

KINETIC MODELS FOR THERMAL DEGRADATION OF STRENGTH OF FIRE-RETARDANT-TREATED WOOD

Jerrold E. Winandy

Research Wood Scientist

and

Patricia K. Lebow

Mathematical Statistician

USDA Forest Service¹

Forest Products Laboratory

One Gifford Pinchot Drive

Madison, WI 53705-2398

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ABSTRACT

Several types of kinetics-based thermal degradation models were evaluated to predict strength loss of fire-retardant-treated wood as a function of cumulative thermal exposure. The data were taken from previous tests and reports on small, clear specimens of southern pine treated with six different fire-retardant chemicals and subjected to various durations of a steady-state exposure at different temperatures and relative humidity levels. We found that the single-stage full model approach was superior to traditional two-stage approaches. When constrained to using a two-stage approach, the best alternative two-stage model was a nonlinear model with additive error for each temperature, followed by a weighted regression across temperatures. The advantages of the nonlinear-weighted two-stage model were the maximized fit and more random error structure when compared to other two-stage models.

Keywords: Fire retardant, treatment, plywood, lumber, thermal degrade, modeling, kinetics.

INTRODUCTION

The initial reduction in strength of fire-retardant-treated wood material apparently does not change over time, as indicated by more than 50 years of field experience for exposures at or near room temperature. However, field problems of additional reductions in strength capacity have developed in some situations where fire-retardant-treated material is exposed to elevated temperatures (APA 1989a; LeVan and Collet 1989; NAHB 1990). For example, for plywood sheathing in severely de-

graded roofs, service life has ranged from only 1 to 8 years (APA 1989a; NAHB 1990).

The effects of fire-retardant treatments and the mechanisms that cause thermal-related failure were reported previously (LeVan and Winandy 1990). Research has shown that the magnitude of wood degradation depends on the fire-retardant formulation (LeVan et al. 1990); exposure temperature and relative humidity (Winandy et al. 1991); construction details that dictate roof temperatures; and ventilation, which together with construction details, dictates wood moisture content in roof systems (Heyer 1963; Rose 1992). Previous studies specifically evaluated strength loss of matched solid-wood specimens exposed at 130°F (54°C) and 180°F (82°C) for up to 5 months (LeVan et al. 1990) or exposed at 150°F

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(66°C) for up to 18 months (Winandy 1995). These reports were not conclusive in determining whether the relationship between strength loss and temperature/duration of exposure is linear or nonlinear.

Several kinetics-based models for thermal degradation have been proposed (Millet and Gerhards 1972; Woo 1981; APA 1989b; Pasek and McIntyre 1990; Winandy et al. 1991). These previous models each assumed first-order kinetic theory and involved a two-step process based on logarithmic transformations of the data. The advantages and disadvantages of this classic approach are specifically listed in the section on Traditional Models.

The objective of this report was to use the combined data set from previous studies to compare previous models and to develop an optimal mechanistic reaction-rate model based on kinetic theory. That model can then be used to identify those fire-retardant chemicals that are most susceptible to accelerated thermal degradation and to provide guidance on in-service temperature levels at which that acceleration might occur. Future plans call for us to validate our model by evaluating 3- and 4-year exposures, then applying that model as a tool to project serviceability assessments.

EXPERIMENTAL METHODS

Experimental materials

Data used for the model were obtained from previous research (LeVan et al. 1990; Winandy 1995). In these studies, small, clear $\frac{5}{8}$ -in.- (16-mm-) tangential by $1\frac{3}{8}$ -in.- (35-mm-) radial by 12-in.- (305-mm-) long test specimens were cut from nominal 1-in.- (19-mm-) thick vertical-grain southern pine lumber. The specimens were sorted into 161 modulus of elasticity (MOE) and density matched groups of 30 specimens each and pressure treated with various fire retardants (Table 1) to approximately 3.5 lb/ft³ (56 kg/m³) retention. The specimens were kiln-dried after treatment at a mild maximum dry-bulb temperature of 120°F (49°C) to a final moisture content of 12%. They were then exposed at either 80°F (26°C)/30%

TABLE 1. *Fire-retardant chemicals.*

| Chemical | Abbreviation |
|---|--------------|
| Phosphoric acid | PA |
| Monoammonium phosphate | MAP |
| Borax-boric acid | BBA |
| Guanylurea phosphate/boric acid | GUP/B |
| Dicyandiamide-formaldehyde-phosphoric acid | DPF |
| Diethyl-N,N-bis(2-hydroxy-ethyl)aminomethyl phosphonate | OPE |
| Untreated | UNT |

relative humidity (RH), 130°F (54°C)/73% RH, and 180°F (82°C)/50% RH for up to 5 months (LeVan et al. 1990) or at 150°F (66°C)/75% RH for up to 18 months (Winandy 1995). After each environmental exposure and prior to mechanical testing, all specimens were conditioned at 74°F (23°C) and 65% RH to constant weight.

The equilibrated specimens were tested in flat-wise bending using a span of 9 in. (22.9 mm), center-point loading, and a loading rate of 0.19 in./min (4.8 mm/min). Mechanical testing was performed at intermittent times over a 4-year period. An analysis of the effect of these staggered test periods showed that the data could be combined (Winandy 1995).

The results of these studies conclusively showed that the phenomenon of fire-retardant-related thermal degrade was directly related to exposure temperature and duration of that exposure and to the dissociation potential of the fire-retardant formulation in question (Fig. 1). A more detailed description of the experimental design and test results was previously reported (LeVan et al. 1990; Winandy 1995).

