsius per minute. The three commercial pellets exhibited consistent thermal behaviour, with decomposition onset temperatures falling within narrow ranges. The experimental sample showed substantially different behaviour, including a downward shift in the decomposition onset temperatures of hemicellulose and cellulose by 23 and 41 degrees Celsius, respectively, an elevated endothermic peak temperature consistent with stronger moisture binding, and a residual mass of 10 percent, which was six to ten times higher than that of the commercial pellets. These findings document that incorporating digestate fundamentally alters the thermal behaviour of wood pellets.

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INTRODUCTION

In recent decades, wood pellets have established themselves as one of the most important solid fuels produced from renewable biomass, owing primarily to their high energy density, standardised shape, low combustion emissions, and the possibility of automated combustion in modern boilers used in residential heating, industrial facilities, and combined heat and power generation (Grønli *et al.* 2002; Skreiberg *et al.* 2011; Guo *et al.* 2015). The European Commission has included them among the key components of the strategic energy policy guiding the transition to renewable sources, which has resulted in growing demand for pellets within the European Union, including Slovakia. In Slovakia, pellets are produced predominantly from the sawdust of Norway spruce (*Picea abies*), which represents the dominant wood species in the forestry and wood-processing industries (Kistler *et al.* 2012).

Alongside the growth in pellet production, interest is also increasing in their combination with non-traditional additives that could broaden the range of valorisable

biomass feedstocks. One of the promising additives is solid digestate (the separated fraction obtained after anaerobic fermentation) from biogas plants, which represents a by-product of the agricultural and municipal fermentation of organic material. The use of digestate in pellets has been analysed by several authors (Kratzeisen *et al.* 2010; Cathcart *et al.* 2021; Czekała 2021), showing that digestate improves the economics of pelletisation and enables the circular utilisation of residual materials. Beyond these economic and circular economy considerations, the incorporation of digestate can also influence the physical and mechanical quality of the pellets. Because solid digestate is rich in proteins and other nitrogen organic compounds, it may act as a natural binder that promotes inter-particle bonding and can improve pellet hardness and mechanical durability during handling, transport and storage (Kratzeisen *et al.* 2010; Czekała 2021). This mechanical benefit, together with the nutrient value of the residual material means that adding digestate particularly at low proportions may remain attractive despite its higher ash content. At the same time, however, digestate alters the chemical and physical nature of the fuel, substantially increasing the content of inorganic components (ash), polar nitrogen-containing groups, and alkali metals, which can fundamentally affect the thermal behaviour of pellets during heating and combustion and may also adversely affect combustion equipment.

Wood pellets containing digestate additives have not yet been sufficiently characterised by thermoanalytical methods. Existing studies have largely focused on standard ENplus A1 or A2 class pellets and their energy potential, whereas systematic data on the thermal degradation of pellets with digestate additives in an oxidative atmosphere remain limited. Yet it is precisely the experimental data obtained from DSC and TGA that are needed. The decomposition temperatures of hemicellulose, cellulose, and lignin, the enthalpies of the reactions, and the content of inorganic residue that constitute an essential input for the design of combustion equipment. The data are needed for the assessment of the efficiency of these fuels, and the evaluation of their combustion behaviour. These performance attributes are expected to influence the potential applications of the modified pellets, including from a safety perspective. Without these data, it is not possible to responsibly assess the safety, efficiency, and environmental impacts of the combustion of alternative pellet formulations. The importance of experimental data further increases when they are systematically aggregated into publicly available materials databases, such as the Phyllis2 database maintained by the Netherlands Organisation for Applied Scientific Research (ECN.TNO 2022), which provide reference values for the comparison of fuel formulations and serve as input for the numerical modelling of combustion processes and the kinetics of thermal decomposition. When combined with spatial analyses in a geographic information system (GIS) environment, characterisation data on individual pellet formulations can significantly contribute to the identification of suitable local sources of biomass and digestate, the optimisation of the siting of pelletisation lines, and the quantification of supply-chain sustainability at the regional level (Einarsson and Persson 2017).

In this context, it is important to note that the characterisation of the thermal behaviour of a fuel forms part of a broader system for ensuring the reliability and resilience of energy infrastructure, in which every alternative energy source must be properly tested and validated before being introduced into routine operation (Rehak *et al.* 2019). In the field of fire safety, the testing of materials under the influence of heat is considered a fundamental tool for the quantification of risk during storage and handling, whether it concerns conventional structural materials, protective equipment (Kubás *et al.* 2024), or

fuels. For wood pellets, the ignition temperature and the flash point are routinely determined in accordance with ISO 871, which employs the Setchkin furnace and provides rapid and comparable data on the reactivity of samples. In a previous study, these parameters were determined for the same set of Norway spruce pellet samples and experimental pellets containing digestate (Bóna *et al.* 2025), where it was found that the addition of digestate increases the ignition temperature (from 420 to 450 °C) and at the same time alters the activation energy of combustion. However, these results describe the behaviour of pellets only within a short heating time window at a specific temperature and do not provide detailed information on the sequence of thermal processes that take place prior to ignition itself.

It is precisely this gap in the knowledge of thermal characteristics that can be filled by simultaneous thermal analysis, combining differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), which makes it possible to quantify, in a single experiment, the heat flow, mass changes, characteristic decomposition temperatures, and reaction enthalpies over a wide temperature range (Magdziarz *et al.* 2017). DSC provides information on endothermic processes (moisture evaporation, phase transitions) and exothermic processes (decomposition and oxidation reactions), whereas TGA quantifies mass losses in the individual stages of thermal degradation of the lignocellulosic complex (Grønli *et al.* 2002; Vyazovkin *et al.* 2014). For samples containing mineral additives, DSC and TGA additionally make it possible to identify the catalytic effects of alkali metals, which accelerate the decomposition of polysaccharides and shift the temperatures of maximum decomposition towards lower values (Di Blasi *et al.* 2009; Wang *et al.* 2022).

The aim of this study was therefore to provide a comprehensive set of DSC and TGA data for four wood pellet samples, comprising commercial Norway spruce pellets of ENplus A1 class from Slovakia, commercial Norway spruce pellets of ENplus A2 class from Slovakia, commercial Norway spruce pellets of ENplus A1 class from Ukraine, and experimental pellets prepared from a mixture of spruce sawdust and digestate from a biogas plant in a mass ratio of 1:1. This corresponds to a digestate content of 50 wt%, well above the loadings at which digestate is typically employed as a minor additive. In the present formulation the digestate therefore acts as a co-substrate rather than an additive. The spruce raw material used to prepare the experimental sample ISE originated from the same source as the commercial A2 spruce pellets (ISA2). Sample ISA2 therefore serves as the digestate-free spruce reference for the experimental formulation. The parameters investigated were the decomposition temperatures of hemicellulose and cellulose, the enthalpies of the endothermic and exothermic reactions, the content of inorganic residue, and the comparison of thermal behaviour. The data obtained build upon the previous characterisation of the same set of samples in terms of ignition temperature and flash point (Bóna *et al.* 2025) and provide a complementary picture of the thermal decomposition of pellets, which is essential for the responsible assessment of their applicability.

