Representation of coal and coal derivatives in process modelling

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Synopsis

This paper provides guidelines on performing mass and energy balance modelling involving coal and coal derivatives. Usually, the inputs to a pyrometallurgical process would be specified in terms of elements and compounds. Reliable thermochemical data is more widely available for species involving uniquely defined, relatively smaller molecules. However, in the case of coal, the molecules are extremely large and not uniquely defined. Consequently, modelling processes involving coal and its derivatives involve several potential pitfalls. These are outlined in the present paper.

It was found that coal proximate analysis should not be regarded as absolute; it could vary with several parameters, including heating rate. For modelling, the use of ultimate analyses should be considered a preferable option to proximate analyses, where 'fixed carbon' and 'volatiles' are not defined in terms of chemical composition. Significant errors could be incurred if the larger molecules are neglected during calculation of the calorific value (CV) of coal gas (the gas liberated when coal is heated in the absence of oxygen).

For elemental analysis determination, the oxygen content (which is calculated by balance) should be checked to ensure it is within the expected range. For representation of sulphur in coal, one should avoid double-counting due to SO_3 in the ash analysis.

Potentially, oxygen in coal could be represented as O_2, H_2O, CO, or CO_2. However, use of some of these species without considering the experimentally determined gross CV leads to significant errors in the energy balance. If coal enthalpy is calculated from elemental analyses without correction, representation of coal oxygen as $H_2O_{(l)}$ gives reasonable accuracy. Coal volatiles could be represented by a complex mixture of compounds, even using different oxygen-containing species than these four, provided the enthalpy is corrected.

It is recommended that an 'enthalpy correction value' be incorporated in energy balances involving combustion, devolatilization, or conversion of coal and coal derivatives, e.g. coke, char, or tar. That would imply that proximate analysis, elemental analysis, as well as the gross CV would be required for all solid or liquid coal-derived substances being modelled. No other correction due to carbon being present in a form other than graphite should be used, as that would imply double-counting some effects.

Keywords
coal properties, process modelling, proximate analysis, energy balance, enthalpy.

Introduction

Coal is possibly the most heterogeneous substance used in the minerals industry, especially that sector involving processing at high temperatures. Coal derivatives include coke, char, tar, pitch, and coal gas which are important commodities in industry.

Coal is used extensively in the metallurgical industry for widely different purposes, *e.g.* electrical power generation, reductant manufacturing (coke and char), as well as gasification, which allows the value of coal to be extended to a wide range of chemical products. Pulverized coal injected into the blast furnace (for the purpose of decreasing coke consumption) is subjected to significantly different conditions than pulverized coal used for power generation. Reductants such as anthracite fed to an open arc smelting process are subjected to rapid rates of heating. Lump coal fed into the Corex (Institute for Industrial Productivity, 2012a), smelt-reduction, or rotary kiln direct reduction (DR) processes (Institute for Industrial Productivity, 2012b) is subjected to reducing conditions as well as a relatively rapid rate of heating.

It is therefore important to understand the physiochemical properties of coal as they relate to different applications in order to extract maximum value from available coal resources. Process modelling plays an important role in extracting this value through a detailed understanding of the quality and physiochemical properties of coal and its derivatives. This paper highlights some of the relevant issues and potential pitfalls in the modelling of coal, focusing on the application of proximate and ultimate analysis of coal, with specific reference to oxygen content, and the effect of different assumptions regarding its representation on the calculated calorific value (CV).

Current evaluation methods for coal include proximate analysis, total sulphur, and CV. Proximate analysis includes moisture, volatiles, ash, and fixed carbon yields. (Note the preference for the word 'yields' in this context, as opposed to 'contents'. That is because coal actually contains minerals and not ash. Ash is the remnants of minerals after

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complete oxidation of the coal. Most often these analyses are not adequate to fully describe the behaviour of the coal in the specific process. Technologists, especially in the fields of power generation and coke-making, properly consider the results of a number of additional tests, *e.g.* elemental analyses, ash analysis, ash fusion temperature, and coal petrography. Coke-makers consider coal plasticity tests (*e.g.* Gieseler fluidity and dilatation), and those involved in power generation consider coal reactivity, especially from drop tube oven results.

The use of mathematical modelling in metallurgical and chemical processes

Mass balance modelling is simply based on the law of conservation of mass. Although the concept is simple, there are potential pitfalls associated with these calculations, especially for coal. The same applies to energy balances, which are based on the enthalpy function. Considerable time has elapsed since the initial development of the field of thermodynamics and introduction of, for example, the concept of Gibbs free energy (Bodner Group, 2014). Nowadays, exploiting the concept of Gibbs free energy minimization is easier than previously, due to the availability of useful databases, software, and computers.

Usually one would specify an input to a pyrometallurgical process in terms of elements and compounds. However, in the case of coal the molecules are extremely large, and not uniquely defined. Reliable thermochemical data is more widely available for species involving uniquely defined, relatively simpler molecules.

Nevertheless, it is essential to understand the limitations of mathematical modelling. The quality of the output depends on the following:

- Accuracy of inputs
- Understanding of the process
- Validity of assumptions
- Intent of the model
- Inherent limitations of modelling
- The level of skill of the person undertaking the task, including the use of checks and balances
- The time allowed for execution of the task, which if not enough, could force the person to make unjustified assumptions.

