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Chemical and thermal characterization of wood biomass from non-native tree species in the steppe zone of Ukraine

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The growing demand for sustainable and renewable energy sources highlights the importance of exploring biomass from non-native tree species in Ukraine's steppe zone. This study aims to investigate the chemical composition and thermal decomposition characteristics of wood from non-native tree species (*Acer negundo*, *Robinia pseudoacacia*, *Quercus rúbra*, *Ailanthus altissima*) to evaluate their potential as biomass for energy production. Key wood parameters such as pH, buffering capacity, extractive content, and structural polymers (cellulose, hemicellulose, lignin) were analyzed, revealing significant interspecies variation linked to their biochemical traits and adaptation levels. Thermogravimetric analysis identified three main stages of thermal decomposition and demonstrated differences in thermal stability and decomposition rates among species. Notably, *A. negundo* exhibited the highest thermal decomposition rate, while *R. pseudoacacia* showed superior buffering capacity. Correlations between chemical composition and thermal degradation energy requirements suggest that species with higher cellulose and lignin content demand greater activation energy for thermo-oxidative breakdown. These findings indicate that non-native tree species, including invasive ones, represent promising biomass sources for energy generation. Moreover, their utilization could serve as a sustainable strategy for controlling species with invasive characteristics, thereby contributing to biodiversity preservation and ecological balance in the region.

Keywords: non-native tree species with invasive characteristic; chemical composition; thermal decomposition; thermogravimetric analysis.

Introduction

The restoration of the forest fund within the steppe zone of Ukraine will require the search for forest-forming tree species that will be adapted to the climatic and soil conditions of the disturbed ecosystems and capable of fulfilling practical function. Plantations of fast-growing trees capable of rapidly generating above-ground biomass with significant energy potential may become one of the types of restored forest plantations. Biomass of fast-growing plants, which is composed of carbon, is one of the best renewable solutions for replacing fossil fuels resources in many applications. It can be used in the energy sector to produce heat, electricity and transport fuels (Ali et al., 2024). In general, it will allow the restoration of disturbed forest plantations and harvesting of biomass that can be used to address the problem of energy resources shortages, especially in local communities in the southeastern steppe zone.

The process of using biomass with wood processing by thermochemical means is a promising alternative for many energy purposes (Bridgwater, 2003). The most modern thermochemical processes (conversion of biomass by heat) are gasification, pyrolysis and combustion. The application of these approaches will continue to require further research to improve their efficiency for a variety of woody plant species. Fast-growing tree species are increasingly becoming the main choice for plantations, which are the oldest form of reclamation of damaged land (Filcheva et al., 2000). At the same time, the emphasis is placed on those species that produce biomass in a short period of time and are economically important (Singh et al. 2002). Short-rotation plantations not only produce woody biomass for energy quickly, but also store significant amounts of carbon from the soil and air. However, many of the trees used to create such plantations are often recognised as Invasive. Assessment of the impact, prevention of spread, control and management of invasive adventive species are recognised as priority tasks in many strategic international and European documents (Kowarik et al., 2003; Genovesi & Shine, 2004; EU Biodiversity Strategy 2030, 2021). They have an ever-increasing impact on biodiversity and ecosystem functioning. However, many invasive species are still beneficial, especiallywith regard to their biomass and energy use.

Knowledge of the biology and ecology of invasive plant species is a fundamental prerequisite for their successful control (Brown et al., 2005). The characteristic features of invasive species are their ability to expand their secondary area, their ability to penetrate and transform natural and semi-natural plant communities, and their significant impact on the growth and development of other species, which is difficult to control (Sax & Brown, 2000; Prots & Vykhor, 2013). However, to the present day, large-scale projects are focused on the use of invasive tree species for the production of goods and services, especially in developing countries (Low, 2012). Thus, existing forest plantations containing species with significant invasive potential require a search for their appropriate rational use and the development of algorithms for their management. One such mechanism may be the use of plantations with species that show invasive characteristics as a source of aboveground biomass and can be used directly as an energy resource. To achieve these goals, it is necessary to know the main thermal characteristics of biomass which has a significant energy potential that can be assessed using physicochemical models and whose thermal properties can be assessed. In this context, thermal analysis plays a crucial role in characterising the biomass of different woody species (Silva et al., 2024).

