# CHARACTERIZATION OF BIOMASS RENEWABLE ENERGY RESOURCES FROM SOME PERENNIAL SPECIES

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The scope of this study is the evaluation of the energy content and the qualitative characteristics of five perennial biomass species collected from various forest and hill areas in Romania. The compared species are: stone lichen (*Cetraria islandica*), mistletoe (*Viscum album*), knotweed (*Polygonum aviculare*), wheatgrass (*Agropyron repens*) and knapweed (*Centaurium erythraea*). The following characteristics are evaluated: higher heating value (HHV), higher heating value of ash free sample (HHV$_f$), carbon (C), nitrogen (N), moisture, ash content, bulk densities and fuel value index (FVI). Carbon content is the essential characteristic that considerably affects the heating power of fuels. Our data indicate that the studied species are good resources as biofuel in the form of pellets. The specific parameters are determined according to definite standard methods. From among the considered species, *Viscum album* presents the highest heating value, highest carbon content and the lowest moisture content, thus being a satisfactory material for home pellets manufacturing.
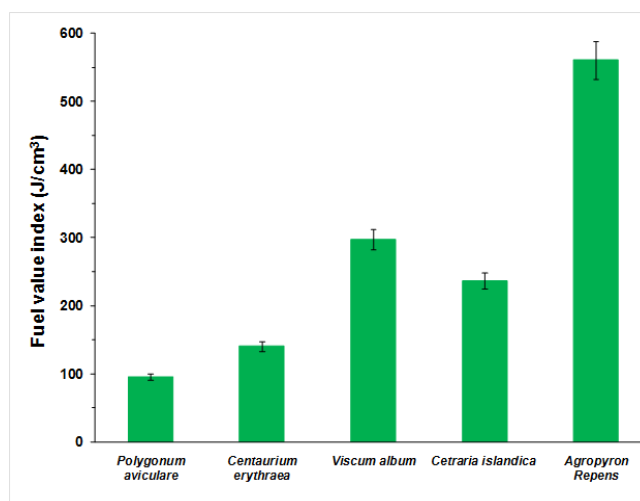
INTRODUCTION

At the moment, both in Roumania and in other European countries, widespread perennial species are evaluated for their possible usage in various sectors of economy.[1,2]

Combustion calorimetry method has a significant capacity for obtaining the results required to define the employ of plant biomass species in the form of pellets as an alternative source of fossil fuels. The form of pellets is the most generally used for solid biofuels as they combine a high energy density and quality standards that ensure easy handling and transportation.

Biomass is the third largest natural source of energy in the world. It is accessible in most countries and its practice may expand the fuel-supply in many circumstances.[3] It frequently refers to plant matter grown or harvested for usage as fuel. Also, it can be used to define animal and plant matter employed for production of fibers, chemicals or heat.

Combustion of biomass is considered to be constructive for the environment in comparison to the use of fossil fuels. The release of carbon dioxide in the combustion process is compensated by its recent absorption by the plants, so-called closed cycle of CO_2.[4] The physical and chemical properties of coals and biomass vary, thus it is essential to determine the chemical composition as this often affects the combustion characteristics.[5] The major difference in the composition of biomass fuels is ash content.

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Fuel made from biomass is ecological and highly energetic. It produces a small amount of ash in the combustion process. Biomass can yield continuous electricity generation and is the only outspread source of renewable heat. The increased usage of biomass as a source of energy (electricity and heat) will contribute to the reduction of CO_2 emissions, increase energy security, and support feasible progress and reconstruction of provincial areas.[6]

Biomass reserves can be split into four conventional classes: wastes (urban and agricultural), forest products, energy crops, aquatic plants.[7] Of the four major groups of biomass, grasses, woody and herbaceous plants are the primary types of importance for generating energy.

Fossil fuels present the disadvantages that are formed during millions of years and when burned, it release "new" greenhouse gases into the atmosphere. Higher performance of a biomass plant means fewer negative effects on the climate, resulting in a decrease of demanding burning firewood, oil, or coal. Species diversity are needed for improved biodiversity and in order to offer a continuous biomass supply for the energy generation sector and for integrated biorefineries and industry.[8]

Perennial energy crops (grasses and trees) are widespread and used because of their low environmental impact than conventional agricultural crops. (see Figure 1).

In Figure 2 are presented the samples after drying in oven, before pressing into pellets.

