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HEAT OF SOME PLANT BIOMASS SPECIES FOR BIOFUELS PRODUCTION

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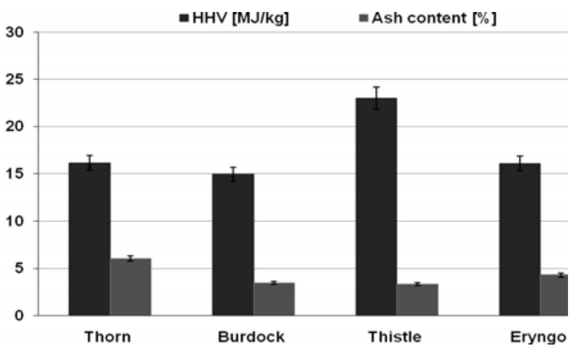
Heating values of plants are very important parameters for characterization material cycle and energy conversion in forest ecosystems. Heating systems can use plants or other organic material. Local biomass resources for heating purposes are suitable and indicated in order to reduce the pollution of atmosphere caused by greenhouse gas emissions. In the present research four biomass species collected from various rural districts near Bucharest, Romania were used: Thorn (*Xanthium spinosum*), Arctium lappa (*Greater burdock*), Milk thistle *(Silybum marianum)* and Eryngo (*Eryngium planum).*The calculated parameters were: higher heating value, ash, moisture, nitrogen contents and bulk densities. The investigated species revealed positive characteristics which make them attractive raw materials for production of solid biofuels in the form of pellets. The obtained results are in a good agreement with literature statements and were calculated according to specific standard methods. From among the investigated species, Milk thistle *(Silybum marianum)* is the most perspective energy crop, having the highest heating value, lowest ash content and lowest moisture content. The determined parameters indicates Milk thistle to be a good material for domestic pellets production and other energy usages.



INTRODUCTION

Biomass is considered one of the main renewable energy resources of the future due to its large potential, economic viability and various social and environmental benefits.[1,2] Biomass absorbs carbon dioxide during growth, and emits it during combustion. Therefore, biomass helps the atmospheric carbon dioxide recycling and does not contribute to the greenhouse effect.[3]

The high cost of fossil fuels and technological progress have made possible the appearance of energy development of biomass systems that allows to obtain energy directly or indirectly by means of combustion, pyrolysis or gasification processes. These development systems are becoming more and more efficient, reliable and clean. Due to this fact, biomass is currently being taken into account as a total or partial alternative to fossil fuels.[4-6]

Biomass is a term used for all organic matter that is derived from plants as well as animals. Biomass resources include wood and wood wastes, agricultural crops and their waste by-products, municipal solid waste, animal wastes, wastes from food processing, aquatic plants and algae.[4] There are competing uses for these resources because of their economic and environmental value. Biomass can be used to generate power, heat and steam, and for the production of transportation fuels. It is also used by the food processing, animal feed, and the wood processing industries.[4] Biomass is composed mainly of cellulose, hemicellulose, lignin, and small amounts of extractives. The suitability of a particular biomass as a potential feedstock for biofuels production

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depends on various characteristics such as moisture content, calorific value, fixed carbon, oxygen, hydrogen, nitrogen, volatiles, ash content, and cellulose/lignin ratio. Agro-industrial by-products, on the other hand, are produced mainly after crop processing.

The whole process of thermal utilization of solid biofuels (fuel supply, combustion system, solid and gaseous emissions) is influenced by the kind of biofuels, its physical characteristics (e.g. particle size, bulk density, moisture content, gross calorific value) and its composition.[6]

Biomass as fuel is fundamentally different from coals in its appearance, diversity, combustion technological characteristics and processes. The emergence of biomass as solid fuel has widened the range of materials to be studied in recent years to an extent that raises the necessity of a critical evaluation of the examination methodology. Due to the diversity (ligneous, oleaginous, herbaceous, chips, saw dust, pellets, etc.) and behavior – different from that of coals – resulting from the rise in temperature, the standard procedures used so far do not always provide reliable data.[7,8]

Biomass combustion results in either heat or electricity. Heat is one of the most important types of energy. Combustion is responsible for over 97 % of the world's bio-energy production.[4] Using local biomass resources it is possible to reduce the pollution of atmosphere caused by greenhouse gas emissions.

There are two fundamental forms of solid biofuels use: (1) "Traditional domestic" use in developing countries, burning firewood or agricultural waste for household cooking, lighting and space heating; (2) "Traditional industrial" and "modern industrial" use, in which industries are experimenting with technologically-advanced thermal conversion technologies.

