IC engine exhaust gas analysis.

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Abstract

A generalised approach, based on linear algebra, is described for processing exhaust gas analyser data. Systematic methods of deriving useful relationships from arbitrary data are proposed, and used to produce several novel and useful results, as well as to show how existing relationships may be derived in forms that involve no approximations. The methods developed lend themselves to automatic real-time assessment of the consistency of gas analyser data, and in the case of inconsistencies, identifying plausible reasons. The approach is also used to develop methods to examine storage and release mechanisms within after-treatment devices, such as oxygen storage/release in three way catalysts, soot oxidation in particle filters, and water condensation/evaporation.

1 Introduction

There is significant prior art related to this topic, and a good review is contained in the paper by Silvis [1], who examines the application and relative merits of some of the many expressions that have been proposed to relate gas species measurements to an engine's air/fuel ratio. It is hoped that this paper will be a useful addition to this field in a number ways:- i) methods of analysis are introduced based on a linear algebra approach, which helps to clarify the process of developing relationships of interest, and the effect of any assumptions on these relationships, ii) a number of new results have been obtained, iii) many new gas analysers for IC engines are appearing, and these analysers deliver new data (e.g. H_2O, hydrocarbon speciation, etc), for which it is useful to have a framework within which the use of this new data can be integrated.

In relating the known (measured or assumed) gas and fuel composition to the unknowns of interest (such as lambda and unmeasured gas species), the problem may be under-constrained, in which case further assumptions are needed, over-constrained, in which case one or more relationship are discarded, or "just right". A common analyser suite leads to a situation where there exist 5 unknowns and there are 6 equations (Eq. 2 to 7 below), and the best-known method for obtaining lambda from exhaust gas analysis in this case (normally attributed to Spindt [2], later extended by Brettschneider [3]), neglects the nitrogen balance (or equivalently that the exhaust mol fractions sum to unity). Simons [4] took an alternative approach for extracting lambda from the same data by neglecting the water gas shift reaction (WGSR). There seems to have been little conjecture concerning what might appear as the arbitrary choice as to which of

the available equations should be discarded, and indeed whether there is any information available via an examination of the discarded equation. New analysers are becoming commonplace, and the issue of how to incorporate and optimise extra "knowns" may be of increased interest.

In the present paper, a linear algebra approach is taken, and this lends itself to a structured examination of what information might be obtained from the discarded relationships when the problem is over-constrained, and in particular information about the consistency of the data. Attention will also be paid to the effect of simplifying assumptions which are often made.

2 Basis of the analysis

The starting point for this endeavor is the combustion equation. In a fairly general form, and in the absence of storage/release mechanisms, this can be written on the basis of one mol of fuel as:-

$$C_nH_mO_xN_y + \lambda t\left(O_2 + uCO_2 + vH_2O + wN_2\right) \Rightarrow n_p\left(X_{CO_2} + X_{CO} + X_{H_2O} + X_{H_2} + X_{O_2} + X_{N_rO_z} + X_{uHC} + X_{N_2}\right) \quad (1)$$

t is the number of mols of O_2 required for the complete combustion of 1 mol of fuel; by inspection $t = n + m/4 - x/2$. The expressions which arise during the analysis are simplified via a nomalisation with n, the average carbon number of the fuel, and all such normalized quantities are denoted with an over-bar. Thus $\bar{t} = 1 + \bar{m}/4 - \bar{x}/2$, where $\bar{m} = m/n$ is the fuel's H/C ratio, and $\bar{x} = x/n$, is the O/C ratio. u, v and w are the ambient quantities of CO_2, H_2O and N_2 per mol of ambient O_2 respectively, and thus v is a variable; all other ambient gases (essentially Ar) are contained in w. n_p is the sum of the exhaust products per mol of fuel, and thus $\bar{n}_p = n_p/n$. The 5 unknowns referred to in the introduction are typically $\lambda, n_p, X_{H_2O}, X_{H_2}, X_{N_rO_z}, X_{N_2}$.

Initially it is assumed that there are no gas storage/release mechanisms between the engine and the gas measurement location. For example during transients, the gases downstream of a TWC (Three Way Catalyst) cannot be represented by Eq. 1, since a considerable quantity of oxygen is stored/released by the TWC's washcoat. In section 4.2 storage/release mechanisms are examined.

2.1 Fuel

$C_nH_mO_xN_y$ is a representation of the fuel, which for pump fuels will be a mix of many compounds; the proportion of fuel components that cannot can be represented within $C_nH_mO_xN_y$ is very small indeed. Nitrogen is included so that natural gas can be included as a fuel. In Brettschneider's analysis [3] he allowed for the fuel to have a water content which was treated separately from the

fuel in the analysis. Certainly water exists in, for example, fuels containing oxygenates such as ethanol. It is not clear what is gained by treating the water-in-fuel separately – except perhaps for a very minor effect via the usual assumption that the fuel composition is the same as the uHC composition (which could be corrected if need be by not making such an assumption). Thus here we assume that any water is included in $C_nH_mO_xN_y$.

2.2 Unburnt fuel, "NO_x" and particulate matter.

It is not assumed a priori that the unburnt hydrocarbons have the same composition as the fuel – though in practice this may be expedient, especially in the absence of speciation data. The unburnt fuel is assumed to be of composition $C_{n'}H_{m'}O_{x'}$ and the mol fraction of this (generally imaginary) compound is X_{uHC}, the sum of the mol fractions of the individual unburnt hydrocarbons. If a FID (Flame Ionization Detector) is employed to measure the uHC, and, as is generally the case, reports on a C_1 basis, then the analyser reports $n'X_{uHC}$. This is a very useful fact since often one only wants to know $n'X_{uHC}$ - which is fortunate as n' often isn't known with any precision. For other analysers, for example the FTIR (Fourier Transform Infra-Red) analyser, extracting the $n'X_{uHC}$ term may not be straightforward, but manufacturers of such devices for exhaust gas analysis may offer a processed output which is "FID equivalent". In this paper the hydrocarbons will in general be represented by the combination $n'X_{uHC}$.

If uHC speciation is available, then $X_{uHC} = \sum_i X_{uHC,i}$, and $n' = \sum_i n'_i X_{uHC,i} \big/ X_{uHC}$, $m' = \sum_i m'_i X_{uHC,i} \big/ X_{uHC}$ etc. The <u>actual</u> mol fraction of uHC will be needed to find the sum of the (wet) exhaust mol fractions $\boldsymbol{S}_{X_i}$, but if only a FID is used, then X_{uHC} has to be estimated using an estimate of n'. As X_{uHC} is usually represents a relatively small contribution to $\boldsymbol{S}_{X_i}$, this procedure will normally be satisfactory.

Any compounds containing only nitrogen and oxygen can be represented by N_rO_z, so $X_{N_rO_z} = \sum_i X_{N_rO_z,i}$, where $r = \sum_i r_i X_{N_rO_z,i} \big/ X_{N_rO_z}$ and $z = \sum_i z_i X_{N_rO_z,i} \big/ X_{N_rO_z}$.

Since under normal engine operation the feed-gas (engine-out) quantity of particulate matter is very small indeed, it is not included in the combustion to feedgas atom balances. However the situation across a Diesel Particle Filter (DPF) during regeneration may lead to a significant differences between the inlet end exit atom balances, and this will be investigated in appendix 8.

2.3 Balance equations and the WGSR

Returning to Eq. 1, 4 atom balances can be made:-

Carbon balance

$$1+u\lambda\bar{t}=\bar{n}_p\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right) \quad 2$$

Hydrogen balance

$$\bar{m}+2v\lambda\bar{t}=\bar{n}_p\left(2X_{H_2O}+2X_{H_2}+\bar{m}'n'X_{uHC}\right) \quad 3$$

Oxygen balance

$$\bar{x}+\lambda\bar{t}\left(2+2u+v\right)=\bar{n}_p\left(2X_{CO_2}+X_{CO}+X_{H_2O}+2X_{O_2}+zX_{N_rO_z}+\bar{x}'n'X_{uHC}\right) \quad 4$$

Nitrogen balance (assuming that there is no nitrogen in the uHC's

$$\bar{y}+2w\lambda\bar{t}=\bar{n}_p\left(rX_{N_rO_z}+2X_{N_2}\right) \quad 5$$

Also we have that the sum of the exhaust mol fractions $\boldsymbol{S}_{\boldsymbol{X_i}}$, where $\boldsymbol{S}_{\boldsymbol{X_i}}\equiv\Sigma X_i$,

$$\boldsymbol{S}_{\boldsymbol{X_i}}=1 \quad 6$$

If the fuel is a hydrocarbon, then the relative quantities of CO_2, CO, H_2O, H_2 are often taken to be related by the water gas shift reaction (WGSR)

$$-X_{co}-X_{H_2O}+X_{CO_2}+X_{H_2}=0$$

If the equilibrium constant for this reaction is K,then

$$K=\frac{X_{CO}X_{H_2O}}{X_{CO_2}X_{H_2}} \quad 7$$

K is available from standard data, and it is often assumed that for engine-out gases, the evaluation of K should be at a temperature of about 1750 K, though the little experimental data available may suggest a lower figure especially post-catalyst [5]. If the gases are fully equilibrated in a catalyst, then perhaps the catalyst temperature should be used. Though it is tempting, in view of these uncertainties, to attempt to avoid the use of the WGSR, given the commonly available analysed exhaust gases, and uncertainties therein, use of the WGSR has been found to be beneficial – and this will be confirmed in what follows. Unless otherwise stated, K is assumed to be that evaluated at 1750 K. When the equations above are manipulated to eliminate the unknowns X_{H_2} and X_{H_2O}, the group $1/2\left(1+X_{CO}/KX_{CO_2}\right)$ frequently appears, and thus the substitution

$$\alpha=\frac{1}{2\left(1+X_{CO}/KX_{CO_2}\right)} \quad 8$$

will be found to be a useful shorthand – note that α is unaffected by the basis for X_{CO_2} and X_{CO} as long as it is the same basis (wet, semi-dry or dry).

2.4 Analyser measurement basis

Analysers typically either measure a sample in its original state (i.e. "wet") or following a drier (usually a chiller) that removes much of the water vapour, and the analysed gases are then in a "semi-dry" state. Here we denote a wet sample as X_i, semi-dry as X_i^+, and completely dry as X_i^*. The last is an imaginary condition, but is useful in the analysis to follow. The different wetness states are related by

$$X_i = X_i^+ \frac{\left(1 - X_{H_2O}\right)}{\left(1 - X_{H_2O}^+\right)},\ X_i = X_i^*\left(1 - X_{H_2O}\right),\ X_i^+ = X_i^*\left(1 - X_{H_2O}^+\right) \qquad 9a\text{-}c$$

where $X_{H_2O}^+$ is the drier exit water mol fraction. The drier typically takes the sampled stream to a dew point of around 5 °C [6], meaning $X_{H_2O}^+ \approx 0.01$. Thus assuming "semi-dry" equates to "dry" introduces approximately a 1% error. Note that if a semi-dry value is available, then the dry value is also known via the drier dew point; however the wet (i.e. actual value) will not be known unless a calculated or measured value for X_{H_2O} is available.

It is commonplace to use approximate relationships relating the gas species measured to lambda etc. The simplifications usually consist of one or more of the following:- ambient CO_2 and H_2O negligible ($u \sim 0, v \sim 0$), no N_2 in the fuel ($y = 0$), and that the unburnt hydrocarbons have the same composition as the fuel ($n' = n, m' = m, x' = x$). In the relationships derived below, results without these approximations are given, along with the approximate forms when all of these approximations are made. Working from the exact forms, any desired combination of simplifying assumptions can be made.

3 Using a linear algebra approach

The aim here is to develop a flexible method of processing whatever analyser data is available. Various combinations of available analyser data and states of "wetness" are examined, and suggestions for a general approach made. The manipulations are largely relegated to appendices. For each situation the relevant equation set is cast in a form suitable for direct matrix inversion. Where tolerably simple algebraic relationships can be derived, this is done. "Spindt" will be used as a short-hand for the Spindt/Brettschneider approaches – these are essentially the same, except for the inclusion/exclusion of some more minor contributors to the atom balances. Particle emissions are not included in the analysis. Note that depending on the mix of analyser measurement bases (wet and/or semi-dry) the same basic approach may lead to rather different relationships.

3.1 Scenario 1:-Wet basis measurements of CO_2, CO, O_2, NO_x and *uHC's*

Wet basis exhaust gas measurement is becoming more common (via the use of FTIR's for example). If wet measurements of $X_{CO_2}, X_{CO}, X_{O_2}, X_{uHC}, X_{N_rO_z}$ (though X_{O_2} is in fact not available from an FTIR) are available, we can use the relationships in Eq. 2 to 7 given above to cast the complete equation set in matrix form, Eq. 10a-f .

$$\begin{bmatrix} -u & X_{CO_2}+X_{CO}+n'X_{uHC} & 0 & 0 & 0 \\ -2v & \overline{m}'n'X_{uHC} & 2 & 2 & 0 \\ -(2+2u+v) & \begin{pmatrix} 2X_{CO_2}+X_{CO}+2X_{O_2} \\ +zX_{N_rO_z}+\bar{x}'n'X_{uHC} \end{pmatrix} & 1 & 0 & 0 \\ -2w & rX_{N_rO_z}+y'X_{uHC} & 0 & 0 & 2 \\ 0 & \begin{pmatrix} X_{CO_2}+X_{CO}+X_{O_2} \\ +X_{N_rO_z}+X_{uHC}-1 \end{pmatrix} & 1 & 1 & 1 \\ 0 & 0 & X_{CO}/KX_{CO_2} & -1 & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ \bar{n}_p X_{H_2O} \\ \bar{n}_p X_{H_2} \\ \bar{n}_p X_{N_2} \end{bmatrix} = \begin{bmatrix} 1 \\ \overline{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix} \quad \text{10a-f}$$

There is one more equation than there are unknowns, so one could then be omitted, giving 5 linear equations in the unknowns, which can be solved by inverting the 5 x 5 matrix, to find the 5 unknowns, namely, $\lambda, \bar{n}_p, X_{H_2O}, X_{H_2}, X_{N_2}$. Below we consider some of the options that have been proposed for solving for the 5 unknowns – in other words which equation is to be ignored in solving for the unknowns.