The plantations of introduced tree species in the steppe and forest-steppe zones were created for different purposes, primarily due to the works on land consolidation to mitigate water and wind erosion in the 1950s and 1960s (Lovynska et al., 2022). In some years, up to 300,000 hectares of forest plantations were planted annually, with introductions of species due to the steppe's climatic conditions. Such species as ash-leaved maple, northern red oak and tree of heaven are quite common introductions to the steppe zone (Kunakh et al., 2022). Ash-leaved maple (*Acer negundo* L.) is a tree species with a high invasive potential, which expands its range and effectively penetrates natural and semi-natural plant communities. Ash-leaved maple is capable of spreading in a variety of natural and anthropogenically transformed habitat types (Dawson & Ehleringer, 1993; Mędrzycki, 2010). *Acer negundo* is adapted for growth on saline and sandy soils, and effectively helps to stabilise ravine slopes. In forestry practice, it has been used to create plantations along roads and for shelterbelt plantations in the steppe zone, as it is characterised by significant drought resistance and rapid growth (Kucher, 2015). Northern red oak (*Quercus rubra* L.) is widely used in forestry in Europe, where it is one of the most common introduced non-native species with a total plantation area of over 350,000 hectares, more than half of which is located in Ukraine (Kucher et al., 2023). Its rapid growth and high survival rate, as well as the significant potential for the use of its wood in carpentry products, have led to the widespread use of this species in forestry in Ukraine (Hayda et al., 2022). Tree of heaven (*Ailanthus altissima* [Mill]. Swingle) is widespread in the plantations of the steppe zone of Ukraine. The dense wood of this tree species is actively used for the manufacture of decorative carpentry and high-quality paper (Kúdela & Mamoňová, 2006). Black locust (*Robinia pseudoacacia* L.) has been widely planted and naturalised in many temperate areas of the world and is considered an invasive species in many regions of Europe (Kleinbauer et al. 2010; Cierjacks et al., 2013) due to its high ability to spread beyond its original cultivation location. It is a nitrogen-fixing tree, and its use for bioenergy production (mainly fuelwood) is expected to increase the phytonutrient content of the soil (Paris et al., 2015).

The purpose of this study is to (i) determine the content of the main structural components of wood – cellulose, hemicellulose, lignin; (ii) investigate the main characteristics of wood thermaldegradation; (iii) establish the relationship between the chemical composition of wood and its thermal degradation; (iv) determine the level of potential for using wood biomass of introduced species as an energy resource. The object of the study is the wood of the trunks of introduced tree species that are widespread in the forest plantations of the steppe zone of Ukraine and show signs of invasiveness: *A. altissima*, *A. negundo*, *Q. rubra*, *R. pseudoacacia*.

Materials and methods

The research was conducted in the Druzhby Narodiv Park, which is located in the left-bank part of the city of Dnipro (48º32'07" N, 35º05'25" E, 79 m above sea level) in a valley-terraced landscape type. The area of the park is 90 hectares. The park's soils are classified as Calcic Chernozem (silty) according to IUSS Working Group WRB (2015). The research objects were trees of the species *A. altissima*, *A. negundo*, *Q. rubra* and *R. pseudoacacia*. Wood samples of each experimental tree species were collected using an increment borer (Haglöf, Sweden, 400 mm). From each experimental tree of a certain species, 3 wood core samples were collected at a trunk height of 1.3 m. From the selected wood core samples for each tree species, a mixed wood sample was formed for further research. Five healthy trees of each species without signs of disease or crown and trunk damage of the same age group (20 to 30 years) were selected for the study. The previous age of the trees was determined visually by morphometric features according to Kunakh et al. (2023) and was refined by counting annual rings on tree cores. Species names of the trees are provided according to the modern POWO database.

