# AN OXY-HYDROCARBON MODEL OF FOSSIL FUELS

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**Abstract**

This paper asserts a new method of analyzing fossil fuels, useful for sorting coals into well defined categories and for the identification of outlying ultimate analysis data. It describes a series of techniques starting with a new multi-variant approach for describing the lower Ranks of coal, progressing to a classical, but modified, single-variant approach for the volatile and high energy Ranks. In addition, for a few special cases, multiple low and high Ranks are also well described by the multi-variant approach. As useful as these techniques are for analyzing fuel chemistry in the laboratory arena, this work was initiated in support of Exergetic Systems' Input/Loss Method. At commercial coal-fired power plants, Input/Loss allows the determination of fuel chemistry based on effluents. The methods presented allow equations to be developed independent of actual combustion stoichiometrics, for improved Input/Loss accuracy in determining "real fuel in real time". PAPER72_Rev30.WPD

**Introduction**

Historically coal chemistry associated with low and non-volatile Ranks has defied descriptive analytics. For these fuels, there has been no technique allowing a predictive capability for fuel chemistry. For example, as seen in Figure 1, Irish Peat has a considerable variability (hydrogen versus carbon) even though the fuel was laid down at broadly the same time across the island. Similarly, a coal mined from the Decker region of the Powder River Basin (PRB) in North America, having an average of 70% dry fuel carbon by weight, cannot reasonably be compared to a coal mined from the Buckskin region of the same PRB having an average of 64% dry carbon. These two PRB coals differ in average dry calorific values by 5.6% (>1535 $\Delta$kJ/kg or >660 $\Delta$Btu/lbm). Figure 2 presents graphical results from several hundred ultimate analyses of coals from 17 PRB regions.

As a further example, there has been little success in explaining the vagaries found in fuel chemistry associated with high energy coals, of the same Rank, but obtained from different continents, herein termed "High Seas" coals. High Seas coals are internationally traded high energy, low water, bituminous coals (similar to hvAb & hvBb), which are often purchased literally when cargo ships are underway. Although High Seas coals typically have uniformity of calorific values, Figure 3 illustrates a significant variability in fuel chemistry. Note that Figures 1 and 2 show poor Coefficients of Determination ($R^2$), 62% for Irish Peat and 77% for PRB coals. The $R^2$ value for the High Seas coals of Figure 3 is better at 91%. However, experience with installing Input/Loss indicated fuels of moderate energy, down to the lignites, the highest $R^2$ for these classical plots rarely exceeded 85% [1].

Davidson [2], in a most comprehensive literature review of the chemistry of coal, notes that several authorities report there appears "to be no accurate method for the determination of molecular weights of coals". Although the authors agree that seeking an <u>absolute</u> molecular weight for a particular coal Rank is a fool's errand, we believe that a consistent <u>normalized</u> molecular weight, if consistently demonstrated, offers the touch-stone for substantiating descriptive analytics. It is true that the examination of molecular patterns of whole Ranks reveals an incredible complexity of interstitial layering, aromatic and aliphatic structures, which suggests that coal is a heterogeneous substance at both the macroscopic and microscopic levels. Nevertheless, we argue that at least at the macroscopic level, a consistently computed molecular
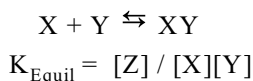
weight, normalized to carbon, offers valid over-checks.

Prior attempts at describing solid fuel chemistry may be reduced to three broad disciplines: a) oxidation pattern recognition, b) molecular structuring models, and c) elemental plots, classically hydrogen versus carbon. Oxidation pattern recognition is exemplified by van Krevelen Diagrams (hydrogen/carbon versus oxygen/carbon plots) [3,4]. However from the view point of descriptive analytics, unmodified van Krevelen Diagrams are not of value, yielding, for example, a Coefficient of Determination ($R^2$) of 33% for Irish Peat, and only 3% for PRB coals. Molecular structuring studies [5] although offering little in terms of analytics per se, have provided solution insight for this work. In this regard, of particular note is the excellent work by Shinn [6].

**An Oxy-Hydrocarbon Approach**

Our ambition was to achieve a fundamental understanding of solid fossil fuels at a molecular level. Throughout, only laboratory generated ultimate analyses were used. It is noted that prior works involving elemental analysis have focused on single-variant relationships: hydrogen = $f$(carbon), oxygen = $f$(carbon), and the like. In the Venn world this is saying that the intersection of a set of carbon concentrations $\{C\}$ and a set of hydrogen concentrations $\{H\}$ is somehow descriptive of the fuel's molecular pattern. Although adequate for high energy coals having low moisture-ash-free (MAF) oxygen, as a two component system it offers little to a molecular understanding of the lower Ranks. Reasons for this include: 1) low Rank coals have high MAF oxygen which must be considered; and 2) volatile Ranks (lvb, mvb, hvAb, hvBb, hvCb) have complexity in –O–, =O and –OH bonding which must be addressed.

This research evolved a recognition that coal's constituents might respond predictably by viewing classical chemical equilibrium of two components, X & Y, not in terms of a resultant XY, but rather in terms of their common tertiary component Z; Z having signatory functionality when considering X to Y bonding patterns. As we shall see, this concept is most applicable to coals having "measurable" concentrations of oxygen and thus favors the lower and middle Ranks. At geological equilibrium ($K_{Equil}$) this thought can be expressed by:

$$X + Y \leftrightarrows XY$$
$$K_{Equil} = [Z] / [X][Y]$$

Simply put, it was believed that multi-variant relationships descriptive of molecular bonding were crucial as explained through their tertiary component. Thus, for example, the intersection of <u>combined</u> carbon plus oxygen concentrations, a set $\{C + O\}$, versus a set of hydrogen concentrations $\{H\}$, properly describes molecular patterns.

