Determination of the Calorific Power of Densified Solid Biofuels

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Abstract: *The present research addresses a current topic in the field of energy production from renewable sources, with the evaluation of the energy potential of biomass, by increasing the calorific power and efficiency of the use of wood in combustion. The current research should start from the determination of the calorific power, to continue with the determination of the influence of humidity, and finally to go on to evaluate the efficiency of the use of wood biomass by increasing the calorific power, by the dry heat treatment in oxygenated environment. In the production of pellets from biomass the costs and the impact on the environment must be taken into account, following the improvement of the composition of the pellets, in order to increase the quality and to reduce the production costs (of the energy consumed) and the increase of the calorific power by identifying some solutions for using the some residues from agriculture.*

Keywords: *Biomass, densification, calorific power*

1. Introduction

The evolution of the sector of production of densified solid biofuels has been growing rapidly in recent years. The solid biofuels market tends to evolve from a local market to an increasingly globalized one. In the created situation, an important role belongs to the knowledge of the factors that influence the quality of solid biofuels, the norms regarding quality control, quality assurance and the specification of the finished product.

In the world the interest for the use of biomass in the form of densified biofuels (pellets, briquettes) has increased, their market is constantly rising. Obviously, this interest is motivated by several factors, of which energy security is placed first.

In recent years, awareness of the possibilities of reducing the consumption of fossil fuels has increased, by replacing them with biofuels from vegetable biomass resulting from agricultural, forestry and industrial activities. [1]

From an energy point of view, the term "biomass" refers to organic matter that can be converted into energy. The main categories of biomass that can be used for this purpose are wood matter, vegetable residues from agriculture and animal residues from animal husbandry, as well as crops and plantations dedicated to energy recovery. In addition, the municipal waste (residues from the cleaning of the trees, maintenance of the parks, etc.), the household waste or some residues from the food industry are considered.

Wood biomass (also called lignocellulosic biomass) consists mainly of lignin (20-25%) and carbohydrates (60-80%). Most of the carbohydrates present in the biomass are poly / oligosaccharide compounds, such as cellulose, hemicellulose, starch and inulin. In addition, small amounts of monosaccharides such as glucose and fructose may be encountered. Although biomass is the most abundant resource on the planet, the use of energy contained in it has a rather low efficiency. This disadvantage is a result, first of all, of the form and state in which this energy source is used, as well as the low efficiency of the classical means of obtaining thermal energy (stoves, fireplaces, ovens, etc.). In this situation, the manufacture of high quality biomass fuels is gaining new strengths, being a current problem for the energy sector.

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2. Densification of biomass

Densification of biomass leads to increased energy efficiency. This is a process that involves two stages:

- pressure compaction of wood material for volume reduction and material agglomeration;
- The lignin contained in the wood is activated by this pressure and glues the wood chips without the need for an additional gluing agent. [2]

The compaction methods have as a common element the pressing operation, through which the thickening of the particles from the primary material is produced, resulting in an increase of the density of the finished product (tablets, pellets, briquettes, etc.).
The operations of agglomeration of biomass particles, depending on the pressure they are subjected to in the working process and the equipment used are described in table 1.

Table 1: Characterization of agglomeration operations

Name of the process	Characteristics
Compression	The method of agglomeration under high pressure by means of pairs of rollers with smooth or profiled surface, which rotate into each other in the feeding area. The material is passed through the space between the rollers and after pressing it increases its density.
Briquetting	Method of agglomeration under pressure of up to 300 MPa, with or without binders, of powdered or granulated materials, in lighters with characteristic geometric shapes, at pressures depending on the characteristics of the raw material and those imposed on the finished product.
Compression as tablets	High pressure agglomeration operation 50… 200 MPa, in individual molds, placed on a rotating disc, from unpolluted powder materials, obtaining tablets.
Pelletizing	Medium pressure agglomeration operation, in ring or flat molds, periodically the material being forced to pass through the holes of the mold, at the exit of the nozzle being cut. Pellets of cylindrical shape, with the determined length, are obtained.
Extrusion	The method of agglomeration at low and medium pressure, in which the material mixed with liquid binders is brought by kneading in a plastic state, after which it is forced to pass through the holes of a mold.