EXPERIMENTAL

Materials

Four wood pellet samples were investigated in this study, comprising three commercially available pellets and one experimental formulation. The samples were selected to enable comparison of two ENplus quality grades (A1 *vs.* A2) of the same wood species, spruce pellets sourced from different geographical origins, and the effect of a high

digestate content on the thermal behaviour of spruce pellets. Sample identifiers, descriptions, and origins are summarised in Table 1.

The three commercial samples (BSA1, ISA2, DSUA1) were obtained directly from manufacturers and a retailer operating in the Žilina Region, Slovakia. All commercial samples consisted of cylindrical pellets with a nominal diameter of 6 mm and a length of 10 to 40 mm, produced by pelletisation from sawdust and wood shavings, in accordance with ISO 17225-2 (2021). The experimental sample (ISE) was prepared by a local Slovak producer as a 1:1 mixture of Norway spruce sawdust (*Picea abies*) and solid digestate from a local agricultural biogas plant, the latter contributing nitrogen-rich organic residues commonly proposed as a slow-release fertilizer carrier. No additional binders or chemical additives were declared by the producer.

All samples were stored in sealed polyethylene bags at laboratory conditions (20 ± 2 °C, relative humidity 45 ± 5%) until analysis. Prior to thermal analysis, pellets were ground in a laboratory mill to a particle size below 0.5 mm and subsequently homogenised; no further drying or chemical pretreatment was applied, in order to preserve the in-use moisture state of the pellets. ISA2 represents the digestate-free spruce counterpart of the experimental sample ISE, both deriving from the same spruce raw material.

Table 1. Wood Pellet Samples Used in This Study

Symbol	Material	Class	Country of origin
ISE	Spruce/Digestate	Experimental	Slovakia
BSA1	Spruce	A1	Slovakia
DSUA1	Spruce	A1	Ukraine
ISA2	Spruce	A2	Slovakia

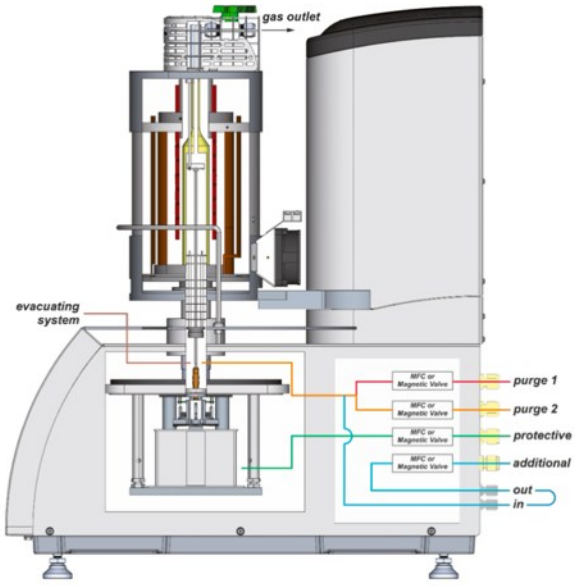

Fig. 1. STA 449 F3 Jupiter® used for DSC and TGA measurements (Netzsch-Gerätebau GmbH 2021)

Simultaneous thermal analysis combining differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was carried out on a STA 449 F3 Jupiter® simultaneous thermal analyser (Netzsch-Gerätebau GmbH, Selb, Germany), equipped with

a TG-DSC sample carrier with type S (Pt/Pt–Rh) thermocouples and platinum crucibles with Al_2O_3 liners. Data acquisition and processing were performed using the Proteus® thermal analysis software (Netzsch-Gerätebau GmbH, Selb, Germany). All thermal analyses were performed at the Fire Research Institute of the Ministry of Interior of the Slovak Republic, Bratislava, Slovakia, which served as the host laboratory for the simultaneous DSC–TGA measurements.

Test Standards

The methodology used in this study followed international and European standards relevant to the thermal analysis of polymeric and lignocellulosic materials. The general principles applied in the thermogravimetric analysis (TGA) of the samples were based on ISO 11358-1 (2022). Although ISO 11358-1 (2022) is intended for polymers, its general principles concerning the selection of the heating rate, atmospheric conditions, sample mass, and interpretation of curves are widely applied in the thermal analysis of lignocellulosic biomass as well. The general procedure for differential scanning calorimetry (DSC) measurements, including baseline correction, peak evaluation, and the determination of characteristic temperatures (onset, peak, and end temperatures), followed ISO 11357-1 (2023).

The simultaneous thermal analyser was calibrated for both temperature and sensitivity prior to the series of measurements, with all calibration, maintenance, and operating procedures carried out strictly in accordance with the manufacturer's instructions (Netzsch-Gerätebau GmbH 2021). All measurements were performed at the Fire Research Institute of the Ministry of Interior of the Slovak Republic, which is an officially designated state expert and testing laboratory. Throughout the experimental campaign, the standard operating procedures of the host laboratory were followed, including verification of instrument calibration, sample handling, and quality assurance protocols, thereby ensuring the traceability of the reported results. It should be noted, however, that each sample was measured in duplicate ($n = 2$, n – number of measurements) in accordance with the general principles of ISO 11358-1 by the same experimental condition. This limited number of replicates is sufficient to indicate the consistency of the measurements.

Methods

Simultaneous thermal analysis, combining differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), enables the concurrent measurement of the heat flow and mass changes of a single sample under a controlled temperature programme. DSC records the difference in heat flow between the sample under investigation and an inert reference, thereby providing information on endothermic and exothermic processes such as moisture evaporation, phase transitions, and decomposition and oxidation reactions. TGA simultaneously monitors the mass loss of the sample due to the release of volatile components, thermal decomposition, and oxidation, allowing the quantification of the individual degradation stages of the lignocellulosic material. The combination of both methods in a single instrument ensures that thermal and mass-related phenomena are recorded under identical conditions and on the same sample mass, which is particularly important when studying heterogeneous natural materials such as wood pellets (Grønli *et al.* 2002; Skreiberg *et al.* 2011).

Prior to measurement, the pellets were manually crushed and homogenised in order to ensure the representativeness of the sample mass and good thermal contact between the sample and the crucible. The samples were not subjected to any additional thermal or chemical treatment before the analysis, thereby preserving their original moisture content corresponding to the storage conditions. For each measurement, platinum crucibles without lids were used, which allowed the free release of gaseous products of decomposition and oxidation during the measurement. The sample mass for each measurement was in the range of 30 to 45 mg, weighed on the analytical balance of the instrument with a precision of ± 0.01 mg. The higher sample mass compared with the typical value of 5 to 20 mg used in thermoanalytical practice (Grønli *et al.* 2002) was chosen due to the heterogeneous nature of the pelletised material, in order to ensure a representative sample for each measurement.

Prior to each series of measurements, the instrument was switched on at least 24 hours in advance in order to achieve thermostatic stability of the balance system (Netzsch-Gerätebau GmbH 2021). The sample was placed in the sample crucible in the front position of the sample carrier, while an empty reference crucible of identical type was placed in the rear position. The mass of the sample and of the reference crucible was entered into the Proteus® measurement software (Netzsch-Gerätebau GmbH 2021).