MODELING

Traditional models

A two-stage Arrhenius-based approach has often been used in modeling fire-retardant reaction rates (e.g., the rate of strength loss over time) (Woo 1981; Pasek and McIntyre 1990; Winandy et al. 1991). Previous studies have not considered alternative model forms in the first stage of a two-stage approach. Although

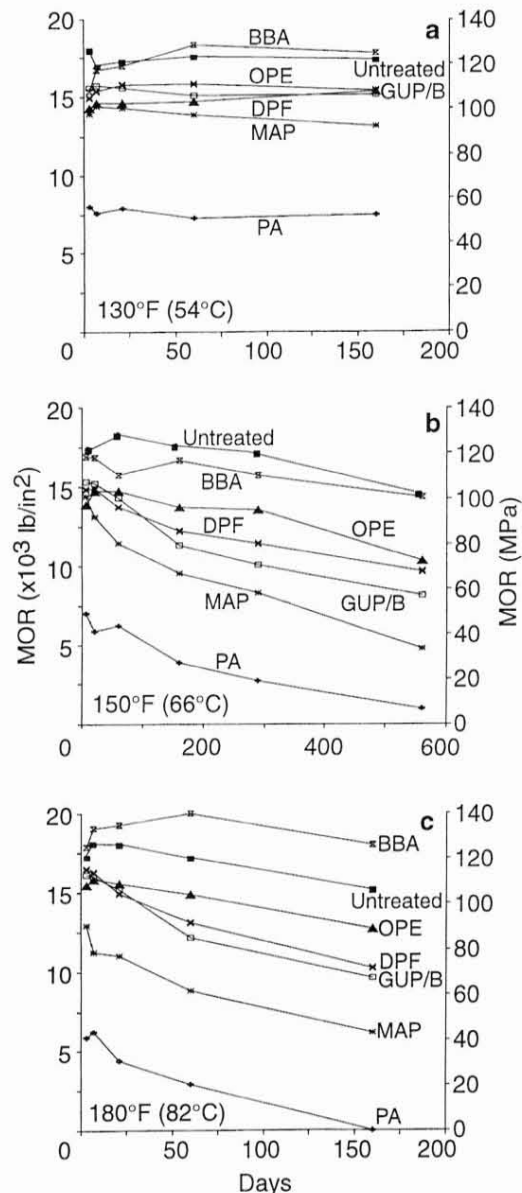


FIG. 1. Effect of extended exposure to elevated steady-state temperatures on bending strength for untreated and fire-retardant-treated wood. (a) 130°F (54°C); (b) 150°F (66°C); (c) 180°F (82°C). BBA is borax-boric acid; DPF, dicyandiamide-formaldehyde-phosphoric acid; GUP/B, guanidurea phosphate/boric acid; MAP, monoammonium phosphate; OPE, diethyl-N,N-bis (2-hydroxyethyl) aminomethyl phosphonate; and PA, phosphoric acid. MOR is modulus of rupture; 1 lb/in.² = 6.894 kPa. (Note differences in scale of x-axis.)

there has been support for both the linear and transformably linear models, we also considered the possibility of the nonlinear model because of its close relationship to other models and its theoretical appeal.

In the first-stage of a traditional two-stage approach, the dependent variable, or a suitable transformation, is defined as a function of time at several temperatures:

linear,

$$Y_{F,T} = b_{F,T} + (-k_{F,T}X) \quad (1)$$

transformed linear,

$$\ln Y_{F,T} = b_{F,T} + (-k_{F,T}X) \quad (2)$$

or nonlinear

$$Y_{F,T} = b_{F,T} \exp(-k_{F,T}X) \quad (3)$$

where

F = fire-retardant chemical

T = temperature of exposure

$Y_{F,T}$ = bending strength (lb/in.²) at T for F

X = time (days) at T for F

$b_{F,T}$, $k_{F,T}$ = model parameters

The same functional form is used at each temperature, and the model parameters are estimated using the appropriate temperature data set. It is often reasonable to assume that at different temperatures, the initial mean strength (in Eqs. (1) or (3)) or the initial mean log strength (in Eq. (2)) will be the same for a particular chemical F. This can be done by forcing the predicted estimates of $b_{F,T}$ (i.e., $\hat{b}_{F,T}$) to be equal at each temperature, which adds another stage to modeling. The belief is that this leads to more accurate rate estimates (Nelson 1990).

Based on kinetic theory, it can be expected that the rates of strength loss over time are dependent on temperature via the Arrhenius theory:

$$k'_F = A_F \exp(-E_{a,F}/RT) \quad (4)$$

where

- k'_F = expected rate constant (adjusted to a common RH)
 A_F = pre-exponential factor
 $E_{a,F}$ = activation energy
 R = gas constant (J/K \times mole)
 T = temperature (K)

Thus, in the second stage of the two-stage approach, the fitted model parameters for each temperature ($k_{F,T}$), which were derived in the first stage, are fit to Eq. (4). Thus, the Arrhenius equation (Eq. (4)) is used to determine each fire retardant's characteristic rate constant of strength loss over the range of temperatures studied. When Eq. (4) is constrained to include only positive strength loss estimates, it can be expressed in terms of natural logarithms as

$$k_F^* = \ln(k'_F) = \ln(A_F) + (-E_{a,F}/RT) \quad (5)$$

This two-stage approach is the classic model-building technique in the study of temperature-mediated (i.e., kinetic) problems for several reasons. Its advantages are that it can discriminate between competing models, it can avoid problems associated with dependent error structures, it is easy to use, and it can quickly provide initial rate estimates. Its disadvantages are that depending on the experimental design and the underlying mechanisms, a two-stage approach may not lead to the best rate estimates, and it can improperly account for (i.e., mask) a time-temperature interaction.

