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

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Abstract

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 correlations 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.

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 $10\% \leq C_{org} < 30\%$ would be of Class 3. Materials with $C_{org} < 10\%$ or with an H/C ratio of $> 0.7 \text{ mol mol}^{-1}$ 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 $< 0.7 \text{ mol mol}^{-1}$. 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 $< 0.4 \text{ mol mol}^{-1}$, 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:

$$Z/C = a_{ZC} \times VM + b_{ZC} \quad (1)$$

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

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

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

$$X = a_X \times VM + b_X \times FC \quad , \quad (4)$$

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

$$X = a_X \times VM + b_X \times FC + c_X \times ASH \quad . \quad (5)$$

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 biochar C_{org} and C_{tot} 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.

TABLE 1 HERE

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:

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

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

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

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

$$\Sigma w_i \times (\varepsilon_i)^2 = \Sigma w_i \times (Y_i - y_i)^2 \quad (i = 1 \text{ to } N), \text{ or in the specific case of Equation (4) for carbon,}$$

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

There are several techniques to calculate the weights ($0 \leq w_i \leq 1$) 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 allowed the initial w_i values to be calculated. The initial w_i values allowed for RLS regression and generated further revised values of ε_i and w_i . Each subsequent iteration resulted in an improved fit. Further information can be found in the Appendix.

Regardless of which correlation was investigated, the goodness of fit between the measured data and the predicted data was calculated. To this end, the weighted (robust) correlation coefficient (r^2), the absolute error (AE), and root mean square error (RMSE) were calculated for each correlation by the following expressions:

$$r^2 = 1 - \frac{\sum [w_i \times (Y_i - y_i)^2]}{\sum [w_i \times (Y_i - Y_{\text{avg}})^2]} ,$$

$$\text{AE (\%)} = \frac{[\sum (|Y_i - y_i| / Y_i)]}{N} , \text{ and}$$

$$\text{RMSE} = [\sum (Y_i - y_i)^2 / N]^{-0.5} \quad (i = 1 \text{ to } N).$$

3. Results

A wide variety of compositions were noted in the biochars. The carbon mass fraction (from elemental analysis) ranged from 19.2 to 93.1 % (on dry basis) and the H/C and O/C mol ratios ranged from 0.06 to 1.80 and 0 to 0.95, respectively. The ash mass fraction ranged from 0.3 to 59.1 %. Based on the IBI and EBF definitions of biochar [3-5], 134 and 154 of the 207 materials would be classified as biochar by EBF and IBI, respectively (using the measured mass fraction of total carbon and H/C and O/C mol ratios); however, nothing was gained by considering O/C ratio in the case of EBF classification. As previously mentioned, EBF uses a more stringent criterion for the biochar carbon mass fraction than IBI and 20 of the materials classified as biochar by the IBI would be classified as bio-carbon minerals by EBF. The collected biochar characterization data have been plotted in a Van Krevelen diagram in Fig. 1. The solid circles below the IBI and EBF limit line (of $\text{H/C} < 0.7 \text{ mol mol}^{-1}$) correspond to the 20 materials

that would be classified as bio-carbon minerals by EBF but as biochars by IBI. Six of the materials had relatively low mass fractions of carbon (<50 %) and high O/C ratio (lower right quadrant in Fig. 1). The data for these six materials came from the same study [11] and had very high ash content. While the IBI allows biochar with carbon mass fractions of <50 %, the higher O/C ratio in these materials would raise questions about their classification as biochar. A similar diagram was provided by Crombie et al. [6] and confirms that biochars created under mild pyrolysis conditions do not meet biochar standards. The solid line in Fig. 1 is the result of RLS regression and can be described by the following expression:

$$H/C = 2.281 \times O/C + 0.151 \quad (r^2 = 0.873). \quad (6)$$

The dashed circle in Fig. 1 corresponds to average biomass composition according to Parikh et al. [13] with a 95 % confidence interval (*t*-statistics). An alternative method for depicting biochar composition is by ternary mol composition diagram [24] (see Appendix).

