Combustion

define some units

$kN := 10^3 \cdot N \quad kPa := 10^3 \cdot Pa$

$MPa := 10^6 Pa \quad kJ := 10^3 \cdot J$

$kmol := 10^3 mol$

combustion of dodecane a parafin of type $C_n \cdot H_{2n}$
(represents diesel fuel) in stochiometric proportions:

$$C_{12} \cdot H_{26} + x \cdot O_2 = y \cdot H_2 \cdot O + z \cdot C \cdot O_2 + heat$$

overkill in this case but general method represented by solution of simultaneous equations from elements involved

$x := 1 \qquad y := 1 \quad z := 1$ initial values for given construct

Given

element:

C $\quad z = 12$

O $\quad x \cdot 2 = y + 2 \cdot z$

H $\quad 26 = 2 \cdot y$

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} := Find(x, y, z) \qquad \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 18.5 \\ 13 \\ 12 \end{pmatrix}$$

so combustion equation is

$$C_{12} \cdot H_{26} + x \cdot O_2 = y \cdot H_2 \cdot O + z \cdot C \cdot O_2 + heat \rightarrow C_{12} \cdot H_{26} + \frac{37}{2} \cdot O_2 = 13 \cdot H_2 \cdot O + 12 \cdot C \cdot O_2 + heat$$

O2 comes with nitrogen: 21% by volume and 23.3% by weight in air (79% N2 by volume and 76.7% N2 by weight - ~ 1% Ar lumped with N2) so ... need 79/21 atoms (volume) N2 for each O2

$18.5 \cdot \frac{79}{21} = 69.6$ and combustion is ...

$$C_{12} \cdot H_{26} + 18.5 \cdot O_2 + 69.6 \cdot N_2 = 13 \cdot H_2 \cdot O + 12 \cdot C \cdot O_2 + 69.6 \cdot N_2 + heat$$

this is on a stochiometric basis (mole basis- i.e. 1 mole of C12H26 combines with 18.5 moles of O2 etc.) or volume basis to convert to weight use molecular weights

$mw\_O2 := 32 \frac{kg}{kmol} \qquad mw\_C12\_H26 := (144 + 26) \cdot \frac{kg}{kmol} \quad mw\_N2 := 28 \frac{kg}{kmol}$

$mw\_H2\_O := (2 + 16) \cdot \frac{kg}{kmol} \quad mw\_C\_O2 := (12 + 32) \cdot \frac{kg}{kmol}$

$$1kmol C_{12} \cdot H_{26} + 18.5 \cdot kmol \cdot O_2 + 69.6 \cdot kmol \cdot N_2 = 13 \cdot kmol \cdot H_2 \cdot O + 12kmol \cdot C \cdot O_2 + 69.6kmol \cdot N_2 + LHV$$

$$\begin{pmatrix} \frac{1kmol \cdot mw\_C12\_H26}{170} C_{12} \cdot H_{26} \ldots \\ + \frac{18.5 \cdot kmol.mw\_O2}{170} \cdot O_2 \ldots \\ + \frac{69.6 \cdot kmol \cdot mw\_N2}{170} \cdot N_2 \end{pmatrix} = \begin{pmatrix} \frac{13 \cdot mw\_H2\_O}{170} \cdot kmol \cdot H_2 \cdot O \ldots \\ + \frac{12kmol \cdot mw\_C\_O2}{170} \cdot C \cdot O_2 \ldots \\ + \frac{69.6kmol \cdot mw\_N2}{170} \cdot N_2 \end{pmatrix} + LHV$$

this is divided by 170 - the molecular weight of C12H26 to express on a per 1 kg fuel basis

$(1kmol) \cdot mw\_C12\_H26 = 170 kg$

for symbolic calculation

result is ... combustion of C12H26 by weight ...

$$1kg\cdot C_{12}\cdot H_{26} + 3.48\cdot kg\cdot O_2 + 11.46\cdot kg\cdot N_2 = 1.38\cdot kg\cdot H_2\cdot O + 3.11\cdot k\ \cdot C\cdot O_2 + 11.46\cdot kg\cdot N_2 + heat$$

weight of air : weight of fuel = air-fuel ratio $\quad air\_fuel\_ratio := 3.48 + 11.46 \quad air\_fuel\_ratio = 14.94$

