Appendix B – Heat of decomposition of coal (dry basis)

The decomposition of coal occurs according to Eq.(115). The coefficients a, b, c, d and z can be calculated from the ultimate analysis of the coal in a dry basis and its moisture content (Eq.(116) to (120)).

$$\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z} \rightarrow \mathrm{C + aH_2 + bO_2 + cN_2 + dS_2 + zZ} \tag{115}$$

$$\mathrm{a} = \frac{\left(\Omega_{\mathrm{H}}^{d}(1-\Omega_{\mathrm{M}}) + \Omega_{\mathrm{M}}\frac{\mathrm{M_{H_2}}}{\mathrm{M_{H_2O}}}\right)/\mathrm{M_{H_2}}}{\Omega_{\mathrm{C}}^{d}(1-\Omega_{\mathrm{M}})/\mathrm{M_C}} \tag{116}$$

$$\mathrm{b} = \frac{\left(\Omega_{\mathrm{O}}^{d}(1-\Omega_{\mathrm{M}}) + \Omega_{\mathrm{M}}\frac{\mathrm{M_{O}}}{\mathrm{M_{H_2O}}}\right)/\mathrm{M_{O_2}}}{\Omega_{\mathrm{C}}^{d}(1-\Omega_{\mathrm{M}})/\mathrm{M_C}} \tag{117}$$

$$\mathrm{c} = \frac{\Omega_{\mathrm{N}}^{d}/\mathrm{M_{N_2}}}{\Omega_{\mathrm{C}}^{d}/\mathrm{M_C}} \tag{118}$$

$$\mathrm{d} = \frac{\Omega_{\mathrm{S}}^{d}/\mathrm{M_{S_2}}}{\Omega_{\mathrm{C}}^{d}/\mathrm{M_C}} \tag{119}$$

$$\mathrm{z} = \frac{\Omega_{\mathrm{Z}}^{d}/\mathrm{M_{Z}}}{\Omega_{\mathrm{C}}^{d}/\mathrm{M_C}} \tag{120}$$

To calculate the endothermal heat of this decomposition by Eq.(121), $q_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z},d}$, it is required to know the enthalpy of the products and reactants. The enthalpy of the products (kcal/mol), as function of temperature in °C, is given by Eq.(122) to (126). It is not necessary to calculate the term $\mathrm{z}h_Z$ because it will appear again in $h_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}}$ and therefore vanishes (ashes are inert).

$$q_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z},d} = h_{\mathrm{C}} + \mathrm{a}h_{\mathrm{H_2}} + \mathrm{b}h_{\mathrm{O}} + \mathrm{c}h_{\mathrm{N_2}} + \mathrm{d}h_{\mathrm{S_2}} + \mathrm{z}h_Z - h_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \tag{121}$$

$$h_{\mathrm{C}} = -0.105 + 2.58 \cdot 10^{-3}\,T + 2.37 \cdot 10^{-6}\,T^2 - 5.8 \cdot 10^{-10}\,T^3 \tag{122}$$

$$h_{\mathrm{H_2}} = -0.142 + 6.7 \cdot 10^{-3}\,T + 3.97 \cdot 10^{-7}\,T^2 \tag{123}$$

$$h_{\mathrm{O_2}} = -0.527 + 8.38 \cdot 10^{-3}\,T \tag{124}$$

$$h_{\mathrm{N_2}} = -0.198 + 6.95 \cdot 10^{-3}\,T + 5.43 \cdot 10^{-7}\,T^2 \tag{125}$$

$$h_{\mathrm{S_2}} = 30.35 + 8.79 \cdot 10^{-3}\,T \tag{126}$$

The enthalpy of coal is computed from its enthalpy of formation and heat capacity by Eq.(127).

$$h_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} = \Delta_{\mathrm{f}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} + \int_{T_{ref}}^{T} c_{p,\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}}\,dT \tag{127}$$

The calculation of both the enthalpy of formation and heat capacity should be performed experimentally. Here we provide empirical equations from literature for its calculation.