If an experiment is composed of subexperiments done in different periods or done in somewhat different conditions, it is best, if possible, to initially examine each subexperiment separately and then combine the data later if deemed appropriate (Bates and Watts 1988). This combination of data may be accomplished in stages or by reanalysis of all the data.

An important consideration in the first modeling stage is how deviations arise in bending strength, $Y_{F,T}$. Typically, the underlying relationship is linear (Eq. (1)); it is assumed that the natural variability arises in a manner that is independent, additive, and distributed with zero mean and constant variance. In such cases,

ordinary least squares is used to solve for parameter estimates. If the underlying relationship is nonlinear (Eq. (3)), and the variability in bending strength appears independent, additive, and distributed with zero mean and constant variance, then nonlinear least squares can be used to derive model parameters. In still other cases where the relationship is nonlinear, but the variability of the response tends to be proportional to its expected value, the logarithmic transformation of the response may stabilize the variance so that it is constant while linearizing the relationship. Then, ordinary least squares can be used to obtain parameter estimates for the transformed linear model (Eq. (2)). In addition, if normality of the deviations is correctly assumed, the parameter estimators based on least-squares methods coincide with the maximum likelihood estimators, which have many desirable statistical properties, including the invariance property. This property allows simple estimator construction of complicated functions of the basic model parameters. For a detailed discussion of assumptions and their implications, especially in regard to nonlinear models, see Seber and Wild (1989, Chap. 2 and 12).

It is important not only to correctly describe the error structure for inference purposes but also to assure that the best estimates for the parameters are calculated. Whereas least squares can be used to obtain parameter estimates for each of the three models considered, to obtain the parameter estimates in the nonlinear model requires initial estimates of the nonlinear parameters and iterative procedures to converge to the least-squares estimates. In this case, initial estimates can be obtained from parameter estimates of the transformably linear model (Snedecor and Cochran 1980).

Full models

A single-stage approach is also feasible for use in modeling reaction rates, especially when the responses are independent, which is usually the case with a destructive measurement that can be measured only once per specimen.

Thus, we will also consider variations of a single-stage (commonly termed full) model, which, in just one step, relates strength loss to time, temperature, and relative humidity. Based on the results of the two-stage model-building process just outlined, substitution of Eq. (4) into Eq. (3) yields

$$Y_F = b_F \exp[-X A_F (H_T/H_0) \exp\{-E_{a,F}/RT\}] \quad (6)$$

or

$$\ln Y_F = \ln(b_F) - X A_F (H_T/H_0) \exp\{-E_{a,F}/RT\} \quad (7)$$

and Eq. (4) into Eq. (1) yields

$$Y_F = b_F - X A_F (H_T/H_0) \exp\{-E_{a,F}/RT\} \quad (8)$$

where

b_F = initial bending strength (lb/in.²) at time ($X = 0$)

H_T = relative humidity during exposure

H_0 = normalized relative humidity at 67% (ASTM 1994)

Note that with the two untransformed types of full model (i.e., Eqs. (6) or (8)), we explicitly specify an initial strength parameter that may be estimated simultaneously with other model parameters. In still another variation, a transformed version of this model could be obtained by taking the logarithms of both sides of Eq. (6) yielding Eq. (7). The differences between Eq. (6), (7), and (8) involve how degrade terms and error terms are entered in and whether a transformation is used to linearize the dependent variable. From Eq. (6) to (8), we can see that we are considering rate of strength loss as a special type of Eyring relationship (i.e., where rate is a function of temperature and one other independent variable). See Nelson (1990) for other Eyring relationships, in addition to detailed discussions of accelerated degradation models including an example of a transformed Arrhenius rate model. Also see Bates and Watts (1988) for discussions of the handling of parameters that are functions of other variables.

Although many statistical software packages

have the capability to obtain estimates of the parameters in Eqs. (6) and (7) via nonlinear least squares, some re-parameterization may be necessary for convergence by reducing correlations between parameter estimates (Box and Draper 1987; Hunter and Atkinson 1966). Since the model includes time and temperature, it allows the inclusion and evaluation of all data, not just subsets of the data with positive rate loss estimates. This avoids trying to fit a regression model to a very small number of points as in the two-stage approach (where there is just one predicted k'_F per fire-retardant treatment at each temperature).

MODELING CUMULATIVE TEMPERATURE EFFECTS

The general modeling concept can be summarized as follows. Two modeling approaches were considered: a two-stage approach and a single-stage full approach. For the two-stage approach, three initial model forms were considered in the first stage to obtain estimates of the rate of strength loss at each exposure temperature. These were the linear (Eq. (1)), transformably linear (Eq. (2)), and nonlinear (Eq. (3)) models. Once estimated in the first stage, these isothermal rate constants ($k_{F,T}$) were considered as independent observations of the dependent variable, which were applied in the second stage using an Arrhenius-type approach to model rate of strength loss as a function of thermal exposure. Hence, the estimated parameters of the second stage were functions of the first-stage parameters.