3.1.1 Spindt

Since the value of X_{N_2} is normally not of interest, omitting 10d (N balance) is perhaps attractive. In fact there are only two equations which contain X_{N_2}, 10d and 10e (sum of the exhaust mol fractions = 1). Thus omitting either equation leaves the other as the only relationship containing X_{N_2}, and so is not required in solving for the other unknowns, λ, n_p, X_{H_2O} and X_{H_2}. The remaining equations can thus be written as Eq. 11a-d:-

$$\begin{bmatrix} u & 1 & 0 & 0 \\ 2v & \overline{m} & 2 & 2 \\ (2+2u+v) & \bar{x} & 1 & 0 \\ 0 & 0 & X_{CO}/KX_{CO_2} & -1 \end{bmatrix} \begin{bmatrix} \lambda\bar{t}/\bar{n}_p \\ 1/\bar{n}_p \\ -X_{H_2O} \\ -X_{H_2} \end{bmatrix} = \begin{bmatrix} X_{CO_2}+X_{CO}+n'X_{uHC} \\ \overline{m}'n'X_{uHC} \\ \begin{pmatrix} 2X_{CO_2}+X_{CO}+2X_{O_2} \\ +zX_{N_rO_z}+\bar{x}'n'X_{uHC} \end{pmatrix} \\ 0 \end{bmatrix} \quad \text{11a-d}$$

Matrix inversion could be used to obtain a numerical solution, but we proceed via Gaussian elimination to obtain algebraic forms (alternatively, equivalently but more tediously, eliminating one unknown at a time can be achieved via substitution). Eliminating X_{H_2O} and X_{H_2}, gives

$$\begin{bmatrix} u & 1 \\ (2+2u+v(1-2\alpha)) & (\bar{x}-\alpha\bar{m}) \end{bmatrix}\begin{bmatrix} \lambda\bar{t}/\bar{n}_p \\ 1/\bar{n}_p \end{bmatrix}=\begin{bmatrix} (X_{CO_2}+X_{CO}+n'X_{uHC}) \\ (2X_{CO_2}+X_{CO}+2X_{O_2}+zX_{N_rO_z}+(\bar{x}'-\alpha\bar{m}')n'X_{uHC}) \end{bmatrix} \quad 12a,b$$

The sum of the product mols per mol of fuel, n_p is then:-

$$\bar{n}_p=\frac{1+u\bar{t}\lambda}{(X_{CO_2}+X_{CO}+n'X_{uHC})} \quad 13$$

and

$$\lambda=\frac{(2X_{CO_2}+X_{CO}+2X_{O_2}+zX_{N_rO_z})+(\alpha\bar{m}-\bar{x})(X_{CO_2}+X_{CO})-B_1}{\bar{t}(2-B_2)(X_{CO_2}+X_{CO}+n'X_{uHC})+B_3} \quad 14$$

Where

$B_1=((\bar{x}-\bar{x}')-\alpha(\bar{m}-\bar{m}'))n'X_{uHC}$

$B_2=(2\alpha-1)v$

$B_3=u\bar{t}(X_{CO}-2X_{O_2}-zX_{N_rO_z}+(2-\bar{x}'+\alpha\bar{m}')n'X_{uHC})$

With $B_1=B_2=B_3=0$, and $z=1$ (*NO* only), the "standard" Spindt relationship in approximate form is recovered. B_1,B_2,B_3 relate to "second order" aspects, respectively the difference between the fuel and the *uHC* composition, ambient humidity, and ambient CO_2. The apparent inclusion of an aspect of the *uHC* composition in the Spindt relationship via n' is illusory if a FID is in use, since $n'X_{uHC}$ is actually what is reported by a FID. The effect on λ of differences between the fuel and *uHC* composition will be via the B_1 term. Eq. 14 allows for situations where the oxides of nitrogen cannot be represented by N_rO_1, (eg NO_2) via the appearance of "z". ("r" has no effect on the value of lambda – see the first paragraph of this section.)

For lean combustion $B_2<<1$, not only because usually $v<<1$ (though in extreme climates it can reach over 0.25 mols H_2O per mol of ambient O_2), but also because $\alpha\sim 1/2$, as $K=O(1)$, and $X_{CO}<<X_{CO_2}$. When both X_{CO} and the absolute humidity are significant then B_2 will be relevant. This is supported by results presented in [3]. The effect of assuming that ambient CO_2 is negligible ($u=0$) is only of relevance (and then only marginally) with very lean mixtures; e.g. at $\lambda\sim 5$ the error incurred in λ is typically around 1% (at present $u\sim 0.00183$ mols ambient CO_2 per mol ambient O_2). Note that as long as the gases are measured on the same basis, Eq. 14 remains valid.

Alternative Gaussian eliminations may be used to lead immediately to other relationships of interest. For example, if the mol fraction of hydrogen was the parameter of interest, then the equation set 11a-f leads, for $u = v = 0$, directly to

$$X_{H_2} = \frac{\overline{m}\left(X_{CO_2} + X_{CO}\right) + \left(\overline{m} - 2\overline{m}'\right)n'X_{uHC}}{2\left(1 + KX_{CO_2}/X_{CO}\right)} \qquad 15$$

If it is wished to evaluate all the exhaust gas species, then all except X_{N_2} are found from Eq. 11a-d. X_{N_2} itself can be obtained from either the nitrogen balance, Eq. 10d, or the sum of the mol fractions equaling unity, Eq. 10e. For experimental data these two alternatives will not yield the same value of X_{N_2}.

3.1.2 Simons

In this approach, the WGSR is neglected, which perhaps has some attraction, as the value of the WGSR equilibrium constant may not be well-established. Eq. 2 to 6 can then be conveniently cast as

$$\begin{bmatrix} u & 1 & 0 & 0 & 0 \\ 2v & \overline{m} & 2 & 2 & 0 \\ (2+2u+v) & \bar{x} & 1 & 0 & 0 \\ 2w & \bar{y} & 0 & 0 & 2 \\ 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \lambda\bar{t}/\bar{n}_p \\ 1/\bar{n}_p \\ -X_{H_2O} \\ -X_{H_2} \\ -X_{N_2} \end{bmatrix} = \begin{bmatrix} \left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) \\ \overline{m}'n'X_{uHC} \\ \left(2X_{CO_2} + X_{CO} + 2X_{O_2} + zX_{N_rO_z} + \bar{x}'n'X_{uHC}\right) \\ rX_{N_rO_z} \\ \left(X_{CO_2} + X_{CO} + X_{O_2} + X_{N_rO_z} + X_{uHC} - 1\right) \end{bmatrix} \qquad 16a\text{-}e$$

The 5x5 matrix contains only constants, so in this form matrix inversion is only required once.

If however algebraic relationships are preferred, then Gaussian elimination yields the result

$$\lambda = \frac{1 - X_{O_2} - X_{N_rO_z}\left(1 - r/2\right) - \left(1/n' + \bar{y}/2 + \overline{m}/2 - \overline{m}'/2\right)n'X_{uHC} - \left(1 + \bar{y}/2 + \overline{m}/2\right)\left(X_{CO_2} + X_{CO}\right)}{\bar{t}\left(\left(w+v\right)\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) - uS_1\right)} \qquad 17$$

Where

$$S_1 = \left(1 - X_{CO_2} - X_{CO} - X_{O_2} - \left(1 - r/2\right)X_{N_rO_z} - \left(1/n' - \overline{m}'/2\right)n'X_{uHC}\right) \qquad 18$$

If the approximation $uS_1 \sim 0$ is made, then the error in lambda will be approximately $100v/w\%$. Now since $w \sim 3.77$, and typically $v < 0.15$, a ~5% error may arise. $u \sim 0.002$ and has a negligible effect.

In approximate form

$$\lambda = \frac{1 - X_{O_2} - X_{N_r O_z}(1 - r/2) - (1/n')n'X_{uHC} - (1 + \bar{y}/2 + \bar{m}/2)(X_{CO_2} + X_{CO})}{w\bar{t}(X_{CO_2} + X_{CO} + n'X_{uHC})} \quad 19$$

3.1.3 Other relationships

Additional results appear in Appendix 1, but it is worth remarking here that only three of the five possible relationships for λ (and three of the six possibilities for X_{N_2}) have been considered so far for this analyser scenario. Also for each possible relationship, the question of what value the discarded relationship might have has not yet been considered.

3.2 Scenario 2:- Wet basis measurement of *uHC*'s, semi-dry measurements of CO_2, CO, O_2, NO_x.

This combination is a somewhat "classic" one, where typically a semi-dry sample is measured by NDIR (non-dispersive infra-red) (for $X^+_{CO}, X^+_{CO_2}$), CLD (chemi-luminescence detector)(for $X^+_{NO+NO_2}$), and para-magnetic (for $X^+_{O_2}$) analysers, but a FID is employed to measure unburnt hydrocarbons, and reports on a wet C_1 basis.

It is more convenient here to use dry (X^*_i) rather than semi-dry (X^+_i) quantities, and these are obtained via Eq. 9c, in the form $X^*_i = X^+_i / (1 - X^+_{H_2O})$. $X^+_{H_2O}$, the dryer exit water vapour content, will be known from the analyser specification, and as noted above, typically $X^+_{H_2O} \sim 0.01$. The Spindt and Simons relationships given above in Scenario 1, (eqs. 14 and 17, with or without approximations) have the drawback that for the more usual analyser scenario now being considered, iteration is required as in eq. 14 all the gas mol fractions have to be on the same basis, wet or semi-dry, and in the case of eq. 17 all wet. Iteration could proceed by guessing an initial value for X_{H_2O}, using this to convert the measured $n'X_{uHC}$ to the same basis as the other species, evaluating λ and an updated X_{H_2O} and so on - convergence is very fast. Silvis [1] argues that such iteration is not an issue with the advent of high speed processors, but since it is easy to find relationships which do not involve iteration, it would seem useful to have them.

Once again the aim is to write the equations derived from the combustion equations in a form suitable for matrix manipulation, as was done in the previous section. In this case however, the semi-dry quantities have a wet "counterpart" – as an example the "all wet" carbon balance, (eq 2)

$$1 + u\lambda\bar{t} = \bar{n}_p(X_{CO_2} + X_{CO} + n'X_{uHC}),$$

becomes

$$-u\bar{t}\lambda+\left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right)\bar{n}_p-\left(X^*_{CO_2}+X^*_{CO}\right)\left(X_{H_2O}\bar{n}_p\right)=1 \qquad 20$$

As in the previous analyser scenario, we have six equations and five unknowns. A useful result is derived using the Spindt method (see next section), but Simons' method does not yield any simple algebraic forms - Appendix 2 gives fuller details. It is again noted that only three of five possible relationships for λ are considered at this stage.

3.2.1 Spindt

By omitting (as in 3.1.1) either the N balance or the $\boldsymbol{S}_{X_i}=1$ equation, a matrix casting of the remaining equations suitable for inversion can be directly obtained from eq. B7. Again, as in 3.1.1, the resulting value of X_{N_2} will depend on which equation was omitted, but all the other quantities will be unaffected. Alternatively algebraic relationships can be obtained for λ in exact or approximate form, as shown in Appendix 2. In "approximate" form it is shown there that

$$\lambda=\frac{\left(2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}+zX^*_{N_rO_z}\right)+\left(\alpha\bar{m}-\bar{x}\right)\left(X^*_{CO_2}+X^*_{CO}\right)}{2\bar{t}\left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}+\alpha\bar{m}'\left(X^*_{CO_2}+X^*_{CO}\right)n'X_{uHC}\right)} \qquad 21$$

Written in terms of semi-dry products (except uHC's), Eq. 21 becomes

$$\lambda=\frac{\left(2X^+_{CO_2}+X^+_{CO}+2X^+_{O_2}+zX^+_{N_rO_z}\right)+\left(\alpha\bar{m}-\bar{x}\right)\left(X^+_{CO_2}+X^+_{CO}\right)}{2\bar{t}\left(X^+_{CO_2}+X^+_{CO}+n'X_{uHC}/\left(1-X^+_{H_2O}\right)+\alpha\bar{m}'\left(X^+_{CO_2}+X^+_{CO}\right)n'X_{uHC}\right)} \qquad 22$$

These are convenient relationships for this analyser scenario. It is equivalent to the standard Spindt relationship, but avoids the need to iterate. The difference from Eq. 15 (all mol fractions on the same basis) is the $\alpha m\left(X^*_{CO_2}+X^*_{CO}\right)X_{uHC}$ term in the denominator.

3.3 Scenario 3:- Wet measurements of CO_2, CO, NO and $uHC's$, O_2 not available

Another common situation is when a measure of O_2 is not available (and this is normally when the other analysers are operating on a "wet" basis). A well-known relationship for this scenario is due to Stivender [7], reproduced for example in Heywood [8, equ 4.66]. In this case, there are an equal number of equations and unknowns, so a "Spindt or Simons or …" issue does not arise. In casting the equation set, O_2 is now an unknown and so (for example) the oxygen balance becomes

$$-\left(2+2u+v\right)\bar{t}\lambda+\left(2X_{CO_2}+X_{CO}+zX_{N_rO_z}+\bar{x}'n'X_{uHC}\right)\bar{n}_p+\left(\bar{n}_pX_{H_2O}\right)+2\bar{n}_pX_{O_2}=\bar{x} \qquad 23$$

Appendix 3 gives a fuller analysis. The relationship for λ in exact form is cumbersome, though as ever, numerical results can easily be obtained by matrix inversion.

In approximate algebraic form ($u = v = y = 0$, and the fuel and uHC have the same composition), then

$$\lambda = \frac{\left(2 - X_{CO} - 2X_{uHC}\right) + \left(\overline{m}\left(\alpha - 1\right) - \bar{x}\right)\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(1 + w\right)\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \qquad 24$$

and the rest of the unknowns are easily determined by back substitution. The relationship due to Stivender is similar but is derived assuming the fuel contains no oxygen, and furthermore the fuel is of the form C_nH_{2n+2}. These restrictions are not required in this expression, which is of trivial additional complexity.

3.4 Scenario 4:- Wet measurements of CO_2, CO, O_2, NO, uHC's and H_2O

With some instruments (e.g. FTIR), a measurement of X_{H_2O} is possible, and this leads to certain opportunities. One of these is be able to remove or at least reduce uncertainties related to the value of the equilibrium constant of the WGSR, as was the case in Simons' approach. In this analyser scenario, we have the luxury of 6 equations and 4 unknowns. If we follow the same elimination order used previously (details in Appendix 4), that is omit either the *N* balance or the $\boldsymbol{S}_{X_i} = 1$ relationship, we find:-

$$\lambda = \frac{\left(2X_{CO_2} + X_{CO} + 2X_{O_2} + X_{H_2O} + zX_{N_rO_z}\right) - \bar{x}\left(X_{CO_2} + X_{CO}\right) + \left(\bar{x}' - \bar{x}\right)n'X_{uHC}}{\bar{t}\left(2 + v\right)\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) + u\bar{t}\left(X_{CO} - 2X_{O_2} - X_{H_2O} - zX_{N_rO_z} + \left(2 - \bar{x}'\right)n'X_{uHC}\right)} \qquad 25$$

In approximate form this is

$$\lambda = \frac{\left(2X_{CO_2} + X_{CO} + 2X_{O_2} + X_{H_2O} + zX_{N_rO_z}\right) - \bar{x}\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \qquad 26$$

Which is (unsurprisingly) similar in form to the Spindt result.

3.5 Scenario 5:- All measured semi-dry except uHCs, no O2 available

This analyser scenario is investigated in Appendix 5. This is a situation with six equations for six unknowns, so direct matrix inversion of the equation set (E7) is possible. There are no simple algebraic formulations, but with assumption $u = 0$ reasonably tractable equations result.

3.6 Species storage and release

There are a significant number of storage/release mechanisms that may be in play in exhaust systems. A universal one is that of water condensation and evaporation during cold starts. Though no results are presented here, an analysis is presented in appendix 7. Particle filtration is another example, and while gas concentration measurements may not be informative during the collection process, regeneration of a DPF may be usefully characterized by such measurements. Once again, though no results are presented here, an analysis is presented in appendix 8.

Other aftertreatment devices, such as LNT's, SCR's and TWC's, would also be amenable to analysis, but only the latter is examined in this paper, both via analysis (appendix 6) and experiment (section 4.2.3).

4 What additional value can be retrieved using the unused information?

In some instances in the 4 scenarios above, when the problem was over-constrained, equation(s) were discarded, with the objective in view being to arrive at an expression for λ. With real data, the choice of which equation(s) are omitted will result in different predictions. Whichever equation(s) are actually neglected, back substitution leads to all other quantities – and conflicting ones. Since we are dealing with experimental data, it is inevitable that discrepancies show up when following this process – for example when all the mol fractions have been determined, the mol fractions will not sum to unity. Here we investigate what value the discarded information might have.

4.1 A simple example – gasoline tailpipe gas analysis at λ~1

An almost trivial example demonstrates that the discarded relationship for a Scenario 2 (Section 3.2) emissions measurement has value. Many automotive gasoline engines run at "lambda one", so that the catalytic after-treatment system can simultaneously and effectively remove CO, uHC and NOx from the exhaust. Apart from CO_2, H_2O, and N_2, typically the post-catalyst gases contain negligible concentrations of other gases.

