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Predicting the heating value of solid manure with visible and near-infrared spectroscopy

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HIGHLIGHTS

- Spectral models predicted feedlot manure HHV within 1.7% with excellent reliability.
- Estimated N and S corrections to HHV reduced spectral prediction by 0.1%.
- VisNIR-DRS models reliably predicted HHV_{daf} based on proximate data within 1.8%.
- Manure-specific HHV_{daf} equations from ultimate data may improve spectral prediction.

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ABSTRACT

Visible and near-infrared spectral data were used to predict the higher heating value (HHV) and dry, ash-free HHV (HHV_{daf}) of solid manure samples collected from cattle fed diets containing wet distillers grains plus solubles (WDGS) in 0%, 15%, 30%, 45%, and 60% dry matter concentrations. The HHV was determined by isoperibol bomb calorimetry and the HHV_{daf} was calculated from an equation based on the HHV and proximate analysis. Spectral models were developed in "The Unscrambler" software. The spectral models based on all treatments with random samples withheld for validation predicted the HHV with excellent reliability within 1.7%; RMSD = 60.19 cal g^{-1} (108 Btu lb^{-1}), RPD = 2.29 (excellent), and bias = −15.29 cal g^{-1} (28 Btu lb^{-1}), using five PLS factors and identifying 129 important wavebands. Accounting for estimated N and S content reduced the predictive accuracy of the spectral models by 0.1% with an RPD = 2.28 (excellent). Spectral models based on all treatments with random samples withheld for validation predicted the HHV_{daf} with acceptable reliability within 2.0% with an RMSD = 96.17 cal g^{-1} (173 Btu lb^{-1}), RPD = 1.17 (acceptable), and bias = −19.83 cal g^{-1} (−37 Btu lb^{-1}), using five PLS (partial least squares) factors and identifying 29 important wavebands. Spectral models reliably predicted the HHV of feedlot manure with accuracy well under the 5% error margin tolerated in practical applications such as feedlot manure gasification.

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1. Introduction

In the context of fuel energy, manure can be partitioned into combustible and noncombustible fractions. The noncombustible fraction contains ash and moisture which are known as the *proximate data* [1]. Ash and moisture are the primary determinants of the higher heating value (HHV) of manure, which is a measure of the gross chemical potential energy per unit of mass (cal g^{-1}, Btu lb^{-1}, or kJ g^{-1}). In previous work, we successfully predicted ash and moisture in unprocessed samples of solid cattle manure using VisNIR-DRS within 4% (db) and 3% (wb) by weight, respectively [2,3], but we do not know if VisNIR-DRS can successfully predict the combustible fraction, known as the HHV_{daf}.

The combustible fraction of manure is volatile matter comprised of complex carbohydrates, proteins, trace organic compounds, and fats, containing primarily C, H, O, N, and S. These five elements are known as *ultimate data* and are determined by *ultimate analysis* [1]. When wet distillers grains with solubles (WDGS) is incorporated in beef cattle diets, the manure-S concentration [4–6] increases linearly with WDGS inclusion rate (% DM)

Abbreviations: db, dry basis; DM, dietary dry matter; HHV, higher heating value; HHV_{daf}, dry, ash-free higher heating value; PLS, partial least squares; RMSD, root mean squared deviation; RPD, ratio of standard error of prediction to the root mean squared deviation; VisNIR-DRS, visible, near-infrared diffuse reflectance spectroscopy; wb, wet basis; WDGS, wet distillers grains with solubles.

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and may affect the HHV_{daf} of the manure. Similarly, WDGS is often higher in N than the feedstuffs it displaces in beef cattle diets [7–10]. Excess dietary N and S are excreted by cattle [11–14]. The composition of WDGS varies with the grain source, processing method, neutral detergent fiber, and ratio of wet grains to solubles [15,16]. We have shown that the inclusion of WDGS in varying proportions in cattle rations had little effect on the prediction by VisNIR-DRS of the noncombustible fraction of manure [6], but we do not know if the inclusion of WDGS in cattle diets affects the ability of VisNIR-DRS to predict the HHV and HHV_{daf} of manure.

The objectives of this study were to (1) determine the potential of VisNIR-DRS to predict the HHV of solid cattle manure using proximate data and (2) determine the effect of accounting for estimated S and N in the samples on the prediction accuracy of the VisNIR-DRS models.

