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Correlating LIBS Coal Data for Coal Property Prediction

Siddharth Deshpande

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Abstract

This report presents results for correlations between coal data derived from laboratory analysis and Laser Induced Breakdown Spectroscopy analysis. LIBS data were used to predict higher order properties of coal using artificial neural network models. Higher order coal properties such as heating value and ash fusion temperature are predicted using LIBS analysis and compared against standard laboratory measurements. Selected formulas for the prediction of coal properties are also presented and compared against the neural network and laboratory results.

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Introduction

Coal is a complex fuel due to its heterogeneous composition and varied properties. Over the past few years, coal fired power plants have begun to burn cheaper and off-design coals in order to reduce their operating costs in order to meet new environmental regulations. A consequence of this is a higher incidence of slagging and fouling of coal ash in the power plant boilers, which poses maintenance problems for power plants. As a result, there has been increased demand for rapid and on-line technology that can be used to measure and monitor the composition and properties of the coal being burned in the power plant boilers.

The composition and related properties of coal are typically characterized by a number of laboratory-based analysis methods collectively known as ultimate analysis, proximate analysis, ash analysis, etc. Each different coal analysis method focuses on determining distinct and specific properties of the coal sample. For example, ultimate analysis is used to determine the elemental composition of coal, and proximate analysis is used to determine properties such as moisture content and heating value of coal. While applying these techniques provides an accurate measurement of the desired parameters, they are also time intensive measurements. In the general case, each of these techniques requires thorough and representative sampling of the batch of coal to be analyzed. Furthermore, depending on the technique to be applied, the samples may require some form of pre-processing prior to combustion and measurement. Using these techniques, it is not possible to both rapidly and accurately obtain measurements of coal properties.

An alternate method of characterizing the higher order properties of coal involves an analysis of the relationships between coal properties and coal composition. In the literature, many such correlations have been reported in the form of formulas or statistical and artificial intelligence-based models. An advantage of this method of characterizing the properties of coal is that given information about the composition of coal, the other useful properties of coal can be quickly estimated to reasonable degree of accuracy.

This report will focus on determining correlations between several higher order coal properties and coal composition data that were collected using Laser Induced Breakdown Spectroscopy (LIBS). In particular, algebraic and statistical correlations from the literature will be compared against Artificial Neural Network (ANN) based models using LIBS data as their input. While ANN models have been successfully used to correlate coal properties with the elemental composition of coal, the analysis presented in this report differs by attempting to directly correlate LIBS spectral data to coal properties using ANN models.

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Description of Related Theoretical Concepts and Physical Principles

Literature Survey for Coal Property Correlations

Heating Value

The heating value (HV) of a fuel is an important property that gives the energy content contained within the fuel. Heating value is usually reported in two forms, which are known as higher heating value (HHV) and lower heating value (LHV). The primary difference between these two values is that the HHV takes water vapor into consideration as a combustion product, while the LHV assumes that water vapor is removed. The heating value of coal that is typically reported is the gross heating value (GHV), or higher heating value (HHV). As this property is important in determining the energy content of the fuel, it is often estimated from the elemental composition of the fuel (Speight, 2005).

Many formulas relating the heating value of coal to its elemental composition are reported in the literature. As part of a survey of formulas for heating values, a list of several common formulas for heating values of different fuels has been compiled by Channiwala and Parikh. In their paper, they list common formulas with the basis and assumptions behind them. All of the formulas compiled by Channiwala and Parikh are published correlations for HHV (MJ/kg) reported on a dry basis. The percent composition values are reported as percent by mass and on a dry basis.

The first reported formula for coal HHV in the literature is the Dulong formula (Eq. 1). The Dulong formula is based on empirical analysis of combustion reactions and the concept of available hydrogen. This formula is reported to be accurate to 1.5% for low oxygen coals. The Dulong formula was developed from an analysis of all coal ranks, however the majority of samples considered in the Dulong study came from bituminous and subbituminous coals. This formula is reported to deviate by 5 − 7%.

$$HHV = 0.3383(\%C) + 1.443\left(\%H - \frac{1}{8}(\%O)\right) + 0.0942(\%S) \qquad (Eq.\,1)$$

The next formulas for coal heating values that are reported in the literature are modifications of the Dulong Formula. Strache and Lant (Eq. 2) better accounts for variances in oxygen content. Steuer (Eq. 3) modifies the Dulong formula by considering the association of oxygen with both hydrogen and carbon. Both of these modifications of the Dulong formula are reported to be accurate to within 2% for all coals. Both of these studies built upon the Dulong study and considered similar coal sampling data as the Dulong study.

$$HHV = 0.3406(\%C) + 1.4324(\%H) - 0.1532(\%O) + 0.1047(\%S) \qquad (Eq.\,2)$$

$$HHV = 0.339\left(\%C - \frac{3}{8}(\%O)\right) + 0.2386\left(\frac{3}{8}(\%O)\right) + 1.444\left(\%H - \frac{1}{16}(\%O)\right)$$
$$+ 0.1046(\%S) \qquad (Eq.\,3)$$

The Vondrecek (Eq. 4) correlation considers the bond energy of carbon and a higher availability of hydrogen in coal as compared to the Dulong Formula. The Vondrecek study considered coal samples from the entire range of coal ranks. The predictions of the Vondrecek formula are reported to be accurate to within 1.5% for all coals; however a listing the specific ranks of coal considered in this study could not be found.

$$HHV = 0.373(\%C) - 0.00026(\%C)^2 + 1.444\left(\%H - \frac{1}{10}(\%O)\right) + 0.1047(\%S) \qquad (Eq.\,4)$$

The Schuster correlation (Eq. 5) is based on an assumption that the heat evolved from combustion of fuels is proportional to the amount of oxygen consumed, and that the constant of proportionality is dependent on the oxygen content of the fuel. This correlation is based on similar coal sample data as the Dulong formula, and therefore is primarily based on a study of bituminous and subbituminous coals. In the literature, this correlation is reported to be superior to the Dulong Formula.

$$HHV = \left(1.0632 + 1.486 * 10^{-3}(\%O)\right) * \left(\frac{\%C}{3} + \%H - \frac{\%O - \%S}{8}\right) \qquad (Eq.\,5)$$

A similar correlation was proposed by Grummel and Davis (Eq. 6). Grummel and Davis made the same assumption regarding the proportionality between the heat evolved and the oxygen content of fuels. Their correlation differs from Schuster's in that the constant of proportionality is assumed to be dependent on the hydrogen content rather than the oxygen content of the fuel. The Grummel and Davis correlation is reported to be accurate within 1.3% for all coals, however, the majority of the coal samples in this study are bituminous and subbituminous.

$$HHV = (0.0152(\%H) + 0.9875) * \left(\frac{\%C}{3} + \%H - \frac{\%O - \%S}{8}\right) \qquad (Eq.\,6)$$

Another major correlation reported was proposed by Seyler (Eq. 7). This correlation is based on the finding that the ratio between the heat of formation and the oxygen content of the fuel is a linear function of the oxygen content of the fuel. Seyler reports that this correlation accurately predicts HHV to within 1%. The specific coal ranks for which this correlation is appropriate were not given in the Channiwala paper.

$$HHV = 0.519(\%C) + 1.625(\%H) + 0.001(\%O)^2 - 17.87 \qquad (Eq.\,7)$$

The Boie correlation (Eq. 8) is a more general correlation that is based on the properties of hydrocarbon fuels. Predictions for HHV from the Boie correlations are reported to be within 1.8% of the true HHV for bituminous and subbituminous coals.

$$HHV = 0.3517(\%C) + 1.626(\%H) + 0.1047(\%S) - 0.111(\%O) \qquad (Eq.\,8)$$

Another general correlation for HHV is the IGT correlation (Eq. 9). The IGT correlation was derived from analyses of the properties of over 700 coal samples. This correlation is reported to be accurate to within 1.2% for all coals. One major difference for the IGT correlation is that it considers the percent ash content of coal. The IGT correlation is primarily based on a study of coals from Illinois.

$$HHV = 0.341(\%C) + 1.323(\%H) + 0.0685 - 0.0153(\%Ash) - 0.1194(\%O + \%N) \quad (Eq.\,9)$$

The final reported correlation for HHV of coal is the Dulong-Bertherlot correlation (Eq. 10). This correlation modifies the original Dulong formula by introducing the effect of nitrogen in the fuel. This correlation is claimed to be superior to the Dulong correlation and is based on a similar coal sample set as the Dulong formula.

$$HHV = 0.3414(\%C) + 1.4445(\%H) - \frac{(\%N + \%O - 1)}{8} + 0.093(\%S) \qquad (Eq.\,10)$$

In addition to their survey of correlations in the literature, Channiwala and Parikh also worked to develop a unified correlation for heating value based on all the others reported. In order to achieve their unified correlation, Channiwala and Parikh collected data from various fuels including coal, natural gas and biomass from the literature. The resultant compendium of data for all fuels was verified by back-checking with the most proven correlations for the fuels. In this case, the Boie correlation (Eq. 8), the IGT correlation (Eq. 9), and the Grummel and Davis correlation (Eq. 6) were used to verify the data.

