WHEN YOU NEED TO BE SURE

CyFlex® Knowledge Article

Reactant Stream Composition and Molecular Weight

Author: Daniel Oren

July 9, 2019

The composition and molecular weight of the reactant streams must be specified as inputs to the calculations described in the *Burned Gas Composition* document. Some reactant streams are so common that they warrant specific discussion.

Dry Air

The concentrations of oxygen, nitrogen, argon, and carbon dioxide in dry "Cummins standard" combustion air are assumed to be :

$$y_{O_2,dry\ air} = 0.20946 \quad \text{rsc.1}$$

$$y_{N_2,dry\ air} = 0.78087 \quad \text{rsc.2}$$

$$y_{Ar,dry\ air} = 0.00934 \quad \text{rsc.3}$$

$$y_{CO_2,dry\ air} = 0.00033 \quad \text{rsc.4}$$

The molecular weight of "Cummins standard" air is

$$M_{air,dry} = 28.9646 \quad \text{rsc.5}$$

Wet Air

Combustion air is seldom dry unless you are using compressed air as a source. The amount of water vapor in combustion air drawn from the atmosphere can be determined from the measured barometric pressure P_{bar} and the measured vapor pressure, P_{vap}. If we assume a composition vector of the form

$$y_{dry\ air,wet\ air}\left(y_{O_2,dry\ air}O_2 + y_{N_2,dry\ air}N_2 + y_{Ar,dry\ air}Ar + y_{CO_2,dry\ air}CO_2\right) + y_{H_2O,wet\ air}H_2O$$

the number of moles of dry air per mole of wet combustion air, $y_{dry\ air,wet\ air}$, and the number of moles of water vapor per mole of wet combustion air, $y_{H_2O,wet\ air}$, can be calculated based on vapor and barometric pressure measurements using

$$y_{dry\ air,wet\ air} = \frac{P_{bar} - P_{vap}}{P_{bar}} \quad \text{rsc.6}$$

and

$$y_{H_2O,wet\ air} = \frac{P_{vap}}{P_{bar}} \quad \text{rsc.7}$$

The molecular weight of wet combustion air is given by

$$\begin{aligned} M_{wet\ air} &= y_{dry\ air,wet\ air} M_{dry\ air} + y_{H_2O,wet\ air} M_{H_2O} \\ &= \frac{\left(P_{bar} - P_{vap}\right) M_{air,dry} + P_{vap} M_{H_2O}}{P_{bar}} \end{aligned}$$ rsc.8

Natural Gas

Natural gas composition is measured with a gas chromatograph and provided directly in the form of mole fractions of methane, ethane, propane, isobutane, nbutane, pentanes, hexanes and higher, hydrogen, carbon monoxide, nitrogen, oxygen, and carbon dioxide. The composition vector is then given by

$$y_{methane,nat\ gas} CH_4 + y_{ethane,nat\ gas} C_2H_6 + y_{propane,nat\ gas} C_3H_8 + y_{isobutane,nat\ gas} C_4H_{10} +$$

$$y_{nbutane,nat\ gas} C_4H_{10} + y_{pentanes,nat\ gas} C_5H_{12} + y_{hexanes,nat\ gas} C_6H_{14} + y_{hydrogen,nat\ gas} H_2 +$$

$$y_{hexanes,nat\ gas} C_6H_{14} + y_{hydrogen,nat\ gas} H_2 + y_{carbon\ monoxide,nat\ gas} CO + y_{nitrogen,nat\ gas} N_2 +$$

$$y_{oxygen,nat\ gas} O_2 + y_{carbon\ dioxide,nat\ gas} CO_2$$

The molecular weight of the natural gas stream is given by

$$\begin{aligned} M_{natural\ \ gas} = \; & y_{methane} M_{CH_4} + y_{ethane} M_{C_2H_6} + y_{propane} M_{C_3H_8} + y_{isobutane} M_{C_4H_{10}} + \\ & y_{nbutane} M_{C_4H_{10}} + y_{pentanes} M_{C_5H_{12}} + y_{hexanes} M_{C_6H_{14}} + y_{hydrogen} M_{H_2} + \\ & y_{carbon\ monoxide} M_{CO} + y_{nitrogen} M_{N_2} + y_{oxygen} M_{O_2} + y_{carbon\ dioxide} M_{CO_2} \end{aligned}$$ rsc.9

Liquid Fuels

Composition

There are a variety of ways for specifying liquid fuel composition. We provide three alternatives in the composition variable: atom weight fractions, equivalent composition, and atom mole fractions.