2. Materials and methods

2.1. Sample collection and gravimetric analyses

We obtained 120 samples of solid cattle manure collected for a companion study [6] from beef cattle (*Bos taurus*) fed diets formulated with WDGS included at 0%, 15%, 30%, 45%, and 60% of dry matter (DM). The samples were sealed in identical plastic bags and preserved at -12 °C.

The samples were brought to room temperature and subsamples taken for gravimetric analyses of moisture and ash. The moisture content on a wet basis (% wb) was calculated for each treatment from three measurements of each subsample according to a procedure recommended for manure analysis [17]. The same subsamples were prepared according to ASTM Standard E1757-01 [18] for crude ash analysis by dry oxidation according to ASTM Standard E5865-11a [19]. Ash determination was conducted in an ashing furnace (Model F-A1730, Argo Thermodyne Co., Bangalore, India) with procedural enhancements as described in [2]. The ash content on a dry matter basis (% db) was calculated from three measurements of each subsample.

2.2. Calorimetric procedures

The HHV and HHV_{daf} values were calculated in the companion study [6] with and without HNO_3 and H_2SO_4 corrections based on the N and S fractions of the manure. An H_2SO_4 correction of 13.75 cal g^{-1} (24.75 Btu lb^{-1}) for every 1.0% S was calculated based on the heat of formation of H_2SO_4 from SO_2. This is consistent with the correction of 14 cal g^{-1} (25.2 Btu lb^{-1}) recommended by the instrument manufacturer.

A standard HNO_3 correction of 8 cal g^{-1} was automatically applied by the bomb calorimeter to account for N_2 contained in the bomb atmosphere, but this did not account for N contained within the sample material. Unlike H_2SO_4 corrections, HNO_3 corrections for N in sample material vary depending on the type of matter and on the proportions of various molecules in which N is found in the sample [20–22]. We applied an additional HNO_3 correction of 4.93 cal g^{-1} (8.87 Btu lb^{-1}) for every 1.0% N in the sample based on the heat of formation of HNO_3 from N_2. There is no standardized HNO_3 correction for manure samples, but this is a reasonable value based on those determined for cellulosic materials such as livestock feeds and bovine fecal matter [17,18].

Both HNO_3 and H_2SO_4 corrections were based on bulk mean N and S concentrations measured from treatment-wide composite samples, not the unique N and S content of the individual samples. Although current ASTM, ISO, and other standardized methods differ in their treatment of determining acid corrections, all require the titration of bomb washings [10–12]. Schroeder [22] emphasized that although sample-specific acid corrections by titration are most desirable, "average" corrections are preferred over no corrections. Titration data from bomb washings were not available in this study.

In the companion study [6], the HHV_{daf} values were calculated from the observed moisture, ash, and corrected HHV of each manure sample using the following equation:

$$HHV_{daf} = \frac{HHV}{(1-A)(1-M)} \quad (1)$$

in which HHV_{daf} is the dry, ash-free higher heating value (cal g^{-1}), HHV is the measured higher heating value corrected for N and S content (cal g^{-1}), A is the ash content (% db), and M is the moisture content (% wb).

2.3. Spectral analyses

A Field-Spec 3 spectrometer fitted with a hand-held probe (AgriSpec, ASD Inc., Boulder, CO) was used to measure reflectance of each manure sample in wavebands from 350 to 2500 nm with spectral resolutions of 3 nm at 700 nm and 10 nm at 1400 and 2100 nm. The probe featured a spot size of 10 mm and an internal halogen light source with a color temperature of 2901 ± 10 K. Reflectance was set to 100% with a Spectralon white reference panel placed inside a plastic bag identical to those containing the manure samples. The samples were scanned three times through their plastic bags, and the instrument calibration was verified after every twenty samples.

Prior to analysis by VisNIR-DRS, the samples had settled resulting in an accumulation of finer particles on the underside of the bags. When predicting moisture and ash content in previous studies, we determined that scans of unprocessed manure produced superior models than scans of dried or milled manure [2], and scans of the coarse, unsettled manure in bags strongly outperformed models built from scans of the fine, settled particles [3]. Therefore, we scanned the manure on the coarse side of each sample bag at three separate, non-overlapping locations.

2.4. Spectral data processing

The raw spectral data were processed using custom statistical computing code written in R [23] (R Foundation for Statistical Computing, Vienna, Austria) following the procedures of Brown et al. [24] as described in Sakirkin et al. [25]. Spectral models based on the first derivative of the raw reflectance predominate in published literature; however, some researchers have reported better prediction accuracy with models based on the second derivative because it effectively removes the confounding effects of particle size [26,27]. The first derivative of the raw reflectance with respect to wavelength ($\partial r/\partial \lambda$) was used in all models because we have found it to be consistently superior in predicting manure characteristics [2,3] when compared to the raw spectra and the second derivative of the raw spectra.