The pellets are produced by chopping sawdust, chippings, furrows, tree shells, fodder, etc. and pressing of the material obtained through a mold. The heat resulting from friction is sufficient for softening the lignin. By cooling, the lignin becomes rigid and binds the material. The pellets have a cylindrical or spherical shape with a diameter of less than 25 mm (fig. 1 a). The briquettes (fig. 1 b) are usually rectangular or cylindrical in shape and are obtained by pressing together the sawdust, chippings, furrows or tree shells in a piston or screw press. Because in the manufacture of pellets recyclable raw materials are used, they are of an ecological nature, so we can consider them fuels with clean combustion and an alternative of heating with a stable cost. They are much cheaper than natural gas and the calorific power is almost double that of wood: 1 kg pellets can produce 4.7 kW or 17 MJ / kg.


a


b

Fig. 1.
a-Pellets b-Briquettes

The main advantages of wood biomass densification are:
• Increased density of compressed material (from 80-150 kg / m^3 for straw or 200 kg / m^3 for wood sawdust up to 600-700 kg / m^3 for final products);
• Higher caloric power and a homogeneous structure of compressed products;
• Low moisture content (less than 10%).
The raw material used for the production of pellets and briquettes must meet certain physical characteristics, important during the densification process:

• Material fluidity and adhesive capacities (different additives can be used as well lubricants or binders, for granting the respective characteristics);
• Predetermined dimensions of the particles of the raw material (a very fine crumb thereof it can lead to increased cohesion properties, causing a reduced flow of material);
• Material hardness (too much hardness of the particles creates difficulties in the densification process). [9]

2.1 Biomass pelletizing. Description of the pelletizing process

Pellets, also called "liquid wood", are fibrous products obtained from chips, sawdust, chop from vegetable debris or dedicated energy crops, pressed under high pressure. The characteristic of the pellet is that it has a much lower humidity than firewood, which gives a much higher thermal efficiency.
Pelletizing is a mechanical pressing of the material at much smaller dimensions and with much higher density. Pellets are solid fuels with low moisture content, obtained from sawdust, wood chips, or even tree bark, wood dust from industrial wood processing plants, as well as from unused trees from logging. The resins and binders naturally occurring in sawdust have the role of keeping the pellets compact and therefore they do not contain additives. Wood pellets are environmentally friendly, economical and CO_2-neutral fuels, mostly produced from sawdust and wood scraps, compressed at high pressure without additives for bonding. They are cylindrical in shape, usually measuring between 6-10 mm in diameter and 10-30 mm in length. [6]
The combustion is adjustable, making it possible to reduce the emission of harmful substances. The process of producing pellets involves subjecting the biomass to high pressures and forcing it to pass through the cylindrical holes of a mold. When exposed to appropriate conditions, the biomass "fuses" into a solid mass. This process is called extrusion. Certain types of biomass (mainly wood) naturally form good quality pellets, while other types of biomass (feed, herbaceous biomass, etc.) may require additives to serve as "binders" that keep the pellets bound. The stages of the pellet production process are: humidity control, extrusion, cooling and packing / storage. The material subjected to the pelletizing process must meet two essential conditions: the size of the chips between 30-50 mm and the maximum humidity 15%. In this regard, a pellet manufacturing line will include equipment for drying the raw material, chopping and pelleting.

2.2 Equipment for biomass pelletizing

The usual system for making pellets is the extrusion of the chopped material through a mold provided with a series of holes.
In general, pellet presses are the main equipment in a pellet production line. The technical characteristics of a pellet press greatly influence the quality and productivity. These characteristics are generally the size of the mold, the speed of the mold and the distance between the working elements.
The material, with the help of rollers, is pressed through the mold, thus forming the pellets. On the outside of the mold a knife cuts the pellets to the desired length. After extrusion the pellets reach the temperature of 90-100˚C and are transported to the refrigerator, where their temperature drops to 25˚C. It fixes lignin and strengthens the product, helping to maintain its quality in storage and transport. Finally, they are sieved so that the residual debris is separated and reused in the process. Dust-free pellets are ready for storage, transported to packing equipment and stored.

A pelletizing equipment, fig. 2 is composed of:
- helical feed system with dosing role of the compaction material;
- funnel for directing the compaction material;
- pellet press;
- drive gear motor;
- order cabinet.

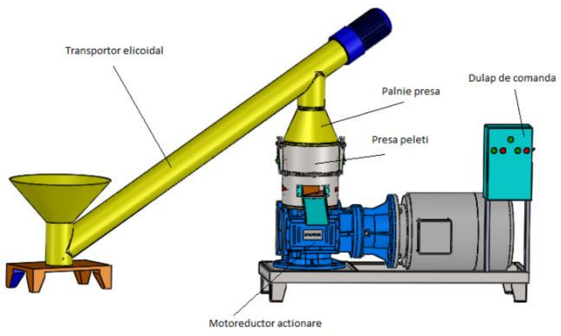

Fig. 2. Press pellets with feed and dosing with helical conveyor [5]

The most common devices used for pelletizing are those with mold and one or more pressing rollers. These are available in two constructive variants:
- with fixed mold and movable rollers
- with rotary mold and fixed rollers (with rotation movement only around its own axis).

