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Effect of the carbon oxidation state of biomass compounds on the relationship between GCV and carbon content

G. Toscano*, G. Riva, E. Foppa Pedretti, D. Duca

Dipartimento di Scienze Agrarie, Alimentari ed Ambientali, Università Politecnica delle Marche, Via Brecce Bianche, 60131 Ancona (AN), Italy

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ABSTRACT

The gross calorific value of biomass is an important parameter for its applications for energy purposes. It represents the enthalpy of the complete combustion of a fuel, including the latent heat of water formed by the process. Several mathematical relationships are proposed in the literature to calculate the gross calorific value (GCV) of biomass fuels, using some characteristics as proximate analysis, ultimate analysis and chemical composition analysis. All these formulae were obtained by a mere application of statistical data elaboration, in some cases collected from literature and not from direct experimental analysis. In this study an investigation on the relationships between the chemical composition of the biomass compounds and their GCVs has been carried out. More than 650 biomass samples have been analyzed to develop four mathematical relationships between GCV and carbon content, considering the average oxidation state (C_{ox}) of the biomass compounds.

1. Introduction

The evaluation of Gross Calorific Value (GCV) is a fundamental step in several applications of biomass for energy purposes [1–4]. The measurement of this parameter requires a specific calorimeter device and the conditions defined in EN 14918 [5] for solid biofuel and ASTM D240 for liquid biofuels [6].

Some Authors have proposed methods for determining GCV through mathematical relationships between GCV and biomass characteristics [1–4,7–12] in order to reduce the complexity, time consuming and the related costs of the laboratory determinations. Among them, elemental analysis and proximate analysis are the most important to be considered. These models are different from each other: the resulting predictions could be therefore very different and the accuracy of a correlation must be evaluated to make a proper selection [3]. The inaccuracy may be attributed to several reasons: the limited biomass samples used for its derivation, the analysis methods used in the biomass characterization and the method of deriving the formulae are the most important ones [3].

Furthermore, the GCV is a function of the energy chemical bounds in the biomass and converted into heat energy by the combustion process [2]: the variability of the biomass chemical structure determines reduction in the accuracy of the GCV prediction mathematical relationship based on element composition. This element has been investigated in the present work in order to improve the performance of the GCV prediction models. The biomass chemical composition and its relationship with the energy content have been introduced before of the description of the experimental work.

* *Corresponding author*. Tel.: +39 071 2204297; fax: +39 071 2204167.
E-mail address: g.toscano@univpm.it (G. Toscano).

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2. Biomass, structures and their energy content

The term "biomass" refers to a very wide number of heterogeneous materials whose origin comes from the photosynthesis reaction, a process in which the organisms use the sunlight energy to produce carbohydrates from carbon dioxide and water. The word biomass derives from Greek (bio = life and mass = unspecified amount) and generally indicates non-fossilized organic materials originated from plants, animals and microorganisms. Biomass includes different kind of material deriving mainly from agriculture, forestry and marine fields. Their components include cellulose, hemicelluloses, lignin, extractives, lipids, fat, proteins, simple sugars, starches, water, hydrocarbons, ash and other compounds [13,14]. Their presence depends on the biomass type. For instance, proteins and lipids, typical of animal biomass, are also contained in vegetable biomass (e.g. oilseed crop) and in some microalgae [15]. Hemicelluloses, cellulose and lignin are the three main components of lignocellulosic biomass, in particular forest and agriculture materials [16,17]. The variability of the composition of these macromolecules depends on the kinds of biomass and its component (e.g. wood, branch, barks, shell, leaves, straw, pits and so on). Other minor components, like pectin, protein, extractives, resins, terpenes, gums and others may also be included [14,17,19]. In trees, cellulose is generally about 40–50% of the dry weight and the amount of lignin in wood species varies from 20% to 40%, but on average stood at 25% [15]. For lignocellulosic macromolecules literature proposes several formulae for cellulose, polysaccharide also known as glucan and glucosan and for hemicelluloses polysaccharide also known as xylan, polyose and pentosan. The ratios between the main elements are quite homogeneous, though the hemicelluloses composition, more irregular than cellulose, can vary in hardwood and softwood. The composition variability increases for the lignin components. It has been reported that lignin is a phenolic polymer whose structure can be represented by $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9 \div 1.7}]_n$. It is known that hemicelluloses is a polymer with a basic structure of $(C_5H_8O_4)_m$ and m as the degree of polymerization. The basic structure of cellulose can be denoted by $(C_6H_{10}O_5)_m$ [18,19]. The lipids have a different structure. These compound are esters derived from glycerol and fatty acids. The fatty acids composition depends on the kind of oilseed plant and structure can be generally represented by $C_nH_{(2n \pm s)}O_2$ where s is the number of insaturation. Therefore, in these compounds the carbon atoms make a number of different bonds with hydrogen and oxygen changing the energy produced by their combustion which depends on the number and type of molecule's chemical bonds [20,21]. Covalent bonds between carbon and hydrogen are energy-rich and it takes about 418 kJ to break 1 mol (6.023×10^{23}) of carbon–hydrogen (C–H) bonds [20,21].