The heat of formation of coal is normally calculated from its heat of combustion and the heats of formation of the combustion products (Eq.(128)). Substituting the values for the heats of formation (water as liquid, $T_{ref} = 25$ °C), Eq.(128) results in Eq.(129) (in kcal/mol).

$$\Delta_{\mathrm{f}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} = \Delta_{\mathrm{c}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} + \Delta_{\mathrm{f}}h^{T_{ref}}_{CO_2} + \mathrm{a}\Delta_{\mathrm{f}}h^{T_{ref}}_{H_2O} + 2\mathrm{c}\Delta_{\mathrm{f}}h^{T_{ref}}_{NO_2} + 2\mathrm{d}\Delta_{\mathrm{f}}h^{T_{ref}}_{SO_2} + \mathrm{z}\Delta_{\mathrm{f}}h^{T_{ref}}_{Z} \tag{128}$$

$$\Delta_{\mathrm{f}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} = \Delta_{\mathrm{c}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} - 94.05 - 68.31\mathrm{a} + 15.87\mathrm{c} - 141.89\mathrm{d} + \mathrm{z}\Delta_{\mathrm{f}}h^{T_{ref}}_{Z} \tag{129}$$

The heat of combustion can be measured experimentally or calculated from empirical correlations. Here we provide the revised IGT correlation for the heat of combustion of coal, as a function of the ultimate analysis, in a dry basis (Eq.(130)) [36], in kcal/g. In the case of biomass fuel, the Eq.(131) is preferred [37] (the rest of the methodology would be the same).

$$\Delta_{\mathrm{c}}h^{d,T_{ref}}_{\mathrm{coal}} = 8.1488\Omega_{\mathrm{C}}^{d} + 31.62\Omega_{\mathrm{H}}^{d} - 2.8647(\Omega_{\mathrm{O}}^{d} + \Omega_{\mathrm{N}}^{d}) + 1.6344\Omega_{\mathrm{S}}^{d} - 0.3658\Omega_{\mathrm{A}}^{d} \tag{130}$$

$$\Delta_{\mathrm{c}}h^{d,T_{ref}}_{\mathrm{biomass}} = 8.34\Omega_{\mathrm{C}}^{d} + 28.15\Omega_{\mathrm{H}}^{d} - 2.470\Omega_{\mathrm{O}}^{d} - 0.3607\Omega_{\mathrm{N}}^{d} + 2.401\Omega_{\mathrm{S}}^{d} - 0.504\Omega_{\mathrm{A}}^{d} \tag{131}$$

In order to convert this value to wet basis and $\mathrm{kcal/mol_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}}$ (Eq.(132)), it is necessary to know the molar weight of $\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}$, and therefore the composition of the ashes.

$$\Delta_{\mathrm{c}}h^{T_{ref}}_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} = \Delta_{\mathrm{c}}h^{d,T_{ref}}_{\mathrm{coal}}(1-\Omega_{\mathrm{M}})\mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \tag{132}$$

Ashes are usually a mixture of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, MnO and P_2O_5 (Eq.(133)). The values of z_i can be calculated as in Eq.(120), from the weight fraction in a dry basis (Eq.(134)). The molar weight is thus calculated by Eq.(135).

$$\mathrm{Z_z \equiv (SiO_2)_{z_1}(Al_2O_3)_{z_2}(Fe_2O_3)_{z_3}(CaO)_{z_4}(MgO)_{z_5}(MnO)_{z_6}(P_2O_5)_{z_7}} \tag{133}$$

$$\mathrm{z_i} = \frac{\Omega^d_{\mathrm{Zi}}/\mathrm{M_{Zi}}}{\Omega^d_{\mathrm{C}}/\mathrm{M_C}} \tag{134}$$

$$\mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z} = M_C + aM_{H_2} + bM_{O_2} + cM_{N_2} + dM_{S_2}} + \sum_i \mathrm{z_i M_{Z_i}} \tag{135}$$

Regarding the heat capacity, it can be calculated as a weighted sum by mass fractions of the following components: moisture, fixed carbon, primary volatile, secondary volatile and ash. Assumed that the volatile matter in a dry, ash-free basis exceeding 10% should be considered as the primary, and up to 10% as the secondary volatile matter (Eq.(136), in kcal/g-K). If the volatile matter content in a dry, ash-free basis is less than 10%, there are only secondary volatiles [38], and therefore Eq.(137) should be used instead. To change units to kcal/mol-K, Eq.(138) is used.

$$c_{p,\mathrm{coal}} = \left[\Omega_{\mathrm{M}} c_{p_{\mathrm{M}}} + (1-\Omega_{\mathrm{M}})\left(\Omega^d_{\mathrm{FC}} c_{p_{\mathrm{FC}}} + \left(\Omega^d_{\mathrm{VM}} - 0.1(1-\Omega^d_{\mathrm{Z}})\right) c_{p_{\mathrm{PV}}} + 0.1(1-\Omega^d_{\mathrm{Z}}) c_{p_{\mathrm{SV}}} + \Omega^d_{\mathrm{Z}} c_{p_{\mathrm{Z}}}\right)\right] \tag{136}$$

$$c_{p,\mathrm{coal}} = \left[\Omega_{\mathrm{M}} c_{p_{\mathrm{M}}} + (1-\Omega_{\mathrm{M}})\left(\Omega^d_{\mathrm{FC}} c_{p_{\mathrm{FC}}} + \Omega^d_{\mathrm{VM}} c_{p_{\mathrm{SV}}} + \Omega^d_{\mathrm{Z}} c_{p_{\mathrm{Z}}}\right)\right] \tag{137}$$

$$c_{p,\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} = c_{p,coal} \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \tag{138}$$