It is proposed that a unique relationship exists between C–O and C=O chemical bonds and fuel hydrogen, that is, for all C–O and C=O bonds found in a given Rank of coal, a unique relationship exists with its particular hydrogen content. And concomitantly, oxygen and hydrogen bonds (–O–, –H– and –OH) form as a function of the material's particular carbon content.

However, when considering the system of C–H bonding as a function of fuel oxygen, the presence of the hydroxyl group must be taken into account as it affects the independence of the tertiary oxygen. It has been well established that the hydroxyl group influences the poorer Ranks, but declines through the non-volatile Ranks until it is essentially non-existent in anthracite [7,8]. Such findings derive from extraordinary laboratory analysis, not routine industrial testing (e.g., ASTM D3176 [9]). For the case of the volatile Ranks undergoing pyrolysis, it is assumed that the volatiles will disengage predominately at the –O– bond [10], forming a hydroxyl. The authors believe that there is a hydroxyl influence on reported ultimate analyses for volatile Ranks given the effects of vigorous laboratory heating associated with industrial testing (while reducing moisture during sample preparation). This has influenced our Oxy-Hydrocarbon Model as discussed below.

In summary, we suggest a multi-variant approach to fossil fuel analytics. This is saying that uniqueness lies in the chemical bonding patterns, not in $\{C\}$, $\{H\}$ and $\{O\}$ as separate data sets, but rather in what is clearly observed when the set $\{C + O\}$ representing chemical bonds are related to the tertiary $\{H\}$. Thus when taken in combination, bonding patterns play out descriptive of a unique fuel. Furthermore, the intersection of sets leads directly to a normalized molecular weight (based on C, H and O).

Multi-variant plots employing MAF molar quantities produce outstanding fits as observed through Coefficients of Determination; $R^2$ values are typically greater than 98%. For example, Figure 4 is a plot of Irish peat, of MAF molar diatomic hydrogen <u>plus</u> MAF molar diatomic oxygen versus MAF molar carbon showing an $R^2$ value of 98.91%; see Eq.(1) below. Figure 5 for PRB coals produces an $R^2$ value of 99.77%. Figure 6 for High Seas coals produces an $R^2$ value of 99.78%. Note that all plots were produced using the same databases.

Further, it was found that MAF molar carbon plus MAF molar diatomic oxygen versus MAF molar diatomic hydrogen was equally successful; see Eq.(2) below. This latter technique was then extended to an even broader range of fuels; for set $\{C + O\}$ the collection of an, sa, subA, subB, subC & ligA fuels present an equal potential.

Note that in these equations and graphs, hydrogen and oxygen quantities are expressed in the diatomic rather than monatomic, but only as a convenience for consistency with stoichiometric relationships used by the Input/Loss Method. Clearly, $R^2$ values using the monatomic will be identical (care being taken in conserving a consistent MAF base).

Although the MAF molar carbon plus MAF molar diatomic hydrogen versus MAF molar diatomic oxygen, Eq.(3), was successful for non-volatile Ranks, $R^2$ values were not consistently as high as for Eq.(1) or Eq.(2). To address the fact that the –OH radical forms at the expense of C–H bonding, a so-called "hydroxyl factor" ($I_{OHC4}$) was placed on the hydrogen term, then correlated against the oxygen/carbon ratio; see Eq.(4). Correlations were also studied against oxygen. The use of the oxygen/carbon ratio is no panacea. With a unity hydroxyl factor, $R^2$ produced using Eq.(4) is actually less than that produced using Eq.(3) for many Ranks. However, in combination with an optimized hydroxyl factor, a net improvement is seen for the lower and mid-Ranks. For example, the worth of using the oxygen/carbon ratio for PRB coal (versus just oxygen) was 12%, the balance attributable to an optimized $I_{OHC4}$. In summary, use of Eq.(4) increased $R^2$ values significantly for the well oxygenated Irish Peat, Greek lignite and lignite A as would be hoped; marginal improvement was observed for the mid-Ranks, non-volatile coals. Notably the hydroxyl factor appears reasonably behaved, trending to unity for the high Ranks. An exception is the High Seas coal which, being similar to hvAb and hvBb, may well be influenced by industrial testing methods.

In achieving multi-variant fits of ultimate analysis data with $R^2$ values of 98% and better, it is proposed that this level of predictability not only portends a molecular understanding of the Oxy-Hydrocarbon composition of the fuel but also reflects the homogeneity of the originating organic material. This is clearly the case for the non-volatiles. Indeed, even given the vagaries of notoriously variable fuels such as Powder River Basin coals, it was hoped that a basic O-H-C pattern would arise, a genesis understanding at the MAF level, and it does.

We have termed these relationships the Oxy-Hydrocarbon (OHC) Model. The OHC Model is described by the following relationships:

$$\alpha_{MAF-H} + \alpha_{MAF-O} = J_{OHC1} + K_{OHC1}\,\alpha_{MAF-C} \quad (1)$$
$$\alpha_{MAF-C} + \alpha_{MAF-O} = J_{OHC2} + K_{OHC2}\,\alpha_{MAF-H} \quad (2)$$
$$\alpha_{MAF-C} + \alpha_{MAF-H} = J_{OHC3} + K_{OHC3}\,\alpha_{MAF-O} \quad (3)$$
$$\alpha_{MAF-C} + I_{OHC4}\,\alpha_{MAF-H}$$
$$= J_{OHC4} + K_{OHC4}\,(\alpha_{MAF-O}/\alpha_{MAF-C}) \quad (4)$$

where:

$\alpha_{MAF-C}$ = Moles of carbon per mole of MAF fuel
$\alpha_{MAF-H}$ = Moles of $H_2$ per mole of MAF fuel

$\alpha_{MAF-O}$ = Moles of $O_2$ per mole of MAF fuel
$I_{OHCk}$ => Hydroxyl factor chosen to maximize $R^2$
$J_{OHCk}$ & $K_{OHCk}$ => Regression constants.