A set of data was taken from an engine mounted on a dynamometer test bed, equipped with a gas analysis system with a wet basis measurement of uHC's, and semi-dry measurements of CO_2, CO, O_2, NO. The semi-dried gases were passed through a chiller with an effective temperature of 5 °C, giving $X^+_{H_2O} = 0.0086$. The fuel was assayed and found to have H/C and O/C ratios:- $\overline{m} = 1.763$, $\overline{x} = 0.015$. The ambient (dry air) CO_2 concentration was taken as 390 ppm so $u = 0.00186$, and the ambient relative humidity was 60% at 25 °C, ($v = 0.091$). Because the $\boldsymbol{S}_{X_i} = 1$ relationship will be used here, in principle a value for n' is required (see section 2.2), but as $n'X_{uHC}$ is negligible, this is not needed.

The data analysed was averaged from a 10 s period when the running conditions were very stable, under closed loop control. The average UEGO reading was 0.9948, with a standard deviation of 0.00042. The average emissions figures, as measured, ppm semi-dry, except uHC which was ppm wet (C1), were as in Table 1.

$X^+_{CO_2}$	X^+_{CO}	X^+_{NO}	$X^+_{O_2}$	$n'X_{uHC}$	UEGO
162442	57	0.92	11.2	8.25	0.9948

Table 1 Measured post-catalyst exhaust gas

lambda						S_{X_i}
	Omit eq. 10a (C bal')	Omit eq. 10b (H bal')	Omit eq. 10c (O bal')	Omit eq. 10d or 10e (N bal' or $S_{X_i}=1$)	Omit eq. 10f (WGSR)	Omit eq. 10d ($S_{X_i}=1$)
u,v incl.	1.1592	0.9436	0.9436	0.99975	0.8801	1.0435
$u=v=0$	1.1510	0.9459	0.9459	0.99976	0.8848	1.0408

Table 2 Computed lambda's and S_{X_i} (uncorrected)

Table 2 shows the value of λ predicted from the data in Table 1, obtained by matrix inversion when each of the Eq. 10a-f was omitted in turn to remove the over-constraint. The upper entries include u,v, the lower entries do not – clearly the errors introduced by assuming $u=v=0$ are small. (The "Omit eq 10d or 10e" column corresponds to the Spindt method, and the "Omit 10f" column to the Simons method). The last column gives the value of S_{X_i} (the sum of the exhaust mol fractions) when and omitting the $S_{X_i}=1$ equation (all other methods have $S_{X_i}=1$ by definition). As far as the lambda prediction result is concerned, it makes no difference for the Spindt method whether the N balance or $S_{X_i}=1$ equation is omitted (see discussion in 3.1.1).

An immediate conclusion is that only the Spindt method has resulted in a realistic prediction of λ. There is no doubt that the engine is running at very close to $\lambda=1$. The Spindt relationship gives $\lambda=0.9997$ (the slightly richer UEGO result of 0.9948 is expected, as is argued in a recent paper [9]). The fact that the Spindt method makes a good prediction of λ in this case is unsurprising – from the Spindt relationship (Eq. 22) in approximate form (see also the aside following Eq. B9), it is apparent that for conditions where the noxious emissions and oxygen are virtually negligible that $\lambda \neq f\left(X_{CO_2}\right)$. However it is important to note that this insensitivity only exists at close to $\lambda=1$, i.e. when the noxious emissions and oxygen can be in low concentration.

By contrast, from the Simons expression, Eq. 17 (and ignoring the fact that this is an all wet expression), we have $\lambda \sim \left(1-\left(1+\bar{y}/2+\bar{m}/2\right)X_{CO_2}\right)/w\bar{t}X_{CO_2}$, and the prediction of lambda will be sensitive to the value of X_{CO_2}. One begins to see the reason that the Spindt method is popular!

Nevertheless, all the methods should give the same value of λ and we now enquire why they do not. Inspection of input data forces the conclusion that only the fuel composition and/or the

$X^{+}_{CO_2}$ measurement can be responsible – the only other inputs are measurements of gases which are of negligible concentration.

$X^{+}_{CO_2}$	λ	X_{H_2O}	X_{CO_2}	X_{CO}	X_{H_2}	X_{N_2}	$\overline{m}$	$\overline{x}$	S_{X_i}
162441	0.99976	141758	140623	49.5	206	757890	1.763	0.015	1.040527
162441	0.99936	122009	143859	50.7	176	733900	0.826* 1.763	0.015	1.000000
162441	0.99928	140934	140758	49.5	205	718050	1.763	11.2* 0.015	1.000000
0.955* 162441	0.99928	136230	135146	50.0	208	728363	1.763	0.015	1.000000

Table 3 Lambda and composition predictions using corrected data

Via Table 3, effect of the fuel composition and the $X^{+}_{CO_2}$ measurement is examined; for simplicity the near-zero quantities of *NOx*, *O2* and *uHC*'s have been ignored, and the approximate form ($u = v = 0$) of the relationships used. In the first row, the first entry is the measured (i.e. semi-dry) value of $X^{+}_{CO_2}$. λ has already been computed (Table 2) and to convert the measured semi-dry quantities to a wet basis (so that S_{X_i} can be computed), the value of X_{H_2O} is required - Eq. B12b; this permits the evaluation of $X_{CO_2}, X_{CO}, X_{O_2}$ from the semi-dry measurements, and X_{H_2} is given by Eq. B13. Finally, for X_{N_2} we can use either the *N* balance (Eq. B14b) or the $S_{X_i} = 1$ (Eq. B15) option. Arbitrarily the first option is taken so the "problem" with the data appears as an $S_{X_i} \neq 1$ issue, rather than an *N* imbalance.

In the three subsequent rows, the correction factor necessary to give $S_{X_i} = 1$ is computed. It is seen that the H/C ratio needs to be multiplied by 0.826, the O/C ratio by 11.2, and $X^{+}_{CO_2}$ by 0.955.

For gasoline an H/C ratio, $\overline{m} = 0.826 * 1.763 = 1.465$ is absurd, and an O/C ratio $\overline{x} = 11.2 * 0.015 = 0.168$ would be equivalent to a x10 exceedance of the allowed oxygenates for this fuel standard. Thus the only available candidate responsible for the majority of the error is the $X^{+}_{CO_2}$ measurement, either as a gain or offset error, or a calibration gas issue, of ~4.5%

Thus at this commonplace running condition, a simple check can be made on the consistency of some of the input data. Based on the manufacturer's specifications, a 4.5% error is towards, but inside, the limits quoted. It is also seen how little the modifications have on the predicted λ . This

is unsurprising, based on the discussion above about the form of the Spindt expression for $\lambda \approx 1$ when $X^*_{CO_2} >> X^*_{CO}, X^*_{O_2}, X^*_{uHC} \& X^*_{NO}$.

4.2 Gasoline feedgas gas plausibility analysis at during a catalyst oxygen storage test.

This example relates to the same set-up (engine, gas analysers, as in the previous example), but here lambda is stepped between various values. The engine speed and load are constant. At some points in this test cycle (which was not originally intended as producing data for this paper), switching between lambda values is very rapid, and this data is not examined, as response time and time delay differences between the analysers becomes dominant. Thus portions of the record has been omitted from the figures below.

This situation introduces significant additional complexity, but once again the over-constrained nature of the problem means that plausibility checks can be made on the data, and furthermore suggest, in the case of inconsistencies, what the likely cause might be. In these tests the fuel assay was $\overline{m} = 1.86,$ and $\bar{x} = 0.015$, and the ambient relative humidity was 50% at 25 °C, ($v = 0.076$ mols H_2O/mol O_2).

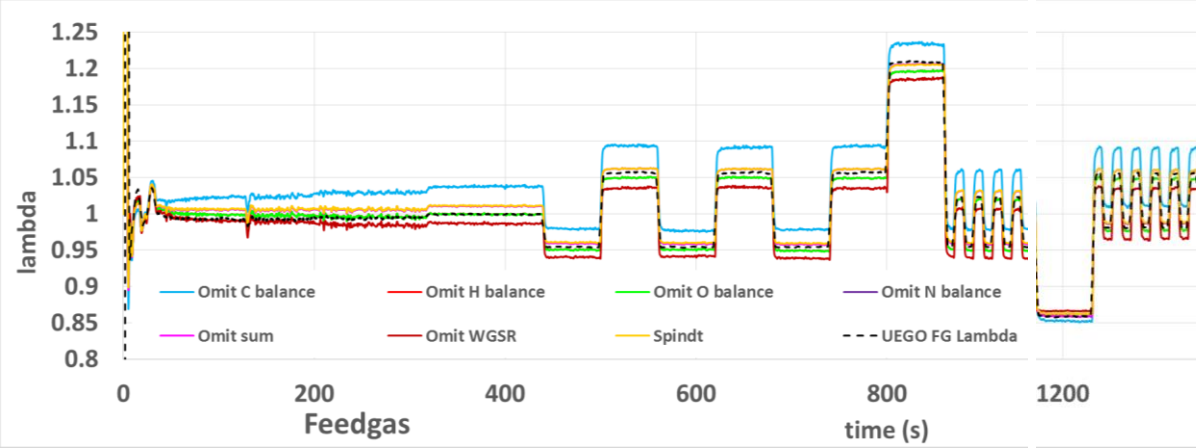

Figure 1. Raw data lambda predictions by a variety of methods (see text).

Fig 1 shows the feedgas (FG) value of λ reported by a UEGO sensor, and also the predictions of λ obtained by omitting each of the available relationships (carbon balance, hydrogen balance, etc), as described in the previous section (in other words fig 1 is the equivalent of Table 2, but for many test points). Also an approximate Spindt calculation (neglecting ambient CO_2 and H_2O) using Eq. A4b is shown. Unsurprisingly, since Spindt is based on omitting either the N balance or the $\boldsymbol{S}_{X_i}$ balance, these results lie virtually exactly on one another. The data between 0 and 400 s is included, though during this time the engine is being warmed up.

Fig 2 shows how each prediction method relates to an imbalance in the associated conservation equation. In the case of omitting the carbon balance for example (equ. 2), for real data there will

be a difference between the "input" carbon, $n+u\lambda t$, and the "output" carbon $n_p\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)$, and this might be expressed as

$$C_{imbalance}=100\left(1-\frac{n_p\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)}{n+u\lambda t}\right) \qquad 27$$

And similarly for *H*, *O*, and *N*. For $\boldsymbol{S}_{X_i}$, an equivalent expression is

$$Sum_{imbalance}=100\left(1-\boldsymbol{S}_{X_i}\right) \qquad 28$$

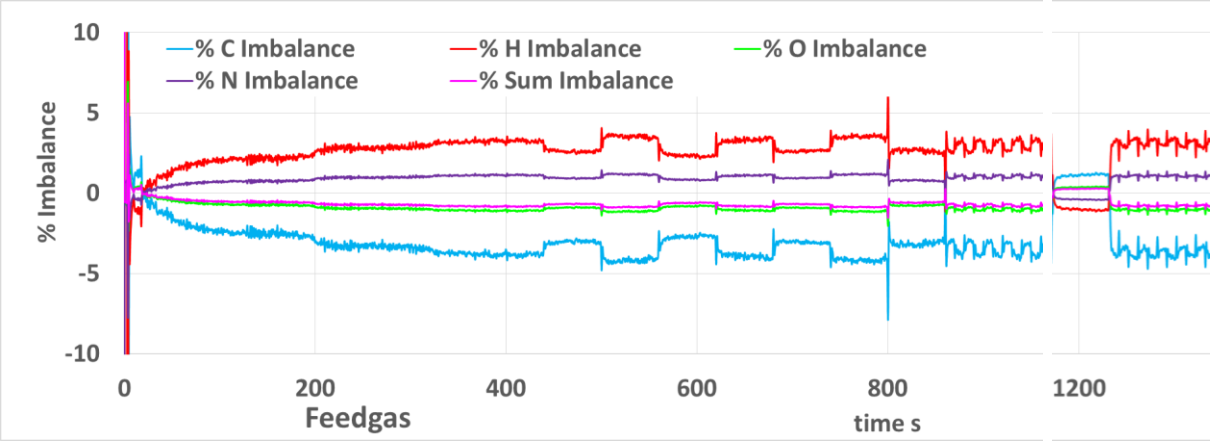

Figure 2. Imbalances calculated by a variety of methods (see text).

Bearing in mind the λ predictions from the Fig. 1, it is seen that balance errors of the order of 1% or less seem not to impact significantly on the prediction of λ.

In the case of omitting the WGSR, there will be a difference between the assumed value of K (i.e. that evaluated at 1750 K), and the value based on the measured X_{CO_2}, X_{CO} and the computed X_{H_2}, X_{H_2O}. Thus we might write

$$K_{imbalance}(\%)=100\left(1-\frac{1}{K_{assumed}}\frac{X_{CO}X_{H_2O}}{X_{CO_2}X_{H_2}}\right) \qquad 29$$

$K_{imbalance}$ defined in this way has the problem that with real data, when lean of stoichiometry, X_{H_2} can be very small, and the resulting value of $K_{imbalance}$ can be unphysical.

An alternative definition for $K_{imbalance}$ could be

$$K_{imbalance}=C_1\left(K_{assumed}X_{CO_2}X_{H_2}-X_{CO}X_{H_2O}\right) \qquad 30$$

where the constant C_1 is chosen to make these two definitions of $K_{imbalance}$ similar for rich and stoichiometric conditions. Figure 3 illustrates the issues clearly. "K Imbalance %" is that defined

in Eq. 29, while "K Imbalance" is that from Eq. 30, with $C_1 = 20000$. The "problem" at 800 – 850 s, where $\lambda \sim 1.2$, is clearly seen, due to X_{H_2} being ~ zero.

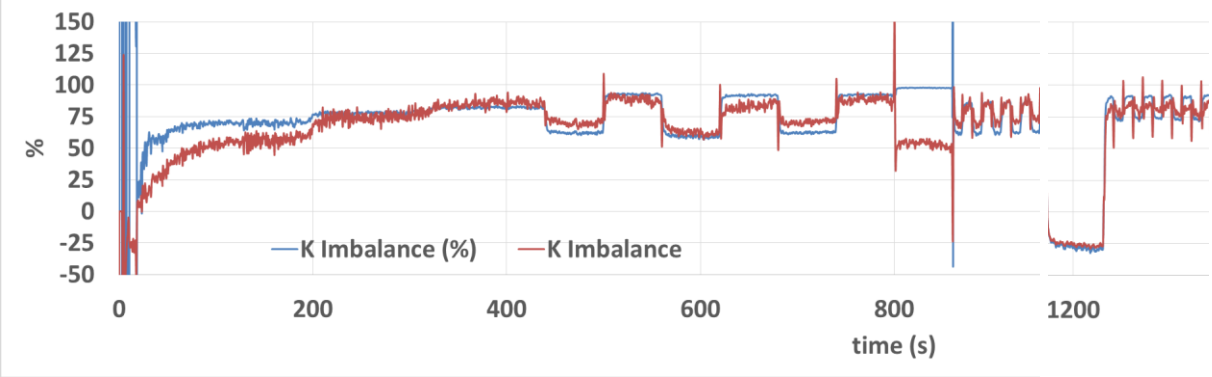

Figure 3. "K" imbalances as per Eq. 29 and 30.

4.2.2 Data plausibility investigation, feedgas.

As in the case of post-catalyst stoichiometric data, the question again arises as to what is causing the differences in the λ predictions, and the associated imbalances. Unlike the previous case, there is no unique answer, given the nature and quantity of the data available. For example it is possible, by modifying the WGSR equilibrium constant for every data point, to get the data to satisfy all the other balance constraints at every data point. The range of WGSR equilibrium temperatures required are however completely outside the range of reasonableness. The scant data available does not suggest that significant deviations from the "classic" 1750 K are likely. The fuel assay could be challenged, but no single, "reasonable" fuel composition leads to data consistency.

