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BIOMASS AND THE THERMO-PHYSICAL-CHEMICAL PROPERTIES OF THIS RELATED TO THE COMPACTION PROCESS

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ABSTRACT: The paper presents the main sources of biomass used in the process of compaction for obtaining briquettes and pellets. Were identified the main thermo-physical-chemical properties by types of agricultural and forestry solid biomass. It also presents the methods and materials used to obtain thermo-physical-chemical properties of agricultural and forestry biomass.
KEYWORDS: compaction, energy, thermal-physical-chemical properties

INTRODUCTION

The biomass expresses the totality of the agricultural vegetal production that can be converted into different forms of energy. The agricultural production consists of primary and secondary production.

The main vegetal agricultural production is converted into bio alimentary-energy and the secondary vegetal agricultural production constitutes the main source of biomass which usually can be transformed into thermal energy.

According to the European Union legislation, the biomass is the biodegradable fraction of products and waste from agriculture, forestry domain and the related industries of them, as well as the biodegradable fraction of industrial and municipal waste.

The main chemical composition of biomass is:

Lignin ($C_{40}H_{44}O_6$) = 15 - 30 %;

Cellulose ($C_6H_{10}O_5$) = 40 - 45 %;

hemi-cellulose = 20-35 %.

The limits of variation of the three main components are determined by species. The long polymers of cellulose are used by plants to build the fibers which confers solidity to the plant iar lignina acţionează ca un liant which keeps the cellulose fibers linked. For the manufacture of pellets, the lignin content has to be as high. For a high calorific value it is necessary that the reports O / C and H / C to be as small.

The main secondary agricultural products which can be converted into thermal energy are:

the straws and chaff of straw cereals (wheat, rye, barley, orzo, rice and oats);

corn stalks and loafs;

sunflower and rape stalks;

haulms of soy, peas and beans;

vine ropes;

branches of fruit trees.

The calorific power of biomass is correlated with its chemical composition. Thus, the calorific power increases with increasing the content of lignin. The cellulose has a lower calorific power than the lignin because of the high degree of oxidation. The hydrocarbon content also increases the calorific power of biomass. The calorific power can be calculated according to the chemical composition.[1,2]

Van Loo S and J.Koppejan propose in the paper Handbook of Biomass Combustion and Co-firing, Twente University Press, 2002 the following calculation formulas for the calorific power [7]:

$$Q = 88,9 \ (LC) + 16821,8 \ [kJ/kg] \qquad (1.1)$$

where: (LC) is the content of lignin reported to the dry state and deprived of ash.

$$Q = 196 \ Cf + 14119 \ [kJ/kg] \tag{1.2}$$

where: Cf is fixed carbon content of biomass.

$$Q = 33500 \ C + 14300 \ H - 15400 \ O - 14500 \ N \ [kJ/kg] \tag{1.3}$$

where: C is carbon content [%], H is the content in hydrogen [%],

O is the oxygen content (%) and N is the content of nitrogen [%].

Tillman D.A. established in the work Biomass Cofring: the technology, the experience, the combustion consequences, Biomass Bioenergy 2000, the following formula for calculating the calorific power [6]:

$$Q = 349,1 \ C + 1178,3 \ H + 100,5 \ S - 15,1 \ N - 103,4 \ O - 21,4 \ A \ [kJ/kg] \tag{2}$$

Transforming biomass into thermal energy by burning imposes certain moisture values of fuel as follows:

the maximum humidity of biomass for burning in conventional combustion plants = 25 %;

the maximum humidity of biomass for burning in specific combustion plants = 60 %;

optimum humidity of biomass for burning = 7 - 10 %;

maximum humidity of biomass for gasification = 35 %;

the maximum humidity of biomass for transformation into pellets or briquettes = 10 %.

Analyzing the data concerning the moisture values arise that for the use of biomass by burning, it is necessary to dry it. The high humidities of biomass from the time of burning negatively influence the technical condition of the combustion plant.

To increase the density of the solid fuels from biomass and to enable the automation of the burning process, at present is used the transformation of biomass into pellets or briquettes.

The pellets are obtained by grinding the sawdust, shavings, branches or tree barks and pressing the obtained dust into a mold. The heat resulting from friction softens the lignin which by cooling binds the dust obtained from biomass. Since there is no glue used to manufacture of pellets, very important is the lignin content of the used biomass. Thus, from the composition of pellets should not miss the resinous wastes. After shape, the pellets can be with circular or square section, the most common being the pellets with circular section.

The large size pellets require biomass with high lignin content. For this reason the most widespread are the pellets with the diameter of 5 mm and the length of 5 or 10 mm.