Derivation of first stage of traditional model

When considering the traditional two-stage kinetic model-building approach, the nonlinear and transformably linear models are attractive because as time progresses they will never predict a strength value below zero. In contrast, a linear model can predict negative strength, which is undesirable. However, the simplicity of a linear model often outweighs the additional complications of a nonlinear or

TABLE 2. Root mean-squared error (RMSE) and R^2 of three model types.

| Chemical | RMSE | | | R^2 | | |
|----------|--------|---------------|-----------|--------|---------------|-----------|
| | Linear | Transformable | Nonlinear | Linear | Transformable | Nonlinear |
| PA | 1,629 | 1,579 | 1,562 | 0.62 | 0.64 | 0.65 |
| MAP | 2,047 | 1,973 | 1,962 | 0.70 | 0.72 | 0.72 |
| BBA | 1,907 | 1,912 | 1,909 | 0.14 | 0.14 | 0.14 |
| GUP/B | 2,162 | 2,097 | 2,082 | 0.60 | 0.62 | 0.62 |
| DPF | 1,963 | 1,947 | 1,941 | 0.46 | 0.47 | 0.48 |
| OPE | 1,991 | 2,015 | 2,004 | 0.33 | 0.31 | 0.32 |
| UNT | 1,759 | 1,766 | 1,763 | 0.24 | 0.23 | 0.24 |

transformably linear model, depending on the intended use of the model.

In our study, scatterplots of the raw data did not clearly indicate which of the three models most adequately describes the relationship between strength loss and cumulative thermal exposure. A comparison of mean strength loss versus cumulative thermal exposure for several chemical treatments supported the hypothesis of a nonlinear or transformably linear relationship (Fig. 1). However, the general error structure of our most extensive, long-range data set (i.e., the 150°F [66°C] data (Winandy 1995) did not support the assumption of transformed error. With the exception of phosphoric acid (PA), the error structure appeared random and lacked a systematic trend of progressively decreasing error as mean MOR decreased. If such a trend had existed, it would have often been stabilized by an appropriate transformation of the response. However, because such a trend did not exist, a logarithmic transformation of the strength values altered its inherent variability by inappropriately exaggerating the error in the lower strength data while masking the influence of the error in the higher strength data. This appeared to hold true for the data for 130°F (54°C) and 180°F (82°C) as well, but as stated by LeVan et al. (1990), analysis was inconclusive because the test involved only 160 days of exposure.

An extensive examination of the plots of bending strength loss versus time for specimens treated with each fire-retardant chemical system evaluated led us to believe that the data set emulates a nonlinear model with additive disturbances. However, because this was not

the conclusive model of choice for describing the relationship between strength loss and cumulative exposure, all three models were fit and analyzed. To compare goodness-of-fit between the three models, the root mean squared error (RMSE) of each treatment was compared (Table 2). Note that to compare the models on the same scale, the fitted values for the transformably linear model were obtained by the inverse transformation (i.e., $\hat{y} = \exp[\ln \hat{y}]$) where \hat{y} is a predicted strength value. Additionally, an R-square (R^2) statistic could be calculated as a function of the RMSE, with the interpretation of the proportion of the variation in y about its mean that is attributed to the fitted model (R^2 , in Kvålseth 1985). Recalling that minimized RMSE (equivalently, maximized R^2 in this case) is desirable, we noted that the nonlinear model fit the data as well as, or slightly better than, either the linear or transformably linear models.

Since interpretations of simple summary fit statistics can be problematic, it is imperative to investigate the suitability of each model by supplemental analysis of residual error (observed minus fitted). Plots of the residual error from the transformably linear model appeared to display a systematic pattern that is usually associated with nonconstant variability. Furthermore, the residual plots from the linear models appeared slightly nonlinear. Both patterns suggested a systematic lack-of-fit. Also, normal probability plots of the residuals supported the normality assumption for the linear and nonlinear models more so than for the transformably linear model.

Meanwhile, with the exception of phos-

TABLE 3. Parameter estimates for various models.^a

| Chemical | Linear | | Transformable | | Nonlinear | |
|----------|-------------------|-------------------|-------------------|---|-------------------|---|
| | $\hat{b}_{F,150}$ | $\hat{k}_{F,150}$ | $\hat{b}_{F,150}$ | $\hat{k}_{F,150}$ ($\times 10^{-4}$) | $\hat{b}_{F,150}$ | $\hat{k}_{F,150}$ ($\times 10^{-4}$) |
| PA | 6,485 (182.7) | 11 (0.7) | 8.82 (0.037) | 34.4 (1.38) | 7,061 (219.3) | 33.1 (3.03) |
| MAP | 13,218 (229.6) | 16 (0.8) | 9.51 (0.026) | 19.6 (0.98) | 13,773 (253.0) | 19.4 (1.24) |
| BBA | 16,786 (214.0) | 4 (0.8) | 9.72 (0.013) | 2.6 (0.50) | 16,796 (218.4) | 2.5 (0.53) |
| GUP/B | 14,876 (242.5) | 13 (0.9) | 9.61 (0.022) | 12.3 (0.83) | 15,254 (256.9) | 12.8 (0.94) |
| DPF | 14,542 (220.2) | 9 (0.8) | 9.58 (0.019) | 8.1 (0.71) | 14,701 (231.4) | 8.1 (0.75) |
| OPE | 14,826 (223.3) | 7 (0.8) | 9.60 (0.018) | 5.9 (0.67) | 14,846 (234.2) | 5.3 (0.69) |
| UNT | 17,143 (197.4) | 5 (0.7) | 9.75 (0.012) | 3.3 (0.46) | 17,155 (202.7) | 3.2 (0.49) |

^a Standard errors in parentheses; $\hat{k}_{F,T}$ and $\hat{b}_{F,T}$ refer to values in appropriate Eqs. (1), (2), and (3).

phoric acid, the residual plots from the nonlinear model with additive error were more well-behaved in comparison to the plots from the other model forms. That is, they exhibited a less systematic (i.e., non-random) error structure than did the linear or transformable models. Parameter estimates for each model form in the first stage of a two-stage approach at 150°F (66°C) are given in Table 3.