Atom Mole Fractions

When specified in terms of atom mole fractions, the equivalent molecular formula for the fuel has the form

$$C_{y_{C,liquid\ \ fuel}} H_{y_{H,liquid\ \ fuel}} O_{y_{O,liquid\ \ fuel}} N_{y_{N,liquid\ \ fuel}}$$ rsc.10

where

$y_{V,\ liquid\ fuel}$ = *mole fraction of V atoms per mole of total atoms making up the fuel molecule*

Like mole fractions of component gases, the sum of the atom mole fractions will always be one. Specifying the composition in terms of atom mole fractions allows us to treat the fuel in a way that is roughly equivalent to the way we deal with gaseous fuels so we always convert fuel composition information provided in other forms to this format.

Equivalent Composition

An equivalent composition can be specified in the form of a fuel having the molecular formula

$$C_\varepsilon H_\sigma O_\tau N_\zeta \qquad \text{rsc.11}$$

This allows us to handle the case of a pure fuel such as dodecane which would be specified as $\varepsilon = 12$, $\sigma = 26$, $\tau = 0$, $\zeta = 0$ as well as combinations of fuels for which ε, σ, τ, and ζ can be scaled to non-integer values to reflect the relative amounts of the pure fuels that make up the mixture. This approach is described in some detail in many standard textbooks on internal combustion engines.

We can also use this method if we want to assume a H:C atom ratio for the fuel. Commonly used values for diesel are usually in the range of 1.80 to 1.85. If we want to specify a H:C ratio of 1.85 for example, then we would set $\varepsilon = 1$, $\sigma = 1.85$, $\tau = 0$, $\zeta = 0$. As long as we properly specify the ratio of C:H:O:N, the atom mole fractions that we compute for use in the burned gas composition calculations will work out correctly since any multiplier will cancel out in the next set of equations described below.

Given the equivalent composition, we can calculate the atom mole fractions using

$$y_{C,liquid\ fuel} = \frac{\varepsilon}{\varepsilon+\sigma+\tau+\zeta} \qquad \text{rsc.12}$$

$$y_{H,liquid\ fuel} = \frac{\sigma}{\varepsilon+\sigma+\tau+\zeta} \qquad \text{rsc.13}$$

$$y_{O,liquid\ fuel} = \frac{\tau}{\varepsilon+\sigma+\tau+\zeta} \qquad \text{rsc.14}$$

$$y_{N,liquid\ fuel} = \frac{\zeta}{\varepsilon+\sigma+\tau+\zeta} \qquad \text{rsc.15}$$

Atom Weight Fractions

Atom weight fractions are commonly used by laboratories that do fuel analysis to specify the fuel composition. To see how the weight fractions relate to the atom mole fractions, consider an equivalent fuel composition of the form specified above. The mass of an equivalent fuel molecule would be given by

$$m_{equiv\ fuel} = \varepsilon M_C + \sigma M_H + \tau M_O + \zeta M_N \qquad \text{rsc.16}$$