The briquettes are obtained by pressing the sawdust mixed with wood chips, tree branches or tree barks using a piston or screw press. For the mixture binding a synthetic binder is used. The average diameter of briquettes is of 25 mm.

By pelleting or briquetting the density increases to 600 - 700 kg / m³ and the calorific power to more than 17 MJ / kg depending on the type of biomass used. [4]

MATHERIAL AND METHOD

Were conducted series of experimental campaigns which aimed the determination of the following thermo-physical-chemical characteristics of different types of biomass:

humidity;

content of volatile substances;

fixed carbon content;

the content of inerts;

the lower calorific power.

The experimental procedure consisted of the following steps:

Drying and sampling;

Pyrolysis;

Combustion;

Determination of lower calorific power.

Drying and sampling. Moisture content

Different samples were taken of forest and agricultural biomass in natural state. After about two months storage the samples were chopped with a chopper. After chopping was performed their drying in the laboratory oven (figura 1), at the temperature of 105 °C, for 24 hours.

Figure 1. The drying stove

Figure 2. The mill

In order to determine the moisture content, the samples were weighed before and after drying with an analytical balance. After drying, was performed the mechanical grinding of samples with the mill (with knives) shown in Figure 2.

The samples thus prepared (dried and ground) were kept in an oven, at the temperature of 105 ℃, until the time of superior thermal processing (pyrolysis and combustion).

Volatile substances content

Objective: For determining the content in volatile substances, the samples obtained after drying stage were subjected to a medium temperature pyrolysis process.

For pyrolysis (and for combustion) of biomass was used an electrical furnace (Figure 3 and 4) produced by Nabertherm, type L9/11/SW: with trolley, balance, swing door and nominal operating temperature (maximum) of 1100 ℃.
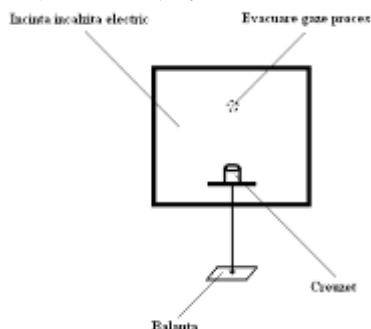

Figure 3. Schematic diagram of electric furnace

Figure 4. Electric furnace

It starts the electrical furnace, is set the working temperature at 600 ℃ and the heating time.

Is extracted a certain amount of a sample from the drying oven, is introduced into a metal crucible and weigh this amount with the analytical balance.

Once the oven temperature reached 600 ℃, it is inserted into the crucible containing the sample and let for 30 minutes (or until the full release of volatiles).

Upon the completion of pyrolysis process, the crucible is removed from the furnace by means of some gloves and pliers, is covered with the lid and weigh again, to determine the amount of volatiles released (by difference).

The operation is repeated for each type of biomass.

The fixed carbon content and inerts

Objective: The samples obtained in the first stage are subjected to a combustion process, for the determination of total carbon fixed, respectively of the one of inerts.

It starts the electrical furnace, the working temperature is set to 1100 ℃, the heating time and working time to 60 min. Is extracted a certain amount of a sample from the drying oven, is introduced into a metal crucible and weigh this amount with the analytical balance. The crucible is left uncovered, without lid, to allow the air (oxygen) necessary for burning to get in contact with the sample.

At the furnace temperature of 1100 ℃, is introduced the crucible and it is left for at least 15 minutes or until the complete oxidation of the sample of biomass (it may be necessary to remove the crucible and mix the contents this being performed in the case of insufficient aeration inside the oven, after which take place the insertion into the furnace of the crucible again, for a new period of oxidation). After the sample completely burned, the crucible is removed from the furnace and weighed. Since the crucible is removed from the furnace at high temperature (orange-red), on the balance is placed an asbestos plate, with the role of thermal insulation.

Inserting and removing of the crucible from the furnace shall be made only with gloves and clippers. The operation is executed for each type of biomass.

Determination of lower calorific power

Was used to determine of calorific value a calorimetric system type C 200, Figure 5 with the following components:
    calorimeter itself;
    calorimetric bomb;
    the nacelle;
    the burning adapter;
    the oxygen station;
    the analytical balance with the accurate of 0.1 mg.

Figure 5. The calorimeter

Is inserted into nacelle the sample of material for determining the calorific power and weigh. Is attached a thread of cotton in the center of the ignition wire and is insert with the other end into the sample, to propagate the combustion inside of this. Is inserted the nacelle located in its holder into the calorimetric bomb and is hermetically closed. The bomb is then filled with oxygen at a pressure of 20-30 bar using the oxygen station, connected to an oxygen cylinder. To the bomb it attaches the ignition adapter and then is placed in the calorimeter inner vessel. Is poured about 2 liters of demineralized water into the calorimeter tank, following the level indicator.