The pH and the buffering capacity of wood were determined according to Król et al. (2017). Wood ash content was determined according to the NREL procedure (Sluiter et al., 2008). The content of substances soluble in cold water was determined by extraction with distilled water at 23 ± 2 °C for 48 hours and the content of substances soluble in hot water was determined by extraction with distilled water at 100 °C for 3 hours, according to ASTM D1110-21 (2021); the content of extractives soluble in an alcohol-toluene mixture (1:2 by volume) was determined using a Soxhlet apparatus, according to ASTM D 1107-2021 (2021). The cellulose content was determined by the method of Chen et al. (2018), which is based on the dissolution of lignin and hemicelluloses in a nitrogen-alcohol mixture (1:4) by boiling for 1 hour (one cycle) and washing the wood. Four treatment cycles were performed, after which the insoluble cellulose content was determined by the weight method. The content of hemicelluloses was determined by acid hydrolysis with a 2% HCl solution, at low boiling for 3 h (Gao et al., 2014). Klason lignin (insoluble lignin) was determined by the weight method after hydrolysis of desiccated wood with 72% sulfuric acid solution, according to NREL/TP-510-42618 standard (Sluiter et al., 2011). The total lignin content was calculated by the formula:

$$L = 100 - A - C - H - E,$$

where: A – ash content (%); C – cellulose content (%); H – hemicellulose content (%); E – extractive substances content (%).

A comparative thermogravimetric analysis of woody plant biomass samples from tree species was carried out to obtain information about the wood thermal. The analysis was performed using the derivatograph Q-1500D of the 'F. Paulik-J. Paulik-L. Erdey' system.

Samples of stem wood biomass, each 100 mg weight, were analysed dynamically at a heating rate of 10 °C/min in an air atmosphere. Aluminium oxide was used as the reference substance. Differential thermogravimetric (DTG), thermogravimetric (TG) and differential thermal analysis (DTA) were used to assess the thermochemical changes occurring in the wood biomass of the studied tree species. DTG is a mathematical differential curve of mass change, which is the temperature derivative of the mass change function of the substance under study dP/dT = f(T), i.e. the derivative of P = f(T) (Broido, 1969). The DTG curve can be used to determine the temperature of the start and end of the reaction, and the peak of the curve can be used to determine the temperature of the maximum speed of the reaction. Tan & Stotta (1989) described the differential thermal analysis (DTA) of wood in an oxidising environment and pseudo-fluidised layers and suggested using its data to determine the method of chemical treatment and burning of wood. As a criterion for assessing the degree of thermal degradation of natural polymers, the activation energy of thermo-oxidative degradation was taken, i.e. the excess energy required to destroy the chemical bonds that form the main chain of the polymer under the influence of light and air oxygen. In this study, we used TG curves to determine the activation energy of thermo-oxidative degradation of biomass samples of trunk components according to the method of Broido (1969). To do this, the double logarithm value for the relevant temperature was calculated using the following relationship:

$$\ln\left(\ln\frac{100}{100-\Delta m}\right) = -\frac{E}{R}\cdot\frac{1}{T}$$

where m – the sample mass (%); E – the activation energy (kJ/mol); R – the universal gas constant (8.314 J/(mol•K)); T – the temperature (K).

The equations and their correlation coefficients were determined by analyzing the curves constructed in the coordinates of the Broido equation for different temperature ranges corresponding to the stages of moisture evaporation, volatile organic substances and the stages of decomposition of cellulose, hemicellulose and lignin. All the results obtained were treated by statistical methods using the StatGraphics Plus 5 software package at the significance level $P < 0.05$.

