Estimation of Thermophysical and Transport Properties

A.1 Density Calculations

Gas Phase

For low pressure gaseous mixtures, ideal gas equation can be employed.

High Pressure Correction

For gaseous mixtures at high pressures, a simple but effective method known as “Kay’s rule” can be used. Here pseudocritical temperature and pressure of the mixture have to be evaluated first given by the relations

\[ T_{cm} = \sum x_i T_{ci}, \quad P_{cm} = \sum x_i P_{ci} \]

Where \( x_i, T_{ci}, \) and \( P_{ci} \) are species mole fraction, critical temperature and critical pressure respectively. Then reduced temperature and pressure are obtained using

\[ T_r = \frac{T}{T_{cm}} \quad \text{and} \quad P_r = \frac{P}{P_{cm}} \]

and \( Z \) (compressibility factor) at \( T_r \) and \( P_r \) is read from the compressibility chart. Finally the gaseous mixture density is given by

\[ \rho_{g,m} = \frac{P}{Z R_u T} \]

where, \( R_u = R_g / MW \)

\( R_u \) is the universal gas constant, \( MW \) is the molecular weight.

For mixing of air and fuel vapour, the mixing rule is given by [51]

\[ \rho_{g,\text{air-fuel-mix}} = \left( \frac{2}{3} \rho_g + \frac{1}{3} \rho_{\text{air}} \right)^{-1} \]

Another approach for high pressure gaseous mixture calculations is by using any of the given analytical equations of state, (Table 3.1). In the present work, both Kay’s rule and Soave-Redlich-Kwong Equation of State (EOS) are tried and it is observed that there is not much difference in the calculated values of gas mixture densities.
**Liquid Phase**

Modified Rackett Technique [144]

\[ \rho = \frac{1}{V_s} \]

\[ V_s = \frac{RT}{P_c} Z_{RA} \left[ 1 + \left(1 - T_c \right)^{2/3} \right] \]

\[ Z_{RA} = 0.29056 - 0.08775 \omega, \text{ where } \omega \text{ is Pitzer’s acentric factor, } V_s \text{ is the saturated liquid molar volume in } \text{cm}^3/\text{mol}, \text{ } R \text{ is the universal gas constant, } P_c \text{ is in bar.} \]

Hankinson and Thomson have presented the following correction for liquid mixture densities [144]

\[ \frac{V_{sm}}{V_m^*} = V_R^{(0)} \left[ 1 - \omega_{SRK} V_R^{(5)} \right] \]

\[ \omega_{SRK} = \omega_m = \sum_i x_{ni} \omega_i \]

\( \omega_{SRK} \) is acentric factor wrt SRK EOS. \( V_{sm} \) is the saturated molar volume of the mixture and \( V_m^* \) is the characteristic mixture molar volume (\text{cm}^3/\text{mol}), generally within 1 to 4 percent of the critical volume.

\[ V_R^{(0)} = 1 + a \left( 1 - T_r \right)^{1/3} + b \left( 1 - T_r \right)^{2/3} + c \left( 1 - T_r \right) + d \left( 1 - T_r \right)^{4/3} \]

\[ 0.25 < T_r < 0.95 \]

\[ V_R^{(5)} = \left[ e + f T_r + g T_r^2 + h T_r^3 \right] \left( T_r - 1.00001 \right) \]

\[ 0.25 < T_r < 1.0 \]

\[ T_{sm} = \sum_i x_i T_{ci} \text{ (by Kay’s Rule)} \]

\[ T_r = \frac{T}{T_{sm}}, \text{ } T = 298K \]

Values of the constants are

\[ a = -1.52816 \quad b = 1.43907 \]

\[ c = -0.81446 \quad d = 0.190454 \]

\[ e = -0.296123 \quad f = 0.386914 \]

\[ g = -0.0427258 \quad h = -0.0480645 \]

Pure characteristic volume is given as
\[ V^* = \frac{RT}{P_e} (a + b \omega_{SRK} + c\omega^2_{SRK}) \]

For Paraffins

\[ a = 0.2905331 \]
\[ b = -0.08057958 \]
\[ c = 0.02276965 \]

For liquid mixtures

\[ V^*_m = 1/4 \left[ \sum x_i V^*_i + 3(\sum x_i V^{*1/3}_i)(\sum x_i V^{*2/3}_i) \right] \]