The studied plants were harvested from the spontaneous flora of Prahova Valley (Roumania) in June-October 2019. Common knotgrass (*Polygonum aviculare*), despite its name, is not a grass, but is actually related to the docks. It has wiry stem that grow along the ground and is a weed of waste ground, gardens and arable fields.[9] *Polygonum aviculare* is native to Europe, but has been extensively introduced elsewhere. It is now a widespread weed in nearly all the temperate regions of the world and, more locally, in warmer climates.[10]

In Canada, *Polygonum aviculare* is mostly known as a nuisance weed of lawns, sidewalks and paved areas, and large sums are spent annually to control it.[11] *Polygonum aviculare* is also very common in Slovakia, being represented by four species.[12]

Cetraria islandica (stone lichen) from *Parmeliaceae Family* is found in Northern and Eastern Europe, Siberia and North America and in middle ranged and alpine mountains in Germany, North Italy, Czech Republic, Slovakia, Poland and Russia. Its habitat is in damp places, usually on rocks and the bark of trees, especially conifers.[13] It is also found in Britain, all over Europe, especially in the Arctic region. Species from *Cetraria islandica* are found in Kopaonik, Serbia, a renewed interest in lichens being developed in recent years in this country.[14] In our country, the lichen flora is high on the waste dump of Rosia Montana.[15]
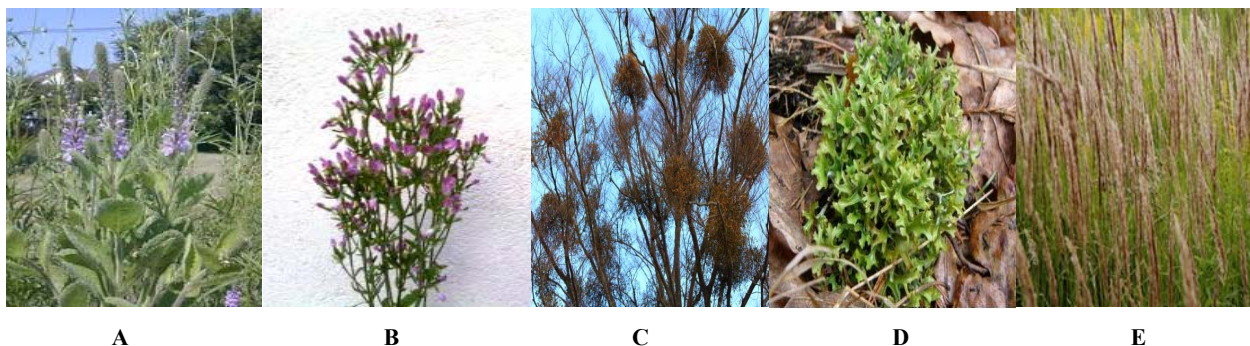

Fig. 1 – The investigated biomass perennial species: A – *Polygonum aviculare*; B – *Centaurium erythraea*; C – *Viscum album*; D – *Cetraria islandica*; E – *Agropyron repens*. (https://en.wikipedia.org/).
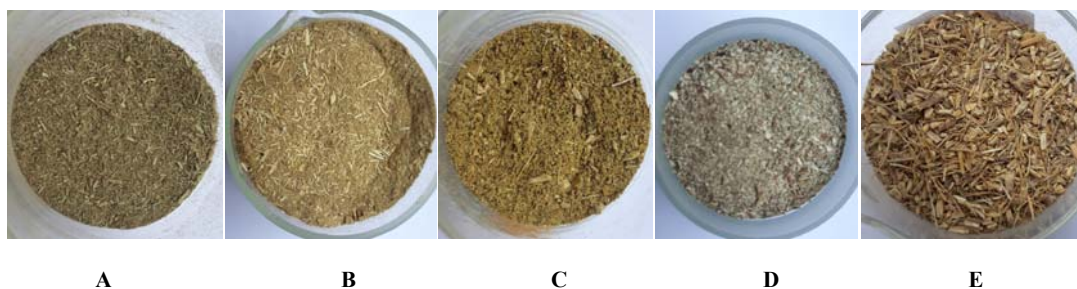

Fig. 2 – The grass powders after drying. A – *Polygonum aviculare*; B – *Centaurium erythraea*; C – *Viscum album*; D – *Cetraria islandica*; E – *Agropyron repens*.