Proximate analysis

Moisture content

Preparation of a new coal sample would include air-drying the coal at ambient temperatures or at elevated temperatures not exceeding 40°C (SANS 589:2009, 2009). The apparently dry coal obtained is referred to as 'air-dry'. The mass loss from wet coal to 'air-dry' coal is referred to as 'free moisture content'. A sample of air-dry coal, after appropriate sample preparation techniques (including milling), is heated to a temperature of between 105°C and 110°C, and the associated mass loss is referred to as 'residual or inherent moisture'. The sample is then referred to as 'dry' or 'absolutely dry'. Total moisture content of the coal sample is calculated as follows:

$$\%\text{Total moisture} = \%\text{Free moisture} + \%\text{Inherent moisture} \quad [1]$$

Some coals liberate additional moisture (water of crystallization) when heated to temperatures higher than about 105°C. This moisture reports as part of the volatile content. In the case of highly porous coal derivatives such as coke or char, the drying method prescribes temperatures between 120°C and 200°C, with additional care to ensure that no further mass loss occurs before recording the mass (SANS 579:2005, 2005).

Proximate analysis calculation

Proximate analysis is usually carried out on an air-dry coal sample. Results include inherent moisture, volatiles, and ash yields, while the balance is allocated to fixed carbon, with all values expressed on an air-dry basis, as follows (SANS 17246:2011, 2011):

$$\%\text{Fixed C} = 100\% - (\%\text{Moisture} + \%\text{Volatiles} + \%\text{Ash}) \quad [2]$$

Note that sulphur remaining in the residue would report to 'fixed carbon'. The values on an air-dry basis could be converted to an absolute dry base, *e.g.* by applying the following conversion:

$$\%\text{Fixed C}_{(\text{dry})} = \%\text{Fixed C}_{(\text{air dry})} / (1 - (\%\text{ Inherent moisture})/100) \quad [3]$$

During modelling and reporting of modelled results, care should be exercised to specify all analyses as 'wet as-received', 'air-dry', or 'dry' and to use the appropriate conversion factors to avoid errors.

Coal volatiles

During determination of the volatile content of coal, a small milled sample is inserted in a crucible and covered by a lid. The crucible is loaded into a muffle furnace at 900°C for a duration of 7 minutes (SANS 50:2011, 2011). The mass lost, after subtracting the moisture content, is referred to as 'volatiles content' or volatiles yield.

For determination of ash yield, the coal is subjected to oxidizing conditions. The temperature is limited to 850°C to minimize the loss of volatile compounds such as K_2O and Na_2O.

According to Rosenqvist (1974), '*The proximate analysis gives the percentage of "moisture", "volatile matter", "fixed carbon" and "ash". Each of these is determined by standardized procedures, and different values would be obtained if different procedures were used.*' Procedures were standardized by ISO, ASTM, and other organizations.

Some operators who are less familiar with coal could treat the results from proximate analyses as if they were absolute. However, considering the quote from Rosenqvist and observing the extent to which actual processes differ from the procedures for proximate analysis, behaviour not in line with proximate analysis should actually be expected. Therefore it should not be surprising if the actual performance of coal, *e.g.* during charring or coke-making, deviates from what would be expected if the characteristic were calculated on the basis of the proximate analysis.

One example of actual results deviating from proximate analysis data is the observation that rapid heating tends to increase the volatile yield. Most noticeably, that decreases the yield of fixed carbon (Niksa, 1995).

Composition and representation of volatiles

Coal volatiles are partly organic and partly inorganic in origin. Water vapour and carbon dioxide from clay and carbonate minerals are the main inorganic volatiles. Some effects of inorganic volatiles are as follows:

- They do not contribute combustible species that could increase the CV
- Their liberation could be associated with endothermic reactions, which would neutralize part of the exothermic reaction heat from combustion
- They could adversely affect ignition of the coal.

Not all the water from clays is liberated at approximately 105°C, as the remainder (crystal water) is bound in chemical compounds that decompose at higher temperatures. These volatiles of inorganic origin are referred to as 'inert volatiles' (Porter and Ovitz, 2014). Coal volatiles could also be subjected to secondary reactions after initial liberation – for example, in the case of tar from slot coke-making ovens, in which thermal cracking occurred during contact with surfaces at a higher temperature than that of initial release. Thermal cracking (Chiu and Hong, 1983) involves the formation of pyrolytic carbon, smaller molecules (such as H_2), and modified hydrocarbon compounds. Pyrolytic carbon is deposited in the coke pores during carbonization, which increases the yield of fixed carbon significantly (Chiu and Hong, 1983). If the process being modelled involves thermal cracking, appropriate assumptions would be required, which should be based on evidence from experimental work or plant observations.

Condensable hydrocarbons in coal volatiles represent a modelling challenge. Condensable hydrocarbons contain numerous compounds, for which detailed analyses are seldom available. Tars in particular contain numerous compounds with very large molecular structures and which are thermally unstable. Representation of tar with a simpler species or mixture of species of smaller molecular mass with well-known thermodynamic data is advantageous. In this regard it could be mentioned that benzene (C_6H_6) has a high carbon content of 92.3%, in the same order of magnitude than typical tar from slot coke-making ovens. For quick calculations where approximate results are required, benzene could be used to represent tar. Light oils, also referred to as BTX, contain benzene, toluene, and xylene. As benzene predominates in the composition of these light oils, it could also represent this group of compounds where approximate results are required (Powell, 1945).

Representation of volatiles for coal gas CV calculation

The large molecules of condensable hydrocarbons do not make a major contribution to the volume of coal gas. However, they do make a significant contribution to both the CV and carbon content of the gas. According to Powell, typical coke oven gas from a by-product coke oven contains about 0.65% by volume light oils (after tar removal, but before BTX removal) (Powell, 1945).

In Table I, composition by volume of coal gas from a typical by-products coke-making oven, given by Powell, is presented, together with the percentage contribution of each individual component of that gas analysis to the calculated CV of the gas mixture (23.93 MJ/Nm^3 in this instance). If only the contributions of hydrogen, carbon monoxide, and methane are taken into account, the calculated gas CV would be only 82.5% of the accurate value, assuming that the given calculated value is the accurate one. Light oils, which represent only 0.65% of the volume of the gas, contribute almost 4% of the gas CV.