After concluding that the nonlinear model best described the 150°F (66°C) data, the 180°F (82°C) data (reported in LeVan et al. 1990) were modeled with similar results in that the nonlinear model fit the data better than did the linear or transformed linear models. However, the 130°F (54°C) data fit only slightly better, which was probably related to the general lack of a temperature effect on strength at 130°F (54°C). Since the 80°F (27°C) specimens showed no strength loss over the test period of 160 days and were only tested at two time periods, the data from these specimens were not included in further development of the model.

Derivation of second stage of traditional model

The rates of thermal degrade experimentally derived in the first stage of our two-stage ap-

proach were adjusted to 67% RH as follows:

$$k'_{F,T} = k_{F,T}(H_0/H_T) \quad (9)$$

where

$k_{F,T}$ = rate of strength loss at test

$k'_{F,T}$ = rate of strength loss normalized to RH (at 67% [ASTM 1994])

This consensus adjustment was used in the recent ASTM D-5516-94 Standard (ASTM 1994) for testing fire-retardant-treated plywood, with justification for such an adjustment given by Winandy et al. (1991). Given the adjusted rate constant estimates for the effect of cumulative thermal exposure on bending strength of fire-retardant-treated wood, the appropriateness of a kinetic-rate-based model based on Arrhenius theory can be determined.

The logarithms of these adjusted rate values for Eq. (5) and estimates of their error are given in Table 4 and shown in Fig. 2 for each of the seven treatments at the three tested temperatures. The predicted rate values ($\hat{k}^*_{F,T} = \ln \hat{k}'_{F,T}$) for each model form in Table 4 are denoted by the midpoints (as indicated by a negative sign) of the vertical lines. The vertical line at each temperature (K^{-1}) designates the approximate 95% confidence interval for that $k^*_{F,T}$ estimate as determined using a first-order

TABLE 4. Logarithms of adjusted standard rate constants for Eq. (5).^a

| Chemical | Temp. (°F) | True nonlinear | | Transformed linear | |
|----------|---------------|-------------------|-------|--------------------|-------|
| | | $\hat{k}_{F,T}^*$ | SE | $\hat{k}_{F,T}^*$ | SE |
| PA | 130 | -8.15 | 1.26 | -7.90 | 1.06 |
| | 150 | -5.82 | 0.09 | -5.79 | 0.04 |
| | 180 | -4.00 | 0.16 | -4.04 | 0.12 |
| MAP | 130 | -7.73 | 0.46 | -7.56 | 0.39 |
| | 150 | -6.36 | 0.06 | -6.35 | 0.05 |
| | 180 | -5.10 | 0.11 | -5.13 | 0.09 |
| BBA | 130 | — | — | — | — |
| | 150 | -8.41 | 0.21 | -8.38 | 0.19 |
| | 180 | -8.43 | 1.36 | -8.60 | 1.62 |
| GUP/B | 130 | -8.51 | 0.78 | -8.49 | 0.75 |
| | 150 | -6.77 | 0.07 | -6.82 | 0.07 |
| | 180 | -5.35 | 0.10 | -5.34 | 0.09 |
| DPF | 130 | — | — | — | — |
| | 150 | -7.23 | 0.09 | -7.23 | 0.09 |
| | 180 | -5.48 | 0.10 | -5.46 | 0.09 |
| OPE | 130 | — | — | — | — |
| | 150 | -7.66 | 0.13 | -7.54 | 0.11 |
| | 180 | -6.33 | 0.18 | -6.30 | 0.17 |
| UNT | 130 | -11.38 | 13.11 | -11.17 | 10.71 |
| | 150 | -8.16 | 0.15 | -8.13 | 0.14 |
| | 180 | -6.61 | 0.20 | -6.52 | 0.18 |

^a Dash denotes that the $-k_{F,T}$ estimate was positive.
°C = (°F - 32) (0.55).

Taylor Series (Batts and Watts 1988). The duration of exposure, degree of variation, and lack of response (i.e., too little strength loss) hinder the calculation of good estimates of strength loss for the 130°F (54°C) data.

However, except for borax/boric acid, $k_{F,T}^*$ is always negatively related to the inverse of temperature, based on the estimates at 180°F (82°C), the estimates at 150°F (66°C), and some estimates at 130°F (54°C) (e.g., as exposure time or temperature increases and strength decreases). This provides support for an Arrhenius-type approach.

With so few temperature data points, it is difficult to decide the best way to combine them to develop a useful, predictive model for rate constants that can also be used with the first-stage model for strength prediction. This second stage of model development can be considered in two ways. First, a straight line can be fit using least squares to three-point (or in some cases two-point) estimates. This is termed

TABLE 5. Regression coefficients and root mean-squared errors for various two-stage and single-stage model forms.