Viscum album L. or European mistletoe belongs to the family of the *Loranthaceae*.[16] It is a semi-parasitic plant and grows on several types of trees, especially pine, poplar, apple trees etc. It is native to Europe and Western and Southern Asia.[17-19] It is found in Austria, Czech Republic, Denmark, Estonia, Germany, Lithuania, Poland, Slovak Republic, Spain, Slovenia. Barney *et al.* (1998) listed 452 species, subspecies, varieties and hybrids in 96 genera of 44 families as potential hosts.[20] In the east it occurs in the Ukrainian Carpathians, and also to some extent in the other parts of Western Ukraine and the Crimean Peninsula. Although there are many varieties of mistletoe, including the American (*Phorandendron serotinum* or *Phorandendron flavescens*), the European (*Viscum album* L), and the Korean (*Viscum album* L. *coloratum*), most investigative work has been done on European mistletoe.[21]

Different species of *Viscum album* are capable of parasitizing a large number of host species. The European mistletoe (*Viscum album*) from the family *Viscaceae* is able to infest more than 380 woody taxa in Europe. At the begining of the 20th century, less than 10% of Hungary was infested. The distribution area was centralized in the Transdanubian Mountains, and no mass occurrence was noticed elsewhere. Since then, the infested area has almost tripled, and heavily infested forests can be observed in numerous parts of Hungary, especially in the Northeast Area of the Hungarian Great Plain. The most infested macroregion of Hungary is Western Transdanubia, the only region where all three different subspecies can be found. The increased mistletoe occurrence can be attributed to several factors, including human impact and larger forest area.[22]

In Roumania, *Viscum album* occurs only on Silver fir (*Abies alba Mill.*) and is one of the most significant biotic factors that has affected silver fir stands.[19] Silver fir occurs naturally only in the Carpathian Mountains, mainly in mixed forests with beech and spruce on an estimated area of 0.9 mil. ha.

Viscum album causes important damages and wood degradation. According to the Flora of RPR (1952) in Romania, *Viscum album abietis* was spread in the Northern part of Eastern Carpathians (Maramures and Bucovina) and Focşani area (Dealul Lung and Pelticu forest). According to Zuber,[16] in Roumania mistletoe is spread in Northern part of Roumanian Carpathians and in Banat Mountains.

Agropyron repens (*Elymus repens*) or couch grass, is a perennial grass that is a problematic weed in a wide range of crops.[23] *Elymus repens* is a serious agricultural and horticultural weed mainly in temperate climates in the Northern Hemisphere and to some extent in cool climates at higher altitudes within warmer regions. It is particularly important in the northernmost, cooler, agricultural areas, where it seems to be more competitive in perennial crops than further south.[24] It is reported as an important weed of coffee in higher, cooler areas of New Guinea and is found in scattered sites in the cooler mountain valleys of Central and South America. The occurrence of this species in temperate climates and its absence in the warm tropics may be due to difficulties in producing rhizomes at higher temperatures.[25]

The species grow on many types of soil, both mineral and organic. It seems to be most competitive on fertile soils, rich in nitrogen and with a good water supply and is less successful on very acid or very dry, shallow soils.[24]

Elymus repens occurs through Europe in habitats of various types. It is a species native to Eurasia that has been introduced to North America, where it is a troublesome invasive weed. According to literature,[26] there are 1081 plants from 302 populations covering Central Europe and adjacent countries: Austria (8 populations), Bulgaria (2 populations), Czechia (169), Germany (13), Hungary (20), North Macedonia (2), Moldova (3), Poland (14), Romania (6), Slovakia (39), Slovenia (5), Serbia (7) and Ukraine (14).

In Roumania is widely spread in agricultural crops.[27]

Centaurium erythraea is a variable biennial or annual found throughout Europe, mainly on calcareous soils and dry grassy places, including sand dunes and chalky uplands.[28] There are about 14 species of *Centaurium* in Europe. The Flora of Turkey [29] gives five *Centaurium* species, including *Centaurium erythraea*.[30]

European centaury is native from Western Europe to Pakistan and Northern Africa and introduced in North and South America and Australia.

In Roumania, *Centaurium erythraea* is found in meadows, the edge of the plain forests to the hill area. In Greece exist five subspecies of *Centaurium erythraea* and in Italy is present in all regions. In the Netherlands the species is quite common in the coastal areas and not rare in the Southern part of the country and along the rivers. In Czech Republic the species is rather common in open mesophilous grasslands and sometimes also on disturbed habitats like the fallows.

