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Estimation of Energy Potential for Solid Pyrolysis By-Products Using Analytical Methods

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Abstract

Waste can be converted into energy and value-added products by thermo-chemical processes. Pyrolysis represents the thermal degradation of the material under a non-oxidant atmosphere leading to generation of three products: char—solid, oil—liquid and pyrolysis gas. Pyrolysis process means a complex mechanism of reactions, endothermic and/or exothermic chemical reactions that occurs simultaneously and/or subsequently. The use of lignocellulosic and plastic waste for energy purposes leads to the production of solids that could replace much of the conventional fuels once energy conversion technologies will prove profitable. In this chapter the authors proposed to describe, analyze and apply analytical methods for the heating value estimation of the solid products generated by pyrolysis of different wood and plastic materials. Our results obtained by experimental studies and empirical formulas will be evaluated and compared. The impact of the thermo-chemical process operational conditions on the variation of chars and biochars heating value will be also discussed in this chapter.

Keywords: analytical pyrolysis, heating value, biomass, plastic

1. Introduction

Today, the society concentrates on technological forces to switch the energy generation from conventional sources to renewables. This global tendency evolved due to the use of more clean, alternate and reusable energy sources. Denmark has already produced 44% of its electricity needs with renewable wind power and it intends to require at least 50% of its energy needs to come from renewable sources by 2030 [1]. The Scottish Government aims to generate 100% of Scotland's electrical power from renewable energy by 2020. Also, India plans nearly 60% of electricity capacity from non-fossil fuels by 2027. Waste and biomass are inevitable products of society. The main challenge for the future generations is to investigate how to manage large quantities of these fuels in a sustainable way. The energy content (heating value) represents a key factor of the waste, which determines how much energy can be extracted from it. Wood, cardboard or plastic waste is one of the main components of the municipal solid wastes (MSW), residential types respectively. These energy resources could be exploited by thermal processes to produce solids fuels with valuable energy content. Cellulosic and plastic residues, despite others exhaustible or expensive materials, could be used to produce fuels with valuable energy content.

The impact of biomass properties and operational conditions of pyrolysis processes on physical and chemical properties of the biochar has been already discussed [2–4], but insufficient materials are published concerning the relation between biomass and plastic based waste types and the energy content of chars and biochars. The present work brings contributions with critical analytical data regarding this correlation. This could help to identify optimum types of waste to be treated to produce chars valuable for their energy potential in a variety of pyrolysis units. Therefore, the research concentrates on theoretical and experimental studies that could give more clues about the heating value of the chars generated from five types of waste. So, we proposed to obtain viable experimental results applicative at industrial level and give some ideas how use the chars obtained or how to replace some materials with these lignocellulosic/plastic wastes. These could solve environmental problems that affect in the present the entire world.

2. Calorimetry: instrumentation and analysis

Calorimetry is the science dedicated to the measuring of heat. This represents the amount of energy exchanged within a given time interval in the form of a heat flow [5]. Since its foundation in 1780, the calorimetry meets varied and successful uses in many fields. The modern calorimetry has some targeted fields: material science, life science (biology, medicine and biochemistry), pharmacy and food science, environmental control analysis, safety investigations and determinations of energy content of fuels, search of new alternative energy sources.

During the past century, the classical methods of calorimetry have not known many changes, only microelectronic and computer science get progress allowing to develop new types of calorimeters and open new fields of application.

Each calorimetric experiment has three stages very well defined:

- The calorimetric part assumes the accurate determination of the energy generated in the reaction.
- The chemical part involves the characterization of the initial and final states.
- The transformation of the results obtained in the calorimetric experiment to a standard-state combustion energy at 298.15 K, from which a standard enthalpy of formation can be calculated [6].

2.1 Units

Heat cannot be measured by a direct method. Consequently, heat must be determined by means of its effects. The oldest unit quantity of heat is the calorie. This was defined in terms of the heating of water. A traditional definition specifies that 1 calorie is the amount of heat required to raise the temperature of 1 gram of water by 1°C, from 14.5 to 15.5°C (American Physical Society). Conversion relation between calorie and joule:

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ J} = 0.2388459 \text{ cal}$$

Nowadays, the International System of Unit recommend joule as unit for heat. Another common unit for heat is British thermal unit (Btu), that is the English system analog of the calorie.

$$1 \text{ Btu} = 251.9958 \text{ cal}$$

The last unit is the International Table (IT) calorie that has been adopted in the publications of the Energy Information Administration of the U.S. Department of Energy (DOE/EIA) [7] and of the International Energy Agency of the Organization for Economic Co-operation and Development (OECD/IEA) [8].

2.2 Calorimeters

The calorimeter represents an instrument used in calorimetric testing (calorimetry) that allows to measure the amount of heat released or absorbed in chemical or physical reactions. It can determine heat content, latent heat, specific heat, and other thermal properties of substances. The design of a calorimeter is based on a container with a temperature thermocouple through which the thermal phenomenon is investigated. The container communicates with the environment by its insulating walls that have some thermal resistance.