To determine the unified correlation, Channiwala and Parikh attempted to fit a number of algebraic expressions to the data using regression methods. The best correlation for HHV that was determined from this analysis is listed below (Eq. 11). This correlation is reported by the authors to be accurate to within 3% for all hydrocarbon fuels. It is important to note that the unified correlation (Eq. 11) has been developed as a general formula for HHV for hydrocarbon fuels and not for specific ranks of coal (Channiwala & Parikh, 2001).

$$HHV = 0.3491(\%C) + 1.1783(\%H) + 0.1005(\%S) - 0.1034(\%O) - 0.0151(\%N) - 0.0211(\%Ash) \qquad (Eq.\,11)$$

Calculations of heating value have also been achieved using Multivariate Regression and Artificial Neural Network (ANN) techniques. A paper written by Mesgroghli, Jorjani, and Chelgani considers the use of both approaches, and puts forward a comparison of the results from the application of the two techniques.

The regression based techniques used by Mesgroghli, Jorjani and Chelgani consider the multivariable relationships between the HHV of coal and various parameters determined from ultimate and proximate analyses. All of the coals considered in this study were sampled from coal mines in the United States, with the majority of the samples coming from bituminous and subbituminous coals. Using a least square regression method, the correlation coefficients for C, H, H_{ex} (Hydrogen exclusive of moisture), N, O, O_{ex} (Oxygen exclusive of moisture), sulfur, ash, moisture and volatile matter with HHV were determined. Then, using a stepwise procedure, multivariable equations between the various parameters and the HHV were determined. The three best recorded equations are presented in Table 1.

Table 1: Best-Correlatated Multivariable Equations for HHV (MJ/kg). All parameters are in %mass. Source: (Mesgroghli, Jorjani, & Chelgani, 2009).

HHV (MJ/kg) equations	R^2
$HHV = 37.777 - 0.647(M) - 0.387(A) - 0.089(VM)$	0.97
$HHV = -26.29 + 0.275(A) + 0.605(C) + 1.352(H) + 0.84(N) + 0.321(S)$	0.99
$HHV = 6.971 + 0.269(C) + 0.195(N) - 0.061(A) - 0.251(O_{ex}) + 1.08(H_{ex}) - 0.21(M)$	0.995

In addition to considering equations derived from multivariable regression, the paper also develops ANN-based models for the estimation of HHV of coal. Three specific ANN-based models are developed in this paper. The ANN based models developed in this study are feed forward networks that execute training using error back propagation (EBP). The ANNs developed consist of an input layer, a single hidden layer and EBP training. In order to validate the ANN models, their performance is evaluated by considering the correlation between the predicted HHV and the actual HHV. More detailed information regarding the three ANN models is provided in Table 2 below.

Table 2: Details for ANN models for HHV. Source: (Mesgroghli, Jorjani, & Chelgani, 2009).

Inputs	Training Set Size	Testing Set Size	Validation Set Size	No. of Input Nodes	No. of Hidden Layer Nodes	R^2
Ash, VM, M	2000	1740	800	3	10	0.95
C,H,N, O, S, Ash	2000	1740	800	6	10	0.92
C, H_{ex}, N, O_{ex}, S, Ash, M	2000	1740	800	7	10	0.97

In order to achieve valid comparisons between the two general methods of estimating

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HHV, Mesgroghli, Jorjani and Chelgani developed three specific models for each method using similar input parameters. Then, using the correlation coefficients, the developed models could be reasonably compared. Based on the results from their analysis, the paper concludes that both techniques provide highly reliable correlations, however the regression technique is preferred due to its relative simplicity as compared to the ANN-based method. That being said, the ANN-based method has an advantage in that it can better handle nonlinear relationships between input parameters and HHV (Mesgroghli, Jorjani, & Chelgani, 2009).

Volatile Matter

The volatile matter of coal is defined as the constituents of coal, excluding moisture, that depart in the form of gases and vapors during pyrolysis (Speight, 2005). A number of correlations have been proposed between volatile matter and other constituents of coal. Many such correlations between volatile matter and the hydrogen-carbon ratio in coal are proposed by C.H. Fisher. Fisher surveyed literature for volatile matter correlation and used petrographic data to plot curves relating volatile matter content to various Hydrogen-Carbon ratios. Fisher noted that the relationships were linear for coals containing anthraxylons and constituents such as fusains, attrital matter, durains and spores, which he termed as 'bright coals'. The samples of the 'Bright Coals' that were used by Fisher were stated to be from a Pittsburgh, PA coal mine. The linear equations of the observed correlations have fair accuracy for anthraxylons of all ranks and for the other constituents.

Fisher starts his study by introducing a formula developed by Seyler (Eq. 12), which characterizes 'bright coals' containing anthraxylons, vitrains and clarains. The Seyler formula applies for these coals if constituents are reported on a dry, mineral matter free basis.

$$\%VM = 10.61(\%H) - 1.24(\%C) + 84.15 \qquad (Eq.\,12)$$

Other formulas from the literature that were put forward in the Fisher paper are the Seyler logarithmic formula (Eq. 13), Diederich's formula (Eq. 14), and Seyler's quadratic formulas (Eq. 15), (Eq. 16). These formulas were applied to the same coal samples as the rest of the correlations in the Fisher study.

$$\%H = 2.8 * \log(\%VM) + .95 \qquad (Eq.\,13)$$

$$\%H = \%VM * \left(\frac{7.35}{\%VM + 10}\right) - 0.013 \qquad (Eq.\,14)$$

$$\%H = 0.1292(\%VM) - 0.00156(\%VM)^2 + 2.69 \qquad (Eq.\,15)$$

$$\%C = 0.299(\%VM) - 0.01334(\%VM)^2 + 90.79 \qquad (Eq.\,16)$$

In addition to the formulas in the literature, Fisher noted relationships between the

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square of a hydrogen to carbon ratio and volatile matter for coals containing high amounts of vitrains and clarains (Eq. 17), and coals containing other banded constituents (Eq. 18) (Fisher, 1938).

$$\%VM = \frac{13}{12}\left(\frac{100(\%H)}{\%C}\right)^2 - 7.6 \qquad\qquad (Eq.\,17)$$

$$\%VM = \frac{17}{18}\left(\frac{100(\%H)}{\%C}\right)^2 + 2.3 \qquad\qquad (Eq.\,18)$$

More recently, Vassilev, Vassileva, Baxter and Andersen authored a paper that outlines a number of correlations between many different constituents of coal. Using a broad database of coal sampling data from 37 separate sites (majority are bituminous or subbituminous coals), the paper presents correlations between specific properties or elemental compositions such as fixed carbon versus hydrogen. In particular, the paper finds that Volatile Matter is positively correlated with moisture, oxygen, and hydrogen, and negatively correlated with ash, carbon, and nitrogen (to name a few). The paper lists positive and negative correlations, as well as their correlation coefficients. Table 3 below is an excerpt from a table in the paper, which notes significant correlation coefficient values for coal constituents with volatile matter (Vassilev & Vassileva, 2010).

Table 3: Significant Positive (+) and Negative (-) correlation coefficient values for Volatile Matter (97th and 95th Confidence Interval). Source: (Vassilev & Vassileva, 2010).

Symbol	Significant Correlation Coefficient Values
VM	H(+0.58), O (+0.55), Mineral Matter(+0.43), K(-0.52), Ash(-0.46), C(-0.42)

Percent Ash Content

The Ash content of coals is defined to be the residue that is found after coal is combusted. The ash follows from the remnant of the incombustible matter in coal after it is burned. In general, the ash content of coal is comprised of mineral matter. One potential correlation for ash content is with Silicon. In a paper written by Hicks O'Reilly and Koppenaal, the percent ash content in coal is proposed to be strongly correlated with the percent silicon content in coal. Using various spectroscopic techniques to analyze coal ash samples from West Virginia and Kentucky, Hicks, O'Reilly and Koppenaal produced linear-least fit (Eq. 19) and logarithmic (Eq. 20) correlations for percent ash content as a function of silicon content. The logarithmic correlations are reported to be accurate to within 1.8%. Reported values for the constants and the correlation coefficients can be found in Tables 4 and 5 (Hicks, O'Reilly, & Koppenaal).

$$\%Ash = p(\%Si) + q \qquad\qquad (Eq.\,19)$$

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$$\%Ash = a(\%Si)^b \hspace{4cm} (Eq.\,20)$$

Table 4 Linear Correlations for %Ash from %Si. For equation 19. Source: (Hicks, O'Reilly, & Koppenaal).