**Tabulated Results by Rank**

High consistency has been found for a number of fossil fuels as shown in Tables 1, 2 and 3. All but the (C + $H_2$) relationships of Table 3 produce $R^2$ values predominately greater than 98%. Table 4 presents results of applying Eq.(4). As discussed, the predictive worth of Eq.(4) for non-volatile Ranks diminishes as fuel oxygen decreases and for low oxygen fuels may be easily replaced by Eq.(3). Indicated are the improvements in $R^2$ values as compared with Eq.(3). In summary, these equations describe the inherent carbon, hydrogen and oxygen make-up of a fossil fuel, its Oxy-Hydrocarbon construct.

**Mathematical Singularity**

An obvious criticism of these analyses is, given that MAF C + $H_2$ + $O_2$ + $N_2$ + S = 1.0, it becomes obvious that a plot of (C + $H_2$) versus ($O_2$ + $N_2$ + S) produces a straight line with a negative unity slope, unity intercept and unity $R^2$ ... a question of mathematical singularity arises. Arguments allowing resolution of such criticism include:

a) The sum of nitrogen and sulphur, listed in Table 3, is generally less than 1%, supporting the criticism, especially considering that oxygen is determined by difference; i.e., suffering from an accumulation of errors. However, this sum does not yield the intercept $J_{OHC3}$, given zero oxygen; indeed there is no observable correlation between this sum and Eq.(3)'s intercept. Note that the sum of oxygen, nitrogen and sulphur, ranging from 13.7% for peat, to 1.4% for anthracite, again offers no observable correlation with $J_{OHCk}$ or $K_{OHCk}$.

b) The variation in the slopes ($K_{OHCk}$) associated with Eqs.(1) & (2) is not consistent, presumably representative of natural variations in the fuels. No slopes are the same for a given Rank: $K_{OHC1}$, $K_{OHC2}$, $K_{OHC3}$. Further, consider that for Irish Peat: $K_{OHC1} < K_{OHC2} < K_{OHC3}$. However such patterns are far from the norm as seen with sub-bit A, etc., again supporting natural variations.

c) If false information is being generated, then plotting different Ranks on the same figure should reveal visual inconsistencies, thus supporting (or not) the technique's ability to identify outlying data associated with a given Rank. Figure 7 demonstrates that plotting

**TABLE 1:**
**MAF Molar Fuel Diatomic Hydrogen + Diatomic Oxygen**
**versus MAF Molar Fuel Carbon**

| Rank | $J_{OHC1}$ | $K_{OHC1}$ | $R^2$ (%) |
|---|---|---|---|
| Irish Peat | 1.026586 | -1.062057 | 98.91 |
| Greek Lignite (ligB) | 0.971701 | -0.978878 | 99.19 |
| Lignite A (ligA) | 0.967175 | -0.961524 | 97.53 |
| Sub-bituminous C (subC) | 0.978943 | -0.980892 | 98.17 |
| Sub-bituminous B (subB) | 0.989200 | -0.995069 | 99.43 |
| Powder River Basin | 0.986835 | -0.988635 | 99.77 |
| Sub-bituminous A (subA) | 0.990659 | -0.997212 | 99.50 |
| High Seas Commercial | 1.009397 | -1.025647 | 99.78 |
| Semi-anthracite (sa) | 0.986130 | -0.991377 | 98.60 |
| Anthracite (an) | 0.989047 | -0.993931 | 99.80 |

**TABLE 2:**
**MAF Molar Fuel Carbon + Diatomic Oxygen**
**versus MAF Molar Fuel Diatomic Hydrogen**

| Rank | $J_{OHC2}$ | $K_{OHC2}$ | $R^2$ (%) |
|---|---|---|---|
| Irish Peat | 0.972121 | -0.935400 | 97.09 |
| Greek lignite (ligB) | 0.988563 | -1.016521 | 97.23 |
| Lignite A (ligA) | 1.000259 | -1.029894 | 98.04 |
| Sub-bituminous C (subC) | 0.996934 | -1.020298 | 98.47 |
| Sub-bituminous B (subB) | 0.992464 | -1.000103 | 99.33 |
| Powder River Basin | 0.996057 | -1.006130 | 99.73 |
| Sub-bituminous A (subA) | 0.994627 | -1.008012 | 99.42 |
| High Seas Commercial | 0.980482 | -0.958190 | 99.71 |
| Semi-anthracite (sa) | 0.993794 | -1.004406 | 97.99 |
| Anthracite (an) | 0.994791 | -1.003952 | 99.74 |
| Generic Non-Volatile (an, sa, subA, subB, subC, ligA) | 0.995497 | -1.011011 | 99.95 |

**TABLE 3:**
**MAF Molar Fuel Carbon + Diatomic Hydrogen**
**versus MAF Molar Fuel Diatomic Oxygen, Eq.(3), and Residuals**

| Rank | $J_{OHC3}$ | $K_{OHC3}$ | $R^2$ (%) | $N_2$ + S | $O_2 + N_2 + S$ |
|------|-----------|-----------|-----------|-----------|------------------|
| Irish Peat | 0.979681 | -0.903732 | 96.86 | 0.0079 | 0.1374 |
| Greek Lignite (ligB) | 0.986963 | -1.028534 | 97.45 | 0.0164 | 0.1357 |
| Lignite A (ligA) | 0.986805 | -0.925322 | 90.73 | 0.0078 | 0.0800 |
| Sub-bituminous C (subC) | 0.982440 | -0.868727 | 88.91 | 0.0087 | 0.0759 |
| Sub-bituminous B (subB) | 0.992029 | -0.993473 | 95.75 | 0.0076 | 0.0698 |
| Powder River Basin | 0.995394 | -1.017100 | 98.99 | 0.0056 | 0.0636 |
| Sub-bituminous A (subA) | 0.987991 | -0.917961 | 95.55 | 0.0075 | 0.0630 |
| High Seas Commercial | 0.991261 | -0.998360 | 97.22 | 0.0079 | 0.0355 |
| Semi-anthracite (sa) | 0.992139 | -0.927044 | 88.07 | 0.0070 | 0.0183 |
| Anthracite (an) | 0.994587 | -1.029322 | 94.61 | 0.0057 | 0.0140 |