There are many types of calorimeters used for measurement of the heat. The most common are:

- *Bomb calorimeters*—they are isolated devices with a constant volume. Since the volume does not change, the instruments measure the heat evolved under constant volume, q_v ,

$$q_v = C \times dT \text{ [J]}, \quad (1)$$

where dT is the temperature increase. The q_v so measured is also called the change in internal energy, dE . Note that.

$$dE = q_v = C \times dT \text{ [J]} \quad (2)$$

- *Differential scanning calorimeters*—represent an important tool in thermal analysis. If a calorimeter measures the heat into or out of a sample, a differential calorimeter measures the heat of sample relative to a reference. The difference in the quantity of heat necessary to increase the temperature of the sample starting from the reference temperature is measured as a function of temperature. In the last years, the methods of thermal analysis have been widely accepted in analytical chemistry. Differential scanning calorimeters are often used in many industries—from pharmaceuticals and polymers, to nanomaterials and food products.
- *Isothermal titration calorimeters*—they are based on a technique (isothermal titration calorimetry—ITC) used in quantitative studies of an extensive variety of biomolecular interactions. They directly measure the heat that is either released or absorbed during a biomolecular binding event. Isothermal titration calorimetry (ITC) is a valid method to investigate biological reactions with high sensitivity and accuracy at a constant temperature [9].
- *Calvet-type calorimeters*—they are not so often used. They can measure the enthalpy change during sublimation reactions and the behavior of a material. In case of these calorimeters, the detection is based on a three-dimensional flux meter sensor. There is no calibration and standard methods required for this type of calorimeters. The calibration can be achieved at a constant temperature, in heating and cooling modes, while the system can manage temperatures up to 1600°C. Calvet microcalorimeter is one of the most known type of

heat conduction calorimeter [10], SETARAM Instrumentation being the only producer of these categories instruments.

During this chapter we focused on oxygen bomb calorimeters. These type of calorimeters have a wide range of uses, but their mainly applicability are in the coal industry, i.e., coal fired power stations, iron and steel plants, cement plants and other users of coal. Also, they are often used in other non-coal related industries. Some examples for this case are:

- animal feeds—to determine their nutritional value,
- animal digestion of feeds, dairy products and other foods to measure the caloric value,
- ammunition propellants are analyzed for their effectiveness,
- liquid fuels can also be analyzed in a similar way to coal.

Other important applicability of the bomb calorimeters is the use in colleges, universities or research institutes, where these instruments could bring a contribution to teaching or to experimental and development research that is performed in many departments. But the main applications for oxygen bomb calorimeters are:

- Solid and liquid fuel testing,
- Waste and refuse disposal,
- Food and metabolic studies,
- Propellant and explosive testing,
- Fundamental thermodynamic studies,
- Educational training.

3. High heating value

The heating value or calorific value defines the energy content of a fuel. It is one of the most important properties to evaluate the fuel quality and a key parameter in the development of any energetic application. The heating value is the amount of heat released during the complete combustion of a specific fuel quantity at standard conditions, pressure 1 atm and temperature 25°C. Generally, it is measured in energy content (Joule, Calorie, British Thermal Unit- Btu or Watt-hours-Wh) per specific quantity (mass or volume) of the combusted fuel. The specific quantity is given by the fuel physical state: molar, gram or kilogram for solid fuels, liter for liquid fuels and cubic meter for gaseous fuels.

The fuel heating value can be classified as Higher or Lower Heating Value (LHV). The High Heating Value (HHV) otherwise known as heat of combustion or Higher Calorific Value or Gross Calorific Value (GCV) or Gross Energy or Upper Heating Value is the total amount of energy released during the fuel complete combustion per fuel specific quantity. The LHV, also known as Net

Heating Value or Net Calorific Value, is determined by subtracting the latent heat of vaporization produced during the complete combustion of the fuel from the HHV [11].

The heating value can be estimated theoretically based on the proximate, ultimate and chemical analysis composition of the fuel by using dedicated empirical formulas or experimentally by employing an adiabatic calorimetric bomb, which measures the enthalpy change between reactants and products [12–14].

3.1 Theoretical estimation of the heating value

Although the calorimeter instrument is easy to use and relatively accurate, it might not always be accessible to researchers. The earliest and most used empirical correlation for the HHV estimation was developed by Dulong by in end of nineteenth century, based on the ultimate analysis of coal [15]. One century later, Tillman [16] developed the simplest heating value prediction formula for woody biomass based on the fuel carbon content.