**High Pressure Correction**

From the modified HBT (Hankinson-Brobst-Thomson) method, for liquid mixtures at high pressures [13]

\[ V_m = V_{sm} \left( 1 - c \ln \frac{\beta + P}{\beta + P_{sm}} \right) \]

\( V_m \) is the mixture molar volume at high pressure, \( P_{sm} \) is the mixture vapour pressure and \( P \) is the given pressure.

\[ \beta = P_{sm} \left( -1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3} \right) \]

\( T_r \) is determined using Kay’s rule, then

\[ T_r \text{ or } T_r = \frac{T}{T_{sm}}, \ T = 298K \]

\[ e = \exp \left( f + g \omega_{SRK} + h\omega^2_{SRK} \right) \]
\[ c = j + k\omega_{SRK} \]
\[ a = -9.070217 \quad b = 62.45326 \]
\[ d = -135.1102 \quad f = 4.79594 \]
\[ g = 0.250047 \quad h = 1.14188 \]
\[ j = 0.0861488 \quad k = 0.0344483 \]

\[ P_{sm} = (0.291 - 0.08\omega_{SRK})R_m T_{sm} / V_{sm} \]

\[ R_m = \frac{R}{MW_m}; \ MW_m = \sum x_i MW_i \]

\[ V_{cj} = 1/8 \left( V^{1/3}_c + V^{1/3}_j \right)^3 \]
\[ V_{mn} = \sum_i \sum_j x_i x_j V_{ij} \]

\[ \alpha = \left( 35 - \frac{36}{T_m} \right) - 96.736(\log_{10} T_m) + T_m^6 \]

\[ P_{m}^{(1)} = 4.86601 \left( \log_{10} T_m \right) + 0.03721754 \alpha \]

\[ P_{m}^{(0)} = 5.8031817 \left( \log_{10} T_m \right) + 0.07608141 \alpha \]

\[ \log_{10} P_m = P_m^{(0)} + \omega_{sk} P_m^{(1)} \]

\[ P_m = P_m^{(0)} \cdot P_m^{(1)} \]

**A.2 Specific Heat Calculations**

**Gas Phase**

For the estimation of low pressure (ideal gas) specific heats, a number of polynomial or other functional forms are available in literature, one form is given as [144]

\[ C_{pg}^o = \left( a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \right) \times R \]

\[ C_{pg}^o \] is the ideal gas specific heat in J mol\(^{-1}\) K\(^{-1}\) and \( R \) is the universal gas constant in J mol\(^{-1}\) K\(^{-1}\), then \( C_{pg}^o \) for a mixture is given by mass fraction weighted averaging as:

\[ C_{pg}^o = \sum y_{pg} C_{pg}^o \]

Finally, \( C_{pg}^o \) for air-fuel vapour mixture can be evaluated by using 1/3 rule for composition.

**High Pressure Correction**

From the Lee-Kesler method, for gaseous mixtures [144]

\[ (C_{pg} - C_{pg}^*)_m = (\Delta C_{pg})_m = (\Delta C_{pg})_{m}^{(0)} + \omega_m (\Delta C_{pg})_{m}^{(1)} \]

Where, \((\Delta C_{pg})_{m}^{(0)}\) is the simple fluid contribution, \((\Delta C_{pg})_{m}^{(1)}\) is the deviation function, \( R \) is the universal gas constant and \( \omega_m \) is Pitzer’s acentric factor for the mixture.

If Lee-Kesler method is to be used for gaseous mixtures at high pressures, then Lee-Kesler mixing rules have to be used which are given as follows
\[ T_{cm} = \frac{1}{V_{cm}^{\frac{1}{4}}} \sum_i \sum_j x_i x_j V_{cij}^{\frac{1}{4}} T_{cij} \]
\[ V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \]
\[ \omega_m = \sum_i x_i \omega_i \]
\[ T_{cij} = (T_{cij} T_{cij})^{\frac{1}{2}} k_{ij} \]

\( k_{ij} \) is the binary interaction coefficient

\[ V_{cij} = \frac{1}{8} \left( V_{cij}^{\frac{1}{3}} + V_{cij}^{\frac{1}{3}} \right)^3 \]
\[ P_{cm} = (0.2905 - 0.085 \omega_m) R_m T_{cm} / V_{cm} \]

Now, \( T_m = T / T_{cm}, P_m = P / P_{cm} \)

Then, \( (\Delta C_{pg})^0_m \) and \( (\Delta C_{pg})^1_m \) are taken from tables [144], and \( C_{pgm} \) at high pressure is evaluated, and finally \( C_{pg} \) of air and fuel vapour mixture at high pressure.

