JOURNAL OF ENERGY SYSTEMS

2021, 5(4)

2602-2052 DOI: 10.30521/jes.962474 Review Article

Bio-energy characteristics of black pine (*Pinus nigra Arn.*) hydrodistillation waste products

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Submitted: 05.07.2021
Accepted: 25.10.2021
Published: 31.12.2021

Abstract: The present study aimed to investigate the physicochemical and energy characteristics of *Pinus nigra* Arn. (Pinaceae family) coniferous biomass used after the production of essential oil. The biomass, comprised of needles and needles with twigs, was milled and subjected to sieve analysis, thus producing three groups of particle fractions (between 384 and 413 μm). The infrared spectrum was recorded as 4000–400 cm^{-1}. The results from the study revealed significant differences in the phytochemical composition. Particle fractions were characterized in terms of moisture content (7.10-7.95%), ash (1.96-2.89%), cellulose (21.30-29.20%), total chlorophyll (225.54-896.04 μg/g), total carotenoids (23.52-145.43 μg/g), and polysaccharides (0.14-2.06%). The basic energy indices used in the assessment of biomass potential as conditional fuel were calculated as follows: calorific value (16748.79-16877.86 kJ/kg), the density of wood biomass (390.99-421.17 kg/m^3), and heat equivalent (0.224-0.243 J/m^3).

Keywords: *Bio-energy, Renewable, Pellets, Pinus nigra, Waste products*

Cite this paper as: Fidan, H., Stankov, S., Petkova, N., Bozadziev, B., Dimov, M., Lazarov, L., Simitchiev, A., & Stoyanova, A., Bio-energy characteristics of black pine (*Pinus nigra Arn.*) hydrodistillation waste products. *Journal of Energy Systems* 2021; 5(4): 326-335, DOI: 10.30521/jes.962474

1. INTRODUCTION

The presence of high greenhouse gas emissions, air pollution, the strong growth of global transport, which has led to increased fuel demand, has given impetus to significant research efforts to develop bioenergy derived from biomass [1,2,3]. On the other hand, the modern world's environmental challenges enhanced the need to look for alternative solutions for renewable energy sources. Waste recovery is an essential economic process for producing renewable energy, combined with its additional benefit, which is the cleaning of the environment. Different sectors worldwide inevitably have significant amounts of biomass residues [4,5,6,7,8,9]. Waste can be a promising raw material for bioenergy due to its efficiency; therefore, economically viable technologies were developed for its usage. However, there are several limitations to biomass residues and waste as an immediate energy resource. Primarily, the production of bioenergy waste is still not as profitable as fossil fuels based on developed modern technologies [10,11,12,13]. Still, waste for bioenergy production is not so economically viable due to the high cost of combustion, gasification, and pyrolysis technologies. The high energy required for the waste pre-treatment process can limit the commercialization of technological waste to bioenergy. However, the processing of waste into bioenergy can lead to the release of unwanted and harmful by-products into the atmosphere [2].

Biomass is a renewable resource and is considered an alternative raw material for sustainable energy in all industrial livestock farms. In industrialized countries, a wide range of raw materials is available to produce biofuels, including agricultural and forest residues, industrial waste, and municipal solid waste. Unlike biofuels derived from edible food crops, much of the biofuels of widespread interest to the research community are generated from lignocellulosic materials, such as wood and biomass residues [1,6].

Unlike biomass, which is grown for energy purposes, biomass residues and waste are generated together with by-products. Biomass could be categorized into primary, secondary, and tertiary groups. Primary residues are usually generated during the plantation of target crops and forest products [4,5,7]. Secondary residues are obtained after food crops have been processed into the final product form. Examples of secondary residues are wood chips, coffee husks, rice flakes, sugar cane, and palm kernel cake. On the other hand, the third group of residues becomes available for consumption after consuming humans and animals. Biomass residues and waste, wood and agricultural residues (primary and secondary biomass residues), cooking oil wastes (tertiary biomass residues), and microalgae biomass demonstrate their promising potential [2].