Similarly, in Table II, composition by volume of coal gas from low-temperature carbonization (Powell, 1945) is presented. This gas has an even higher CV of 27.5 MJ/Nm^3, compared to 23.9 MJ/Nm^3 for by-product coke oven gas. Similar to the case of low-temperature carbonization, hydrogen, carbon monoxide, and methane contribute only 67.8% of the gross CV. The contributions, especially by substances containing at least two carbon atoms, are large and omission of them would results in significant errors. In the case of low-temperature carbonization gas, light oils represent about 1.5% of the gas volume; however, they contribute almost 8% of the gas CV.

Table I

Coal gas composition from by-product coke oven and its contribution to gross calorific value (Powell, 1945)

Species in unwashed coke oven gas from by-products plant			Volume % of gas species	% Contribution to gross CV	% Combined contribution to gross CV
Major gas constituents	Hydrogen	H_2	56.70	30.24	82.5
	Methane	CH_4	29.60	49.17	
	Nitrogen	N_2	0.90	0.00	
	Carbon monoxide	CO	5.70	3.05	
	Carbon dioxide	CO_2	1.70	0.00	
	Ethylene	C_2H_4	2.45	6.45	
Minor and trace gas constituents	Ethane	C_2H_6	1.28	3.72	13.59
	Propylene	C_3H_6	0.34	1.31	
	Propane	C_3H_8	0.80	0.33	
	Butylene	C_4H_8	0.16	0.81	
	Butane	C_4H_{10}	0.02	0.11	
	Acetylene	C_2H_2	0.05	0.12	
	Hydrogen sulphide	H_2S	0.70	0.73	
Oxygen		O_2	0.00	0.00	0.00
Light oils		C_6H_6*	0.65	3.96	3.96
Total percentage			100.33	100.00	100.00
Gas CV including all components:				23.93	MJ/Nm^3

*: Benzine represents light oils.

Table II

Coal gas composition from low-temperature carbonization and its contribution to gross calorific value (Powell, 1945)

Species in unwashed coke oven gas from by-products plant			Volume % of gas species	% Contribution to gross CV	% Combined contribution to gross CV
Major gas constituents	Hydrogen	H_2	33.5	15.5	67.8
	Methane	CH_4	32.0	46.8	
	Nitrogen	N_2	1.1	0.0	
	Carbon monoxide	CO	11.7	5.4	
	Carbon dioxide	CO_2	11.0	0.0	
	Ethylene	C_2H_4	0.92	2.11	
Minor and trace gas constituents	Ethane	C_2H_6	3.80	9.61	24.31
	Dimethylethylene (3 isomers)	C_4H_8	0.51	2.25	
	Propylene	C_3H_6	0.87	2.90	
	Propane	C_3H_8	1.33	4.79	
	Butane	C_4H_{10}	0.28	1.31	
	Isobutane	C_4H_{10}	0.09	0.42	
	1,3–Butadiene	C_4H_6	0.002	0.01	
	Acetylene	C_2H_2	0.00	0.00	
	Hydrogen sulphide	H_2S	1.00	0.91	
Oxygen		O_2	0.00	0.00	0.00
Light oils		C_6H_6*	1.498	7.94	7.94
Total percentage			100.33	100.00	100.00
Gas CV including all components:				27.53	MJ/Nm^3

*: Benzine represents light oils.

Liberation of volatiles at high temperatures

The residue from the proximate analysis test in which 'volatiles' were determined is by no means free from volatile elements like H, O, N, and S. Most of the remaining volatile elements are liberated only at temperatures higher than 900°C, and even exceeding 2000°C. In a Lurgi packed-bed gasifier sampling campaign, Bunt and Waanders found that 10% of the coal nitrogen, as well as 0.75% of coal hydrogen, remained in the residue after reaching a temperature of at least 1000°C (Bunt and Waanders, 2008).

For a detailed mass balance on a process that produces reductants, or even one where coal is converted to char for consumption in the process itself, such as the DR kiln, the extent of liberation of H, O, N, and S, as well as the remaining carbon that is associated with the volatiles, should be carefully considered.

If coke or char is heated to very high temperatures (higher than *e.g.* 1500°C) in the absence of oxygen to effect graphitization or to drive off the remaining H, N, S, and O, the ash composition could also be expected to change. Volatile oxides (such as K_2O and Na_2O) would be driven off to a large extent. Most remaining ash oxides could react with carbon at these temperatures, forming volatile oxides such as $SiO_{(g)}$ and $Al_2O_{(g)}$. A notable exception to this behaviour is iron, which does not readily form a volatile reaction product. Under such conditions, iron would exist in the reductant as metallic iron or perhaps FeS (instead of an oxide of iron). That explains why the ash composition of graphite has a significant or dominant Fe_2O_3 content (during determination of the ash composition, iron or FeS would oxidize to form Fe_2O_3). Another effect of these high-temperature reactions is the consumption of some carbon in forming these volatile oxides.

Ultimate (elemental) analysis

The char residue from the proximate analysis test for determination of 'volatiles' is by no means free from volatile elements like H, O, and N. Therefore 'fixed carbon' is not defined in terms of its elemental composition. As we have seen, 'volatiles' is also not defined in terms of elemental composition.

For mass and energy balance studies it is advisable to base calculations on the ultimate analysis instead of the proximate analysis of the coal. Reasons for this include the following:

- ➤ The percentage fixed carbon could be a function of certain parameters such as heating rate, gas pressure, and secondary reactions involving the volatiles
- ➤ The composition of 'fixed carbon' is not defined in an elemental sense, as it could contain residual sulphur, hydrogen, nitrogen, and oxygen
- ➤ The composition of 'volatile matter' is also not defined in an elemental sense, as it could contain numerous compounds in varying quantities.