**Liquid Phase**

The equation modified by Bondi, suggested originally by Rowlinson for low to high pressure pure liquid and liquid mixtures [144] is

\[ C_{pg} - C_{pg}^o \frac{R_u}{T_r} = 1.45 + 0.45(1 - T_r)^{-1} + 0.25 \omega \left[ 17.11 + 25.2(1 - T_r)^{1/3} T_r^{-1} + 1.742(1 - T_r)^{-1} \right] \]

\( C_{pg}^o \) is ideal gas low pressure specific heat at \( T_r, R_u \) is universal gas constant.

\[ T_r = \frac{T}{T_c}, \quad T = 298K, \quad P_r = \frac{P}{P_c}, \quad \text{then} \]

\[ C_{pg,\text{fuelmix}} = \sum_f y_f C_{pg} \]

**A.3 Thermal Conductivity and Viscosity Calculations**

An easier method for evaluating thermal conductivity (\( W / mK \)) of gaseous mixtures is provided by Law and Williams [54], then

\[ \lambda_m^* = 0.4 \lambda_F(T) + 0.6 \lambda_e(T) \]

Here \( F \) and \( \infty \) denote fuel vapour and ambience respectively, where as \( T \) is the average of fuel boiling point and flame temperatures \( T_b \) and \( T_f \) respectively.
**Gas Phase**

For low to moderate pressure gaseous mixtures, $\lambda_m^+$ can be calculated using Wassiljewa Equation [144]

$$\lambda_m^+ = \sum_{i=1}^{n} \frac{y_i \lambda_i}{y_i + \sum_{j=1}^{n} y_j A_{ij}}$$

where, $\lambda_m^+$ = thermal conductivity of the gaseous mixture

$\lambda_i$ = thermal conductivity of pure $i$

$y_i, y_j$ = mole fraction of components $i$ and $j$

From Mason and Saxena Modification [144]

$$A_{ij} = \left[ 1 + \left( \frac{\eta_i}{\eta_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2$$

$$\frac{1}{\eta} \left( \frac{M_i}{M_j} \right)^2 = A_{ij}$$

$A_{ij}$ = $(\eta_i / \eta_j)(M_i / M_j)A_{ij}$, where $\eta_i$ and $\eta_j$ are pure component gas viscosities, $M_i$ and $M_j$ are molecular weights.

For pure, low pressure gases, Stiel and Thodos [144] suggested

$$\lambda^+ = \left[ 1.15 + \frac{2.03}{C_v / R} \right] \frac{\eta M'}{M}$$

$C_v$ is in $kJ / kmolK$

$\eta$ is the viscosity in $Ns / m^2$

$M'$ is the molecular weight in $kg / mol$

$R$ is the universal gas constant, then $\lambda$ is in $W / mK$

Estimation of low pressure pure gas viscosity for the above formula is done using Chung et al. relation [144]

$$\eta = 40.785 \frac{F_v (MT)^{1/2}}{V_c^{2/3} \Omega_v}$$

$\eta$ is the viscosity in $\mu P$

$M$ is the molecular weight in $g / mol$

$T$ is the temperature in $K$
$V_c$ is the critical volume in $cm^3/mol$

$\Omega_c$ is viscosity collision integral, given as

$$\Omega_c = [A(T^*)^{-\beta} + C[\exp(-DT^*)] + E[\exp(-FT^*)]$$

for $0.3 \leq T^* \leq 100$

$A = 1.16145$ ; $B = 0.14874$ ; $C = 0.52487$

$D = 0.77320$ ; $E = 2.16178$ ; $F = 2.43787$

$T^* = 1.2593T_r$

$$F_c = 1 - 0.2756\omega + 0.059035\mu^4 + \kappa$$

Here, $\kappa$ is a special correction for highly polar substances such as alcohols and acids.

$\mu$ is dimensionless dipole moment

$$T_r = T / T_c,$$ where $T_c$ is the reduced temperature.

