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Short communication

Simple models for estimating helium density of coals

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Abstract

In the present paper a set of 75 coal samples in the ASTM ranking range of anthracite to lignite from different countries have been used to obtain correlations between helium density (HD_{dmmf}) and compositional parameters in terms of H/C, O/C and O/H atomic ratios. Based on dry, mineral-matter-free (dmmf) basis helium density is estimated according to the following expression:

$$HD_{dmmf} = 1.5856 - 0.418462\left(\frac{H}{C}\right) + 0.468039\left(\frac{O}{C}\right) + 0.160189\left(\frac{O}{H}\right)$$

$$HD_{dmmf} = 1.6211 - 0.467168\left(\frac{H}{C}\right) + 0.692099\left(\frac{O}{C}\right)$$

The absolute average percentage errors and correlation coefficients of above two models are found to be 1.30; 0.96 and 1.31; 0.96 respectively. Statistical analysis and comparison of the models with other two earlier models suggest the superiority of present models over earlier one.

Keywords: Coal; Helium density; Modelling; Physical properties of coal; Correlation; Atomic ratio

1. Introduction

Helium density is considered to be an important fundamental property of coal. It is useful in giving information about the coal structure. In coal it varies in a systematic manner during coalification from lignite to anthracite. The porosity of coal can be predicted from the knowledge of helium density and particle density (mercury density). Helium density, therefore, is a property of the coal surface. Because of importance of helium density, it requires adequate attention while examining the structure of coal as well as in the area of coal utilization. Properties of coal surfaces play an important role in a number of coal utilization technologies. Coal flotation, coal liquid mixtures, hydrogenation, co-processing, coking properties, and coal dehydration all depend on the chemical nature of the coal surface. Because of its immense utility, several attempts have been made to estimate it, solely from a knowledge of the chemical composition of coal.

Neavel et al. [1] proposed a correlation for the estimation of helium density (HD_{dmmf}) using weight percentage of carbon, hydrogen, oxygen and sulphur elements in coal on dry, mineral-matter-free basis. The correlation may be expressed as

$$HD_{dmmf} = 0.01545\ (C) - 0.03709\ (H) + 0.02182\ (O) + 0.01573\ (S) \quad (1)$$

But, the correlation [1] does not hold good for low-rank coals. Mazumdar [2] stressed the need of precise estimation of helium density, so that, it can be used in routine evaluation of aromaticity (fa) of coal and other structural parameters. He gave following model for the estimation of helium density.

$$HD_{dmmf} = 1.714 - 0.686\left(\frac{H}{C}\right) + 1.0\left(\frac{O}{C}\right) + 1.0\left(\frac{N}{C}\right) + 0.5\left(\frac{H}{C} - 0.6\right)^2 \quad (2)$$

But, the accuracy of correlation [2] appears to fall off progressively in highly oxygenated coals. It also does not perform well with coals having low oxygen content.

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Oxygen is an integral component of coal, and its inclusion with other elements in the form of atomic ratios yielded better correlations between various parameters [3–5]. In relation to oxidation studies of coal, Singh [3] found good correlations between oxidation time and atomic ratios of H/C, O/C, O/H and O/S. Acidic functional groups are considered to be important characteristics in coal structure. This fact was validated by Singh [4] where he established a linear relationship between total acidity with the atomic O/H ratio, and carboxyl acidity with the O/C ratio. The correlation coefficients of these relationship were 0.996 and 0.98, respectively. In another studies, Singh and Kakati [5,6] found a correlation coefficient of 0.98 between specific energy and atomic ratios of O/C and O/H. In addition, Singh [7] established a linear relationship between acid equivalents of generated humic acids and the atomic O/C ratio. In microwave desulphurization studies Singh and Kakati [8–9] developed a number of strong correlations (correlation coefficient values between 0.97 and 0.99) between sulphatic, pyritic, organic and total desulphurization efficiencies and atomic ratios of H/C and O/C. In these studies they found strong correlation between pyritic sulphur removal efficiency and helium density with a correlation coefficient of 0.995. They also obtained [8] good correlation between organic sulphur efficiency and helium density with a correlation coefficient of 0.97.