The measurements were performed in a dynamic atmosphere combining a protective and a purge atmosphere, which together simulate the composition of air at a controlled flow rate. The protective atmosphere of the balance system consisted of nitrogen (N_2) at a flow rate of 20 mL/min, while the purge atmosphere in the sample chamber consisted of oxygen (O_2) at a flow rate of 20 mL/min and nitrogen (N_2) at a flow rate of 80 mL/min. These conditions enable the monitoring of both oxidative and pyrolytic processes, which are typically involved in the thermal degradation of biomass in real combustion equipment. The sample chamber composition corresponds to an oxygen fraction was deliberately chosen to approximate the oxygen content of ambient air and thereby to reproduce the oxidative conditions relevant to the combustion of solid biofuels in real equipment. This composition is essentially equivalent to synthetic air. The oxidative and inert components were metered separately through the instrument's mass-flow controllers, which allows independent control of each gas and is compatible with the separate inert protective atmosphere (N_2, 20 mL/min) required to protect the microbalance.

The temperature programme consisted of a linear heating ramp from 30 to 700 °C at a constant rate of 20 °C/min. The choice of heating rate represents a compromise between measurement sensitivity and the resolution of individual thermal events. Higher rates increase sensitivity but reduce the resolution of closely spaced transitions, whereas lower rates provide better resolution at the cost of an extended measurement time. The value of 20 °C/min is commonly used in the thermal analysis of biomass and allows the comparison of the obtained results with the literature. Each sample was measured twice (n = 2) in order to verify the reproducibility of the results.

The experimental design was intended to characterise the digestate-containing formulation as a combustible fuel and to benchmark it against commercial spruce pellets, rather than to deconvolute the thermal contributions of the individual fuel. The thermal behaviour of solid digestate on its own has been reported previously (Dziedzic *et al.* 2021), and the digestate-free spruce counterpart is represented in the present set by sample ISA2.

RESULTS AND DISCUSSION

The differential scanning calorimetry (DSC) results are summarised in Table 2. The results include the enthalpy of the endothermic reaction ΔH_{endo} (J/g), the enthalpy of the exothermic reaction ΔH_{exo} (J/g), the endothermic peak temperature t_{pendo} (°C), which corresponds to the release of moisture and the onset of thermal destabilisation of the material, as well as the peak temperatures of the first ($t_{p1.st}$) and second ($t_{p2.st}$) stages of exothermic decomposition (°C). For each sample, two independent measurements were performed (n = 2). When interpreting the DSC curves of lignocellulosic materials, it is important to bear in mind that the first exothermic peak ($t_{p1.st}$) corresponds mainly to the decomposition of hemicellulose and cellulose, whereas the second exothermic peak ($t_{p2.st}$) is attributed to the high-temperature decomposition of lignin and the oxidation of the carbonaceous residue, both proceeding in an oxidative atmosphere (Grønli *et al.* 2002; White and Dietenberger 2010). Because the decomposition ranges of these constituents overlap, particularly in an oxidative atmosphere, these peaks are interpreted as reflecting predominant contributing processes.

Endothermic Area

The endothermic peak temperature values (t_{pendo}) ranged from 103.6 to 125.9 °C, with the highest average values recorded for the experimental sample ISE (125.2 °C), whereas the commercial Norway spruce pellets BSA1, DSUA1, and ISA2 reached average temperatures of 111.7, 111.4, and 106.2 °C, respectively. The shift of the ISE endothermic peak towards higher temperatures indicates a stronger binding of moisture in the structure of the material, which is consistent with the presence of polar nitrogen-containing groups from the digestate additive that form hydrogen bonds with water molecules. Similar shifts of the endothermic peak towards higher temperatures in biomass with the addition of organic nitrogen have also been described in the literature (Skreiberg *et al.* 2011; Dziedzic *et al.* 2021).

The two replicate values of the enthalpy of the endothermic reaction ΔH_{endo} differed markedly for several samples, most notably ISE 57.4 to 147 J/g; for BSA1 8.5 to 56.9 J/g). It should be emphasised that this scatter was confined to ΔH_{endo} alone. For the same runs, the characteristic temperatures and the exothermic enthalpy ΔH_{exo} were reproducible. An instrumental malfunction or a systematic preparation error would be expected to affect all measured parameters rather than a single one. The fact that only ΔH_{endo} varied therefore points to a physical origin rather than to a problem with the equipment or the measurement. The varying value corresponds to the integral of the low temperature moisture desorption peak. This is governed by the amount and local distribution of physically bound water in each small aliquot. Wood pellets are hygroscopic and internally heterogenous, so the local moisture content of individual samples can differ appreciably even within homogenised batch, because samples were deliberately analysed at their in-use moisture content. This proportionality between the moisture desorption enthalpy and the water content of woody biomass has been demonstrated directly by DSC for spruce and other wood species, with a near-linear correlation between the measured enthalpy and moisture content (Bryś *et al.* 2016). Despite this variability, the average ΔH_{endo} values for the ISE sample (102.2 J/g) were substantially higher than those of the commercial Norway spruce pellets (BSA1 32.7 J/g; DSUA1 22.1 J/g; ISA2 52.5 J/g), again indicating a higher content of bound water in the experimental formulation.

Exothermic Area

The peak temperatures of the first exothermic peak ($t_{p1.st}$), which in an oxidative atmosphere correspond to the maximum rate of decomposition of hemicellulose and partly of cellulose, ranged for the three commercial Norway spruce pellets within a narrow interval of 327.5 to 340.2 °C (average values 333.9 to 338.5 °C). These values are consistent with the literature for spruce wood (Grønli *et al.* 2002; Bartocci *et al.* 2017; Magdziarz *et al.* 2017) and confirm that the commercial pellets BSA1, DSUA1, and ISA2 exhibit mutually comparable thermal behaviour despite their different origin (Slovakia *vs*. Ukraine) and quality class (A1 *vs.* A2).

The ISE sample showed a substantially lower average temperature $t_{p1.st}$ = 311.5 °C, *i.e.*, approximately 22 to 27 °C lower than the commercial Norway spruce pellets. This shift towards lower temperatures might be attributed to a catalytic effect of inorganic constituents present in the digestate, possibly alkali and alkaline earth metals such as K and Ca, which are known to accelerate the decomposition of polysaccharides. However, the elemental and ash composition of the samples was not determined in this study. A similar reduction in the maximum decomposition temperature of polysaccharides in the presence of alkali metals has been documented by several authors in TGA studies of biomass with mineral additives (Di Blasi *et al.* 2009; Wang *et al.* 2022).

The temperatures of the second exothermic peak ($t_{p2.st}$) correspond, in an oxidative atmosphere, to the combustion of the carbonaceous residue (char) and the high-temperature oxidation of lignin. For BSA1, DSUA1, and ISE, the average values fell within the interval of 450.9 to 462.4 °C, which is consistent with the literature concerning the exothermic peak of lignin during the heating of wood in an oxidative atmosphere (White and Dietenberger 2010).

The ISA2 sample exhibited the largest scatter of this parameter between repetitions (368.7 °C in the first measurement *vs.* 457.1 °C in the second measurement). This extreme difference probably does not reflect the actual behaviour of the material but is a consequence of the heterogeneity of the sample or of a different positioning of the sample within the crucible at the low sample mass and manual preparation. The second measurement of ISA2 (457.1 °C) was in good agreement with the other Norway spruce samples and is recommended to be considered the more representative one. For a more robust characterisation, it would be advisable in future studies to increase the number of repetitions and to standardise the milling of the sample using a mechanical mill.