The legal requirements for production, transport and trade of biofuels require very precise measurements of physical parameters such as energy content (calorific value, moisture, ash content, volatile content etc). These properties are essential for the optimization of the combustion processes.[9,10] While estimating the energy potential of the biomass, one should take into account the following parameters: origin of biomass (energy crops, by-product), type of biomass, amount of energy, energy conversion process, calorific value.

A group of plants dedicated to the energy purposes is quite numerous. The species studied in the present work are as follow: Thorn (*Xanthium spinosum*), *Arctium lappa* (Greater burdock), Milk Thistle (*Silybum marianum*), Eryngo (*Eryngium planum*).

The amount of crops and its humidity are the two factors deciding whether the plant is suitable for the energy purposes or not. The amount of crops of the investigated plants depends on their species, genotype, environmental conditions (type of soil), planting arrangement, number of seasons and the harvesting date. Another important parameter of the biomass is its caloric value. The calorific value of plant is defined as the amount of heat energy released during the combustion of a specified amount of it. Calorific values are also important indices for evaluating material and they are classified into two types: gross calorific value (GCV) or caloric value on oven-dry weight basis, and ash-free calorific value (AFCV) or calorific value on ash-free basis. When studying calorific values of plants, GCV and AFCV are usually considered together.[11] The biomass is not a pure material, so the caloric value may differ within the same type.[12]

Thorn (*Xanthium spinosum*) is a much branched annual herb, often 0.3–0.6 m in height, but sometimes up to 1 m tall and 1.5 m across. Pitcher stated that *X. spinosum* had been introduced to at least 39 countries, though records for many more are available and the real figure may be higher still.[13] It is widely distributed in the Mediterranean region, Europe, Australia, parts of Africa, South America and North America, though is only rarely found in the tropics.[14] *X. spinosum* can be found growing in a wide variety of habitats. Holm *et al.*[14] described *X. spinosum* as mainly a pasture or meadow weed, growing along roads and in disturbed areas and abandoned fields, also being sometimes common around waterholes and along floodplains, canals, ditches, creek flats, river terraces, and other moist places. It can also be common weed in cultivated fields, stock yards and abandoned settlements. *X. spinosum* has proved remarkably adaptable to a wide range of climates and other environmental conditions, with the exception only of very cold polar/tundra conditions and very hot and dry or moist lowland tropical climates. In tropical regions it is generally only found at high altitudes. It appears to show no specific requirements regarding soil type. *X. spinosum* is a highly invasive weed that is capable of growing under a range of environmental conditions. Being highly invasive, *X. spinosum* can compete both directly and indirectly with native species, alter habitats and, when present on river banks, can increase soil erosion and affect water flow and quality.

Fig. 1 – The studied biomass plant species.

Arctium lappa, commonly called **greater burdock** is a biennial plant, rather tall, reaching as much as 3 m (10 ft). It has large, alternating, cordiform leaves that have a long petiole and are pubescent on the underside. This species is native to the temperate regions. It is naturalized almost everywhere and is usually found in disturbed areas, especially in soil rich in nitrogen.[15]

Milk thistle *(Silybum marianum)* is an annual or biennial plant of the Asteraceae family. Milk thistles can grow to be 30 to 200 cm (12 to 79 inch) tall, and have an overall conical shape. Milk thistle (*Silybum marianum*) is a thorny plant presenting decorative leaves with a white pattern of veins and purple flower heads. The plant originates from mountains of the Mediterranean region, where it forms scrub on a rocky base.[16] In Romania, milk thistle is a niche crop with huge potential, especially considering that is not a very demanding plant, which can bring smallholders profits upwards of 2.500 euros per hectare.[17] With an inherent reputation of being a competitive weed, milk thistle has an aggressive vegetative growth rate, allowing this crop to produce a relatively high amount of biomass within a relatively short period of time.[18]

Eryngo (***Eryngium planum)***, known as or **blue eryngo**, or **flat sea holly**, is a species of flowering plant in the family Apiaceae, native to the area that includes central and southeastern Europe and central Asia. It is an herbaceous perennial thistle growing to 50 cm (20 inch) with branched silvery-blue stems, and numerous small blue conical flowerheads surrounded by spiky bracts in summer.[19]

Thermochemical characterization of the products which are the object of this study involves performing the following experimental determinations: combustion calorimetry determinations for obtaining: a)- calorific power of the products and other combustion characteristic parameters; b)- ash quantity resulting from combustion; c)- nitric acid present in the calorimetric bomb solutions; d)- the nitrogen content of the product. The calorimetry of combustion has important practical applications, as follows: the study of substances used in drugs synthesis;[20] the study of fossils fuels components;[21,22] the environment to biomass exploitation[8] and disaster prevention.[23,24]

The purpose of the study was to evaluate the suitability of the selected biomass plants for heating. Beside the calorimetric measurements, the following physical characteristics will be determined: the bulk densities of the samples, moisture content, and ash content.