In the process of coal hydrogenation Singh [10] found strong correlations between the total conversion and helium density with correlation coefficient of 0.97. He also established good correlation between benzene soluble product yield and helium density with correlation coefficient of 0.95. Recently Singh [11] established a linear relationship between the specific energy and helium density with a correlation coefficient of 0.996 for oxidised coals. Oxidised coals are equivalent to low rank coals. This is in agreement with the earlier statements of Neavel [12] who reported that oxidation is essentially equivalent to reducing the coal rank. Very recently, Singh and Kakati [13] found good correlation between mercury density (MD_{dmmf}) and compositional parameters of H/C, O/C and O/H atomic ratios with a correlation coefficient of 0.96 and absolute percentage error of 1.18%. In relation to the study of coal structure, Van Krevelen [14] recommended the use of dimensionless parameters, such as H/C and O/C ratios. Berkowitz [15] also stressed the use of atomic percentages instead of mass percentages.

In view of its importance and potentiality, an attempt has been made in the present study to correlate helium density (HD_{dmmf}) with atomic ratios of H/C, O/C and O/H.

1.1. Data and method

Coal is an organic rock and highly heterogeneous in nature containing carbon, hydrogen, oxygen, sulphur, nitrogen, and many minerals. Coals differ in 'rank' and there is no single parameter of rank. Rank generally refers to the percentage of carbon by weight and heating value of coal on a mineral-matter-free basis. The mineral matter content and composition generally change due to the reactions occurring in the process of coalification. In the process of coalification an increase in carbon content in coal resulted in a gradual reduction of oxygen. Partial oxidation or weathering of coal is a continous, and natural coalification process which can change the coal properties in terms of specific energy [5,6], helium density, acidity values [4], aromaticity, etc. This indicates that oxygen is an integral component of coal and therefore, its association with other elements, in terms of atomic ratios may be a better correlation variable between related parameters. The molecular structure of coal on the other hand can also be adequately represented by atomic O/C ratio [14] and helium density [2].

Accordingly a wide selection of 75 coals of different ranks varing from lignite to anthracite from different countries USA [16–19] (lignite to anthracite), Japan [20] (lignite to anthracite) and Canada [21] (lignite to semi-anthracite) were considered for the development of the model. The ultimate analysis and helium density on dry-mineral-matter-free basis(dmmf) of various coals are presented in Table 1. The ranges of composition, helium density, and atomic ratios of H/C, O/C and O/H on dmmf basis are given in Table 2. The parr formula was used for conversion to the dmmf basis. This basis was selected because in general, models utilizing the ultimate analysis and dmmf basis perform better than those using the proximate analysis and dry basis. Neavel et al. [22] made a comparison of the estimation of oxygen by difference against the oxygen by neutron activation and reported that it serves as an independent check on the accuracy of the combined elemental analyses. The overall mean difference for the 66 coals was — 1% with a standard deviation of 0.93 about the mean. They further mentioned that the estimate of oxygen content by difference did not significantly reduce the accuracy of the estimation procedure, and was more practical than more complex estimates. Because of comparable accuracy of oxygen estimation by difference, Neavel et al. [1], Mazumder [2] and Singh [3,4,7,10,11] and Singh and Kakati [5,6,8,9,13] used the oxygen content data based on difference in their correlations. It means the oxygen estimation by difference is well within the range of experimental errors. Added to this, the correlations, where ratios of elements in terms of H/C, O/C and O/H are involved, the error will be further minimised because of association of errors both in the numerator and denominator in the equation. Hence, the oxygen contents determined by difference was used in the proposed models. Therefore, compositional parameters in terms of the atomic ratios H/C, O/C, O/H, O/S, S/C and N/C were selected for development of the model.

The measured value of true density depends upon the measuring fluid to be used for determining the true density. The fluid to be used, should not react chemically, should not be adsorbed on the material and it should have very small molecular size. Small molecular size of the fluid is necessary,