**TABLE 4:**
**MAF Molar Fuel Carbon + Hydroxyl Factored Hydrogen**
**versus MAF Molar Ratio of Diatomic Oxygen/Carbon, Eq.(4)**

| Rank | $I_{OHC4}$ | $J_{OHC4}$ | $K_{OHC4}$ | $R^2$ (%) | Comment |
|------|-----------|-----------|-----------|-----------|---------|
| Irish Peat | 0.7780 | 0.895208 | -0.431411 | 98.38 | Improved (+1.52%) |
| Greek Lignite (ligB) | 0.7980 | 0.902258 | -0.465179 | 98.75 | Improved (+1.30%) |
| Lignite A (ligA) | 0.9350 | 0.964755 | -0.560722 | 91.75 | Improved (+1.02%) |
| Sub-bituminous C (subC) | 0.9280 | 0.958077 | -0.518650 | 89.75 | Improved (+0.84%) |
| Sub-bituminous B (subB) | 0.9240 | 0.967009 | -0.605362 | 96.72 | Improved (+0.97%) |
| Powder River Basin | 0.9280 | 0.971158 | -0.621657 | 99.10 | Slight improvement |
| Sub-bituminous A (subA) | 0.9500 | 0.972574 | -0.590137 | 96.17 | Slight improvement |
| High Seas Commercial | 0.9025 | 0.966255 | -0.706477 | 98.85 | Improved (+1.63%) |
| Semi-anthracite (sa) | 0.9820 | 0.988620 | -0.723776 | 88.58 | Slight improvement |
| Anthracite (an) | 0.9790 | 0.992213 | -0.894030 | 94.76 | No improvement |

most Ranks using Eq.(1) indicates the general viability of Table 1; at least for the <u>non-volatile Ranks</u>. Figure 7 indicates that: Irish Peat is not comparable to Greek lignite; the slopes of the lower Ranks are not those for the mid-Ranks. However the high volatile Rank of hvAb <u>does not</u> support. This is most interesting, as the hvAb data pattern suggests a degradation of the correlation is due (it is believed) to the present of volatiles; the same patterning was observed in lvb, mlb, hvBb and hvCb Ranks. Figure 8, based on Eq.(3), for the non-volatile Ranks produces different slopes and intercepts (note outlying subC data), and confirms Table 3's viability.

Finally, the relationship of MAF fuel oxygen with carbonates found in the fuel's mineral matter may also represent a source of error. The problem arises when a portion of a fuel sample is used to determine mineral matter content by firing at high temperature and for a sufficient length to reduce all organics. With fuels such as Irish peat where the mineral matter is largely composed of carbonates, a false determination of the fuel ash is possible given $CO_2$ production from calcination. Such an effect may be quite important, if not complex for some fuels (and certainly for PRB coals, peats and lignites). The authors have experimented with the washing of PRB and Irish Peat with dilute hydrochloric acid prior to analysis to determine the magnitude of carbonate effects on resultant ultimate analyses. In addition, this will result in compounding error given that oxygen is computed by difference. However for the purpose of this work, it was desired that the OHC Model be required to function as a predictive tool of ultimate analyses generated using industrial testing methods. If errors are being made in not accurately assigning "fuel oxygen", recorded by an ultimate analysis, versus carbonates (i.e., misrepresenting fuel ash) and/or errors from difference analysis, then the authors argue for consistency with the reported industrial ultimate analyses. Again, the authors strongly suspect that industrial testing methods may adversely influence calorimetrics of volatile Ranks.

**Molecular Weight of Coal**

It occurs that Eqs.(1), (2) and (3) representing three unknowns can be solved for molecular representations of the fuel. Normalizing to carbon, a $CH_mO_n$ formulation can be quickly evaluated, taking account of a conversion to monatomic hydrogen and oxygen; this ignores nitrogen and sulphur. The results presented in Table 5 indicate a striking consistency;

offering a touch-stone for substantiating the OHC Model. The on a computed calorific value which is mineral matter free, but reflects a "natural inherent moisture"; although D388's designations are now commonplace, it is awkward when applied. In Europe, there are seemingly as many coal categories in use as countries. If using the ISO procedures [13], coal is categorized as either hard or soft depending on ash-free calorific value. Sub-groups under ISO are classified by volatile matter, coking properties, etc. resulting in a three-digit numbering system. No known system employs ultimate analysis data to classify coals; at best proximate analyses are employed. It is not hard to understand that such standards have received criticism. It is therefore suggested that the ASTM and ISO standards be replaced capitalizing on the techniques taught through this work. Suggested is following procedure for categorizing coals:

1)      analyze fuel samples fo the same Rank;
2)      form Oxy-Hydrocarbon relationships using Eqs.(1), (2) and (3), invoking Eq.(4) where necessary; and
3)      solve for the fuel's normalized molecular formulation from which a confirmatory category (or outlying data) may be observed.

