

# MASS LOSS MODEL FOR CHAR FORMING POLYMERS

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The basic mechanism of the pyrolysis of char forming polymers has been described as a generalized process consisting of primary and secondary thermal decomposition events. The primary decomposition step occurs through a free radical intermediate with generation of a primary gas and disproportionation to hydrogenated tar and hydrogen-deficient primary char residue. The primary char decomposes by dehydrogenation to form the secondary gas and a thermally stable char. This pyrolysis scheme accounts qualitatively for the low char yield of hydrogen-rich polymers. In the absence of hydrogen atoms, polyaromatic free radical nuclei can recombine to form crosslinks or stable, non-volatile species (char) which resist further decomposition.

A simple result for the mass loss history of a char forming polymer for use in fire models is obtained by recognizing that the important process with respect to material flammability is the fuel generation rate at or near the decomposition ( $\approx$  surface burning) temperature. With this in mind the following assumptions can be made: 1) thermolysis of primary chemical bonds in the polymer is the rate-limiting step for isothermal mass loss, 2) mass loss proceeds through an active intermediate which is a stationary state, 3) primary gas production and char formation are simultaneous processes whose magnitude and rate constants are large compared to successive products and rate processes (i.e., secondary char formation), and 4) conditions are anaerobic in the pyrolysis zone so that oxidation reactions may be neglected in the mass loss model. The above assumptions lead to a simplified kinetic scheme for polymer pyrolysis which reduces gas and char formation to a single step involving parallel decomposition reactions of the active intermediate as shown in Figure 1.

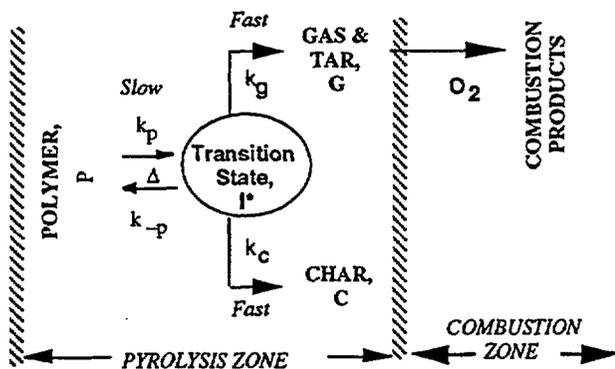


Figure 1. Kinetic mass loss model for polymer combustion

The rate equations for the instantaneous mass of polymer, P, reactive intermediate, I\*, primary gas, G, and primary char, C, according to Figure 1 are

$$\frac{dP}{dt} = -k_p P + k_{-p} I^* \quad (1)$$

$$\frac{dI^*}{dt} = k_p P - (k_{-p} + k_g + k_c) I^* \quad (2)$$

$$\frac{dG}{dt} = k_g I^* \quad (3)$$

$$\frac{dC}{dt} = k_c I^* \quad (4)$$

With  $I^* \ll P, G, C$ , the total mass balance in terms of the initial mass,  $m_0$ , is

$$m_0 = P + G + C + I^* \approx P + G + C \quad (5)$$

while the sensible mass of the sample (as measured for example in a TGA experiment) is

$$m = P + C + I^* \approx P + C \quad (6)$$

The solution for the mass loss history of a char forming polymer at constant temperature from Equations 1-6 and the four assumptions is

$$\frac{m}{m_0} = Y_c + (1 - Y_c) e^{-k_p t} \quad (7)$$

where  $k_p$  is the forward pyrolysis rate constant and  $Y_c = k_c / (k_c + k_g)$  is the equilibrium char yield at a particular temperature. Equation 7 also describes the mass loss history of filled polymer systems having an inert filler loading fraction  $Y_c$  which is not temperature dependent.

Equation 7 was used to fit thermogravimetric data for anaerobic, isothermal, mass loss histories of a crosslinked phenolic triazine thermoset resin at temperatures ranging from 350–450C using  $k_p$  and  $Y_c$  as adjustable parameters. Experimental data for the isothermal mass loss histories are shown as solid symbols in Figure 2 while the solid lines are the best fit of Equation 7 to the experimental data using  $k_p$  and  $Y_c$  values listed in Table 1.

Figure 3 is an Arrhenius plot of the pyrolysis rate constants,  $k_p$ , listed in Table 1 as  $\ln[k_p]$  versus  $1/T$ . The activation energy  $E_a$  for pyrolysis of phenolic triazine resin obtained

from the slope in Figure 3,  $E_a = 165$  kJ/mol, is approximately half of the value obtained for these same data from n-th order kinetics while the frequency factor,  $A = 10^9$  sec<sup>-1</sup>, determined from the intercept is essentially the square root of the value determined from non-charring first-order kinetics.