Table 1
Elemental analysis and helium density of 75 coals

Sl No.	C	H	S	N	O	HD_{dmmf}
1	80.61	5.59	5.59	1.60	6.61	1.3050
2	79.44	5.19	0.22	1.22	13.93	1.3360
3	87.84	5.07	0.95	1.42	4.72	1.2820
4	90.92	4.70	0.66	1.31	2.41	1.3160
5	91.97	4.75	0.91	1.92	.45	1.3470
6	84.59	5.66	2.46	2.12	5.17	1.2852
7	85.46	5.78	1.34	1.89	5.53	1.3012
8	88.45	5.93	1.40	1.91	2.31	1.3101
9	86.66	5.95	1.27	1.89	4.23	1.3035
10	87.67	5.72	0.68	1.87	4.06	1.2847
11	89.06	5.52	0.43	2.01	2.98	1.3157
12	89.20	5.40	0.64	1.90	2.56	1.3067
13	91.72	4.67	0.39	1.57	1.65	1.3246
14	91.60	4.64	0.70	1.52	.54	1.3666
15	92.63	4.04	0.69	1.42	1.22	1.4007
16	89.50	5.00	0.83	1.00	3.67	1.3300
17	88.30	4.90	0.65	0.25	5.90	1.3200
18	83.80	5.70	0.88	1.50	8.12	1.2800
19	81.30	5.70	1.80	1.00	10.00	1.2700
20	79.90	5.20	4.30	1.50	9.10	1.2500
21	77.20	5.60	7.40	1.10	7.40	1.2700
22	75.50	5.30	3.30	1.00	14.90	1.3000
23	71.70	5.20	0.90	1.30	20.90	1.3500
24	71.20	5.20	0.69	0.56	22.35	1.4000
25	92.36	3.81	1.12	0.61	2.10	1.3811
26	89.51	4.70	1.73	1.71	2.35	1.3260
27	88.04	5.26	1.06	1.72	3.92	1.2947
28	86.50	5.42	1.55	2.15	4.38	1.2802
29	81.92	5.71	1.26	1.72	9.39	1.2915
30	79.33	5.38	0.84	1.46	12.99	1.3226
31	75.44	5.13	0.66	1.74	17.03	1.3388
32	74.45	5.43	0.57	1.68	17.87	1.3345
33	71.52	4.82	0.66	1.52	21.48	1.3652
34	72.70	5.10	0.50	1.60	20.10	1.3469
35	76.80	5.90	0.40	1.30	15.60	1.2884
36	77.80	6.00	0.20	1.10	14.90	1.2676
37	78.10	5.90	2.70	0.80	12.50	1.2797
38	79.80	5.50	0.90	1.00	12.80	1.2999
39	81.10	6.00	0.30	1.60	11.00	1.2731
40	83.40	6.20	0.30	1.70	8.40	1.2779
41	84.50	6.10	1.10	1.20	7.10	1.2631
42	86.20	6.30	0.30	1.90	5.30	1.2741
43	87.20	5.80	0.30	1.30	5.40	1.2861
44	86.60	5.80	0.70	1.60	5.30	1.2950
45	87.60	5.30	0.30	1.70	5.10	1.3091
46	88.40	5.20	0.50	1.60	4.30	1.3084
47	89.00	5.00	0.70	1.70	3.60	1.3176
48	90.70	4.80	0.70	1.30	2.50	1.3459
49	70.80	4.60	1.20	1.20	22.20	1.4391
50	72.70	5.20	0.80	1.50	19.80	1.4037
51	75.80	5.10	0.50	1.70	16.90	1.4295
52	71.60	4.20	0.40	1.70	22.10	1.4547
53	75.00	4.40	0.20	1.10	19.30	1.4513
54	73.40	4.40	1.20	1.80	19.20	1.4482
55	75.70	4.10	0.50	1.20	18.50	1.4697
56	74.40	5.00	0.60	1.50	18.50	1.4176
57	73.70	4.60	0.80	1.40	19.50	1.4063
58	74.10	4.30	0.50	2.00	19.10	1.4348
59	75.80	5.40	0.90	1.80	16.10	1.3709
60	76.00	4.40	0.10	1.50	18.00	1.4047
61	75.90	4.40	0.30	1.70	17.70	1.4295
62	76.60	4.40	0.10	1.80	17.10	1.4174
63	75.80	4.70	0.50	1.70	17.30	1.4098
64	72.80	5.20	1.00	1.00	20.00	1.3830
65	70.90	5.00	1.10	1.10	21.90	1.3916
66	69.60	4.00	1.10	1.30	23.60	1.4428
67	73.70	5.60	0.20	0.80	19.70	1.3579
68	74.80	4.40	0.20	1.00	19.60	1.4186
69	76.50	5.60	4.50	1.20	12.20	1.2900
70	63.30	4.60	1.50	0.47	30.13	1.4500
71	83.90	2.20	0.10	1.50	12.30	1.5613
72	78.20	3.00	0.20	1.50	17.10	1.5093
73	78.50	2.90	0.80	1.70	16.10	1.5233
74	83.70	2.40	0.70	1.90	11.30	1.5385
75	86.30	2.20	0.60	2.20	8.70	1.5534

Table 2
Ranges of composition, atomic ratios, ASTM ranking and helium density of 75 coal samples