2.5. Model development

Partial least squares (PLS) regression models were developed in "The Unscrambler" software [28] to predict the HHV_{daf} of the samples. The models were built on mean-centered data using a segmented cross-validation PLS method and were validated with a test-set holdout. The segments for cross-validation were chosen randomly and comprised four percent of the calibration dataset. The Unscrambler uses a standard, non-linear, iterative PLS algorithm and can be allowed to determine automatically the number of factors to include in each PLS model by minimizing the residual variance of the calibration cross-validation. We permitted the

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software to choose the optimal number of PLS factors, but we verified that the number was reasonable by inspecting the model performance statistics. If over-fitting or other errors occurred we set the number of PLS factors manually by choosing the optimal number based on the residual variances of the early components. The RMSD (root mean squared deviation), RPD (ratio of prediction to standard deviation), bias, and number of PLS factors were considered in the evaluation and comparison of model performance. Suitable RPD limits for soils are appropriate for use with manure and are suggested to be: <1.6, poor; 1.6–2.0 acceptable; and >2.0, excellent [29].

To investigate the spectral difference between dietary treatments, six different VisNIR-DRS models were created and used to predict HHV and HHV_{daf}. In the first model, eight-tenths of all samples were randomly selected as a calibration set ($n = 96$) and the remaining samples used as a validation set ($n = 24$). In the remaining five models, each dietary treatment was held out of the calibration set ($n = 96$) in turn and then used as a validation set ($n = 24$), which gave a conservative estimate of prediction accuracy. We chose eight-tenths of the samples, as opposed to an arbitrary two-thirds, in the first model to eliminate any effect resulting from differences in calibration and validation set sizes.

To investigate the spectral similarity among dietary treatments, convex hull biplots of the first two principal components of the first derivatives were created for each treatment using the R programming environment. Islam et al. [30] found that a convex hull biplot of the first two principal components based on spectral data provides a simple and rapid method for visually assessing the differences and similarities among groups of samples. The distribution of the samples on the plot, in terms of area and proximity, indicates the relative degree of variability and spectral similarity among the samples. These characterizations can be extended to the combined effects of physical and chemical properties, which are well predicted by UV, visible, and IR spectra. Principal component decomposition of the first derivative spectra and convex hull calculations were performed in R.

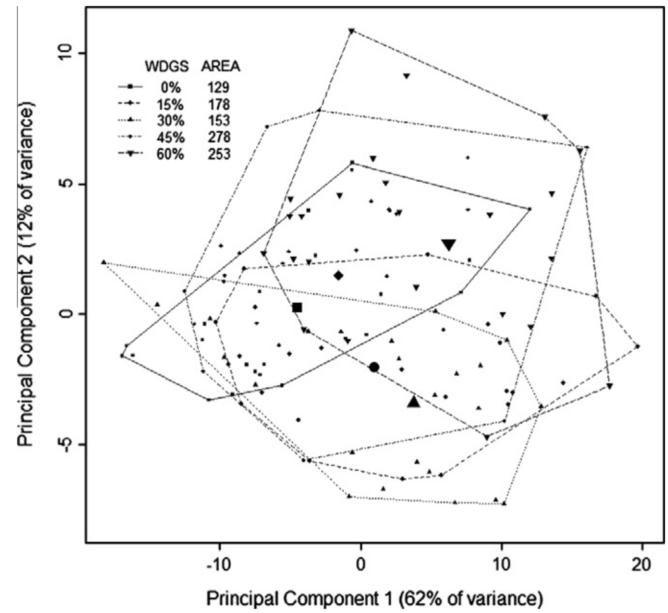

Fig. 1. Convex hull biplots of the first two principal components of the VisNIR spectra from manure samples, grouped by the inclusion level of WDGS (wet distillers grains plus solubles) included in the finishing cattle diets. The large symbols denote the weighted geometric centroid of each respective polygon.