In order to insure complete combustion,air is usually supplied in excess, see example below. Products would include air i.e. O2 and N2

to analyze combustion process use first law ...

steady state, steady flow process ... $\quad m\_dot = flow\_rate$ (5.46)

$$\frac{d}{dt}Q_{c\_v} + \sum_n m\_dot_{i_n}\cdot\left(h_i + \frac{V_i^{\,2}}{2} + g\cdot z_i\right) = \sum_n m\_dot_{e_n}\cdot\left(h_e + \frac{V_e^{\,2}}{2} + g\cdot z_e\right) + \frac{d}{dt}W_{c\_v} \qquad (5.47)$$

work, KE and PE = 0 .. $\quad Q\_dot_{c\_v} + m\_dot_f\cdot h_f + m\_dot_a\cdot h_a = m\_dot_p\cdot h_p \quad$ p = products

conservation of mass ... $\quad m\_dot_p = m\_dot_f + m\_dot_a$

$$\frac{Q\_dot_{c\_v}}{m\_dot_f} = \frac{m\_dot_p}{m\_dot_f}\cdot h_p - \left(h_f + \frac{m\_dot_a}{m\_dot_f}\cdot h_a\right) = \left(1 + \frac{m\_dot_a}{m\_dot_f}\right)\cdot h_p - \left(h_f + \frac{m\_dot_a}{m\_dot_f}\cdot h_a\right)$$

or per unit mass ... $\quad Q_{c\_v} = H_P - H_R \quad$ R = reactants

To quantitatively calculate this equation the basic approach would include accounting for the enthalpy of formation of each of the entities in the process. To avoid repeatedly accounting for the enthalpy of formation of various fuels a calculation (measurement) is done at a standard condition and then specific processes need only account for the deviation from this standard. The standard chosen was 25 deg C and atmospheric pressure (100 kPa) - designated the zero (0) subscript. e.g. the enthalpy of formation of C -> CO2 such that 1 kmol C combines with 1 kmol O2 to yield 1 kmol CO2 gives off 393,522 kJ/kmol. This measurement for fuels is accomplished and the net result is tabulated as the heating value. If the H2O in the products is liquid it is the higher heating value (HHV), if the H2) is vapor - the heating value is the lower heating vaue (LHV). The difference is due to the heat of vaporization being extracted as heat.

$$Q_{c\_v\_0} = H_{P0} - H_{R0} = -heating\_value$$

negative as heating value usually expressed as positive negative Q in first law indicates heat given off

some typical values ...

.	HHV	LHV	sp_gr
.	$\frac{kJ}{kg}$	$\frac{kJ}{kg}$	.
distillate	45900	43000	0.825
heavy_bunker	42900	40600	1.014
dodecane = diesel	47470	44109	_
octane = gasoline	47893	44425	_

from Prof. Carmichael's notes and Table 12.3 in Van Wylen and Sonntag. dodecane and octane are in liquid form. Vapor form has slightly higher value - same concept as HHV vs LHV that is ...

$$Q_{c\_v\_0\_octane} = H_{P0} - H_{R0} = -\text{heating\_value} = -47893\,\frac{kJ}{kg}$$ fuel as liquid, water in preoduct as liquid

this enables us to write ...

$$Q_{c\_v} = H_P - H_R = H_P - H_{P0} - \left(H_R - H_{R0}\right) + \left(H_{P0} - H_{R0}\right) = H_P - H_{P0} - \left(H_R - H_{R0}\right) - \text{heating\_value}$$

or ... writing for boiler, ...

$$-Q_{c\_v} = -Q_B = H_R - H_{R0} - \left(H_P - H_{P0}\right) + \text{heating\_value}$$ QB on unit mass basis

or on a specific enthalpy basis ...

$$-\frac{Q\_dot_{c\_v}}{m\_dot_f} = -Q_B = h_f - h_{f0} + \frac{m\_dot_a}{m\_dot_f}\cdot\left(h_a - h_{a0}\right) - \left(1 + \frac{m\_dot_a}{m\_dot_f}\right)\cdot\left(h_p - h_{p0}\right) + \text{heating\_value}$$

so ... in calculation of boiler process, need only to look up heating value for fuel - appropriate to its state as gas or liquid and water product state as gas or liguid (HHV or LHV) then "correct" heat for deviation from standard state using gas tables or other estimates.
With this result can calculate boiler efficiency ...