Coal Ash%	Slope (p)	Intercept (q)	Error in Estimation of %Ash	Correlation Coefficient
4.6-27.3	2.48	4.33	2.41	0.890
6.5-27.3	2.94	2.88	1.73	0.941
6.5-27.3	3.00	2.69	1.71	0.943

Table 5 Logarithmic Correlations for %Ash from %Si. For Equation 20. Source: (Hicks, O'Reilly, & Koppenaal)

Constant (a)	Constant (b)	Correlation Coefficient
6.82	0.525	0.917
5.82	0.652	0.919
5.72	0.663	0.902

In addition to this proposed correlation, the paper written by Vassilev, Vassileva, et al, reports a number of positive and negative correlations for Ash in coal. The paper states that the current understanding of correlations for ash yield in coal is poor due to its complex character as Ash is simultaneously produced from mineral matter, organic matter, and fluid matter during coal combustion, and it is therefore difficult to determine the source of the ash. The significant correlations for ash content are shown in Table 6 below (Vassilev & Vassileva, 2010).

Table 6 Significant Positive (+) and Negative (-) correlation coefficient values for Ash content (97th and 95th Confidence Interval). Source: (Vassilev & Vassileva, 2010).

Symbol	Significant Correlation Coefficient Values
A	S (+0.57), K (+0.50), Al (+0.47), FC (-0.66), VM (-0.46)

Ash Fusion Temperature

The Ash fusion temperature of coal is a measure of the behavior of the ash residue of the coal at high temperatures such as those that exist in furnaces. Generally, at high temperatures, the ash residue tends to fuse into a glass-like slag material which needs to be periodically cleaned out of the furnace. A measure of the ash fusion temperature is important in determining the operating conditions of the coal fired boiler. There are four temperatures that are measured and reported as ash fusion temperatures. First, there is the initial deformation temperature (IT), which is the temperature at which a sample of coal ash first starts to deform. The next measure is the softening temperature (ST), at which the ash sample fuses down to a spherical lump. The third measure is the hemispherical temperature (HT), at which the ash sample fuses down to a hemisphere such that the height is half the width of the

base. The final measure is the fluid temperature (FT), at which the ash sample fuses into a flat, glassy layer (Speight, 2005).

The majority of sources in the literature reported correlations between ash fusion temperatures and ash composition. This approach is reported in a paper by Ozbayoglu and Ozbayoglu, who conducted a study on ash fusion temperatures for Turkish coals. This study developed both linear and nonlinear correlations for the estimation of ash fusion temperature. The linear correlation developed in this study is shown as Equation 21, and the nonlinear correlation for ash fusion temperature is shown in Equation 22. The inputs for these two equations are listed in Tables 7 and 8. The constants l_i and c_i are equation constants for the linear and nonlinear correlations respectively. These equation constants were determined using statistical methods (Ozbayoglu & Ozbayoglu, 2005).

$$T\,(°C) = l_1 + l_2(SV) + l_3(B) + l_4(A) + l_5(DR) + l_6(R_{250}) + l_7(Ash) + l_8(SG) + l_9(HGI) + l_{10}(MM) + l_{11}(SiO_2) + l_{12}(Al_2O_3) + l_{13}(Fe_2O_3) + l_{14}(CaO) + l_{15}(MgO) + l_{16}(K_2O) + l_{17}(Na_2O) \qquad (Eq.\,21)$$

$$T\,(°C) = c_1(SV)^{c_2}(B)^{c_3}(A)^{c_4}(DR)^{c_5}(R_{250})^{c_6}(Ash)^{c_7}(SG)^{c_8}(HGI)^{c_9}(MM)^{c_{10}}(SiO_2)^{c_{11}} * (Al_2O_3)^{c_{12}}(Fe_2O_3)^{c_{13}}(CaO)^{c_{14}}(MgO)^{c_{15}}(K_2O)^{c_{16}}(Na_2O)^{c_{17}} \qquad (Eq.\,22)$$

Table 7 : Parameters considered for linear and nonlinear correlations for Ash Fusion Temperature. Source: (Ozbayoglu & Ozbayoglu, 2005).

Parameter Symbol	Parameter Definition
SV – Silica Value	$SV = SiO_2/(SiO_2+Fe_2O_3+CaO+MgO)$
B – Base	$B = Fe_2O_3+CaO+MgO+K_2O+Na_2O$
A – Acid	$A = SiO_2+Al_2O_3+TiO_2$
R_{250}	$R_{250} = (SiO_2+Al_2O_3)/(SiO_2+Al_2O_3+Fe_2O_3+CaO)$
DR – Dolomite Ratio	$DR = (CaO+MgO)/(Fe_2O_3+CaO+MgO+K_2O+Na_2O)$
Ash	% Ash composition
SG	Specific Gravity of Coal
HGI	Hardgrove Grindability Index of coal
MM	% Mineral Matter Composition
SiO_2	% SiO_2 composition
Al_2O_3	% Al_2O_3 + TiO_2 composition
Fe_2O_3	% Fe_2O_3 composition
CaO	% CaO composition
MgO	% MgO composition
K_2O	% K_2O composition
Na_2O	% Na_2O composition

Table 8 : linear and nonlinear regression equation constants for three ash fusion temperatures. Source: (Ozbayoglu & Ozbayoglu, 2005).

	T (°C) = Softening Temp		T (°C) = Melting Temp.		T (°C) = Fluid Temp.	
No. (i)	l_i	c_i	l_i	c_i	l_i	c_i
1	1516.9	1159.4	1518.8	522.74	3040	335.17
2	-1123	-0.731	-121	-0.597	-3327	-0.452
3	-561.4	-0.067	-1288	-0.117	-1101	-0.009
4	2087.3	-0.372	2816.1	3.1897	4149.7	3.855
5	-53.41	-0.103	0	0	-72.07	0.0547
6	-2767	0.819	-4166	-0.394	-4900	0.445
7	284.71	0.0841	-107.5	-0.021	-213.9	-0.033
8	310.6	0.2787	355.82	0.0963	363.41	0.1116
9	-2.46	-0.108	2.55	0.0374	3.28	0.0518
10	-30.65	-0.003	0.0083	0	120.16	0.0155
11	1140.1	0.3625	857.98	-1.983	-3.017	0
12	949.64	-0.013	1960.5	-0.242	2224.6	-0.37
13	-539.6	-0.034	266.24	0.056	-1539	0.0708
14	-293.1	0.0728	524.64	0.0171	-1526	-0.013
15	1341.8	-0.031	282.3	-0.008	942.69	-0.071
16	-2448	-0.004	-7105	0.0078	-3231	0.023
17	1379.9	-0.031	2194.6	0.0076	4254.5	0.0042
R - coeff	0.874	0.955	0.864	0.963	0.84	0.934

The only paper to provide direct correlations between various ash fusion temperatures and coal composition was the one written by Vassilev, Vassileva, et al. In this paper, significant correlations and their correlation coefficients for elements in coal and the ST, HT and FT (softening, hemispherical and fluid ash fusion temperatures) are reported. These correlations are provided in Table 9 (Vassilev & Vassileva, 2010).

Table 9 Significant Positive (+) and Negative (-) correlation coefficient values for three Ash Fusion Temperatures (97th and 95th Confidence Interval). Source: (Vassilev & Vassileva, 2010).

Symbol	Significant Correlation Coefficient Values
ST	Al (+0.69), Ti (+0.67), C (+0.56), FC (+0.56), Gp (-0.52), Mg (-0.46), O (-0.46) H (-0.43)
HT	Al (+0.70), Ti (+0.66), C (+0.58), Si (+0.52), FC (+0.46), Ca (-0.65), Mg (-0.47), O (-0.58)
FT	Al (+0.69), Ti (+0.69), C (+0.64), FC (+0.48) Si (+0.44), SO_3 (-0.72), Ca (-0.57), O (-0.56)

Slagging and Fouling Indices

Slagging and fouling are the two main types of deposits that form within coal fired boilers. Slagging deposits typically occur in the parts of the boiler where coal ash deposits are

easily exposed to radiation from the flame. Fouling deposits tend to occur as the coal fly ash cools down, and typically form in areas that are not directly exposed to the flame of the boiler. The occurrence of these deposits results in a reduction in the effectiveness of heat transfer between the combustion in the boiler and the water used to produce steam. Due to the consequences that slagging and fouling deposits have on the operation of a coal-fired power plant, it is important to estimate the propensity of coal to form such deposits. The estimation of the slagging and fouling propensity of coal is done using slagging and fouling indices (Manton, Williamson, & Riley, 1996).