Up to now, various empirical formulas, models and correlations have been improved or developed for the predication of the HHV using the proximate or ultimate analysis of the fuel such as: fossil fuels/waste [17], biomass [18, 19], refused derived-fuels [20], commingled wastes [21, 22]. However, sometimes the models can have their limitations, due to their wide variety on fuels applications, that can be homogeneous (e.g., fossil fuels and biomass) or heterogenous (refused derived fuels, solid recovered fuels, municipal solid waste) such as:

- the equations based on the elemental analysis are generally more accurate than those based on proximate analysis [12];
- usually, the weight of the moisture or ash free basis or both, is undefined in the equation, limiting its accuracy;
- for precise values, even for homogenous wastes, like biomass, Özyuğuran and Yaman, show the necessity to create models for each subclasses (e.g., herbaceous, woody or agricultural waste) [23];
- sometimes the same model can be reproduced based on different units (i.e., kcal/kg, kJ/kg, Btu/lb, etc.) leading to confusion [24].
- some studies suggest the creation of personalized models, based on the fuel derivation/application, country/region, to avoid the over or under prediction [25, 26].

3.2 Estimation of the high heating value from ultimate or proximate analysis

In the absence of calorimeter instrument, the HHV can be estimated based on the elemental, proximate or physical analysis of the fuel.

Based on a comprehensive literature review the most common equations for the appropriate estimation of the HHV of biomass, commingled biomass-plastic waste, municipal solid waste (MSW), coal and char are summarized in **Table 1**. Ten correlations for each type of analysis (ultimate and proximate) were studied in order to establish the wide applicability and versatility of the formulas by considering cellulose, hemicellulose, lignocellulose and plastic polymers-based waste.

Eq no.	Name of the author/source	Original equation	U.M.	Recommend fuel type	Ref.
Estimation of the high heating value from ultimate analysis					
1	Sheng and Azevedo	$HHV = 0.3259C + 3.4597$	MJ/kg	Biomass	[12]
2	Tillman	$HHV = 0.4373C - 1.6701$	J/kg	Biomass	[27]
3	REM model	$HHV = 36C + 120H - 16O$	MJ/kg	Biomass-plastic	[21]
4	Friedl et al.	$HHV = 3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20,600$	kJ/kg	Biomass	[28]
5	Dulong	$HHV = 7831C + 35,932H - O/8 + 1187O + 578N$	kcal/kg	Waste	[29]
6	Yacio	$HHV = 0.336C + 1.418H - 0.0145O + 0.0941S$	MJ/kg	Coal/refuse	[30]
7	Dermirbas	$HHV = 0.335C + 1.423H - 0.154 * O - 0.145N$	J/kg	Waste/biomass	[31]
8	Dulong	$HHV = 144.5C + 609.6H - 76.2O + 40S + 10N$	Btu/lb	Waste/coal	[32]
9	Boie	$HHV = 35.2C + 116.2H + 6.3N + 10.5S + 11.1O$	MJ/kg	Waste/biomass	[21]
10	Scheurer-Kestner	$HHV = 81(C - 3O/4) + 342.5H + 22.5S + 171O/4 - 6(9H + W)$	kcal/kg	Waste	[25]
Estimation of the high heating value from proximate analysis					
11	García et al.	$HHV = 18,300 - 3.98A^2 - 112.10A$	kJ/kg	Biomass	[32]
12	Yin	$HHV = 0.1905VM + 0.2521FC$	MJ/kg	Biomass	[19]
13	Cordero et al.,	$HHV = 354.3FC + 170.8VM$	kJ/kg	Biomass	[33]
14	Phichai et al.	$HHV = 157.34(VM + FC) + 4243.97$	kJ/kg	Biomass	[34]
15	Bento	$HHV = 44.75VM - 5.85W + 21.2$	kcal/kg	Refuse/char	[25]
16	Kathiravale et al	$HHV = 356.047VM - 118.035FC - 5600.613$	kJ/kg	MSW	[35]
17	Soponpongpipat et al.	$HHV = 35.4879 - 0.3023A - 0.1905VM$	MJ/kg	Chars/coal	[36]
18	Özyüğuran, et al.	$HHV = 167.2 - 1.449VM - 1.562FC - 1.846A$	MJ/kg	Biomass	[23]
19	Kieseler et al.	$HHV = 0.4108FC + 0.1934VM - 0.0211A$	MJ/kg	Chars	[37]
20	Parikh et al.	$HHV = 0.3536FC + 0.1559VM - 0.0078A$	MJ/kg	Biomass	[38]

HHV, high heating value; U.M., unit measure; C,H,N,S,O, wt% of carbon, hydrogen, nitrogen, sulphur, oxygen content; W, wt% total moisture content; A, wt% of ash, dry basis; VM, wt% volatile matter; FC, wt% of fixed carbon.

Table 1.

Most common equations used for high heating value prediction.

As seen from **Table 1**, most empirical formulas are linear regression models, build based on the mass fractions (weight) or percent of the fuel principal elements and constant coefficients. The simplest equations for the HHV prediction from the ultimate or proximate analysis consider only the carbon (C) fuel content (Eqs. (1, 2)), or ash (A) (Eq. (11)), respectively. Besides these two elements, the reliability of the results increases with the augmentation of the chemical or physical elements used partly or fully in the formulas: hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), chlorine (Cl) or fixed carbon (FC), volatile matter (VM) and moisture (W). Over more Eqs. (2, 5, 8, 16) represent one of the most known and used equations in the exact science area, while the rest have been proposed, adjusted or improved in the last in several decades [15, 19].

