Immediate measurement of fuel characteristics of bio-char using NIRS

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Abstract. Low temperature pyrolysis is effective to improve the fuel quality of wheat straw and corn stover. To determine the pyrolysis condition and fully utilizing the solid product (bio-char), the fuel characteristics of the bio-char should be measured. It costs a lot of time and money to finish all the measurement, which really retards the development of the biomass industry. This study is supposed to immediately predict the proximate analysis parameters, ultimate analysis parameters and heat value of sixty-five bio-char using NIRS. The results show the fuel characteristics of the bio-char vary in a very big range. The NIRS models can predict the VM, FC, ash, HHV, oxygen, carbon, hydrogen contents of the bio-char accurately. The $R_c$ and $R_{cv}^2$ value are all bigger than 0.92 and the RPD are bigger than 3.59. The NIRS models can also tell the high or low content of moisture and nitrogen. Only for the sulphur, more work need to do to improve the accuracy of the NIRS models. Predicting the fuel characteristic of the bio-char only by scanning the NIR spectrum, which costs only 10 seconds, will really be helpful for the biomass industry.

1. Introduction

Biomass is with high moisture content, low energy density and high oxygen content, which makes it more difficult and expensive to use than fossil fuel [1-2]. Thermochemical treatment can improve the quality of biomass and make it a better solid fuel. Du et al reported the fuel properties of biomass after thermochemical treatment are even better than the coal with high volatile [3]. The solid product after thermochemical treatment is called bio-char, which is a kind of enrichment of carbon atoms. What’s more, the fuel characteristics of bio-char is related to the thermochemical operating conditions [1]. To determine the proper operating conditions, the fuel characteristics, such as industrial analysis, element analysis, heat value of the bio-char are needed. It costs a lot time and money to get the data using traditional methods. Along with the thermochemical treatment, the bonds- C-H, O-H, C-O changed [2]. The information of C-H, O-H, C-O bonds have absorption in the near infrared (NIR) spectra. What’s more, the NIR spectra contains more chemical and physical information of the sample [4], which makes is potential to realize the prediction of the fuel characteristics of bio-char using NIRS.
In this study, the fuel characteristics of sixty-five bio-char from different thermochemical treatment - thirteen different final temperature (from 200 to 500 °C, 25 °C temperature of a point), two different heating rate (10 K/min and 20 K/min) and two nitrogen purging rate (100 ml/min and 200 ml/min) - were predicted using NIRS.

2. Materials and methods

2.1. Biomass samples
Wheat straw (WS) and corn stover (CS) were used in this study, which were collected from China's Shandong province in 2013. After collection, the sample were milled to pass the 250μm sieve. The chemical composition, industrial composition, element composition and heat value of the sample were shown as table 1.

| Sample/% | Cellulose | Semi-cellulose | Lignin | WSC | Moisture | VM | Ash |
|----------|-----------|----------------|--------|-----|----------|----|-----|
| WS       | 41.49     | 20.54          | 19.14  | 0.98| 3.35     | 70.75| 7.49|
| CS       | 37.41     | 14.98          | 21.58  | 6.55| 2.60     | 74.19| 6.04|

| Sample/% | FC | C  | H   | N   | S  | Heat Value (MJ/Kg) |
|----------|----|----|-----|-----|----|-------------------|
| WS       | 18.41 | 43.50 | 5.81 | 0.63 | 0.48 | 42.10            |
| CS       | 17.17 | 44.19 | 5.28 | 0.79 | 0.25 | 43.45            |

2.2. Bio-char preparation experiment and the calculation of the fuel characteristics
The bio-char was prepared using the tube furnace. According to the existing research [3, 5], a total of thirteen ending temperature (200-500 °C, per 25 °C), two heating rate (10 and 20 °C/min) and two nitrogen purging flow (100 and 200 ml/min) were chosen for the preparation, resulting in sixty-five bio-char samples.

The proximate analysis parameters are measured using thermal gravimetric analyser (TGA) from TA(USA) according to other researchers’ method [6]. First, heat the furnace from room temperature to 105°C at heating rate of 10°C/min, hold for 40 min in nitrogen. The mass loss in this period is supposed to be the moisture. Second, heat the furnace from 105°C to 900°C at a heating rate of 10°C/min, hold for 20 min in nitrogen. The mass loss in this period is supposed to be the volatile matter (VM). Third, change the purge gas to be air, burn the furnace at 900°C and hold for 30 min. The mass loss in this period is supposed to be the fix carbon (FC). The remaining weight is ash.

The ultimate analysis parameters are measured using the elemental analyser from Elementar (Germany) according to ASTM E777 -08, AOAC Official Method 990.03 protein (crude) in Animal Feed and ISO351. The content of oxygen is calculated according to the formula: O%=100%-C%-H%-N%-S%.

The high heat value (HHV) is calculated using the formula [7]: HHV = 3.55C2 - 232C - 2230H+ 51.2C×H+ 131N+ 20 600.