Common slagging indices for coal are reported in a paper written by McLennan, Bryant, Bailey et. al. This paper reports three common indices for coal slagging, along with an estimation of the slagging potential for each index considered. The study was conducted using samples of high rank Australian coals. The three common coal slagging indices are shown in Table 10. For the ash fusibility, the IDT is the initial deformation temperature and the HT is the hemispherical ash fusion temperature of the coal. For the coal ash viscosity, the $T_{250(ox)}$ and the $T_{1000(red)}$ values are the 250 poise temperature of coal for oxidizing conditions and the 1000 poise temperature for coal for reducing conditions respectively. The F_s value is a correlating factor for viscosity, however its value was not reported in the study (McLennan, Bryant, Bailey, Stanmore, & Wall, 1999).

Table 10: Three slagging and fouling Indices for high rank coals. Source: (McLennan, Bryant, Bailey, Stanmore, & Wall, 1999).

		Slagging Potential			
Index	Calculation	Low	Medium	High	Severe
Ash Fusibility (T °C)	$$\frac{4(IDT) + HT}{5}$$	>1343°C	1232-1343°C	1149-1232°C	<1149°C
Viscosity (poise)	$$\frac{T_{250(ox)} - T_{1000(red)}}{975F_s}$$	<0.5	0.5-0.99	1.0-1.99	>2.0
Ash Chemistry (% comp.)	$$\frac{(Fe_2O_3 + CaO + MgO + K_2O + Na_2O) * S}{SiO_2 + Al_2O_3 + TiO_2}$$	<0.6	0.6-2.0	2.0-2.6	>2.6

Trace Elements

Trace elements in coal are general inorganic constituents of coal that are not part of the organic coal substance. The trace elements in coal form the majority of mineral matter in coal, but can also take the form of heavy metals. A number studies have been performed to determine trace element affinities in coal. In general, these studies relate trace element concentrations to total sulfur, sulfur compounds, and organic or inorganic matter (Speight, 2005).

In their paper, Xiao-hua, Han-cai, and Lu-xian modeled the relationship between trace elements and 3 species of sulfur in coals, namely, organic sulfides, inorganic sulfides and sulfates. The study reported regression models (Eq. 23) between trace elements and the three types of sulfur compounds. This study used samples from Chinese bituminous coals. These relations are presented in table 11 below. The form of the regression models is shown in Equation 23, where X_1, X_2 and X_3 are percentages of sulfates, inorganic sulfides and organic sulfides respectively, a_1, a_2, and a_3 are constants. Y represents the concentration (µg/g) of the trace element in the coal (Xiao-hua, Han-cai, & Lu-xian, 1998).

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 \qquad\qquad (Eq.\,23)$$

Table 11 Regression Models for Trace Elements and Three species of sulfur. Source: (Xiao-hua, Han-cai, & Lu-xian, 1998).

Trace Element	Regression Equation	Correlation Coefficient
Be	$Y = 0.145 - 2.76(X_1) + 0.0389(X_2) + 0.122(X_3)$	0.776
Cd	$Y = -0.952 + 11.27(X_1) + 3.23(X_2) + 3.23(X_3)$	0.9966
Co	$Y = 6.49 - 12.43(X_1) + 2.38(X_2) + 1.03(X_3)$	0.9671
Pb	$Y = -51.47 + 791.3(X_1) + 57.5(X_2) + 67.93(X_3)$	0.990
Cu	$Y = -7.99 + 248.8(X_1) + 0.0389(X_2) + 0.122(X_3)$	0.997
Cr	$Y = -37.98 + 588.6(X_1) + 5.33(X_2) + 41.69(X_3)$	0.6278
Ni	$Y = 81.24 - 716.1(X_1) - 1.49(X_2) - 58.25(X_3)$	0.9871
As	$Y = -75.11 - 925.3(X_1) + 15.19(X_2) + 98.94(X_3)$	0.3934

Another study on trace element affinities in coal was performed by Conaway. In his thesis, Conaway briefly outlines basic affinities of trace elements to organic matter, mineral matter, and sulfur compounds. He then presents correlation coefficients and regression models for a number of trace elements for three separate coal samples. The Parr Formula (Eq. 24) is used to estimate mineral matter and organic matter concentrations in the study. Conaway developed a multiple regression model (Eq. 25) relating trace element concentration to the concentration of ash, pyritic sulfur and organic matter forming materials. C_i represents the concentration of a specific species of trace element I, and the constants M_a, M_{pyr}, M_{OM} are regression coefficients for each of the three input values. Table 13 shows the regression coefficients for samples from the Coalburg WV coal mine (Conaway, 2001).

$$\%Organic\ Matter = 100 - (\%Mineral\ Matter)$$
$$= 100 - \big(1.8(\%Ash) + 0.55(\%S)\big) \qquad\qquad (Eq.\,24)$$

$$C_i = M_a(\%ash) + M_{pyr}(\%Pyritic\ Sulfur) + M_{OM}(\%Organic\ Matter) \qquad (Eq.\,25)$$

Table 12 Normalized Regression Coefficients for Coalburg WV coal samples. Source: (Conaway, 2001).

Normalized Regression Coefficients											
	Sb	As	Be	Cd	Cr	Co	Pb	Mn	Hg	Ni	Se
Ash forming materials (M_a)	0	0	0	0.2766	0.8146	0	1.0	0.004	0	0.0062	0
Pyritic Matter materials (M_{pyr})	1.0	1.0	0	0.7197	0	0.3101	0	0.996	1.0	0.9894	1.0
Organic Matter materials (M_{OM})	0	0	1.0	0.0037	0.1854	0.6899	0	0	0	0.0142	0

Laser Induced Breakdown Spectroscopy

Laser Induced Breakdown Spectroscopy (LIBS) is a form of atomic emission spectroscopy that can be used to determine the composition of a sample. In principle, LIBS systems operate by exciting a sample using a high energy pulsed laser (typically a Nd:YAG 1064nm laser) to atomize it. For most LIBS systems, the laser is pulsed at its targets for time intervals on the order of ~ 4 ns, releasing optical radiation as a small portion of the sample is burned off. This optical radiation is typically analyzed through the use of optical emission spectrometry. As seen in Figure 1, the spectral data that are obtained from LIBS measurements can be output as a plot of intensity versus wavelength, where the different wavelengths correspond to different elements and the intensity of each spectral line corresponds to the relative concentration of the element in the sample. The intensity measurement follows from a detector that measures counts of photons of different wavelengths that are released when the sample is excited by the laser. It is important to note that as opposed to a single wavelength, a spread of wavelengths typically corresponds to an element. This can be seen in Figure 1 where multiple peaks are shown to correspond to Silicon and Iron respectively. In order to obtain a single measurement for the concentration of a particular element, the spectra data are typically normalized by integrating across a spread of wavelengths that are known to correspond to a particular element. Once the spectral measurements are taken, they must then be interpreted to determine the elemental composition of the sample.
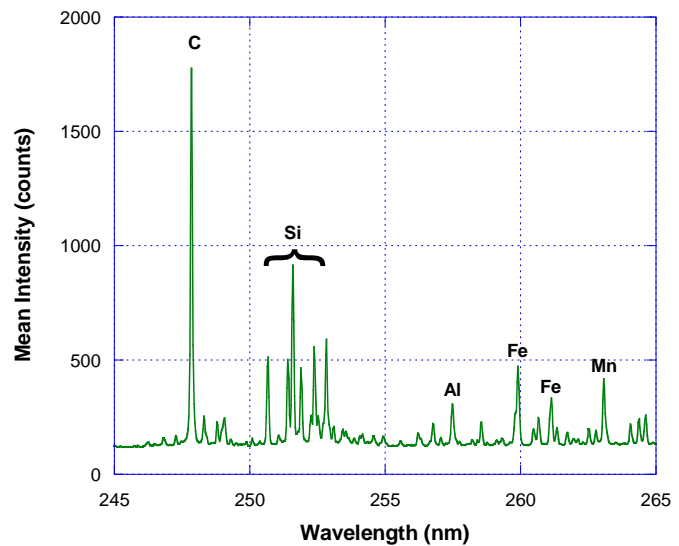
Figure 1: Coal LIBS Spectrum

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The LIBS measurement technique is particularly advantageous for rapid on-line coal analysis as measurements are taken without destroying or heating the sample. In addition, the LIBS technique does not require the samples of coal to be specially prepared for analysis. In addition, the LIBS technique has been proven to be relatively accurate with a high degree of repeatability. The primary limitation of the LIBS technique is the sensitivity of the detector that is used for the spectral analysis. (Fortes and Moros, 2012).