It is worth noting in order to use or create dedicated empirical formulas, the experimental determination of the chemical–physical characteristic of the fuel is need. In this case dedicated laboratory instruments are necessary. The proximate analysis could be established by using a thermogravimetric analyzer (TG), following the ASTM D7582-12. In the absence of the TG analyzer, the drying oven and the calcination furnace can be used. Thus, for woody-biomass the content of moisture is determined according to ASTM standard method 871-82, for volatile matter (VM) with ASTM D5832-98 (2014) and ash with ASTM D1102-84 (2013). The fixed carbon content (FC) is always determined by difference considering the sum of total moisture (if available), volatile matter and ash. The elementar analyzer is used for the ultimate analysis determination adopting ASTM D5373 – 08. Usually the oxygen (O) is obtained by subtracting the rest of the determined chemical elements carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and chlorine (Cl) from the total content ($O = 100 - C - H - N - S - Cl$) or by subtracting the carbon (C), hydrogen (H) and ash from the matter ($O = C - H - Ash$).

3.3 Proximate and ultimate analyses data on biomass and plastic waste

The validation of the HHV predication models presented in the preceding section was made by using the characterization of three biomass-based waste (cherry wood, cardboard and newspaper waste) and two types of plastic waste, polypropylene (PP) and high-density polyethylene (HDPE) waste. The waste sampling, along with the analytical and empirical procedure for the ultimate and proximate analysis of the newspaper, cardboard, PP and HDPE resulted from the selective collection of the municipal solid waste were former presented in previews researches made by the authors [39, 40]. The cherry wood waste elemental and proximate composition was obtained after a generic review of the former literature [41, 42]. The summaries of the ultimate and proximate analysis are presented in **Table 2**.

Sample	Ultimate analysis [wt%]						Proximate analysis [wt%]			
	C	H	N	S	O	Total	V.M.	F.C.	Ash	Total
Newspaper	47.00	7.00	2.00	1.00	43.00	100.00	88.4	3.5	8.1	100.00
Cardboard	48.00	8.00	2.00	1.00	41.00	100.00	87.5	6.6	5.9	100.00
Cherry wood waste	49.52	5.81	0.31	0.02	44.34	100.00	84.9	15	0.1	100.00
PP	85.50	12.50	1.20	0.10	0.70	100.00	99.13	0.27	0.6	100.00
HDPE	84.70	14.47	0.11	0.12	0.60	100.00	99.74	0.06	0.2	100.00

Table 2.
 Summaries of ultimate and proximate analysis [39, 43].

4. Experimental determinations

The experimental research was developed adopting a bench scale pyrolysis system and an oxygen bomb calorimeter with the purpose to investigate alternative energy sources from residue material as light packaging waste and wooden biomass.

Calorimetry experiments were performed for the solid products (chars) generated by biomass and light packaging waste (LPW) pyrolysis processes and with a calorimetric bomb IKA C200. Testing were completed for five types of chars resulted from waste pyrolysis: biochars produced from woody biomass and mixers of biomass and plastic based material.

4.1 Collection and preparation of the samples

Five types of materials were considered and analyzed in the present chapter. Cherry sawdust was the wooden biomass used to produce biochar samples and it was collected from furniture industry. The configuration, the procedure to get the reduced dimensions and characterization of the cherry wood and the others plastic based materials were previously detailed described in other works [43, 44]. Other four LPW mixtures representative for Eastern Europe, coming from the MSW selective collection were used: Mix 1 (paper and cardboard mixture—in equal proportion), Mix 2 (plastic solid waste mixture—HDPE, PP, PET—in equal proportion), Mix 3 (90% paper & cardboard waste mixture and 10% plastic solid waste mixture), Mix 4 (67% paper & cardboard waste and 33% plastic solid waste).

Pyrolysis processing was applied to cherry wood, resulting in a series of 12 samples of cherry biochars, 36 samples of LPW mixtures respectively. So, a total of 48 samples were prepared for measurements of high heating values by using the oxygen bomb calorimeter.

4.2 Processing for char samples production

To obtain the solid pyrolysis by-products that can be used as fuel with high calorific energy content, pyrolysis processes were completed through a laboratory scale pyrolyser. **Figure 1** explains the general schema of the reactor. The furnace temperature was very well controlled to achieve the desired heating rate and temperature for samples thermal-chemical treatment as the furnace is equipped with an automatic integrated control for heating. The tubular batch reactor worked in a discontinuous mode, so the waste sample was placed in a crucible of refractory steel W4541 with tubular parallelepiped form and then this was introduced in the furnace. Each sample of the cherry biomass was weighted trying to keep the mass constant at 25 g. The total amount of the mixture that entered in the crucible was in a range 25–30 g depending on the form and structure of the waste fractions.