The masses of individual atoms are given by

$$m_{C,equiv\ fuel} = \varepsilon M_C \qquad \text{rsc.17}$$

$$m_{H,equiv\ fuel} = \sigma M_H \qquad \text{rsc.18}$$

$$m_{O,equiv\ fuel} = \tau M_O \qquad \text{rsc.19}$$

$$m_{N,equiv\ fuel} = \zeta M_N \qquad \text{rsc.20}$$

The atom weight (mass) fractions are given by

$$wf_{C,liquid\ fuel} = \frac{m_{C,equiv\ fuel}}{m_{equiv\ fuel}} = \frac{\varepsilon M_C}{m_{equiv\ fuel}} \quad \text{rsc.21}$$

$$wf_{H,liquid\ fuel} = \frac{m_{H,equiv\ fuel}}{m_{equiv\ fuel}} = \frac{\sigma M_H}{m_{equiv\ fuel}} \quad \text{rsc.22}$$

$$wf_{O,liquid\ fuel} = \frac{m_{O,equiv\ fuel}}{m_{equiv\ fuel}} = \frac{\tau M_O}{m_{equiv\ fuel}} \quad \text{rsc.23}$$

$$wf_{N,liquid\ fuel} = \frac{m_{N,equiv\ fuel}}{m_{equiv\ fuel}} = \frac{\zeta M_N}{m_{equiv\ fuel}} \quad \text{rsc.24}$$

These formulas can be rearranged to give

$$\varepsilon = \frac{wf_{C,liquid\ fuel} m_{equiv\ fuel}}{M_C} \quad \text{rsc.25}$$

$$\sigma = \frac{wf_{H,liquid\ fuel} m_{equiv\ fuel}}{M_H} \quad \text{rsc.26}$$

$$\tau = \frac{wf_{O,liquid\ fuel} m_{equiv\ fuel}}{M_O} \quad \text{rsc.27}$$

$$\zeta = \frac{wf_{N,liquid\ fuel} m_{equiv\ fuel}}{M_N} \quad \text{rsc.28}$$

From which we can calculate the atom mole fractions using

$$y_{C,liquid\ fuel} = \frac{\varepsilon}{\varepsilon + \sigma + \tau + \zeta} = \frac{\frac{wf_{C,liquid\ fuel} m_{equiv\ fuel}}{M_C}}{\frac{wf_{C,liquid\ fuel} m_{equiv\ fuel}}{M_C} + \frac{wf_{H,liquid\ fuel} m_{equiv\ fuel}}{M_H} + \frac{wf_{O,liquid\ fuel} m_{equiv\ fuel}}{M_O} + \frac{wf_{N,liquid\ fuel} m_{equiv\ fuel}}{M_N}} = \frac{\frac{wf_{C,liquid\ fuel}}{M_C}}{\frac{wf_{C,liquid\ fuel}}{M_C} + \frac{wf_{H,liquid\ fuel}}{M_H} + \frac{wf_{O,liquid\ fuel}}{M_O} + \frac{wf_{N,liquid\ fuel}}{M_N}} \quad \text{rsc.29}$$

$$y_{H,liquid\ fuel} = \frac{\frac{wf_{H,liquid\ fuel}}{M_H}}{\frac{wf_{C,liquid\ fuel}}{M_C} + \frac{wf_{H,liquid\ fuel}}{M_H} + \frac{wf_{O,liquid\ fuel}}{M_O} + \frac{wf_{N,liquid\ fuel}}{M_N}} \quad \text{rsc.30}$$

$$y_{O,liquid\ fuel} = \frac{\frac{wf_{O,liquid\ fuel}}{M_O}}{\frac{wf_{C,liquid\ fuel}}{M_C} + \frac{wf_{H,liquid\ fuel}}{M_H} + \frac{wf_{O,liquid\ fuel}}{M_O} + \frac{wf_{N,liquid\ fuel}}{M_N}} \quad \text{rsc.31}$$

$$y_{N,liquid\ fuel} = \frac{\dfrac{wf_{N,liquid\ fuel}}{M_N}}{\dfrac{wf_{C,liquid\ fuel}}{M_C} + \dfrac{wf_{H,liquid\ fuel}}{M_H} + \dfrac{wf_{O,liquid\ fuel}}{M_O} + \dfrac{wf_{N,liquid\ fuel}}{M_N}}$$ rsc.32

Molecular Weight

To maintain consistency with the gaseous composition calculations and to avoid complications associated with the various ways an equivalent fuel can be specified, we define the molecular weight in terms of an equivalent molecule having the form

$$C_{y_{C,liquid\ fuel}} H_{y_{H,liquid\ fuel}} O_{y_{O,liquid\ fuel}} N_{y_{N,liquid\ fuel}}$$ rsc.33