In Kurdistan, *Centaurium erythraea* is quite common and it is easily found in nature, mainly in low temperature zones (places close to mountains and some valley areas).[31]

The aim of the study is to establish if the selected biomass are suitable for energy purposes. Thus, higher heating value (HHV), higher heating value of ash free sample (HHVf), nitrogen, carbon, bulk density, moisture, ash content and fuel value index (FVI), are determined after combustion experiments.

RESULTS AND DISCUSSION

Plant raw materials, which may be a potential heating biomass source are highly varied, thus knowledge on them is essential.

The calorific value of plant is defined as the amount of heat energy released during the combustion of a specified amount of it. In this study, the heating value of the studied species is expressed as higher heating value (HHV) and higher heating value of ash free sample (HHV_f), the latter being calculated after subtraction of ash from the weight of HHV determination. In Table 1 are shown the values obtained for HHV_f (MJ/kg), bulk density (kg/m^3) and nitrogen content (%). Six replicates have been made. The experimental results show that the HHV_f increases in order: *Cetraria islandica, Agropyron repens, Polygonum aviculare, Centaurium erythraea, Viscum album* (Table 1).

Carbon is the major burning component of a fuel; it can yield energy in the form of heat, and then converted into other forms of energy such as steam and electricity.

The total organic carbon content (TOC) is determined through dry combustion, from the difference between the initial mass sample and the residue after combustion, is obtained the burned organic mass, then calculating the total organic carbon content (TOC) by applying the correction factors in accordance to the standards of the method.

The removal of water from the sample is essential during the determination of TOC by the dry combustion methods. Dry chemistry techniques can be divided into two phases, namely, sample combustion and sample quantitation. The sample combustion technique is previous described.[32] The end product of the combustion is CO_2 which is quantitated by gravimetric technique using adsorption bulbs.[33] Biomass has less carbon content than coal. Dry combustion method is considered the most accurate method because ensures oxidation of all organic carbon.[34,35] For calculating the total organic carbon (TOC), the following formula is used:[36]

$$TOC(\%) = Organic Carbon(g)/W(g) \quad (1)$$

where $W(g)$ is dry sediment analysis weight (g).

In this study, solid fuels made of plant biomass are studied as an alternative to fossil coals. The carbon content of a sample is the contribution that carbon makes to the total mass of the sample. The carbon content of vegetation is notably constant for a large variety of species, and is ranged between 45 and 50%.[37,38]

Variation of the carbon content is presented in Figure 3.

From the studied species, *Viscum album* presents the highest carbon content, about 43.5%, closed to literature values[37,38] and the lowest carbon content is found in *Cetraria islandica* about 39.8%. The higher content of carbon present in the biomass species, the higher will be the thermal energy.

Table 1

HHV$_f$ (MJ/kg), bulk density (kg/m^3) and nitrogen content (%) for the selected perennial species

Species	Higher heating value of ash free sample (HHV$_f$) ± S.D. (MJ/kg)	Bulk density (kg/m^3)	Nitrogen content (%)
Polygonum aviculare	17.75±0.1	0.1893±0.02	0.36±0.04
Centaurium erythraea	18.57±0.3	0.1726±0.02	0.31±0.03
Viscum album	21.32±0.2	0.2988±0.05	0.3±0.03
Cetraria islandica	16.39±0.1	0.1467±0.02	0.23±0.02
Agropyron repens	17.21±0.6	0.2797±0.04	0.38±0.05