3. Determination of the calorific power of densified biomass samples (pellets and briquettes)

The calorific power of biomass is correlated with its chemical composition. Thus, the calorific power increases as the lignin content increases. Cellulose has a lower calorific power than lignin due to the high degree of oxidation. The hydrocarbon content also increases the calorific power of the biomass. The calorific power can be calculated according to the chemical composition. 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 calorific power, [3]:

$$Q = 88.9\,(LC) + 16821.8\ [kJ/kg] \tag{1}$$

in which LC is the lignin content related to the dry and ash-free state.

$$Q = 196\ Cf + 14119\ [kJ/kg] \tag{2}$$

where: Cf is the fixed carbon content of the biomass.

$$Q = 33500\ C + 14300\ H - 15400\ O - 14500\ N\ \ [kJ/kg] \tag{3}$$

in which:

- C is the carbon content [%], H is the hydrogen content [%]
- O is the oxygen content (%) and N is the nitrogen content [%].

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 heat power, [4]:

$$Q = 349.1\ C + 1178.3\ H + 100.5\ S - 15.1\ N - 103.4\ O - 21.4\ A\ [kJ/kg] \tag{4}$$

in which C, H, S, N, O, A are the carbon, hydrogen, sulfur, nitrogen, oxygen and ash contents relative to the anhydrous state, expressed as a percentage.
Table 2 shows the calorific power values for the main solid biomass fuels, [4].

Table 2: The calorific power of the main solid biomass fuels, [4]

No. crt.	Fuel type	Calorific power of dry substance [MJ/kg]
1.	Wheat straw	18.3
2.	Barley straw	18.0
3.	Rice straw	15.2

3.	Corn cobs (stems)	16.2
5.	Cobs	17.4
6.	Stems of sunflower (sticks)	21.8
7.	Peel sunflower seeds	16.2
8.	Soybean spices	18.1
9.	Ropes of vines (humidity 7%)	16.5
10.	Fruit tree branches (7% humidity)	15.2
11.	Lamppost stems	18.4
12.	Fire wood	15.5
13.	Wood pellets or sawdust briquettes	17.1
13.	Charcoal	31.8
15.	Vegetable waste (stems, leaves, shells)	12.6

From the analysis of the data presented in table 2, it is found that the highest calorific power is obtained for the sunflower stems. The calorific power of solid biomass fuels is much lower than the conventional fuels (average calorific power of diesel fuel 42.34 [MJ / kg].

3.1 Determination of the lower calorific power of densified biofuels by means of the bomb calorimeter

The principle and method of determining the calorific power with the help of the bomb calorimeter is to determine the amount of heat released by burning a known quantity of fuel (approximately 0.5 g) and giving it to the calorimetric system comprising a known quantity of water (2700 ml at the temperature of 22 ... 25^{o}C), whose temperature is recorded. The combustion of the samples takes place in a vessel made of stainless steel, which is inaccessible to the acids resulting from the combustion of the fuel, capable of withstanding the high pressures developed during the explosive combustion of the investigated fuel.
The sample of material for determining the calorific power is placed in the cradle and weighed. Attach a cotton thread (fig. 3) to the center of the ignition wire and insert it with the other end into the sample, to propagate the combustion inside it. Insert the nacelle in its support into the bomb calorimeter and seal it tightly (fig. 4). The pump is then filled with oxygen at a pressure of 20-30 bar through the oxygen station, connected to an oxygen cylinder. The ignition adapter (fig.5) is attached to the bulb and then inserted into the calorimeter's inner vessel. Pour about 2 liters of demineralized water into the calorimeter tank, following the level indicator.

Fig. 3. Binding the cotton thread to the tungsten filament of the device

Fig. 4. Oxygen pressurization of the combustion vessel

To prepare the measurement, enter the measured weight of the sample, the type of operation to be performed (calibration or actual measurement), the type of the bomb calorimeter and the correction values for the heat generated by the combustion of the cotton yarn (the default value is entered in the measurement menu, 50 J) or from other sources.
When everything is ready, the calorimeter cover is closed (Fig. 6) and the unit starts the measurement operation. First the inner vessel is filled with water, then the combustion is carried out, the final step being to equalize the temperatures of the inner and outer vessels, by transferring heat from the inner vessel to the outer one. When this has happened, the measurement process is complete and the measured calorific power is displayed.

