Equivalent Bond Method: Using Source and Target Matrices to Specify Equivalent Fuels

When a gaseous fuel begins to combust, it undergoes pyrolysis as a first step. Pyrolysis is a literal undoing by fire of parent fuel molecules. This disassembly process means that fuel mixtures containing the same number and types of bonds will generate similar pyrolysis products, and thereby similar combustion properties – e.g., heating value, CO and NO_x production, etc. The following method, termed the *equivalent bond method*, is a matrix algebraic process for specifying a (simpler) target fuel having the same number and kinds of bonds as a (more complex) source fuel.

Let **s** be a vector holding the component fractions of a source fuel mixture of interest; for example,

$$\mathbf{s}^{\mathsf{T}} = \begin{pmatrix} y_{\mathrm{H2}} & y_{\mathrm{CH_4}} & y_{\mathrm{C_2H_4}} & y_{\mathrm{C_2H_6}} & y_{\mathrm{C_3H_6}} & y_{\mathrm{C_3H_8}} & y_{\mathrm{C_4H_8}} & y_{\mathrm{C_4H_{10}}} \end{pmatrix}$$

where y refers to the mole fraction of the subscripted species and $^{\mathsf{T}}$ is the transpose operator. Furthermore, let **b** stand for a vector holding the numbers of all possible bonds of interest; for example: $\mathbf{b}^{\mathsf{T}} = \begin{pmatrix} n_{\mathrm{H-H}} & n_{\mathrm{C-H}} & n_{\mathrm{C-C}} & n_{\mathrm{C=C}} \end{pmatrix}$, where $n_{\mathrm{H\text{-}H}}$ is the number of hydrogen-hydrogen bonds; $n_{\mathrm{C\text{-}H}}$ is the number of carbon-hydrogen bonds; $n_{\mathrm{C\text{-}C}}$ is the number of carbon-carbon single bonds; and, $n_{\mathrm{C=C}}$ is the number of carbon-carbon double bonds. Once **b** and **s** are specified, a bond matrix for the source fuel, **S**, is found by filling each row with the numbers of bond types specified in $\mathbf{b}^{\mathsf{T}}$. For the present case $\mathbf{b}^{\mathsf{T}} = \begin{pmatrix} n_{\mathrm{H-H}} & n_{\mathrm{C-H}} & n_{\mathrm{C-C}} & n_{\mathrm{C=C}} \end{pmatrix}$ and this leads to

$$\mathbf{s} = \begin{pmatrix} \underline{\text{component}} \\ y_{\mathrm{H2}} \\ y_{\mathrm{CH_4}} \\ y_{\mathrm{C_2H_4}} \\ y_{\mathrm{C_2H_6}} \\ y_{\mathrm{C_3H_6}} \\ y_{\mathrm{C_3H_8}} \\ y_{\mathrm{C_4H_8}} \\ y_{\mathrm{C_4H_{10}}} \end{pmatrix} \quad \mathbf{S} = \begin{pmatrix} \underline{n_{\mathrm{H\text{-}H}}} & \underline{n_{\mathrm{C\text{-}H}}} & \underline{n_{\mathrm{C\text{-}C}}} & \underline{n_{\mathrm{C=C}}} \\ 1 & 0 & 0 & 0 \\ 0 & 4 & 0 & 0 \\ 0 & 4 & 0 & 1 \\ 0 & 6 & 1 & 0 \\ 0 & 6 & 1 & 1 \\ 0 & 8 & 2 & 0 \\ 0 & 8 & 1 & 1 \\ 0 & 10 & 3 & 0 \end{pmatrix}$$

(The headings in the vector and matrix are for reference and not part of the matrix proper.)

Therefore, **S** is completely determined by the bond structure and bonds of interest of each fuel component*; mathematically, this is codified via Equation (1) or graphically by Figure 1.

$$\mathbf{b} = \mathbf{S}^{\mathsf{T}}\mathbf{s} \tag{1}$$

* For example, C_3H_6 has no H−H bonds, six C−H bonds, one C−C bond, and one C=C bond. Expressed as a row in the bond matrix (**S**) this is (0 6 1 1). Since C_3H_6 is the fifth entry in the **s** vector, therefore, the fifth row of the **S** matrix is (0 6 1 1).