Artificial Neural Networks

In addition to the algebraic and statistical correlations between coal properties and coal composition that are reported in the literature, this report will consider correlations that are derived from artificial neural network (ANN) models. The ANN models were used to correlate the spectral data from LIBS measurements with the relevant higher order properties of coal.

Artificial neural networks (ANNs) are a set of computational models that are inspired by the operation of central nervous systems. In natural nervous systems, neural signals are transmitted to and received by neurons through syna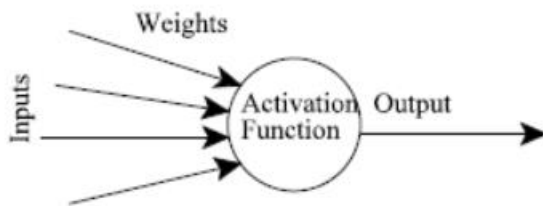pses. If the strength of the signal is beyond a certain threshold, then the neuron is activated, making it send new signals to other neurons. In ANN modeling, the natural neural system is modeled computationally. In the ANN case, input signals are both sent and received by nodes. These signals are all assigned weights, which represent the strength of the signal. Depending on the weight assigned to an input signal and an activation function, the node to which it travels may or may not be activated, resulting in the transfer of an output signal. This is illustrated in Figure 2.

Figure 2: Artificial Neural Network Node. (Gershenson)

Artificial neural networks are formed by combining several layers of nodes. The operation of an ANN model will differ depending on the weights assigned to the signals that are input and output to and from nodes. ANN modeling requires the use of algorithms to determine the appropriate weights in order to obtain the output that is desired. The process of altering the weights is called training. The primary applications for artificial neural network modeling are in pattern recognition, and forecasting. There are many different types of algorithms that can be used in ANN modeling. The differences between them typically lie in the activation functions, or in the architecture of the network. For the LIBS data that are analyzed in this report, two common ANN models were used. The two models that were considered were Error Back Propagation (EBP) and Radial Basis Function (RBF) networks.

A general mathematical algorithm for artificial neural networks is shown in Equation 26 below. In Equation 26, v_i are the output neurons that are being fed information from input

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neurons v_j through the use of weights, w_{ij} and a transfer function or activation function $g(a_i)$. For an EBP network, the transfer function g is typically linear or sigmoid. For an RBF network, g is a radial basis function. The primary difference between an EBP network and an RBF network is how the weights are updated using activation functions. (Peterson and Rognvaldsson, 1991).

$$v_i = g(a_i) \sum_j (w_{ij} v_j) \qquad\qquad (Eq. 26)$$

The EBP algorithm is a supervised learning algorithm that can be used to model patterns within a data set. The term 'supervised learning' refers to the fact that the training dataset that is input to the system consists of paired sets of inputs and outputs. An ANN that operates on an EBP algorithm will first consider the training data to infer a function between the input and the output, and then use a testing set to validate the function. EBP algorithms are also known as feed forward networks in that the training pattern that is generated is fed forward through the network in order to generate the desired output. Back propagation is then used to calculate the error for the outputs for individual inputs against other such pairs in the training set. The network is trained until the level of error falls below a specified value.

A radial basis function network (RBF) operates by calculating radial basis functions of the inputs to individual nodes in the network. The output from each node is determined by the linear combination of the radial basis functions of the inputs to the node. A radial basis function is a function whose output is only dependent on the distance between its input and a 'center'. In the case of ANN modeling, the 'center' is typically the desired output value that is specified in the data set. RBF networks are considered a fast alternative to EBP networks (Neusciences, 2000).

Determination of Data used in Analysis

In order to determine correlations between higher order properties of coal and coal composition, it was first necessary to select the appropriate input and output data for the different models to be considered. The output data comprised of higher order properties of coal such as the higher heating value and the ash fusion temperature of coal. The input data for the various models differed depending on the type of model and the availability of data.

Data for a total of 50 samples of coal across 10 separate sampling locations was used for data analysis. For these samples, the coal data were collected in two forms: Standard Laboratory data and LIBS data. The standard laboratory data followed from coal analysis techniques such as ultimate analysis and proximate analysis and provided information for both the composition and the properties of the coal sample. The LIBS data were collected from LIBS experiments that were conducted on the coal samples. The LIBS data were more limited in that the spectral information could only be used to predict the composition of elements such as Al, Ca and Fe. While in theory it could be possible to determine the concentration of many other elements in the coal sample, the LIBS dataset in this case was limited to carbon and metals.

In the case of the algebraic correlations between coal composition and coal properties, the input data for the algebraic models depended on the requirements of the model that was selected. One such algebraic model is Fisher's vitrain formula for volatile matter in coal (Eq. 17). In the case of this model, the inputs are specified as the dry percent composition values for Oxygen and Hydrogen in coal sample. These values were then directly input into the formula in order to estimate a value for the volatile matter of the coal sample.

For the ANN models that were considered, the input dataset that was used was limited to spectral data for a few metals and for carbon, while the output data remained the same (coal property information derived from laboratory measurements). Instead of converting the information in the spectral data to the elemental composition of coal, the spectral data were input into the neural networks. This was done in order to reduce the amount of error in the estimation of the output value. In terms of ANN modeling, the nature of the input data was not a factor due to the fact that the spectral data were directly paired with the appropriate output data. The LIBS models were then trained to determine patterns between the input and output data and use the patterns to estimate the value of the output given new inputs of the same form.

Procedure for Artificial Neural Network Modeling

The analysis using artificial neural network models for LIBS spectra data was performed using Neuframe Professional 4. Neuframe is a software package for data analysis using artificial intelligence methods such as ANNs. While Neuframe is capable of data analysis using a number of different algorithms for pattern recognition, clustering, and data mining, the analysis that was performed on the LIBS data was restricted to only two of the available algorithms. The two algorithms for neural network training that were selected were the Error Back Propagation algorithm and the Radial Basis Function algorithm. The primary reason why these particular algorithms were selected was that they are both particularly applicable for pattern recognition in datasets where the input values are clearly paired with the output values. In other words, the EBP and RBF algorithms allow for the creation of general purpose supervised learning neural network models.

Preparation of Datasets for Input to Model

In order to perform data analysis using Neuframe, it was first necessary to select the appropriate data set to be input to the software program. This meant selecting the input parameters and the desired output parameters for the modeling. The input parameters used were quantities such as the Dolomite Ratio and Silica Ratio, which were calculated from the LIBS spectral data. The parameters that were determined from laboratory analysis, such as Heating Value and Ash Fusion Temperature were selected as the desired outputs for the neural networks.

Before data can be input to Neuframe for analysis, it needs to be separated into a training set and a query set. This is illustrated in Figure 3. The training set consists of randomly selected rows of paired input and output parameters. For the 50 samples that were used for this analysis, the training set that was chosen typically consisted of between 30 and 40 rows of data. The purpose of the training set is to pass data into the neural network in order for it to learn patterns between the input parameters and the output parameters. The query set consisted of all 50 rows of data. After

Figure 3: Example Neuframe DataView

the neural network is trained using the training set, the query set is used to test the network. The outputs for running the neural network using the query set are the neural network predictions of the output parameters.

Training the Artificial Neural Network

In order to train a neural network model to accurately predict a desired output parameter, a number of options are available in order to optimize the network's performance. The first condition that can be varied is the size of the training set. By increasing the size of the training set, the pattern between the input and output parameters that is determined by the neural network can be improved as it is developed using more of the overall data set. Another consequence of increasing the size of the training set is a decrease in the number of output data points that were predicted by the network without being used to train the network. It is important to ensure that enough data points are not used for training in order to ensure that the model can be adequately validated. The best test for an ANN model is to apply a trained model to a new set of data for prediction.