All the measurements are repeated two times.

2.3. NIRS spectra collection and establishment of NIRS prediction model
Spectrum 400(PerkinElmer, USA) was used to collect the spectra (Figure 1). Sample cup (diameter = 1.5cm, height = 1cm) is put on the window of the integrating sphere. The cup will be filled up with sample and made flat with a blade. And it will spin when collect the spectra. Spectra of samples were collected in diffuse reflection mode in the range of 10 000-4 000 cm$^{-1}$ at a resolution of 8 cm$^{-1}$. Internal reference was used for the spectrometer. Each spectrum is the average of 30 scans. Each sample was measured in triplicate and the results were averaged. The average spectrum would be used as final spectrum.
All NIR models were developed using PLS toolbox based on the MATLAB R2008a software (Math works Corporation, USA). Firstly, spectra were pretreated by autoscale, First derivative or Second derivative, smoothing (Sav-Gol), SNV or MSC respectively or some group of them. Then using original or pretreated spectra, a partial least squares (PLS) regression was calculated to determine the quantitative relation between the spectral variable and the straw analysis characteristics.

The best model was chosen according to $R_c$, RMSEC, $R_{cv}$ and RMSECV. The accuracy of the model was evaluated by $R$, RMSEC, RMSECV, RSD and RPD. The RPD statistic compares the RMSEP with the range of the calibration parameter measured as, the standard deviation (SD) of the values obtained in the reference analysis [8]. The RSD is calculated as $\text{RMSEP} \times 100\% / \text{Mean}_v$. The RSD is the index of the accuracy of the prediction of the models.

3. Results and discussion

3.1. NIRS spectra of all bio-char samples

Figure 2a shows fourteen spectra of original and biochar samples of wheat straw, used to discuss the influence of different termination temperatures on the NIRS spectra of biochar. According to figure 2a, there are significant differences in NIRS spectra of bio-char at different termination temperatures, mainly including the following four significant changes:

1. The absorbance value increases sharply along with the increase of the final temperature. The main reason is the colour of the sample deepened along with the increase of final temperature, which results in the increase of the absorbance.

2. The peaks of 6600-7100, 5400-6200 and 4500-5000 cm$^{-1}$ weaken gradually along with the increase of the final temperature and disappear at 300 °C, which are mainly comes from stretching vibration of N-H, O-H, C-H, S-H and C=O bonds in cellulose, water and protein in the straw.

3. The peak at 4600 cm$^{-1}$ gradually forms after 300 °C, which is the information of the stretching vibration of C-H and C=O bonds from produced aldehyde.

4. The peaks of 5000-5400 and 4200-4400 cm$^{-1}$ weaken gradually along with the increase of the final temperature and disappear at 425 °C, which are mainly comes from stretching vibration of C=O, O-H, N-H and C-H bonds from cellulose, starch and carboxylic acid compounds in the straw.

The PCA calculation results of the spectra were shown as figure 2b. Seen from the temperature, the distribution is a symmetrical u-shape. For the PC2 scores, it decreases and then increases with the increase of the temperature. The turning point is at 325 °C. While for the PC3, it increases and then decreases with the increase of the temperature. The turning point is at 275 °C. All these information reflect the different chemical composition and physical state of biochar after different terminal temperature treatment.
3.2. Prediction results of the NIRS models

The proximate analysis parameters were shown as table 2. The moisture of bio-char is very low, with the average content of 2.76%. The contents of VM and FC have a very broad range, with a gap bigger than 60% and 50%, respectively. The maximum HHV of bio-char is 24.33MJ/Kg, which is even higher than some coal.

The statistical data of the best model are shown as table 2. Considering all statistical data, the NIRS models can predict the fixed carbon, ash content, HHV and volatile matter accurately. The $R_c^2$ and $R_{cv}^2$ values are all bigger than 0.94 and the RPDs are bigger than 4.25. The prediction model are based on the information of the NIR spectra contains, which was discussed earlier. However, for the prediction of moisture, the model can only tell the high or low contents. More work is needed to improve the accuracy.

![Figure 2. NIRS spectra and the PCA distribution of bio-char.](image)