Pure gas viscosities at low and high pressure can also be calculated by methods provided by Lucas. Wilke formula can be used for determining viscosities of low pressure gaseous mixtures.

Lucas Method [144]

(for gas phase viscosity calculations)

$\xi$ is the reduced inverse viscosity in $(\mu P)^{-1}$, given as $\xi = 0.176 [T_c / MW^3 P_r^4]^{1/6}$ ; $T_c$ is in K, $MW$ is in $g/mol$ and $P_r$ in bars.

Then, $\eta \xi = \left[0.807T_r^{0.618} - 0.357 \exp(-0.449T_r) + 0.340 \exp(-4.058T_r) + (0.018)\right]F_p^0$

$$T_r = \frac{T}{T_c}$$, $F_p^0$ is a correction factor equal to unity for the present case, and $\eta$ is in $\mu P$.

Mixing rules given by Wilke method [144] can be adopted.

$$\eta_{mix} = \frac{x_1 \eta_1}{x_1 + x_2 \phi_{12}} + \frac{x_2 \eta_2}{x_2 + x_1 \phi_{21}},$$ parameters $\phi_{12}$ and $\phi_{21}$ are given as

$$\phi_{12} = \frac{\left[1 + (\mu_2 / \mu_1)^{1/2} \left(M_2 / M_1\right)^{1/4}\right]^2}{2\sqrt{2}\left[1 + \left(M_1 / M_2\right)\right]^{1/2}},$$

$$\phi_{21} = \frac{\left[1 + (\mu_1 / \mu_2)^{1/2} \left(M_1 / M_2\right)^{1/4}\right]^2}{2\sqrt{2}\left[1 + \left(M_2 / M_1\right)\right]^{1/2}}$$

subscripts 1 and 2 denote the components, $x$ is the mole fraction and $\eta$ is the viscosity.
High Pressure Correction

For high pressure viscosity of gaseous mixtures, corresponding state method provided by Lucas [13] can be applied.

Another method for estimating viscosities of pure gas or gaseous mixtures at low to high pressures can be determined from Bird et al.[159].

\[ \mu = \mu_r \mu_c \]
\[ \mu_c = 7.70M^{1/2}P^{2/3}T_c^{-1/6} \]

Here, \( \mu_c \) is the critical viscosity in micropoises (\( \mu P \)), \( M \) is the molecular weight in \( g/mol \), \( T_c \) in \( K \), \( P_c \) in \( atm \), and \( \mu_r \) is the reduced viscosity, calculated from [159] using \( P_r = P/P_c \) and \( T_r = T/T_c \), where \( T \) and \( P \) are reference temperature and pressure.

Following mixing rules suggested by Yorizane et al. can be used for high pressure gaseous mixtures [144]

\[ T_{\text{m}} = \frac{\sum_i \sum_j x_i x_j V_i T_i}{V_{\text{m}}} \]
\[ V_{\text{m}} = \sum_i \sum_j x_i x_j V_i \]
\[ \omega_{\text{m}} = \sum x_i \omega_i \]
\[ Z_{\text{m}} = 0.291 - 0.08 \omega_{\text{m}} \]
\[ P_{\text{m}} = Z_{\text{m}} R T_{\text{m}} / V_{\text{m}} \]

\( R \) is the universal gas constant
\[ MW_{\text{m}} = \sum_i x_i MW_i \]
\[ T_{ij} = (T_i T_j)^{1/2} \]
\[ V_{ij} = 1/8 \left[ V_i^{1/3} + V_j^{1/3} \right]^3 \]
\[ T_{\text{m}} = T_R / T_{\text{m}} \], where \( T_R \) is the reference temperature in \( K \)
\[ P_{\text{m}} = P / P_{\text{m}} \]

From Roy and Thodos formula [144]
\[ \Gamma_m = 210 \left( \frac{T_m M_m^{1/4}}{P_m^{1/4}} \right) \]

\( \Gamma_m \) is the reduced inverse thermal conductivity \([W / mK]^{-1}\) of mixture at high pressure, \(T_m\) is the mixture critical temperature in Kelvin, \(M_m\) is the mixture molecular weight in g/mol, \(P_m\) is the mixture critical pressure in bar.