The second term of the right side of Eq.(127) can be written as Eq.(139) showing the separate contribution of each component.

$$\begin{aligned} &\int_{T_{ref}}^{T} c_{p,\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}}\, dT \\ &= \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \Omega_{\mathrm{M}} \int c_{p_{\mathrm{M}}} dT + \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \Omega^d_{\mathrm{FC}} (1-\Omega_{\mathrm{M}}) \int c_{p_{\mathrm{FC}}} dT \\ &+ \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} (\Omega^d_{\mathrm{VM}} + 0.1\Omega^d_{\mathrm{Z}} - 0.1)(1-\Omega_{\mathrm{M}}) \int c_{p_{\mathrm{PV}}} dT \\ &+ \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} (0.1 - 0.1\Omega^d_{\mathrm{Z}})(1-\Omega_{\mathrm{M}}) \int c_{p_{\mathrm{SV}}} dT + \mathrm{M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}} \Omega^d_{\mathrm{Z}} (1-\Omega_{\mathrm{M}}) \int c_{p_{\mathrm{Z}}} dT \end{aligned} \tag{139}$$

The last addend of this equation, together with the last one of Eq.(129), are equal to the term $\mathrm{z}h_Z$ appearing in Eq.(121), and therefore these terms vanishes when computing $q_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z},d}$.
The integrals of the heat capacities are given by Eq.(140) to Eq.(144) in kcal/g, and T given in °C [38]. In the case of ashes, a more accurate value could be computed as weighted sum of the contributions of the components of the ashes, because the composition of the ashes is known (it was used to calculate the molar weight of the coal). Nevertheless, the error of Eq.(144) is minor for ashes with high weight fractions of SiO_2 and Al_2O_3, as it is usually the case. Moreover, it is not necessary to compute it because it vanishes.

$$\int_{25°C}^{T} c_{p_{\mathrm{M}}} dT = -0.025 + 10^{-3} \cdot T \tag{140}$$

$$\int_{25°C}^{T} c_{p_{\mathrm{FC}}} dT = -4.3331 \cdot 10^{-3} + 1.6491 \cdot 10^{-4} \cdot T + 3.4009 \cdot 10^{-7} \cdot T^2 - 1.3999 \cdot 10^{-10} \cdot T^3 \tag{141}$$

$$\int_{25°C}^{T} c_{p_{\mathrm{PV}}} dT = -1.0130 \cdot 10^{-2} + 3.9508 \cdot 10^{-4} \cdot T + 4.0505 \cdot 10^{-7} \cdot T^2 \tag{142}$$

$$\int_{25°C}^{T} c_{p_{\mathrm{SV}}} dT = -1.7930 \cdot 10^{-2} + 7.0959 \cdot 10^{-4} \cdot T + 3.0508 \cdot 10^{-7} \cdot T^2 \tag{143}$$

$$\int_{25°C}^{T} c_{p_{\mathrm{Z}}} dT = -4.5469 \cdot 10^{-3} + 1.8013 \cdot 10^{-4} \cdot T + 6.9998 \cdot 10^{-8} \cdot T^2 \tag{144}$$

Through this methodology, the heat of decomposition of any coal can be calculated. As example, the calculation for the coal in **Table 7** is presented in **Table 8**. The temperature at which $q_{\mathrm{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z},d}$ is calculated corresponds to the temperature at which the coal is injected in the blast furnace. For this example, we assume 50 °C.

Table 7. Example of a coal analysis.