The biomass generated from forestry and garden, park, food, kitchen, and waste from processing is increasing. Therefore, it is necessary to use biomass' efficiency by increasing its energy consumption and through innovative approaches to its combustion [3,5]. Biomass obtained from various plant sources is an inexhaustible energy source during combustion due to its ability to consume as much carbon as it absorbs during its growing season. This ability places biomass in the group of renewable energy sources producing clean or "green" energy. Its main advantage is to lower greenhouse gas emissions compared to conventional fuels [4,11]. Forest waste, part of the timber industry, is a source of biochar, bio-oil, biofuels, energy pellets, and electricity produced by thermochemical conversion methods [2,13]. In recent years, chips are various raw materials that remain as waste in the agricultural, food, essential oil, timber, and other industries. They are considered and used as a potential source of biomass for the production of pellets and briquettes. The circular economy and its connection to the bio-energy supply are objects of the economic growth of the countries [5].

The potential of biomass used for extraction of phytochemicals can be cogenerated by the construction of modern combustion plants providing over 60% of the total energy produced in the region, meeting the needs of public buildings or households [6]. Many authors have conducted studies on some physical,

chemical, and energy characteristics of biomass. They reported data for pellet characteristics obtained by soybean culture, sugarcane bagasse, eucalyptus wood [1], waste from agriculture [7], industrial wood wastes, and peach stone [8], and waste from woody juniper [9].

The primary source of wood for energy needs in Bulgaria is forests that occupy about 34% of the country's territory. Conifers - white pine, black pine, spruce, fir, and other species, occupy about 18% of forest plantations. Apart from being a source of wood, coniferous plants are also processed to obtain essential oils, with the main application in the perfume, cosmetics industry and medicine [10]. After the essential oil extraction, this in coniferous plants is mainly consisted in the leaves and thin branches, as well as in the wood. Large amounts of waste remain, which are utilized for the production of various biomasses: energy wood chips, tree bark, wood pellets, wood briquettes, *etc.* [11,12], and for the preparation of other products [10].

In order to appropriately apply bioenergy efficiency in the recovery of biomass from the timber or processing industry, it is necessary to assess its bioenergy potential, both from a consumer point of view and from the management of waste products. The characteristics of the input biomass determined the production of pellets, which is a multi-stage process [13].

With the community's increasing interest in using alternative energy sources, which are waste products from the agricultural sector, light, and heavy industry, a large part of the research was focused on their application in the goals of the green economy. The department of wood processing of coniferous species for fuels and timber in Bulgaria provides over 2.5% of the gross domestic product, which is related to the generation of large quantities of coniferous biomass, which is waste for their subject of activity. In turn, essential oils of coniferous species are associated with producing cosmetic, pharmaceutical, and agricultural products for plant protection. In the conditions of the circular economy, this is associated with the generation of large quantities of coniferous biomass, which does not find subsequent application, except for the production of coniferous biofertilizers. Therefore, the aim of the present study was to investigate the characterization of the physicochemical and energy performance of *Pinus nigra* Arn. coniferous biomass, mainly used in essential oil production, with the potential for inclusion in bioenergy products.

2. MATERIAL AND METHODS

Plant material. The needles with thin twigs of black pine (*P. nigra* Arn., family Pinaceae) growing in Bulgaria were used. The raw material was collected during the spring of 2020. The species has been identified in Agricultural University, Plovdiv. Before processing, the raw material was cut into particle size 1.5-2.5 cm. It was processed by hydrodistillation into a laboratory distillation apparatus according to the British Pharmacopoeia, modified by [14] under the following conditions: Duration 3 h, raw material: Water ratio = 1:10.

After hydrodistillation, the waste material was subjected to drying by adjusting the humidity (75±2%) and the thickness of the layer of material 2-3 cm. Forced air circulation (0.2 m/s) was provided in the drying rooms (25°C), ensuring even drying and avoiding the development of molds. The biomass was separated on sieve bases and was periodically stirred mechanically during drying process.