The study will contribute to obtain the necessary information for efficiently use of solid biofuels as alternative energy source. An increased use of biomass for energy purposes is reflected in positive socio-economic effects on regional and national level. The present work will complete the data bases regarding the characteristics of solid biofuels from biomass. The analysis of calorific power, nitrogen content, density etc. of studied products will help to choose the most advantageous in terms of energy production, pollution and transport costs. Some of obtained results are likely to provide valuable information to those processing the biomass plants.

RESULTS AND DISCUSSION

Plant raw materials, which may be a potential heating biomass source are highly varied, thus knowledge of their characterization is essential.[25] The aim of the research was to evaluate the variety of plant biomass qualitative properties for production of solid fuel. By choosing suitable plants, high dry matter biomass solid fuel products can be obtained. Calorimetry is considered as the most influential analyse, since it gives the exact data about the heating value of a specific sample.[26] The calorific value, ash, moisture and nitrogen content and bulk densities of the plant biomass samples were determined using the method described above. The obtained results are presented in Table 1.

Heat of combustion is one of the main physical and chemical parameters of solid fuels. The ash content is one of the major qualitative characteristics of plant biomass. The ash content should not surpass 5–7% under the conditions of correct stockpile. Nevertheless, the experience shows that the ash content can reach even 20%.[27] Our values are in agreement with literature statement which reported that ash content of herbaceous biomass may reach values up to 10%.[28] Another author reported an ash content for hay (grass) of 6.33%, close to our value for thorn and higher comparing to burdock, thistle and eryngo.[29] The lower is the ash content, the better is suitability of fuels for thermal utilization.[30] The research carried out by authors[31] proves that the ash level in biomass is lower than in case of the majority of coal. High ash content causes high dust emission and negatively influences the combustion efficiency.

In Table 1, the heating value of the studied species is expressed as higher heating value (HHV) and higher heating value of ash free sample (HHVf). The later was calculated after substraction of ash from the weight of the HHV determination biomass samples. The higher heating value of the studied species ranged from 14.94 MJ/Kg to 23.02 MJ/Kg. HHVf increased proportionally with the removal of ash and was the highest in milk thistle compared with the values for thorn, arctium lappa, and eryngo. Generally, the highest calorific values are typical for biofuels made of wood biomass. The quality of the fuel is affected by the chemical composition of the biomass. Biomass proteins contain nitrogen. During combustion it completely transforms into gaseous state. The nitrogen content of the studied species varied between 0.088 and 0.563% and was the highest in thistle. The nitrogen content of biomass varies from 0.2% to more than 1%.[32] Fuel-bound nitrogen is responsible for most nitrogen oxide (NOx) emissions produced from biomass combustion. Lower nitrogen content in the fuel should lead to lower NOx emissions. An important indicator in the choice of fuel is fuel density or bulk density, as it affects the transportation and storage of the fuel. Bulk densities (Kg/m^3) varied from 0.24 to 0.76%.

Eryngium planum presents the highest moisture content of 7.79 % and milk thistle, the lowest one of 2.37 %.

Below are plotted the variation of higher heating value (HHVf, MJ/kg) versus ash content (%) (Figure 2) and moisture content (%) (Figure 3).

It can be observed from Figures 2 and 3 that the lower is the ash and moisture content, the higher is the heating value. Moisture in biomass generally decreases its heating value. Our results plotted in Figure 3 are in agreement with the statement of Pushpa[33] which highlighted the impact of the product moisture content on the combustion behavior and calorific power values.

