PARTICLE SIZE LIMITATIONS DUE TO HEAT TRANSFER IN DETERMINING PYROLYSIS KINETICS OF BIOMASS

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A simplified heat transfer model is analyzed in order to estimate an upper bound for biomass particle size in conducting experimental pyrolysis kinetics. In determining intrinsic kinetic rates, it is desirable that the entire particle be at reactor temperature for the duration of the chemical reaction. By comparing characteristic times for reaction rates versus heat up rates, an approximate boundary for particle size can be constructed as a function of temperature; above this boundary, the reaction rate is strongly heat transfer dominated, and below the boundary the reaction rate is kinetically controlled. Using parameters for cellulor pyrolysis, it is estimated that a 100 μ particle will be heat transfer limited due to internal heat transfer at temperatures above 500°C.

In order to experimentally determine kinetic parameters for pyrolysis decomposition of biomass materials, it is typically assumed that the reactions are first order with respect to mass and that the solid material is at uniform temperature. As the reaction temperature is increased, the kinetic rates eventually become faster than the associated heat transfer rates (internal and external). At higher temperatures, the decomposition rate becomes heat transfer limited, and any kinetic interpretation must include a transport model of the process. Since the temperature region over which the transition from kinetic control to heat transfer control takes place is a strong function of particle dimension, it is important for the kineticist to use relatively small particles if the temperature uniformity assumption is made. A simplified model will be presented for determining the particle size limit for the kinetic controlled regime.

In this development, several simplifying assumptions are made in order to achieve readily interpreted results. Within the region of interest, that is the transition from a kinetic rate controlled mechanism to that influenced by heat transfer limitations, the assumptions are reasonable and lead to meaningful results. The goal is to quantify the dimension referred to as "thermally thick" and to develop an understanding of how this characteristic dimension changes with temperature. The rationale is to define the region in which kinetic data may be safely interpreted without the necessity to model the heat and mass transfer process.

In the light of recent work by Chan and Krieger (1), it is clear that transport limitations play an important role in governing the overall rate of solid decomposition for large particles. Several detailed and well developed solutions are available (2, 3, 4, 5), however, an interpretation of what these considerations mean to the kineticist is needed.

Model Development and Solution

The simplest geometry to assume is that of the semi-infinite slab of defined thickness. There is also some practical justification as wood chips could be so described. The starting energy equation (simplified) is

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial X^2} + k_{rx} \lambda \rho \qquad 1)$$

k_{rx} = 1st order rate constant

λ = heat of reaction

ρ = particle density

The energy transport due to volatile evolution and diffusion is neglected, recognizing that the resulting solution will hold only for relatively slow (compared to heat transfer) kinetic rates. Since this is the region of interest, no loss of information results. In addition, recognizing that we are considering cases for relatively slow kinetic reactions or for initial rate studies, it is also assumed that we have constant densities and constant physical properties.

The reaction rate coefficient is "exponential" with temperature, however a linearized form expanded about the reactor temperature results in significant simplification and is justified since the rate drops so rapidly with temperature. It also turns out that the region of primary interest is within about 10°C of the reactor temperature, so that a linearized rate constant is a good approximation:

$$k_{rx} = k_o \left\{ 1 + \frac{E}{RT_o^2} (T-T_o) \right\} \qquad 2)$$

k_o = rate coefficient at T_c

If we define dimensionless coordinates

$$\tau = t/(\rho C_p B^2/k)$$

$$\xi = \frac{X}{B}$$

where 2B = particle thickness

and a dimensionless temperature

$$\phi = \frac{T-T_o}{T_1-T_o}$$

T_o = surface temperature

T_1 = initial temperature

the energy equation reduces to

$$\frac{\partial \phi}{\partial \tau} - \frac{\partial^2 \phi}{\partial \xi^2} - \alpha \gamma \phi = \alpha \qquad \text{where } \alpha = \frac{-\rho \lambda k_o B^2}{k(T_1-T_o)} \qquad 3)$$

$$\gamma = \frac{E(T_1-T_o)}{RT_o^2}$$

The initial condition is

$$\phi(0) = 1 \qquad \text{from } T(x,o) = T_1 \tag{4}$$

and the boundary conditions used are

$$\text{i)} \quad \frac{\partial\phi}{\partial\xi}(0,\tau) = 0 \qquad \text{symmetry about } x = 0 \tag{5}$$

$$\text{ii)} \quad \phi(1,\tau) = 0 \qquad \text{from } T = T_o \text{ at } x = B$$

The second boundary condition assumes that the surface temperature can be specified with high external heating fluxes available using fluid beds, radiation, or other devices. It is important to note that external heat transfer is also often limiting and that the estimate to be presented here for an upper bound particle dimension would need to be revised downward in such cases.

This "initial-boundary value" problem can be solved analytically following the development in Bird, et. al. (6) or Carslaw and Jaeger (7).