Results

The characteristics of the wood trunks of the studied tree species are given in Table 1. The wood of the investigated species is sufficiently different by the value of pH, and ranges from 4.44–7.24. Only the wood of *A. negundo* is characterised by a pH value close to neutral, while the other studied species have a value of this parameter that indicates an acidic reaction. Among the studied species, the most acidic pH value is characterised by the wood of *Q. rubra*. The pH value of the aqueous extract characterises the content of weak water-soluble acids in the wood, while the alkaline buffering capacity is a broader characteristic, as it additionally indicates the content of organosoluble acids, acid groups of hemicelluloses, acetyl groups in hemicelluloses and acid groups of lignin that react with alkali. The studied species significantly differ in buffering capacity, the highest of which is in *R. pseudoacacia* wood.

The ash content of wood is determined by the content of mineral components: it was insignificant in the studied tree species, with the highest level of mineral components demonstrated by *R. pseudoacacia* wood. The studied species varied significantly in the content of extracted compounds. The maximum amount of substances extracted by cold, hot water and ethanol-toluene solution in *Q. rubra* was 25.28%, while the lowest value of 10.15% was recorded in *A. negundo*.

Table 1
Wood properties of the investigated tree species

Species	pH	Buffer capacity, mmol/100 g	%	Extracted compounds, %		
				cold water	hot water	ethanol/ toluene
A. negundo	7.24	2.32	1.05	3.19	4.60	2.36
A. altissima	5.56	1.74	0.87	6.58	7.84	4.28
Q. rubra	4.44	5.20	0.73	9.61	11.03	4.64
R. pseudoacacia	5.24	9.59	0.29	6.57	8.66	5.40

The distribution of structural components of wood in all studied species has the same trend. the content decreased in the following range: cellulose, hemicellulose, lignin and Klason lignin (Fig. 1). However, species-specific distributions of these components were found. In cellulose content, *A. negundo* and *A. altissima* were close, while *R. pseudoacacia* and *Q. rubra* had slightly lower content. The hemicellulose content had the opposite trend. *A. altissima* wood had the same content of hemicellulose and lignin, while *R. pseudoacacia* wood contained two times less lignin than hemicellulose, with almost the same amount of lignin as cellulose.

Thermal destruction of wood biomass of all studied tree species occurred in three stages: 1 – evaporation of water and volatile compounds, 2 – decomposition of hemicellulose, cellulose and the least thermally stable lignin components, 3 – destruction of thermally stable lignin fragments (Table 2).

The first stage of thermal destruction occurred in the temperature range from 20 to 120 °C. It is quite natural that the removal of free and bound moisture is an endothermic process with a relatively high (~65 kJ/mol) activation energy. The process was quite slow; the maximum rate did not exceed 12.7%/min. The extreme point with the maximum intensity of the destruction process was observed at a temperature of 90 °C. The mass loss was insignificant, namely 3.8% in *A. negundo*, 3.4% in *A. altissima*, 4.4% in *Q. rubra*, 3.5% in *R. pseudoacacia* (Fig. 2).