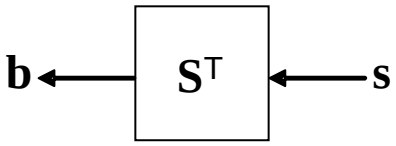

Figure 1, pictorial representation of the transformation of source to bond vector via $\mathbf{S}^T$.

Now we desire to produce a target fuel blend (codified as target fuel vector **t**) that has many fewer components but still contains the identical number and type of bonds as the source fuel. This will be accomplished with a transformation matrix (**T**). Figure 2 depicts the process in an analogous way to Figure 1.

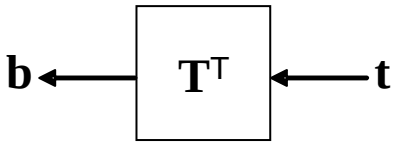

Figure 2, pictorial representation of the transformation of target to bond vector via $\mathbf{T}^T$.

Then, analogous to Equation (1), we arrive at Equation (2).

$$\mathbf{b} = \mathbf{T}^T\mathbf{t} \tag{2}$$

Since **b** is already known, once we decide upon the components for **t**, **T** is determined. For example, if $\mathbf{t}^T = \begin{pmatrix} y_{H2} & y_{CH4} & y_{C3H6} & y_{C3H8} \end{pmatrix}$ then **T** becomes

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 4 & 0 & 0 \\ 0 & 6 & 1 & 1 \\ 0 & 8 & 2 & 0 \end{pmatrix} \tag{3}$$

Since we have four kinds of bonds, we have chosen **t** to comprise four target components containing them. This gives a square invertible matrix, one of two requirements for the equivalent bond method to be useful.* The goal is now to obtain **t**.

From Equation (2) and per the rules of matrix algebra, we may derive

$$\mathbf{t} = (\mathbf{T}^T)^{-1}\mathbf{b} \tag{4}$$

For the present case, Equation (5) gives $(\mathbf{T}^T)^{-1}$ the solution to the case at hand.

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* The other requirement is that the target fuel components are able to *bracket* the source components. We shall describe this second requirement in more detail later.

$$\left(\mathbf{T}^{\mathsf{T}}\right)^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/4 & -1 & -1/2 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1/2 & -1/2 \end{pmatrix} \tag{5}$$

Equating (2) with (1) gives $\mathbf{S}^{\mathsf{T}}\mathbf{s} = \mathbf{T}^{\mathsf{T}}\mathbf{t}$. Solving for **t** leads to a single transformation matrix from **s** to **t**.

$$\mathbf{t} = (\mathbf{T}^{\mathsf{T}})^{-1}\mathbf{S}^{\mathsf{T}}\mathbf{s} \tag{6}$$

We shall refer to $(\mathbf{T}^{\mathsf{T}})^{-1}\mathbf{S}^{\mathsf{T}}$ as the **X** matrix. Then

$$\mathbf{t} = \mathbf{X}\mathbf{s} \qquad \text{where } \mathbf{X} = (\mathbf{T}^{\mathsf{T}})^{-1}\mathbf{S}^{\mathsf{T}} \tag{7}$$

For the present case, this results in

$$\mathbf{X} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1/2 & 1/2 & 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & -1/2 & 1/2 & 0 & 1 & 1/2 & 1/2 \end{pmatrix} \tag{8}$$

That is

$$\mathbf{t} = \begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_3H_6} \\ y_{C_3H_8} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 1/2 & 1/2 & 0 & 0 & -1/2 & -1/2 \\ 0 & 0 & 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & -1/2 & 1/2 & 0 & 1 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_2H_4} \\ y_{C_2H_6} \\ y_{C_3H_6} \\ y_{C_3H_8} \\ y_{C_4H_8} \\ y_{C_4H_{10}} \end{pmatrix} \tag{9}$$

Figure 3 depicts the process.