$$\eta_B = -\frac{Q\_dot_{c\_v}}{m\_dot_f\,HHV} = \frac{-Q_B}{HHV} = \frac{HV + \left(h_f - h_{f0}\right) + \frac{m\_dot_a}{m\_dot_f}\cdot\left(h_a - h_{a0}\right) - \left(1 + \frac{m\_air\_dot}{m\_fuel\_dot}\right)\cdot\left(h_p - h_{p0}\right)}{HHV}$$

if for example, the fuel and air entering the boiler are at standard conditions (25 deg C, atmospheric pressure) and the H2O in the exhaust is vapor, the boiler efficiency becomes ...

$$\eta_B = \frac{LHV - \left(1 + \frac{m\_air\_dot}{m\_fuel\_dot}\right)\cdot\left(h_p - h_{p0}\right)}{HHV}$$

$$h_a - h_{a0} = 0$$

$$h_f - h_{f0} = 0$$

As an example, let's consider the effect of exhaust (stack) temperature on efficiency ... the calculations are straight-forward but extensive. We will specify combustion with 15 % excess air of dodecane ...

The calculation of enthelpy of the products is the challenge. Either it can be done by "unlumping" the participants or forming a weighted average of the product enthalpies.

example ... combustion of dodecane with 15 % excess air, fuel and air entering at standard conditions, H2O exhaust as vapor, estimate efficiency of the combustion process with exhaust temperature of 120, 230, and 340 deg C. An additional calculation at 226.85 deg C will be done to check the calculations. Assume also 1.5 % heat loss to environment.

from above ..result is ... combustion of C12H26 by weight ... adjusted for 15 % excess air ... and using the LHV

$$1\text{kg}\cdot C_{12}\cdot H_{26} + \left(3.48\cdot \text{kg}\cdot O_2 + 11.46\cdot \text{kg}\cdot N_2\right)\cdot 1.15 = \begin{bmatrix} 1.38\cdot \text{kg}\cdot H_2\cdot O + 3.11\cdot \text{kg}\cdot C\cdot O_2 + 11.46\cdot \text{kg}\cdot N_2 \ldots \\ + \left(3.48\cdot \text{kg}\cdot O_2 + 11.46\cdot \text{kg}\cdot N_2\right)\cdot 0.15 \end{bmatrix} + \text{LHV}$$

which is same as ... athough we will use elemental expression for enthalpy calculation - probably could use air parameters

$$C_{12}\cdot H_{26} + (3.48 + 11.46)\cdot 1.15\cdot \text{air} = 1.38\cdot H_2\cdot O + 3.1\cdot C\cdot O_2 + 11.46\cdot N_2 + (3.48 + 11.46)\cdot 0.15\cdot \text{air} + \text{LHV}$$

weighted average statement ....

$$h_p - h_{p0} = \frac{\begin{bmatrix} m\_H2\_O\cdot\left(h_{H_2\cdot O} - h_{H_2\cdot O\cdot 0}\right) + m\_C\_O2\cdot\left[h_{C\cdot O_2} - \left(h_{C\cdot O_2\cdot 0}\right)\right] \ldots \\ + m\_N2\cdot\left(h_{N_2} - h_{N_2\cdot 0}\right) + (m\_O2 + m\_N2)\cdot 0.15\cdot\left(h_{air} - h_{air\cdot 0}\right) \end{bmatrix}}{m\_H2\_O + m\_C\_O2 + m\_N2 + (m\_O2 + m\_N2)\cdot 0.15}$$

where m_xx is mass of the entity

to calculate enthalpies at non-standard conditions use constant-pressure specific heats from Table A.9 of Van Wylen and Sonntag ...

$$\theta = \frac{T}{100}$$

O2 $$C_{po\_O2}(\theta) := 37.432 + 0.020102\cdot\theta^{1.5} - 178.57\cdot\theta^{-1.5} + 236.88\cdot\theta^{-2}\ \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}$$