FIGURE 1 HERE

3.1. Correlation of H/C and O/C mol ratios to proximate analysis results

When correlations between H/C and O/C and proximate analysis results (VM, FC and ASH) were evaluated, the correlations with the highest robust correlation coefficients were as follows (Fig. 2):

$$H/C = 0.397 \times VM/FC + 0.251 \quad (r^2 = 0.725) \quad (7)$$

$$O/C = 0.188 \times VM/FC + 0.035 \quad (r^2 = 0.857) \quad (8)$$

FIGURE 2 HERE

Other correlations for H/C and O/C mol ratios are shown in the Appendix together with errors. As an alternative to directly correlate H/C and O/C to VM and FC; individual C, H, and O

composition may be correlated to VM, FC, and ASH [Equations (4), (4A), (4B), (4C) and (5)] before creating the mol ratios.

3.2. *Correlation of C, H, and O mass fractions to proximate analysis results*

The measured and predicted mass fractions of C, H, and O, using the relationships that resulted in highest correlation coefficients, are shown in Fig. 3. As is noted, the correlation coefficient for carbon was quite good ($r^2=0.94$); however, lesser correlations were noted for hydrogen and oxygen, where greater scatter existed.

FIGURE 3 HERE

The correlations in Fig. 3 are listed below and other correlations (and graphs) are provided in the Appendix,

$$C = 0.474 \times VM + 0.963 \times FC + 0.067 \times ASH \quad (r^2 = 0.936) \quad (9)$$

$$H = 0.074 \times VM + 0.012 \times FC - 0.052 \times VM/FC \quad (r^2 = 0.687) \quad (10)$$

$$O = 0.469 \times VM + 0.010 \times FC - 0.069 \times ASH \quad (r^2 = 0.837) \quad (11)$$

3.3. *Classification of biochars using proximate analysis results*

Using the relationships above [Equations (7)–(11)] and others (see Table 1 and Appendix), the carbon mass fraction and the H/C mol ratio were calculated from the proximate analysis results (VM, FC, and ASH) and the information was used to classify the reviewed biochars. This method was compared with the classification based on ultimate (CHO) analysis results. The best results are shown in Table 2.

TABLE 2 HERE

As noted, one of the better techniques (Line 1, Table 2) resulted in 27 false positives (FP = prediction identified the material as biochar, while the ultimate analysis did not) and 13 false negative (FN = prediction did not identify material as biochar, while the ultimate analysis did) in the case of IBI's classification scheme. When compared with EBF's classification scheme, the best technique gave 26 false positive and 9 false negative classifications.

4.0 Discussions

The data in Fig. 1 can be compared with theoretical and practical pyrolysis results. It is well known that pyrolysis gas predominantly consists of CO, CO₂, H₂, CH₄, and others [34] and Antal and Grønli [35] showed that the theoretical pyrolysis decomposition of cellulose resulted in gases that have the combined molecular formula of C_{6.00}H_{25.7}O_{13.3}. The same reference [35] also refers to an earlier experimental estimation study, where pyrolysis of cellulose resulted in mass loss with a combined molecular formula of C_{6.00}H_{18.7}O_{12.0} and that pyrolysis of wood resulted in mass loss with a combined molecular formula of C_{6.00}H_{15.0}O_{8.33}. Other researchers [36-38] have proposed a two-phased loss system, where dry biomass undergoes dehydration (loss of H₂O) followed by aromatization (apparent loss of H₅O) [37]. Assuming that the loss mainly occurs from the volatile matter, the loss of these compounds from an average biomass material can be displayed (as colored arrows) in the Van Krevelen diagram (Fig. 4). Of the above predictive losses from literature, the dehydration reaction (loss of H₂O) and loss of C_{6.00}H_{25.7}O_{13.3} from the VM fraction of the biomass closely describe the experimental data, represented by the solid line (see Figs. 1 and 4). Calculated, the solid line (in Figs. 1 and 4) represents an apparent loss of H_{2.28}O_{1.00} [see Equation (6)]. The arrowheads in Fig. 4 represent the atomic composition

where at least one of the elements (C, H, or O) is exhausted from the biomass VM mass fraction by the loss of the compounds indicated in the legend (see Appendix for calculation details).

FIGURE 4 HERE

The assumption that pyrolysis mainly alters the biomass VM fraction, consisting mainly of cellulose and hemicellulose, is not unreasonable. Shafizadeh and Sekiguchi [39] measured the aromatic structures created during pyrolysis of cellulose and concluded that a maximum of 2.5 % of cellulose carbon was converted into aromatic carbon structures and the rest was volatilized. Keiluweit et al. [21] proposed a pyrolysis decomposition scheme for plant-derived biochar depending on charring intensity (pyrolysis temperature); this scheme suggested that the masses of non-volatile matter (FC) and ash are constant and independent of pyrolysis conditions; only VM is impacted (through mass loss) by pyrolysis. As a consequence, the mass ratio of FC and ASH should not be impacted by pyrolysis temperature. To test this assumption, the FC/ASH ratio was plotted as a function of pyrolysis temperature (Fig. 5) for the data reviewed and when sufficient data were available (i.e., where pyrolysis temperature was varied in a suite of tests).