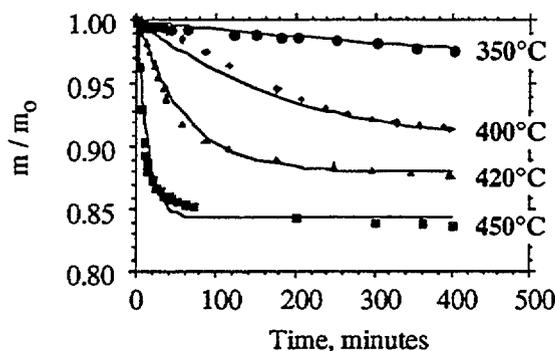


Figure 2. Mass loss history of phenolic triazine at 350, 400, 420, and 450°C. Solid lines are fit of Equation 7.

Table 1.  
Best Fit  $k_p$  and  $Y_c$  Values for Isothermal Pyrolysis of Phenolic Triazine Thermoset Resin

T (°C)	$k_p$ (sec <sup>-1</sup> )	$Y_c$
350	$1.4 \times 10^{-5}$	0.92
400	$8.5 \times 10^{-5}$	0.90
420	$2.7 \times 10^{-4}$	0.88
450	$1.2 \times 10^{-3}$	0.84

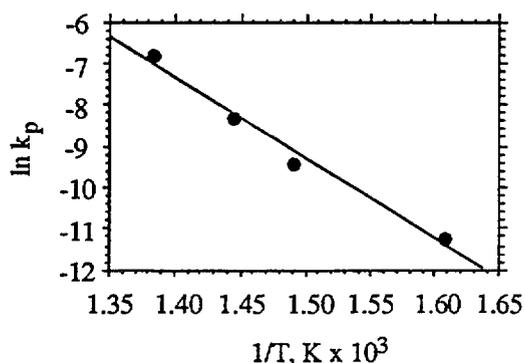


Figure 3. Plot of  $\ln[k_p]$  versus reciprocal temperature for phenolic triazine resin.

Assuming an Arrhenius form for the gasification and charring rate constants,  $k_g$  and  $k_c$ , Equation 7 can be rearranged to give

$$\ln\left[\frac{1-Y_c}{Y_c}\right] = \ln\left[\frac{A_g}{A_c}\right] - \left[\frac{E_g - E_c}{R}\right] \frac{1}{T} \quad (8)$$

so that a plot of  $\ln[(1-Y_c)/Y_c]$  versus  $1/T$  has a slope proportional to the difference in activation energies for gas and char formation. Figure 4 shows such a plot constructed from the isothermal char yields in Table 1. The slope gives  $(E_g - E_c) = +30$  kJ/mol and the intercept,  $A_g/A_c = 17$ . This result indicates char formation is favored over volatile production by 30 kJ/mol consistent with the high char yield of this material.

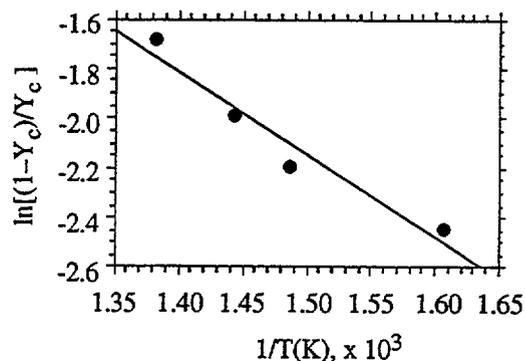


Figure 4. Plot of the natural logarithm of  $(1-Y_c)/Y_c$  versus reciprocal temperature for the phenolic triazine resin.

The rate constants for phenolic triazine resin pyrolysis, char and gas formation can be substituted into Equation 7 to allow calculation of the mass loss as function of temperature at different heating rates. Results of these calculations are shown in Figure 5 as solid lines. Symbols are data from thermogravimetric experiments at constant heating rates of  $\beta = 1, 5,$  and  $20$  K/min. It is seen that the predicted mass loss of the phenolic triazine resin calculated from Equation 7 is in excellent agreement with data up to the secondary mass loss event ( $T > 600^\circ\text{C}$ ) which was neglected in the present derivation. The dashed line is the calculated equilibrium char yield ( $\beta = 0$ ) as a function of temperature.

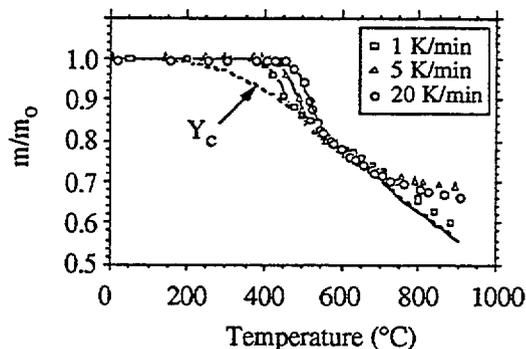


Figure 5. Measured and calculated mass loss of phenolic triazine resin in TGA at constant heating rates of  $\beta = 1, 5,$  and  $20$  K/min.