| Chemical | $\ln(\hat{A}_F)$ | | $\hat{E}_{a,F}$ | | RMSE |
|---------------------------------|------------------|--------|-----------------|--------|---------|
| | Intercept | SE | Slope | SE | |
| Nonlinear-weighted ^a | | | | | |
| PA | 33.4 | 3.76 | 110.5 | 10.72 | 1,825.9 |
| MAP | 21.2 | 2.54 | 77.6 | 7.23 | 2,195.3 |
| BBA | −8.6 | 28.93 | −1.3 | 82.73 | 2,582.0 |
| GUP/B | 23.9 | 2.52 | 86.5 | 7.22 | 2,101.8 |
| DPF | 30.1 | 2.99 | 105.0 | 8.37 | 2,145.6 |
| OPE | 20.6 | 4.79 | 79.5 | 13.50 | 2,092.2 |
| UNT | 24.9 | 5.30 | 93.1 | 15.16 | 1,933.2 |
| Nonlinear-linear ^a | | | | | |
| PA | 44.3 | 14.28 | 142.2 | 41.55 | 1,847.2 |
| MAP | 25.7 | 5.38 | 90.8 | 15.61 | 2,180.2 |
| BBA | −8.6 | 28.93 | −1.3 | 82.73 | 2,540.5 |
| GUP/B | 31.5 | 8.82 | 108.5 | 25.64 | 2,192.1 |
| DPF | 30.1 | 2.99 | 105.0 | 8.37 | 2,141.0 |
| OPE | 20.6 | 4.79 | 79.5 | 13.50 | 2,086.8 |
| UNT | 48.5 | 147.17 | 161.8 | 428.58 | 2,054.0 |
| Single-stage full model | | | | | |
| PA | 41.0 | 2.65 | 131.8 | 7.42 | 1,790.7 |
| MAP | 28.2 | 1.86 | 97.4 | 5.19 | 2,151.6 |
| BBA | −3.2 | 11.16 | −13.8 | 31.43 | 2,519.4 |
| GUP/B | 20.8 | 1.89 | 77.5 | 5.28 | 2,092.1 |
| DPF | 23.4 | 2.27 | 85.9 | 6.36 | 2,115.5 |
| OPE | 12.5 | 4.32 | 56.6 | 12.12 | 2,071.3 |
| UNT | 16.8 | 4.31 | 69.9 | 12.06 | 1,921.7 |

^a Two-stage model (first stage-second stage).

the "linear second-stage" approach and is shown by the heavily dashed lines in Fig. 2. Second, a weighted regression can be fit to the three points using the inverses of the variance of the point estimates as weights. This approach is termed the "weighted second-stage" approach. It is sometimes employed in life-testing analysis to obtain parameter estimates (Nelson 1990). The weighted approach reduces the influence of the highly variable 130°F (54°C) data, where little or no degrade was detected, in the prediction of strength loss at higher temperatures. The weighted approach is given by the dotted lines in Fig. 2. The parameter estimates of activation energy and pre-exponential constant calculated by these two approaches are given in Table 5. The standard errors for both the linear and weighted second-stage models are derived as functions of the variances of the original $\hat{k}_{F,T}$ values. For fire-re-