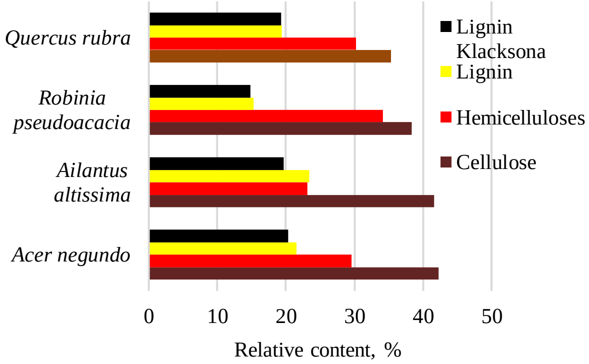
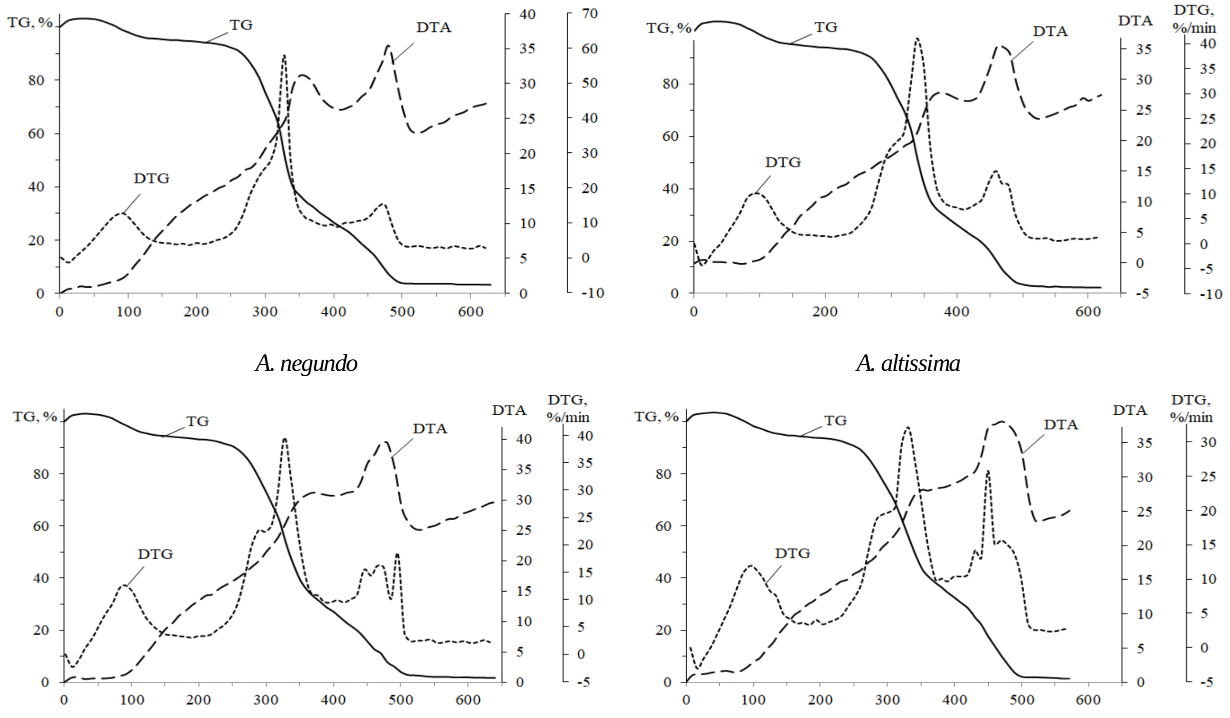


Fig. 1. Structural components of wood of the studied species

Table 2
Thermal features of the tree species' wood decomposition

Species	Stage	Interval, °C	Extreme point,C°	Max. rate, % min	Weight loss, %	*Ea*, kJ/mol
A. negundo	1	20–120	90	12.6	3.8	65.4
	2	240–390	330	57.9	67.8	71.9
	3	390–600	460	12.3	96.8	24.0
A. altissima	1	20–120	100	9.9	3.4	65.5
	2	240–390	340	41.1	68.7	62.8
	3	390–600	450	12.3	97.7	27.1
Q. rubra	1	20–120	90	12.6	4.4	177.4
	2	240–390	330	39.5	66.9	62.3
	3	390–600	430/460	15.4/18.4	98.3	27.3
R. pseudoacacia	1	20–120	90	11.9	3.5	114.1
	2	240–390	330	32.1	61.9	56.9
	3	390–600	450	25.8	98.5	41.6



A. negundo

A. altissima

Q. rubra

R. pseudoacacia

Fig. 2. The mass loss (TG), the differential-thermogravimetric (DTG) and the differential thermal analysis (DTA) curves for the wood of the investigated species

The second stage was divided into two phases: in the temperature range of 240–390 °C, hemicellulose (pentosans and hexosans), cellulose, and the least thermally stable lignin components decomposed. In this temperature interval, at 330 °C, the highest intensity of wood thermal degradation was observed, which probably reflected the beginning of the destruction of the least stable lignin fragments). The studied species differed in the values of the maximum intensity of thermal decay (%/min): 57.9 – *A. negundo*, 41.1 – *A. altissima*, 39.5 – *Q. rubra*, 32.1 – *R. pseudoacacia*, with a small peak at 300 °C (corresponding to the destruction of cellulose components). The activation energy in this temperature range is ~72 kJ/mol. The weight loss of the wood samples is also the highest in this temperature range and was 67.8% for *A. negundo*, 68.7% for *A. altissima*, 66.9% for *Q. rubra*, and 61.9% for *R. pseudoacacia*.