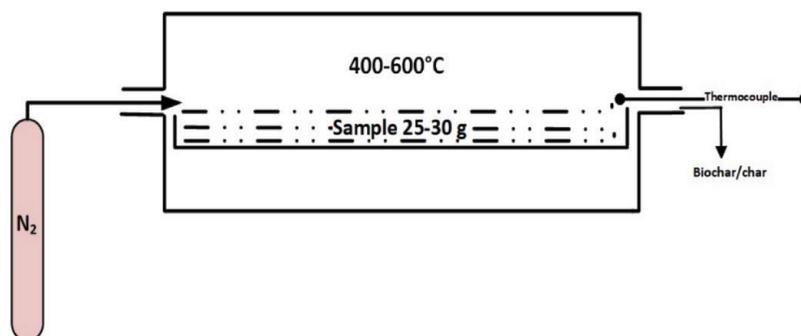


Figure 1.
Simplified scheme of the pyrolysis batch reactor.

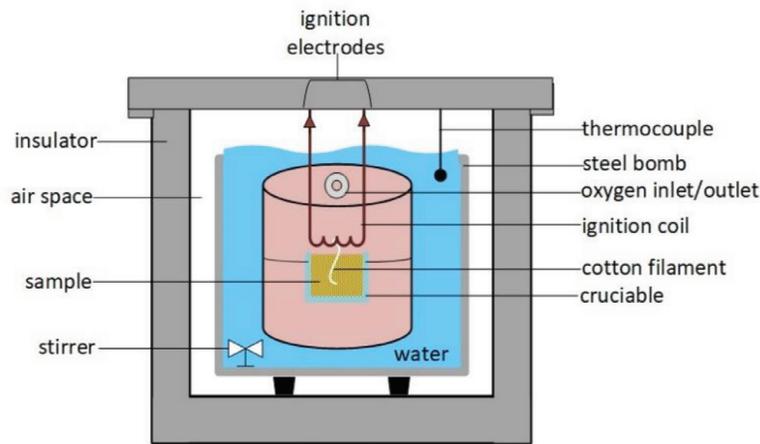


Figure 2.
Calorimetric system.

The reactor was heated by electrical resistances until the temperature of the process has reached the desired value. At this moment the biomass waste sample was introduced in the reactor, where an inert atmosphere was maintained throughout the pyrolysis processing by inserting a nitrogen flow of about 1 l/min. For the types of the materials analyzed in this chapter, the pyrolysis processing was conducted in almost the same conditions: temperature: 400, 500 and 600°C, atmospheric pressure, inert gas: purified N₂ (99.9995%) at a gas pressure 50–100 kPa; only the process time was different: 30 min for cherry wood and 60 min for municipal solid waste types. Considering previously results of our experimental research [45] that demonstrated heating value is not very much influenced by the treatment time during the pyrolysis processes but depends more on the process temperature [46], it is valuable to discuss and compare here the actual experimental results. All pyrolysis experiments were done in triplicates.

4.3 Procedure for HHV measurement

Experimental determinations of the high heating value in case of the five types of pyrolysis chars were performed in the laboratory conditions: combustion of the sample under specific conditions in a C200 system according to ASTM D2015-96 standard (1998). C200 (**Figure 2**) can be used to determine the calorific value for solids or liquids samples by engagement an adiabatic bomb calorimeter that allows to measure the heat of reactions involving gases.

The measuring of the samples calorific power involves the following steps:

- a. Melting the crucible and weighing the sample using a high precision electronic balance;
- b. Inserting the sample into a small plastic bag;
- c. Positioning the filament (a cotton yarn). It binds in the middle of the firing wire.
- d. Place the crucible on the support and insert the filament into the crucible, over which the material sample is placed;
- e. Turning of the bomb;
- f. Transporting the bomb to the oxygen station. Insert oxygen for about 3 minutes into the bomb at a pressure of 30 bar.

- g. Transporting the bomb to the calorimeter. Attaching the bomb to the ignition fitment, then insert it into the calorimeter. Fit it in its intended place and then close the calorimeter.
- h. Fill the IKA C200 calorimeter tank with water until the level indicator indicates the water level at a position between the minimum level and the maximum level.
- i. Digital operation with the device display. Enter the values corresponding to the sample mass and the lower calorific value of the bag into which the sample is introduced.
- j. After the apparatus displays the value of the calorific value, the water tank is emptied.
- k. Positioning the gas removal device on the top of the calorimeter bomb.
- l. Press and the gases are exhausted.
- m. Opening the sample, removing the filament and cleaning the crucible with alcohol.

All the calorimetric measurements for the determination of biochars and chars HHV were performed in triplicates.