To prepare the measurement, is inserted in the menu of measurement the measured weight of the sample, the type of operation that will be performed (calibration or measurement itself), the type of calorimeter bomb and the correction values for the heat generated by the combustion of the cotton yarn (default value is 50 J) or from other sources.

When everything is ready, the lid of the calorimeter is closed and the device starts the operation of measurement. Firstly the inner vessel is filled with water, then the combustion is carried out, the final stage consisting in equalizing of internal and external vessel temperatures, by the transfer of heat from the inside to the outer vessel. When this is happened, the measurement process ends and the measured calorific power value is displayed. [1, 2]

The device calculates the calorific power under the following assumptions:

the temperature of the fuel and of the combustion products is of 25ºC;

the water contained in the fuel and the water formed by burning of hydrogen are in liquid state at the end of the process (the device measures the high calorific power);

the atmospheric nitrogen was not oxidized;

the gaseous products of combustion are: O_2, N_2, CO_2 si SO_2;

ash may be formed.

RESULTS

The volatile content was calculated as follows:

$$Volatile\ content\ in\ the\ dry\ basis = \frac{Initial\ mass - Final\ mass}{Initial\ mass} \times 100[\%] \ ,$$

where the initial mass and the final mass being those weighed before and after the pyrolysis process;

$$Volatile\ content\ in\ the\ wet\ basis = Volatile\ content\ in\ the\ dry\ basis \times \frac{100 - Humidity}{100}[\%],$$

The volatile matter content on types of biomass agricultural and forestry determined are presented in Table 1. Observații: The samples may partially oxidize (in a higher degree than that due to the amount of oxygen existing in the waste), due to the penetration of a quantity of air in the crucible during the performance of pyrolysis process, which affects the results.

Table 1 - The volatile matter content

Type of biomass	Initial mass [g]	Final mass [g]	Volatile content in the dry basis [%]
Agricultural	19.95	5.37	73.08
Forestry	14.35	2.70	81.18

Table 2 - The inerts content

Type of biomass	Initial mass [g]	Final mass [g]	Volatile content in the dry basis [%]
Agricultural	5.02	4.88	2.7
Forestry	4.76	4.707	1.1

The inerts content is presented in Table 2. Naturally, the highest percentage of incombustible substances it has the agricultural biomass.

Through difference was determined and the fixed carbon content:

Fixed carbon = 100 – (Humidity + Volatiles + Incombustible)

The fixed carbon content in the agricultural biomass was: 16.83%

The fixed carbon content in the wooden biomass was: 14.47%

Observations: In the case of combustion, occur the problem of incomplete oxidation, because of the imperfect contact of air with the sample (because of the crucible shape, of the dimensions of sample etc.), of the insufficient air movement (the lack of permanent ventilation etc.).

The lower calorific power for the forestry biomass is represented in Table 3.

These elements are part of both the main constituents of wood namely:

cellulose: 50 – 55%

lignin: 20 – 30%

hemicellulose: 25 – 30%

as well as of the secondary ones such as:

resins: 1 – 5%

mineral substances: 0.2 – 1.2%

tannin, coloring matters, etc.

Tabel 3 - Experimental results by types of forestry biomass

Species	C [%]	H [%]	O [%]	N [%]
- Oak	48.9	5.9	43.1	2.1
- Beech	48.5	6.3	45.3	-
- Ash	49.4	6.1	44.5	-
- Poplar	49.7	6.3	44.0	-
- Lime	49.4	6.9	43.1	0.6
- Fir	49.9	6.4	43.7	-
Mean (LAU)	50	6	43	1

Besides the main constituents listed which are of organic nature, in the wood composition enters and mineral substances which after burning form the ash. Mineral substances representing 0.2 to 1.2% from the weight of dry wood are:

potassium: 10 – 25%;
sodium: 1 – 5%;
calcium: 20 – 45%;
magnesium: 3 – 15%;
manganese oxide: 1 – 8%;
iron oxide: 1 – 4%;
silicon dioxide: 1 – 3%;
phosphoric acid: 2 – 10%;

Table 4 - The ash content of wood

Species	Ash %
Pine	0.39
Beech	0.17
Oak	0.51
Birch	0.39

Table 5 - The calorific power of wood

Humidity of the wood	Calorific power
40 %	11600 kJ/ kg
10%	16709 kJ/kg

The composition of ash of various wood species is almost homogeneous and is characterized on average by the following data: 35% CaO, 16% Na_2O + K_2O, 7% MgO, 5% MnO, 3% Fe_2O_3, 3% Al_2O_3, 20% CO_2, 5% SO_3, 4% P_2O_5, 2% SiO_2.