Thus again attention falls on the gas analysis data. We will initially assume that any "issues" with the calibration data can be corrected via a gain and offset:-

$$X_{k,true} = m_k X_k + c_k \qquad 31$$

Though nonlinearities might also be relevant, they are not considered here. It will be assumed that only corrections to $X^*_{CO_2}, X^*_{CO}, X^*_{O_2}$ are appropriate, as all other measured gases are typically in much lower concentrations, and do not affect the balance equations significantly.

Starting at 400s, (figure 1) 18 running conditions were identified where the running condition was reasonably stable, and the analyser data was averaged over these periods. Thus for each running state i, we have the averaged values $X^{*,i}_{CO_2}, X^{*,i}_{CO}, X^{*,i}_{O_2}, X^{*,i}_{N_rO_z}, n'X^i_{uHC}$, and the "true" values of the first three, are $X^{*,i}_{CO_2,true} = m_{CO_2} X^{*,i}_{CO_2} + c_{CO_2}$ etc., where the m_k, c_k and were assumed

constant throughout the test. It must be emphasised again that there is not a unique answer to the question "what's wrong" – all that can be said with certainly is that something(s) is (are) wrong, and that perhaps the most likely cause is related to the $X^*_{CO_2}, X^*_{CO}, X^*_{O_2}$ measurements.

A linear least squares approach was used to attempt to find the most likely 5 values of the m and c.The residuals are the imbalances defined above, six in number, denoted $B(k)$.

The objective is to minimise these imbalances, for every running condition *i*. In other words we wish to minimise S, where $S = \sum_{k=1}^{6}\sum_{i=1}^{n} B(k,i)$, by adjusting the 6 values of the m and c. Now $B(k,i) = f(x_{k,i}, \beta)$. where the $x_{k,i}$ are the analyser data, and if β is the vector containing the adjustable parameters, and the best fit is obtained when $\frac{\partial S}{\partial \beta_j} = 2\sum_{i=1}^{n} B(k,i)\frac{\partial B(k,i)}{\partial \beta_j} = 0,\ j = 1,2,....m$. Assuming a linear model is sufficient, then $f(x,\beta) = \sum_{j=1}^{m} \beta_j \phi_j(x)$. If we let $Z_{ij} = \frac{\partial f(x_i,\beta)}{\partial \beta_j} = \phi_j(x_i)$, then the least squares estimate of the adjustment to be made to the x_i is $\hat{\beta} = (Z^T Z)^{-1} Z^T y$.

There are thus 6 "fits" being made simultaneously, one for each imbalance relationship. Though the problem could be formulated to be a single optimization problem, this detracts to some extent from the ability to get a sense of what is physically "going on". Generally speaking the imbalances responded similarly to the adjustments being suggested.

Figure 4 shows the λ predictions following the fitting process. Due to the limited number of data points, (essentially there were only 5 distinct λ values), it was found that making simultaneous gain and offset changes was problematic. Instead, only the gains were adjusted, and the zero offsets were assumed to be those measured at the beginning of the test when the analysers were sampling air. In the case of oxygen this was estimated from the reported concentration of ambient air. The gains applied to the raw *CO2*, *CO* and *O2* data were 0.985, 1.065 and 1.019 respectively. Once again, it should be noted that calibration gases may have been implicated in the issues identified here.

From Fig. 4 it is clear that the fit is now much better, though not so good while the engine is warming up – which perhaps indicates a changing WGSR equilibration temperature. The Spindt prediction is from the raw data, and is thus identical to that in figure 1. It is intriguing that the UEGO λ measurement is not the same as that predicted from the gas analysis, but is almost identical to that of a UEGO model (green dots), described in [9]. Perhaps most surprising is the "error" at λ~1, which is about 0.01. This bias is due to the fact that $X_{CO} \sim 8000$ ppm, and $X_{H_2} \sim 2300$ ppm at this condition – much bigger values than would be predicted at equilibrium.

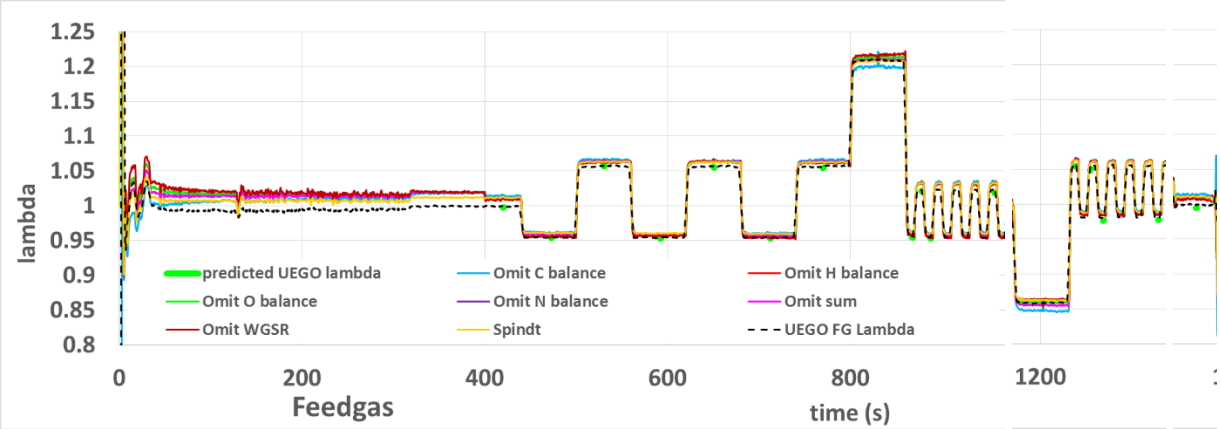

Figure 4

Figure 5 shows that the imbalances are virtually negligible following the adjustments, except during transients, which is to be expected, due to data alignment issues.

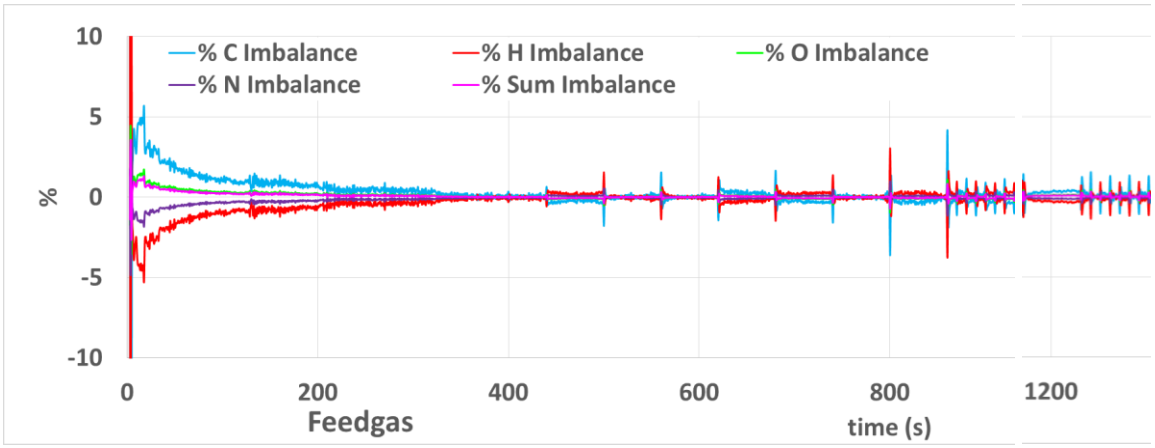

Figure 5

Though not shown, the WGRS balance is also significantly better, the maximum deviation being less that 10%.

It is striking that the predictions of λ by most of the "methods" are good, with the exception of omitting the carbon balance, and to a lesser extent, the oxygen balance. This seems to be a fairly general conclusion based on the analysis of other data. The Spindt method corresponds to both the "omit N" balance and "Omit sum" balance, and these are generally rather accurate in predicting lambda.

4.2.3 Data error investigation, tailpipe.

We now turn to the post-catalyst gases. This is the same data set as used in the previous section, and the corrected feedgas composition is used. There is the extra issue here that storage and

release of oxygen occurs, and this needs to be included in the balance equations, which are developed in Appendix 6. The analyser suite is identical to that used for the feedgas. The five unknowns are the post-catalyst (subscript "pc") quantities, $n_{pc}, X_{H_2,pc}, X_{H_2O,pc}, X_{N_2,pc}$, and the $n_{O_2,released}$. The four atom balance equations, and $\mathbf{S}_{\mathbf{X_i}} = 1$ are thus sufficient to solve for the unknowns, but there is no extra equation with which to test the plausibility of the data. The WGSR remains unused, but due to uncertainty about the appropriate equilibrium temperature, it seems unattractive to use it to drive the solution.

When investigating catalyst oxygen storage, pre- and post-catalyst UEGO sensors are often employed, and these sensors were present for these tests – Fig. 6.The difference between the sensors' output, when combined with the exhaust flow rate, give an indication of the oxygen stored on the catalyst.

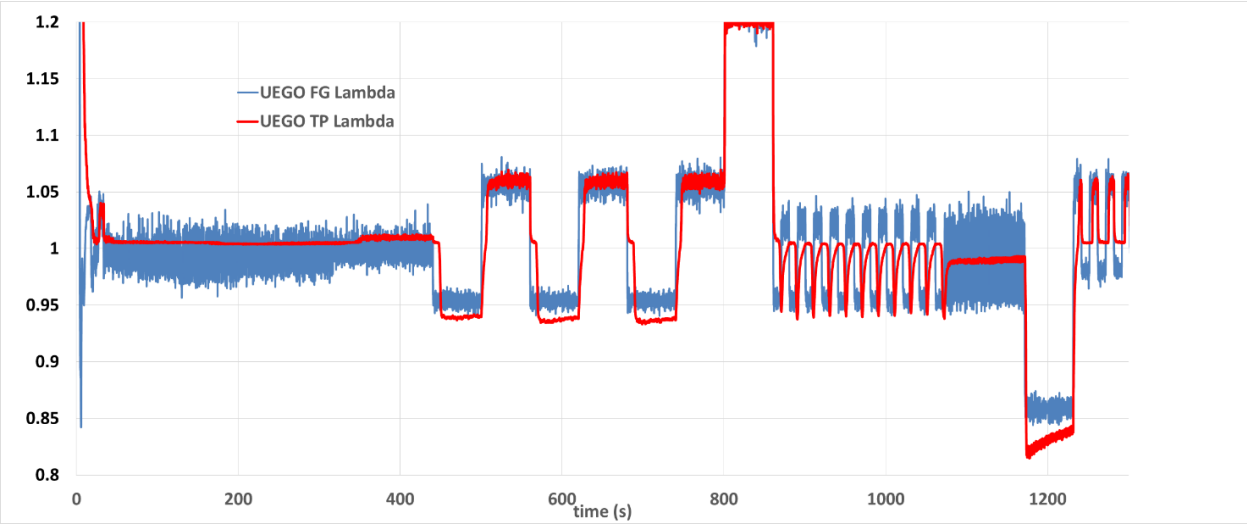

Figure 6. Feedgas and Tailpipe UEGO sensor measurements

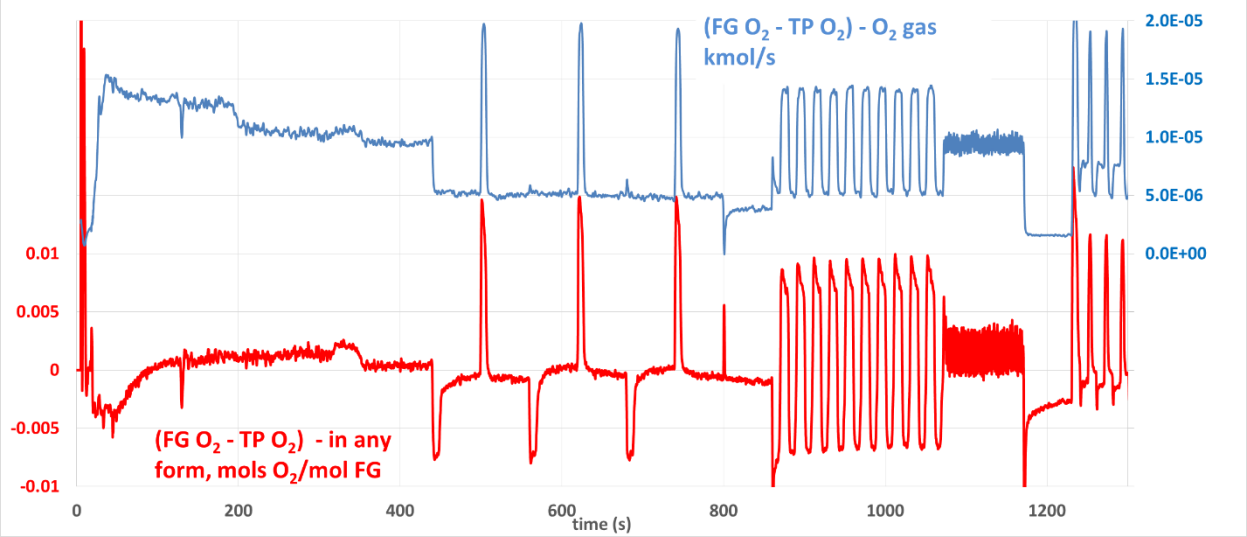

Figure 7. Oxygen storage/release in a TWC:- difference in O_2 gas flow (blue), and an O atom flow (red) between inlet and outlet.

Figure 7 shows two methods of looking at the oxygen balance across the TWC. The red trace shows the quantity of oxygen, in any form, that is released or adsorbed, based on an oxygen atom balance. We would expect that this quantity would be zero at steady state, this seems to be the case – though if one were designing a testing regime, occasional periods of extended steady state running would be a useful feature from this point of view, where any deviation from zero would be interpreted as analyser drift.

The storage and release profiles are rather different, in particular the "two-stage" oxygen release following a lean to rich transition, seen particularly between 440 and 500 s. The sites on the TWC with which oxygen may be via the oxidation state of the precious metal, and that of the ceria and cerium/zirconium/oxygen compounds in the wash coat [10].
The difference between the FG and TP (tailpipe – i.e. post-catalyst) oxygen gas flux (blue trace) is that of actual oxygen gas, so unsurprisingly it has a rather different characteristic. There is never other than a loss of oxygen gas through the catalyst, especially during rich to lean transitions, when a very fast rate of oxygen gas consumption is seen. Striking is that between 440 s and 800 s, there is an almost constant oxygen gas consumption, except during the rich to lean transitions. This corresponds (roughly speaking) to complete reaction of either O_2 gas with CO gas (lean conditions), or TWC stored O_2 with CO (rich conditions).

The behaviour during the very rich excursion beginning at 1170 s is also interesting. Unlike the rich intervals beginning at 440, 560 and 680 s, there is virtually no evidence of a "prompt" oxygen release, which is because the preceding very rapid switching was net rich. Instead there an ever-decreasing rate of extraction of "harder to access" oxygen in the washcoat – the second feature of the "two-stage" oxygen release. Comparison with the UEGO data of figure 6 shows broadly matching features, but the two stage oxygen release is not evident.

The overall conclusion is that significantly more insight into the oxygen storage/release processes may be available via this technique. It is a pity that no plausibility check on the post-catalyst gases could be made, but it is unlikely that the qualitative discussion above would be affected due to small % errors in the gas analysis. The actual quantity of oxygen stored and released may be calculated from figure 7 if the fuel or air flow rate is known together with λ.

It is also interesting to calculate a value for the equilibrium constant K of the WGSR from the measured (CO_2, CO) and calculated (H_2, H_2O) data, post catalyst. This is shown in figure 8. It might be expected that under rich conditions the computed value of K would be physical, and this is indeed the case. The K value computed for the rich regions with $\lambda \sim 0.95$ is about 0.5, which corresponds to a temperature of about 650 C. However at around 1200 s, when $\lambda \sim 0.85$, the computed value of K corresponds to unphysical catalyst temperatures (e.g. K=1.5 corresponds to an equilibrium temperature of 960 C.