Knowing the normalized molecular formulation also affords the opportunity to evaluate the fuel's relative calorific value. Using the Input/Loss relationship between chemical binding energies and elemental constituents [11] given by Eq.(5), below, ignoring fuel sulphur and normalizing to anthracite, a relative measure of MAF calorific value is produced as shown in Table 5. The easily observed trend in relative calorific values demonstrates the robust nature of the Oxy-Hydrocarbon approach for non-volatile coals. Of course caution must be exercised when using Eq.(5) with a fixed O-H-C chemistry for each Rank; on the other hand, it supports the general observation of a constant MAF calorific value found for most Ranks.

$$CV_{Rel} = [\, k_O\, \alpha_{MAF\text{-}O} + k_C\, \alpha_{MAF\text{-}C} + k_H\, \alpha_{MAF\text{-}H}\,]/\,(CV_{AN}\, N_{MAF\text{-}Fuel}) \qquad (5)$$

where:

$CV_{Rel}$ = Relative MAF Calorific Value
$CV_{AN}$ = Calorific Value of Anthracite
$N_{MAF\text{-}Fuel}$ = Normalized molecular weight of MAF fuel using C, H and O;

and:

if $\alpha_{MAF\text{-}O}/\alpha_{MAF\text{-}C} \leq 0.25$:     $k_O$ = -178387.22
                                $k_C$ = 183591.92
                                $k_H$ = 78143.678;

**TABLE 5:**
**Reduction of Multi-Variant Analysis to a Normalized Molecular Weight**
**of Coal ($CH_mO_n$), and Relative MAF Calorific and Effluent $CO_2$ Indices**

| Rank | Hydrogen (m) | Oxygen (n) | Normalized Molecular Wt. (using C, H and O) | Relative Calorific Value, $CV_{Rel}$, % | Relative Mass Effluent $CO_2$, % | Relative Effluent $CO_2$ per $CV_{Fuel}$, % |
|---|---|---|---|---|---|---|
| Irish Peat | 1.0942 | 0.4534 | 20.367 | 59.78 | 78.77 | 182.82 |
| Greek Lignite (ligB) | 1.0788 | 0.4249 | 19.897 | 61.84 | 80.63 | 180.93 |
| Lignite A (ligA) | 0.8299 | 0.2219 | 16.398 | 78.38 | 97.83 | 173.21 |
| Sub-bituminous C (subC) | 0.8688 | 0.2084 | 16.221 | 80.33 | 98.90 | 170.84 |
| Sub-bituminous B (subB) | 0.8348 | 0.1900 | 15.892 | 82.13 | 100.95 | 170.56 |
| Powder River Basin | 0.8136 | 0.1751 | 15.633 | 83.69 | 102.62 | 170.14 |
| Sub-bituminous A (subA) | 0.7661 | 0.1640 | 15.407 | 84.56 | 104.13 | 170.88 |
| High Seas Commercial | 0.7340 | 0.0766 | 13.977 | 96.27 | 114.78 | 165.44 |
| Semi-anthracite (sa) | 0.4803 | 0.0283 | 12.948 | 101.08 | 123.90 | 170.08 |
| Anthracite (an) | 0.2600 | 0.0191 | 12.579 | **100.00** | 127.54 | 176.98 |
| Graphite | 0.0000 | 0.0000 | 12.011 | 100.11 | 133.57 | 185.13 |
| Methane | 4.0000 | 0.0000 | 16.043 | 138.76 | **100.00** | **100.00** |

**Table 6: $L_{10}$ vs. MAF Molar Diatomic Oxygen**

| Rank | $G_{OHC1}$ | $H_{OHC1}$ | $R^2$ (%) |
|---|---|---|---|
| Irish Peat | 11.749578 | -33.669627 | 98.96 |
| Greek Lignite (ligB) | 11.922373 | -35.957530 | 99.27 |
| Lignite A (ligA) | 12.448910 | -39.311755 | 97.94 |
| Pennsylvania Bit. Waste (Gob) | 12.520164 | -40.942945 | 92.68 |
| Sub-bituminous C (subC) | 12.434765 | -39.130897 | 97.58 |
| Sub-bituminous B (subB) | 12.601279 | -41.266314 | 98.82 |
| Powder River Basin | 12.772919 | -43.423015 | 99.61 |
| Sub-bituminous A (subA) | 12.565156 | -40.587183 | 98.72 |
| High Seas Commercial | 12.798506 | -45.549042 | 96.56 |
| Semi-anthracite (sa) | 12.721190 | -43.261728 | 94.71 |
| Anthracite (an) | 12.554270 | -39.570934 | 93.12 |

**Table 7:**
**$L_{10}$ vs. MAF Molar Fuel Carbon + Diatomic Hydrogen**

| Rank | $G_{OHC2}$ | $H_{OHC2}$ | $R^2$ (%) |
|---|---|---|---|
| Irish Peat | -24.087573 | 36.492909 | 98.43 |
| Greek Lignite (ligB) | -22.184593 | 34.500349 | 99.21 |
| Lignite A (ligA) | -27.384762 | 40.214575 | 96.63 |
| Pennsylvania Bit. Waste (Gob) | -35.328433 | 48.873806 | 94.65 |
| Sub-bituminous C (subC) | -28.664285 | 41.636430 | 95.03 |
| Sub-bituminous B (subB) | -27.727421 | 40.593960 | 98.57 |
| Powder River Basin | -29.529120 | 42.485604 | 99.65 |
| Sub-bituminous A (subA) | -30.125654 | 43.155046 | 98.43 |
| High Seas Commercial | -32.463721 | 45.674256 | 99.55 |
| Semi-anthracite (sa) | -31.027299 | 44.067901 | 95.90 |
| Anthracite (an) | -24.934121 | 37.685859 | 94.58 |

if $\alpha_{MAF-O}/\alpha_{MAF-C} > 0.25$:     $k_O$ = -171240.10
$\qquad\qquad\qquad\qquad\qquad$ $k_C$ =  183034.60
$\qquad\qquad\qquad\qquad\qquad$ $k_H$ =  78685.355.