Fig. 5. Inserting the bomb calorimeter into the calorimeter

Fig. 6. Closing the calorimeter lid to start burning the biofuel sample

Fig. 7. The bomb calorimeter cooler

The device calculates the calorific power according to the following hypotheses:
- the temperature of the fuel and of the combustion products is 25 °C;
- the water contained in the fuel and the water formed by the combustion of hydrogen are in liquid state at the end of the process (the device measures the higher calorific power);
- atmospheric nitrogen was not oxidized;
- the gaseous products of the combustion are: O_2, N_2, CO_2 and SO_2;
- ash can form.

These elements are part of both the main constituents of wood, namely: [6]:
- cellulose: 50 - 55%
- lignin: 20 - 30%
- hemicellulose: 25 - 30%

as well as from secondary ones, such as:
- resins: 1 - 5%
- mineral substances: 0.2 - 1.2%
- tannin, coloring matter, etc.

In addition to the main constituents, listed, which are organic in nature, the wood composition also includes mineral substances that, as a result of burning, form ash.
The mineral substances, representing 0.2 - 1.2% by weight of dry wood are, [6]:
- 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%

The ash composition of different 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, [6].

3.2 INOE 2000-IHP test results

The tests were carried out on 2 types of pellets made on 2 types of pellet presses, these being realized within a project developed by INOE 2000-IHP in collaboration with 2 companies S.C. TECHNICAL ECO CDI S.R.L. Bucharest and S.C. ROLIX IMPEX SERIES SRL Bucharest. Following the tests for determining the lower calorific power for densified biofuels obtained from different types of biomass, the following values were obtained:
- In softwood pellets made with the TECHNICAL ECO press, the average lower calorific power was 18.477 MJ / kg, for an average humidity of 7.62%;
- In softwood pellets made with ROLIX press, the average lower calorific power was 17, 873 MJ / kg, for an average humidity of 8.64%;

The results of the determinations, presented in table 3, represent the average of the instantaneous calorific powers measured in 29 points, for each 5 samples from the pellets obtained with the two presses.

Table 3: The results of the tests regarding the lower calorific power of the biofuels densified pellets / briquettes

Test	Test no.	Determination		
		Average humidity, (U), [%]	**Lower calorific power (q_i), [MJ/kg]**	**Unburned combustible substance, (S_{cn}) [g/kg]**
Softwood pellets (Tehnic Eco)	1	7.62	18.654	5.15
	2		18.347	4.35
	3		18.516	3.55
	4		18.432	3.82
	5		18.440	3.01
	Average		**18.477**	**3.97**
Softwood pellets (Rolix)	1	8.64	17.869	8.51
	2		17.821	8.95
	3		17.592	9.71
	4		18.045	8.80
	5		18.043	7.25
	Average		**17.873**	**8.64**

NOTE: Moisture is the average humidity of the samples.

4. Conclusions

• Densified biofuels (pellets, briquettes) are obtained from recyclable raw materials, they are ecological in nature, so they can be considered clean burning fuels;
• Densification (pelleting, briquetting) represents the most efficient method of increasing the energy density and the calorific power of the biomass; the calorific value of pellets and briquettes is almost double that of wood (1 kg pellets can produce 4.7 kW or 17 MJ / kg);
• Lower calorific power of the pellets tested: 18.477 MJ / kg (softwood pellets obtained with TECHNICAL ECO press), respectively 17.873 MJ / kg (softwood pellets obtained with ROLIX press), allows them to be classified in EN plus A1 class (16500 ≤ Q ≤ 19000 kJ / kg);
• Pellet presses with a flat mold with which the pellets tested were produced in order to determine the lower calorific power (presses designed and manufactured by IHP in collaboration with the companies TEHNIC ECO and ROLIX, partners in the project "Eco-innovative technologies for biomass waste recovery", under Operational Program Competitiveness 2014-2020) meet the technical-functional parameters imposed for this type of equipment; the pellets meet the quality criteria of the standards in force regarding the physical-mechanical properties (diameter, length, bulk density, mechanical strength);

• The humidity significantly influences the lower calorific power and the quantity of the combustible substance found in the densified biofuels; for the same type of biomass, the difference of 1.02% humidity determines the decrease of the lower calorific value by 0.60 MJ / kg and the increase of the quantity of the fuel substance burned by 4.67 g / kg.

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