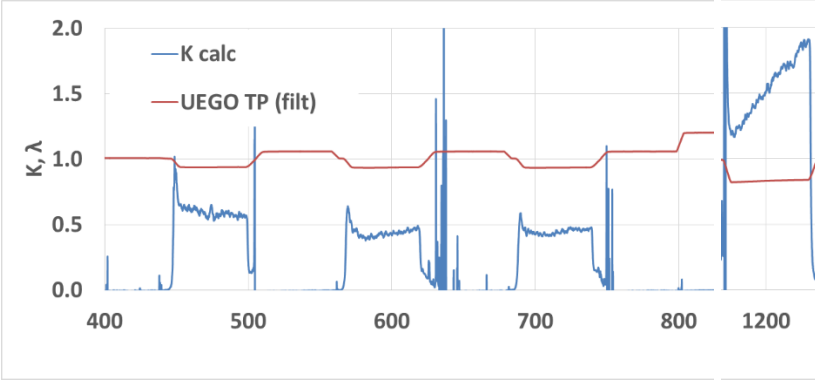

Figure 8 Equilibrium WGSR equilibrium constant prediction

4.3 Diesel feedgas and post LNT+CSF gas analysis during a WLTP drive cycle.

Some data from a diesel engine test is reproduced below. In fig 9 the feedgas S_{X_i} and 5 predicted equivalence ratios, following the same procedure as described in section 4.2 (based on emissions measurements and a fuel assay). It is apparent that S_{X_i} is about 1% high on average, and with significantly larger excursions during transients. Also the agreement between the predictions of equivalence ratio differ significantly, especially that found when the carbon balance is omitted (shown by a dotted line).

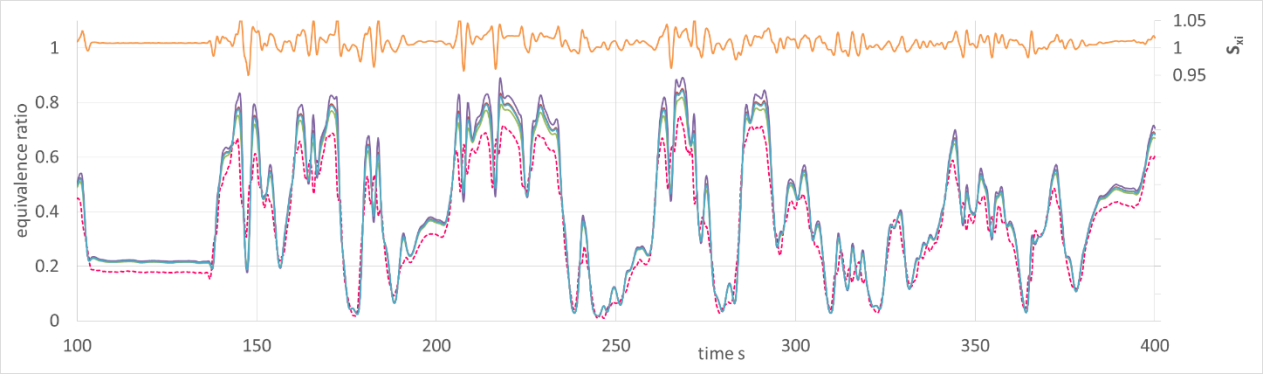

Figure 9 Predictions of the feedgas equivalence ratio and S_{X_i} .

As well as the small steady state offset in S_{X_i} , it is interesting here to try and determine the origin of the large deviations in S_{X_i} during transients. Here the main "levers" are CO_2 and O_2, all other measured gases being of small concentration. One immediate check that needs to be made is whether there is a relative time delay between the analyser channels. One way to do this is to

look at how the standard deviation in S_{X_i} varies if time delays/advances are artificially introduced in each analyser channel. This procedure indicated no synchronisation issues.

In the same way as in the previous section, we can iterate (on gain correction factors for CO_2 and O_2 in this case) to find the values that minimize the difference between the 5 methods of computing λ, and the deviation of S_{X_i} from unity. The result of this procedure is shown in figure 10. Here five of the equivalence ratio methods virtually lie on one another - only the "omit C balance", and then only during transients, exhibits differences from the others, and this difference correlates with the small but finite deviations from unity of S_{X_i}, the standard deviation of which is now 0.0046. The reason for this behaviour is not clear.

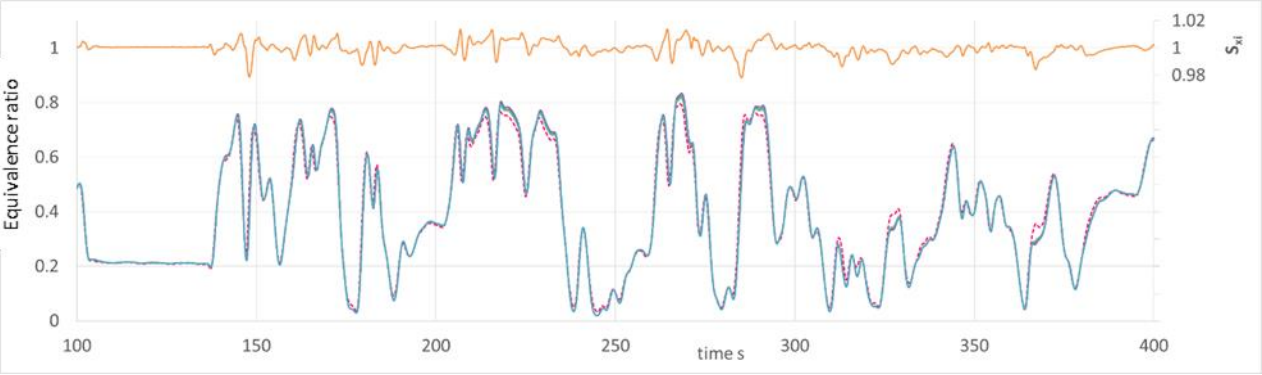

Figure 10 Feed-gas equivalence ratio and S_{X_i} computed from corrected data.

5 Conclusions

We have attempted in this paper to demonstrate how a linear algebra approach can be used to significantly reduce or eliminate the need to perform the length and tedious algebraic manipulations that are often seen in this topic – Brettschneider's paper (3) is an example. The approach has been used to clarify the origin, and approximations involved in some of the better-know relationship in use, and introduced new formulations which may be found of use – for example a form of the Spindt/Brettschneider relationship for lambda when the constituent analyser inputs are in there original form (wet and dry).

The second main theme how the approach can be used to check for the consistency of experimental data, and it has been demonstrated for both gasoline and diesel engines how data from a specific exhaust gas analyser might be need "attention".

Finally the method has been used to look at storage phenomena, experimentally in the case of oxygen in a three-way catalyst, and relationships have been derived for soot regeneration and water condensation.

Acknowledgements

The permission of Jaguar Land Rover Limited to use data for this paper from JLR powertrains is gratefully acknowledged.

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Nomenclature

AFR	Air to fuel ratio
K	equilibrium constant of the water gas shift reaction (WGSR)
m, m'	(see n, n')

$\overline{m}$ fuel H/C ratio, $\overline{m} = m/n$

$\overline{m}'$ uHC (unburnt hydrocarbon) H/C ratio, $\overline{m}' = m'/n'$

n mean fuel composition is $C_n H_m O_x N_y$

n' mean uHC (unburnt hydrocarbon) composition is $C_{n'} H_{m'} O_{x'}$

n_p mols of exhaust gas per mol of fuel

r mean "NO_x" composition is $N_r O_z$

$\boldsymbol{S}_{X_i}$ sum of the wet exhaust gas mol fractions ($\boldsymbol{S}_{X_i} \equiv \sum_i X_i$)

t $t = n + m/4 - x/2$

$\bar{t}$ $\bar{t} = 1 + \overline{m}/4 - \bar{x}/2$

u mols CO_2 per mol O_2 of O_2 in ambient air

v mols H_2O per mol of O_2 in ambient air

w mols N_2 per mol of in ambient air (i.e. w includes everything except ambient O_2, CO_2 and H_2O – essentially argon)

x, x' (see n, n')

$\bar{x}$ fuel O/C ratio, $\bar{x} = x/n$

X_i wet (actual) mol fraction of exhaust component i

X_i^* dry mol fraction of exhaust component i

X_i^+ semi-dry mol fraction of exhaust component i

y (see n)

z (see r)

Greek symbols

α $1/\left(2 + 2X_{CO}/KX_{CO_2}\right)$

λ $AFR/AFR_{stoichiometric}$

Appendix 1. Wet basis measurements of CO_2, CO, O_2, NO_x and $uHC's$

The balances from the combustion equation (Eq. 3 – 8) can be written in matrix form as :-

$$\begin{bmatrix} -u & X_{CO_2}+X_{CO}+n'X_{uHC} & 0 & 0 & 0 \\ -2v & \overline{m}'n'X_{uHC} & 2 & 2 & 0 \\ -(2+2u+v) & \begin{pmatrix}2X_{CO_2}+X_{CO}+2X_{O_2}\\ +zX_{N_rO_z}+\bar{x}'n'X_{uHC}\end{pmatrix} & 1 & 0 & 0 \\ -2w & rX_{N_rO_z}+y'X_{uHC} & 0 & 0 & 2 \\ 0 & \begin{pmatrix}X_{CO_2}+X_{CO}+X_{O_2}\\ +X_{N_rO_z}+X_{uHC}-1\end{pmatrix} & 1 & 1 & 1 \\ 0 & 0 & X_{CO}/KX_{CO_2} & -1 & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \overline{n}_p \\ \overline{n}_p X_{H_2O} \\ \overline{n}_p X_{H_2} \\ \overline{n}_p X_{N_2} \end{bmatrix} = \begin{bmatrix} 1 \\ \overline{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix} \qquad \text{A1a-f}$$

<u>Brettschneider/Spindt</u>

In this case, either Eq. 6 or 7 is omitted, and then Eq. 7 or 6 can be eliminated, to give

$$\begin{bmatrix} -u & X_{CO_2}+X_{CO}+n'X_{uHC} & 0 & 0 \\ -2v & \overline{m}'n'X_{uHC} & 2 & 2 \\ -(2+2u+v) & \begin{pmatrix}2X_{CO_2}+X_{CO}+2X_{O_2}\\ +zX_{N_rO_z}+\bar{x}'n'X_{uHC}\end{pmatrix} & 1 & 0 \\ 0 & 0 & X_{CO}/KX_{CO_2} & -1 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \overline{n}_p \\ \overline{n}_p X_{H_2O} \\ \overline{n}_p X_{H_2} \end{bmatrix} = \begin{bmatrix} 1 \\ \overline{m} \\ \bar{x} \\ 0 \end{bmatrix} \qquad \text{A2a-d}$$

We can further manipulate A2 to derive the Brettschneider relationship. Adding twice equation A2d to Eq. A2b allows Eq. A8d to be removed. Multiplying Eq. A2b by α , and subtracting it from Eq. A2c allows the removal of Eq. A8c to give:-

$$\begin{bmatrix} -u & \left(X_{CO_2}+X_{CO}+n'X_{uHC}\right) \\ (2+2u+v-2v\alpha) & -\begin{pmatrix}2X_{CO_2}+X_{CO}+2X_{O_2}\\ +zX_{N_rO_z}+(\bar{x}'-\alpha\overline{m}')n'X_{uHC}\end{pmatrix} \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \overline{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \alpha\overline{m}-\bar{x} \end{bmatrix} \qquad \text{A3a,b}$$

Eliminating $\overline{n}_p$ between these two equations gives

$$\lambda = \frac{\left(2X_{CO_2}+X_{CO}+2X_{O_2}+zX_{N_rO_z}\right)+\left(\alpha\overline{m}-\bar{x}\right)\left(X_{CO_2}+X_{CO}\right)-\left(\left(\bar{x}-\bar{x}'\right)-\alpha\left(\overline{m}-\overline{m}'\right)\right)n'X_{uHC1}}{\bar{t}\left(2-(2\alpha-1)v\right)\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)+u\bar{t}\left(X_{CO}-2X_{O_2}-zX_{N_rO_z}+\left(2-\bar{x}'+\alpha\overline{m}'\right)n'X_{uHC}\right)} \qquad \text{A4a}$$

This is the full form, with no approximations, other than those inherent in the original combustion equation. In approximate form this becomes

$$\lambda = \frac{\left(2X_{CO_2} + X_{CO} + 2X_{O_2} + zX_{N_rO_z}\right) + \left(\alpha\overline{m} - \bar{x}\right)\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \qquad \text{A4b}$$

By back substitution all the remaining unknowns are found, with approximate forms (where different) in $\{\ \}$:-

$$\bar{n}_p = \frac{1 + u\bar{t}\lambda}{\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \quad \left\{= \frac{1}{\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)}\right\} \qquad \text{A5a,b}$$

$$X_{H_2O} = \frac{\bar{x} + \left(2 + 2u + v\right)\bar{t}\lambda}{\bar{n}_p} - \left(2X_{CO_2} + X_{CO} + 2X_{O_2} + zX_{N_rO_z} + \bar{x}'n'X_{uHC}\right)$$

$$\left\{= \frac{\bar{x} + 2\bar{t}\lambda}{\bar{n}_p} - \left(2X_{CO_2} + X_{CO} + 2X_{O_2} + zX_{N_rO_z} + \bar{x}'n'X_{uHC}\right)\right\} \qquad \text{A6a,b}$$

$$X_{H_2} = \frac{\left(v\lambda\bar{t} + \overline{m}/2\right)}{\bar{n}_p} - \left(X_{H_2O} + \frac{\overline{m}'n'X_{uHC}}{2}\right) \qquad \left\{= \frac{\overline{m}}{2\bar{n}_p} - \left(X_{H_2O} + \frac{\overline{m}'n'X_{uHC}}{2}\right)\right\} \qquad \text{A7a,b}$$

(or from the WGRS, $X_{H_2} = \dfrac{X_{CO}}{KX_{CO_2}} X_{H_2O}$)

The value of X_{N_2} is given by either

$$X_{N_2} = \frac{w\bar{t}\lambda}{\bar{n}_p} - \frac{rX_{N_rO_z}}{2} \qquad \text{A8}$$

or

$$X_{N_2} = 1 - \left(X_{CO_2} + X_{CO} + X_{O_2} + X_{H_2O} + X_{H_2} + X_{N_rO_z} + X_{uHC}\right) \qquad \text{A9}$$

And for experimental data in general these values will be different.

Simons

An alternative approach is due to Simons [4], who omitted the WGSR from the equations set. In view of the uncertainty in the value of the equilibrium constant for this reaction this may be useful. Thus the equation set A1a-f with Eq. A1f (the WGSR) removed, leaves 5 equations with 5 unknowns, so matrix inversion may be used directly to find the unknowns. Alternatively, Gaussian elimination yields

$$\lambda\bar{t} = \frac{1 - X_{O_2} - X_{N_rO_z}(1 - r/2) - (1/n' + \bar{y}/2 + \bar{m}/2 - \bar{m}'/2)n'X_{uHC} - (1 + \bar{y}/2 + \bar{m}/2)(X_{CO_2} + X_{CO})}{((w+v)(X_{CO_2} + X_{CO} + n'X_{uHC}) - A_4 u)}$$

A10a

Where $A_4 = (1 - X_{CO_2} - X_{CO} - X_{O_2} - (1 - r/2)X_{N_rO_z} - (1/n' - \bar{m}'/2)n'X_{uHC})$

Or in approximate form

$$\lambda = \frac{1 - X_{O_2} - (1 - r/2)X_{N_rO_z} - X_{uHC} - (1 + \bar{m}/2)(X_{CO_2} + X_{CO})}{w\bar{t}(X_{CO_2} + X_{CO} + n'X_{uHC})} \qquad \text{A10b}$$

It is interesting to note that these expressions do not include then fuel's oxygen/carbon ratio, $\bar{x}$, though of course the mol fractions within the expression implicitly do include $\bar{x}$.

