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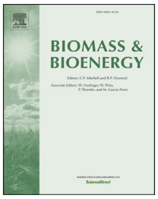

Research paper

Biochar characterization and a method for estimating biochar quality from proximate analysis results

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A R T I C L E I N F O

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Biochar has gained significant interest in the literature, mainly for its ability to improve soil quality and sequester carbon. This work investigated if results from proximate analysis could be used to assess the quality of the biochar. Normally, ultimate analysis results are used for this purpose. A large set of data was collected from literature and various mathematical correlation were investigated to determine if quality parameters such as carbon mass fraction and H/C and O/C mol ratios could be estimated from proximate analysis results. It was determined that the mass fraction of carbon in the biochar could be correlated to the mass fractions of volatile matter (VM), fixed carbon (FC), and ash (ASH) by the relationship $C = 0.474 \times VM + 0.963 \times FC + 0.067 \times ASH$. The mass fraction of oxygen in biochar could also be correlated to VM, FC, and ASH, while hydrogen was best correlated to a relationship with VM, FC, and VM/FC. Atomic ratios, such as H/C and O/C, used for biochar classification by international standards and carbon sequestration potential, were best correlated to VM/FC by the expressions $H/C = 0.379 \times VM/FC + 0.251$ and $O/C = 0.188 \times VM/FC + 0.035$. The developed correlations were proven to accurately classify biochar when the biochar had been made at ≥400 °C.

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1. Introduction

Developing correlations between simplified and complex techniques for biochar characterization would be beneficial because simplified techniques, such as proximate analysis, can be carried out by with less sophisticated equipment and at lower cost [1,2]; however, it is the results of the complex techniques, such as ultimate analysis, that generally are used to determine the quality of the biochar.

The International Biochar Initiative (IBI) proposed three general classes of biochar determined by the organic carbon content [3,4]. Biochar with a C_{org} mass fraction of $\geq 60\%$ would be of Class 1, biochar with $30\% \leq C_{org} < 60\%$ would be of Class 2, and biochar with and $10\% \leq C_{org} < 30\%$ would be of Class 3. Materials with $C_{org} < 10\%$ or with an H/C ratio of >0.7 mol mol^{-1} would not be classified as biochar. The IBI did not directly address the stability of biochar carbon other than to state that the H/C_{org} mol ratio should be used to determine carbon stability. They argued that the H/C_{org} ratio is preferred over the O/C_{org} mol ratio because H is determined experimentally, while O is a value often estimated from the difference of the content of other major components [3]. The European Biochar Foundation (EBF) has also developed its biochar classifications [5]. According to EBF, the carbon mass fraction must exceed 50% (on a dry basis) and the H/C_{org} ratio must be <0.7 mol mol^{-1}. In concurrence with the IBI, EBF state that H/C_{org} measurement are preferred over O/C_{org} measurements and, while the O/C_{org} ratio should be <0.4 mol mol^{-1}, the carbon content together with the H/C_{org} ratio is sufficient to classify the material as a biochar. Biochars with carbon mass fractions <50% are referred to as bio-carbon-minerals by the EBF. In addition to IBI and EBF, a variety of research groups [6–10] have linked carbon stability (when biochar is added to soil) to biochar carbon content and atomic ratios (mainly O/C).

The H/C and O/C mol ratios, have been shown to correlate fairly well with mass fraction of VM from biochar proximate analysis on a dry or dry ash-free basis [6,7,11]. The same ratios (H/C, O/C) have also been correlated to mass fraction of FC [6,12]. These correlations for H/C and O/C as functions of VM and FM can be described as:

$$Z/C = a_{ZC} \times VM + b_{ZC} \tag{1}$$

$$Z/C = a_{ZC} \times VM/(VM + FC) + b_{ZC} \tag{2}$$

$$Z/C = a_{ZC} \times FC + b_{ZC}\ , \tag{3}$$

where Z represents H and O. The constants a_{ZC} and b_{ZC} are specific

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to the individual Z/C ratios (H/C and O/C).

Correlation between elemental composition (C, H, and O) and proximate analysis results for un-charred biomass was investigated by Parikh et al. [13] as a method to estimate the energy values of materials, which at the time were often correlated to elemental composition [14]. With over 200 data points, they concluded that mass fractions of C, H, and O in biomass could be calculated with absolute error limits of <5% from the proximate analysis results [13]. The best correlation was in the form of

$$X = a_X \times VM + b_X \times FC\,, \tag{4}$$

where X represent mass fraction in biomass of C, H, and O with the element-specific constants a_X and b_X. This equation is interesting because it implies that dry biomass exists as two organic fractions, VM and FC, and that these organic fractions have fixed mol compositions of $C_{6.00}H_{9.74}O_{4.71}$ and $C_{6.00}H_{5.84}O_{2.15}$, respectively. These are similar to cellulose and lignin compositions ($C_{6.00}H_{10.0}O_{5.00}$ and $C_{6.00}H_{6.96}O_{2.09}$) [15].

