Fuel 214 (2018) 640–646

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Optimal use of condensed parameters of ultimate analysis to predict the calorific value of biomass

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ARTICLE INFO

Keywords:
Biomass
Calorific value prediction
Elemental analysis
Ultimate analysis

ABSTRACT

Higher heating value (HHV) and lower heating value (LHV) of 39 biomass species that include woody samples, herbaceous materials, agricultural residues, juice pulps, nut shells, etc. were predicted based on elemental analysis results. Simple linear equations were developed in which C, H, N, S, and O contents exist and the prediction performance of these empirical equations was evaluated comparing the experimental and the predicted values of calorific values according to the criteria of mean absolute error (MAE), average absolute error (AAE), and average bias error (ABE). For this purpose, equations that include parameters changing from only C to sum of C, H, N, S, and O were tested to compare the prediction performance of each additional parameter. It was concluded that, the use of only two parameters including carbon and extra one element either nitrogen or oxygen is optimal to predict the calorific value. These condensed forms of ultimate analysis-based equations gave r^2 values changing in the range of 0.9219–0.9572. Improving effects of additional parameters are rather limited and the addition of H and S contents did not lead so significant improvement in prediction performance.

1. Introduction

Efficient use of biomass energy is of great interest since biomass is a sustainable and renewable energy resource and it includes every type of carbonaceous materials except fossil fuels [1]. In this context, various organic wastes such as agricultural and forestry residues, bagasse, MSW (municipal solid waste), RDF (refuse derived fuel), biosolids, industrial wastes, long grasses, barks etc. can be evaluated as alternative fuels provided that their energy potential is worth considering in energetic purposes [1]. In this context, sustainable use of biomass in power plants is of great concern and co-combustion systems that burn coal and biomass usually suffer from the variations of the biomass properties particularly in the calorific value [2]. It is troublesome to foresee the biomass characteristics without applying test procedures in case of waste biomass species that usually have complex structures and a number of constituents. In addition, herbaceous samples and waste materials may contain high contents of mineral matter (inorganics) that lead formation of high yields of ash and also their calorific values are usually very low [1]. For these reasons, the calorific value of such wastes is regarded as the most significant parameter that defines the fuel quality. The calorific value of biomass is directly measured by burning a specimen in a calorimeter under controlled conditions. On the other hand, estimation of the calorific value based on the chemical composition of biomass has also been in great demand when reliable analysis results are present. Macromolecular ingredients such as hemicellulose, cellulose, and lignin account for the most of the organic part of biomass while some others including starch, proteins, triglycerides, lipids, etc. also co-exist. Accordingly, some kinds of biomasses particularly woody ones are generally defined as lignocellulosic. On the other hand, although these macromolecular ingredients are consisted of three elements (C, H, and O), their molecular configurations are highly different in each case. Cellulose $(C_6H_{10}O_5)_n$ is the primary structural component in the cell wall, and it has long chain polymers with high degree of polymerization [1,3]. Hemicellulosics $(C_5H_8O_4)_n$, which are soluble in weak alkaline solutions, are complex polysaccharides that accompany cellulose in the cell walls, and xylan is the most abundant form of hemicellulosics [1]. Besides, lignin is a phenolic polymer that is the only aromatic ingredient in biomass [4]. Since these ingredients are connected with weak ether bonds, even moderate external effects like thermal/chemical treatments can easily disintegrate this unity. In addition, all of these ingredients are very rich in oxygen and hence the calorific value of biomass is not comparable with those of high rank coals that contain less oxygen content. The distribution of these macromolecular structures in biomass shows discrepancy depending on the type of material. That is, Kumar et al. [5] listed the breakdown of these ingredients for a number of biomass resources including grasses, straw, hardwoods, softwoods, nut shells, wastes, manure, etc. and concluded that the highest cellulose content is in paper (up to 99%), while the

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https://doi.org/10.1016/j.fuel.2017.10.082
Received 4 October 2016; Received in revised form 20 December 2016; Accepted 18 October 2017

Nomenclature

AAE	average absolute error
ANN	artificial neural network
ABE	average bias error
FC	fixed carbon
HHV	higher heating value
LHV	lower heating value
LSR	least squares regression
MAE	mean absolute error
MLR	multiple linear regression
MSW	municipal solid waste
OLS	ordinary least squares
RDF	refuse derived fuel
RMSD	root mean square deviation
VM	volatile matter