Then finally using either of the three relations for excess thermal conductivity corrections for gaseous mixtures, we have

\[
(\lambda_m - \lambda_m^0)\Gamma_m Z_m^3 = 1.22 \times 10^{-2}[\exp(0.535\rho_m) - 1] \quad \rho_m < 0.5
\]

\[
(\lambda_m - \lambda_m^0)\Gamma_m Z_m^3 = 1.14 \times 10^{-2}[\exp(0.67\rho_m) - 1.069] \quad 0.5 < \rho_m < 2.0
\]

\[
(\lambda_m - \lambda_m^0)\Gamma_m Z_m^3 = 2.60 \times 10^{-2}[\exp(1.155\rho_m) - 2.016] \quad 2.0 < \rho_m < 2.8
\]

here, \(\lambda_m\) is the high pressure thermal conductivity of mixture in \([W / mK]\), \(Z_c\) is the critical compressibility factor of the mixture, and the reduced mixture density \(\rho_m = V_m / \rho_m\), where \(V_m\) is in \(m^3 / kmol\) calculated using Soave-Redlich Kwong Equation of State [160]. Thermal conductivities of fuel vapour mixtures calculated above for low and high pressure can be used to determine thermal conductivities of air-fuel vapour mixtures by applying 1/3 rule.

**Liquid Phase**

From Latini et al.[144]

\[ \lambda_L = A(1 - T)_{0.38} \]

\(\lambda_L\) is the thermal conductivity of liquid in \([W / mK]\)

\(T_r = T / T_c\), \(T = 298K\)

\[ A = \frac{A^*T_b^\alpha}{M^\beta T_c^\gamma} \]

\(T_b\) is the normal boiling temperature in K at 1 atm,

\(T_c\) is the critical temperature in K

\(M\) is the molecular weight in kg/kmol

For paraffins (family of saturated hydrocarbons),
\[ A' = 0.00350; \quad \alpha = 1.2; \quad \beta = 0.5; \quad \gamma = 0.167 \]

By Filippov Equation [144]

\[ \lambda_m = y_{10}\lambda_1 + y_{20}\lambda_2 - 0.72y_{10}y_{20}(\lambda_2 - \lambda_1) \]

where, \( \lambda_1, \lambda_2 \) are pure component thermal conductivities, selected in such a way so that \( \lambda_2 \geq \lambda_1 \), and \( y_{10}, y_{20} \) are liquid phase mass fractions of the two components.

**High Pressure Correction**

Using graphical method suggested by Lenoir [144]

\[ \frac{\lambda_{L_2}}{\lambda_{L_1}} = \frac{L_2}{L_1}, \quad \lambda_{L_1} (W/mK) \rightarrow \text{at 1 bar, 298 K} \]

\[ L_1 \rightarrow P_1, T_1; \quad L_2 \rightarrow P_2, T_2 \]

\( L_1 \) and \( L_2 \) can be determined from the graph as a function of \( P_r \) and \( T_r \) and hence, \( \lambda_{L_2} (W/mK) \) can be determined at high pressure. In the same way, Fillipov method can be employed for liquid mixture thermal conductivity at high pressures.

**Property Calculations for Biodiesel Fuel**

**Methyl Linoleate (Sunflower Oil Fatty Acid Methyl Ester)**

*Molecular Formula:* \( C_{19}H_{34}O_2 \)

*Molecular Weight:* 294.476 g/mol

*Chemical Structure:* \( CH_3(CH_2)_4CH=CH(CH_2)CH=CH(CH_2)_7-COO-CH_3 \)

**Table A.1 Estimation of \( \Delta_T, \Delta_P, \Delta_b \) and \( \Delta_y \) for Calculating Critical Properties and Boiling Point of Biodiesel Liquid Fuel (Methyl linoleate)**

<table>
<thead>
<tr>
<th>Group</th>
<th>Ambrose Method</th>
<th>Joback Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta_T )</td>
<td>( \Delta_P )</td>
</tr>
<tr>
<td>Carbon atoms in alkyl groups</td>
<td>0.138</td>
<td>0.226</td>
</tr>
<tr>
<td>Corrections double bonds</td>
<td>-0.050</td>
<td>-0.065</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliphatic functional group (-CO-O-)</td>
<td>0.330</td>
<td>0.470</td>
</tr>
<tr>
<td>( \Sigma )</td>
<td>2.852</td>
<td>4.634</td>
</tr>
</tbody>
</table>
Where, \( T_b = 198 + \sum \Delta_{b^i} \), \( V_c = 17.5 + \sum \Delta_{v^i} \), \( T_c = T_b \left[ 1 + \left( 1.242 + \sum \Delta_T \right)^{-1} \right] \),

\[ P_c = M \left( 0.339 + \sum \Delta_P \right)^{-2} \]