Ultimate analysis involves determination of the carbon, hydrogen, nitrogen, and total sulphur content of air-dry coal. Ash (from the proximate analysis) is also used in the formula. Oxygen is determined as the balance of the elemental analysis, as follows:

$$\%O = 100\% - \%\ \text{Inherent moisture} - \%Ash - \%C - \%H - \%N - \%S \qquad [4]$$

Note that neither oxygen nor hydrogen contained in the inherent moisture, nor in the ash-forming oxides, form part of the reported coal oxygen content (ASTM Designation D 3, n.d.).

For elemental analysis done on a Leco apparatus, it is important to ensure the apparatus is calibrated with a sample that more or less resembles the sample being tested. If, for example, an anthracite sample is analysed while a bituminous coal reference sample is used, significant error could occur. Such an error is often evident from the oxygen content (which is calculated by difference), which can sometimes be reported as a negative value. Figure 1 shows typical oxygen contents of South African coals plus four imported hard coking coals (Schoeman and Boshoff, 1996), and Table III contains the proximate and ultimate analyses, as well as the calorific values, of this set of data. The lowest oxygen contents were found for anthracites, ranging from zero to 2%. Note, however, that oxygen contents up to about 4% are not uncommon for anthracitic coals. Hard coking coals generally have relatively high rank and high vitrinite content (Falcon, 2013) and low oxygen contents , of the order of 2–4%.

Other South African bituminous coals have oxygen contents of generally between 7% and 11%. High-inertinite coals from the Free State have relatively high oxygen contents of about 9%, and are also noteworthy due to high ash (a relatively high ash content implies a relatively low carbonaceous content).

If the ultimate analysis is used to represent coal or coal derivatives entering a process, additional care would have to be taken, especially regarding sulphur and oxygen.

Representation of sulphur in coal

As mentioned previously, 'fixed carbon' would also include sulphur reporting in the residue of the proximate analysis test. Under the oxidizing conditions in a pulverized fuel boiler, sulphur could be oxidized to SO_2, which generally involve exothermic reactions. However, under the reducing conditions prevailing in the blast furnace or Corex processes, sulphur cannot be oxidized to SO_2, but forms H_2S instead. Consequently, oxidation of that part of the 'fixed carbon' cannot contribute to any exothermic heat generated for those processes. Sulphur in coal can exist in pyritic, sulphatic, and organic forms. Under oxidizing conditions, organic and pyritic sulphur would oxidize exothermally to SO_2. However sulphatic sulphur is already in an oxidized form. Sulphatic sulphur does not constitute a high percentage of the sulphur in South African coals (Schoeman and Boshoff, 1996).

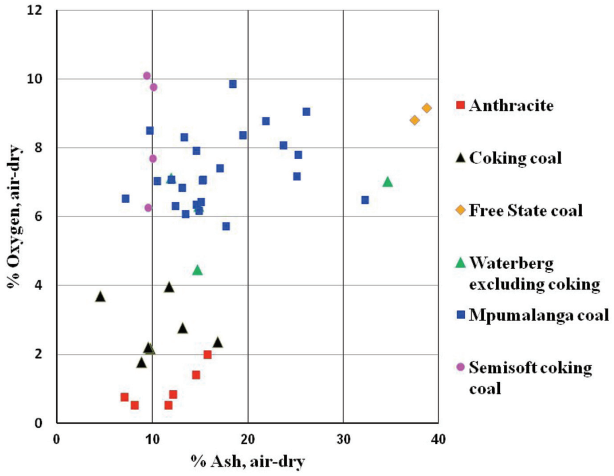

Figure 1 – Oxygen contents of South-African coals and four imported hard coking coals (Schoeman and Boshoff, 1996)

It is advisable to use the total sulphur content from the elemental analysis as input sulphur into a model. Using the SO_3 from the ash analysis could imply that part of the sulphur would be double-counted. On the other hand, omitting SO_3 would cause missing mass in the mass balance, which is probably preferable to double-counting sulphur. SO_3 in the ash is particularly related to calcium, which combines sulphur as $CaSO_4$. Calcium sulphate forms during the ashing of the coal for ash composition determination; however, it would not necessarily form in any given process. Generally, CaSO4 would form at temperatures of around 900°C under oxidizing conditions.

If coal is devolatilized instead of combusted, reducing conditions prevail and pyrite would decompose at temperatures in the range 300–600ºC (Rausch, 1975) according to:

$$FeS_2 \rightarrow FeS + ½ S_2(g) \qquad [5]$$

This would affect the analysis of forms of sulphur, a topic that is beyond the scope of this paper.

Presumably, basing a representation of coal on the mineralogical analysis would be the ultimate goal. The percentage of mineral matter in the coal could be linked by approximation with the ash, as well as certain other parameters, by the King-Maries-Crossley formula (Karr, 1978), provided those parameters are available:

$$MM = 1.09A + 0.5S_p + 0.84CO_2 - 1.1SO_3 + 0.5Cl \qquad [6]$$

where

MM is mineral matter (% by mass)
A is ash content (% by mass)
S_p is pyritic sulphur in the coal (% by mass)
CO_2 is carbon dioxide that originates from the mineral matter in the coal (%)
SO_3 is sulphur trioxide in the ash (%)
Cl is the chlorine in the coal (%).

Representation of oxygen in coal

South African coals have too high an oxygen content to be ignored for all calculations involving elemental analysis. In principle, representing the oxygen as O_2, can be considered, or replacing some of the hydrogen or carbon of the coal to form compounds such as H_2O, CO, or CO_2. According to Powell (1945), free oxygen is present in coal gas only as a result of air leakage or introduction of air after the gas has left the carbonization chamber. Relatively small amounts of oxygen could also be associated with air originally present in the voidage between the coal particles plus that in the pores or adsorbed within the coal during charging. Therefore, from these considerations, assuming the coal oxygen to be O_2 seems to be the least accurate assumption.