4.4 Results, comparison, and discussions

4.4.1 Theoretical high heating value of pyrolysis chars

The HHVs of the biomass and polymer-based materials were predicted by using 20 equations presented in **Table 1**. The ultimate and proximate analysis for each type of material, presented in **Table 2** were used for the application of the formulas. **Table 3** shows the newspaper, cardboard, cherry wood, PP and HDPE waste HHV-predicted values obtained using the equations presented in **Table 1**. To avoid confusion and compare more easily the results, all the predicted values were normalized, by using the same reference unit measure [kJ/kg]. The comparison of the data was made based on: the HHV predicted mean value generated by the equations, standard deviation (STD) by analyzing all the equations from each type of determination (ultimate or proximate analysis), HHV of the material obtained with the calorimeter (HHV experimental) and STD by comparing the predicted and experimental results.

From the elemental analysis models, the HHVs predicted from biomass-based materials (newspaper, cardboard and cherry wood) varies between 21,273 and 23,034 kJ/kg, while the plastic-waste ranges between 44,111–46,017 kJ/kg with a STD of ≈ 6000 –7000 kJ/kg. By comparing only, the data obtained using the equations, the trend lines plotted in **Figure 3** report homogenies correlation between the results for most equations. However there are some visible exceptions since for plastic based materials Eq. (3, 4) underestimate the predicted HHV with almost 30%, while Eq. (7) for plastic and Eqs. (7, 8, 11) for biomass-based waste overestimates it. For some correlations inconsistent results can be observed while comparing the mean HHV predicted v.s. HHV experimental. For a better evaluation of the correlation the mean absolute error (MAE) was determined. The MAE evaluates the accuracy of the HHV predicted to the experimental one. In this case, lower values tending to 0% indicate good accuracy of a specific correlation. The MAE negative values indicate the underestimation of the results, while the positive their

High heating value (HHV) [kJ/kg]														
Estimation of the high heating value from ultimate analysis											Data comparison			
Eq. no.	1	2	3	4	5	6	7	8	9	10				
Type of waste/ name of the author/s	Sheng and Azevedo	Tilman	REM model	Friedl et al.	Dulong 1	Yacio	Demirbas	Dulong 2	Boie	Scheurer- Kestner	HHV predicted mean value	STD all eq.	HHV experimental [39, 43]	STD (Predicted v.s. experimental)
Newspaper	18,777	18,883	18,440	19,035	28,107	25,189	18,794	18,117	29,682	21,328	21,635	4154	14,183	3726
Cardboard	19,103	19,320	20,320	19,726	29,810	26,972	20,860	20,226	30,974	23,025	23,034	4297	15,387	3823
Cherry wood waste	19,598	19,985	17,653	19,632	27,116	24,201	17,984	16,975	29,102	20,486	21,273	3926	17,500	1887
PP	31,324	35,719	45,668	53,718	46,825	46,452	46,148	46,347	44,785	44,125	44,111	5925	42,772	670
HDPE	31,063	35,369	47,760	56,915	49,491	48,980	48,857	48,887	46,715	46,137	46,017	7046	45,783	117
Estimation of the high heating value from proximate analysis											Data comparison			
Eq. no.	1	2	3	4	5	6	7	8	9	10				
Type of waste/ name of the author/s	García et al.	Yin	Cordero et al.	Phichai et al.	Bento	Kathiravale et al	Soponpongpipat et al.	Özyüğüran, et al.	Kieseler et al.	Parikh et al.	HHV predicted mean value	STD all eq.	HHV experimental [39, 43]	STD (Predicted v.s. experimental)
Newspaper	17,131	17,723	16,339	18,704	25,422	25,461	16,199	16,571	18,363	14,956	18,687	3533	14,183	2252
Cardboard	17,500	18,333	17,283	19,050	25,253	24,774	17,036	16,572	19,509	15,929	18,931	3121	15,387	1772
Cherry wood waste	18,289	19,955	19,815	19,962	24,766	22,857	19,284	16,573	22,580	18,539	20,189	2328	17,500	1345
PP	18,231	18,952	17,027	19,884	27,431	29,662	16,422	16,575	19,270	15,545	19,731	4544	42,772	11,520
HDPE	18,277	19,016	17,057	19,947	27,545	29,904	16,427	16,575	19,310	15,569	19,797	4607	45,783	12,993

Table 3.
The HHVs prediction based on ultimate and proximate analysis.

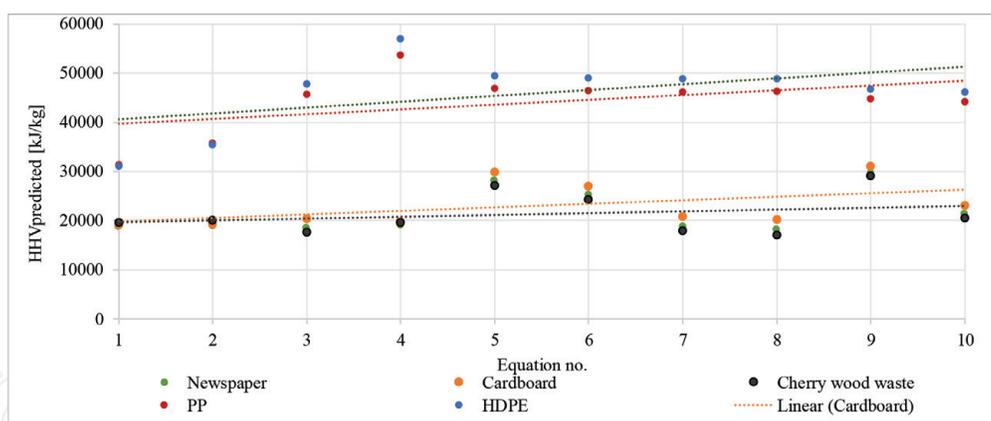


Figure 3. Comparison of the HHV-predicted values based on ultimate analysis.