Physical and chemical characteristics. The biomass was grounded on a Schule laboratory pin crusher (Germany) at a peripheral pin speed of 64 m/s and a load of 30 kg/h. The required degree of grinding is achieved as a result of seven consecutive passes of the supernatants separated over a sieve with apertures of 500 μm through the crusher and collection of the separations of the grindings in a total fraction. The sieve analysis of the obtained ground product (less than 500 μm) was performed using a laboratory sieve operator LP-200, including five sieve frames with dimensions of 200 x 200 mm and the precise openings of the sieves. The sieving lasts for 3 minutes, at a sieve operator speed of 180 min^{-1} [12]. The moisture

content of the biomass was determined by drying to constant weight at 105 °C [12], and the results from the chemical analyses were given on a dry weight basis (dw). The ash content was determined according to AOAC, 2005, by igniting the samples at 550°C for 5 hours [12]. The infrared spectrum was recorded using a Nicolet iS 50 (Thermo Scientific, USA) FT-IR spectrometer in the frequency region of 4000–400 cm^{-1}, with the samples embedded in KBr matrixes. The total chlorophylls and carotenoid contents were measured, according to the methods described by [15], and [16]. The total soluble carbohydrate content was determined according to the method reported by [17]. Sucrose, glucose, and fructose were analysed by HPLC method [18]. The cellulose content was determined following the method of [19].

Energy characteristics. The heating value (kJ/kg), density of wood biomass (kg/m^3), and heat equivalent (J/m^3) were calculated according to the method [12].

Statistical analysis. The measurements were performed in triplicate and the results were presented as the mean value of the individual measurements with the corresponding standard deviation (SD), using Microsoft Excel.

3. RESULTS AND DISCUSSION

Sieve analysis. The biomass origin and its moisture, temperature, and grinding system influenced the susceptibility to digestion [20]. The primary fractioned amounts of ground biomass are presented in Table 1. The data showed that the density of distribution of the three samples fractions had similar values in the studied range of size classes. Therefore, the similar average diameters (between 384 and 413 μm) of the particles of the three samples were determined. According to our results, the particle size distribution was uneven. The reason for this could be considered with the different strength in the structure of the vegetative plant parts. The highest distribution density was reported in class size 500/355 μm. Larger particles predominated, mainly from the woody part of the branches, which had higher strength and significantly impact resistance, despite of their low humidity. The finer sieving fractions were composed of ground green needles from pine twigs, and they were easier to grind. The digestion of the biomass and the particle size determined the density of the obtained pellets and, at a later stage, the rate of their combustion [20].

Table 1. Fractional characteristic of P. nigra biomass

Size class, μm	Needles with twigs			Needles (sample 1)			Needles (sample 2)		
	m, g	m, %	qi*,mm^{-1}	m, g	m, %	qi, mm^{-1}	m, g	m, %	qi, mm^{-1}
000 – 132	2.0	0.015	0.11	6.8	0.057	0.43	15.6	0.130	0.98
132 – 150	0.5	0.004	0.22	0.4	0.003	0.19	0.5	0.004	0.23
150 – 180	0.5	0.004	0.13	0.3	0.003	0.08	0.4	0.003	0.11
180 – 200	3.0	0.023	1.15	3.3	0.028	1.38	1.7	0.014	0.71
200 – 280	5.0	0.038	0.48	3.4	0.028	0.36	1.2	0.010	0.12
280 – 355	2.0	0.015	0.20	0.6	0.005	0.07	0.7	0.006	0.08
355 – 450	64.0	0.481	5.34	44.5	0.373	4.14	45.4	0.378	4.20
450 – 500	56.0	0.421	8.42	60.0	0.503	10.06	54.6	0.455	9.09
Σ, g	33.0			119.3			120.1		
Medium diameter, μm	413.9			407.4			384.7		

*Note: qi- density of distribution

The particle size distribution of the biomass and the density of distribution of the fractions in the sample needles with twigs are presented in the Table 2. The grinding process and the granulometric evaluation of the biomass provided information on the degree of fragmentation of the particles during the production of the pellets in the presence of pressure. By reducing the volume of the particles, an adequate adhesion between them is ensured without changing the shape of the pellets and forming air pores [21]. The size of the biomass digestion corresponds to the digestion rates recommended by other authors [22] for biomass from plant species used for pellet production.