Proximate analysis			Ultimate analysis		
Moisture (Ω_M)	8.5	wt.% (wet basis)	C (Ω_C^d)	54.57	wt.% (dry basis)
Fixed carbon (Ω_{FC}^d)	25.83	wt.% (dry basis)	H (Ω_H^d)	3.21	wt.% (dry basis)
Volatile matter (Ω_{VM}^d)	53.00	wt.% (dry basis)	O (Ω_O^d)	15.59	wt.% (dry basis)
Ash (Ω_Z^d)	21.17	wt.% (dry basis)	N (Ω_N^d)	1.07	wt.% (dry basis)
			S (Ω_S^d)	4.39	wt.% (dry basis)
			Z (Ω_Z^d)	21.17	wt.% (dry basis)
Ash composition (wt.% dry basis)					
SiO_2 (Ω_{Z,SiO_2}^d)	Al_2O_3 ($\Omega_{Z,Al_2O_3}^d$)	Fe_2O_3 ($\Omega_{Z,Fe_2O_3}^d$)	CaO ($\Omega_{Z,CaO}^d$)	MgO ($\Omega_{Z,MgO}^d$)	MnO ($\Omega_{Z,MnO}^d$)
12.58	6.48	1.32	0.55	0.22	0.02

Table 8. Steps for the calculation of the heat of decomposition of coal at $T_{coal} = 50\ °C$.

Term	Equation	Value	Units
a	(116)	0.4632	$mol_{H2}/mol_{CH2aO2bN2cS2dZz}$
b	(117)	0.1640	$mol_{O2}/mol_{CH2aO2bN2cS2dZz}$
c	(118)	0.0084	$mol_{N2}/mol_{CH2aO2bN2cS2dZz}$
d	(119)	0.0151	$mol_{S2}/mol_{CH2aO2bN2cS2dZz}$
z_{SiO2}	(134)	0.0461	$mol_{SiO2}/mol_{CH2aO2bN2cS2dZz}$
z_{Al2O3}	(134)	0.0140	$mol_{Al2O3}/mol_{CH2aO2bN2cS2dZz}$
z_{Fe2O3}	(134)	0.0018	$mol_{Fe2O3}/mol_{CH2aO2bN2cS2dZz}$
z_{CaO}	(134)	0.0022	$mol_{CaO}/mol_{CH2aO2bN2cS2dZz}$
z_{MgO}	(134)	0.0012	$mol_{MgO}/mol_{CH2aO2bN2cS2dZz}$
z_{MnO}	(134)	0.0001	$mol_{MnO}/mol_{CH2aO2bN2cS2dZz}$
z_{P2O5}	(134)	0.0000	$mol_{P2O5}/mol_{CH2aO2bN2cS2dZz}$
$M_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z}$	(135)	24.05	$g_{CH2aO2bN2cS2dZz}/mol_{CH2aO2bN2cS2dZz}$
$\Delta_c h_{coal}^{d,T_{ref}}$	(130)	4.979	$kcal/g_{dry\ coal}$
$\Delta_c h_{CH_{2a}O_b N_{2c} S_{2d} Z_z}^{T_{ref}}$	(132)	109.6	$kcal/mol_{CH2aO2bN2cS2dZz}$
$\Delta_f h_{CH_{2a}O_b N_{2c} S_{2d} Z_z}^{T_{ref}} - z\Delta_f h_Z^{T_{ref}}$	(129)	-18.12	$kcal/mol_{CH2aO2bN2cS2dZz}$
$\int_{25°C}^{T} c_{p_M} dT$	(140)	0.0250	$kcal/kg_M$
$\int_{25°C}^{T} c_{p_{FC}} dT$	(141)	0.0086	$kcal/kg_{FC}$
$\int_{25°C}^{T} c_{p_{PV}} dT$	(142)	0.0106	$kcal/kg_{PV}$
$\int_{25°C}^{T} c_{p_{SV}} dT$	(143)	0.0252	$kcal/kg_{SV}$
$\int_{T_{ref}}^{T} c_{p,CH_{2a}O_b N_{2c} S_{2d} Z_z}\, dT - M_{CH_{2a}O_b N_{2c} S_{2d} Z_z} \Omega_Z^d (1-\Omega_M) \int c_{p_Z} dT$	(139)	0.2543	$kcal/mol_{CH2aO2bN2cS2dZz}$
$h_{CH_{2a}O_b N_{2c} S_{2d} Z_z} - zh_z$	(127)	-17.86	$kcal/mol_{CH2aO2bN2cS2dZz}$
h_C	(122)	0.0298	$kcal/mol_C$
h_{H_2}	(123)	0.1940	$kcal/mol_{H2}$
h_{O_2}	(124)	-0.1081	$kcal/mol_{O2}$
h_{N_2}	(125)	0.1509	$kcal/mol_{N2}$
h_{S_2}	(126)	30.79	$kcal/mol_{S2}$
$q_{CH_{2a}O_{2b}N_{2c}S_{2d}Z_z,d}$	(121)	18.43	$kcal/mol_{CH2aO2bN2cS2dZz}$