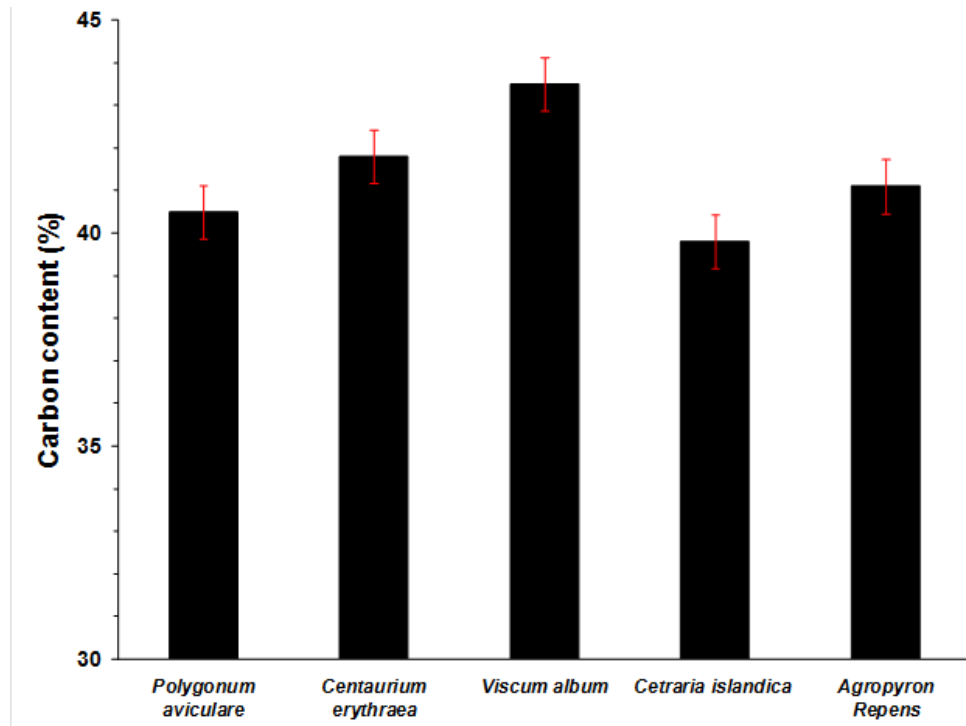S.D. – standard deviations of the mean

Fig. 3 – Values of carbon content for studied plants.

Ash and moisture content

The required features for a high quality perennials is the high combustion ability, high heat output and low ash content.[39] Ash is composed of minerals, inorganic substances that remain after burning the fue.[40] Ash is one of the essential generated secondary products. High ash content involves more charges related to ash evacuation and storage of combustion devices.[41] Higher ash content causes difficulties to combustion automation. Although ash is not pollutant, high ash contents may confuse home and industrial users of biofuels, eroding and fouling machinery. However, some quantities of ash in fuel is needed since in case of a great furnace, it protects the grate against overheating.[42] The ash content is estimated using EN 14775:2009. Solid biofuel: Determination of Ash content. The ash quantity is calculated through weighing of the bomb crucible before and after combustion.[43]

The variation of HHV (MJ/kg), ash and moisture content (%) for the studied species is plotted in Figure 4.

From Figure 4 is find out that from ecological point of view, *Cetraria islandica* pellets present a convenience due to the low ash content of 1.11%. The ash content of our samples varies between 1.11–5.28%, in agreement with literature statements. An interval of acceptance for the ash content of plant biomass is up to 10%, being influenced by the biomass type, soil type, fertilization and the maturity of the plants.[44]

In the literature, there are many works on characterizing and obtaining the calorific values for a large series of biomass species. Komlajeva *et al.* studying a group of perennial grasses widely distributed across Europe, such as reed canary grass (*Phalaris arundinacea* L.), an ideal biofuel source in Latvia,[45] hemp (*Cannabis sativa* L.), sunflower (*Helianthus annuus* L.), reported the calorific values of about 16.8 MJ·kg^{-1} in good agreement to the value reported by our group for *Polygonum aviculare* (16.81 MJ·kg^{-1}), differences being found in the ash content. The ash content should not surpass 5–7%. This requirement is fulfilled by our studied species, but the Latvian ones ranged from 3.1 to 12.8%.