Table 2. Particle size distribution and distribution density of ground biomass

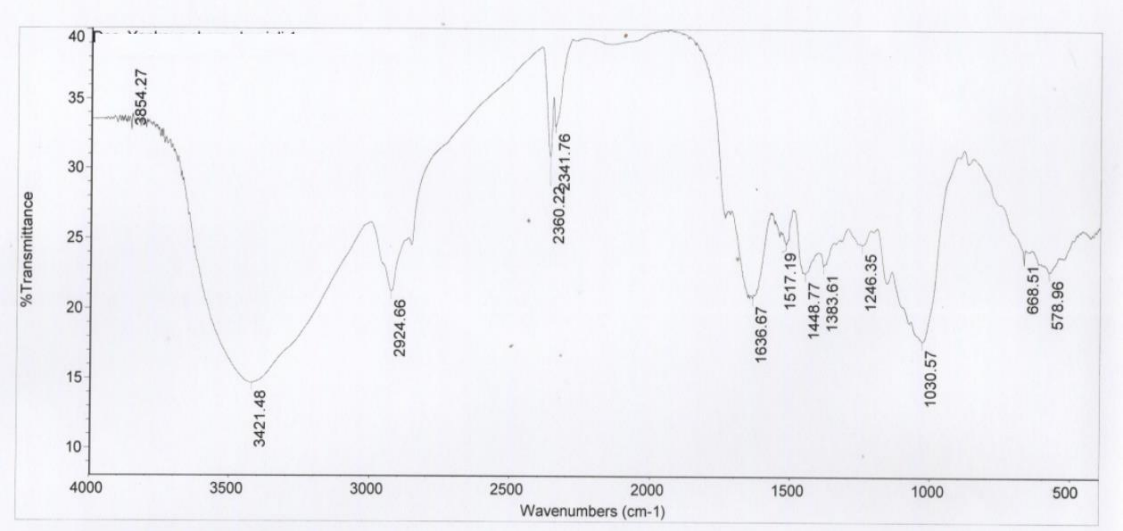
№	Slieve light opening, x_i, mm	Mass part, ΔD_i [-]	Class width, Δx_i, mm	Density of distribution, $q_i=\Delta D_i/\Delta x_i$, mm^{-1}
1	0 – 0.132	0.421	0.132	0.11
2	0.132 – 0.150	0.481	0.018	0.22
3	0.150 – 0.180	0.015	0.030	0.13
4	0.180 – 0.200	0.038	0.020	1.15
5	0.200 – 0.280	0.023	0.080	0.48
6	0.280 – 0.355	0.004	0.075	0.20
7	0.355 – 0.450	0.004	0.090	5.34
8	0.450 – 0.500	0.015	0.050	8.42

Physical and chemical indices. The IR spectrum of biomasses is shown in Table 3. All three samples contained OH group, which was confirmed by the absorption bands in the three samples (for needles with twigs (3423 cm^{-1}), for sample 1 (3421 cm^{-1}), and for sample 2 (3432 cm^{-1})), which is further confirmed at the absorption strips for the sample of needles with twigs (2362 cm^{-1}), sample 1 (2360 cm^{-1}) and sample 2 (2361 cm^{-1}). For the twig needle sample, an absorption band appeared at 1735 cm^{-1}, a characteristic band for an aldehyde carbonyl group. All three samples have characteristic absorption bands for *cis*- a double bond of the type HRC=CR'H, respectively at 1636, 1637, and 1637 cm^{-1}. The sample of twig needles and sample 1 had absorption bands at 1517 cm^{-1}, characteristic of an aromatic nucleus band (oscillations for γ C=C). It is noteworthy that in the sample of needles with stems and sample 1 there are characteristic bands of aromatic and vinyl ethers of the type =C–O–C, γ as C–O–C, at a wavelength of 1262 and 1246 cm^{-1}, which is absent in sample 2. Additionally some bands typical for carbohydrates, especially lignin and cellulose were observed (Table 3) that could be explained with high cellulose content in samples. A band around 1457 cm^{-1} was due to deformation of lignin CH_2 and CH_3 and 1636 cm^{-1} was typical for stretching of the C=C and C=O lignin aromatic ring. A band at 1735 cm^{-1} was assigned to C=O stretching of unconjugated hemicellulose while the band at 2925 cm^{-1} was due to asymmetrical stretching oh CH_2 and CH. Our observation coincided with the bands reported in literature [23] which denoted the characteristics of cellulose. The obtained diffraction peaks corresponded to the previously reported [24] showed the difference in the intensities of the peak maxima in the three samples. The obtained carbon bands took into account the carbon fraction obtained in the thermochemical processes. Smaller bands with a visibly smaller volume showed C – C bonds presence and the emergence of additional energy forces forming small volumes, but relatively good conducting electrochemical waves [25]. The biomass of tree species was composed mainly of cellulose, hemicellulose, and lignin substances. Thus, it was lignocellulose biomass that contained about 50% carbon and 6 to 10% hydrogen [26, 27].