FIGURE 5 HERE

The dashed lines in Fig. 5 correspond to trends that are not statistically significant ($p=0.95$, t -statistics), while the two solid lines correspond to trends that are statistically significant. As noted, significant scatter existed for materials with low ash content (i.e., high FC/ASH ratio). For the cases where the FC/ASH ratios were less than 10, the trends were flat indicating that the absolute masses of FC and ash (or at least the FC/ASH mass ratios) in the biochars were unaffected by pyrolysis temperature.

4.1. *Correlation of H/C and O/C to proximate analysis results*

Previous researchers have correlated H/C and O/C to VM, FC, or VM/(VM+FC) [6, 7, 11, 12]. Here, better correlations (i.e., higher robust r^2) with VM/FC were found [Equations (7) and (8)]; however, other correlations were superior when considering regression parameters such as absolute error (AE) or RMSE (see Appendix). The correlations with the lowest AE were based on VM, while the lowest RMSE were found in correlations with VM, in the case of H/C, and with VM/(VM+FC), in the case of O/C.

4.2. *Correlation of C, H, and O mass fractions to proximate analysis results*

Carbon, H, and O mass fractions has been correlated to proximate analysis results for biomass and coal [13, 16]. When applied (with parameters for biomass and coal), these correlations failed to estimate C, H, and O mass fractions in biochar (see Appendix). In terms of robust r^2 , the C and O mass fractions in biochar were best correlated to VM, FC, and ASH by the same type of correlation [Equation (5) in Table 1 and Equations (9) and (11)] previously found accurate for coals [16] but with different parameter values. Hydrogen, H, was best correlated to a more complex expression with VM, FC and VM/FC [Equation (4B) in Table 1 and Equation (10)] but this was only slightly better than the correlation type developed for coals [Equation (5)]. The correlation type, previously used for biomass [Equation (4)], resulted in a fit with correlation coefficients of 0.93, 0.63, and 0.80 for C, H, and O, respectively. Equation (4) provides some benefit as it allows us to estimate the molecular formulas of the VM and FC fractions in the biochar, just as in the case of biomass (see Introduction). Based on Equation (4), the molecular formula of VM was calculated to be $C_{6.00}H_{9.77 \pm 1.52}O_{3.98 \pm 1.18}$. Statistically, this composition is the same as VM in biomass ($C_{6.00}H_{9.74}O_{4.71}$) and in cellulose ($C_{6.00}H_{10.0}O_{5.00}$). Based on Equation (4), the molecular formula of FC was calculated to be $C_{6.00}H_{1.06 \pm 1.37}O_{0.04 \pm 10.3}$,

which is statistically not the same as FC in biomass ($C_{6.00}H_{5.84}O_{2.15}$) and indicate an enrichment of the carbon fraction in FC. This implies that mass loss from the FC fraction also occurs during slow pyrolysis. For that to take place and keep the FC/ASH mass ratio constant, an approximately equal mass of VM would need to be converted into FC. The formation of aromatic structures in chars from cellulose has been investigated as a function of pyrolysis temperature [39] and it showed that the composition changed from a theoretical $C_{6.00}H_{10.0}O_{5.00}$ of untreated cellulose to $C_{6.00}H_{10.4}O_{5.00}$ (virtually unchanged) at 300 °C, to $C_{6.00}H_{4.40}O_{1.10}$ at 400 °C, and to $C_{6.00}H_{3.20}O_{0.90}$ at 500 °C. Thus, the scheme represented in Fig. 6 may be an appropriate characterization of biomass pyrolysis. As suggested in the figure, some of the VM content in biomass may be measured as VM in the biochar, while some of the VM in biomass may be measured as FC in the biochar because the pyrolysis caused this change, while a third portion of VM in the biomass is volatilized in the pyrolysis process. While the figure shows biomass-to-biochar conversion, it could also represent conversion of a low-temperature biochar to a higher-temperature biochar.