C_O2 $$C_{po\_C\_O2}(\theta) := -3.7357 + 30.529\cdot\theta^{0.5} - 4.1034\cdot\theta + 0.024198\cdot\theta^{2}\ \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}$$

given in kJ/kmole*K so divide by molecular weight to get kJ/kg*K

N2 $$C_{po\_N2}(\theta) := 39.060 - 512.79\cdot\theta^{-1.5} + 1072.7\cdot\theta^{-2} - 820.40\cdot\theta^{-3}\ \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}$$

H2_O $$C_{po\_H2\_0}(\theta) := 143.05 - 183.54\cdot\theta^{0.25} + 82.751\cdot\theta^{0.5} - 3.6989\cdot\theta\ \frac{\text{kJ}}{\text{kmol}\cdot\text{K}}$$

$$T := \left[\begin{pmatrix} 120 \\ 230 \\ 340 \\ 500 - 273.15 \end{pmatrix} + 273.15\right]\cdot K \quad \theta T := \frac{T}{100K} \quad \theta T = \begin{pmatrix} 3.93 \\ 5.03 \\ 6.13 \\ 5 \end{pmatrix} \quad T = \begin{pmatrix} 393.15 \\ 503.15 \\ 613.15 \\ 500 \end{pmatrix} K \quad T_0 := (25 + 273.15)K$$

$$500 - 273.15 = 226.85$$

integrate $dh = C_p \cdot dT$ with variable change to θ. $h_{H\_2OT} = \left(h_{H_2 \cdot O} - h_{H_2 \cdot O \cdot 0}\right)$ etc....

$i := 0..3$

H2_O

$$h_{H\_2OT_i} := \frac{\left(\displaystyle\int_{\frac{T_0}{K \cdot 100}}^{\frac{T_i}{K \cdot 100}} C_{po\_H2\_0}(\theta) \cdot 100\, d\theta \right| \frac{kJ}{kmol}\Bigg)}{mw\_H2\_O} \qquad h_{H\_2OT} = \begin{pmatrix} 178.81 \\ 390.4 \\ 609.19 \\ 384.25 \end{pmatrix} \frac{kJ}{kg}$$

C_O2

$$h_{C\_O2T_i} := \frac{\left(\displaystyle\int_{\frac{T_0}{K \cdot 100}}^{\frac{T_i}{K \cdot 100}} C_{po\_C\_O2}(\theta) \cdot 100\, d\theta \right| \frac{kJ}{kmol}\Bigg)}{mw\_C\_O2} \qquad h_{C\_O2T} = \begin{pmatrix} 84.39 \\ 191.77 \\ 307.3 \\ 188.57 \end{pmatrix} \frac{kJ}{kg}$$

N2

$$h_{N2T_i} := \frac{\left(\displaystyle\int_{\frac{T_0}{K \cdot 100}}^{\frac{T_i}{K \cdot 100}} C_{po\_N2}(\theta) \cdot 100\, d\theta \right| \frac{kJ}{kmol}\Bigg)}{mw\_N2} \qquad h_{N2T} = \begin{pmatrix} 99.01 \\ 214.22 \\ 331.66 \\ 210.9 \end{pmatrix} \frac{kJ}{kg}$$

O2

$$h_{O2T_i} := \frac{\left(\displaystyle\int_{\frac{T_0}{K \cdot 100}}^{\frac{T_i}{K \cdot 100}} C_{po\_O2}(\theta) \cdot 100\, d\theta \right| \frac{kJ}{kmol}\Bigg)}{mw\_O2} \qquad h_{O2T} = \begin{pmatrix} 88.02 \\ 193.2 \\ 302.34 \\ 190.13 \end{pmatrix} \frac{kJ}{kg}$$

these data could also have been obtained from gas tables. as a check the values for the reference temperature were obtained fromTable A.11 of VW &S - taken from the gas tables

$h_{H\_2OT_3} \cdot mw\_H2\_O = 6916.45 \frac{kJ}{kmol}$ 6920 in table A.11

$h_{C\_O2T_3} \cdot mw\_C\_O2 = 8297.06 \frac{kJ}{kmol}$ 8314 in table A.11

$h_{N2T_3} \cdot mw\_N2 = 5905.1 \frac{kJ}{kmol}$ 5912 in table A.11

$h_{O2T_3} \cdot mw\_O2 = 6084.08 \frac{kJ}{kmol}$ 6088 in table A.11

now calculate weighted average ... separating air into N2 and O2 h.prod is weighted average of products