The third stage of wood thermal destruction is carried out in the temperature range of 390–600 °C, during which the degradation of thermally stable lignin fragments occurs, the content of which expires at a temperature of about 520 °C, and subsequently the separation of heavy pitches and the burning of coke residue.

As for the thermal degradation of the wood of the introduced wood species, due to the greater similarity of their chemical composition, the curves of dependence on DTA at this stage differ to a lesser extent (Fig. 2). The final stage of thermo-oxidative degradation was in the temperature range of 450–640 °C. In this temperature range, the decomposition of all organic matter of biomass, including lignin, is completed with the formation of mineralised residues of small mass. Of the introduced species studied, the highest exothermic effect (T = 450–480 °C) accompanies the process of thermo-oxidative destruction in red oak wood samples, followed by black loust, and then for tree of heaven. For boxelder maple, the thermal effect is the smallest among all samples.

Discussion

The peculiarities of thermal degradation processes are primarily caused by the composition of the structural components of plant biomass. The dependence of the thermal characteristics of wood pyrolysis on its chemical composition, namely on the content of cellulose, hemicellulose and lignin, has been shown in some works (Yang et al., 2007; Apaydın & Mutlu, 2023).

Wood properties, such as the content and quality of the extractives, the ratio of the main biopolymer components, such as hemicellulose, cellulose and lignin, determine the parameters of thermal decomposition. The chemical composition of plant tissues is species-specific. The wood of deciduous tree species on average contains: libriform 43–75%, elements of conductive tissue, fibres – 20–40%, medullary rays 10–20%, and wood parenchyma 2–13% (Silva da Silva et al., 2024).

Figure 3 shows a comparative analysis of the composition of the main components of the wood of the species investigated in our work.

The highest content of cellulose and of Klason lignin among the studied species is characterised by *A. negundo*, hemicellulose – *R. pseudoacacia*, lignin – *A. altissima*, which is aligned with the work of other authors (Vanholme et al., 2019; Li et al., 2024).

The dependence of mass loss (Δm) on the temperature of wood destruction of the studied tree species was described by mathematical modelling, the results of which are shown in Figure 4 and Table 3. Comparison of the general equations of wood thermal decomposition with other studies shows that the use of linear equations to describe the mass loss of wood during thermal decomposition is a common approach in thermogravimetric analysis (Poletto et al., 2012; Bryś et al., 2018). Similarly to the above works, we obtained linear equations that appropriately describe the dependence of mass loss for all the species studied, because it has the high coefficients of determination R^2.

The thermal behaviour of natural polymers such as cellulose, hemicellulose and lignin varies significantly. It depends on the chemical structure, degree of polymerisation and crystallinity (Yang et al., 2007; Bryś et al., 2016; Apaydın & Mutlu, 2023). The thermal decomposition of polysaccharides occurs in a relatively small temperature range (El-Sayed & Mostafa, 2020). Lignin decomposition occurs over a wider temperature range than the degradation of polysaccharides (Brebu & Vasile, 2010; Várhegyi, 2017). Other wood compounds (inorganic ions and extractive compounds) affect the decomposition of the above-mentioned natural polymers. The study by Brebu et al. (2013) of the extracted materials of *R. pseudoacacia* showed that the thermal decomposition of extractive substances occurs in two main stages: the first stage occurs between 130 and 250 °C, and the second – between 250 and 550 °C. The temperature intervals obtained as a result of our experiment showed slightly different outcomes, with a range of higher values. This applies not only to representatives of the species *R. pseudoacacia*, but also to other studied species. The range of extractive substance temperatures was about 1.5 times higher for the two established stages compared to the results of the authors. The thermal decomposition of different types of lignin was studied and the results of lignin behaviour in different wood species were shown. Of the species studied by the authors, common oak lignin decomposed at the highest temperatures. Similar observations were observed in this study for the species from genus *Quercus*.