Exothermic Enthalpy

The total exothermic enthalpy ΔH_{exo} represents the sum of the heat released during the oxidative decomposition of the organic fraction of the biomass and serves as an indicator of the energy potential of the fuel in an oxidative atmosphere. The average values of ΔH_{exo} reached 7.45×10^3 J/g (ISE) > 6.28×10^3 J/g (ISA2) > 6.06×10^3 J/g (DSUA1) > 5.47×10^3 J/g (BSA1). The ISE sample thus exhibited the highest exothermic enthalpy among all the samples examined, which is at first sight surprising given its higher inorganic content (approximately 10 % ash residue from TGA) and the correspondingly lower proportion of organic matter per unit sample mass. This apparent contradiction may be explained by the conditions under which ΔH_{exo} is determined and, tentatively, by a catalytic role of the inorganic constituents present in the digestate. ΔH_{exo} from the DSC measurement is recorded during dynamic heating under a limited supply of oxygen, where the magnitude of the integrated heat signal depends strongly on the reactivity of the organic matter and on the presence of catalytically active species.

Table 2. Results of DSC

Symbol	N.	ΔH_{ENDO} (J/g)	ΔH_{EXO} (J/g)	t_{pendo} (°C)	t_{onset} (°C)	$t_{p1.st}$ (°C)	$t_{p2.st}$ (°C)
ISE	1.	147	7270	124.6	360.3	316.1	477.6
ISE	2.	57.4	7630	125.9	353.7	306.9	447.2
BSA1	1.	56.9	5670	119.8	327.5	340.2	456.9
BSA1	2.	8.49	5270	103.6	313.3	327.5	444.9
DSUA1	1.	14.1	6380	105.8	332.5	338.5	451.6
DSUA1	2.	30.1	5740	117.1	330.5	338.5	464.3
ISA2	1.	45.5	6400	104.1	325.0	334.3	368.7
ISA2	2.	59.7	6160	108.2	327.9	336.9	457.1

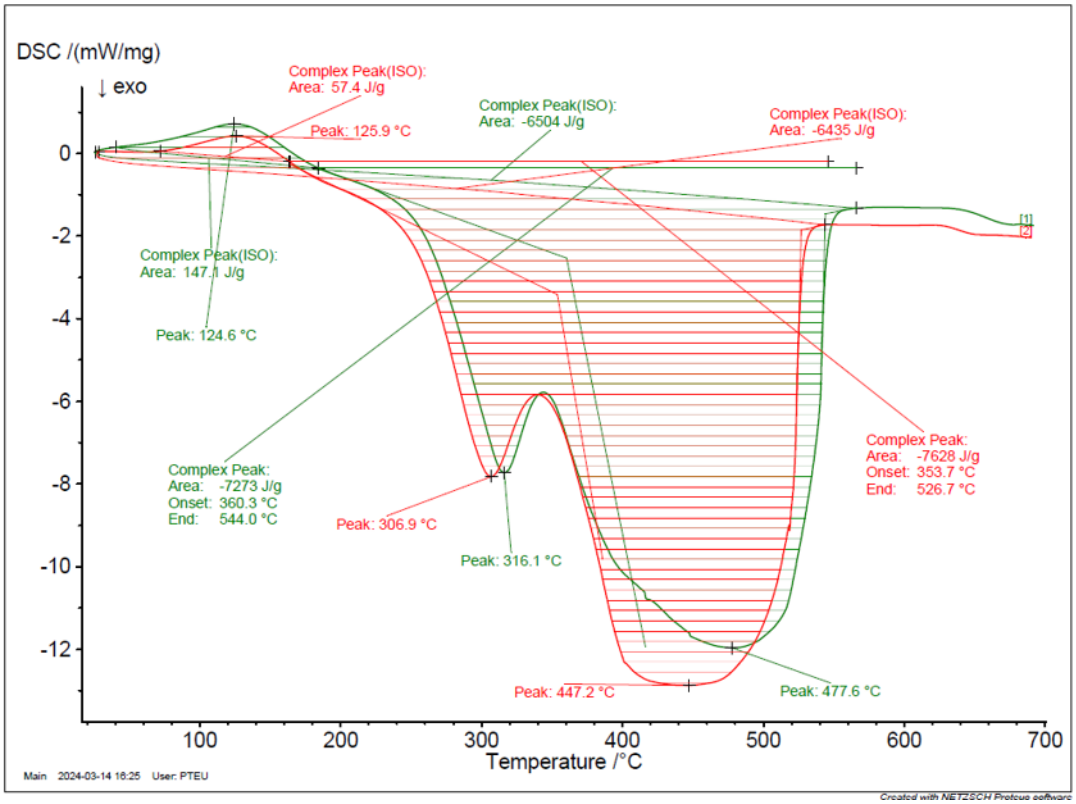

Fig. 1. DSC curves of ISE 1. Legend: The green color corresponds to the first measurement, and the red color represents the second measurement.

If catalytically active alkali and alkaline earth metals are present in the digestate, they could accelerate the oxidative decomposition of polysaccharides at lower temperatures, leading to a more intense and rapid release of heat within the DSC temperature window. Under this interpretation, higher ΔH_{exo} value of ISE does not indicate a higher energy content of the fuel. In fact, its higher ash content means less combustible matter per unit mass. It indicates that the inorganic constituents of the digestate catalyse the oxidative decomposition of the organic matter, causing a greater proportion of the heat to be released within the DSC temperature range and thus producing a higher integrated exothermic signal. The DSC curves are the resulting record of the measurement on figures below. Thanks to the software programme, it is possible to quantify the individual parameters mentioned above.

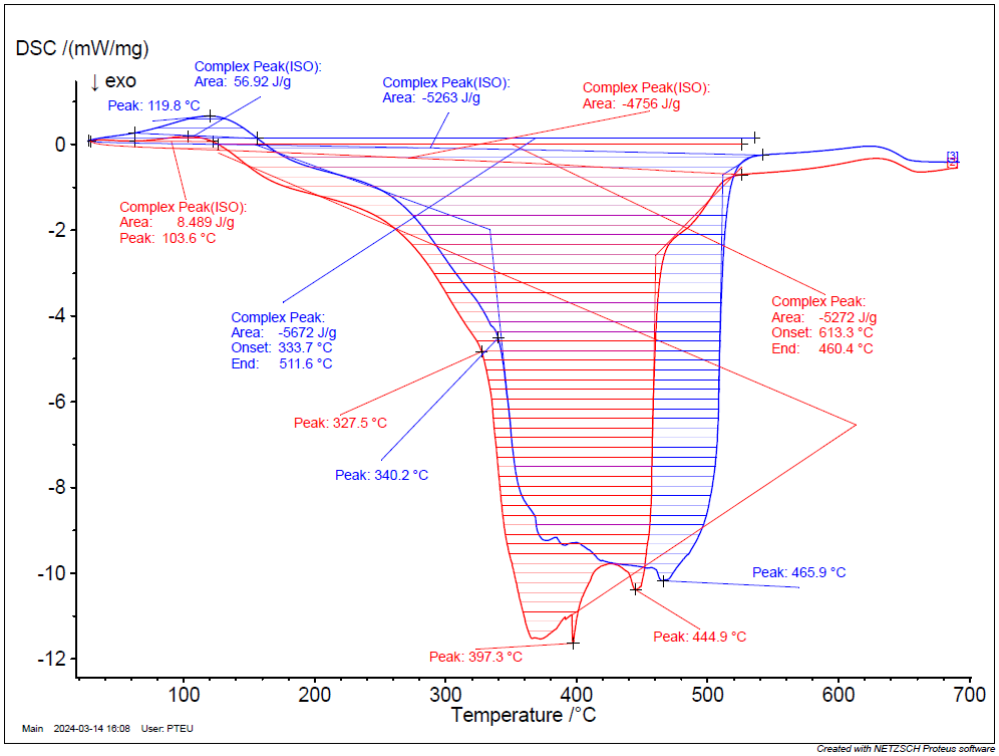

Fig. 2. DSC curves of BSA 1. Legend: The blue color is for the first measurement and the red color is for the second measurement.

