Full Length Article

Prediction of carbon, hydrogen, and oxygen compositions of raw and torrefied biomass using proximate analysis

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Daya Ram Nhuchhen

Mechanical Engineering, Dalhousie University, Halifax, NS B3H 4R2, Canada

HIGHLIGHTS

- Examine if the existing correlation can be used to predict the elemental compositions of torrefied biomass.
- Analyze different forms of new correlations using data from raw and torrefied biomass.
- Validate the selected correlations with another set of published data.
- Compare the existing and selected new correlations.
- Only new correlations are applicable for torrefied biomass.

ARTICLE INFO

ABSTRACT

Elemental compositions of biomass are essential for designing energy conversion systems. Only a few correlations to estimate the elemental compositions using the proximate analysis of raw biomass have been published so far. Recently researches on biomass torrefaction have been increasing significantly, which require performing an elemental analysis of the torrefied biomass. Torrefaction affects both the proximate and elemental analyses of biomass. Therefore, this study examines if the existing correlations can be deployed or not for estimating carbon, hydrogen, and oxygen compositions of the torrefied biomass. For this, estimation errors were calculated for the existing correlations using data from the torrefied biomass. Results suggest that existing correlations were not suitable for predicting the elemental compositions of the torrefied biomass. New correlations were proposed using a wide range biomass, including both raw and torrefied biomass (447 samples). New correlations $C = -35.9972 + 0.7698VM + 1.3269FC + 0.3250ASH$, $H = 55.3678 - 0.4830VM - 0.5319FC - 0.5600ASH$, and $O = 223.6805 - 1.7226VM - 2.2296FC - 2.2463ASH$ were selected for future use. These correlations have the MAE of 2.58%, 0.41%, 2.60%, the AAE of 5.23%, 9.94%, 8.79%, the ABE of 0.45%, 2.82%, 2.01%, and the R^2 of 0.83, 0.70, 0.84 corresponding to the measured values of C, H, and O, respectively. The selected correlations were also validated and compared with the existing correlations using another set of data that includes raw, washed, torrefied, and carbonized biomass. Selected new correlations could be used for predicting carbon, hydrogen, and oxygen compositions in the raw and torrefied biomass, especially those biomasses which have negligible nitrogen and sulfur contents.

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1. Introduction

Biomass is widely available renewable energy resources with balanced CO_2 emissions and absorption. Physical, chemical and thermodynamic properties of biomass are essential parameters for designing any energy systems [1]. For instance, the higher heating value (HHV), which gives the energy content of biomass, is considered to be an important fuel parameter for a design of the combustion system [2]. The elemental compositions of biomass

are also necessary to analyze the overall process of any thermo-chemical conversion methods. The elemental compositions help to predict the flue gas flow rate, air requirement, and flue gas compositions in the combustion process. The experimental method of finding the elemental compositions is, however, costly and requires a sophisticated equipment [3]. It also needs highly skilled engineers or analysts [4–6]. Therefore, having proper correlations for predicting the major elemental compositions would always be an asset for a design engineer. However, only a few such studies [7–9] are available in the literature so far. While the correlation by Vakkilainen [9] is limited only to the black liquor, correlations by

Parikh et al. [7] and Shen et al. [8] are applicable for a wide range of biomass. The range of data points considered by Parikh et al. [7] for volatile matter, fixed carbon, ash, carbon, hydrogen and oxygen contents of biomass are 57.2–90.6%, 4.7–38.4%, 0.12–77.7%, 36.2–53.1%, 4.4–8.3%, and 31.4–49.5%, respectively, Shen et al. [8], on the other hand, have used the data points in the range of 57.2–90.6%, 9.2–32.8%, 0.1–24.6%, 36.2–53.1%, 4.7–6.6%, and 31.4–48.0% for *VM*, *FC*, *ASH*, *C*, *H*, and *O*, respectively. While Parikh and his co-workers neglected the effect of ash compositions on the elemental analysis, Shen and his colleagues discussed the importance of ash measurement and proposed new correlations including the ash compositions. Shen et al. [8] found correlations with a better prediction compared to those developed by Parikh et al. [7]. However, these correlations are purely based on raw biomass and some chars.

Recently, interest on biomass torrefaction because of its ability to improve heating values, hydrophobicity, grinadlbility, flowability and combustion characteristics of biomass have increased significantly. Studies have found that the torrefaction of biomass has changed components of both proximate and ultimate analyses. More on the effect of torrefaction on biomass and the technologies of torrefaction are reviewed in different papers [10–14]. Reported results suggest that torrefaction reduces volatile matter (*VM*) of biomass and increases fixed carbon and ash (*ASH*) contents per unit weight of the torrefied biomass. Reduction in volatile matter of the torrefied biomass is due to the solid mass loss contributed by the mild pyrolysis of hemicellulose, cellulose, and lignin during torrefaction process [15]. Decomposition of hemicellulose and depolymerization of cellulose and lignin compositions of biomass are two major reactions of the torrefaction process that release different light volatile gases including non-condensable gases (carbon dioxide, and carbon monoxide) and condensable gases (water, methanol, and carboxylic acids) [16]. As a result, it increases the fuel ratio, making biomass more comparable with the fuel ratio of coal (lignite) [17]. This then improves the flame stability [12] and reduces the burnout rate of biomass [18]. Due to the decomposition and depolymerization reactions that favor decarboxylation and deoxygenation of biomass [19], the torrefaction process increases the carbon content of biomass and reduces the hydrogen and oxygen contents. This is due to the removal of different light volatile gases that have high hydrogen and oxygen atoms. This then moves the biomass from the right-hand side of the Van-Krevelen diagram to the left side (towards the coal side) [20].