FIGURE 6 HERE

4.3. *Classification of biochars*

When attempting to classify the biochar per IBI and EBF standards using the developed correlations, it resulted in approximate 35–40 incorrect classifications (Line 1, Table 2). While these error rates may sound high, a review of the specific errors yielded important considerations. For example, when considering the IBI carbon mass fraction requirement (>10 %), the method of determining mass fraction [Equation (9)] never failed. When considering the EBF carbon mass fraction requirement (>50 %), the method of determining carbon mass fraction

[Equation (9)] only failed three times. Two of these were for cow manure biochars (700 °C pyrolysis temperature) and the third was a rice hull biochar (350 °C pyrolysis temperature). Thus, most of the misclassifications were due to error in the estimation of the H/C ratio by Equation (7). This is not surprising as the correlation and error rate for this equation was worse than for the C correlation [Equation (9)]. Interestingly, in all but four cases, the misclassified materials (40 for IBI and 35 for EBF) were pyrolyzed at 300–450 °C and the majority of those (34 out of 36 for IBI and 30 out of 31 for EBF) were pyrolyzed at 300–400 °C. Two of the four biochars that were misclassified and pyrolyzed at >450 °C were a coconut shell biochar and an eucalyptus wood char [14] where the validity of the proximate analysis results is questionable (i.e., unreasonable high VM values for these pyrolysis temperatures and considered severe outliers in RLS regression). The remaining two misclassified biochars by Equation (7) were poultry manure/sawdust blend biochars pyrolyzed at 500–550 °C. Taking into account the pyrolysis temperature and the questionable literature data for two biochars, only five biochars pyrolyzed at ≥ 400 °C were misclassified as EBF biochars and only eight biochars pyrolyzed at ≥ 400 °C were misclassified as IBI biochars. (These have been bolded (EBF) and underlined (IBI) in the Appendix data table.) Thus, it can be concluded that the best developed correlations, can be used to classify biochars with very low error rates as long as the pyrolysis temperature is ≥ 400 °C. The method was tested on 8 biochars created at 600 °C from a variety of raw materials [8] and on 18 biochars created at 450–650 °C from pine wood chips, wheat straw, and wheat straw pellets [40]; all, but one, of these biochars were correctly classified as EBF and IBI biochar using the developed relationships.

The lack of fit for the chars pyrolyzed below 400 °C is not unexpected. This pyrolysis temperature range is where significant compositional changes occur and it is where biomass

charring begins or charring is very slow [35]. The thermal degradation of hemicellulose occurs at 200–260 °C, cellulose at 240–350 °C, and lignin at 275–500 °C [41]. Shafizadeh and Sekiguchi [39] reported that aromatic structures and significant changes in the H/C ratio occur during cellulose charring between 350–400 °C. According to that study, only 2.5 % of the carbons in cellulose ends up in the aromatic structure of char and this occurs around 400 °C, after which no more carbon is lost and carbon densification occurs by additional loss of H and O. The same increase in aromatic carbon groups, at the expense of other functional groups, was also observed in pyrolysis of grass and wood at 400 °C [21]. When all is considered, it raises the question whether or not material pyrolyzed below 400 °C is a fully charred material or if it should be considered a transitional material, like others have proposed [21]. Shafizadeh and Sekiguchi use the term “stable” to describe chars created above 400 °C [39]. Pyrolysis temperature is not the only aspect to consider—pyrolysis time is also important; for example, the aromaticity during pyrolysis of sawdust at 400 °C has shown to change significantly when the pyrolysis time increased from 0.5 to 4 to 8 h [42], again suggesting a transitional state when short pyrolysis times are used. Thus, depending on the biomass source and the pyrolysis conditions, these transitional materials may be closer in composition to a biomass while others may be closer in composition to a char. The correlations that are appropriate for biochars are not expected to work on transitional materials in all cases.

4.4. Predicting carbon stability from proximate analysis results

As mentioned in the Introduction, atomic ratios (mainly O/C) have been used to estimate C stability. Spokas [7] found a relationship between the O/C ratio and biochar half-life and qualitatively stated that for biochar with an O/C ratio of $<0.2 \text{ mol mol}^{-1}$, the half-life would be