The Dulong formula (Rosenqvist, 1974) allows estimation of the gross CV of coal as calculated from the elemental analysis:

$$NCP = 81C + 340(H - O/8) + 22S \qquad [7]$$

where

NCP is gross CV in kCal/kg (1 kCal = 4.184 kJ)
C, H, O, and S are the mass percentages of these elements in an absolute dry coal sample.

Table III

Proximate and ultimate analyses and calorific values of South African coals and four imported hard coking coals (Schoeman and Boshoff, 1996)

		Proximate analysis (air-dry base), mass%				Gross CV, (air-dry base), MJ/kg	Ultimate analysis (air-dry base), mass %				
		Moisure	Volatile matter	Ash	Fixed carbon		C	H	N	S (total)	O
Anthracites	A	21	6.0	12.1	79.8	30.31	79.56	2.64	1.96	0.81	0.83
	B	2.4	7.7	15.7	74.2	29.17	75.07	2.85	1.56	0.43	1.99
	C	1.7	9.1	14.5	74.7	29.78	76.42	3.18	1.93	0.86	1.41
	D	1.8	7.7	11.6	78.9	30.44	79.34	3.20	2.10	1.44	0.52
	E	1.9	5.3	8.1	84.7	32.07	83.66	2.84	1.80	1.17	0.53
	F	1.6	5.4	7.0	86.0	32.46	85.09	2.87	1.80	0.88	0.76
Coking coals	G	1.5	31.0	11.7	55.8	30.53	74.61	4.82	1.95	1.44	3.98
	H	1.1	21.8	13.1	64.0	30.77	76.07	4.38	1.92	0.66	2.77
	I	0.7	24.0	8.8	66.5	32.94	80.99	5.08	2.08	0.58	1.77
	J	1.1	30.8	4.5	63.6	33.54	82.30	5.35	1.09	1.96	3.70
	K	0.7	27.8	9.7	61.8	32.45	79.64	5.11	1.62	1.05	2.17
	L	0.7	22.9	9.5	66.9	32.51	80.37	4.89	1.78	0.56	2.21
	M	0.8	22.0	16.8	60.4	30.38	73.33	4.40	1.67	0.63	2.37
Free State coals	N	5.9	19.3	37.4	37.4	16.27	43.76	2.66	1.07	0.41	8.80
	O	6.8	20.5	38.7	34.0	15.59	41.12	2.71	1.00	0.50	9.17
Waterberg coals	P	2.2	26.4	34.6	36.8	20.43	50.63	3.56	1.17	0.82	7.02
	Q	2.9	24.9	14.8	57.4	27.30	70.10	3.78	1.40	0.71	6.31
	R	2.9	24.2	14.7	58.2	27.40	71.90	3.86	1.50	0.67	4.47
	S	2.4	23.4	11.9	62.3	27.95	72.38	3.90	1.63	0.66	7.13
Mphumalanga coals	T	4.2	23.6	25.1	47.1	21.94	57.91	3.25	1.42	0.96	7.16
	U	4.9	22.6	26.1	46.4	20.87	54.92	3.06	1.29	0.68	9.05
	V	4.5	24.3	21.9	49.3	22.23	59.07	3.30	1.33	1.12	8.78
	W	3.2	26.8	12.4	57.6	27.98	71.31	4.27	1.73	0.78	6.31
	X	3.1	25.9	13.5	57.5	27.89	70.79	4.30	1.75	0.49	6.07
	Y	2.6	31.7	10.5	55.2	29.56	72.69	4.81	1.85	0.52	7.03
	Z	2.7	23.9	14.6	58.8	27.39	70.17	4.07	1.55	0.57	6.34
	AA	2.4	29.2	7.2	61.2	30.69	77.03	4.62	1.82	0.41	6.52
	AB	2.0	27.0	15.3	55.7	27.47	69.42	4.24	1.67	0.30	7.07
	AC	2.0	24.9	17.1	56.0	26.51	66.77	4.05	1.60	1.08	7.40
	AD	2.9	27.2	17.7	52.2	25.94	66.40	4.00	1.71	1.58	5.71
	AF	2.6	27.1	15.2	55.1	27.16	68.64	4.10	1.76	0.65	7.05
	AG	4.3	25.6	19.5	50.6	23.96	61.78	3.72	1.39	0.95	8.36
	AH	2.2	20.8	32.3	44.7	20.86	53.77	3.09	1.27	0.90	6.47
	AI	3.6	27.0	14.6	56.4	26.68	67.78	4.11	1.62	0.39	7.90
	AJ	3.0	25.4	13.3	58.3	27.44	69.20	4.06	1.55	0.58	8.31
	AK	4.0	24.1	18.4	53.5	23.89	62.20	3.33	1.40	0.83	9.84
	AL	3.5	22.3	13.1	61.1	27.06	70.29	3.80	1.64	0.84	6.83
	AM	2.9	18.9	14.9	63.3	27.03	70.09	3.62	1.69	0.63	6.17
	AN	4.8	24.2	25.3	45.7	21.83	56.19	3.42	1.30	1.19	7.80
	AO	2.7	26.6	15.1	55.6	27.65	69.29	4.22	1.64	0.63	6.42
	AP	3.2	31.3	9.7	55.8	28.94	71.65	4.57	1.80	0.58	8.50
	AQ	3.2	24.2	23.7	48.9	23.14	59.32	3.59	1.45	0.68	8.06
	AR	2.1	28.5	12.0	57.4	28.23	71.60	4.33	1.67	1.23	7.07
Semisoft coking coal samples	AS	3.1	35.2	9.4	52.3	29.27	70.20	4.92	1.39	0.88	10.11
	AT	2.6	37.0	9.5	50.9	29.79	73.86	5.27	1.52	0.99	6.26
	AU	2.5	36.9	10.1	50.5	29.16	70.44	4.74	1.49	0.97	9.76
	AV	2.9	35.6	10.0	51.5	29.43	72.09	4.82	1.44	1.06	7.70

The formula implies that oxygen decreases the contribution of hydrogen to the gross CV. This suggests that oxygen is combined with hydrogen in coal, probably as $H_2O_{(l)}$, or at least the thermal effect thereof seems to be an acceptable approximation.