The molecular weight is then given by

$$M_{liquid\ fuel} = y_{C,liquid\ fuel} M_C + y_{H,liquid\ fuel} M_H + y_{O,liquid\ fuel} M_O + y_{N,liquid\ fuel} M_N$$ rsc.34

Molar Flow Rate

The molar flow rate of the liquid fuel stream can be calculated just as we do for a gas using

$$x_{liquid\ fuel} = \frac{\dot{m}_{liquid\ fuel}}{M_{liquid\ fuel}}$$ rsc.35

This approach is entirely consistent with our approach to gaseous fuels and avoids the need to introduce a multiplier to put the burned gas equations on a moles per mole of fuel carbon basis.

Liquid Solutions

Urea in pure form is a solid that decomposes if heated to its melting point. For use in SCR systems, it is commonly dissolved in water. The solution is usually described in terms of the weight fraction of urea. Other solutes and solvents are possible, so we will develop the formulas here in a more general way and then use urea as an example.

Composition

If we consider a solution of *a* moles of solute in *b* moles of solvent, we can come up with an equivalent composition similar to what we used for fuel

$$a\,(C_{\varepsilon_{solute}} H_{\sigma_{solute}} O_{\tau_{solute}} N_{\zeta_{solute}}) + b\,(C_{\varepsilon_{solvent}} H_{\sigma_{solvent}} O_{\tau_{solvent}} N_{\zeta_{solvent}})$$
$$\Rightarrow C_{\varepsilon_{solution}} H_{\sigma_{solution}} O_{\tau_{solution}} N_{\zeta_{solution}}$$ rsc.36

To get this in the form of mole fractions, we can write

$$y_{C,solution} = \frac{\varepsilon}{\varepsilon+\sigma+\tau+\zeta} = \frac{a\,\varepsilon_{solute} + b\,\varepsilon_{solvent}}{a(\varepsilon+\sigma+\tau+\zeta)_{solute} + b(\varepsilon+\sigma+\tau+\zeta)_{solvent}} \quad \text{rsc.37}$$

$$y_{H,solution} = \frac{\sigma}{\varepsilon+\sigma+\tau+\zeta} = \frac{a\,\sigma_{solute} + b\,\sigma_{solvent}}{a(\varepsilon+\sigma+\tau+\zeta)_{solute} + b(\varepsilon+\sigma+\tau+\zeta)_{solvent}} \quad \text{rsc.38}$$

$$y_{O,solution} = \frac{\tau}{\varepsilon+\sigma+\tau+\zeta} = \frac{a\,\tau_{solute} + b\,\tau_{solvent}}{a(\varepsilon+\sigma+\tau+\zeta)_{solute} + b(\varepsilon+\sigma+\tau+\zeta)_{solvent}} \quad \text{rsc.39}$$

$$y_{N,solution} = \frac{\zeta}{\varepsilon+\sigma+\tau+\zeta} = \frac{a\,\zeta_{solute} + b\,\zeta_{solvent}}{a(\varepsilon+\sigma+\tau+\zeta)_{solute} + b(\varepsilon+\sigma+\tau+\zeta)_{solvent}} \quad \text{rsc.40}$$

Given a weight fraction of solute, wf_{solute}, we can write

$$wf_{solute} = \frac{m_{solute}}{m_{solution}} = \frac{m_{solute}}{m_{solute}+m_{solvent}} = \frac{a\,M_{solute}}{a\,M_{solute} + b\,M_{solvent}} \quad \text{rsc.41}$$

This equation can be rearranged and solved for the ratio of *a* to *b*

$$\frac{a}{b} = \frac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}} \quad \text{rsc.42}$$

