Course Name: Theory of Fire Propagation (Fire Dynamics)

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Week – 03

Lecture – 03

Module 2 – Review of thermo-chemistry, chemical equilibrium & kinetics

Heat calculation for multicomponent fuel:

Consider LPG that typically contains 0.03% CH_4, 0.96% C_2H_6, 13.31% C_3H_8, 10.22% C_3H_6, 30.23% i-C_4H_{10}, 25.32% n-C_4H_{10}, 3.98% C_4H_8, 5.03% i-C_4H_8, 4.99% trans-2-C_4H_8, 3.64% cis-2-C_4H_8, 1.96% i-C_5H_{12} and 0.33% n-C_5H_{12}, by volume. Volume fractions translate to mole fractions. For example, mole fraction of propane, $X_{propane}$, in LPG is 0.1331.

Molecular weight of LPG is obtained by a chain mixing rule called Kay's rule, given as,

$$MW_{LPG} = \sum (X_i \times MW_i).$$

Here, X_i is the mole fraction of the i_{th} species and MW_i is its molecular mass. Molecular mass of LPG is obtained as 54.2 kg/kmol.

Standard enthalpy of formation of LPG is obtained using similar chain rule, given as,

$$\bar{h}^{0}_{f,LPG} = \sum \left(X_i \times \bar{h}^{o}_{f,i} \right) \ \ kJ/mol$$

It should be noted that if mass fractions of the constituents of LPG have been given, then, the values of enthalpies of formation of individual species used in the calculations should be specific to mass (kJ/kg). These are obtained by dividing the molar enthalpy of formation (kJ/kmol) of a component by its molecular mass (kg/kmol). Mixture enthalpy of formation (for LPG) may be converted back to molar form by using the molecular mass of the mixture, MW_{LPG}. Global single step reaction of LPG and air, as shown earlier, is written as,

$$C_{3.77}H_{8.98} + 6.015(O_2 + 3.76N_2) \rightarrow 3.77CO_2 + 4.49H_2O + 22.6N_2$$

Standard heat of reaction of LPG and air is calculated as,

$$\dot{Q} = 3.77\bar{h}_{f,CO_2}(298) + 4.49\bar{h}_{f,H_2O}(298) - \bar{h}_{f,\,LPG}(298)$$

Standard heat of reaction of LPG:

Substituting the values of heat of formation, the standard heat of reaction for LPG-air reaction is:

$$\dot{Q} = 3.77(-393.52) + 4.49(-241.83) - (-90.3) = -2479.1 \text{ kJ/mol} - \text{LPG}$$

Here, standard heat of formation of LPG calculated using mixing rule, based on the composition considered is -90.3 kJ/mol.

Lower heating value is: 2479.1×1000/54.2 = 45740 kJ/kg-LPG.

Heat of reaction per mol of O_2: -2479.1/6.015= -412.15 kJ/mol-O_2.

Heating value per kg of O_2: 412.15x1000/32= 12880 kJ/kg-O_2, or 12.88 MJ/kg-O_2.

Enthalpy of formation of solid fuel:

Percentages of volatiles and fixed carbon (flammable components) and elemental composition of C, H, O, N, and S can be determined. A consolidated fuel in terms of $C_xH_yO_zN_p$ can be formulated, and the values of x, y, z, and p can be evaluated using the data from proximate and ultimate analyses. For calculating the heat of reaction, enthalpy of formation of the consolidated fuel is required. For this, composition of volatiles in terms of species such as CH_4, C_2H_2, C_2H_4, CO, H_2, O_2 and N_2, are required. These can be determined by heating the solid fuel in an inert environment and determining the proportions of these gases using gas chromatography. If the heating value of the solid fuel is determined by calorimetry, then it can be used to calculate its enthalpy of formation.

Flame temperature:

Flame temperature is an important parameter that affects the fire propagation, ignition of neighboring commodities and their mass loss rates. Flame temperature is affected by the heat loss to surroundings. Maximum temperature in a given space is attained if the heat loss is zero. That is,

$$\dot{Q} = 0 = \sum_{1}^{N} \dot{n}_i \bar{h}_i(T_P) - \sum_{1}^{M} \dot{n}_i \bar{h}_i(T_R)$$

Therefore, the enthalpy of the reactant mixture, calculated at T_R, is equal to the enthalpy of the product mixture, calculated at T_P, when there is no heat transfer to the surroundings. T_P will be the maximum temperature attainable for the given conditions and is called the adiabatic flame temperature.

Adiabatic flame temperature:

Calculation of enthalpy of the reactant mixture is straightforward, as seen in the heat calculations. To calculate the maximum product temperature, the exact proportions of the species constituting the products should be known. If complete combustion is assumed, then for a stoichiometric reactant mixture, CO_2, H_2O and N_2, in some proportions, would contribute to the product mixture. Adiabatic flame temperature calculated by balancing the enthalpies of the reactant and product mixtures for this case (theoretical case without dissociation) is generally found to be much higher than the measured value. This is because dissociation of the major product species has not been considered in the above procedure.

Equilibrium flame temperature:

Only when the exact proportions of the species in the product mixture are taken in to account considering dissociation of species such as CO_2, H_2O and so on, a realistic value of adiabatic flame temperature can be obtained. In order to evaluate the exact product species, the concept of chemical equilibrium is used. The flame temperature calculated using equilibrium approach is found to be closer to the measured values. Equilibrium codes such as NASA CEA can be used to obtain equilibrium flame temperature.

Example calculation – no dissociation:

Consider char (solid carbon) initially at 298 K burns in the air in a furnace. Airflow is measured to be 150% theoretical air. Since this is a case with excess air, the resultant temperature is expected to be low and the chance of dissociation is also small. Therefore, neglecting the dissociation of CO_2 formed, the adiabatic flame temperature is calculated as illustrated below. Combustion reaction is written in the form:

$$C(s) + 1.5(O_2 + 3.76N_2) \rightarrow CO_2 + 0.5O_2 + 5.64N_2$$

Enthalpy of reactant is zero (naturally occurring elements at 298 K). Enthalpy of product is calculated using the expression:

$$H_P = \left[\bar{h}_{f,CO_2}(298) + \Delta\bar{h}_{CO_2}\left(T_p\right)\right] + 0.5\Delta\bar{h}_{O_2}(T_P) + 5.64\Delta\bar{h}_{N_2}(T_P)$$