>1000 y. For an O/C ratio of between 0.2–0.6 mol mol⁻¹, the half live would be between 100–1000 y and for an O/C ratio >0.6 mol mol⁻¹, the half-life would be <100 y. In the current investigation, good correlation between the O/C mol ratio and VM/FC mass ratio existed in the form of Equation (8). According to this, a VM/FC ratio of <0.88 g g⁻¹ would predict a biochar with a half-life of more than 1000 y. Likewise, a VM/FC ratio of >0.88 g g⁻¹ and <3.0 g g⁻¹ would reflect an O/C ratio >0.2 mol mol⁻¹ and <0.6 mol mol⁻¹ and predict a biochar with a half-life between 100 and 1000 y. The O/C ratio has also been correlated to carbon stability by the Edinburgh stability tool [6], which is based on chemical oxidation by hydrogen peroxide and estimates what fraction of biochar carbon is predicted to be stable. Using their data, the following robust correlation was derived:

$$\text{Stable C mass fraction} = 1.00 - 2.24 \times \text{O/C} \quad (r^2 = 0.713), \quad (15)$$

where O/C can be estimated from Equation (8) to yield

$$\text{Stable C mass fraction} = 0.921 - 0.422 \times \text{VM/FC} \quad (16)$$

A recalcitrance potential (R₅₀) for biochar has been proposed by some researchers as a measure of biochar carbon stability [8-10]. It has been shown that this property (or measurement) correlates very well with ash-free carbon mass fraction (C_{afb}) through a linear relationship [9].

Using their data, the following robust correlation was derived:

$$R_{50} = 0.170 \times C_{afb} + 0.00479 \quad (r^2 = 0.881), \quad (17)$$

where Equation (9) together with the known ash mass fraction of the biochar from the proximate analysis can be used to estimate C_{afb}, for a final correlation of

$$R_{50} = 170 \times (0.474 \times \text{VM} + 0.963 \times \text{FC} + 0.067 \times \text{ASH}) / (100 - \text{ASH}) + 0.00479 \quad (18)$$

Based on the R_{50} value, Zhao et al. [10] proposed that the carbon sequestration potential (CS) could be used to estimate the mass fraction of carbon in the biochar feedstock that would be recalcitrant when the biochar was added to soil. The CS was defined as

$$CS = (\text{biochar yield, g/g}) \times C_{BC} \times R_{50} / C_F, \quad (19)$$

where C_{BC} and C_F is the mass fractions of carbon in the biochar (BC) and feedstock (F), respectively. These values can be estimated from feedstock and biochar proximate analyses results by the Parikh et al. relationship [13] and Equation (9), again showing the usefulness of the developed correlations.

In a comprehensive review of the stability (or persistence) of biochar in soil, Lehmann et al. [43] suggested two relationship [Equations (20) and (21)] to correlate either the mean residence time (MRT expressed in years) or the mass fraction of carbon that would remain after 100 y (BC_{+100}) to the H/C_{org} mol ratio.

$$MRT = 4501 \times e^{-3.2 \times (H/C_{org})} \quad (20)$$

$$BC_{+100} = 1.05 - 0.616 \times H/C_{org} \quad (21)$$

The H/C mol ratio was found to be well correlated to the mass ratio VM/FC through Equation (7). Provided that the assumption of $C_{org} \sim C_{tot}$ holds, we can arrive to the following expressions:

$$MRT = 4501 \times e^{-1.3 \times VM/FC - 0.80} \quad \text{and} \quad (22)$$

$$BC_{+100} = 0.895 - 0.245 \times VM/FC \quad . \quad (23)$$

However, the authors point out that the methods [Equations (20) and (21)] are not sufficient for accurate prediction, possibly due to local variability in soil conditions [43]. They also advocate more complex models of carbon stability based on pools of carbons, which have different stability functions and propose that, at least, a two-pool system should be considered, representing pools of less persistent carbon and more persistent carbon. It is tempting to link

these pools to the VM and FC fractions in the biochar but no attempt to study this appears to have been made.

Finally, the H/C mol ratio and FC/C mass ratio has been used to predict aromaticity [44], which in turn has been mentioned as important aspects of carbon stability in biochar [43]. As we have shown, both these quantities are either directly available from proximate analysis or predictable from the correlations developed herein.

5. Conclusions

In conclusion, it was estimated that the atomic composition of the volatile mass fraction of biochar (VM) was very similar to its composition in biomass, but that the fixed carbon (FC) fraction of biochar was enriched in carbon compared to the biomass. The mass loss during pyrolysis was estimated to come from a loss of volatiles (gas and condensable) with an overall apparent composition of $\text{H}_{2.28}\text{O}_{1.00}$ (not including carbon). It was shown that correlations could be developed between simplified and complex techniques for biochar characterization; i.e., proximate analysis results (VM, FC, and ASH) could be used in lieu of ultimate analysis results through various correlations. Specifically,

- H/C and O/C mol ratios correlated best with the VM/FC mass fraction ratio,
- C and O mass fractions correlated best with mass fractions of VM, FC, and ASH, and
- H mass fraction correlated best with VM, FC, and VM/FC.