### Table 2. Prediction results of the proximate analysis parameters and HHV using NIRS.

| Proximate analysis parameters/% | Moisture | VM | FC | Ash | HHV (MJ/Kg) |
|-------------------------------|---------|----|----|-----|-------------|
| Number of the sample          | 66      | 67 | 67 | 65  | 63          |
| Min.                          | 0.51    | 18.08 | 17.17 | 6.04 | 17.29      |
| Max.                          | 6.13    | 79.52 | 68.41 | 26.88 | 24.33      |
| Mean                          | 2.76    | 43.07 | 45.10 | 17.87 | 21.34      |
| SD                            | 1.19    | 19.69 | 16.41 | 6.07  | 1.90       |
| CV                            | 43.21   | 45.72 | 36.38 | 33.95 | 8.92       |
| PLS Components                | 4       | 5   | 5  | 4   | 4           |
| Pretreatment                  | Autoscale | Autoscale | Autoscale | Autoscale | Autoscale |
| $R_c^2$                       | 0.72    | 0.98 | 0.97 | 0.96 | 0.96       |
| $R_{cv}^2$                    | 0.67    | 0.98 | 0.96 | 0.95 | 0.94       |
| RMSEC                         | 0.59    | 2.60 | 3.05 | 1.25 | 0.37       |
| RMSECV                        | 0.64    | 3.02 | 3.43 | 1.33 | 0.45       |
| RSD                           | 23.22   | 7.01 | 7.61 | 7.44 | 2.10       |
| RPD                           | 1.86    | 6.52 | 4.78 | 4.56 | 4.25       |

The ultimate analysis parameters were shown as table 3. The carbon content of bio-char increases from 43.50% to 68.60%, which is more than some coal [3].

The statistical data of the best model are shown as table 3. According to the data, the NIRS model can predict the oxygen content perfectly. The $R_c$ and $R_{cv}$ values are all bigger than 0.99 and the RPDs are bigger than 11. For the prediction of carbon and hydrogen content, the NIRS models can predict them accurately. The $R_c$ and $R_{cv}$ values are all bigger than 0.92 and the RPDs are bigger than 3.59. The NIR spectra contain a lot of information of the C-H, O-H, C-O and C=O bonds, which is the basis
of the prediction. For the prediction of the content of nitrogen, the NIRS model can only tell the high or low contents. Unfortunately, the NIRS model cannot predict the sulphur content. Because there is not much information of sulphur in the NIR spectra. And the content of sulphur is really low.

| Ultimate analysis parameters/% | C     | O     | H     | N     | S     |
|--------------------------------|-------|-------|-------|-------|-------|
| Number of the sample           | 67    | 67    | 65    | 67    | 66    |
| Min.                           | 43.50 | 5.97  | 1.71  | 0.63  | 0.25  |
| Max.                           | 68.60 | 43.45 | 5.81  | 1.36  | 1.18  |
| Mean                           | 57.41 | 19.54 | 3.32  | 1.11  | 0.74  |
| SD                             | 6.78  | 11.41 | 1.05  | 0.18  | 0.22  |
| CV                             | 11.81 | 58.38 | 31.71 | 15.95 | 29.69 |
| PLS Components                 |       |       |       |       |       |
| Pretreatment                   | Autoscale | Autoscale | Autoscale | SNV,Autoscale | Autoscale |
| Rc$^2$                         | 0.94  | 0.99  | 0.93  | 0.84  | 0.42  |
| Rcv$^2$                        | 0.92  | 0.99  | 0.92  | 0.76  | 0.33  |
| RMSEC                          | 1.66  | 0.95  | 0.27  | 0.06  | 0.17  |
| RMSECV                         | 1.89  | 1.04  | 0.27  | 0.08  | 0.18  |
| RSD                            | 3.29  | 5.31  | 8.18  | 7.02  | 23.95 |
| RPD                            | 3.59  | 11.00 | 3.88  | 2.27  | 1.24  |

4. Conclusion
This study is supposed to immediately predict the fuel characteristics of sixty-five bio-char using NIRS. The results show the fuel characteristics of the bio-char vary in a very big range. The NIRS models can predict the VM, FC, ash, HHV, oxygen, carbon, hydrogen contents of the bio-char accurately. The Rc and Rcv$^2$ value are all bigger than 0.92 and the RPD are bigger than 3.59. The NIRS models can also tell the high or low content of moisture and nitrogen. Only for the sulphur, more work need to do to improve the accuracy of the NIRS models. Predicting the fuel characteristic of the bio-char only by scanning the NIR spectrum, which costs only 10 seconds, will really be helpful for the biomass industry.

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References
[1] H Abdullah, D Mourant, CZ Li ; H Wu. Energy Fuels, 2010, 24: 5669-5676.
[2] T A. Lestander, M Rudolfsson. Green Chem., 2014, 16: 4906-4913.
[3] S Du, W Chen, J A Lucas. Bioresource Technol., 2014, 161: 333-339.
[4] B. Sander, J. J. Wagner, M. Jakob, L. Jane, E. S. Balling. Ind. Crop. Prod., 2010, 31(2): 321-326.
[5] S W Park, C H Jang, K R Baek, J K Yang. Energy, 2012, 45: 676-685.
[6] D. Medic, M. Darr, A. Shah, B. Potter, J. Zimmerman. Fuel, 2012, 91: 147-154.
[7] P McNamee, L I Darvell, J M Jones. Biomass Bioenergy, 2015, 5: 1-10.
[8] C Lomborg, J B Holm-Nielsen, P Oleskowicz-Popiel, K. H. Esbensen. Bioresource Technol., 2009, 100(5): 1711-1719.