Another set of conditions that can be varied are the specific algorithm parameters for the different models that can be created. In the case of the EBP model, the algorithm parameter that can be altered is the maximum percent error between the output target and the output prediction that is acceptable during training. By reducing the maximum acceptable percent error, the accuracy of the ANN model should increase, however, the time that is required to train the model will
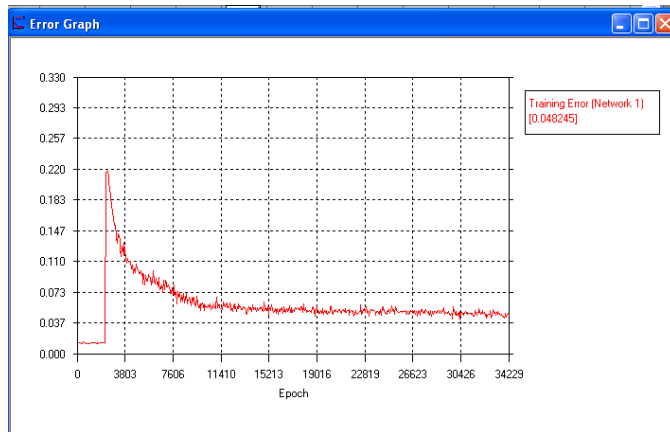

Figure 4: Training Error Plot in Neuframe

Note: The information contained in this report is proprietary and owned by the Lehigh University Energy Research Center and the Energy Research Company (ERCo).

increase. Figure 4 shows how the error in training can be monitored while the network is training. For ANN models using the RBF algorithm, the corresponding algorithm parameter is the size of the acceptable radius between points. In the case of the RBF model, the radius operates as a control on the maximum allowable difference between the desired output and the model's prediction. By lowering the acceptable radius, the RBF model is expected to be more accurate, however, the training time for the model will be increased accordingly.

A third option that can be used to optimize a neural network is to modify the network architecture. Figure 5 shows an example neural network in Neuframe. When modifying a neural network in this manner, the parameters that can be modified are the number of hidden layers in the model, the size of the hidden layers, or the transfer functions between the network layers.

The ANN model shown in Figure 5 is a standard 3 – layer EBP neural network. This means that it has a single input layer, a single hidden layer and an output layer. As can be seen in the Neuframe screenshot, the program gives the user the ability to modify the number of nodes in each layer and the transfer function between the layers. By modifying the number of hidden layers, or the number of nodes in the hidden layers, the complexity of the neural network can either by increased or deacreased accordingly. The other parameter that can be modified is the transfer function between the nodes in different layers of the network. The available transfer functions are
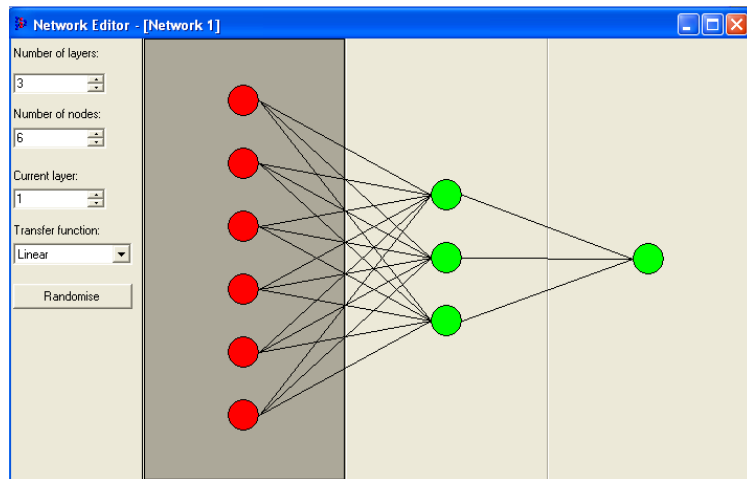

Figure 5: Example Neural Network in Neuframe

linear, sigmoid and tanh. Modifying the transfer function between layers changes how weights are applied to different quantities in the model. While it was not possible to determine the exact effect of modifying the network architecture on the results obtained from the neural network, the general observation that could be made was that more complex networks tended to be, the longer it took to train the networks.

Presentation and Discussion of Results

Artificial neural network models were developed for a total of eight output parameters. The parameters that were predicted using ANNs were Heating Value, Volatile Matter, Ash Content, Ash Fusion Temperature, Slagging Index, Iron content and Sulfur content. In developing ANN models, the input parameters used were all calculated values from the LIBS spectral data, and consisted of the silica ratio, base, acid, R250, Dolomite Ratio and intensity values for Carbon. Definitions for these input parameters can be found in Table 7. The ANN models that were developed for these 8 output parameters were used to predict values for the output based on the LIBS input values and were directly compared against values that were measured using the standard laboratory analysis techniques. In addition to ANN models, where possible, algebraic correlations from the literature were also used to predict the output parameters and were compared against laboratory measurements.

The general results for the ANN correlations are shown in Table 13. In all cases, the ANN models that were developed were 3 – layer models. Given the spread of the ANN model predictions, the plots showing the results all display the spread of the ANN data to ± 2σ. Both the R^2 correlation coefficient value and the root mean square error (RMSE) values shown were used to assess the performance of the ANN models. Root mean square error is a measure of the difference in the values predicted by a model versus values determined through actual observation. The formula for RMSE that was used is shown in Equation 27 below, where y_i and $\hat{y}_i$ are actual and predicted values respectively for a total of n sets of predictions.

$$RMSE = \sqrt{\frac{\sum_i^n (y_i - \hat{y}_i)^2}{n}} \qquad (Eq. 27)$$

Table 13: Summary of ANN model results

ANN Model (model type)	No. of Input Nodes	No. of Hidden layer nodes	Training Set Size	Testing Set Size	R^2 coefficient	RMSE value
HHV - (EBP)	6	3	30	20	0.988	76.16
VM – (EBP)	6	3	35	15	0.910	3.68
Ash – (EBP)	6	5	35	15	0.903	2.38
Tf – (EBP)	6	3	30	20	0.951	101.684
Fe_2O_3 – (RBF)	6	23	40	10	0.992	0.759
Slagging Index – (EBP)	6	3	40	10	0.96	0.171
S – (EBP)	6	3	40	10	0.95	0.261

The analysis for Heating Value of coal was conducted for the HHV of the samples on a moisture and ash free basis (MAF). The predictions from the ANN model were directly

compared against actual heating value data from laboratory analysis and the Dulong Formula (Eq. 1) from the literature. The Dulong Formula was selected for this comparison as it showed better results as compared to other formulas in the literature. In addition, the Dulong Formula is a more general formula and is applicable to many types of coal. In the case of the Dulong Formula, the output needed to be corrected for ash content as the formula predicts HHV on a dry basis only. The R^2 correlation coefficient value for the Dulong formula is 0.952. The results for the analysis for Heating Value can be seen in Figure 6.
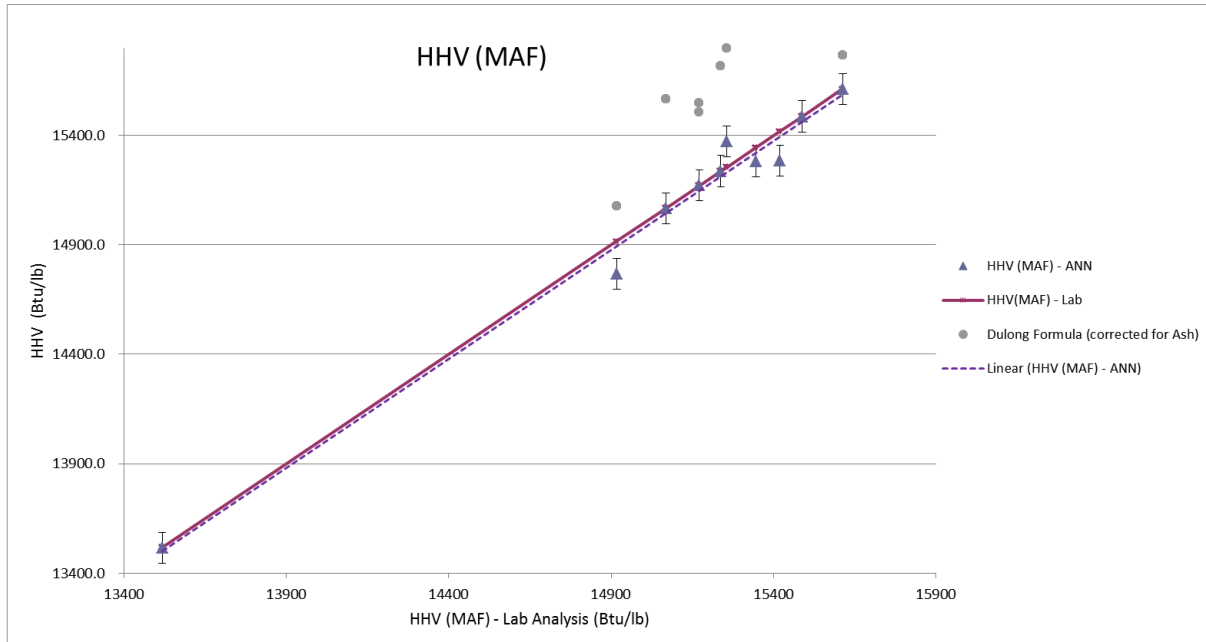
Figure 6: Results for HHV