Table 1

Physicochemical parameters of the selected biomass plant species

Species	Higher heating value (HHV) (MJ/kg)	Higher heating value of ash free sample (HHVf) (MJ/kg)	Moisture content (%)	Ash content (%)	Bulk density (kg/m^3)	Nitrogen content (%)
Thorn (*Xanthium spinosum*)	16.15±0.11	17.19±0.04	5.01	6.07±0.41	0.2524	0.306±0.28
Arctium lappa (Greater Burdock)	14.94±0.22	15.48±0.17	6.05	3.48±0.76	0.4214	0.31±0.04
Milk thistle (*Silybi mariani*)	23.02±0.15	23.87±0.17	2.37	3.35±0.14	0.76	0.563±0.029
Eryngo (*Eryngium planum*)	16.08±0.06	16.72±0.14	7.79	4.32±0.15	0.2451	0.088±0.001

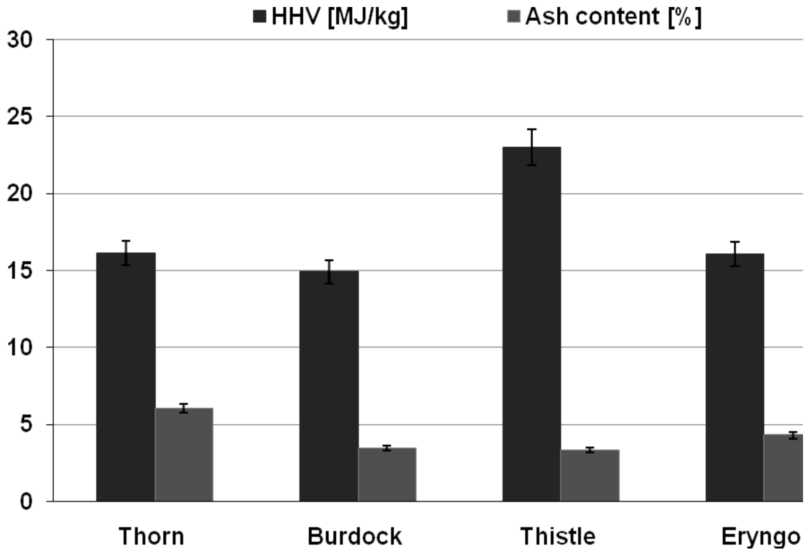

Fig. 2 –Variation of higher heating value (HHVf, MJ/Kg) *versus* ash content (%).

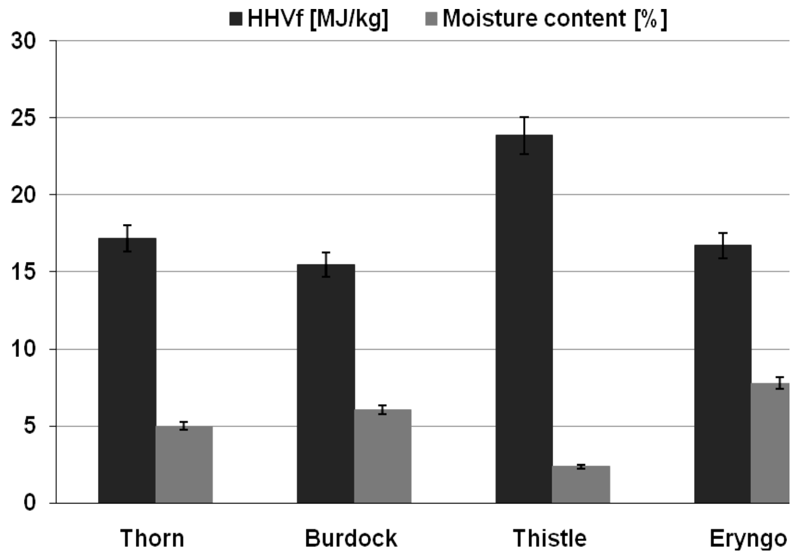

Fig. 3 – Variation of higher heating value (HHV, MJ/kg) *versus* moisture content (%).

EXPERIMENTAL

Materials

Sample description

The determination of calorific value of the biomass resulted from several plant species was taken into account. Material for research was perennial species of herbaceous plants: **Thorn (*X. spinosum*), *Arctium lappa* (greater burdock), Milk thistle *(Silybum marianum),* Eryngo (*Eryngium planum).*** Material for the research was harvested in November-December 2016 from the local areas and the further measurements of biomass properties were performed in the Laboratory of Chemical Thermodynamics of Institute of Physical Chemistry Ilie Murgulescu of the Romanian Academy in accordance with European Union standards for solid biofuel. The favorable period of collecting biomass is the beginning of winter because low temperatures (specially the negative ones), accelerates drying and enable moisture to drop below 10%.[35]

Samples of about 0.6–0.8 g were cut. The samples were pressed into pellets of 6 mm diameter, their length ranged from 10 to 40 mm. The pellets were weighed with a Mettler-Toledo analytical balance, model XP6 with an accuracy of $\pm 2\cdot 10^{-6}$ g. The biomass samples are dried at 105 ± 2 °C until constant in mass in a ventilated oven in order to determine the water content. Constancy in mass is defined as a change not exceeding 1 mg in mass during another phase of heating during a period of 60 minutes.