Finally, in addition to relative calorific values, it is of interest to judge fuels based on the relative mass of effluent $CO_2$ per unit of fuel and per unit of fuel energy relative to methane, given its common use as a standard against which coals are oftentimes judged. Table 5 presents such data on a relative scale normalized to methane. The relative mass effluent $CO_2$ per unit of fuel is simply the ratio of molecular weights of $CO_2$ to fuel, $N_{CO2}/N_{MAF-Fuel}$, normalized to methane. The relative mass of effluent $CO_2$ per unit of fuel energy is determined as $(kg_{CO2}/kJ)_{MAF-Fuel}/(kg_{CO2}/kJ)_{Methane}$. Results indicate a more complex response than read in the popular press. For example, although Irish peat produces 21.23% less mass of effluent $CO_2$ than methane, per unit mass of fuel, given its low calorific value (82.82%) more effluent $CO_2$ is produced per unit of thermal output.

The consistent data progression seen in Table 5 belies the notion of unrelated or non-uniform data apparent in Tables 1, 2 and 3. We contend that when examining the O-H-C pattern for a large range of non-volatile coals, a unified picture emerges of originating organic material being slowly modified from a carbohydrate to an oxy-hydrocarbon, with younger fuels (peats and lignites) containing a considerable oxygen content, losing first oxygen and then, later, hydrogen in a progression towards anthracites (if not base carbon).

Table 5 leads to the conclusion that MAF fuel oxygen content is the defining variable–hence the name Oxy-Hydrocarbon.

**Ranking and Over-Checking of Fuels**

The consistency of Table 5 also suggests that these findings can be used to over-check laboratory ultimate analyses. Such over-checks could include both categorizing fuels and identifying outlying data (e.g., subC data in Figure 8). Also, using the type of data represented by Table 5 will reveal and define the occasional strange fuel.

One such fuel is Bear Canyon coal. Although a western US coal, it is mined in Utah outside the Powder River Basin. Bear Canyon computes as $CH_{0.9197}O_{0.0762}$, a molecular weight of 14.158. The oxygen content of this coal indicates a hvAb or hvBb coal while its hydrogen content indicates a lignite A or B. Further, its MAF calorific value is 98.41% relative to anthracite. Since Bear Canyon coal has little water content, the OHC Model suggests it as being most environmentally friendly, it being closer to methane than any other known coal producing only 59.78% more effluent $CO_2$ per $CV_{Fuel}$ when compared to methane.

It must be noted that the ASTM D388 [12] standard which specifies Ranks of coal, and whose broad categories are widely used in North America, judges high energy coals on MAF "fixed carbon" and MAF volatile matter (using proximate analysis data). The lower energy coals are judged classified by volatile matter, coking properties, etc. No known system employs ultimate

analysis data to classify coals; at best proximate analyses are employed. It is not hard to understand that such standards have received criticism, and thus it is suggested that the ASTM and ISO standards be replaced by the techniques outlined here.

**The $L_{10}$ Factor**

The above work, although useful in analyzing fossil fuels and for interrogating lab results, does not complete the task of allowing solution (a series of independent equations) to system stoichiometrics associated with power plants, leading to As-Fired fuel chemistry. Two general problems need to be addressed in the context of commercial power plants: 1) there will always be fewer equations than unknowns; and 2) there are many practical difficulties in measuring combustion effluents. Computing fuel chemistry based on combustion effluents–given the vagaries associated with large commercial steam generators, and the measurement of plant effluents–requires recognition of the difficulties involved and the extreme sensitivities to measured data:

All instrumentation has error, especially that associated with effluent measurements.

- Many times a power plant's more precise effluent measurements may be found at the air heater inlet (Economiser outlet), and not at the air heater outlet (Stack). This requires knowledge of the air heater in-leakage, differentially affecting effluent $H_2O$, $CO_2$ and $O_2$ measurements.
- Effluent measurements are taken either wet or dry, requiring conversion to a common base.
- It can be demonstrated that the ambient $O_2$ concentration in combustion air may vary significantly depending on the system's location, weather inversions, leakage of flue gas into air intakes, etc.
- Computed system stoichiometrics may have great sensitivity to dry effluent $CO_2$, but often times this measurement is made on a wet basis and thus directly affected by the accuracies of the measured (or assumed) effluent moisture.

To solve these problems, in parallel with and guided by the development of the Oxy-Hydrocarbon Model, a new factor, termed $L_{10}$, was developed. $L_{10}$ displays a high degree of predictability for a wide range of fuels, including Irish peat, Powder River Basin coals and High Seas coals. The $L_{10}$ Factor allows an independent equation to be written. In addition, its corrected value, $L_{10\text{-corr}}$ as defined by Eq.(9), is essentially constant and thus useful in correcting instrumentation error. A constant $L_{10\text{-corr}}$ may be employed by the Input/Loss

Method multi-dimensional minimisation techniques as a "stake-in-the-ground" allowing correction of any effluent measurement error (actually any parameter which can affect system stoichiometrics may be corrected [14,15,17]). No matter the value of $L_{10}$, that is the actual MAF chemistry being fired may be far from the norm given actual or erroneous measurements, the corrected value, termed $L_{10\text{-corr}}$, will be forced constant by minimization techniques given adjustment to any parameter affecting system stoichiometrics. This assures that the computed fuel chemistry produces an $L_{10}$ which is valid for a given Rank (i.e., it lies on a line suggested by regression constants presented in Table 6 or 7, as seen below). In summary, the computed fuel chemistry will respond to corrections made in effluent measurements ($H_2O$, $CO_2$ and $O_2$), upon which it is based and through which a newly computed $L_{10}$ will achieve a constant factor quantified by $L_{10\text{-corr}}$.