Several proposed molecular structures of coal have been published by various authors (Given, 1960; Wiser, 1973). If we consider a proposed structure of vitrinite, we observe that most oxygen is present in C–O–H, less in C–O–C bonds, and some C=O bonds are also found (Shinn, 1984). From such a structure oxygen would not be liberated as O_2.

From the vitrinite structure in Figure 2, the coal would preferably be represented by a small number of species with less complex molecular structure and known thermodynamic properties. Even studying the type of bonds does not help much in suggesting which species would best represent oxygen in the coal. However, whatever species are chosen, the mass balance should be satisfied (it should reflect the elemental composition of the coal) and the energy balance should be satisfied. Potentially one could choose any one of O_2, H_2O, CO, or CO_2.

The effect of the choice of a compound to represent oxygen in coal on the results obtained is illustrated by the simple hypothetical 'process' in Figure 3. Table IV gives the assumed composition of the hypothetical coal used in this study. The hypothetical coal is simplified by assuming it is dry and the ash has only one constituent: SiO_2. One kilogram of this coal is oxidized with 2.25 kg oxygen to yield an off-

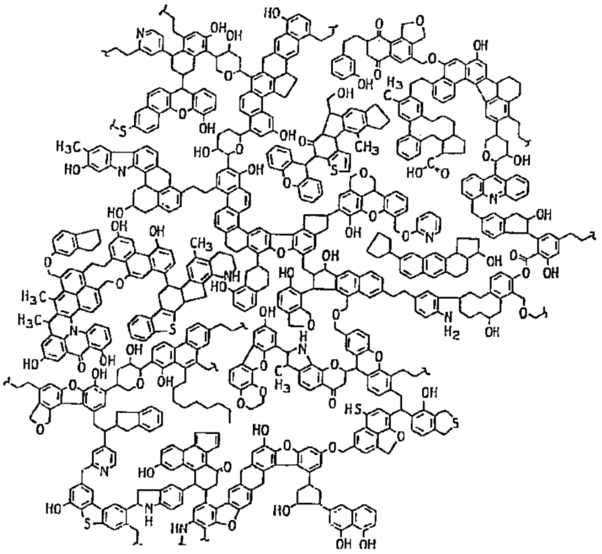

Figure 2 – Vitrinite coal structure (Shinn, 1984)

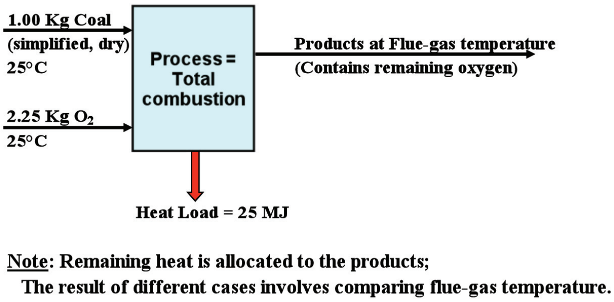

Figure 3 – Hypothetical 'process': illustration of study on assumptions of a compound to represent oxygen in coal

gas containing surplus O_2. The hypothetical heat load of the process is 25.00 MJ. The remaining heat is allocated to the flue-gas. The flue-gas temperature is calculated for different assumptions. Flue-gas temperatures were determined for coal oxygen represented as:

- O_2
- $H_2O_{(l)}$
- CO
- CO_2.

In principle, coal could be represented by a mixture of species, including oxygen-containing species other than those from list above. However, the list was chosen to illustrate a concept that could be applied to any valid selection of species. The Ex Mente™ Easy Thermo program was used to perform the equilibrium calculation.

Table V gives the resulting flue-gas temperatures from this study. For the four cases, the flue-gas temperature varied between 807°C and 1128°C, which suggest that the choice of

Table IV

Hypothetical example of coal oxygen representation by different compounds

Representation according to assumptions on oxygen

Assume the coal is dry and contains only one ash item: SiO_2

Assume the Gross CV of the coal is:	30.0	MJ/kg (dry)
Mass Coal input:	1.0	kg

Input		
	Mass %	Mass, g
%C	75.0	750.0
%H	4.0	40.0
%N	2.0	20.0
%S	1.0	10.0
%O	8.0	80.0
%SiO_2	10.0	100.0
Total	100.0	1000.0

	Represented contents according to different assumptions on coal oxygen			
	Assumption 1: O_2	Assumption 2: H_2O	Assumption 3: CO	Assumption 4: CO_2
	gram	gram	gram	gram
C (graphite)	750.0	750.0	689.9	720.0
H_2	40.0	29.9	40.0	40.0
N_2	20.0	20.0	20.0	20.0
S	10.0	10.0	10.0	10.0
O_2	80.0			
SiO_2	100.0	100.0	100.0	100.0
H_2O		90.1		
CO			140.1	
CO_2				110.0
Total	1000.0	1000.0	1000.0	1000.0

Table V

Flue-gas temperatures from representation of coal oxygen by different molecules in the hypothetical example

	Assumption 1: O_2	Assumption 2: H_2O	Assumption 3: CO	Assumption 4: CO_2
Flue-gas temperature, °C	1128	807	1006	909

the compound to represent oxygen in coal has a significant influence on the accuracy of modelling.

From fundamental analysis of the problem, there are at least four different reasons why any representation of coal could be inaccurate as far as the energy balance is concerned.