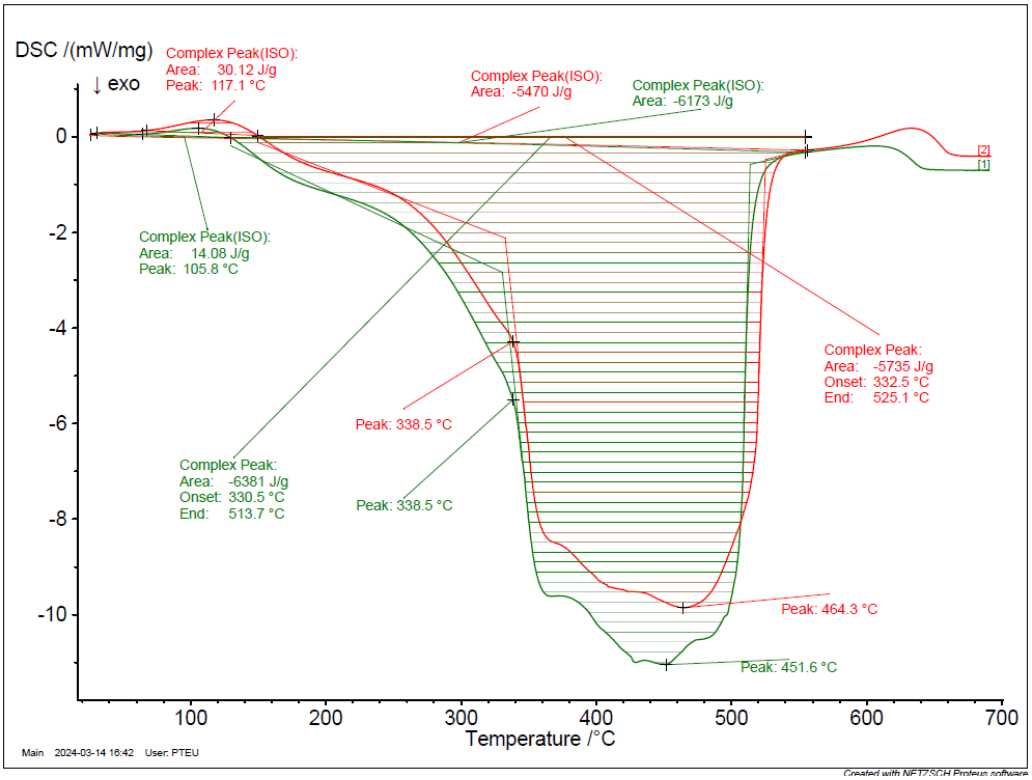

Fig. 3. DSC curves of DSUA1. Legend: Green color is the second measurement, and red color presents the first measurement.

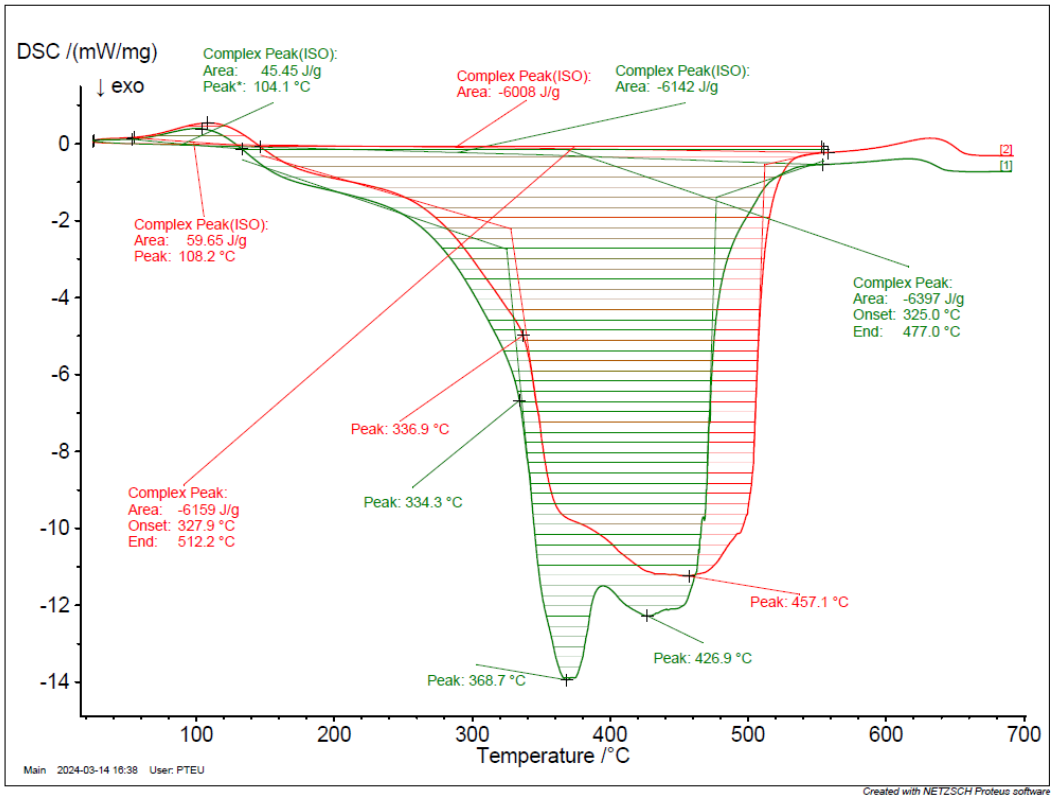

Fig. 4. DSC curves of ISA 2. Legend: Green color corresponds to the first measurement, and red color presents the second measurement.

In DSC analysis, the temperature T_{onset} (the beginning of the process) is interpreted as the temperature at which a demonstrable onset of the thermal event occurs (Tureková *et al.* 2019). The cited authors refer to the "limit of thermal stability" (Table 2), which thus represents the temperature at which the material begins to degrade massively. The temperature $T_{peak} = T_p$ represents the point of the maximum rate of the reaction, in the given case the thermal decomposition or pyrolysis of the samples (Höhne *et al.* 2003).