Method and equipments

Gross calorific value was determined experimentally using a calorimeter Parr 6200 and according to "EN 14918:2009. *Solid biofuels: determination of calorific value*".

Combustion calorimetric determinations were performed using an isoperibolic Parr Instruments 6200 Combustion Calorimeter provided with a combustion bomb, inner volume ≈ 300 mL. The work pressure is 35 atmospheres and high purity oxygen (99.995 %) is use for combustion. The calorimeter operating unit consists of a temperature-controlled water jacket with a built-in circulating system and an electric heater, a microprocessor, a high precision electric thermometer, a display for data entry and viewing the results, multiple options in regard to handling thermochemical corrections too. The 6200 Calorimeter will automatically make all calculations necessary to produce a gross heat of combustion for the sample and produces a corrected temperature rise, being provided with software and digital hardware.

The calorimeter is previously calibrated by combustion of benzoic acid (CAS 65-85-0) supplied by Parr Company, from ten calibration experiments, using samples weighing ~ 1g, and the calorimetric constant (ε_{calor}=10054.4±0.7 JK^{-1}) is obtained. The device is equipped with a software that calculates the average value of the constant; it will also calculate the heat of combustion of the sample for each hand experience, with mentioned corrections. The identification of key parameters affecting the calorific value (moisture, ash content) was performed. The solutions presented in calorimetric bomb after the combustion experiment were analyzed in order to determine the amount of nitric acid formed, by titration of final bomb solutions with a 0.1 N NaOH solution. The titration will be made using an automatic digital biurette (maximum resolution 0.001 mL) and a pH-meter (inoLab 720 pH). The nitrogen content of the product was calculated from the quantity of nitric acid formed.

The procedure described in the technical standard "EN 14775:2009. *Solid biofuel: Determination of Ash content*" was used to estimate ash content. Ash quantity was calculated through weighing of the bomb crucible before and after combustion using the formula[35]:

$$A_C = \frac{(m_3 - m_1)}{(m_2 - m_1)} \cdot 100 \quad ,\% \qquad (1)$$

where
m_1 – mass of an empty crucible, g;
m_2 – mass of crucible with a sample, g;
m_3 – mass of crucible with ash residue, g.

In order to determine the moisture content, the procedures provided by the following technical standard is taken into account: EN 14774-3:2009. *Solid biofuel. Determination of moisture content, oven dry method. Part 3: moisture in general analysis sample*. The moisture content was reported in percent.

Based on the measurement of dry mass of each sample, the gross calorific value (GCV) was measured with the oxygen bomb calorimeter. Five runs were performed for each sample, and the arithmetic mean was regarded as the GCV. Finally, the ash-free calorific value was calculated by: AFCV = GCV/ (1- ash mass/total oven-dried mass).[11]

Bulk density

Moisture content and bulk density after grinding are important properties for downstream processing. The bulk densities of the samples were measured following the Standard Method CEN/TS 15103 [34] and were determined after drying, by weighing of a certain volume of product. The average bulk density was calculated from five measurement series per sample.

CONCLUSIONS

The main conclusion that may be drawn from the present study, summarizing the results of the parameters determined for the selected species, is the positive characteristics which make them attractive raw materials for production of solid biofuels in the form of pellets.

Based on the obtained results it was stated, that, from among the investigated species, Milk thistle (*Silybum marianum*) is the most perspective energy crop among the tested plants, having the highest heating value of 23.87 MJ/Kg, lowest ash content (3.35%) and lowest moisture content (2.37%). The determined parameters indicates Milk thistle to be a good material for domestic pellets production and other energy usages.

The heating values for the selected crops are in agreement with the literature standards EN14961-3, the minimum value should be 15.5 MJ/Kg.[35]

The relevance and applications of the present study: an increased use of biomass for energy purposes is reflected in positive socio-economic effects on regional and national level. The present studies will complete the data bases regarding the characteristics of solid biofuels from biomass. The analysis of heating values, moisture, ash, nitrogen content, density etc. of studied products will help to choose the most advantageous in terms of energy production, pollution and transport costs. Some of obtained results are likely to provide valuable information to those processing the biomass plants.

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