3. Results and discussion

The HHV of the samples ranged from 3303.9 to 3601.5 cal g^{-1} (5947–6483 Btu lb^{-1}), and the HHV_{daf} ranged from 4742.7 to 4899.6 cal g^{-1} (8537–8819 Btu·lb^{-1}). The fuel value of this manure was within the expected range for manure collected from pens with paved surfaces [25]. Descriptive statistics for the moisture (% wb) and ash (% db) content, the observed HHV uncorrected for N and S content, the observed HHV corrected for N and S content, and the HHV_{daf} calculated using Eq. (1) from the corrected HHV are presented in Table 3. Detailed results were reported in the companion study [6].

Convex hull biplots based on spectra of the samples (Fig. 1) confirmed that in general, the treatments are spectrally similar. The first and second principal components used in the biplots represented 57% and 82% of the spectral variation. Each treatment hull was largely coextensive with the others, indicating shared physical and chemical characteristics sensitive to detection by VisNIR-DRS. The hulls associated with the 45% and 60% WGDS samples had a larger area than the other rations indicating a greater degree of spectral variability. Conversely, the 60% WDGS hull contained the largest amount of non-intersecting area and featured a centroid with greater displacement relative to the origin than the other treatments, indicating unique spectral features which may result from differences in manure composition.

The software successfully chose the optimal number of PLS factors ranged from three to five for most models which. However, it failed to do so in two HHV_{daf} models. It chose double the number of PLS factors in the HHV_{daf} models based on 15% and 45% WDGS when compared to the other HHV and HHV_{daf} models. Further, the 15% and 45% WDGS models had much higher RMSD and lower RPD values when compared to others, and the software did not identify any significant wavebands for the 45% WDGS model indicating an error. We inspected the residual variances for the early principal components of these two models and chose five as a more reasonable number of PLS factors for both. We recreated the 15% and 45% WDGS models using five PLS factors which eliminated the significant waveband error and produced results consistent with those of the other HHV and HHV_{daf} models.

Historically, a dry, ash-free fuel value of 4722 cal g^{-1} (8500 Btu lb^{-1}) has been accepted for use in Eq. (1) [1,31]. An RMSD value of 100 cal g^{-1} (180 Btu lb^{-1}) is approximately equivalent to an error of 2% of this value. This error is well below the 10% engineering factor of safety used in gasifier design and is acceptable in practical terms for use in industrial applications [32]. The VisNIR-DRS spectral models based on calorimetry data uncorrected for estimated S and N content predicted HHV within 1.7%. When the HNO_3 and H_2SO_4 corrections were applied, the model predicted HHV within 1.8%. The model based on all treatments with random samples withheld from calibration for validation predicted the HHV uncorrected for N and S with the following results: RMSD = 60.19 cal g^{-1} (108 Btu lb^{-1}), RPD = 2.29 (excellent), and bias = −15.29 cal g^{-1} (28 Btu lb^{-1}), using five PLS factors and identifying 129 important wavebands[1] (Table 1). Fig. 2 presents a plot of the regression coefficients over wavelength (nm) of this particular model. The number of important wavebands used in each of the six models ranged from 113 to 156, with 133 common important wavebands among three or more models. Wavebands common among three or more models were 360–380, 400–580, 600, 620, 680, 690, 770–980, 1020–1050, 118, 1210–1320, 1390, 1400, 1420–1510, 1540–1640, 1660–1710, 1730–1780, 1820–1870,

[1] Important wavelengths are determined by The Unscrambler software which identifies variables with the largest positive or smallest negative value. Variables with large factor loadings (coefficients) in early components have the most variation and explain the greatest proportion of the difference between samples.

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Table 1
Visible near-infrared spectral models predicting HHV uncorrected for N and S content and HHV corrected for N and S content based on manure samples cattle fed steam-flaked corn-based diets with increasing amounts of wet distillers grains plus solubles (WDGSs). In the first model, eight-tenths of all samples were selected as a calibration set ($n = 96$), and the remaining were used as a validation set ($n = 24$). In the remaining models, each ration was held out of the calibration set ($n = 96$) in turn and was then used as a validation set ($n = 24$).