Characteristics	Minimum	Maximum
Ultimate analysis (wt.% dmmf)		
Carbon	63.3	92.63
Hydrogen	2.2	6.30
Nitrogen	0.25	2.20
Sulphur	0.10	7.40
Oxygen (by difference)	0.45	30.13
H/C (atomic ratio)	0.3038	0.9190
O/C (atomic ratio)	0.0037	0.3570
O/H (atomic ratio)	0.0060	0.3711
ASTM ranking	Lignite	Anthracite
Helium density	Hd_{dmmf} 1.25	1.4007

because, it can penetrate the fine pores of the material whose density is to be determined. Helium, with a kinetic diameter of 0.26 nm can rapidly penetrate the open pore structure of coal [20,21]. The true density was obtained experimentally determined by Neavel et al. [1], Parkash [16], Agrawal [17], Fujii and Tsuboi [20] and Ng et al. [21] using helium displacement method in a volumetric apparatus. The measured values then corrected for mineral matter content basis. Accordingly, the following correlation formula was used to correct the measured density for mineral matter content.

$$HD_{dmmf} = 3 \times HD_{mmc} \frac{(100 - A)}{(300 - A \times HD_{dmmc} A)}$$

where, HD_{dmmf} is the correct density of coal on dry-mineral-matter-fre basis. HD_{mmc} is the measured density of coal on mineral matter content basis. A represents the weight percent of ash in the coal.

1.2. Model development

The application of principal component analysis (PCA) reveals that first three atomic ratios H/C, O/C and O/H are of great significance contributing together of 90.6% of the original variance in the original data set. Next three atomic ratios O/S, S/C and N/C together describe rest 9.4% of the total variance. Considering the small contribution of the fourth and subsequent variables (O/S, S/C and N/C), they were

Table 3
Performance parameters of various models for predicting helium density generated from the same data set of 75 coal samples

Eq. No.	Basis	Absolute avg. % error	% Deviation		Coal samples giving error				Data points		Correlation Coefficient	Source
			Min.	Max.	<1%	<2%	2% to 3%	>3%	under estd.	over estd.		
Eq. (1)	dmmf	2.52	−4.62	7.37	22.67	40.00	60.00	26.67	36.0	64.0	0.88	Neavel [1]
Eq. (2)	dmmf	2.54	−5.74	8.00	24.00	46.67	53.33	34.67	29.33	70.67	0.94	Mazumdar [2]
Eq. (3)	dmmf	1.30	−5.49	3.49	44.00	81.33	18.67	5.33	48.00	52.00	0.96	Present work
Eq. (4)	dmmf	1.31	−5.40	3.71	42.67	78.67	21.33	5.33	50.70	49.30	0.96	Present work

excluded as critical variables. These findings are in good agreement with the work of Haenel [23] who reported that the change in concentration of sulphur and nitrogen with coalification is less significant.

Thus, the helium density can be described as a combination of three atomic ratios of H/C, O/C and O/H. Through inspection of the correlation matrix of the components, it was found that atomic ratios of H/C, O/C and O/H are of prime importance.

Accordingly, the following simple and multiple linear regression models with correlation coefficients of 0.96 in each case were obtained:

$$\mathrm{HD_{dmmf}} = 1.5856 - 0.418462\left(\frac{\mathrm{H}}{\mathrm{C}}\right) + 0.468039\left(\frac{\mathrm{O}}{\mathrm{C}}\right) + 0.160189\left(\frac{\mathrm{O}}{\mathrm{H}}\right) \quad (3)$$

$$\mathrm{HD_{dmmf}} = 1.6211 - 0.467168\left(\frac{\mathrm{H}}{\mathrm{C}}\right) + 0.692099\left(\frac{\mathrm{O}}{\mathrm{C}}\right) \quad (4)$$

The coefficients of these equations are statistically significant (using the *t*-test) at the 0.001 level. Another multiple linear regression equation including O/S, S/C and N/C was also considered, but was not significant at 0.05 level. It is evident from Eq. (3) that the coefficient of atomic O/C is the greatest and that of atomic O/H ratio is the lowest. The absolute average % error, standard deviation, correlation coefficients, and other performance parameters of earlier models1-2, and the new models shown in Eqs. (3) and (4) are given in Table 3. The tabulation is based on both the experimental published data [16–21] (ultimate analysis and experimental values of helium density) and estimated values (predicted helium density, avg. % error, % deviation, % error, data points under and over estimated, correlation coefficients) for all the four Eqs. (1) to (4). The performance parameters listed in Table 3 are based on the same data set of 75 coal samples.