For endothermic reactions (λ = negative):

$$\phi = \phi_{ss} + \phi_t \tag{6}$$

ϕ_{ss} = steady state solution

ϕ_t = transient solution

$$\phi_{ss} = \frac{1}{\gamma}\left[\frac{\exp(\sqrt{\alpha\gamma}\xi) + \exp(-\sqrt{\alpha\gamma}\xi)}{\exp\sqrt{\alpha\gamma} + \exp - \sqrt{\alpha\gamma}} - 1\right] \tag{6a}$$

$$\phi_t = e^{-\alpha\gamma\tau} \sum_{o}^{\infty} C_n \, e^{-[(n+\frac{1}{2})\pi]^2\tau} \cos(n+\tfrac{1}{2})\pi\xi \tag{6b}$$

$$\text{with } C_n = \frac{2(-1)^m}{(n+\frac{1}{2})\pi}\left[1 + \frac{1}{\gamma} - \frac{1}{\gamma}\left(\frac{1}{1+\frac{\alpha\gamma}{(n+\frac{1}{2})^2\pi^2}}\right)\right]$$

Cellulose and wood pyrolysis are thought to be endothermic (3, 5), however for completeness the solution for exothermic reactions is also given:

$$\phi = \phi_{ss} + \phi_t \tag{7}$$

$$\phi_{ss} = \frac{1}{\gamma}\left[\frac{\cos\sqrt{\alpha\gamma}\,\xi}{\cos\sqrt{\alpha\gamma}} - 1\right] \qquad 7a)$$

$$\phi_t = e^{+\alpha\gamma\tau}\sum_{o}^{\infty} C_n\, e^{-[(n+\frac{1}{2})\pi]^2\tau}\cos[(n+\tfrac{1}{2})\pi\,\xi\,] \qquad 7b)$$

$$Cn = \frac{2(-1)^n}{(n+\frac{1}{2})\pi}\left[1 + \frac{1}{\gamma} - \frac{1}{\gamma}\left(\frac{1}{1 - \frac{\alpha\gamma}{(n+\frac{1}{2})^2\pi^2}}\right)\right]$$

The solutions presented are composed of a steady state and a transient solution. The steady state solution is correct mathematically but does not represent a true steady state solution for real situations, with time varying densities and physical properties. We can nevertheless develop useful information from this solution if we recognize its limitations. Figure 1 shows the analytical solution (Equation 6) for ϕ as a function of ξ and τ for typical values of α and γ.

Defining the Region Free of Heat Transfer Limitations

Solid decomposition reactions are difficult to conduct in a totally repeatable and precise manner. The main difficulties are associated with sample uniformity, sample location in the reactor, temperature, and composition.

It could be argued that, since rates are repeatable only to within, say, 10 to 20% accuracy, that the temperatures within the sample should also be within the same limit. This means that if the local rate is everywhere within this 10 to 20% limit, then we can define an allowable temperature profile associated with this position dependent reaction rate. In the present case, with the center of the particle being the coolest, we may determine the temperature at the center associated with 90% (or 80%) of that at the reactor temperature, T_o.

Using an Arrhenius expression for the rate constant, k, we have the temperature limit, T_ℓ, defined as follows:

$$T_\ell = \frac{T_o}{1 - \frac{R\,T_o}{E}\ln 0.9} \qquad 8)$$

This in turn defines a minimum centerline particle temperature and dimensionless temperatures

$$\phi_\ell = \frac{T_\ell - T_o}{T_1 - T_o} \qquad 9)$$

As a first attempt to fix an appropriate particle size, we can estimate, from Equation 6, the time required for the temperature at the centerline to reach T_ℓ, or ϕ_ℓ. This time can then be used to estimate an approximate extent of reaction to determine how much of the particle may have pyrolyzed in that time period. The actual extent of reaction would be lower since the particle is not uniformly at T_o; the estimate or particle size limits will therefore be conservative.

Specific Examples of Cellulose Kinetics

The results of examining cellulose decomposition as a specific case are shown in Figure 2. Example calculations for 450°C are shown as follows:

$$\frac{d\rho}{dt} = - k \rho \qquad 10)$$

where $k = 9.32(10^{11})\exp(-35960/RT)\ \text{min}^{-1}$ (ref. 8)

The time to reach 10% (ρ/ρ_o=0.9) decomposition at reactor temperature is then determined by integrating to get

$$t_{10} = \frac{\ln 0.9}{-k_o} = .0084 \text{ min} \qquad 11)$$

The dimensionless time, τ, associated with this 10% decomposition value is dependent on particle size

$$\tau_{10} = \frac{t_{10}}{(\rho C_p B^2/k)} \qquad 12)$$

Using literature values for cellulose properties

$\rho = 0.5\ g/cm^3$

$C_p = 0.32$ cal/g-°C

$k = 0.0003$ cal/(cm-sec-°K)

$\lambda = -100$ cal/g

the following mathematical procedure was conducted. For a given temperature and and particle size, the time required for the centerline temperature to reach that temperature (T_ℓ) associated with 90% of the ultimate rate was determined. This heat up time was then compared to the kinetic time for 10% decomposition. The particle size was then increased and the calculation repeated.

