Jansen et al. (2024) Pyrolysis and gasification of …

Appendix A

Justification for the use of Equation 4

The transient local temperature in a solid may be computed by solution of Fourier II, i.e.,

$$C_P \rho \frac{\partial T}{\partial t} = \kappa \nabla^2 T - \sum S_i \tag{A.1}$$

The S values are heat sources or sinks. For pyrolysis, when we use a single endothermic enthalpy sink and in 1D, A.1 becomes

$$\frac{dT}{dt} = \frac{\kappa}{C_P \rho} \frac{d^2T}{dx^2} - \frac{\Delta H^{\circ}_{rxn} d\alpha}{C_P \, dt} = \alpha_T \frac{d^2T}{dx^2} - \frac{\Delta H^{\circ}_{rxn}}{C_P} f(\alpha) k(T) \tag{A.2}$$

Using the fact that if, for any given control volume the reaction is complete, then $f(\alpha) = 1$, along with the rough approximations

$$\frac{d^2T}{dx^2} \approx \frac{2\delta T}{(\delta t)^2} \text{ and } \frac{dT}{dt} \approx \frac{\delta T}{\delta t} \tag{A.3}$$

one may make the substitution

$$\frac{\delta T}{\delta t} \approx \alpha_T \frac{2\delta T}{(\delta x)^2} - \delta T k(T) \tag{A.4}$$

Cancelling the δTs, and using $\tau = \delta t$ as the characteristic time for the full reaction, and $L_c = \delta x$ as the characteristic length – typically the radius for a spherical object – one has

$$\frac{1}{\tau} \approx \frac{2\alpha_T}{L_c^2} - k(T) \tag{A.5}$$

Multiplying through by the denominators and rearranging, one arrives at

$$\tau \approx \frac{L_c^2}{2\alpha_T} + \frac{L_c^2}{2\alpha_T} \tau k(T) \tag{A.6}$$

Using the approximation

$$L_c^2 \approx 2\alpha_T \tau \tag{A.7}$$

for the second term on the RHS, one arrives at the quadratic

$$\tau \approx \frac{L_c^2}{2\alpha_T} + \tau^2 k(T) \quad \underset{\text{or}}{} \quad \tau^2 k(T) - \tau + \frac{L_c^2}{2\alpha_T} \approx 0 \tag{A.8}$$

Completing the square

$$\tau \approx \frac{1 \pm \sqrt{1 - 4k(T)\dfrac{L_c^2}{2\alpha_T}}}{2k(T)} \tag{A.9}$$

For very small object sizes, L_c approximates zero, the second term in the discriminant becomes zero and, taking only the positive value for the square root as physical, the characteristic time for the reaction approximates

$$\tau_0 \approx \frac{2}{2k(T)} = \frac{1}{k(T)} \tag{A.10}$$

I.e., the reaction time is independent of heat-transfer effects, and is simply the inverse of the inherent reaction constant. The subscript zero indicates negligible sample size. Substituting A.10 back into A.8, and using the subscript *pyrolysis* for the full process, one obtains

$$\tau_{pyrolysis} = \frac{L_c^2}{2\alpha_T} + \tau_0^2 k(T) = \frac{L_c^2}{2\alpha_T} + \tau_0 \frac{k(T)}{k(T)} = \tau_0 + \frac{L_c^2}{2\alpha_T} \tag{A.11}$$

or more simply

$$\tau_{pyrolysis} = \tau_0 + \tau_{HT} \tag{A.12}$$

splitting the pyrolysis time into the sum an intrinsic kinetic and a heat-transfer component.