- Amorphous carbon in coal is at a higher free energy as well as enthalpy state compared to graphite. This is illustrated in Figure 4. The difference of about 5 kcal/mole C (1 kcal = 4.184 kJ) equates to about 1.0 MJ/kg for coal containing 60% C, or up to about 1.5 MJ/kg for higher grade coals (having higher carbon content). Coke carbon is associated with a free energy state intermediate between coal and graphite. For modelling purposes, thermodynamic values for graphite are generally available and used
- Depending on the assumption of how oxygen in the coal is represented, significant differences in calculated energy requirement or consumption for the same process could occur
- Energy is required for liberation of the organic volatiles. However, this value is usually not known for a specific coal
- Energy is consumed during pyrolysis of inorganic compounds such as clays and carbonates (associated with 'inert volatiles', as discussed).

For pyrometallurgical modelling involving solid carbon, as well as for tar, results from the bomb calorimeter can be used to calibrate the enthalpy balance. These results represent real behaviour, while calculated results could be inaccurate as previously explained. Such a calibration procedure should rectify inaccuracies resulting from all the reasons mentioned, including the choice of a compound to represent oxygen in coal.

It is hereby suggested that the calculated CV should be compared with the experimentally obtained CV, and the balance used as a correction for the enthalpy of the coal or coal derivative. In principle, this approach is also shared by Peacey and Davenport (1979) for the purpose of modelling the injection of coal and other hydrocarbons into a blast furnace. The balance between calculated CV and gross heat of combustion yields the heat of formation of a hydrocarbon from the elements. That indicates that the assumption is made of O_2 representing oxygen in coal, instead of *e.g.* $H_2O_{(l)}$ which, from the discussion above seems to be a more logical choice.

Subsequently, the effects of determining the correction value were studied for each of the four cases (where four different species were selected to represented oxygen in coal) to determine the effect of using each correction value on the predicted flue-gas temperature of the hypothetical process (see Table VI). The strategy involved calculating a coal enthalpy correction value as follows:

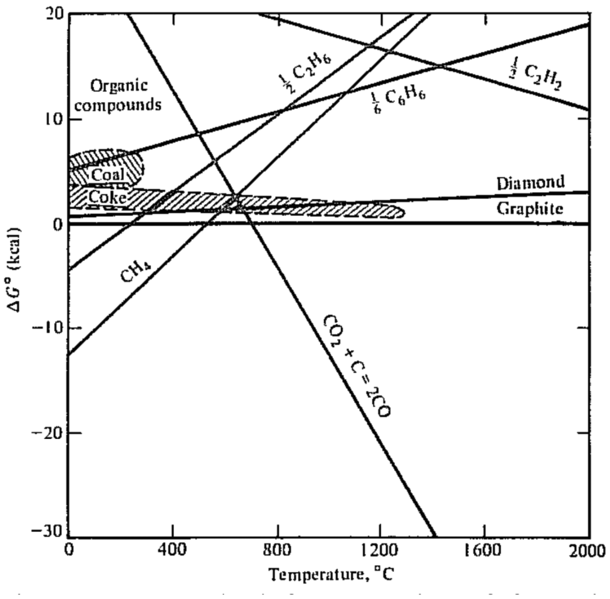

Figure 4 – Standard free energies of formation of various carbon compounds relative to graphite (Rosenqvist, 1974)

$$\text{Coal enthalpy correction value} = \text{Gross CV} - \text{Calculated CV} \quad [8]$$

The unit of this correction value would be MJ/kg. By adding the enthalpy correction value (which could be either positive or negative) to the calculated CV, the CV would be corrected to represent the experimentally determined gross CV. For the present hypothetical study, the coal enthalpy correction value was calculated for each of the four cases, where oxygen in the coal was represented by different species. Subsequently, the coal enthalpy (where carbon is assumed to be graphite by default) was corrected by the correction value, and the corrected flue gas temperatures were calculated (Table VI).

A different coal enthalpy correction value is obtained for every compound assumed to represent oxygen. However, the corrected off-gas temperature is the same for all the different assumptions, namely 1074°C. Since the values, including the coal CV, used in this example are hypothetical, this does not provide proof of which compound best represents oxygen in coal.

Clearly. whatever the choice of the compound to represent oxygen in coal, the correction value yields the same correct flue-gas temperature, as the correction value itself depends on the choice of a compound to represent oxygen.

Table VI

Results from hypothetical example, including use of the coal enthalpy correction value

	Assumption 1: O_2	Assumption 2: H_2O	Assumption 3: CO	Assumption 4: CO_2
Flue-gas temperature before correction, °C	1128	807	1006	909
Coal enthalpy correction value, MJ/kg coal	0.247	-1.183	-0.306	-0.737
Flue-gas temperature after correction, °C	1074	1074	1074	1074

Nevertheless, it seems important that the correction yields a relatively accurate result. One could refer to the correction term as the 'energy of decomposition of the volatiles'. However, that would suggest that, after devolatilization, no correction term would be required, while the form of carbon (graphite *vs*. amorphous carbon or coke) is still of importance. To designate the correction term, 'heat of formation of a hydrocarbon' (the approach by Peacey and Davenport, 1979) would yield an accurate result. However, the representation of oxygen as O_2 could seem conflicting, as studies suggest that oxygen would not be liberated from coal as O_2 (except for minute quantities originating from the pores in the coal).

Although H–O bonds are not the only way oxygen is combined in coal (Figure 2), representing oxygen in coal by $H_2O_{(l)}$ seems to be a logical choice. The question arises about the general accuracy of predicting the CV of South African coals by calculating from elemental analysis without using the correction procedure. Data for the same set of coals as for Figure 1 was used for this purpose. The theoretical CV was calculated by the following formula, which was derived from the heats of combustion of the species in this study:

$$CV_{(calc)} = 0.3276{*}\%C + 1.4179{*}\%H - 0.1787{*}\%O + 0.0926{*}\%S \qquad [9]$$

where

$CV_{(calc)}$ is the calculated gross CV of the coal on an air-dry base (MJ/kg)
%C: % carbon (air-dry base)
%H: % hydrogen (air-dry base)
%O: % oxygen (air-dry base)
%S: % total sulphur (air-dry base).