$m\_H2\_O := 1.38$ $m\_C\_O2 := 3.1$ $m\_N2 := 11.46 \cdot 1.15$ $m\_O2 := 3.48 \cdot 0.15$

$$h_{prod} := \frac{h_{H\_2OT} \cdot m\_H2\_O + h_{C\_O2T} \cdot m\_C\_O2 + h_{N2T} \cdot m\_N2 + h_{O2T} \cdot m\_O2}{m\_H2\_O + m\_C\_O2 + m\_N2 + m\_O2} \qquad h_{prod} = \begin{pmatrix} 102.26 \\ 223.16 \\ 347.73 \\ 219.65 \end{pmatrix} \frac{kJ}{kg}$$

$LHV := 44109 \frac{kJ}{kg}$ $HHV := 47470 \frac{kJ}{kg}$

$$\eta_B = \frac{LHV - \left[\left(1 + \frac{m\_air\_dot}{m\_fuel\_dot}\right) \cdot \left(h_p - h_{p0}\right)\right.}{HHV}$$

$air\_fuel\_ratio = \frac{m\_air\_dot}{m\_fuel\_dot} = 14.94$ in stochiometric combustion

in this case $air\_fuel\_ratio := 14.94 \cdot 1.15$

heat loss accounted for by reucing net heat from combustion * 0.985

$$\eta_B := \frac{LHV - (1 + air\_fuel\_ratio) \cdot h_{prod}}{HHV} \cdot 0.985 \qquad \eta_B = \begin{pmatrix} 0.877 \\ 0.831 \\ 0.784 \\ 0.832 \end{pmatrix}$$

if we had just calculated the products individually, instead of the weighted average ...

$$C_{12} \cdot H_{26} + (3.48 + 11.46) \cdot 1.15 \cdot air = 1.38 \cdot H_2 \cdot O + 3.1 \cdot C \cdot O_2 + 11.46 \cdot N_2 + (3.48 + 11.46) \cdot 0.15 \cdot air + LHV$$

$$\eta_B := \frac{LHV - \left(1.38 \cdot h_{H\_2OT} + 3.1 \cdot h_{C\_O2T} + 11.46 \cdot 1.15 \cdot h_{N2T} + 3.48 \cdot 0.15 \cdot h_{O2T}\right)}{HHV} \cdot 0.985 \qquad \eta_B = \begin{pmatrix} 0.877 \\ 0.831 \\ 0.784 \\ 0.832 \end{pmatrix}$$

effect of excess air

$$air\_fuel\_ratio = \frac{m\_air\_dot}{m\_fuel\_dot} = 14.94$$ in stochiometric combustion

$$exc\_air := \begin{pmatrix} 0.1 \\ 0.15 \\ 0.25 \end{pmatrix}$$ $$j := 0..2$$

$m\_H2\_O := 1.38$ $m\_C\_O2 := 3.1$ $m\_N2_j := 11.46\cdot(1 + exc\_air_j)$ $m\_O2_j := 3.48\cdot exc\_air_j$

$$h_{prod_{i,j}} := \frac{h_{H\_2OT_i}\cdot m\_H2\_O + h_{C\_O2T_i}\cdot m\_C\_O2 + h_{N2T_i}\cdot m\_N2_j + h_{O2T_i}\cdot m\_O2_j}{m\_H2\_O + m\_C\_O2 + m\_N2_j + m\_O2_j}$$

$$h_{prod} = \begin{pmatrix} 102.51 & 102.26 & 101.82 \\ 223.75 & 223.16 & 222.11 \\ 348.71 & 347.73 & 345.99 \\ 220.23 & 219.65 & 218.62 \end{pmatrix} \frac{kJ}{kg}$$

in this case $air\_fuel\_ratio_j := 14.94\cdot[(1 + exc\_air)_j]$

heat loss accounted for by reucing net heat from combustion * 0.985

$$\eta_{B_{i,j}} := \frac{LHV - (1 + air\_fuel\_ratio_j)\cdot h_{prod_{i,j}}}{HHV}\cdot 0.985 \qquad \eta_B = \begin{pmatrix} 0.878 & 0.877 & 0.874 \\ 0.834 & 0.831 & 0.825 \\ 0.789 & 0.784 & 0.774 \\ 0.836 & 0.832 & 0.826 \end{pmatrix}$$