Ration (% WDGS) Validation set	ALL Random	0 Ration	15 Ration	30 Ration	45 Ration	60 Ration
HHV (nitric and sulfuric acid correction not applied)						
RMSD cal g^{-1} (Btu lb^{-1})	60.19 (108.3)	72.05 (129.7)	57.12 (102.8)	99.20 (178.6)	54.43 (98.0)	94.63 (170.3)
RPD	2.29	1.73	1.49	0.60	1.71	1.22
Bias cal g^{-1} (Btu lb^{-1})	−15.29 (−27.5)	27.50 (49.5)	−36.08 (64.9)	−85.58 (154.0)	−13.38 (24.1)	74.08 (133.3)
Important wavebands (count)	129	168	155	153	161	157
PLS factors	5	4	5	3	4	3
HHV (nitric and sulfuric acid correction applied)						
RMSD cal g^{-1} (Btu lb^{-1})	62.14 (111.9)	70.07 (126.1)	56.32 (101.4)	59.32 (106.8)	54.94 (98.9)	75.51 (135.9)
RPD	2.28	1.78	1.52	1.01	1.72	1.53
Bias cal g^{-1} (Btu lb^{-1})	−14.88 (−26.8)	21.21 (38.2)	−33.08 (59.5)	−40.00 (72.0)	−6.04 (10.9)	53.38 (96.1)
Important wavebands (count)	150	114	151	156	155	113
PLS factors	5	5	5	5	4	4

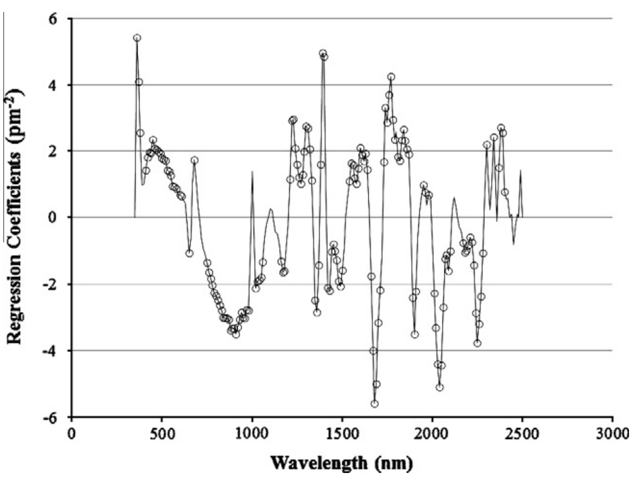

Fig. 2. Plot of the regression coefficients over wavelength (nm) of a VisNIR-DRS model predicting the HHV of manure. The model was based on the first derivative with respect to wavelength (pm^{-1}), and wavebands ($n = 129$) important to the model are indicated by circles on the plot.

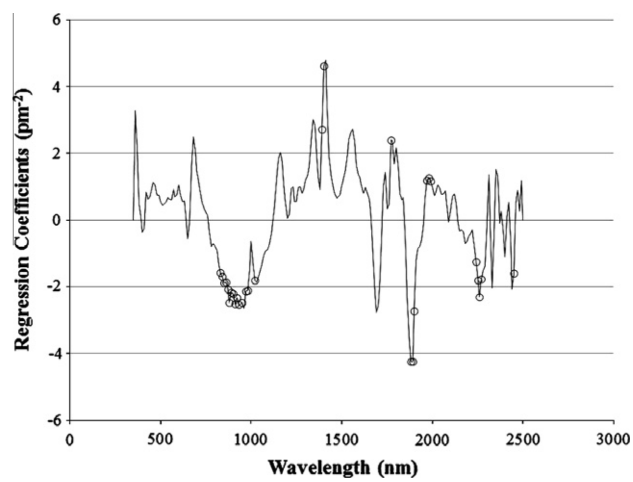

Fig. 3. Plot of the regression coefficients over wavelength (nm) of a VisNIR-DRS model predicting the HHV_{daf} of manure. The model was based on the first derivative with respect to wavelength (pm^{-1}), and wavebands ($n = 29$) important to the model are indicated by circles on the plot.

1890–1910, 1950, 2010–2060, 2090, 2100, 2170–2200, 2230–2270, 2300, 2340, and 2370–2400 nm.

The HHV_{daf} based on the corrected HHV was predicted within 2.0%. Recall that the HHV_{daf} was derived from the proximate analysis, treatment-wide S and N values for HNO_3 and H_2SO_4 corrections, and a simple equation (Eq. (1)). The model based on all treatments with random samples withheld from calibration for validation predicted HHV_{daf} within 1.8% and produced an RMSD = 96.17 cal g^{-1} (173 Btu lb^{-1}), RPD = 1.17 (acceptable), and bias = −19.83 cal g^{-1} (−37 Btu lb^{-1}), using five PLS factors and identifying 29 important wavebands (Table 2). Fig. 3 presents a plot of the regression coefficients over wavelength (nm) of this particular model. The remaining five models based on treatment-wise holdouts had lower RPD values and variable RMSD values ranging from 53.68 to 115.82 cal g^{-1} (97–208 Btu lb^{-1}). The number of important wavebands used in each of the six models ranged from 10 to 136, with 20 common important wavebands among three or more models. Wavebands common among three or more