overestimation. Eqs. (5, 9, 10) and Eqs. (5, 7–12) can predict the HHVs for biomass-based wastes and plastics-based wastes respectively, with MAE lower than 10%, indicating their versatile applicability.

From the proximate analysis models, for all studied materials the HHVs predicted varies between $\approx 18,600$ and $30,000$ kJ/kg with a STD reaching to almost $12,000$ kJ/kg for the plastic-based waste as shown in **Figure 4**. For plastic-based materials, the HHV predicted is different from HHV experimental, for all 10 studied equations. In all cases the predicted energetic value is underestimated. This is further strengthened by MAE that varies between -31 and -66% . In this case the validity of the correlations towards their universal usage on the defined type of materials is uncertain. Good correlation can be noticed for cherry wood waste. The latter is confirmed by the mean percentage error that tends to zero and is lower than 15% for Eqs. (13–16), (19), (22). For the other biomass-based waste (newspaper and cardboard) adequate MAE varying between 4%–20% are registered for Eqs. (13–16, 19–22). Eqs. (17) and (18) are overestimating the predicted newspaper and cardboard HHV with 60–80%. By analysis the equations correlated with the number of elements considered, we can conclude that the heating value is mainly a function of ash content or volatile matter. The previous statement is supported also by literature [25]. In conclusion the accuracy of the results increases with the numbers of elements correlated with ultimate and proximate analysis considered in the prediction formulas. Furthermore, higher correlations accuracies have been registered in the case of ultimate analysis usage. The current statement is supported by former investigations presented by Menikpura and Basnayake [47].

4.4.2 Experimentally determined high heating value of pyrolysis chars

The results concerning the caloric energy of the chars resulted from pyrolysis of the wood cherry and four PSW and PCW mixes (Mix 1, Mix 2, Mix 3, Mix 4) could be a support to provide energy fuels valuable for energy systems. From this point of view, it is evident to underline the energy content of the generated chars. So, a challenge for this experimental research was to discuss the way how type of waste marks changes on the high heating value of the pyrolysis chars. There were significant differences in the caloric value of the chars resulted from wood waste vs. light packaging wastes (LPW). These can be clearly observed in **Figure 5**.

In case of the cherry wood pyrolysis, the increase of process temperature leads to more energy valuable products. The maximum value of HHV ($30,043$ kJ/kg) was determined for the biochars obtained from pyrolysis at 600°C and marks these

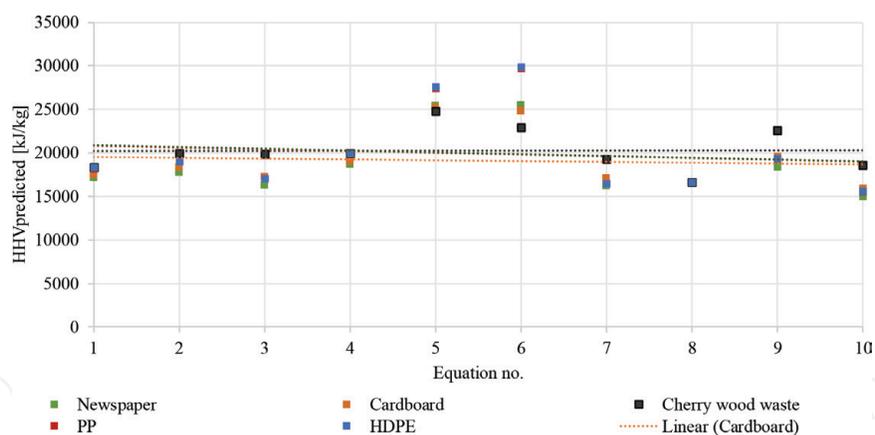


Figure 4. Comparison of the HHV predicted values based on proximate analysis.