Substituting into the mole fraction equations gives

$$\boxed{\begin{aligned}
y_{C,solution} &= \frac{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}\varepsilon_{solute} + \varepsilon_{solvent}}{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}(\varepsilon+\sigma+\tau+\zeta)_{solute} + (\varepsilon+\sigma+\tau+\zeta)_{solvent}} && \text{rsc.43}\\
y_{H,solution} &= \frac{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}\sigma_{solute} + \sigma_{solvent}}{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}(\varepsilon+\sigma+\tau+\zeta)_{solute} + (\varepsilon+\sigma+\tau+\zeta)_{solvent}} && \text{rsc.44}\\
y_{O,solution} &= \frac{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}\tau_{solute} + \tau_{solvent}}{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}(\varepsilon+\sigma+\tau+\zeta)_{solute} + (\varepsilon+\sigma+\tau+\zeta)_{solvent}} && \text{rsc.45}\\
y_{N,solution} &= \frac{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}\zeta_{solute} + \zeta_{solvent}}{\dfrac{wf_{solute}\,M_{solvent}}{(1-wf_{solute})M_{solute}}(\varepsilon+\sigma+\tau+\zeta)_{solute} + (\varepsilon+\sigma+\tau+\zeta)_{solvent}} && \text{rsc.46}
\end{aligned}}$$

Urea Example

Consider a solution of 32.5% by weight of urea in water

$$a\,(NH_2)_2CO \quad + \quad b\,H_2O \quad \Rightarrow \quad C_{\varepsilon_{solution}}H_{\sigma_{solution}}O_{\tau_{solution}}N_{\zeta_{solution}}$$ rsc.47

So

$$\begin{aligned}
wf_{urea} &= 0.325 \\
\varepsilon_{urea} &= 1 \\
\varepsilon_{water} &= 0 \\
\sigma_{urea} &= 4 \\
\sigma_{water} &= 2 \\
\tau_{urea} &= 1 \\
\tau_{water} &= 1 \\
\zeta_{urea} &= 2 \\
\zeta_{water} &= 0 \\
M_{urea} &= 60.07[g/mol] \\
M_{water} &= 18.0153[g/mol]
\end{aligned}$$

and

$$\frac{wf_{urea}\,M_{water}}{(1-wf_{urea})M_{urea}} = \frac{0.325(18.0153)}{(1-0.325)60.07} = 0.1444$$

$$(\varepsilon+\sigma+\tau+\zeta)_{urea} = 1+4+1+2 = 8$$

$$(\varepsilon+\sigma+\tau+\zeta)_{water} = 0+2+1+0 = 3$$

$$\frac{wf_{urea}\,M_{water}}{(1-wf_{urea})M_{urea}}(\varepsilon+\sigma+\tau+\zeta)_{urea}+(\varepsilon+\sigma+\tau+\zeta)_{water}$$
$$= 0.1444(8)+3 = 4.155$$

Finally

$$y_{C,solution} = \frac{0.1444(1)+0}{4.155} = 0.0348$$

$$y_{H,solution} = \frac{0.1444(4)+2}{4.155} = 0.6203$$

$$y_{O,solution} = \frac{0.1444(1)+1}{4.155} = 0.2754$$

$$y_{N,solution} = \frac{0.1444(2)+0}{4.155} = 0.0695$$

Molecular Weight

As with liquid fuels, we define the molecular weight in terms of an equivalent molecule having the form

$$C_{y_{C,solution}} H_{y_{H,solution}} O_{y_{O,solution}} N_{y_{N,solution}}$$ rsc.48

The molecular weight is then given by

$$\boxed{M_{solution} = y_{C,solution} M_C + y_{H,solution} M_H + y_{O,solution} M_O + y_{N,solution} M_N}$$ rsc.49

Molar Flow Rate

The molar flow rate of the solution stream can be calculated just as we do for a gas using

$$\boxed{x_{solution} = \frac{\dot{m}_{solution}}{M_{solution}}}$$ rsc.50

This approach is entirely consistent with our approach to gaseous fuels and avoids the need to introduce a multiplier to put the burned gas equations on a moles per mole of fuel carbon basis.

Gas/Liquid Mixtures

Not documented at this time. Can be added if needed.