Table 2
Visible near-infrared spectral models predicting HHV_{daf} based on manure samples from cattle fed steam-flaked corn-based diets with increasing amounts of wet distillers grains plus solubles (WDGSs). In the first model, two-thirds of all samples were selected as a calibration set ($n = 80$) and the remaining one-third was used as a validation set ($n = 40$). In the remaining models, each ration was held out of the calibration set ($n = 96$) in turn and was then used as a validation set ($n = 24$).

HHV_{daf}						
Ration (% WDGS) Validation set	ALL Random	0 Ration	15 Ration	30 Ration	45 Ration	60 Ration
RMSD cal g^{-1} (Btu lb^{-1})	96.17 (173.1)	104.90 (188.8)	53.68 (96.6)	54.67 (98.4)	115.82 (208.5)	109.80 (197.6)
RPD	1.17	0.92	1.10	0.88	0.73	0.74
Bias cal g^{-1} (Btu lb^{-1})	−19.8 (−35.6)	−39.63 (71.3)	−0.21 (−0.4)	−0.92 (−1.7)	87.25 (157.1)	−82.07 (147.7)
Important wavebands (count)	29	136	26	37	133	33
PLS factors	5	4	5[a]	5[a]	5	5

[a] The maximum number of PLS factors was set manually.

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Table 3
Descriptive statistics for the moisture (% wb) and ash (% db) content, the observed HHV uncorrected for N and S content, the observed HHV corrected for N and S content, and the HHV_{daf} calculated using Eq. (1) from the corrected HHV of manure samples ($n = 120$) from cattle fed steam-flaked corn-based diets with increasing amounts (0%, 15%, 30%, 45%, and 60%) of wet distillers grains plus solubles (WDGSs).

Statistic	Moisture (% wb)	Ash (% db)	HHV uncorrected (cal g^{-1})	HHV corrected (cal g^{-1})	HHV_{daf} (cal g^{-1})
Mean	9.35	21.05	3488.97	3463.15	4838.63
Minimum	5.92	18.14	3126.76	3095.29	4590.52
Maximum	20.25	22.71	3739.49	3723.05	5129.92
Standard deviation	2.77	1.04	134.90	137.65	91.73
Sample variance	7.66	1.09	18199.31	18946.57	8415.18

models were 830–920, 940–950, 1020–1030, 1340, 1400–1410, 1580, and 1870–1880 nm.

The reduction in model performance when predicting HHV_{daf} as compared to HHV indicates that a more robust equation accounting for one or more of C, H, S, O, and N content would improve the prediction accuracy when compared to Eq. (1). In the past, sophisticated equations that require the ultimate analysis, such as the Boie equation [32], have proven useful for estimating the HHV_{daf} of manure. However, these equations were not developed specifically for use with manure and were based on combustion characteristics of hydrocarbon fuels and other biomass fuels. The introduction of WDGS to beef cattle diets and its effects on the HHV_{daf} of manure may reduce the applicability of equations previously considered appropriate. Furthermore, the accepted HHV_{daf} of 4722 cal g^{-1} (8500 Btu lb^{-1}) may be too low. Therefore, the development of an equation to predict the HHV_{daf} of cattle manure more precisely is planned for a future investigation.

4. Conclusions

The spectral models based on the HHV observed by bomb calorimetry predicted the HHV of feedlot manure within 1.7% with excellent reliability. For practical purposes, this is more than adequate for industrial applications where an error of 5% or more is tolerated. Acid corrections are not necessary in VisNIR-DRS models to obtain an HHV prediction accuracy or reliability acceptable for use in feedlot manure gasification. Applying estimated HNO_3 and H_2SO_4 acid corrections based on N and S content measured in bulk samples (i.e. not individual samples) of the manure marginally reduced the accuracy and reliability of the HHV spectral models. However, applying precise HNO_3 and H_2SO_4 acid corrections to individual samples may improve model performance. Sophisticated equations developed specifically for manure and based on the ultimate data may improve the spectral prediction of HHV_{daf} when compared to Eq. (1). The HHV_{daf} value and sophisticated equations currently accepted for estimating the HHV_{daf} of manure may be less appropriate when WDGS is incorporated in beef cattle diets.

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