highest hemicellulose content is in leaves (up to 88%). This study also revealed that the highest lignin content is in nut shells (up to 40%), while Daud and Ali [6] reported even higher lignin content up to 53.4% in palm shell. For such reasons, calorific value estimations based on ultimate (elemental) analysis results are reasonable since this method does not depend on the source of macromolecules and only considers the contents of C, H, N, S, and O elements in biomass. In fact, this method has been applied to estimate the calorific value of coal for very long times. That is, Channiwala and Parikh [7] arranged chronologically the milestone investigations on higher heating value (HHV) estimations of coal based on proximate analysis (volatile matter, fixed carbon, and ash yields) and ultimate analysis (C, H, N, S, and O contents) results that dated back to Dulong Equation of 1880's. Unfortunately, in case of biomass, the presence of cellulose, hemicellulosics, lignin, proteins, lipids, extractives, tannins, etc. makes this prediction much more difficult and therefore rather sophisticated equations should be used for a safe prediction. However, the analysis of these compounds is time-consuming and requires specialized analysts, and furthermore the repeatability of these analytical experiments is not always high. In addition, some alternative parameters may also be considered in case of waste materials. In this context, Khan and Abu-Gharah [8] developed an equation to predict HHV of MSWs based on the primary combustible components such as paper, plastic, rubber, leather, and food.

There have been studies to predict the calorific value of biomass from analysis results. HHV (higher heating value) or LHV (lower heating value) of biomass were predicted using proximate analysis [9–13] and ultimate analysis results [7,9,10,14–18]. Motghare et al. [19] estimated HHVs by calculations based on proximate analysis and ultimate analysis of some waste biomass species and concluded that ultimate analysis suits well to some waste biomass species, while for others proximate analysis gave better results. Mainly four different methods including proximate analysis, ultimate analysis, physical/chemical composition, and ANN (artificial neural network) have been tested to predict HHV or LHV and the first two of which have commonly been applied [20]. HHV estimations can be performed based on MLR (multiple linear regression) models of analysis data and OLS (ordinary least squares) regression [9,14]. But, the main concern encountered for prediction of HHV is that the predicted values and the measured values may seriously differ from each other and the coefficients of determination (r^2) are unsatisfactorily low when full set of high number of biomass samples are considered. There exist examples of very low r^2 in many different papers where lignocellulosic materials were used [21–23]. Whereas r^2 values which are very near to 1 were reported when the predictions were repeated using coal samples [24,25]. Thus, the results of some studies indicate that samples grouped in the forms of subsets whose analysis results change in relatively narrow intervals may show more sensitive predictions [9]. In contrast, some studies also exhibit highly acceptable prediction performances. That is, Friedl et al. [14] tested the prediction of HHVs of 154 biomass samples considering linear and non-linear parameters of C, C^2, H, C × H and N and determined that r^2 was 0.943. However, consideration of high number of parameters in empirical equations makes the equations awkward and they become impractical. Therefore, these equations should be as concise as possible for convenient use.

In this paper, HHV and LHV predictions for full set of wide range of waste biomass samples were carried out using linear equations that contain various combinations of ultimate analysis parameters (C, H, N, S, and O) to decide how condensed forms of these equations are convenient to estimate the calorific value. Furthermore, the constant values in these linear equations were also taken into consideration as an independent parameter and the effects of presence or absence of these constants in estimation performance were interpreted. Likewise, many of the samples used in this study have not been investigated in calorific value estimation studies in literature yet. For example, fruit juice pulps, specific agricultural residues, stalks, stems, etc. are unusual materials investigated in the same study due to handling problems and easy decomposition.

2. Materials and methods

2.1. Biomass characterization

Thirty-nine different biomass species used in this study were provided either from companies operating in food/beverage industries in Turkey or collected from agricultural/forestry sector.

These samples were kept in open trays to get air-dried specimens and then the particle size was reduced to lower than 250 μm by milling and sieving. The proximate analysis was performed according to ASTM standards, while Leco TruSpec® CHN ultimate equipment with Leco TruSpec® S module was employed to perform the ultimate analysis. HHV was determined by IKA C2000 calorimeter from which LHV was calculated from HHV using the following simplified equation [26]:

$$LHV = HHV - \left[\left(\frac{18.015*H}{2}\right) + \%moisture\right]*5.85 \quad (1)$$

These characterization tests were repeated several times to assure the reproducibility of the data that repeatability for ultimate analysis results were within ± 0.5%, while it was up to ± 5% for calorific value determination.

2.2. Methodology

Four different criteria that include HHVs with and without constants and LHVs with and without constants were regarded for estimation of the heating values. For which, twenty-four equations were employed to the experimental data and Table 1 presents which parameters are included in these equations. (+) signs in Table 1 mean "Yes-this parameter is included", while (−) signs mean "No-this parameter is excluded". MAE (mean absolute error), AAE (average absolute error), ABE (average bias error), and RMSD (root mean square deviation) which are four different forms of estimation errors, were considered to compare the prediction performances. The formulas of these criteria for HHV are given below.

$$\mathrm{MAE} = \frac{1}{n}\sum_{i=1}^{n} |HHV_{(p)_i} - HHV_{(e)_i}| \quad (2)$$

$$\mathrm{AAE} = \frac{1}{n}\sum_{i=1}^{n} \left|\frac{HHV_{(p)_i} - HHV_{(e)_i}}{HHV_{(e)_i}}\right| \times 100 \quad (3)$$