Heat Transfer Model Development

To obtain the sample temperature transient during the experiments, it is essential to determine the heat transfer regimes from the furnace to the reactor and the reactor to the sample. For this, the Biot number (Bi) and Thermal Thiele Modulus (M) were used. The former is defined by:

$$Bi = \frac{h}{\lambda_R / L_{c_w}} \tag{S1}$$

where h is the convective heat coefficient, λ_R is the thermal conductivity of the reactor, and L_{c_w} is the wall thickness. Since the area of the vent opening is ~0.7% of the area of the reactor top surface, the effect of the vent was neglected. Table S1 summarizes the parameters used for the heat transfer modeling, indicating that the value of Bi is 0.0003, which is significantly smaller than 1, and means the reactor wall temperature is uniform. To calculate the temperature of the reactor wall, the heat rate equals to:

$$\frac{dQ(t)}{dt} = hA_W(T_F - T_w(t)) \tag{S2}$$

where A_W is the reactor surface area, T_F is the furnace set temperature, and $T_w(t)$ is the reactor wall temperature. In addition, the total heat required to increase the reactor temperature, $Q(t)$, is given by:

$$Q(t) = mc_{p_w}(T_w(t) - T_{o_w}) \tag{S3}$$

where m, c_{p_w}, $T_w(t)$ and T_{o_w} represents the mass, heat capacity of the reactor wall, reactor wall temperature, and initial temperature of the reactor wall, respectively. Introducing Equation (S2) into (S3) yields:

$$T^*(t) = 1 - \left(1 - \frac{T_{o_w}}{T_F}\right)e^{-\frac{t}{\tau_R}} \tag{S4}$$

where $T^*(t)$ is defined as $T^*(t) = \frac{T_S(t)}{T_F}$, with $T_S(t)$ representing the temperature of the surface of

the sample, and τ is the characteristic time of the reactor wall, defined as $\tau_R = \frac{mc_{p_W}}{hA_W}$.

For the heat transfer from the reactor walls to the sample, both convection and conduction take

place. As the sample is touching the reactor wall, it is essential to know the thermal contact

resistance R'', which is estimated to be 2.6×10^{-4} m^2-K/W in this case (Bergman et al., 2011). In

addition, the thermal resistance for convection from the reactor wall to the sample can be calculated

through the following:

$$R_{conv} = \frac{1}{hA} \tag{S5}$$

In Table S1 R_{conv} was calculated to be 9.69 K/W, which is significantly greater than the contact

resistance with this specific area (0.0003 K/W). The contact resistance was neglected in this case.

Table S1. Estimated values of the parameters used for the heat transfer modeling.

Parameter	Value	Source
h, W/m^2-K	10	(Bergman et al., 2011)
λ_R for reactor, W/m-K	45	(Peet et al., 2011)
λ_S for sample, W/m-K	0.4	(De Carvalho et al., 1996)
ρ (apparent), kg/m^3	508.5	Measured in this study
c_{p_W} for reactor wall (apparent), J/kg-K	490	(Bergman et al., 2011)
c_{p_S} for sample (apparent), J/kg-K	1400	(Bergman et al., 2011)
L_{c_R} for reactor, m	0.0013	Measured in this study
L_{c_S} for sample, m	0.003	Measured in this study
A_R for reactor, m^2	0.05	Measured in this study
A_S for sample, m^2	0.0103	Measured in this study
R_{conv} for thermal resistance for convection, K/W	9.69	Current result
R'' for thermal contact resistance, m^2-K/W	0.0003	(Bergman et al., 2011)
R' for reaction rate, kg/m^3-s	1.2	Measured in this study
Bi for furnace to reactor	0.0003	Current result

M for sample	0.05	Current result
τ_s for sample	484.2	Current result

Therefore, M, related to the reaction propagation within the sample, can be used to indicate whether the sample temperature is uniform during the reaction, given by:

$$M = \frac{R'}{\lambda_S / (c_{p_s} L_{c_S}^{2})} \tag{S6}$$

With R' is the degradation reaction rate, λ_S is the thermal conductivity of the sample, c_{p_s} is the heat capacity of the sample and L_{c_S} is the characteristic length of the sample.

The value of M for in this study was calculated using the highest degradation rate, representing the worst-case scenario, and the value was found to be 0.05 (see Table S1). This number is significantly smaller than 1, indicating that the reaction rate of the particles was much slower than the reaction propagation within the sample. As a result, the sample particle temperature equilibrates faster than the reaction rate, and thus the sample temperature was assumed to be uniform during the thermal degradation reaction.

To calculate the temperature of the sample, the sample heat rate is given by:

$$\frac{dQ(t)}{dt} = \frac{T_w(t) - T_s(t)}{R_{tot}} \tag{S7}$$

For the heat transfer from the reactor wall to the sample, the total thermal resistance can be calculated by the following:

$$R_{tot} = \frac{1}{hA} + \frac{L}{k_S A} \tag{S8}$$

combining Equations (S7) and (S8), yields:

$$\frac{dQ(t)}{dt} = \frac{T_w(t) - T_s(t)}{\frac{1}{hA} + \frac{L}{\lambda_S A}} \tag{S9}$$

where, $T_w(t)$ denotes the temperature of reactor wall, k_s denotes the thermal conductivity of the sample. And $Q(t)$ is the heat required to heat the sample to a certain temperature, or

$$Q(t) = mc_{p_s}\left(T(t) - T_{o_s}\right) + mh_r \tag{S10}$$

where m is the sample mass, c_{p_s} is heat capacity of the sample, $T(t) = T_s(t)$, T_{o_s} is the initial temperature of the sample and h_r is the enthalpy of reaction. Since MPW used in this study consists of various types of plastics, the enthalpy of reactions at a similar temperature range was estimated to be 0.0126-0.148 kJ/kg (Zhao et al., 2017). Since the value mh_r is significantly smaller than $mc_p(T(t) - T_o)$ (estimated to be 525 kJ/kg for the 400°C experiments), this term was neglected in this study. Combining Equations (S9) and (S10), yields:

$$T^*(t) = 1 - \left(1 - \frac{T_{oS}}{T_W}\right)e^{-\frac{t}{\tau_s}} \tag{S11}$$

where $T^*(t)$ is defined as $T^*(t) = \frac{T(t)}{T_W}$, and τ_s is the characteristic time of the sample, defined as $\tau_s = \frac{k_s m c_{p_S}}{hA(\lambda_S + hl)}$.

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