Considering the fact that there will be major changes in the proximate and ultimate analyses of the torrefied biomass. As these changes in the properties of biomass vary with the operating conditions of the torrefaction process, the existing correlations for raw biomass will not be able to incorporate the changes in the fuel properties of biomass after torrefaction. So, it would be worth noting that existing correlations will have large estimation error in predicting the elemental compositions of the torrefied biomass and new correlations have to be devised to address those changes in properties of biomass after torrefaction. New correlations that included a wider range of data than the existing correlations will have a better accuracy of prediction. Since such correlations are targeted mainly for those users of biomass in boilers who do not have all experimental facilities to test, a good correlation with less error only could help them to determine accurate controlling information for the operation of the boiler. It then helps to run a boiler smoothly, improving the reliability of the power plant operation. In addition to this, these new correlations could also be used to validate the experimental results from the elemental analyzer.

Though one may argue that the current expressions are valid for a wide range of biomass materials, hence such correlations can be useful to determine the elemental compositions of the torrefied biomass. This study, therefore, answers if the existing correlations

can predict the elemental compositions of torrefied biomass or not. This study used data presented by the author in his previous work, which verifies the HHV correlations. This work is divided into: (i) reviewing the published correlations to predict the elemental compositions of biomass using proximate analysis, (ii) examining if the currently available correlations can be used to predict the elemental compositions of the torrefied biomass or not, (iii) developing new forms of correlations using a large number of published data of the proximate of the raw and torrefied biomass, and (iv) validating and comparing the selected new correlations with the existing correlations using another set of data.

2. Methodology

The data points considered in this study are reviewed from different kinds of the published literature and are reported in supplementary file (Table S1 [21–50] and Table S2 [2,21–47,51–64]). Table S1 shows how proximate and ultimate analyses were changed at different operating conditions after the torrefaction process compared those data with the raw biomass presented in Table S2. One can note that ranges of *VM*, *FC*, *ASH*, *C*, *H*, and *O* of raw biomass materials are 47.70–93.60%, 0.67–36.10%, 0.01–48.70%, 19.12–56.30%, 2.00–7.36%, and 25.18–49.50%, respectively. Corresponding components of the proximate and ultimate analyses of torrefied biomass materials are 13.30–88.57%, 11.25–82.74%, 0.08–47.62%, 35.08–86.28%, 0.53–7.46%, and 4.31–44.70%, respectively. This information clearly tells that the ranges of the proximate and ultimate analyses were varied significantly after torrefaction process. For example, the minimum value of volatile matter is reduced to 13.30% whereas the carbon content is increased to 88.57%. This confirms that new scheme has to be developed with the new range of data including torrefied biomass. The collected data are in wt.% dry basis. Some data, which are, other than in dry basis originally in the published literature, were also converted into the dry basis. Though the collected data points have nitrogen and sulfur contents, they are very small compared to the carbon, hydrogen, and oxygen contents. Therefore, the author focuses mainly on the finding the correlations only for carbon, hydrogen, and oxygen. One may, however, argue that the oxygen content can be obtained by difference method (by subtracting *C*, *H*, *N*, *S*, and *ASH* compositions from 100%) and does not require correlation. But, having correlation for oxygen content will avoid the necessity of nitrogen and sulfur contents and assist in validating the oxygen content if the difference method was to be adopted to find the oxygen content.

Before validating the existing correlations, three major compositions of raw and torrefied biomass were plotted with different components of the proximate analysis. These plots analyze the distribution of the elemental compositions (mainly carbon, hydrogen, and oxygen contents) with the proximate analysis.

In order to validate if the existing correlations can be used or not, existing correlations were used to predict the elemental compositions of the torrefied biomass (Presented in Table S1). The deviation between the predicted and measured values was examined by calculating the estimation errors.

Tables S1 and S2 were then merged to determine new correlations using the principle of the least sum square error in the Microsoft Excel. Different forms of the new correlations were selected from the correlations presented in Parikh et al. [7] and Shen et al. [8] for analysis purpose. Some more additional forms of possible correlations were also analyzed. Estimation errors for the existing correlations were also calculated using both raw and torrefied biomass to determine their suitability in a wider range of biomass types.