<table>
<thead>
<tr>
<th>Group</th>
<th>a</th>
<th>b \times 10^2</th>
<th>c \times 10^4</th>
<th>d \times 10^6</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-CH_3)</td>
<td>0.6087</td>
<td>2.1433</td>
<td>-0.0852</td>
<td>0.01135</td>
<td>×2</td>
</tr>
<tr>
<td>(&gt; CH_2)</td>
<td>0.3945</td>
<td>2.1363</td>
<td>-0.1197</td>
<td>0.002596</td>
<td>×12</td>
</tr>
<tr>
<td>(HC = CH)</td>
<td>0.9377</td>
<td>2.9904</td>
<td>-0.1749</td>
<td>0.003918</td>
<td>×2</td>
</tr>
<tr>
<td>(COO - O -)</td>
<td>2.7350</td>
<td>1.0751</td>
<td>0.0667</td>
<td>-0.009230</td>
<td>×1</td>
</tr>
<tr>
<td>(\sum)</td>
<td>10.5618</td>
<td>36.9781</td>
<td>-1.8899</td>
<td>0.052458</td>
<td></td>
</tr>
</tbody>
</table>

Table A.3 Estimation of \( \sum n_i c_i \) for Calculating Thermal Conductivity of Liquid Fuel at 298 K

<table>
<thead>
<tr>
<th>Group</th>
<th>Contribution</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-CH_3)</td>
<td>9.04</td>
<td>2</td>
</tr>
<tr>
<td>(&gt; CH_2)</td>
<td>6.47</td>
<td>12</td>
</tr>
<tr>
<td>(CH = CH)</td>
<td>5.53</td>
<td>4</td>
</tr>
<tr>
<td>(COO - (esters))</td>
<td>13.41</td>
<td>1</td>
</tr>
<tr>
<td>(\sum n_i c_i)</td>
<td>131.25</td>
<td></td>
</tr>
</tbody>
</table>

Table A.4 Estimation of \( \sum n_i \Delta H \) for Calculating the Enthalpy of Formation of Liquid Fuel at 298 K

<table>
<thead>
<tr>
<th>Group</th>
<th>( \Delta_h )</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-CH_3)</td>
<td>-76.45</td>
<td>×2</td>
</tr>
<tr>
<td>(&gt; CH_2)</td>
<td>-20.64</td>
<td>×12</td>
</tr>
<tr>
<td>(CH = CH)</td>
<td>37.97</td>
<td>×4</td>
</tr>
<tr>
<td>(COO)</td>
<td>-337.92</td>
<td>×1</td>
</tr>
<tr>
<td>(\sum)</td>
<td>-586.62</td>
<td></td>
</tr>
<tr>
<td>Constants</td>
<td>0.3 ≤ φ ≤ 1.0</td>
<td>1.0 &lt; φ ≤ 1.6</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td>0.92 ≤ θ &lt; 2</td>
<td>2 ≤ θ ≤ 3.2</td>
</tr>
<tr>
<td>A</td>
<td>2361.7644</td>
<td>2315.7520</td>
</tr>
<tr>
<td>α</td>
<td>0.1157</td>
<td>-0.0493</td>
</tr>
<tr>
<td>β</td>
<td>-0.9489</td>
<td>-1.1141</td>
</tr>
<tr>
<td>λ</td>
<td>-1.0976</td>
<td>-1.1807</td>
</tr>
<tr>
<td>a_1</td>
<td>0.0143</td>
<td>0.0106</td>
</tr>
<tr>
<td>b_1</td>
<td>-0.0553</td>
<td>-0.0450</td>
</tr>
<tr>
<td>c_1</td>
<td>0.0526</td>
<td>0.0482</td>
</tr>
<tr>
<td>a_2</td>
<td>0.3955</td>
<td>0.5688</td>
</tr>
<tr>
<td>b_2</td>
<td>-0.4417</td>
<td>-0.5500</td>
</tr>
<tr>
<td>c_2</td>
<td>0.1410</td>
<td>0.1319</td>
</tr>
<tr>
<td>a_3</td>
<td>0.0052</td>
<td>0.0108</td>
</tr>
<tr>
<td>b_3</td>
<td>-0.1289</td>
<td>-0.1291</td>
</tr>
<tr>
<td>c_3</td>
<td>0.0827</td>
<td>0.0848</td>
</tr>
</tbody>
</table>
We start from the equation representing combustion reaction between fuel:

\[ C_n^m H_m O_l^k N_k \] and air at equivalence ratio \( \phi \) and products subject to temperature \( T \) and pressure \( P \) attain equilibrium. The number \( n \) and \( m \) should be non-zero while \( l \) and \( k \) may or may not be zero. \( n,m,l \) and \( k \) are the atoms of carbon, hydrogen, oxygen and nitrogen respectively in the fuel. Here \( x_1 \) through \( x_{12} \) are mole fractions of the product species and \( x_{13} \) represents the moles of fuel that will give one mole of products.

\[
x_{13} \left[ C_n^m H_m O_l^k N_k + \frac{n+m/4-l/2}{\phi} \{O_2 + 3.7274N_2 + 0.0444Ar\} \right] \\
\rightarrow x_1H + x_2O + x_3N + x_4H_2 + x_5OH + x_6CO + x_7NO + x_8O_2 + x_9H_2O + x_{10}CO_2 + x_{11}N_2 \\
+x_{12}Ar
\]

The left side of the equation may be written as:

\[
x_{13} [nC + mH + rO_2 + r'N_2 + r''Ar], \text{ where} \\
r = \frac{l}{2} + r_o \\
r' = k/2 + 3.7274r_o \\
r'' = 0.0444r_o \\
r_o = \frac{(n + m/4 - l/2)}{\phi}
\]

Atomic balance for different elements provides the following equations:

\[
C \text{ balance: } x_6 + x_{10} = n \ x_{13} \quad (B.2) \\
H \text{ balance: } x_1 + 2x_4 + x_2 + 2x_9 = m \ x_{13} \quad (B.3) \\
O \text{ balance: } x_2 + x_5 + x_6 + x_7 + 2x_8 + x_9 + 2x_{10} = 2r \ x_{13} \quad (B.4) \\
N \text{ balance: } x_3 + x_7 + 2x_{11} = 2r' \ x_{13} \quad (B.5) \\
Ar \text{ balance: } x_{12} = r''x_{13} \quad (B.6)
\]

The condition that sum of all products mole fraction equals unity requires:

\[
\sum_{i=1}^{12} x_i = 1 \quad (B.7)
\]
We need seven equations more which are provided by the criteria of equilibrium among combustion products to solve for the 13 unknowns and are expressed by the following reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Partial Pressure</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1/2H_2 \Leftrightarrow H$</td>
<td>$P^{1/2}/x_4^{1/2}$</td>
<td>$K_1 = x_1 P^{1/2}/x_4^{1/2}$ (B.8)</td>
</tr>
<tr>
<td>$1/2O_2 \Leftrightarrow O$</td>
<td>$P^{1/2}/x_8^{1/2}$</td>
<td>$K_2 = x_2 P^{1/2}/x_8^{1/2}$ (B.9)</td>
</tr>
<tr>
<td>$1/2N_2 \Leftrightarrow N$</td>
<td>$P^{1/2}/x_{11}^{1/2}$</td>
<td>$K_3 = x_3 P^{1/2}/x_{11}^{1/2}$ (B.10)</td>
</tr>
<tr>
<td>$1/2H_2 + 1/2O_2 \Leftrightarrow OH$</td>
<td>$P^{1/2}/x_4^{1/2}x_8^{1/2}$</td>
<td>$K_5 = x_5 / x_4^{1/2}x_8^{1/2}$ (B.11)</td>
</tr>
<tr>
<td>$1/2O_2 + 1/2N_2 \Leftrightarrow NO$</td>
<td>$P^{1/2}/x_4^{1/2}x_{11}^{1/2}$</td>
<td>$K_7 = x_7 / x_4^{1/2}x_{11}^{1/2}$ (B.12)</td>
</tr>
<tr>
<td>$H_2 + 1/2O_2 \Leftrightarrow H_2O$</td>
<td>$P^{1/2}/x_4^{1/2}x_8^{1/2}$</td>
<td>$K_9 = x_9 / x_4^{1/2}x_8^{1/2}P^{1/2}$ (B.13)</td>
</tr>
<tr>
<td>$CO + 1/2O_2 \Leftrightarrow CO_2$</td>
<td>$P^{1/2}/x_6^{1/2}x_8^{1/2}$</td>
<td>$K_{10} = x_{10} / x_6^{1/2}x_8^{1/2}P^{1/2}$ (B.14)</td>
</tr>
</tbody>
</table>