2. Results and discussion

Performance of various models can be easily highlighted through Table 3. It is seen from Table 3 that Eqs. (1) and (2) gave the absolute average % error of 2.52% and 2.54%, whereas new models Eqs. (3) and (4) yielded the error values of 1.30% and 1.31%, respectively. On comparison of Eqs. (3) and (4), it is seen that the introduction of atomic O/H ratio as an additional variable in Eq. (3), resulted a marginal improvement in the absolute average percentage error of 0.01%. In terms of percentage minimum and maximum deviations values in both the new Eqs. (3) and (4) are again found to be superior to the earlier Eqs. (1) and (2).

The column labelled <1%; >1% but <2%; >2% but <3% and >3% in Table 3 show the percentage samples within a specified error range predicted by earlier and new models. It is clear from Table 3 that using Eqs. (1) and (2), 22.67% and 24% coal samples gave <1% error. In the case of Eqs. (3) and (4), the number of coal samples which yielded error <1% is found to be 44% and 42.67%, respectively. Likewise using Eqs. (1) and (2), 40% and 46% coal samples gave <2% error. But in the case of Eq. (3) and (4) the number of coal samples which gave errors <2% are found to be 81.33% and 78.67%, respectively. Similarly, using Eqs. (1) and (2), 26.67% and 34.67% of coal samples gave >3% error. But, in case of Eqs. (3) and (4), only 5.33% of coal samples yielded error >3%. On comparison of Eq. (3) and (4), it is clear that the introduction of atomic O/H ratio in Eq. (3) is found to be beneficial in reducing the errors at various column labelled <1%, <2%; and between 2% and 3%.

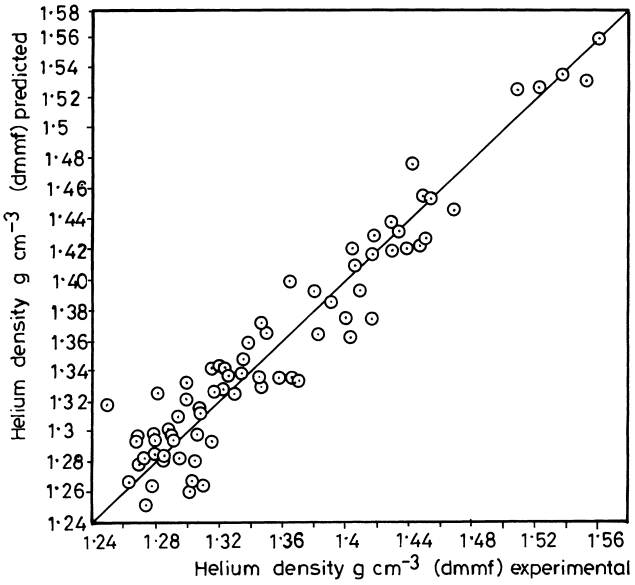

Fig. 1. Relation between experimental values of helium density ($\mathrm{HD_{dmmf}}$) and those predicted by Eq. (3).

In relation to the percentage data points under or over estimated, it is clear that all the earlier models are seriously biased whereas models 3 & 4 perform well.

It is clear from Table 3 that the earlier models, that of Neavel [1] gives the lowest correlation coefficient (0.88) and that of Mazumdar [2] the highest (0.94) for 75 coal samples considered in the present study. It is important to note that for the same data set, the correlation coefficients of both the new models Eqs (3) and (4) are 0.96, greater than those for earlier models, Eqs. (1) and (2). The relation between experimental and predicted values of helium density on dmmf basis computed by Eq. (3) is presented in Fig. 1. It is clear that the relation is linear with a slope of nearly unity, indicating a good fit.

3. Conclusions

The accuracy of the newly developed correlations, particularly Eq. (3), to estimate the helium density (HD_{dmmf}) of coal is excellent and superior to that of earlier Eqs. (1) and (2). Considering all the performance parameters, Eq. (3) can be recommended as the best model for prediction of the helium density (HD_{dmmf}). This model does not require the additional parameters of (O/S) and (N/C) atomic ratios. It is now possible to predict helium density (HD_{dmmf}) of coal from the knowledge of H/C, O/C and O/H atomic ratios only. The developed models will be of great value, in predicting helium density (HD_{dmmf}) of coals without doing laborious and expensive experimental determinations. The use of mathematical models will be of great significance to engineers and designers who are not directly involved in the research and development and have data of ultimate analysis but also require data for helium density.

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