Appendix 2. Wet basis measurement of *uHC*'s, semi-dry measurements of *CO₂, CO, O₂, NO* .

Writing the balances again, but in terms of dry quantities we obtain:-

Carbon balance

$$-u\lambda\bar{t} + (X^*_{CO_2} + X^*_{CO} + n'X_{uHC})\bar{n}_p - (X^*_{CO_2} + X^*_{CO})(X_{H_2O}\bar{n}_p) = 1 \qquad \text{B1}$$

Hydrogen balance

$$-2v\bar{t}\lambda + \bar{m}'n'X_{uHC}\bar{n}_p + 2(\bar{n}_p X_{H_2O}) + 2(\bar{n}_p X_{H_2}) = \bar{m} \qquad \text{B2}$$

Oxygen balance

$$\begin{aligned} &-(2 + 2u + v)\bar{t}\lambda + (2X^*_{CO_2} + X^*_{CO} + 2X^*_{O_2} + zX^*_{N_rO_z} + \bar{x}'n'X_{uHC})\bar{n}_p \\ &-(2X^*_{CO_2} + X^*_{CO} + 2X^*_{O_2} + zX^*_{N_rO_z} - 1)(X_{H_2O}\bar{n}_p) = \bar{x} \end{aligned} \qquad \text{B3}$$

Nitrogen balance

$$-2w\bar{t}\lambda + rX^*_{N_rO_z}\bar{n}_p - rX^*_{N_rO_z}(X_{H_2O}\bar{n}_p) + 2(X_{N_2}\bar{n}_p) = \bar{y} \qquad \text{B4}$$

Also we have, from $\Sigma X_i = 1$

$$\begin{aligned} &(X^*_{CO_2} + X^*_{CO} + X^*_{O_2} + X^*_{N_rO_z} + X_{uHC} - 1)\bar{n}_p - (X^*_{CO_2} + X^*_{CO} + X^*_{O_2} + X^*_{N_rO_z} - 1)(\bar{n}_p X_{H_2O}) \\ &+ (\bar{n}_p X_{H_2}) + (\bar{n}_p X_{N_2}) = 0 \end{aligned} \qquad \text{B5}$$

and the WGSR can be written as

$$X^*_{CO}(\bar{n}_p X_{H_2O}) - KX^*_{CO_2}(\bar{n}_p X_{H_2}) = 0 \qquad \text{B6}$$

In matrix form:-

$$\begin{bmatrix} -u & \left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right) & -\left(X^*_{CO_2}+X^*_{CO}\right) & 0 & 0 \\ -2v & \bar{m}'n'X_{uHC} & 2 & 2 & 0 \\ -(2+2u+v) & \begin{pmatrix}2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}\\ +zX^*_{N_rO_z}+\bar{x}'n'X_{uHC}\end{pmatrix} & -\begin{pmatrix}2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}\\ +zX^*_{N_rO_z}-1\end{pmatrix} & 0 & 0 \\ -2w & rX^*_{N_rO_z} & -rX^*_{N_rO_z} & 0 & 2 \\ 0 & \begin{pmatrix}X^*_{CO_2}+X^*_{CO}+X^*_{O_2}\\ +X^*_{N_rO_z}+X_{uHC}-1\end{pmatrix} & -\begin{pmatrix}X^*_{CO_2}+X^*_{CO}+X^*_{O_2}\\ +X^*_{N_rO_z}-1\end{pmatrix} & 1 & 1 \\ 0 & 0 & X^*_{CO} & -KX^*_{CO_2} & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ X_{H_2O}\bar{n}_p \\ X_{H_2}\bar{n}_p \\ X_{N_2}\bar{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \bar{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix}$$

B7a-f

Spindt

As with the "all wet" situation (appendix 1), we proceed with the same manipulations to arrive at:-

$$\begin{bmatrix} -u & \left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right) & -\left(X^*_{CO_2}+X^*_{CO}\right) \\ -2v\alpha & \alpha\bar{m}'n'X_{uHC} & 1 \\ -(2+2u+v) & \begin{pmatrix}2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}\\ +zX^*_{N_rO_z}+\bar{x}'n'X_{uHC}\end{pmatrix} & -\begin{pmatrix}2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}\\ +zX^*_{N_rO_z}-1\end{pmatrix} \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ \bar{n}_pX_{H_2O} \end{bmatrix} = \begin{bmatrix} 1 \\ \alpha\bar{m} \\ \bar{x} \end{bmatrix} \qquad \text{B8a-c}$$

Elimination of X_{H_2O}, n_p yields:-

$$\lambda = \frac{\left(2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}+zX^*_{N_rO_z}\right)+\left(\alpha\bar{m}-\bar{x}\right)\left(X^*_{CO_2}+X^*_{CO}\right)+B_1}{2\bar{t}\left(\left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right)+\alpha\left(X^*_{CO_2}+X^*_{CO}\right)\bar{m}'n'X_{uHC}+B_2+B_3\right)}$$

Where

$$B_1 = \left[\alpha\left(\bar{m}'-\bar{m}\right)\left(2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}+zX^*_{N_rO_z}-1\right)+\alpha\left(\bar{m}\bar{x}'-\bar{x}\bar{m}'\right)\left(X^*_{CO_2}+X^*_{CO}\right)+\left(\bar{x}'-\bar{x}\right)\right]n'X_{uHC}$$

$$B_2 = v\left[\left(X^*_{CO_2}+2X^*_{O_2}+zX^*_{N_rO_z}+\left(1+\bar{m}'/2-\bar{x}'\right)\left(X^*_{CO_2}+X^*_{CO}\right)\alpha n'X_{uHC}+\left(1/2-\alpha\right)\left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right)\right)\right]$$

$$B_3 = \frac{u}{2}\left[\left(X^*_{CO}-2X^*_{O_2}-zX^*_{N_rO_z}\right)\left(1+\alpha\bar{m}'n'X_{uHC}\right)+\left(2+\alpha\bar{m}'-\bar{x}'\right)n'X_{uHC}\right]$$

In approximate form($B_1 = B_2 = B_3 = 0$):-

$$\lambda = \frac{\left(2X^*_{CO_2} + X^*_{CO} + 2X^*_{O_2} + zX^*_{N_rO_z}\right) + \left(\alpha\overline{m} - \bar{x}\right)\left(X^*_{CO_2} + X^*_{CO}\right)}{2\bar{t}\left(\left(X^*_{CO_2} + X^*_{CO} + n'X_{uHC}\right) + \alpha\left(X^*_{CO_2} + X^*_{CO}\right)\overline{m}'n'X_{uHC}\right)} \qquad \text{B9}$$

This is a useful form of the Brettschneider/Spindt equation, as it can be used directly without iteration since all the quantities are in the as-measured basis (noting of course that for the quantities measured semi-dry, X_i^+, $X_i^* = X_i^+ / \left(1 - X^+_{H_2O}\right)$, where $X^+_{H_2O}$ is the dryer exit water vapour mol fraction).

As an aside, for the exhaust gases post-catalyst for a gasoline engine running at close to stoichiometric, only gases in significant quantities will be N_2, CO_2, H_2O and thus $\alpha = 1/\left[2\left(1 + X^*_{CO}/KX^*_{CO_2}\right)\right] \approx 1/2$, and Eq. B9 becomes

$$\lambda \cong \frac{2X^*_{CO_2} + \left(\alpha\overline{m} - \bar{x}\right)X^*_{CO_2}}{2\bar{t}X^*_{CO_2}} = \frac{2 + \alpha\overline{m} - \bar{x}}{2 + \overline{m}/2 - \bar{x}} = 1. \qquad \text{B10}$$

In other words, at this condition, the prediction of lambda is virtually independent of the measurement of $X^*_{CO_2}$.

Back substitution of λ from Eq. B9 gives, with approximate forms in $\{\ \}$:-

$$\overline{n}_p = \frac{\left(1 + \left(X^*_{CO_2} + X^*_{CO}\right)\alpha\overline{m} + \left(u + 2v\alpha\left(X^*_{CO_2} + X^*_{CO}\right)\right)\lambda\bar{t}\right)}{\left(X^*_{CO_2} + X^*_{CO} + n'X_{uHC}\right) + \alpha\left(X^*_{CO_2} + X^*_{CO}\right)\overline{m}'n'X_{uHC}}$$

$$\left\{ = \frac{\left(1 + \left(X^*_{CO_2} + X^*_{CO}\right)\alpha\overline{m}\right)}{\left(X^*_{CO_2} + X^*_{CO} + n'X_{uHC}\right) + \alpha\left(X^*_{CO_2} + X^*_{CO}\right)\overline{m}'n'X_{uHC}} \right\} \qquad \text{B11a,b}$$

$$X_{H_2O} = \left(\frac{\overline{m} + 2v\bar{t}\lambda}{\overline{n}_p} - \overline{m}'n'X_{uHC}\right)\alpha \quad \left\{ = \left(\frac{1}{\overline{n}_p} - n'X_{uHC}\right)\alpha\overline{m} \right\} \qquad \text{B12a,b}$$

$$X_{H_2} = \frac{X^*_{CO}}{KX^*_{CO_2}} X_{H_2O} \qquad \text{B13}$$

As in the previous section, there are two choices with respect to obtaining a value for X_{N_2} - one can use either the nitrogen balance or $\boldsymbol{S}_{X_i} = 1$; for real data the value of X_{N_2} will be different. Thus two of the possible matrix inversions only affect the value of X_{N_2}. Using the *N* balance:-

$$X_{N_2} = \frac{\bar{y} + 2w\bar{t}\lambda}{2\bar{n}_p} - \frac{r}{2} X^*_{NO}\left(1 - X_{H_2O}\right) \quad \left\{ = \frac{w\bar{t}\lambda}{\bar{n}_p} - \frac{r}{2} X^*_{NO}\left(1 - X_{H_2O}\right) \right\} \qquad \text{B14a,b}$$

Or using $\boldsymbol{S}_{X_i} = 1$:-

$$X_{N_2} = 1 - \left(X^*_{CO_2}\left(1 - X_{H_2O}\right) + X^*_{CO}\left(1 - X_{H_2O}\right) + X^*_{O_2}\left(1 - X_{H_2O}\right) + X^*_{N_rO_z}\left(1 - X_{H_2O}\right) + X_{uHC} + X_{H_2O} + X_{H_2} \right) \qquad \text{B15}$$

Simons

Using Simons' approach, the unknowns can be found by inversion the 5 x 5 matrix remaining when the WGSR (equation B7f) is removed from B7.

Algebraic relationships are complex, but in approximate form it is possible to show that

$$X_{H_2O} = \frac{\left(B_4 - B_5\right)}{\left(B_4 - 1\right)} \qquad \text{B16}$$

$$\bar{n}_p = \frac{1}{\left(X^*_{CO_2} + X^*_{CO}\right)\left(1 - X_{H_2O}\right) + n' X_{uHC}} \qquad \text{B17}$$

and

$$\lambda\bar{t} = \frac{\left(X^*_{CO_2} + 2X^*_{O_2} + zX^*_{N_rO_z}\right)\left(1 - X_{H_2O}\right) + \left(\bar{x}' - 1\right)n' X_{uHC} + X_{H_2O}}{2\left(\left(X^*_{CO_2} + X^*_{CO}\right)\left(1 - X_{H_2O}\right) + n' X_{uHC}\right)} - \frac{\bar{x} - 1}{2} \qquad \text{B18}$$

where

$$B_4 = \left(wX^*_{CO_2} + 2\left(w+1\right)X^*_{O_2} + \left(2 - r + zw\right)X^*_{N_rO_z} + \left(\bar{m} + 2 - w\left(\bar{x} - 1\right)\right)\left(X^*_{CO_2} + X^*_{CO}\right) \right) / w$$

and

$$B_5 = 2\left(1 - \left(1/n'\right)n' X_{uHC}\right)/w$$

Appendix 3 Wet measurements of *CO₂, CO, NO* and *uHC's – O₂* not available

Another common situation is when a measurement of O_2 is not available (and this is normally when the other analysers are operating on a "wet" basis), and then we have identical relationships for the carbon, hydrogen and nitrogen balance (equations A1, A2, A4), and for the WGSR (Eq. A6), but for the oxygen balance we have to write

$$-\left(2 + 2u + v\right)\bar{t}\lambda + \left(2X_{CO_2} + X_{CO} + zX_{N_rO_z} + \bar{x}' n' X_{uHC}\right)\bar{n}_p + \left(\bar{n}_p X_{H_2O}\right) + 2\bar{n}_p X_{O_2} = \bar{x} \qquad \text{C1}$$

and from $\Sigma X_i = 1$

$$0 + \left(\left(X_{CO_2} + X_{CO} + X_{N_rO_z} + X_{uHC}\right) - 1\right)\bar{n}_p + \left(\bar{n}_p X_{H_2O}\right) + \left(\bar{n}_p X_{H_2}\right) + \left(\bar{n}_p X_{N_2}\right) + \left(\bar{n}_p X_{O_2}\right) = 0 \qquad \text{C2}$$

This results in the set of linear equations

$$\begin{bmatrix} -u & X_{CO_2} + X_{CO} + n'X_{uHC} & 0 & 0 & 0 & 0 \\ -2v & \bar{m}'n'X_{uHC} & 2 & 2 & 0 & 0 \\ -(2+2u+v) & 2X_{CO_2} + X_{CO} + zX_{N_rO_z} + \bar{x}'n'X_{uHC} & 1 & 0 & 0 & 2 \\ -2w & rX_{N_rO_z} & 0 & 0 & 2 & 0 \\ 0 & X_{CO_2} + X_{CO} + X_{N_rO_z} + X_{uHC} - 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & X_{CO}/KX_{CO_2} & -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ X_{H_2O}\bar{n}_p \\ X_{H_2}\bar{n}_p \\ X_{N_2}\bar{n}_p \\ X_{O_2}\bar{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \bar{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix}$$

C3a-f

Which by Gaussian elimination reduces to:-

$$\begin{bmatrix} -u & \left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) & 0 \\ -2v & \bar{m}'n'X_{uHC} & 1/\alpha \\ (2+2u+v+2w) & \begin{pmatrix} X_{CO} + (2-z-r)X_{N_rO_z} \\ +(2/n' - \bar{x}')n'X_{uHC} - 2 \end{pmatrix} & \dfrac{1-\alpha}{\alpha} \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ X_{H_2O}\bar{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \bar{m} \\ -(\bar{x} + \bar{y}) \end{bmatrix} \qquad \text{C4a-c}$$

Hence

$$\bar{n}_p = \frac{1 + u\bar{t}\lambda}{\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \qquad \text{C5}$$

By inspection:-

$$X_{H_2O} = \left(\frac{\bar{m} + 2v\bar{t}\lambda}{\bar{n}_p} - \bar{m}'n'X_{uHC}\right)\alpha \qquad \text{C6}$$

By substitution for n_p and X_{H_2O} in Eq. C4c we obtain

$$\lambda = \frac{\left(2 - X_{CO} - (2-z-r)X_{N_rO_z} - 2X_{uHC}\right) + \left((\alpha - 1)\bar{m} - \bar{x} - \bar{y}\right)\left(X_{CO_2} + X_{CO}\right) - C_1}{2\bar{t}(1+w)\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) + C_2 + C_3} \qquad \text{C7}$$