It was shown that proximate analysis results, together with the above correlations, could be used to classify biochar with low error rates as long as the pyrolysis temperature was ≥ 400 °C. It was also shown that proximate analysis results could be incorporated to predict biochar stability as defined by several methods.

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Mention of trade names, stability indices, or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

Appendix. Supplementary data and information

Supplementary data and information associated with this article can be found, in the online version, at.....

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Table 1. Correlations investigated to use proximate analysis results to other biochar characterization properties. Note that Z/C (as in H/C and O/C) are always mol ratios, while X (as in C, H, or O) and VM, FC, and ASH are expressed as mass fractions.

Eq.	Correlation	Explanation	Reference
(1)	$Z/C = a_{ZC} \times VM + b_{ZC}$ with Z=H or O	Tested with biochar	Crombie et al. [6]; Spokas [7]; Enders et al. [11]
(2)	$Z/C = a_{ZC} \times VM / (VM + FC) + b_{ZC}$	Tested with biochar	Crombie et al. [6]; Enders et al. [11]
(2A)	$Z/C = a_{ZC} \times VM / FC + b_{ZC}$		
(3)	$Z/C = a_{ZC} \times FC + b_{ZC}$	Tested with biochar	Crombie et al. [6]; Ronsse et al. [12]
(4)	$X = a_X \times VM + b_X \times FC$ with X=C, H, or O	Tested with biomass	Parikh et al. [13]
(4A)	#(4) with $b_X = b'_X + c_X / VM$	Tested with biomass	Parikh et al. [13]
(4B)	#(4) with $a_X = a'_X + c_X / FC$		
(4C) ¹	#(4) with $b_X = b'_X + c_X \times FC / (VM + FC)$		
(5) ¹	$X = a_X \times VM + b_X \times FC + c_X \times ASH$	Tested with coal	Krishnaiah et al. [16]

¹See online Appendix for additional forms of the correlations.

Table 2. The accuracy of selected correlation to represent carbon mass fraction and H/C mol ratio of biochar as functions of proximate analysis results and how efficient they for biochar classification. (FP=false positive; FN=false negative)

	Biochars classified by IBI standards (n=207)	Biochars classified by EBF standards (n=207)
C by Eq. (9), H/C by Eq. (7)	40 wrong (27FP, 13FN)	35 wrong (26FP, 9FN)
C by Eq. (9), H/C by Eq. (1)	43 wrong (26FP, 17FN)	39 wrong (23FP, 16FN)
C by Eq. (9), H by Eq. (10)	45 wrong (25FP, 20FN)	39 wrong (24FP, 15FN)
C by Eq. (9), H by Eq. (4C)	48 wrong (25FP, 23FN)	39 wrong (24FP, 15FN)
C by Eq. (9), H by Eq. (5)	47 wrong (26FP, 21FN)	37 wrong (24FP, 13FN)
C and H by Eq. (4)	44 wrong (27FP, 17FN)	34 wrong (25FP, 9FN)
C and H by Eq. (4A)	44 wrong (27FP, 17FN)	34 wrong (25FP, 9FN)
C and H by Eq. (4B)	42 wrong (25FP, 17FN)	35 wrong (23FP, 12FN)

Fig. 1. Van Krevelen diagram constructed from literature biochar data (tabulated in the Appendix). Average biomass composition from Parikh et al. [13].

Fig. 2. The best (highest robust r^2) correlations [Equations (7) and (8)] to estimated H/C and O/C mol ratios from proximate analysis results. Some outliers are outside the scale.

Fig. 3. The best (highest robust r^2) correlations for predicting C, H, and O mass fractions of biochar from proximate analysis results using Equations (9)–(11).

Fig. 4. Predicted data trends representing mass loss by different mechanisms from an average biomass. The solid line is the same line as shown in Fig. 1.

Fig. 5. Fixed carbon-ash mass ratio (FC/ASH) as a function of pyrolysis temperature for selective biochars.

Fig. 6. A simplistic approach to understanding changes occurring in biomass during charring.