Results of Thermogravimetrical Analysis

The results of the thermogravimetric analysis (TGA) for the four wood pellet samples examined are summarised in Tables 3, 4, 5, and 6. For each sample, the following parameters were determined within the individual stages of decomposition: the temperature interval of the process T_i (°C), the onset temperature T_{onset} (°C) defined as the intersection of the tangents to the baseline and to the steepest section of the mass-loss curve, the mass loss Δm (%), and the residual mass C_{rezist} (%) at the end of the given stage. The onset temperature represents the temperature at which a significant deviation of the mass curve from the preceding course occurs and is therefore a suitable indicator of the onset of thermal degradation of the material.

According to the literature consensus, the thermal decomposition of wood biomass proceeds in four main stages (Grønli *et al.* 2002; Yang *et al.* 2007):

Stage I — Drying (from 25 to 160 °C): evaporation of free and physically bound moisture from the sample.

Stage II — Active pyrolysis, decomposition of hemicellulose (from 220 to 350 °C): hemicellulose is the least thermally stable component of the lignocellulosic complex

and decomposes first.

Stage III — Active pyrolysis, decomposition of cellulose (from 315 to 525 °C): cellulose is thermally more stable than hemicellulose and decomposes within a narrower temperature interval at a higher rate.

Stage IV — Final stage (from 690 °C): the end of decomposition; at this temperature, the residual mass is recorded after the burnout of the carbonaceous residue, which corresponds mainly to the inorganic fraction of the sample (ash) and a small amount of thermally undecomposed lignin.

It should be emphasised that this four-stage scheme is a simplification. The thermal decomposition ranges of hemicellulose, cellulose, and lignin overlap substantially, and this overlap is particularly pronounced under oxidative conditions, where the decomposition of the polysaccharides, the oxidation of the carbonaceous residue, and the gradual degradation of lignin proceed concurrently over a wide temperature interval. The assignments made below and in the DSC interpretation should be understood as the predominant rather than the sole contributions to each thermal event.

The mass losses in the first stage of decomposition for all four samples fell within a narrow range of 5.3 to 6.8%, with average values of 6.59% (ISE), 6.67% (BSA1), 5.30% (DSUA1), and 6.31% (ISA2). These values correspond to the typical moisture content of commercial wood pellets reported in the standard specifications (≤ 10%) for ENplus A1 and A2 class pellets (Magdziarz *et al.* 2017). The slightly lower loss in DSUA1 (5.30%) indicates drier storage conditions or a different hygroscopicity of the sample of Ukrainian origin.

In the second stage of decomposition, which corresponds mainly to the decomposition of hemicellulose, the onset temperatures for the three commercial Norway spruce pellets (BSA1, DSUA1, ISA2) fell within a narrow range of 284.9 to 286.1 °C. The mass losses in this stage reached 56.9% to 58.2%, which corresponds to the expected contribution of hemicellulose and the incipient decomposition of cellulose in the thermal–pyrolytic region of wood biomass (Magdziarz *et al.* 2017).

The ISE sample exhibited a substantially lower average onset temperature of 262.5 °C than the commercial Norway spruce pellets, together with a smaller mass loss of 42.8% (compared with an average of 57% for the commercial pellets). This pronounced shift of the onset temperature towards lower values is consistent with a possible catalytic effect of the inorganic constituents of the digestate, potentially alkali and alkaline earth metals (K, Na, Ca, Mg), which are reported to catalyse the dehydration and fragmentation reactions of polysaccharides. Because the elemental composition of the digestate and of the ash was not analysed here, this attribution is proposed as likely explanation rather than a demonstrated mechanism. The decrease in the onset temperature by 23 °C is in good agreement with the range of decreases reported in studies of wood impregnated with alkali salts, which report reductions of the initial decomposition temperatures by 35 to 70 K depending on the type and concentration of the salt (Di Blasi *et al.* 2009; Wang *et al.* 2022).

At the same time, the smaller mass loss in ISE (15% lower than in the commercial pellets) suggests that part of the organic matter that would decompose at this stage in the commercial pellets is, in the case of ISE, either shifted to the subsequent stage or retained as a secondary decomposition product. This phenomenon is also characteristic of alkali and alkaline earth metal catalysed pyrolysis, in which the reaction pathways are redirected towards the formation of char and the release of CO_2 and H_2O at the expense of the release of tarry levoglucosan (Di Blasi *et al.* 2009).

In the third stage of decomposition, predominantly controlled by the decomposition of cellulose and partly by the residual pyrolysis of hemicellulose, the onset temperatures for the commercial pellets BSA1, DSUA1, and ISA2 ranged from 338.6 to 346.5 °C (averages 341.8 to 346.1 °C). These values are typical of the thermal degradation of wood biomass in an oxidative atmosphere (Grønli *et al.* 2002; Magdziarz *et al.* 2017). The mass losses in this stage were in the range of 31.0% to 34.7%, which again documents the mutual comparability of the three commercial Norway spruce pellets despite their different origin and quality class.

The ISE sample again exhibited substantially different behaviour. The onset temperature of cellulose dominated decomposition was 303.3 °C, *i.e.*, 41 °C lower than the average of the commercial pellets. This more pronounced shift in the cellulose decomposition stage would be consistent with the mechanism by which K^+ and Na^+ ions catalyse the dehydration reactions of cellulose and shift the temperature of the maximum rate of decomposition of the glycosidic bonds towards lower values (Di Blasi *et al.* 2009; Wang *et al.* 2022). The mass loss of ISE in this stage (37.9%) was higher than in the commercial samples, which complements the transfer of part of the mass loss from the second stage of decomposition to the third.

The most pronounced difference between the experimental sample ISE and the commercial pellets was observed in the residual mass at the end of the final stage of decomposition. For the commercial pellets, C_{rezist} ranged from 0.67% to 2.18% (averages 1.06% for BSA1, 1.89% for DSUA1, 1.67% for ISA2), which corresponds to the very low ash content typical of high-quality Norway spruce pellets of ENplus A1 and A2 classes. For the ISE sample, the residual mass was 10.07%, *i.e.*, approximately 6 to 10 times higher than for the commercial pellets.

This substantially elevated content of inorganic residue directly confirms the assumed contribution of the digestate to the total inorganic content of the experimental pellet formulation. The higher C_{rezist} value of ISE has three key consequences for the thermal behaviour of this sample:

- The mineral substances present may act a catalytic reserve for the decomposition reactions of polysaccharides and could therefore explain the observed shifts in the onset temperatures,
- The increased ash content reduces the effective calorific value of the fuel,
- From the perspective of practical application in combustion equipment, the substantially higher ash content represents a risk of increased slag formation, corrosive deposits on heat exchangers, and a more frequent need for cleaning of the combustion chambers (Kratzeisen *et al.* 2010; Royo *et al.* 2022).

It should be emphasised that, in the absence of a compositional analysis, the role of specific inorganic constituents cannot be regarded as experimentally demonstrated. The catalytic contribution of alkali and alkaline earth metals is therefore proposed here only as a hypothesis consistent with the observed shift and with the literature. For the precise elemental quantification of the inorganic constituents in ISE and for the verification of the assumed content of alkali metals as catalysts of the observed shifts in thermal degradation, it is recommended that further studies include a dedicated elemental and ash composition analysis.