Where

$$C_1 = \left(\left(\overline{m} - \overline{m}'\right)\left(1-\alpha\right) + \left(\overline{x} - \overline{x}'\right) + \overline{y}\right)n' X_{uHC}$$

$$C_2 = u\bar{t}\left(2 + 2X_{CO_2} + X_{CO} - \left(2 - z - r\right)X_{N_rO_z} + \left(2\left(1 - 1/n'\right) + \overline{x}' - \overline{m}'\left(1-\alpha\right)\right)n' X_{uHC}\right)$$

$$C_3 = v\bar{t}\left(2\left(1-\alpha\right)+1\right)\left(X_{CO_2} + X_{CO} + n' X_{uHC}\right)$$

In approximate form, $C_1 = C_2 = C_3 = 0$, and

$$\lambda = \frac{\left(2 - X_{CO} - \left(2 - z - r\right)X_{N_rO_z} - 2X_{uHC}\right) + \left(\left(\alpha - 1\right)\overline{m} - \overline{x} - \overline{y}\right)\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(1 + w\right)\left(X_{CO_2} + X_{CO} + n' X_{uHC}\right)} \qquad \text{C8}$$

Back substitution gives, with approximate forms in $\{\ \}$:-

$$X_{O_2} = \frac{\overline{x} + \left(2 + 2u + v\right)\bar{t}\lambda}{2\overline{n}_p} - \frac{1}{2}\left(2X_{CO_2} + X_{CO} + zX_{N_rO_z} + X_{H_2O} + x' X_{uHC}\right)$$
$$\left\{ = \frac{2\bar{t}\lambda + \overline{x}}{2\overline{n}_p} - \frac{1}{2}\left(2X_{CO_2} + X_{CO} + zX_{N_rO_z} + X_{H_2O} + x' X_{uHC}\right)\right\} \qquad \text{C9}$$

and

$$X_{H_2} = \frac{X_{CO}}{K X_{CO_2}} X_{H_2O} \qquad \text{C10}$$

and

$$X_{N_2} = \frac{2w\bar{t}\lambda + \overline{y}}{2\overline{n}_p} - \frac{1}{2}rX_{N_rO_z}\left\{ = \frac{2w\bar{t}\lambda}{2\overline{n}_p} - \frac{1}{2}rX_{N_rO_z}\right\} \qquad \text{C11}$$

If $x = y = 0$ (fuel is a pure hydrocarbon), and $z = r = 1$, ($X_{N_rO_z}$ is *NO* only), then Eq. C7 becomes

$$\lambda = \frac{\left(2 - X_{CO} - 2X_{uHC}\right) + \left(\alpha - 1\right)\overline{m}\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(1 + w\right)\left(X_{CO_2} + X_{CO} + n' X_{uHC}\right)} \qquad \text{C12}$$

With the same approximations, substitution of C5 into C6 gives

$$X_{H_2O} = \left(X_{CO_2} + X_{CO}\right)\alpha\overline{m}$$

So C12 can be written as

or

$$\lambda = \frac{\left(2 - X_{CO} - 2X_{uHC}\right) + X_{H_2O} - \overline{m}\left(X_{CO_2} + X_{CO}\right)}{2\bar{t}\left(1 + w\right)\left(X_{CO_2} + X_{CO} + n' X_{uHC}\right)} \qquad \text{C13}$$

Stivender's [7] version of this equation, as given by Heywood, eq 4.66, [8] is:-

$$\lambda = \frac{1}{\bar{t}(1+w)}\left[\frac{1+n'X_{uHC}-X_{CO}/2+X_{H_2O}/2}{\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)}-\frac{\overline{m}}{2}\right] \qquad \text{C14}$$

The two relationships are only equal when $m = 2n + 2$, though this does not lead to serious errors for normal fuels. A more serious restriction is that oxygenates are not included.

Appendix 4 Wet measurements of CO_2, CO, O_2, NO, uHC's and H_2O

Writing the equations 2 – 7 as a set of linear equations, with X_{H_2O} as a known quantity

Carbon balance

$$-u\bar{t}\lambda + \left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)\overline{n}_p = 1 \qquad \text{D1}$$

Hydrogen balance

$$-2v\bar{t}\lambda + \left(2X_{H_2O}+\overline{m}'n'X_{uHC}\right)\overline{n}_p + 2\overline{n}_p X_{H_2} = \overline{m} \qquad \text{D2}$$

Oxygen balance

$$-\left(2+2u+v\right)\bar{t}\lambda + \left(2X_{CO_2}+X_{CO}+2X_{O_2}+X_{H_2O}+zX_{N_rO_z}+\bar{x}'n'X_{uHC}\right)\overline{n}_p = \bar{x} \qquad \text{D3}$$

Nitrogen balance

$$-2w\bar{t}\lambda + rX_{N_rO_z}\overline{n}_p + 2\overline{n}_p X_{N_2} = \bar{y} \qquad \text{D4}$$

Also we have, from $\boldsymbol{S}_{X_i} = 1$

$$\left(\left(X_{CO_2}+X_{CO}+X_{O_2}+X_{H_2O}+X_{N_rO_z}+X_{uHC}\right)-1\right)\overline{n}_p + \overline{n}_p X_{H_2} + \overline{n}_p X_{N_2} = 0 \qquad \text{D5}$$

and the WGSR can be written as

$$X_{CO}X_{H_2O}\overline{n}_p - KX_{CO_2}\overline{n}_p X_{H_2} = 0 \qquad \text{D6}$$

In matrix form:-

$$\begin{bmatrix} -u & \left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right) & 0 & 0 \\ -2v & \left(2X_{H_2O}+\overline{m}'n'X_{uHC}\right) & 2 & 0 \\ -\left(2+2u+v\right) & \begin{pmatrix} 2X^*_{CO_2}+X^*_{CO}+2X^*_{O_2}+ \\ X_{H_2O}+zX^*_{N_rO_z}+\bar{x}'n'X_{uHC} \end{pmatrix} & 0 & 0 \\ -2w & rX^*_{N_rO_z} & 0 & 2 \\ 0 & \begin{pmatrix} X^*_{CO_2}+X^*_{CO}+X^*_{O_2}+ \\ X_{H_2O}+X^*_{N_rO_z}+X_{uHC}-1 \end{pmatrix} & 1 & 1 \\ 0 & X^*_{CO}X_{H_2O}\big/KX^*_{CO_2} & -1 & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \overline{n}_p \\ X_{H_2}\overline{n}_p \\ X_{N_2}\overline{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \overline{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix} \qquad \text{D7a-f}$$

Here there are 6 equations, 4 unknowns. If we follow the same elimination order used previously, that is remove the *N* balance and $\sum_i X_i = 1$ equations, which removes the unknown X_{N_2}, and then X_{N_2} via H balance, we obtain:-

$$\begin{bmatrix} -ut & \left(X_{CO_2}+X_{CO}+n'X_{uHC}\right) \\ -2vt & X_{H_2O}/\alpha+\overline{m}'n'X_{uHC} \\ -\left(2+2u+v\right)t & \begin{pmatrix} 2X_{CO_2}+X_{CO}+2X_{O_2}+ \\ X_{H_2O}+zX_{N_rO_z}+\bar{x}'n'X_{uHC} \end{pmatrix} \\ -2wt & \begin{Bmatrix} 2-2X_{CO_2}-2X_{CO}-2X_{O_2}-2X_{H_2O} \\ -\left(2-r\right)X_{N_rO_z}-2X_{uHC} \end{Bmatrix} \end{bmatrix} \begin{bmatrix} \lambda \\ n_p \end{bmatrix} = \begin{bmatrix} n \\ m \\ x \\ y \end{bmatrix} \qquad \text{D9a-d}$$

If we wish to form a Spindt-like expression, we can use D9a to get the usual expression for $\overline{n}_p$

$$\overline{n}_p = \frac{1+ut\lambda}{\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)} \qquad \text{D10}$$

And then D9c to give

$$\bar{t}\lambda = \frac{\left(2X_{CO_2}+X_{CO}+2X_{O_2}+X_{H_2O}+zX_{N_rO_z}\right)-\bar{x}\left(X_{CO_2}+X_{CO}\right)+\left(\bar{x}'-\bar{x}\right)n'X_{uHC}}{\left(2+v\right)\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)+u\left(X_{CO}-2X_{O_2}-X_{H_2O}-zX_{N_rO_z}+\left(2-\bar{x}'\right)n'X_{uHC}\right)} \qquad \text{D11}$$

Which in "approximate" form gives

$$\bar{t}\lambda = \frac{\left(2X_{CO_2} + X_{CO} + 2X_{O_2} + X_{H_2O} + zX_{N_rO_z}\right) - \bar{x}\left(X_{CO_2} + X_{CO}\right)}{2\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right)} \qquad \text{D12}$$

Appendix 5. All measured semi-dry except uHCs, no O2 available

The balances from the combustion equation (Eq. 2 – 8) can be written:-

Carbon balance

$$-u\bar{t}\lambda + \left(X^*_{CO_2} + X^*_{CO} + n'X_{uHC}\right)\bar{n}_p - \left(X^*_{CO_2} + X^*_{CO}\right)\left(X_{H_2O}\bar{n}_p\right) = 1 \qquad \text{E1}$$

Hydrogen balance

$$-2v\bar{t}\lambda + \bar{m}'n'X_{uHC}\bar{n}_p + 2\left(\bar{n}_pX_{H_2O}\right) + 2\left(\bar{n}_pX_{H_2}\right) = \bar{m} \qquad \text{E2}$$

Oxygen balance

$$\begin{aligned} &-\bar{t}\left(2 + 2u + v\right)\lambda + \left(2X^*_{CO_2} + X^*_{CO} + zX^*_{N_rO_z} + \bar{x}'n'X_{uHC}\right)\bar{n}_p \\ &-\left(2X^*_{CO_2} + X^*_{CO} + zX^*_{N_rO_z} - 1\right)X_{H_2O}\bar{n}_p + 2X_{O_2}\bar{n}_p = \bar{x} \end{aligned} \qquad \text{E3}$$

Nitrogen balance

$$-2w\bar{t}\lambda + rX^*_{N_rO_z}\bar{n}_p - rX^*_{N_rO_z}X_{H_2O}\bar{n}_p + 2\bar{n}_pX_{N_2} = y \qquad \text{E4}$$

Also we have, from $\Sigma X_i = 1$

$$\begin{aligned} &\left(X^*_{CO_2} + X^*_{CO} + X^*_{N_rO_z} + X_{uHC} - 1\right)\bar{n}_p - \left(X^*_{CO_2} + X^*_{CO} + X^*_{N_rO_z} - 1\right)\bar{n}_pX_{H_2O} \\ &+ \bar{n}_pX_{H_2} + \bar{n}_pX_{N_2} + \bar{n}_pX_{O_2} = 0 \end{aligned} \qquad \text{E5}$$

and the WGSR can be written as

$$\frac{X_{CO}}{KX_{CO_2}}\bar{n}_pX^*_{H_2O} - \bar{n}_pX^*_{H_2} = 0 \qquad \text{E6}$$

Written in matrix form:-

$$\begin{bmatrix} -u & \left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right) & -\left(X^*_{CO_2}+X^*_{CO}\right) & 0 & 0 & 0 \\ -2v & \bar{m}'n'X_{uHC} & 2 & 2 & 0 & 0 \\ -\left(2+2u+v\right) & \begin{pmatrix}2X^*_{CO_2}+X^*_{CO}\\ +zX^*_{N_rO_z}+\bar{x}'n'X_{uHC}\end{pmatrix} & \begin{pmatrix}1-2X^*_{CO_2}\\ -X^*_{CO}-zX^*_{N_rO_z}\end{pmatrix} & 0 & 0 & 2 \\ -2w & rX^*_{N_rO_z} & -rX^*_{N_rO_z} & 0 & 2 & 0 \\ 0 & \begin{pmatrix}X^*_{CO_2}+X^*_{CO}\\ +X^*_{N_rO_z}+X_{uHC}-1\end{pmatrix} & \begin{pmatrix}1-X^*_{CO_2}\\ -X^*_{CO}-X^*_{N_rO_z}\end{pmatrix} & 1 & 1 & 1 \\ 0 & 0 & X^*_{CO}/KX^*_{CO_2} & -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ X_{H_2O}\bar{n}_p \\ X_{H_2}\bar{n}_p \\ X_{N_2}\bar{n}_p \\ X_{O_2}\bar{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \bar{m} \\ \bar{x} \\ \bar{y} \\ 0 \\ 0 \end{bmatrix} \quad \text{E7a-f}$$

Matrix inversion solves for the unknowns immediately. This equation set can also be reduced to the following form:-

$$\begin{bmatrix} -u & \left(X^*_{CO_2}+X^*_{CO}+n'X_{uHC}\right) & -\left(X^*_{CO_2}+X^*_{CO}\right) \\ -2v & \bar{m}'n'X_{uHC} & 1/\alpha \\ 2\left(1+u+w\right)+v & \begin{pmatrix}+X^*_{CO}+\left(2-r-z\right)X^*_{N_rO_z}\\ +\left(2/n'-\bar{x}'\right)n'X_{uHC}-2\end{pmatrix} & \begin{pmatrix}1/\alpha-1-X^*_{CO}\\ -\left(2-r-z\right)X^*_{N_rO_z}\end{pmatrix} \end{bmatrix} \begin{bmatrix} \lambda\bar{t} \\ \bar{n}_p \\ X_{H_2O}\bar{n}_p \end{bmatrix} = \begin{bmatrix} 1 \\ \bar{m} \\ -\left(\bar{x}+\bar{y}\right) \end{bmatrix}$$

E8a-c

Once again matrix inversion solves for the unknowns, and the remaining unknowns evaluated by back substitution. An algebraic expression for λ without making any approximations is very cumbersome, and is not given. However, if the approximation $u=v=0$ is made, then

$$\bar{n}_p = \frac{1}{\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right)} \qquad \text{E9}$$

And

$$X_{H_2O} = \alpha\bar{m}\left(X_{CO_2}+X_{CO}\right)+\alpha\left(\bar{m}-\bar{m}'\right)n'X_{uHC}+2\alpha vt\bar{\lambda}\left(X_{CO_2}+X_{CO}+n'X_{uHC}\right) \qquad \text{E10}$$

And then by substitution, λ can be found from

$$2\left(1+w\right)\bar{t}\lambda+\begin{pmatrix}+X^*_{CO}+\left(2-r-z\right)X^*_{N_rO_z}\\ +\left(2/n'-\bar{x}'\right)n'X_{uHC}-2\end{pmatrix}\bar{n}_p+\begin{pmatrix}1/\alpha-1-X^*_{CO}\\ -\left(2-r-z\right)X^*_{N_rO_z}\end{pmatrix}\bar{n}_pX_{H_2O}+\left(\bar{x}+\bar{y}\right)=0 \qquad \text{E11}$$

Also

$$X_{H_2O} = \alpha\bar{m}\left(X_{CO_2}+X_{CO}\right) \qquad \text{E12}$$

$\bar{n}_p$ is given by E9, and substitution of this and X_{H_2O} into E11 gives λ.

Appendix 6 Oxygen storage and release

Across an "after-treatment device", which can react species, as well as absorbing and releasing species (here assumed to be O_2 only) we can write

$q_r = \frac{n_{pc}}{n_p}$, $q_{rO_2} = \frac{n_{O_2,released}}{n_p}$, where q_r is the mols of post-catalyst gases, n_{pc}, per mol of feedgas, n_p and q_{rO_2} is the number of mols of O_2 released, $n_{O_2,released}$, per mol of feedgas n_p.