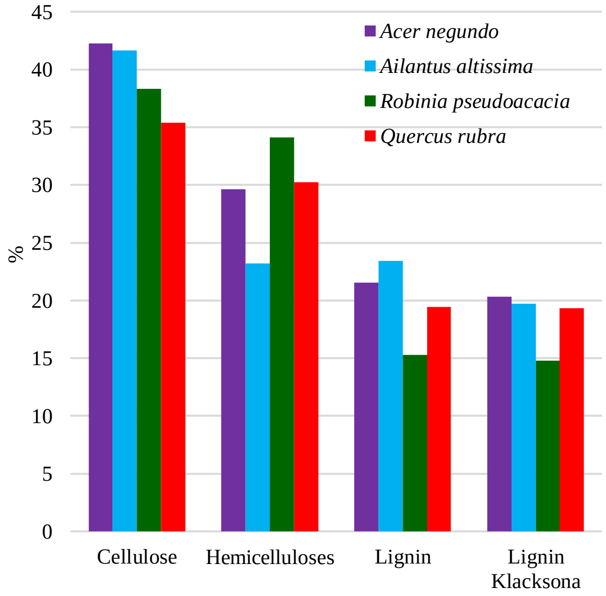


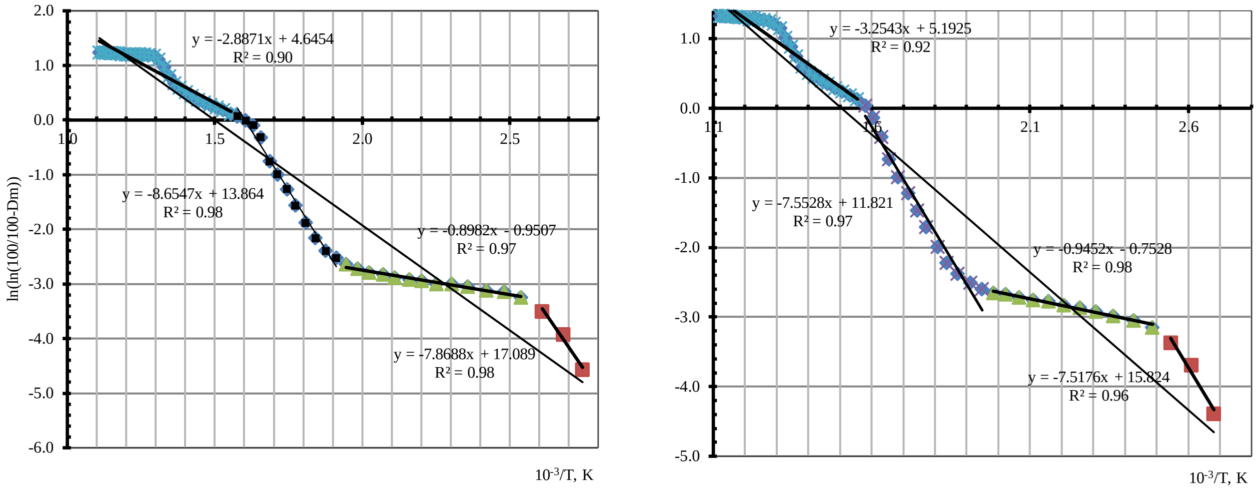
Fig. 3. Comparative characteristics of the content (%) of structural components of wood