Energy flows into the biological materials from the sun by the photosynthesis process in combination with water and carbon dioxide and produces complex organic molecules. Oxidation–reduction (red–ox) reactions are the base of this process. The energy, stored in chemical bonds of the sugars, may originate new bonds by several red–ox reactions. The reduction state of a molecule thus has a higher level of energy than in the oxidized state [21]. These different molecular conditions can be expressed by a carbon oxidation number: this is the charge that the atom would have if both the electrons in any bond are transferred to the more electronegative atoms [22]. In all organic molecules synthesized by photosynthesis process, the carbon has a lower oxidation number in comparison with the CO_2, which represents the maximum oxidation state [23]. The carbon atom reduces its oxidation number if it is linked to a less electronegative atom (as hydrogen) and increases it if linked to a more electronegative atom (as oxygen) [24]. Some theories prove the relationship between the organic molecule energy content and the carbon oxidation number [23].

The parameter that defines the energetic content of the materials is the GCV. It represents the absolute value of the specific energy of combustion for a unit of mass of solid biofuel burned in oxygen in a calorimetric bomb under the specified conditions [5]. In absence of calorimetric data, the GCV of a solid biomass may be estimated by several empirical mathematical relationships between GCV and parameters as elemental analysis, volatile matter, fixed carbon, ash content or lignin composition [1–3,7–9,11,25–27]. Some of these relationships are derived from coal [1]. Some other relationships were obtained on the base of biomass samples with a number lower than 50 [2,7–9]; often the data used to develop the models are collected by literature and not by direct experimental measurements [3,7,8,11,26]. For the latter condition, problems due to the low repeatability and reproducibility of the measurements may have affected the quality of the obtained relationships. Most of them show links of the GCV to carbon (C), hydrogen (H) and oxygen (O) contents. Some relationships concern the linkage between GCV and only the C content [4]. This kind of relationship is interesting for the central role that the carbon atom plays in organic molecules of the biomass and also in their energy content. However, the mathematical relationships proposed by literature don't take into account the aspects connected to the oxidation or reduction carbon atom state. In this work the relationship between GCV and carbon content has been analyzed considering the influence of average oxidation state of the carbon atom in the organic compounds. The study was conducted on a large number of solid and liquid biomass samples and the data were obtained only through analysis carried out in the same laboratory (Biomass Lab – D3A Department of Università Politecnica delle Marche, UNIVPM) adopting the same technical analytical standards and the same measurement systems. The work is part of a wider investigation that the UNIVPM's Biomass Lab is leading on the characteristics, properties and behavior of biomass for energy use.

3. Materials and methods

3.1. *Databases and analysis methods*

Two different databases were considered in this work: the database (DB_e) containing own data concerning measurements carried out by UNIVPM's Biomass Lab and used for developing the mathematical relationship for GCV prediction