Note that Equation [9] is not the result of multiple regression analysis. For the calculation it was assumed the oxygen in coal is present as $H_2O_{(l)}$ and carbon is present as graphite, according to the results depicted in Figure 5. Generally, good agreement between calculated and actual gross CV for all the different coals was found. Nevertheless, percentage errors up to 2.9% were found for this set of coal analyses. In order to increase the accuracy of the energy balance so that it is equal to that obtained from the calorimetric technique, the enthalpy correction term must be utilized.

A positive coal enthalpy correction value could be interpreted from the effect of a carbon form with a higher enthalpy than graphite outweighing the effect of decomposition of the volatiles, and *vice versa*. The purpose of the correction value is to correct the predicted CV to a value equal to that determined in the bomb calorimeter. If the process being modelled involves coal derivatives like coke, char, or tar, it would be advisable to determine the gross CVs of those coal derivatives and calculate enthalpy correction values for them, to be incorporated in the respective energy balances.

It is important to note that, apart from the coal enthalpy correction term, no additional correction value, as suggested by Figure 4, should be used, as that would represent double-counting of effects, which would introduce an error in the calculation process.

Another study was undertaken on the present set of South African coals by representing coal oxygen as O_2 instead of $H_2O_{(l)}$, according to Figure 6. This assumption causes the coal calorific values obtained for the Free State and Mpumalanga coals to be over-estimated. Similar studies for oxygen represented as CO or CO_2 were not included.

Note also that the study is limited to South African coals. It is possible that selecting a different compound to represent oxygen could lead to slightly more accurate predicted CVs for different coals. Nevertheless, the recommendation to determine the CV of the coal and coal derivatives and correct the enthalpy by comparison with the gross CV is a general one.

Conclusions

Coal proximate analysis should not be regarded as absolute; it could vary with several parameters, including heating rate. For modelling, the use of ultimate analysis should be considered a preferable option to proximate analysis, where, 'fixed carbon' and 'volatiles' are not defined in terms of chemical composition. Significant errors could be introduced

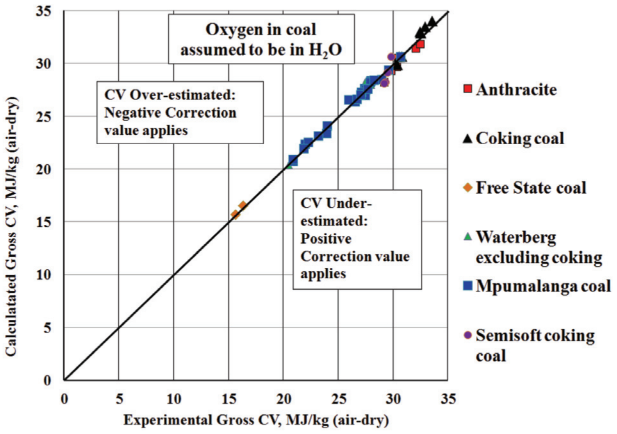

Figure 5 – Calculated vs experimental gross CVs for South African coals and four imported hard coking coals (oxygen assumed to be present as $H_2O_{(l)}$)

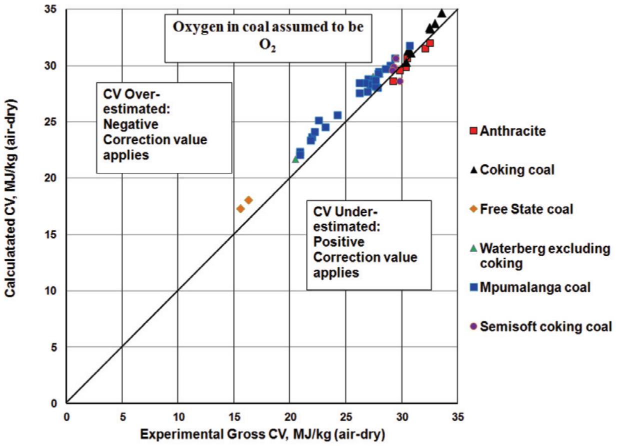

Figure 6 – Calculated vs experimental gross CVs for South African coals and four imported hard coking coals (oxygen assumed to be present as O_2)

if the larger molecules are neglected during calculation of the calorific value (CV) of coal gas (the gas liberated when coal is heated in the absence of oxygen).

For elemental analysis, the oxygen content (which is calculated by balance) should be checked to ensure it is within the expected range. For representation of sulphur in coal, one should be careful to avoid double-counting due to SO_3 in the ash analysis.

Potentially, oxygen in coal could be represented as O_2, H_2O, CO, or CO_2. However, use of some of these species without considering the experimentally determined gross CV introduces significant errors in the energy balance. If coal enthalpy is calculated from elemental analyses without correction, representation of coal oxygen as $H_2O_{(l)}$ gives reasonable accuracy (up to 2.9% error for a set of South African coals). Coal volatiles could be represented by a complex mixture of compounds, even using different oxygen-containing species other than the abovementioned four, provided the enthalpy is corrected.

It is recommended that an 'enthalpy correction value' is incorporated in energy balances involving combustion, devolatilization, or conversion of coal and coal derivatives, *e.g.* coke, char, or tar. That would imply that proximate analysis, elemental analysis, as well as the gross CV would be required for all solid or liquid coal-derived substances being modelled. No other correction due to the form of carbon being different than graphite should be used, as that would imply double-counting some effects.

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