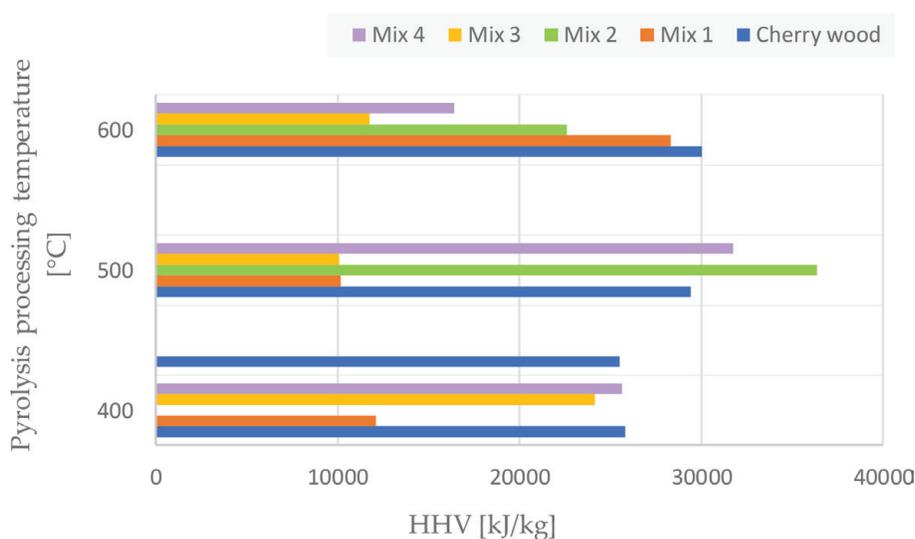


Figure 5. HHV of chars and biochars depending on the pyrolysis process temperature.

as products comparable with a real coal (e.g., semi-anthracite coal—29,500 kJ/kg, bituminous coal—30,200 kJ/kg, anthracite coal—32,600 kJ/kg), while for plastic the maximum value of HHV was 31,378 kJ/kg, obtained at 500°C. If we consider the chars resulted from the LPW mixes, we can conclude there is not any linear increasing/decreasing of the HHV function of the pyrolysis process. Comparing the experimental determinations, it was revealed that for pyrolysis processing, 400°C produces chars with appropriated HHV as value in case of cherry wood, Mix 3 and Mix 4, 500°C in case of cherry biomass and Mix 4 and 600°C for case of cherry wood and Mix 1, respectively. It was already reported that heating value of lignocellulosic biomass type can greatly vary with climate and soil [48]. It is obviously that these factors strongly influence the HHV of wood and of the mixes analyzed in the present research. At lower process temperature of 400°C, for the plastic-based mixtures (Mix 2, Mix 3, Mix 4) the agglutination rate of the char produced increases. At this process temperature, during the experiments, the recovery of the char was obstructed by its high agglutination level, due to plastic incomplete decomposition. In this case, at industrial level, in mixture with other wastes, the deposition of the melted char on the side of the reactor walls might overload it, limiting its recovery from the pyrolysis chamber. In conclusion, the minimal recommend pyrolysis process temperature in case of plastic waste presence should be 500°C.

The closest value of HHV registered for cherry wood and Mix 1 confirming that these two materials have a similar chemical structure and composition. Since all types of biomass have similar carbon mass fraction they have a comparable HHV, between 16,200 and 21,600 kJ/kg [49]. This rule could explain the same tendency for the biochars resulted from wood and Mix 1, respectively. Another aspect to be considered is the ash content that lead to variation of the HHV of the biochar. Experiments of Brewer [50] lead to biochars from corn stover, switchgrass, and hardwood treated by pyrolysis and gasification processes. The results showed that is an inversely proportional relation between biomass ash content and the heating potential of the biochar.

5. Conclusions

In this study analytical methods have been used for the HHV determination of different raw biomass, plastic waste and biomass-plastic waste mixtures and their by-products (biochar and char) resulted from the pyrolysis process. The main conclusion of the present research are listed:

- The comprehensive analysis of the scientific literature revealed that limited information is delivered in the regarding the energy potential of the chars and biochars produced by pyrolysis processing of the waste types analyzed in our research.
- The biomass and plastic wastes presented in this chapter store a significant quantity of energy that can be converted into different energy products depending on the correlation between feedstock properties, operational conditions of the available technology processes and the end use of the obtained products.
- The results generated by using the empirical equations mentioned in the present chapter demonstrates that their accuracy increases with the numbers of elements correlated with ultimate and proximate analysis considered in the prediction formulas.
- In the absence of instrumentation for HHV determination, empirical dedicated formulas can be used based on the ultimate and proximate analysis of the material. The experimental determination of the individual elements and substances is required for further application of the correlations. Twenty prediction formulas for HHV were analyzed. The elemental analysis represents the most essential parameter for determining the fuel heat of combustion. For a better accuracy of the results, the authors suggest the usage of at least three types of different dedicated correlations, considering the main fuel characteristic of the studied fuel.
- The experimental results reported that ash content is the main function in the energy content of biochars/chars. The latter is confirmed by the empirical results, where the heating value is strongly influenced by the ash content or volatile matter.
- Our experimental research revealed the following maximum values for the HHVs of the chars and biochars produced by pyrolysis processes: cherry wood 30,043 kJ/kg at 600°C, PCW 28,335 kJ/kg at 600°C, PSW 36,378 kJ/kg at 500°C, Mix 3 (PCW 90% & PSW 10%) 24,174 kJ/kg at 400°C and Mix 4 (PCW 67% & PSW 33%) 31,732 kJ/kg at 500°C.

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