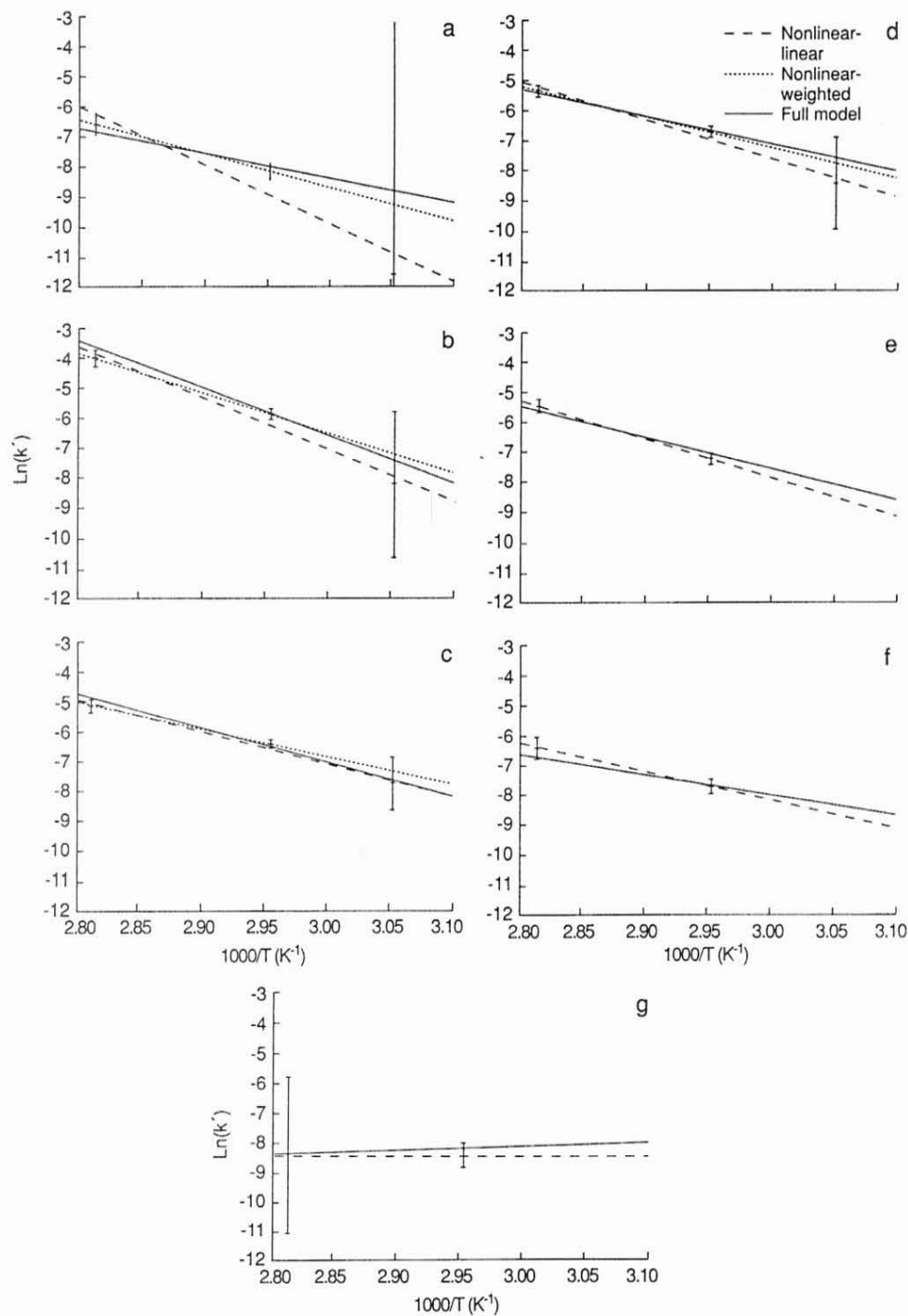


FIG. 2. Parameter estimates of reaction rates using a first-order kinetic theory and a modified Arrhenius approach. The vertical line at each temperature (K^{-1}) designates the approximate 95% confidence interval of the $\ln(k')$ estimate for (a) untreated, (b) phosphoric acid, (c) monoammonium phosphate, (d) guanyurea phosphate/boric acid, (e) dicyandiamide-phosphoric acid-formaldehyde, (f) organophosphate ester and (g) borax-boric acid.

tardant treatments that experience little degrade at 130°F (54°C) (BBA, DPF, and OPE), we basically took the conservative approach by not using a value at 130°F since we felt that this intentional conservative bias would not severely alter interpretations.

In our opinion, results from the weighted regression technique (both parameter estimates and standard errors) seem more appropriate than those obtained from a simple linear regression, especially given that the estimates were obtained from different experiments conducted over different lengths of time with different sampling periods. Since there were no data at time zero, the following approach was used to approximate the effect on model parameters by forcing a common initial strength. An estimate of the initial strength was calculated by a weighted estimate of the $\hat{b}_{F,T}$ values from the nonlinear models used in the first stage. The nonlinear models were refit with this common initial strength. Rate estimates were combined similarly, as described above, using a weighted approach. This evaluation showed that predicted model parameters of the two-stage nonlinear-weighted approach, when constrained to a common intercept, are similar to predicted parameters of a full single-stage model approach.

Single-stage full model

Until this point, we have approached model building using only two-stage solutions to develop parameter estimates. An alternative option to the same model-building approach would be to fit some type of fully nonlinear single-stage model as given by Eqs. (10)–(12) under the assumptions of independence between time periods and temperature, and constancy of error across time periods and temperatures. With a single-stage or full model, we still estimate the same desired parameters, using all the data simultaneously to obtain parameter estimates. Simultaneous “single-step” solutions are often used in “Optimization Statistics” specifically because they can use all the data (i.e., recall previously discussed two-stage models could not deal with negative strength

loss) and they always provide equal or better solutions under the appropriate assumptions (Bates and Watts 1988).

Three single-stage full models were considered as described earlier. Each varies mainly in how error terms are added into the model and each model form explicitly assumes a common intercept for each fire-retardant treatment at time zero. The re-parameterized models considered were:

$$Y_F = b_F \cdot \exp[-X \cdot C_F \cdot (H_T/H_0) \cdot \exp\{-E_{a,F} \cdot [(1/T - 1/T_0) \div R]\}] \quad (10)$$

$$\ln Y_F = \ln b_F - X \cdot C_F \cdot (H_T/H_0) \cdot \exp\{-E_{a,F} \cdot (1/T - 1/T_0)/R\} \quad (11)$$

$$Y_F = b_F - X \cdot C_F \cdot (H_T/H_0) \cdot \exp\{-E_{a,F} \cdot (1/T - 1/T_0)/R\} \quad (12)$$

where

$$T_0 = 341.5 \text{ K } (=155^\circ\text{F, the midpoint between } 130^\circ\text{F and } 180^\circ\text{F})$$

$$\ln C_F = \ln(A_F) - E_{a,F}/(RT_0)$$

The primary differences between the three proposed nonlinear models (Eqs. (10)–(12)) are:

- Equation (10) is an untransformed model in which the total accumulated effects of thermal degrade are multiplied into the model.
- Equation (11) is a transformed version of Eq. (10), which in essence makes the negative effects of thermal degrade on log strength additive. But both Eqs. (10) and (11) have the same underlying functional form.
- Equation (12) is also an untransformed model, but the negative effects of thermal degrade are added into the model, rather than multiplied as in Eq. (10).
- Equation (12) might be expected to fit the data better if the underlying relationship of thermal degrade over time were linear. On the other hand, Eqs. (10) or (11) might be expected to fit the data better if the underlying relationship between thermal degrade

TABLE 6. Goodness-of-fit as indicated by minimum RMSE of three variations of single-stage.

| Chemical | Linear Full (Eq. (12)) | Transformable Full (Eq. (11)) | Nonlinear Full (Eq. (10)) |
|----------|---------------------------|----------------------------------|------------------------------|
| PA | 1,860.08 | 1,824.74 | 1,790.72 |
| MAP | 2,225.74 | 2,175.27 | 2,151.61 |
| BBA | 2,517.69 | 2,526.01 | 2,519.40 |
| GUP/B | 2,143.16 | 2,102.07 | 2,092.11 |
| DPF | 2,135.47 | 2,123.46 | 2,115.55 |
| OPE | 2,064.28 | 2,078.68 | 2,071.25 |
| UNT | 1,920.06 | 1,925.60 | 1,921.70 |

over time were nonlinear asymptotic (i.e., strength can never be ≤ 0).