If the post catalyst (subscript *pc*) species are measured by a MEXA then we have:-

Carbon balance:-

$$\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) = q_r\left(X^*_{CO_2,pc} + X^*_{CO,pc} + n'X_{uHC,pc}\right) - q_r X_{H_2O,pc}\left(X^*_{CO_2,pc} + X^*_{CO,pc}\right) \quad \text{F1}$$

Hydrogen balance:-

$$\left(2X_{H_2O} + 2X_{H_2} + \overline{m}'n'X_{uHC}\right) = q_r\left(2X_{H_2O,pc} + 2X_{H_2,pc} + \overline{m}'n'X_{uHC,pc}\right) \quad \text{F2}$$

Oxygen balance:-

$$\begin{aligned}&\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + zX_{N_rO_z} + \overline{x}'n'X_{uHC}\right) + 2q_{r,O_2}\\ &= q_r\left(2X^*_{CO_2,pc} + X^*_{CO,pc} + 2X^*_{O_2,pc} + zX^*_{N_rO_z,pc} + \overline{x}'n'X_{uHC,pc}\right)\\ &- q_r X_{H_2O,pc}\left(2X^*_{CO_2,pc} + X^*_{CO,pc} + 2X^*_{O_2,pc} + zX^*_{N_rO_z,pc}\right)\end{aligned} \quad \text{F3}$$

Nitrogen balance:-

$$\left(rX_{N_rO_z} + 2X_{N_2}\right) = q_r\left(rX^*_{N_rO_z,pc} + 2X_{N_2,pc}\right) - q_r X_{H_2O,pc}\left(rX^*_{N_rO_z,pc}\right) \quad \text{F4}$$

Sum of the mols:-

$$\begin{aligned}&\left(X^*_{CO_2,pc} + X^*_{CO,pc} + X_{H_2O,pc} + X_{H_2,pc} + X^*_{O_2,pc} + X^*_{N_rO_z,pc} + X_{uHC,pc} + X_{N_2,pc}\right)\\ &- X_{H_2O,pc}\left(X^*_{CO_2,pc} + X^*_{CO,pc} + X^*_{O_2,pc} + X^*_{N_rO_z,pc}\right) = 1\end{aligned} \quad \text{F5}$$

Including the WGSR, we have 6 equations in 5 unknowns, but one of them, the *O_2* balance, drops out immediately as it is the only one with the unknown n_{rO_2} in it.

Then we have 5 equations in 4 unknowns:-

$$\begin{bmatrix} \left(X^*_{CO_2,pc} + X^*_{CO,pc} + n'X_{uHC,pc}\right) & -\left(X^*_{CO_2,pc} + X^*_{CO,pc}\right) & 0 & 0 \\ \overline{m}'n'X_{uHC,pc} & 2 & 2 & 0 \\ rX^*_{N_rO_z,pc} & -rX^*_{N_rO_z,pc} & 0 & 2 \\ \begin{pmatrix} X^*_{CO_2,pc} + X^*_{CO,pc} + X^*_{O_2,pc} \\ + X^*_{N_rO_z,pc} + X_{uHC,pc} - 1 \end{pmatrix} & -\begin{pmatrix} X^*_{CO_2,pc} + X^*_{CO,pc} + X^*_{O_2,pc} \\ + X^*_{N_rO_z,pc} - 1 \end{pmatrix} & 1 & 1 \\ 0 & X^*_{CO,pc} & -KX^*_{CO_2,pc} & 0 \end{bmatrix} \begin{bmatrix} q_r \\ q_r X_{H_2O,pc} \\ q_r X_{H_2,pc} \\ q_r X_{N_2,pc} \end{bmatrix}$$

$$= \begin{bmatrix} X_{CO_2} + X_{CO} + n'X_{uHC} \\ 2X_{H_2O} + 2X_{H_2} + \overline{m}'n'X_{uHC} \\ rX_{N_rO_z} + 2X_{N_2} \\ 0 \\ 0 \end{bmatrix}$$

Making a plausibility check on the post-catalyst data is problematic as the WGSR equilibrium temperature is uncertain. If (as is done in the test case in the main text, section 4.2.3) the WGSR relationship is removed from the equation set, then a unique solution for the unknowns is found, and back substitution into Eq. F3 gives the oxygen storage. The gas composition calculated here will not have a lambda value, in the sense that in general it will not correspond to a composition consistent with Eq. 1. Interpretation of the UEGO sensor response is thus uncertain, except at steady state.

Appendix 7 water condensation and evaporation

During a cold start, significant condensation of water vapour occurs in the exhaust system, including after-treatment devices. Unlike the oxygen storage/release mechanism discussed previously, there is (negligible) reaction associated with this process. Clearly semi-dry and dry measurements of the exhaust composition give no information about how much condensation has taken place, as the measurements will not be affected by the water loss.

We continue to assume that the WGSR contains useful information concerning the engine out gases pre-condensation (the X_i). Let us define

$\overline{n}_p$ as the mols of engine out mols per mol of fuel (as before), normalized by fuel carbon

$\overline{n}_{pc}$ as the mols of "post evaporation/condensation" gases per mol of fuel, normalised

$\overline{n}_{water,cond}$ as the mols of water condensing per mol of fuel, normalized.

Writing the balances as fuel + air = engine out gases (all vapour) = post condensation gases + water condensed, and noting that for all gases except H_2O, we assume $\overline{n}_p X_i = \overline{n}_{pc} X_{i,pc}$, while for H_2O,

$$\bar{n}_p X_{H_2O} = \bar{n}_{pc} X_{H_2O,pc} + \bar{n}_{water,cond}$$

Carbon balance

$$\bar{n} + u\lambda\bar{t} = \bar{n}_p\left(X_{CO_2} + X_{CO} + n'X_{uHC}\right) = \bar{n}_{pc}\left(X_{CO_2,pc} + X_{CO,pc} + n'X_{uHC,pc}\right)$$

Hydrogen balance

$$\bar{m} + 2v\lambda\bar{t} = \bar{n}_p\left(2X_{H_2O} + 2X_{H_2} + \bar{m}'n'X_{uHC}\right) =$$
$$\bar{n}_{pc}\left(2X_{H_2O,pc} + 2X_{H_2,pc} + \bar{m}'n'X_{uHC,pc}\right) + 2\bar{n}_{water,cond}$$

Oxygen balance

$$\bar{x} + \lambda\bar{t}\left(2 + 2u + v\right) = \bar{n}_p\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + zX_{N_rO_z} + \bar{x}'n'X_{uHC}\right) =$$
$$\bar{n}_{pc}\left(2X_{CO_2,pc} + X_{CO,pc} + 2X_{O_2,pc} + zX_{N_rO_z,pc} + \bar{x}'n'X_{uHC,pc}\right) + \bar{n}_{pc}X_{H_2O,pc} + \bar{n}_{water,cond}$$

Nitrogen balance

$$\bar{y} + 2w\lambda\bar{t} = \bar{n}_p\left(rX_{N_rO_z} + 2X_{N_2}\right) = \bar{n}_{pc}\left(rX_{N_rO_z,pc} + 2X_{N_2,pc}\right)$$

Also we have sum mols = 1

$$\bar{n}_{pc}\left(X_{CO_2,pc} + X_{CO,pc} + X_{H_2O,pc} + X_{H_2,pc} + X_{O_2,pc} + X_{N_rO_z,pc} + X_{uHC,pc} + X_{N_2,pc}\right) = \bar{n}_{pc}$$

So, overall, the unknowns are $\bar{n}_p X_{H_2O}, \bar{n}_{pc}, \lambda, X_{H_2O,pc}, X_{H_2,pc}, X_{N_2,pc}, \bar{n}_{water,cond}$, i.e. 7 unknowns. Note that $\bar{n}_p$ and X_{H_2O} cannot be determined independently.

Re-writing the balance equations, but omitting the engine-out component, excepting water, we have (we are measuring the $X_{i,pc}$ not the X_i)

$$\bar{n}_p X_{H_2O} = \bar{n}_{pc} X_{H_2O,pc} + \bar{n}_{water,cond} \qquad \text{G1}$$

Carbon balance

$$1 + u\lambda\bar{t} = \bar{n}_{pc}\left(X_{CO_2,pc} + X_{CO,pc} + n'X_{uHC,pc}\right) \qquad \text{G2}$$

Hydrogen balance

$$\bar{m} + 2v\lambda\bar{t} = \bar{n}_{pc}\left(2X_{H_2O,pc} + 2X_{H_2,pc} + \bar{m}'n'X_{uHC,pc}\right) + 2\bar{n}_{water,cond} \qquad \text{G3}$$

Oxygen balance

$$\bar{x}+\lambda\bar{t}\left(2+2u+v\right)=\bar{n}_{pc}\left(2X_{CO_2,pc}+X_{CO,pc}+2X_{O_2,pc}+zX_{N_rO_z,pc}+\bar{x}'n'X_{uHC,pc}\right)+\bar{n}_{pc}X_{H_2O,pc}+\bar{n}_{water,condensed} \quad \text{G4}$$

Nitrogen balance

$$\bar{y}+2w\lambda\bar{t}=\bar{n}_{pc}\left(rX_{N_rO_z,pc}+2X_{N_2,pc}\right) \quad \text{G5}$$

Also we have sum mols = 1

$$\bar{n}_{pc}\left(X_{CO_2,pc}+X_{CO,pc}+X_{H_2O,pc}+X_{H_2,pc}+X_{O_2,pc}+X_{N_rO_z,pc}+X_{uHC,pc}+X_{N_2,pc}\right)=\bar{n}_{pc} \quad \text{G6}$$

And finally the feedgas WGSR:-

$$K=\frac{X_{CO}X_{H_2O}}{X_{CO_2}X_{H_2}}=\frac{\bar{n}_p}{\bar{n}_{pc}}\frac{X_{CO,pc}X_{H_2O}}{X_{CO_2,pc}X_{H_2,pc}} \quad \text{G7}$$

So, overall, the number of equations and unknowns is equal, seven. In matrix form

$$\begin{bmatrix} -u & \begin{pmatrix}X_{CO_2,pc}+X_{CO,pc}\\+n'X_{uHC,pc}\end{pmatrix} & 0 & 0 & 0 & 0 & 0 \\ -2v & \bar{m}'n'X_{uHC,pc} & 2 & 2 & 0 & 2 & 0 \\ -\begin{pmatrix}2\\+2u\\+v\end{pmatrix} & \begin{pmatrix}2X_{CO_2,pc}+X_{CO,pc}\\+2X_{O_2,pc}+\\zX_{N_rO_z,pc}+\bar{x}'n'X_{uHC,pc}\end{pmatrix} & 1 & 0 & 0 & 1 & 0 \\ -2w & rX_{N_rO_z,pc} & 0 & 0 & 0 & 0 & 2 \\ 0 & \begin{pmatrix}X_{CO_2,pc}+X_{CO,pc}\\+X_{O_2,pc}+X_{N_rO_z,pc}\\+X_{uHC,pc}-1\end{pmatrix} & 1 & 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & -1 & \frac{X_{CO,pc}}{KX_{CO_2,pc}} & 0 & 0 \end{bmatrix} \begin{bmatrix}\lambda\bar{t}\\ \bar{n}_{pc}\\ \bar{n}_{pc}X_{H_2O,pc}\\ \bar{n}_{pc}X_{H_2,pc}\\ \bar{n}_pX_{H_2O}\\ \bar{n}_{water,cond}\\ \bar{n}_{pc}X_{N_2,pc}\end{bmatrix}=\begin{bmatrix}1\\ \bar{m}\\ \bar{x}\\ \bar{y}\\ 0\\ 0\\ 0\end{bmatrix} \quad \text{G8a-g}$$

Which can be solved via matrix inversion.

Appendix 8 DPF Carbon Oxidation

Though the rate of buildup of carbon in a DPF will probably be too small to be seen in a carbon balance, during regeneration this may not be the case. If we assume that the only reaction taking place is the oxidation of carbon, then we can assume that $\bar{n}_p X_i = \bar{n}_{pc} X_{i,pc}$ (subscript *pc* being used to indicate post-DPF) for all gases except *CO*$_2$, *CO* and *O*$_2$ then the analysis is much simplified, and this is the approach taken here, though the full balance equations are first written out.

In a similar manner as the previous two sections, we define

$q_r = \frac{n_{pc}}{n_p}$, $q_{rC} = \frac{n_{C,oxidized}}{n_p}$, where q_r is the mols of post-DPF gases, n_{pc}, per mol of feedgas, n_p, and $q_{r,C}$ is the number of mols of C oxidized, $n_{C,oxidised}$, per mol of feedgas n_p. Writing the equations out on a wet basis, we have

Carbon balance:-

$$\left(X_{CO_2} + X_{CO} + n' X_{uHC}\right) + q_{r,C} = q_r \left(X_{CO_2,pc} + X_{CO,pc} + n' X_{uHC,pc}\right) \qquad \text{H1}$$

Hydrogen balance:-

$$\left(2X_{H_2O} + 2X_{H_2} + \bar{m}' n' X_{uHC}\right) = q_r \left(2X_{H_2O,pc} + 2X_{H_2,pc} + \bar{m}' n' X_{uHC,pc}\right) \qquad \text{H2}$$

Oxygen balance:-

$$\begin{aligned} &\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + zX_{N_rO_z} + \bar{x}' n' X_{uHC}\right) \\ &= q_r \left(2X_{CO_2,pc} + X_{CO,pc} + 2X_{O_2,pc} + X_{H_2O,pc} + zX_{N_rO_z,pc} + \bar{x}' n' X_{uHC,pc}\right) \end{aligned} \qquad \text{H3}$$

Nitrogen balance:-

$$\left(rX_{N_rO_z} + 2X_{N_2}\right) = q_r \left(rX^*_{N_rO_z,pc} + 2X_{N_2,pc}\right) \qquad \text{H4}$$

Sum of the mol fractions:-

$$\left(X_{CO_2,pc} + X_{CO,pc} + X_{H_2O,pc} + X_{H_2,pc} + X_{O_2,pc} + X_{N_rO_z,pc} + X_{uHC,pc} + X_{N_2,pc}\right) = 1 \qquad \text{H5}$$

If the DPF is "active" in some sense, then perhaps the water gas shift reaction will play a part in determining the post-DPF gas composition:-

$$K_{pc} = \frac{X_{CO,pc} X_{H_2O,pc}}{X_{CO_2,pc} X_{H_2,pc}} \qquad \text{H6}$$

Also the *NO*/*NO*$_2$ ratio may be modified, but if the focus is on the regeneration process, changes in the small *NOx* concentration will not be important in the balance equations.

If we were to go via the route of setting up the equations for solution by matrix inversion, the *C* balance can be omitted, as it is the only equation with the unknown $q_{r,C}$ in it. But since even if the water gas shift reaction modifies the CO/CO_2 ratio, the carbon balance will completely dominate the determination of $q_{r,C}$, so it is perhaps appropriate at this stage to introduce the $X_i = q_r X_{i,pc}$ (except for *CO₂*, *CO* and *O₂*) simplification. The only equations which are not then *0 = 0* are the carbon balance

$$\left(X_{CO_2} + X_{CO}\right) + q_{r,C} = q_r\left(X_{CO_2,pc} + X_{CO,pc}\right) \qquad \text{H7}$$

And the oxygen balance

$$\left(2X_{CO_2} + X_{CO} + 2X_{O_2}\right) = q_r\left(2X_{CO_2,pc} + X_{CO,pc} + 2X_{O_2,pc}\right) \qquad \text{H8}$$

The solution to which is

$$q_r = \frac{\left(2X_{CO_2} + X_{CO} + 2X_{O_2}\right)}{\left(2X_{CO_2,pc} + X_{CO,pc} + 2X_{O_2,pc}\right)} \qquad \text{H9}$$

$$q_{r,C} = \frac{\left(X_{CO_2}X_{CO,pc} - X_{CO}X_{CO_2,pc}\right) + 2X_{O_2}\left(X_{CO_2,pc} - X_{CO,pc}\right) - 2X_{O_2,pc}\left(X_{CO_2} + X_{CO}\right)}{\left(2X_{CO_2,pc} + X_{CO,pc} + 2X_{O_2,pc}\right)} \qquad \text{H10}$$

Note that it makes no difference on what basis these gases are measured, as long as it is the same basis for all the gases.