In all cases, the limitation imposed by the steady state (or maximum possible) centerline temperature was first reached. This result validates the basic assumptions used in the derivation. It is therefore apparent that just the steady state portion of the solution can be used to obtain an estimated limit for particle size. Specifically, at the centerline,

$$\phi_{ss} = \frac{1}{\gamma}\left[\frac{2}{\exp(\sqrt{\alpha\gamma})+\exp(-\sqrt{\alpha\gamma})} - 1\right] \qquad 13)$$

Only α depends on particle size, so for a given temperature limit, the particle size associated with that steady state limit is readily calculated. The results of these calculations are shown on Figure 2 for both 10% and 20% deviations from the ultimate rate.

If the heat of reaction is considered to be zero, then the transient solution must be used to determine the particle size limit in the manner as just described. This limit

is also shown on Figure 2 for 10% and 20% deviations from the ultimate rate.

Summary

Using various assumptions as described, it is seen that, for example, a particle dimension of 0.01 cm (thickness = 0.02 cm or 200 microns) might be investigated kinetically up to about 450-500°C without taking transport limitations due to internal particle profiles into account. If external heat transfer to the particle surface is also slow, then even lower temperature limits would occur. In many cases, Equation 13 can be used to estimate the maximum particle size for various values of the dimensionless parameters. It should also be noted that the characteristic dimension for a bed of fine particles would be bed depth rather than particle size.

References

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Figure 1. Temperature Profile vs. Time (Equation 6) with $\alpha = -0.5$, $\gamma = -15$

$$\tau = \frac{t}{(\rho C_p B^2/k)}$$

$$\alpha = \frac{\rho \lambda k_0 B^2}{k(T_1 - T_0)}$$

$$\gamma = \frac{E(T_1 - T_0)}{RT_0^2}$$

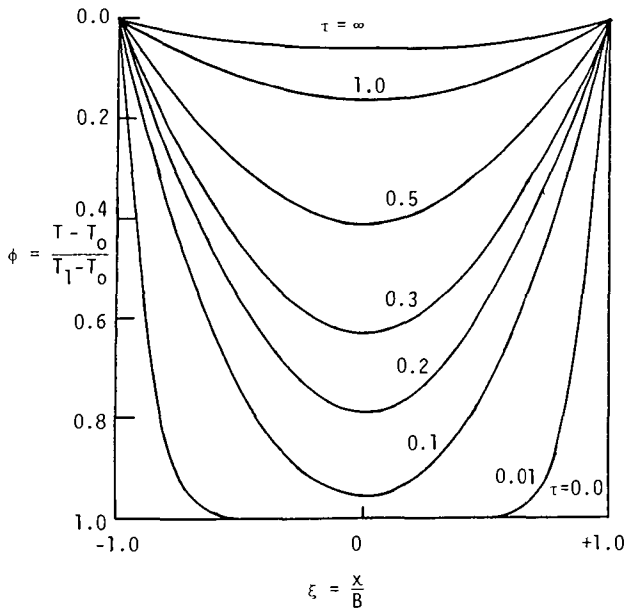
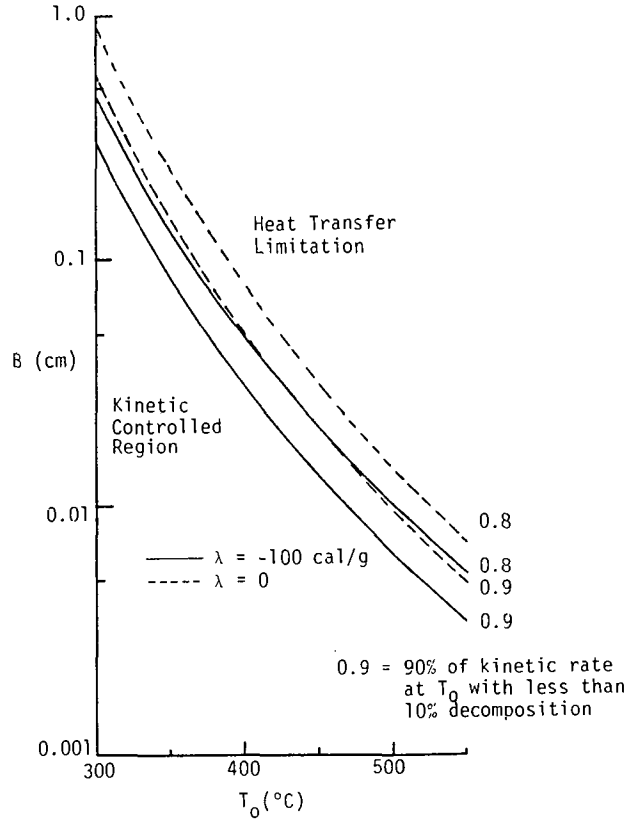
Figure 2. Particle Size Limit vs. Temperature for Kinetic Controlled Region (using parameters for cellulose)