In Greece there is an increased interest on valorification of biomass residues, revealed by the existence of the agricultural crops (cotton, cardoon), forages (*Typha angustifolia*, *Phragmites australis*) and forest (poplar, pine, fir, beech) wastes. There are more than 30 species of cotton plants, but only few are used to supply the world market for cotton. Gravalos *et al.*[46] reported for the cardoon (*Cynara cardunculus*) a gross calorific value of 14.98 MJ·kg^{-1} and a net calorific value of 16.02 MJ·kg^{-1}; the values obtained for cotton are 17.73 MJ·kg^{-1} for gross calorific value and 18.75 MJ·kg^{-1} for the net calorific value respectively, our reported values for *Centaurium erythracea* are close to the results presented above.
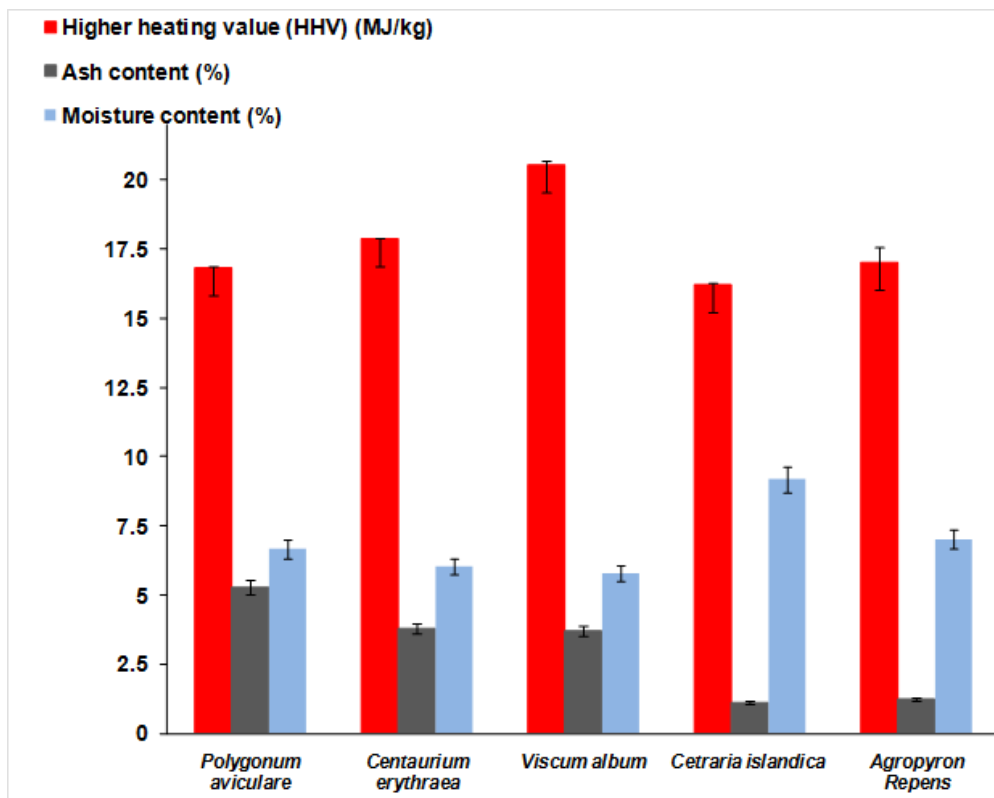
Fig. 4 – Plot of the variation of (HHV), ash and moisture content (%) for the studied species.

The same researchers[46] reported for *Phragmites australis* a gross calorific value of 16.94 MJ·kg⁻¹ and a net calorific value of 17.93 MJ·kg⁻¹, close to our values for *Polygonum aviculare*. The values for *Typha angustifolia* are 17.23 MJ·kg⁻¹ (gross calorific value) and 18.11 MJ·kg⁻¹ (net calorific value) close to *Centaurium erythracea*. Their ash content ranged between 3-6% in agreement to our results.

In Poland, the potential of the biomass is considered an interdisciplinary issue. For the species such as: *Salix viminalis*, *Miscanthus*, *Malvales*, *Phalaris arundinacea*, *Helianthus tuberosus* the calorific values reported, ranged between 15-17 MJ·kg⁻¹.[47] Other species of herbs from Poland are studied by Zabinski *et al.*,[48] leaved stalks of milk thistle (*Silybum marianum*), non-leaved stalks of thyme (*Thymus vulgaris* L.), garden sage (*Salvia officinalis* L.), inflorescence axes of lavender (*Lavandula angustifolia*) and fennel (*Foeniculumcapillaceum Gilib*). Their average value of the heat of combustion is about 20.47 MJ·kg⁻¹, close to our value of 20.53 MJ·kg⁻¹ for *Viscum album*. Our heating values for all the studied species are higher than the heat of combustion reported for biomass milk thistle, of 13.28 MJ·kg⁻¹, which reveal a poorer utility as a solid fuel.