Similarly, the ANN model for Volatile Matter was developed using the LIBS inputs and laboratory data for percent volatile matter on a dry basis. The ANN model predictions were compared against laboratory data and the Fisher-Vitrain correlation from the literature (Eq. 17). The results for the Volatile Matter are shown in Figure 7. The R^2 correlation coefficient for the Fisher correlation is 0.912.
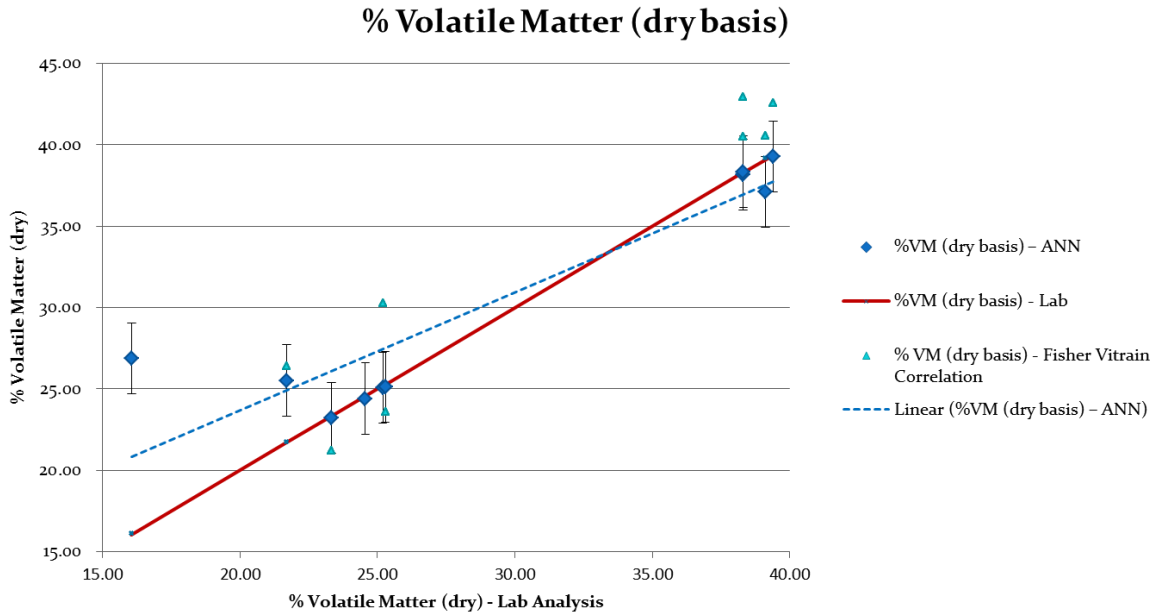
% Volatile Matter (dry basis)

Legend:
- ◆ %VM (dry basis) – ANN
- —— %VM (dry basis) - Lab
- ▲ % VM (dry basis) - Fisher Vitrain Correlation
- ----- Linear (%VM (dry basis) – ANN)

Figure 7: Results for %VM

The results for the ANN model for percent ash content are shown in Figure 8. In the case of ash content, the data from the ANN model were only compared against standard laboratory data for ash percent.
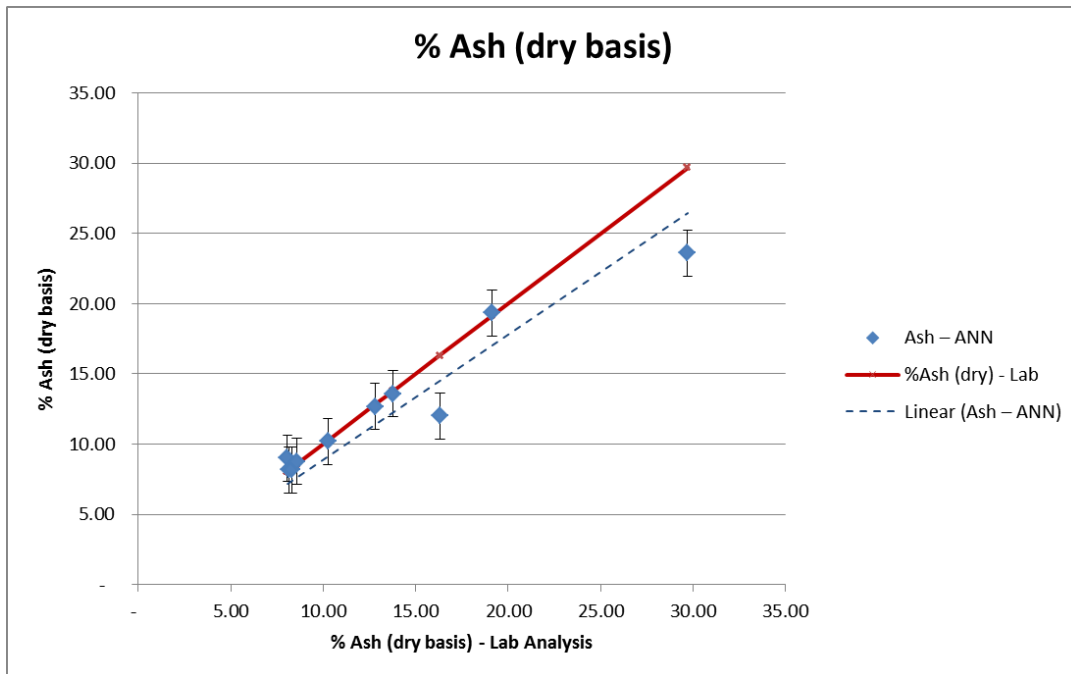

% Ash (dry basis)

Legend:
- ◆ Ash – ANN
- —— %Ash (dry) - Lab
- ----- Linear (Ash – ANN)

Figure 8: Results for Ash Content

Figure 9 shows the results for Ash Fusion Temperature (Tf). While there are 4 different types of ash fusion temperatures, the only one that was considered was the initial ash deformation temperature (IDT).
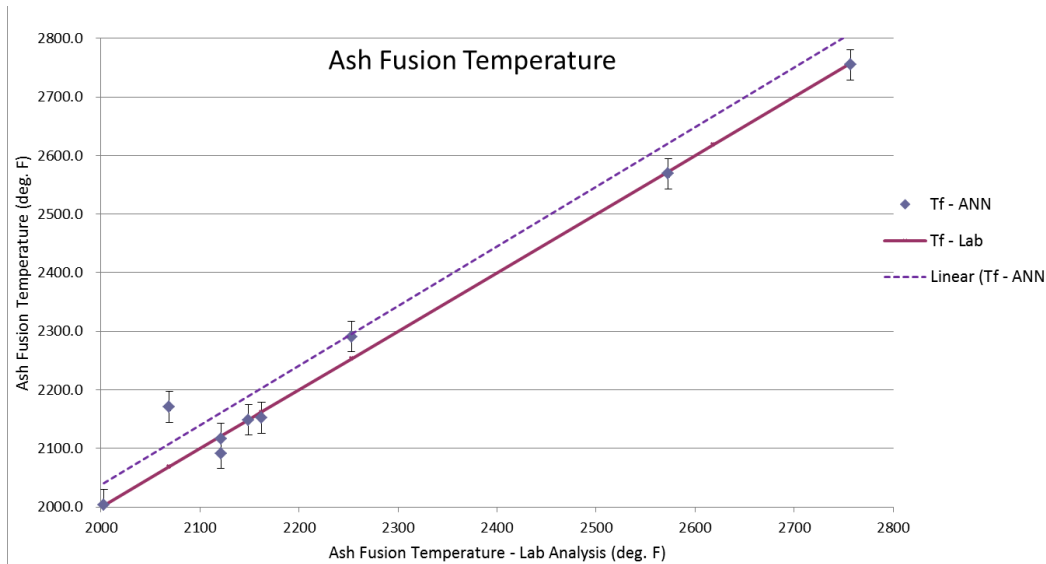