The $L_{10}$ Factor is defined by the following, units of measure being (mass of dry effluent) / (mass of MAF fuel), as based on theoretical combustion of dried fuel. This formulation is the same as: $[1.0 + (\text{Air/Fuel})_{\text{DRY-theor}}]$, the form actually employed:

$$L_{10} \equiv [x_{\text{DRY-theor}} N_{\text{DRY-Fuel}} + a_{\text{DRY-theor}}(1.0 + \Phi_{\text{Ref}})N_{\text{Air}}$$
$$- J_{\text{theor}} N_{\text{H2O}} - x_{\text{DRY-theor}} \alpha_{\text{DRY-Ash}} N_{\text{Ash}}]$$
$$/ (x_{\text{MAF-theor}} N_{\text{MAF-Fuel}}) \qquad (6)$$

where:

$\alpha_{\text{DRY-theor}}$ = Moles of ambient dry oxygen required to theoretically combust dried fuel

$J_{\text{theor}}$ = Moles of effluent moisture based on theoretical combustion of dried fuel

$N_{\text{Air}}$ = Molecular weight of dry combustion air

$N_{\text{Ash}}$ = Molecular weight of dry fuel mineral matter

$N_{\text{DRY-Fuel}}$ = Normalized molecular weight of dried fuel

$N_{\text{MAF-Fuel}}$ = Normalized molecular weight of MAF fuel

$N_{\text{H2O}}$ = Molecular weight of water

$x_{\text{DRY-theor}}$ = Moles of dried fuel based on theoretical combustion

$x_{\text{MAF-theor}}$ = Moles of MAF fuel based on theoretical combustion

$\alpha_{\text{DRY-Ash}}$ = Moles of fuel mineral matter per mole fuel

$\Phi_{\text{Ref}}$ = Reference molar ratio of non-oxygen gases to oxygen in the combustion air and taken as 3.7737254.

The form of Eq.(6) is taken to accent combustion moisture and ash terms to create greater sensitivity to fuel hydrogen. As seen in Tables 6 and 7, when $L_{10}$ is plotted against either MAF molar fuel oxygen or the sum of MAF molar fuel carbon plus MAF molar fuel hydrogen, a high degree of predictability is found. Figure 9 plots $L_{10}$ for High Seas coals against MAF molar fuel carbon plus MAF molar fuel

hydrogen, indicating an $R^2$ value of 99.33%. These relationships can be described by the following:

$$L_{10} = G_{OHC1} + H_{OHC1}\,\alpha_{MAF\text{-}O} \qquad (7)$$
$$L_{10} = G_{OHC2} + H_{OHC2}\,(\alpha_{MAF\text{-}C} + \alpha_{MAF\text{-}H}) \qquad (8)$$

where: $G_{OHCk}$ & $H_{OHCk}$ => Regression constants.

In addition, Figure 9 indicates the results of correcting $L_{10}$ such that a constant value may be created based on the following:

$$L_{10\text{-corr}} \equiv L_{10} - [H_{OHC2}(\alpha_{MAF\text{-}C} - \alpha_{MAF\text{-}C/Ref} + \alpha_{MAF\text{-}H} - \alpha_{MAF\text{-}H/Ref})] \qquad (9)$$

where the reference elemental values ($\alpha_{MAF\text{-}C/Ref}$ and $\alpha_{MAF\text{-}H/Ref}$) are arbitrarily chosen. Figure 9 displays an essentially straight line representation of $L_{10\text{-corr}}$, the corrected. Notably the $L_{10}$ Factor indicates <u>no</u> correlation when plotted against MAF molar fuel carbon plus MAF molar fuel diatomic oxygen, nor against MAF molar fuel diatomic hydrogen plus MAF molar diatomic fuel oxygen.

**Computed Fuel Chemistry**

As to one of the original problems, the on-line computation of fuel chemistry, it may be seen that <u>two independent equations</u> are obtained from, for example, Eq.(3) and the combination of Eqs.(7) and (8). By then writing stoichiometric balances for hydrogen, for oxygen, for carbon and another for sulphur, <u>two more independent equations</u> result, these equations based on stoichiometrics. Further, by recognizing that: $\alpha_{MAF\text{-}O} + \alpha_{MAF\text{-}C} + \alpha_{MAF\text{-}H} + \alpha_{MAF\text{-}S} + \alpha_{MAF\text{-}N} = 1.0$, a <u>fifth equation</u> is available. Five independent equations allow an ultimate analysis to be resolved by matrix solution. There are obviously other combinations; e.g., involving Eq.(4), etc. The resolution of fuel water and fuel ash, by explicit solution, has been well established by Input/Loss [11]. These methods allow determination of a complete fuel chemistry, constructed upon combustion effluent concentrations and in which measurement error in those concentrations is addressed.

**Note on Databases**

Databases of ultimate analyses and calorific values used to develop this work derive from four general sources. Penn State's database [16] was used as containing over 1200 ultimate analyses and associated calorific values from over 400 mines.

- A Power River Basin coal database was used as containing approximately 230 samples from 17 different regions within the Basin, obtained from six Input/Loss PRB installations.
- The High Seas coal database contained 63 coal samples from South Africa, Poland, Russia, Colombia, Indonesia, US and Australia. Actual data was obtained from shipping manifests of power stations actually using such coals: Moneypoint, Republic of Ireland; Brandon Shores, Maryland, US; and Jorf Lasfar, Morocco.
- The Irish Peat database contains approximately 160 samples from 6 different regions within the Republic, notably this data having been collected over a considerable time period, from 1969 through 2005; it was obtained from the Electricity Supply Board.