Table 3. Results of TGA for ISE

ISE Parameter	N.	Stage I - Drying	Thermical degradation		Stage IV – Final stage
			Stage II - Active pyrolysis (hemicellulose)	Stage III - Active pyrolysis (cellulose)	
T_i (°C)	1.	25.8 to 159.1	223.3 to 315.9	315.9 to 542.2	691.4
	2.	27.6 to 158.7	225.6 to 308.8	308.8 to 525.8	690.2
Onset (°C)	1.	-	264.1	306.1	-
	2.	-	260.8	300.5	-
Δm (%)	1.	6.81	44.18	37.11	1.32
	2.	6.37	41.41	38.65	1.11
C_{rezist} (%)	1.	93.10	47.64	10.53	9.21
	2.	93.68	50.68	12.03	10.92

Table 4. Results of TGA for BSA1

BSA1 Parameter	N.	Stage I - Drying	Thermical degradation		Stage IV – Final stage
			Stage II - Active pyrolysis (hemicellulose)	Stage III - Active pyrolysis (cellulose)	
T_i (°C)	1.	27.2 – 155.0	231.6 – 349.7	349.7 – 510.7	692.0
	2.	28.9 – 146.6	231.1 – 339.4	339 – 467.7	690.8
Onset (°C)	1.	-	285.9	345.0	-
	2.	-	285.0	338.6	-
Δm (%)	1.	6.82	57.98	32.35	0.44
	2.	6.52	58.35	32.71	1.07
C_{rezist} (%)	1.	93.05	34.24	1.89	1.45
	2.	93.65	34.46	1.74	0.67

Table 5. Results of TGA for DSUA1

DSUA1 Parameter	N.	Stage I - Drying	Thermical degradation		Stage IV – Final stage
			Stage II - Active pyrolysis (hemicellulose)	Stage III - Active pyrolysis (cellulose)	
T_i (°C)	1.	25.9 – 160.5	235.8 – 351.0	351.0 – 522.1	691.8
	2.	30.8 – 157.5	236.3 – 348.9	348.9 – 511.4	690.1
Onset (°C)	1.	-	286.1	346.3	-
	2.	-	284.9	344.8	-
Δm (%)	1.	5.30	56.88	34.14	0.53
	2.	5.30	56.88	34.68	0.52
C_{rezist} (%)	1.	94.64	36.85	2.71	2.18
	2.	94.54	36.80	2.12	1.60

Table 6. Results of TGA for ISA2

ISA2 Parameter	N.	Stage I - Drying	Thermical degradation		Stage IV – Final stage
			Stage II - Active pyrolysis (hemicellulose)	Stage III - Active pyrolysis (cellulose)	
T_i (°C)	1.	25.6 – 145.8	237.1 – 353.3	353.3 – 509.9	692.1
	2.	25.6 – 135.2	239.8 – 349.3	349.3 – 489.0	690.7
Onset (°C)	1.	-	285.9	346.5	-
	2.	-	285.1	345.7	-
Δm (%)	1.	6.66	56.99	33.07	0.69
	2.	5.96	59.12	30.86	0.79
C_{rezist} (%)	1.	93.22	35.18	2.11	1.42
	2.	93.98	33.56	2.70	1.91

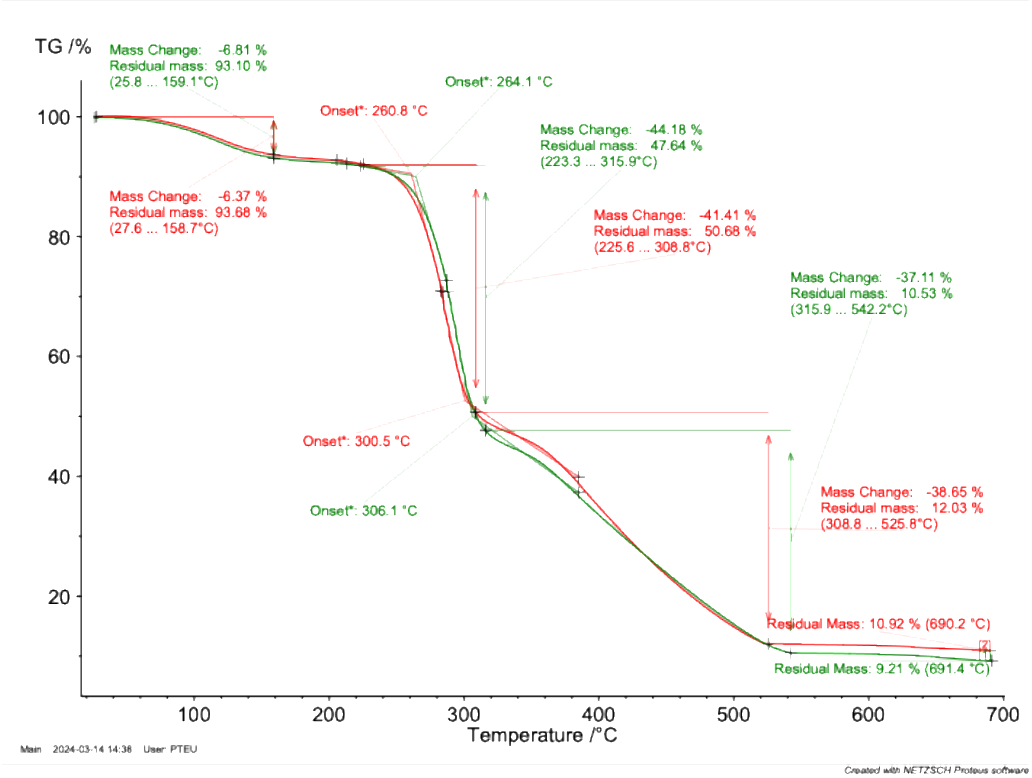

Fig. 5. TG curves of ISE 1. Legend: Green color corresponds to the first measurement, and the red color is for the second measurement.

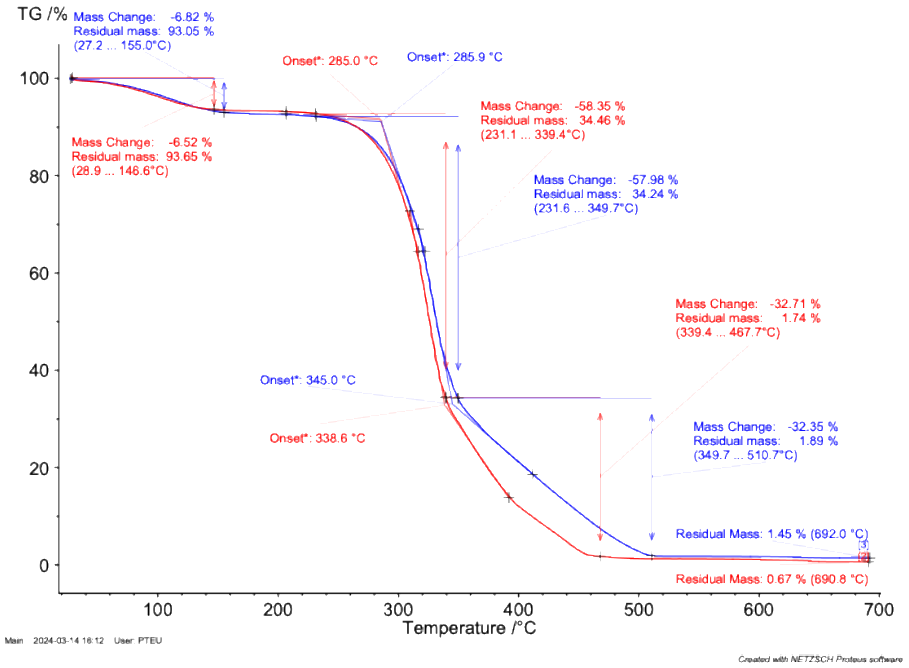

Fig. 6. TG curves of BSA1 1. Legend: The blue color is for the first measurement, and the red color corresponds to the second measurement.