Aleksey *et al.*,[49] studied plant raw material annually renewable in the Russian Federation. Biomass of reed (*Phragmites australis*) and sedge (*Carex nigra*) are collected on back marsh swamp on Karakan pine forest, Novosibirsk Region of Russia. Their higher heating values are 18.18 MJ·kg⁻¹ for reed and for sedge 18.77 MJ·kg⁻¹. In Portugal, Mustelier *et al.*[50] studied esteva (*Cistus ladanifer*), tojo (*Ulex europaeus*), giesta (*Sarothamus scoparius*), feto (*Pteridium aquilium*) and silva (*Rubus ulmifolius*), these being sources for renewable energy from the forest area. Their calorific values range between 16–18 MJ·kg⁻¹ and the ash content is less than 3%, close to our values.

All the studied species are attractive due to the large volume available and invades the forest spaces increasing the risk of large-scale fires. The obtained values are sufficiently high according to literature standards (EN14961-3) to justify the use of a waste energy plant, minimum value should be 15.5 MJ·kg⁻¹.[43]

The density and quality of the product are influenced also by its moisture content.

For determining the moisture content, measurements are carried out in accordance to EN 13183-1:2004 standard. Moisture content (MC) is defined as the mass proportion of water contained in the ground biomass according to formula:[51]

$$MC = (m_0 - m_c/m_0) \cdot 100\% \qquad (2)$$

where m_0 is the mass of the sample before drying and m_c is the mass of dried sample.

The moisture content of the biomass varies with the time of harvest and for some crops can introduce supplementary processing expenses, due to the need to pre-dry, before starting the process.

The literature states that the optimal moisture content ranges between 8–12%. Moisture content exceeding 24% may lead to swelling and fragmentation of pellets rapidly after pressing.[52] The moisture content of pellets obtained from biomass should be between 5% and 10% because lower moisture increases shelf life and density.[53] It is essential to acknowledge that during combustion, the five biomass samples present different moisture content. *Polygonum aviculare*, *Centaurium erythraea* and *Viscum album* are harvested in the summer, the moisture varies from 5.78% to 6.66%, the other crops are harvested in autumn, and hence the moisture content is a little higher and range from 7% to 9%. The moisture content of solid biomass affects the calorific value and the combustion efficiency.

The knowledge of nitrogen content in biomass is important for the evaluation of nitrogen oxides (NO_x) which are atmospheric pollutants. In our samples, nitrogen content varies between 0.23–0.38% and is the highest in *Agropyron repens*. These low values indicate that the emissions of NO_x are lower.

Bulk density

An important feature of biomass materials is their bulk density, or volume bulk density being related to transport and storage costs. Bulk density is determined by using the Standard Method CEN/TS 15103,[53] by weighing of a certain volume of product. Calibrated, constant volume vessel is filled with material and weighted. The bulk density is then calculated as a mass of the sample divided by the vessel volume.

The bulk density varies between 0.14–0.29 kg/m³, this being an important indicator which affects the transportation and storage of the fuel.

Fuel value index

The fuel value index (FVI), which depends upon calorific value, density, moisture and ash content of biomass, is an important and sensitive parameter for screening desirable biofuel plant species.

Fuel value index is introduced to determine their suitability for energy production. The following formula is used:[54,55]

$$FVI = (q_{net} \cdot BD)/(AshC \cdot MC) \qquad (3)$$

where *FVI* is the fuel value index (GJ/m³), q_{net} is the net calorific value (GJ/kg), *BD* is the bulk density (kg/m³), *AshC* is the ash content (%), *MC* is the moisture content (%).

The values of FVI for the selected species are plotted in Figure 5.

In accordance to the literature, higher FVI are obtained for good quality fuels and generally exceed 500 GJ/m³ for these materials.[56] Analysis of the FVI (Figure 5) shows that the studied species applicability for energy production is different. From the plot of Figure 5 results that for all the species except *Polygonum aviculare*, fuel value index exceeds 100 J/cm³, which seems to be a threshold value for application as fuel. The highest FVI is obtained for *Agropyron repens*, followed by *Viscum album*, revealing that these two species can be considered a potentially valuable material for energy production. *Polygonum aviculare*, due to its high ash content presents the lowest FVI among the studied species. The studies of Abbot and Lowore[57] highlighted that the preferable species are among those with the greatest FVI.

EXPERIMENTAL

Materials

Sample description

In this study, local plant material represented by Stone lichen (*Cetraria islandica*), mistletoe (*Viscum album*), knotweed (*Polygonum aviculare*), wheatgrass (*Agropyron repens*) and knapweed (*Centaurium erythraea*) are used. The plant materials are harvested from mountains flora of Roumania in June-October 2019.