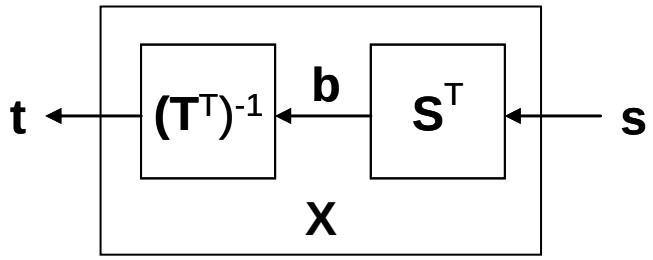

Figure 3, pictorial representation of the transformation of source to target vector via **X**, where $\mathbf{X} = (\mathbf{T}^{\mathsf{T}})^{-1}\mathbf{S}^{\mathsf{T}}$.

For example, according to Equation (9), if $\begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_2H_4} \\ y_{C_2H_6} \\ y_{C_3H_6} \\ y_{C_3H_8} \\ y_{C_4H_8} \\ y_{C_4H_{10}} \end{pmatrix} = \begin{pmatrix} 40\% \\ 30\% \\ 5\% \\ 0\% \\ 2\% \\ 20\% \\ 1\% \\ 2\% \end{pmatrix}$, then $\begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_3H_6} \\ y_{C_3H_8} \end{pmatrix} = \begin{pmatrix} 40\% \\ 31\% \\ 8\% \\ 21\% \end{pmatrix}$ and the reader may verify that both the source and target have identical numbers and kinds of bonds; i.e., $\mathbf{b} = \mathbf{S}^T\mathbf{s} = \mathbf{T}^T\mathbf{t}$.

However, the method may fail if the target vector fails to bracket the source fuel. To see what we mean, consider

$$\begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_2H_4} \\ y_{C_2H_6} \\ y_{C_3H_6} \\ y_{C_3H_8} \\ y_{C_4H_8} \\ y_{C_4H_{10}} \end{pmatrix} = \begin{pmatrix} 40\% \\ 10\% \\ 10\% \\ 1\% \\ 2\% \\ 2\% \\ 0\% \\ 35\% \end{pmatrix}, \text{ then } \begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_3H_6} \\ y_{C_3H_8} \end{pmatrix} = \begin{pmatrix} 40\% \\ -2\% \\ 12\% \\ 50\% \end{pmatrix}.$$

Unfortunately, there is no way to have –2% methane in the target mixture; at least one of the roots is extraneous. This is because with respect to C–H and C–C bonds, the source mixture spans methane to butane but the target mixture spans only methane to propane. So if there is enough butane in the source mixture, it will not be possible to simulate it with methane-propane mixtures. If this happens, it will be necessary to either live with an inexact match or to trade one or more components in the target mixture. As an example of the former method, we may use 0% methane and 52% propane. This gives an approximate match as follows.

$$\text{Source: } \begin{pmatrix} n_{H-H} \\ n_{C-H} \\ n_{C-C} \\ n_{C=C} \end{pmatrix} = \begin{pmatrix} 0.40 \\ 4.64 \\ 1.12 \\ 0.12 \end{pmatrix} \qquad \text{Target: } \begin{pmatrix} n_{H-H} \\ n_{C-H} \\ n_{C-C} \\ n_{C=C} \end{pmatrix} = \begin{pmatrix} 0.40 \\ 4.88 \\ 1.16 \\ 0.12 \end{pmatrix}$$

Although the match is not exact, it is very close and is still likely to be a good simulation for combustion properties such as heating value or NOx formation for a given burner-furnace system.

If an exact match is required, we may change the target mixture to bracket the source fuel – say by using butane in lieu of propane. For the example source fuel an exact match is determined to be as follows.

$$\text{If } \begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_2H_4} \\ y_{C_2H_6} \\ y_{C_3H_6} \\ y_{C_3H_8} \\ y_{C_4H_8} \\ y_{C_4H_{10}} \end{pmatrix} = \begin{pmatrix} 40\% \\ 10\% \\ 10\% \\ 1\% \\ 2\% \\ 2\% \\ 0\% \\ 35\% \end{pmatrix}, \text{ then } \begin{pmatrix} y_{H2} \\ y_{CH_4} \\ y_{C_3H_6} \\ y_{C_4H_{10}} \end{pmatrix} = \begin{pmatrix} 40.0\% \\ 14.7\% \\ 12.0\% \\ 33.3\% \end{pmatrix}.$$