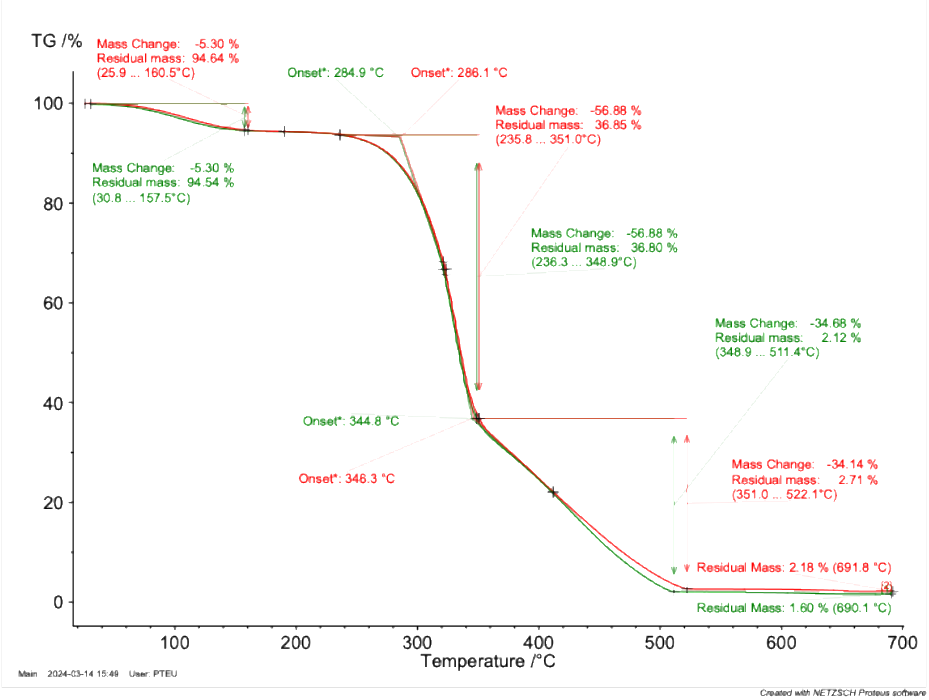

Fig. 7. TG curves of DSUA1 1. Legend: The red color belongs to the first measurement, and green color represents the second measurement.

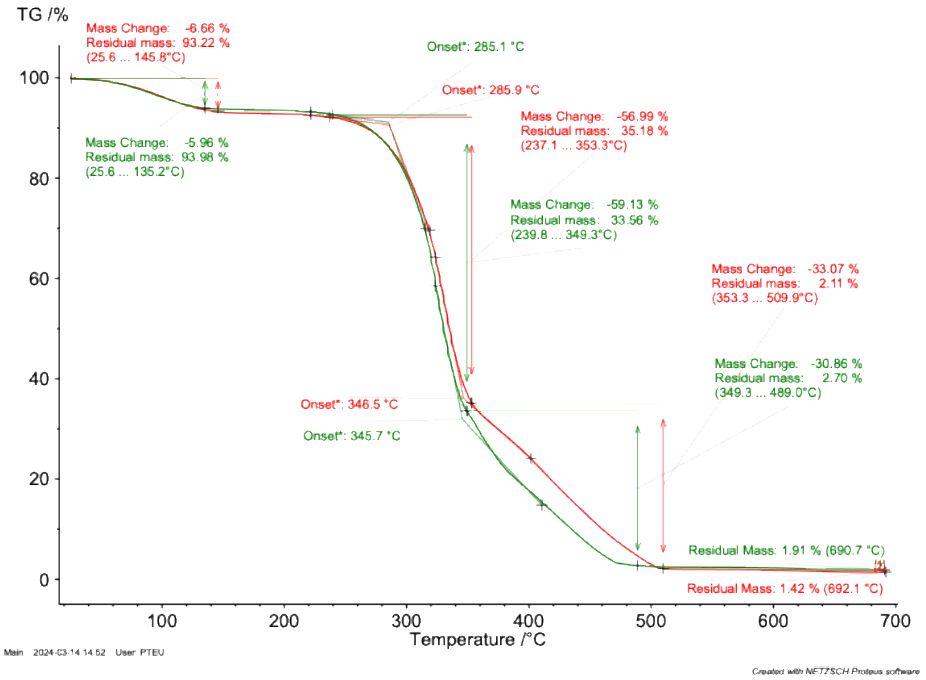

Fig. 8. TG curves of ISA2 1. Legend: The red color indicates the first measurement, whereas the green color represents the second measurement.

CONCLUSIONS

1. At the 1:1 mass ratio investigated here, corresponding to a digestate content of 50wt%, the digestate constitutes a major component of the fuel. At this loading it fundamentally alters the thermal decomposition behaviour of the fuel. The experimental sample ISE exhibited substantially different behaviour from the three commercial Norway spruce pellets without digestate addition in all the parameters investigated, *i.e.*, the onset temperatures of hemicellulose and cellulose decomposition, the DSC peak temperatures, the enthalpies of the endothermic and exothermic reactions, and the residual mass. It follows that this spruce-digestate formulation cannot be evaluated by the same criteria as standard ENplus class wood pellets. These conclusions refer specifically to the 50 wt% formulation and should not be generalised to pellets containing digestate at the lower loadings characteristic of conventional additive use, whose thermal behaviour remains to be characterised in future studies.
2. The three commercial Norway spruce pellets (BSA1, DSUA1, ISA2) exhibited highly reproducible and mutually comparable thermal behaviour despite their different geographical origin (Slovakia *vs.* Ukraine) and quality class (ENplus A1 *vs.* A2). The onset temperatures of hemicellulose decomposition fell within a narrow range of 284.9 to 286.1 °C, the onset temperatures of cellulose decomposition within the range of 338.6 to 346.5 °C, and the residual mass at the end of the temperature programme within the range of 0.67% to 2.18%, which documents the robustness of industrially produced Norway spruce pellets as a fuel across the entire set examined.

3. The residual mass of the experimental sample ISE at the end of the temperature programme reached 10.1%, which is approximately 6 to 10 times higher than that of the commercial pellets (1.06% to 1.89%). This substantially elevated content of inorganic residue directly confirms the dominant contribution of the digestate to the total inorganic content of the experimental formulation and has immediate consequences for the operation of combustion equipment, because the higher ash content reduces the effective calorific value of the fuel and represents a risk of increased slag formation, corrosive deposits on heat exchangers, and more frequent cleaning of the combustion chambers (Kratzeisen *et al.* 2010; Royo *et al.* 2022).

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Conflict of Interest

Authors declare no conflict of interests.

Use of Generative AI

No AI tools were used.

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