Elemental composition has also been correlated to proximate analysis results for coals [16]. In this case, the ash content was found important and the best correlation was in form of

$$X = a_X \times VM + b_X \times FC + c_X \times ASH\,. \tag{5}$$

As the above correlations for coal and biomass did not focus on biochars, these correlations may not fit or may have to be modified for better fit biochar materials. Thus, the objectives of this work were tri-fold.

1. Develop correlations for biochar, allowing elemental composition and H/C and O/C ratios to be estimated from proximate analysis results.
2. Investigate if the correlations could be used for classification of biochar, as defined by IBI and EBF.
3. Use the correlations to relate proximate analysis results to carbon stability, as defined by others, for sequestration purposes.

2. Material and methods

2.1. Data sources

Literature data for biochar were collected and tabulated. In most cases, the original source was used as reference; however, a secondary source was used if the original source was not available. A total of 207 data points from 15 sources were collected [2,6,7,11,14,17–27]. The distinction between C_{org} and C_{tot} is important, since both the IBI and EBF use C_{org} in their qualifying ratios. However, only limited data were available for both C_{org} and C_{tot} in biochar and, considering that most of the biochars data exist for the latter, only C_{tot} was considered here. It should be noted that Enders et al. [11] provided C_{tot} and C_{org} data for a wide range of biochars and concluded that C_{tot} and C_{org} from woody and grass feedstocks were nearly the same but differences were noted when a high degree of ash was present (e.g., for poultry manure and paper mill waste).

The quality of the data was not questioned when selecting the data sources. In five of the sources [6,11,23,25,26], duplicate or triplicate results were evident for either proximate or ultimate analysis. The characterization methods were slightly different but proximate analysis appeared to either directly follow American Society for Testing Materials (ASTM) International methods or similar approaches using a thermogravimetric-based process or equipment. Modifications to standard methods were listed in one case [11], but that appeared more influenced by equipment capability and not by criticism of ASTM methods. ASTM methods for ultimate analysis were quoted by fewer than half of the sources used. More often, a specific instrument for elemental analysis was listed and appeared based on dry combustion techniques. All data were recalculated, as needed, on an ash-containing dry basis. All data have been included in the Appendix. When mol compositions (molecular formulas) are listed in this work, all were based on six carbons for easy comparison with cellulose ($C_6H_{10}O_5$). These molecular formulas should not be taken as steric configurations.

2.2. Correlations and calculations

Several types of correlations between proximate analysis results and mol ratios (H/C and O/C) and CHO composition were investigated. These are described in Table 1 and in the Appendix. All parameters (constants) in the correlations were determined by the method of multiple variables least squares regression [28] using a robust technique.

The robust regression technique is similar to linear regression (i.e., ordinary least squares regression). Ordinary least squares (OLS) regression determines parameters by minimizing the following expression:

$$\sum (\varepsilon_i)^2 = \sum (Y_i - y_i)^2 \ (i = 1 \text{ to } N),$$

where Y_i is the measured value of y (for the i:th data point) and y_i is the predicted value which is calculated by the sought correlating equation (e.g., $y = a \times X + b$). The difference between Y_i and y_i is called the residual error, ε_i. For example, consider Equation (4)—ordinary least square regression for multiple variables determines the parameters a_C and b_C by minimizing

$$\sum [C_i - (a_C \times VM_i + b_C \times FC_i)]^2 \ (i = 1 \text{ to } 207),$$

where C, VM, and FC are expressed as mass fractions. The parameters a_C and b_C are easily computed through matrix algebra. There are several criteria which must be met when using OLS; e.g., that the errors (ε) are normally distributed and have equal variances. Residual errors were graphically inspected and suspected outliers were visible and the data also failed the normality test using the Shapiro-Wilk method [29] as expanded by Royston [30] (see Appendix).

As OLS regression was not found to be an appropriate regression technique, a robust (or weighted) regression technique was used. Robust least squares (RLS) regression is a mathematical process by which the importance of a data point is quantified by a calculated weight. Thus, the method to determine the parameters is revised to minimize the expression.

$$\sum w_i \times (\varepsilon_i)^2 = \sum w_i \times (Y_i - y_i)^2 \ (i = 1 \text{ to } N),$$

or in the specific case of Equation (4) for carbon,

$$\sum w_i \times [C_i - (a_C \times VM_i + b_C \times FC_i)]^2 (i = 1 \text{ to } 207).$$

There are several techniques to calculate the weights ($0 \le w_i \le 1$) but most are based on the size of the residual error (ε_i) for an individual data point and how it compares to the errors of the other data points [31–33]. The weights in this manuscript were calculated via the Tukey biweight technique [31,33]. For the purpose of this manuscript, an iterative process was used by which an initial OLS regression was performed, which allowed initial ε_i values to be calculated. It was followed by data trimming and another OLS regression. This resulted in second set of ε_i values, which in turn