The ash of wood is highlighted by its hard-burnt character and by the fact that it does not melt even in the hottest portions of the firebox. The quantity of ash depends on wood species (Table 4) but was found that it varies depending on the part of tree from which it came, its age and the local growing conditions.

The largest amount results from bark and leaves. Statistically for oak, in strain, the ash reaches up to 0.35%, in bark up to 7.2% and in leaves up to 3.5%. The quantity of ash is inversely proportional to the age of the trees (for the old trees the ash is lower).

The calorific power is influenced by the species and the moisture content (Table 5).The table 6 shows the composition and main physical-chemical characteristics of samples of agricultural biomass analyzed.

Table 6 - Physico-chemical characteristics by agricultural biomass types

Cr. No.	Characteristics		Straws	Corn stalk	Corn cars	Chaffs of flax and hemp
1.	Chemical composition reported to combustible mass [%]	C mc	50	50	50	51
		H mc	6.2	6.2	6.2	6.1
		N mc	0.6	0.6	0.6	0.9
		O mc	43.1	43.1	43.1	41.9
		Sc mc	0.1	0.1	0.1	0.1
		V mc	-	-	-	-
2.	Ash at anhydrous state		2.7	1.8	2.3	2.1
3.	Total sulfur		0.09	0.09	0.09	0.09
4.	Upper calorific power KJ/kg		20.036	20.036	20.036	20.444
5.	Lower calorific power KJ/kg		15.932	15.932	15.932	16.434

CONCLUSIONS

The biomass contributes with 14% to the world consumption of primary energy, and for three-quarters of the world population who lives in the developing countries it represents the most important source of energy. At the European Union level it is expected to create over 300,000 new jobs in rural areas, just by exploitation of biomass. Currently, in EU, 4% of its energy needs is assures from biomass.

In the last hundred years, man intensively exploited the biomass especially as its form fossil of coal, petroleum and natural gases, which led to a major contribution of carbon dioxide in the atmosphere, far beyond "the planet's lungs" (living plants and trees), to consume it during their period of growth. That's why lately, the scientists increasingly recommend, the use of bio-renewable fuels coming from fresh biomass [3, 5].

The fresh biomass can be processed in various ways:

burning - produces heat and electricity;
fermentation - produces biogas;
pressing or pelletisation - produces solid fuel (briquettes or pellets);
distillation - produces liquid fuel (bioethanol and biodiesel).

Regarding the "physical and chemical characteristics by type of agricultural and forest solid biomass", they are the following:

– The physical characteristics: dimensions and shape, the moisture content, the calorific power, bulk density, ash content, granulation, resistance to abrasion, ash melting temperature. The influence the physical properties on the biomass are the following:

dimensions and shape - affects handling and the technology of compaction and burning;
the moisture content - influences the duration of storage, system designing and the calorific power;

the calorific power – is the most important property of a fuel influencing the method of obtaining the thermal energy and compaction plant designing and implicitly of burning;

bulk density – influences the transport, handling and storage of fuel;

ash content – also important characteristic influencing the burning technology, emission of solid particle, the handling and use of ash;

granulation – influences the drying and formation of dust;

abrasion resistance - influences the segregation and the change of quality;

melting temperature of the ash – influences the burning technology, operational safety and control system of the combustion plant.

– *The chemical characteristics of solid fuels obtained from biomass are:*

the content of C – important characteristic influencing the calorific power, should be as high;

the content of O – important characteristic influencing the calorific power, should be as small;

the content of H – important characteristic influencing the calorific power, should be as high;

the content of N – influences the emissions of NOx (toxic) and corrosion;

the content of S – influences the emissions of SOx (toxic) and corrosion;

the content of Cl – influences the emissions of HCl (toxic) and corrosion;

the content of K – influences the use of ash, aerosol formation, corrosion of the combustion plant and reduces the melting temperature of the ash;

the content of Na – influences the aerosol formation, corrosion of the combustion plant and reduces the melting temperature of the ash;

the content of Mg – influences the use of ash and ash melting temperature;

the content of Ca – influences the use of ash, the aerosol formation and increases the melting temperature of the ash;

the content of volatile substances – influences combustion plant designing in order to increase its efficiency;

the content of hard metals – increases the emissions and reduces the possibilities

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