Table 3
Total equation for thermal destruction of wood species

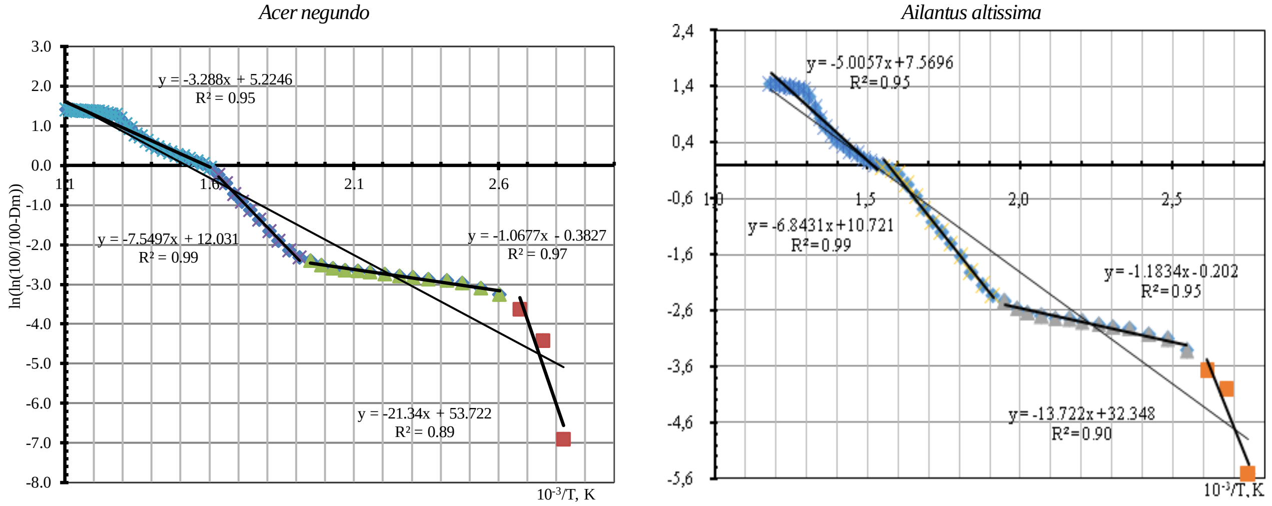
Species	Equation	R^2
A. negundo	Δ*m* = –3.845T + 5.7638	0.94
A. altissima	Δ*m* = –3.9583T + 5.9566	0.94
Q. rubra	Δ*m* = –3.9T + 5.928	0.94
R. pseudoacacia	Δ*m* = –4.003T + 6.0818	0.95

Conclusions

The conducted study of the chemical composition of wood and the characteristics of its thermal decomposition in non-native tree species within the Steppe zone of Ukraine made it possible to identify significant differences between species and their potential as biomass for energy purposes. The main wood parameters – pH level, buffering capacity, content of extractive substances, as well as the amounts of structural polymers, such as cellulose, hemicellulose, and lignin vary significantly depending on the species, which is related to the biochemical features and degree of adaptation of each species.



Acer negundo *Ailantus altissima*



Quercus robur *Robinia pseudoacacia*

Fig. 4. Logarithmic dependence of Δm at thermal destruction of the studied wood species

Thermal analysis revealed three main stages of wood biomass decomposition: moisture evaporation, thermal decomposition of hemicellulose and cellulose, and the breakdown of lignin and thermally stable residues. The activation energy calculated for each of these stages reflected differences in thermal stability and decomposition rate among the species. In particular, A. negundo demonstrated the highest rate of thermal decomposition at the main stage, while *R. pseudoacacia* showed the greatest buffering capacity.The obtained results also confirmed correlations between the chemical composition of the wood and the processes of its thermal decomposition: species with higher contents of cellulose and lignin require more energy for thermo-oxidative degradation. The studied non-native tree species can be effective sources of biomass for energy production, which is important for sustainable development and energy independence in the steppe zone of Ukraine. The use of such species, especially those with invasive characteristics, for biomass production can also serve as a tool for controlling and regulating their spread, thereby contributing to the preservation of biodiversity and ecological balance.

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