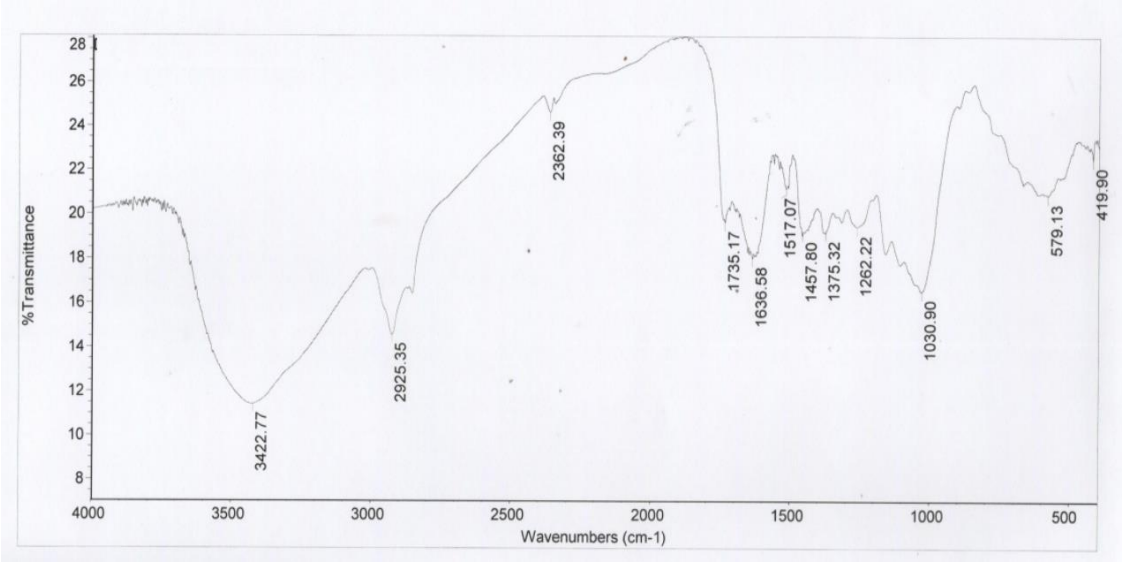
Table 3. IR spectrum of P. nigra biomass

Characteristic bands (cm^{-1})				
Needles with twigs	Needles (Sample 1)	Needles (Sample 2)	Reference data	Group type
3423	3421	3432	3550 – 3400, 3590 – 3420	νOH intra- and intermolecular H – bond
2925	2925	2924	2940 – 2915	ν_{as} $–CH_2–$
2362	2360	2361	3110 – 2362	vibration of γ (OH) bond
1735	1735	1735	1740 – 1720	R – CHO $\nu_{C=O}$; characteristic band of carbonyl group
1636	1637	1637	1665 – 1635	a characteristic band for *cis*- HRC = CR'H bond
1517	1517	-*	1525 – 1475	a characteristic band of the type ν C=C
1458	1449	-	1480 – 1450	linear $–CH_2–$ bond; νC–Hs(CH_2) in pyranose ring, βo–н (OH) for carbohydrates
1375	1384	1384	1385 – 1370	a characteristic band of the type $C(CH_3)_2$
1262	1246	-	1275 – 1200	=C–O–C, ν_{as} C–O–C, aromatic and vinyl
1031	1031	1030	1070 – 1000	trisubstituted aromatic ring γAr – H in positions 1,2,4; νC–O (C–O) from pyranose ring for carbohydrates