Figure 9: Results for Ash Fusion Temperature

The percent iron content in coal was determined by measuring the content of Fe_2O_3. The ANN model that was created to predict output values for Iron differed from the other models in that it was a RBF neural network. The model for Fe_2O_3 is compared against standard laboratory analysis for the same. Results are shown in Figure 10 below.
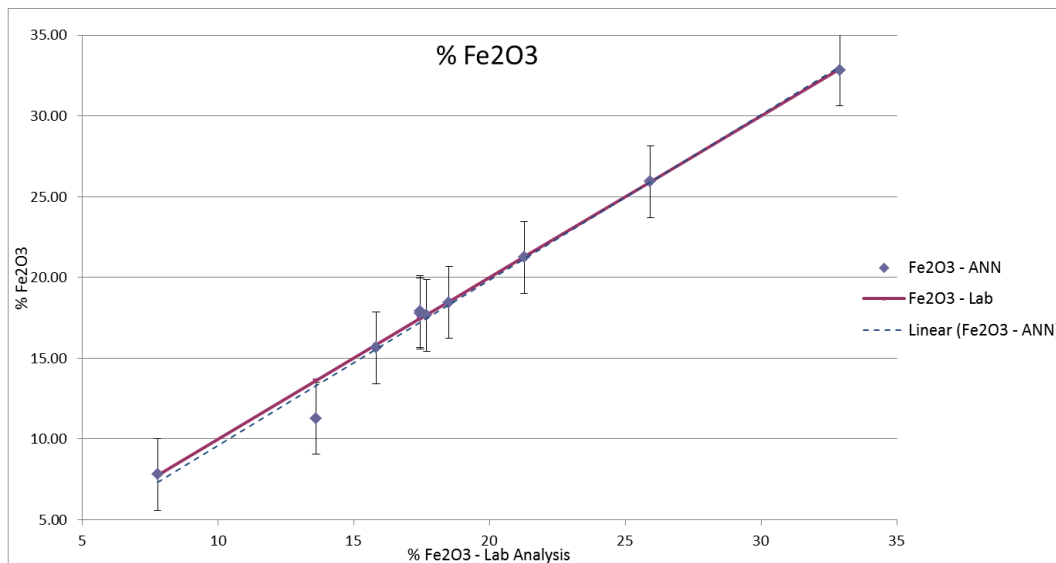

Figure 10: Results for Iron Content

The results for the model developed for the slagging index are shown in Figure 11 below. The predictions from the slagging index model were compared with standard laboratory data. The slagging index that was used in this analysis is comprised of the product between the base/acid ratio and the % Sulfur content of coal.
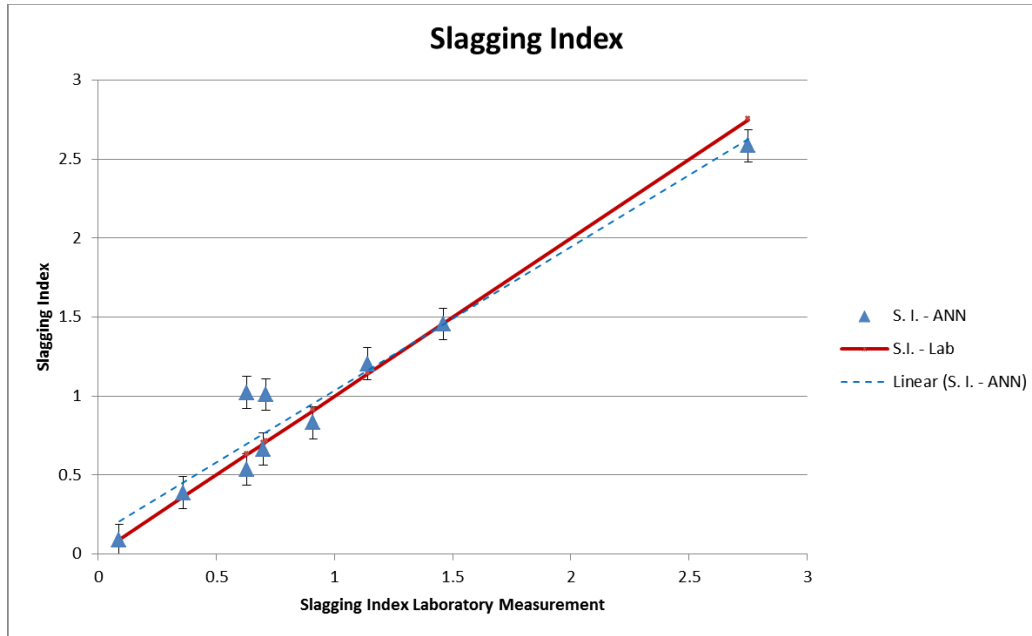

Figure 11: Results for Slagging Index

The final ANN model that was created was for the percent sulfur content. Once again, the predictions from the ANN model were compared directly against the laboratory data. Results for Sulfur are shown in Figure 12 below.
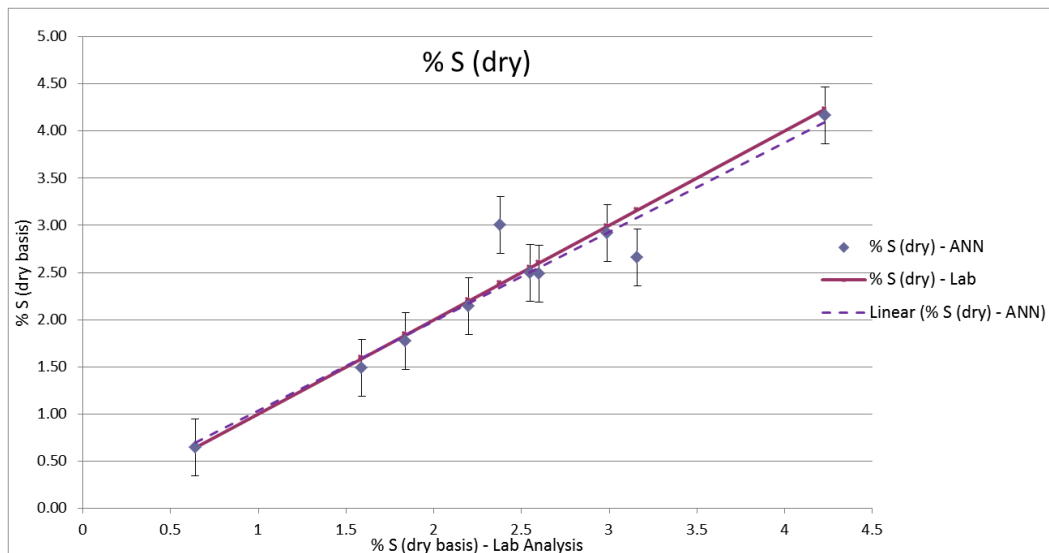

Figure 12: Results for Percent Sulfur

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Conclusions

Based on the results shown in the previous section, it is possible to conclude that for the most part, the ANN models for the output parameters are good estimators of the actual values of the parameters. While the values for the Pearson correlation coefficient (R^2) were relatively high, the spread of the data shows that the results from using these models will vary. The results show that the LIBS data, when input to an ANN model can be used to predict useful properties of coal. Further work will be required in order to optimize the ANN models by testing the models with a new LIBS dataset. By testing the ANN models with an entirely new data set that is removed from the sets used to train the networks, it will be possible to better determine the effectiveness of the neural network models' capability to make accurate predictions about the properties of coal.

In the case of HHV and % VM, where formulas from the literature were also compared, the results show that the predictions from the literature-based do not agree with conclusions that were drawn in the literature regarding these correlations. One possible reason why this is the case is that the data sets used to generate the correlations from the literature were both larger and less broad in terms of sampling as compared to the data used in this report. This difference could partially explain why the results in this report do not show the literature correlations to be as favorable as they are advertised to be.

ME 310 Project Summary

This project was completed in order to satisfy the requirements for the ME 310 project course in the Mechanical Engineering Department at Lehigh University. While this project did not require collaboration with other undergraduate or graduate students at Lehigh University, the work was completed with the Lehigh University Energy Research Center and required collaboration with faculty and staff from the same. Members of the Lehigh University ERC that were consulted for this project were Dr. Carlos Romero, and research scientist, Mr. Zheng Yao.

The initial conditions for this project included the testing setup for and data obtained from LIBS measurements and standard laboratory measurements. These earlier tests were conducted by the Energy Research Center, in collaboration with the Energy Research Company (ERCo). This project did not contain any data collection and was primarily focused on determining correlations between coal data and coal properties from the literature and using ANN models.

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