Method and equipments

After drying in a ventilated oven for 24h at 105±2°C until constant mass, for obtaining the moisture content in accordance to ASTM D1762 (2013) Standard Test Method, the grass powders are pressed in pellets with a manual press. Samples of about 0.5–0.7 g are weighted with a Mettler Toledo balance, XP6 with an accuracy of ±2•10⁻⁶ g. Chemical analyses are carried out at Institute of Physical Chemistry, Chemical Thermodynamics Laboratory, in accordance with European Union standards. Mathematical data processing is employed using the program "Microsoft Excel for Windows 2010".
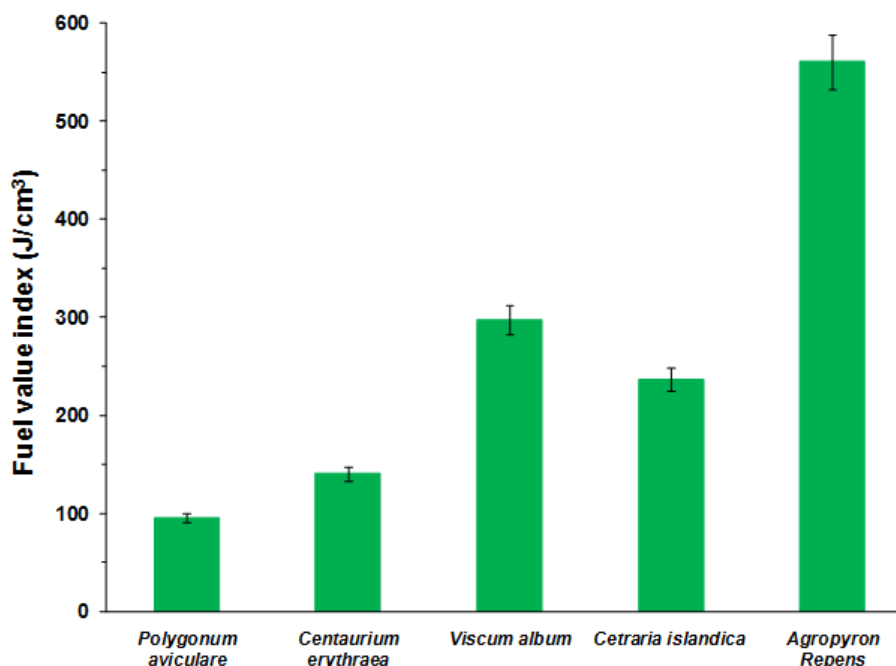
Fig. 5 – The plot of fuel value index (J/cm³) for the studied species.

Experiments are carried out in a bomb calorimeter Parr-6200 at oxygen pressure of 35 atmospheres and high purity (99.995%) for obtaining the gross calorific values, in accordance to "EN 14918:2009. Solid biofuels: determination of calorific value", ASTM D5865 Standard Test Method for Gross Calorific Value of Coal and Coke [58] and standard operating procedure Parr 6000 Calorimeter.[59]

The calorimeter is calibrated with benzoic acid (CAS 65-85-0) supplied by Parr Company, the method is detailed in a previous paper.[32] The identification of key parameters affecting the calorific value (moisture, ash content) is performed. The amount of nitric acid formed is determined by titration of the final bomb solution. The nitrogen content of the product is calculated from the quantity of nitric acid formed.[32]

CONCLUSIONS

Heating value of the biomass plant species is a sensitive parameter and strongly depends on the species, humidity, production technology, soil and climate conditions. The energy content of studied biomass species (on a dry, ash-free basis) is laying in the range 17–21 MJ/kg. This study involves the parameters of density and water content. From among the investigated plants, *Viscum album* and *Agropyron repens* are the most perspective biomass, being good materials for pellets production. All the obtained heating values for the selected species are in accordance with the literature standards. Although these species are of high quality, they are found only in very restrained forest areas and people know less about them or where to look for them.

By replacement of fossil fuels using biomass in order to produce energy will result a net decrease in greenhouse gas emissions. Using biomass as a renewable energy resource remains a useful tool of solving the social-economical problems of this millennium beginning society. Thus, it must be highlighted the valuable effect of regenerating energies not only respecting the environment protection, but also in economical and social areas.

The obtained results will complete the existing databases concerning the properties of solid biofuels from biomass.

Our investigations clearly indicate that the type of biomass used in the process has an important effect on the energy parameters.

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