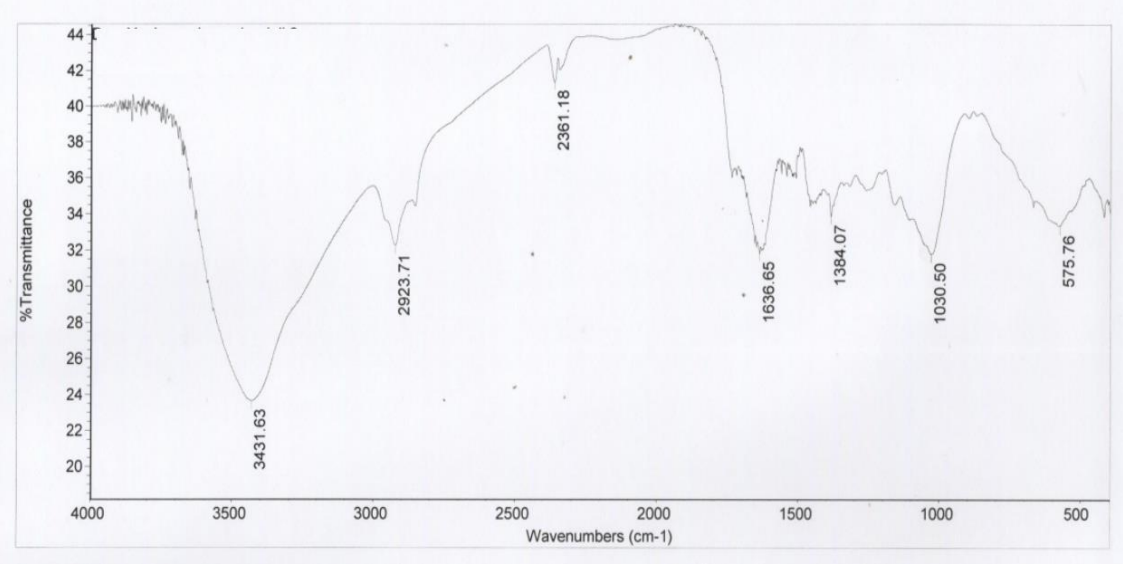
*-not detected



(a) Needles with twigs



(b) Needles (sample 1)



(c) Needles (Sample 2)

Figure 1. IR spectrum of biomasses from P. nigra

The energy characteristics of cellulose and hemicellulose were similar, with about 17.6 and 17.9 MJ/kg, as the energy equivalent of lignin in the biomass composition was decisive in plant species. The experimental FT-IR spectrum of biomasses was presence in Fig. 1.

The results obtained in this study showed that the decomposition of the organic and inorganic components included in the biomass composition caused aggregation zones that changed the thermal costs during pyrolysis. The lingo-polysaccharide amorphous chains involved in the biomass composition shifted the area of the spectral peaks as a result of the different cellular parts and their density, hardness, and strength. The absorption of energy fluxes in the three samples was in close range, with secondary peaks registered in separate zones. This could be explained by the differences in the moisture content of the samples. In areas with absorption-bound water (OH - H), peaks with a larger area were reported. The small spectral differences in the samples studied could be explained by the similar chemical composition, and the small differences were due to the quantitative differences in the absorption-bound water.

The physicochemical data obtained for the composition of the biomass are presented in Table 4. The moisture content was in low levels for plant material and did not exceed 8%, while the ash content varies between 1.96 and 2.89. The results in our study showed that values for ash content were higher than those presented for pine (1.3%) reported by [8] but were comparable to those determined for pine and eucalyptus (0.59-2 69%) by [28]. Higher values of ash content reduced the calorific value of biomass. It is known that lignocellulosic biomass has a low ash content (0.2-1.8%), which is considered as a guarantee for the absence of slag, which is formed in biogenic fuels containing more than 4% ash. Compared to other types of biomass (from 38 to 56%), the lower content of cellulose could be explained by the processed raw material, containing mainly leaves with thin branches bearing them, where the essential oil is deposited. The needles had a higher content of chlorophyll and carotenoids, which could be explained by the photosynthesis that takes place during the spring season when the samples were collected. Results for three years investigation of *P. nigra* subsp. *pallasiana* (Lamb.) Holmboe about seasonal patterns variations in total soluble carbohydrate chlorophyll, carotenoids in needles were reported by [29]. Our data for total soluble sugars were slightly lower than total soluble carbohydrate content in Anatolian black pine, where they varied from 33.60 to 78.26 mg/g [29] and was four times lower than soluble sugar content in Scots pine needles [30]. This could be explained with climate conditions, different variety and seasonal changes in carbohydrate accumulation [29]. Extraction of the essential oil during hydrodistillation changed the structure of the cell walls and increased the reactivity of the subsequent heterogeneous reactions related to combustion [31]. The change in the crystal structure of cellulose during hydrodistillation increased the availability of individual cellulose filaments. It improved the specific contact surface [32], as a result of which combustion could be regulated and used in automated combustion plants.