In total, the analyzed data consists of approximately 1650 ultimate analyses and corresponding calorific values. Although volatile coal data was extensively analyzed, results are not being reported at this time.

**Note on Power Plant Applications**

The OHC Model has been incorporated quite successfully into Exergetic Systems' Input/Loss Method since April 2006. It is currently being β-tested by monitoring a variety of fuels at five selected power plants: Irish peat at West Offaly (Ireland) and at Lough Ree (Ireland); High Seas coal at Brandon Shores Unit 2 (Maryland, US); and PRB at Boardman (Oregon, US) and at Nebraska City Unit 1 (Nebraska, US).

An important question arises as to the accuracy that may be expected from the on-line calculation of fuel chemistry compared to conventional methods. To provide some sense of this and of the importance of a high $R^2$, consider the distribution of data seen in Figure 3 for High Seas coals; it can be described as approximately uniformly distributed about a linear mean. This is important statistically, for one can then envision the effects of increasing the $R^2$ from 90% to a value of 98.5% by simply shrinking the data range. A conservative $R^2$ of 98.5% is important as it encompasses much of the multi-variant data as observed in Tables 1, 2, 3 and 4.

If the range of variation of the type of data exemplified by Figure 3, resulted in an $R^2$ of 98.5%, its effects would translate to a 0.272% error in dry effluent $CO_2$ (say from 15.00% to 15.0408%). Although slight, and if using single-variant analysis without countering effects of hydrogen treatment, this error would result in a 0.90% error in calorific value for the type of fuel seen in Figure 3, at $\pm 263$ $\Delta$kJ/kg ($\pm 113$ $\Delta$Btu/lbm). Although it can be improved using multi-variant analysis, possible use of Eq.(4) and considering the whole of Input/Loss, this level of predictability agrees with the commonly accepted error in measured solid fuel CVs determined between independent laboratories testing split samples, at

$\pm 233 \Delta kJ/kg$ ($\pm 100 \ \Delta Btu/lbm$). Using the $L_{10}$ correction technique described above, it is believed that accuracy of at least this order can be well achieved by Input/Loss.

This last statement is, of course, dependent on a number of factors, not the least of which is the integrity of plant effluent data. Actual problems encountered which can destroy such accuracy statements include the following examples: at one installation, the effluent $CO_2$ instrument was chronically off-line; at another, the effluent $CO_2$ signal was set constant for 6 minute intervals; and at another installation, the effects of effluent $O_2$ stratification was not properly addressed. Though the combination of the OHC Model with Input/Loss contains a powerful mechanism for correcting erroneous effluent measurements, the implementation of some basic quality measurement principles, emphasizing signal consistency, is still required for good results.

**Conclusion**

It is possible to well characterise non-volatile coal using multi-variant analysis techniques. These techniques can lead to the derivation of a fuel's average normalized molecular formulation and calorific value, categorized by Rank. The technique has demonstrated a remarkable consistency and supports understanding of non-volatile coals at the genetic level.

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**Figure 1**



Figure plot — X axis: **MAF Molar Carbon** (0.51 to 0.61); Y axis: **MAF Molar Diatomic Hydrogen** (0.26 to 0.36).

IRISH PEAT (1969-2005)

Hyd = -0.575577(Car) + 0.627790
$R^2$ = 0.619776

**Figure 2**



POWDER RIVER BASIN

MAF Molar Diatomic Hydrogen

Hyd = -0.811119(Car) + 0.810615
$R^2$ = 0.772243

MAF Molar Carbon

**Figure 3**



◆ HIGH SEAS COAL

MAF Molar Diatomic Hydrogen

Hyd = -0.786466(Car) + 0.813654
$R^2$ = 0.907619

MAF Molar Carbon

-13-

**Figure 4**



IRISH PEAT (1969-2005)

Hyd+Oxy = -1.062057(Car) + 1.026586
$R^2$ = 0.989132

MAF Molar Carbon (x-axis)
MAF Molar Diatomic Hydrogen + Oxygen (y-axis)

**Figure 5**



POWDER RIVER BASIN

Hyd+Oxy = -0.988635(Car) + 0.986835
$R^2$ = 0.997698

MAF Molar Carbon (x-axis)
MAF Molar Diatomic Hydrogen + Oxygen (y-axis)

**Figure 6**



Figure 6 plot: x-axis "MAF Molar Carbon" (0.65 to 0.75), y-axis "MAF Molar Diatomic Hydrogen + Oxygen" (0.24 to 0.34). Legend: ◆ HIGH SEAS COMMERICAL. Equation box: (Hyd+Oxy) = -1.025647(Car) + 1.009397, $R^2$ = 0.997759

**Figure 7**



Figure 7 plot: x-axis "MAF Carbon" (0.55 to 0.73), y-axis "MAF Diatomic Hydrogen + Oxygen" (0.25 to 0.45). Legend: Semi-Anth (sa), High Vol A Bit (hvAb), Sub Bit A (subA), Sub Bit B (subB), Sub Bit C (subC), Lignite A, Greek Lignite, Irish Peat

## Figure 8



**Legend:**
- □ Anthracite (an)
- ▲ Semi-Anth (sa)
- △ Sub Bit A (subA)
- ◆ Sub Bit B (subB)
- ■ Sub Bit C (subC)
- ▲ Lignite A
- ◆ Greek Lignite
- ◇ Penn Bit Waste
- □ Irish Peat

X-axis: **MAF Diatomic Oxygen**
Y-axis: **MAF Carbon + Diatomic Hydrogen**

## Figure 9



**Legend:**
- ● HIGH SEAS COMMERICAL
- ■ CORRECTED L10

L10 = 45.674256(Car+Hyd) - 32.463721
R2 = 0.995458

X-axis: **MAF Molar Carbon + Diatomic Hydrogen**
Y-axis: **L10 Factor**

-16-