Here, $P$ is the pressure in atmospheres. The equilibrium constants were then curve fitted from the data in JANAF Tables [161]. The following expression was used:

$$\log K_p = A \ln T + B/T + C + DT + ET^2$$  \hspace{1cm} (B.15)

Where $T$ is the absolute temperature and $A,B,C,D$ and $E$ are constants. The values of constants for the set of reactions (eqns B.8 to B.14) are provided in a tabular form (Table B.1) [141]. The expressions for equilibrium constants can be rearranged to express mole fractions of all products of combustion in terms of $x_4, x_6, x_8$, and $x_{11}$ the mole fractions of $H_2$, $CO$, $O_2$ and $N_2$ respectively.

\[
x_i = C_1 x_4^{1/2}
\]

where, $C_1 = K_1 / P^{1/2}$  \hspace{1cm} (B.16)

\[
x_2 = C_2 x_8^{1/2}
\]

$C_2 = K_2 / P^{1/2}$  \hspace{1cm} (B.17)

\[
x_3 = C_3 x_{11}^{1/2}
\]

$C_3 = K_3 / P^{1/2}$  \hspace{1cm} (B.18)

\[
x_4 = C_5 x_4^{1/2}x_8^{1/2}
\]

$C_5 = K_5$  \hspace{1cm} (B.19)

\[
x_7 = C_7 x_8^{1/2}x_{11}^{1/2}
\]

$C_7 = K_7$  \hspace{1cm} (B.20)

\[
x_9 = C_9 x_4^{1/2}x_8^{1/2}
\]

$C_9 = K_9 P^{1/2}$  \hspace{1cm} (B.21)

\[
x_{10} = C_{10} x_6 x_8^{1/2}
\]

$C_{10} = K_{10} P^{1/2}$  \hspace{1cm} (B.22)
<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2} H_2 \rightleftharpoons H$</td>
<td>0.432168</td>
<td>-0.112464x10^2</td>
<td>0.267269x10^1</td>
<td>-0.745744x10^-1</td>
<td>0.242484x10^-2</td>
</tr>
<tr>
<td>$\frac{1}{2} O_2 \rightleftharpoons O$</td>
<td>0.310805</td>
<td>-0.129540x10^2</td>
<td>0.321779x10^1</td>
<td>-0.738336x10^-1</td>
<td>0.344645x10^-2</td>
</tr>
<tr>
<td>$\frac{1}{2} N_2 \rightleftharpoons N$</td>
<td>0.389716</td>
<td>-0.245828x10^2</td>
<td>0.314505x10^1</td>
<td>-0.963730x10^-1</td>
<td>0.585643x10^-2</td>
</tr>
<tr>
<td>$\frac{1}{2} O_2 + \frac{1}{2} H_2 \rightleftharpoons OH$</td>
<td>-0.141784</td>
<td>-0.213308x10^1</td>
<td>0.853461</td>
<td>0.355015x10^-1</td>
<td>-0.310227x10^-2</td>
</tr>
<tr>
<td>$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftharpoons NO$</td>
<td>0.150879x10^-1</td>
<td>-0.470959x10^1</td>
<td>0.646096</td>
<td>0.272805x10^-2</td>
<td>-0.154444x10^-2</td>
</tr>
<tr>
<td>$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$</td>
<td>-0.752364</td>
<td>0.124210x10^2</td>
<td>-0.260286x10^1</td>
<td>0.259556</td>
<td>-0.162687x10^-1</td>
</tr>
<tr>
<td>CO + $\frac{1}{2} O_2 \rightleftharpoons CO_2$</td>
<td>-0.415302x10^-2</td>
<td>0.148627x10^3</td>
<td>-0.475746x10^1</td>
<td>0.124699</td>
<td>-0.900227x10^-2</td>
</tr>
</tbody>
</table>