Table 4. Physical and chemical indices of P. nigra biomass

Indices	Needles with twigs	Needles (sample 1)	Needles (sample 2)
Moisture, %	7.10 ± 0.61	7.50 ± 0.71	7.95 ± 0.76
Ash, %	2.66 ± 0.20	1.96 ± 0.10	2.89 ± 0.21
Total carotenoids, µg/g	23.52 ± 2.03	145.43 ± 1.22	80.20 ± 0.52
Total chlorophylls, µg/g	225.54 ± 19.54	896.04 ± 8.82	379.05 ± 6.90
- Chlorophyll a	136.81 ± 29.86	688.04 ± 12.34	218.93 ± 11.52
- Chlorophyll b	88.73 ± 8.64	208.74 ± 5.22	152.57 ± 2.32
Total carbohydrates,%	29.12± 1.05	23.43± 1.00	31.12± 0.85
Cellulose, %	26.10 ± 0.25	21.30 ± 0.20	29.20 ± 0.27
Total sugars, %	2.06 ± 0.2	0.28 ± 0.0	0.14 ± 0.0
- Sucrose	0.70 ± 0.0	Not detected	Not detected
- Glucose	0.45 ± 0.0	0.12 ± 0.0	0.05 ± 0.0
- Fructose	0.91 ± 0.0	0.16 ± 0.0	0.09 ± 0.0

The biomass moisture at which the obtained pellets' required density and energy characteristics are provided is in the range between 7.8 - 15%. At the relative moisture values, the plant biomass is well compacted, not too dry, which does not allow its destruction. Stratification is avoided, which is an

essential indicator of the quality and fuel characteristics of the pellets. The value of moisture also depends on the type of material and its composition. Using coniferous biomass containing carbohydrates, resinous substances, and lignin components affects the compaction processes [8, 29].

Energy characteristics. Biomass decomposes with heat release in nature, but this is done very slowly, at temperatures close to the environment. This natural process is used in the use of plant biomass as a fuel source. The calculated energy characteristics are presented in Table 5. The data showed that the calorific values obtained for *P. nigra* biomass in this study were lower than the data in the literature. Our results were comparable to those reported for pine and eucalyptus (16.53-18.13 MJ/kg) pellets by [28] understandably with higher ash and moisture content. Biomass density values obtained in this study were lower than that reported in the literature for other biomass (above 650 kg/m^3) presented by [28, 33]. The differences could be explained by the origin of the raw material, the size of grinding, and moisture content of the plants.

Table 5. Energy indices of P. nigra biomass

Indices	Calorific value, kJ/kg	Density, kg/m^3	Heat equivalent, J/m^3
Needles with twigs	16877.86	421.17	0.243
Needles (sample 1)	16828.26	414.55	0.238
Needles (sample 2)	16748.79	390.99	0.224

The degree of improvement of the individual characteristics of the biomass as an alternative bioenergy resource and the unification of the physical indicators - moisture, particle size, composition, etc. allowed good planning of the processing technology [33]. The melting point of lignin, resinous, and other components in the system led to forming a glassy product, which improves the shape and density.

4. CONCLUSIONS

The results in the present study showed the complexity of applying biomass as an energy source. Several factors in biological systems affect the density and quality of energy products. From the results obtained in the present study, it is clear that the coniferous biomass obtained by distillation of essential oil can be used as a percentage in the composition of bioenergy composite mixtures. Its energy characteristics were calorific value from 16748.79 to 16877.86 kJ/kg, density from 390.99 to 421.17 kg/m^3, and heat equivalent from 0.224 to 0.243 J/m^3. The results from this study may provide an alternative route for residue disposal with the added benefit of energy recovery. The relatively low calorific values are the reason for the impossible use of biomass in its form to provide sufficient energy equivalent and energy density. The subject of future analyses will be the inclusion of biomass in the composition of woody biomass of deciduous species. The distilled raw material will increase the density as a result of the available resinous substances.

Acknowledgments

The authors acknowledge the support by the National Science Fund of Bulgaria, project No KP-06-H36/14.

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