The other parameters were defined previously in Eqs. (6) to (8). The goodness-of-fit for each of the three variations can be compared using the RMSE terms. These RMSE values are given in Table 6. Note that the nonlinear and linear full models (Eqs. (10) and (12)) always displayed minimum RMSE compared to the transformed nonlinear model (Eq. (11)). When comparing the two untransformed nonlinear models, Eq. (10), having an multiplicative effects structure, fit the data better than the nonlinear model employing an additive effects structure (Eq. (12)) in four of seven cases where thermal strength loss was greatest (PA, MAP, GUP/B, DPF). In the three cases where thermal-induced strength loss was minimal or null (BBA, OPE, UNT), the RMSE terms of the two nonlinear models were nearly identical. Accordingly, we selected the nonlinear full model with multiplicative effects and additive error (Eq. (10)) as the preferred model based on a goodness-of-fit test using RMSE as the fit criteria and careful examination of residual plots. Recalling the basic assumptions of the nonlinear models, this result is also appealing because it infers that we could never achieve zero or negative strength.

Comparison of single-stage and two-stage kinetic approaches

We now compare the goodness-of-fit of the best full model (Eq. (10)) to two likely two-

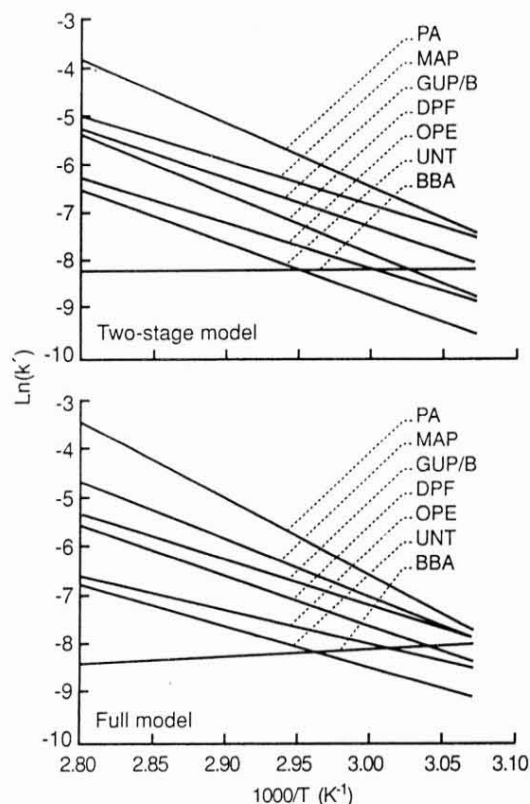


FIG. 3. Predicted reaction rates of different fire-retardant formulations using various approaches: (a) two-stage approach with nonlinear first-stage and weighted regression second-stage, and (b) single-stage full approach.

stage models (the nonlinear-weighted and the nonlinear-linear).

Parameter estimates for $E_{a,F}$ and $\ln(A_F)$ are given in Table 5. In our opinion, the single-stage full model was superior to the weighted linear two-stage approach in that standard error and the RMSE (Table 5) associated with the predictions were much reduced. Furthermore, the full model appeared to fit the combined data set (130°F (54°C), 150°F (66°C), and 180°F (82°C)) as well as or slightly better than the two-stage nonlinear-weighted ([first stage]-[second stage]) approach based on a comparison of RMSE (Table 5) and on a graphical comparison (Fig. 2). Note that the essential difference between the single-stage full model and the nonlinear-weighted two-stage approach is that the predicted reaction rates with

TABLE 7. Results of Monte Carlo simulation of three potential models.^a

| Parameter ^b | Approach estimate | Mean | SD | MSE (true) | MSE ^c (est) |
|------------------------|-------------------|--------|-------|------------|------------------------|
| b | Linear | 13,661 | 158.4 | 25,088 | 4,182 |
| | Weighted | 13,660 | 158.4 | 25,109 | 4,176 |
| | Full | 13,660 | 145.6 | 21,228 | — |
| ln(A) | Linear | 35.32 | 7.21 | 103.10 | 99.59 |
| | Weighted | 33.90 | 2.27 | 37.97 | 35.19 |
| | Full | 28.13 | 1.81 | 3.27 | — |
| E _a | Linear | 100.27 | 20.49 | 427.77 | 394.46 |
| | Weighted | 96.25 | 6.44 | 42.73 | 15.64 |
| | Full | 97.29 | 5.20 | 27.08 | — |

^a True population parameters of $b = 13,665$, $\ln(A) = 28.1725$, and $E_a = 97.4$; 3,000 iterations.

^b b is strength at time 0, A is pre-exponential factor, and E_a is activation energy.

^c Mean-squared error (MSE): (full - linear)² or (full - weighted)².

the full model are greater at higher temperatures ($\geq 150^\circ\text{F}$ ($\geq 66^\circ\text{C}$)) and less at lower temperatures. This can be seen by comparing the predicted k^*_F (rate of thermal degrade) from the single-stage full model (Fig. 3b) to that of the nonlinear-weighted two-stage model (Fig. 3a) across temperature. Thus, the determination of the "best" model form is essential in addressing the critical question of whether thermal degrade of fire-retardant-treated wood in roof systems is more, less, or equally influenced by a limited number of roof exposure hours at higher temperatures ($\geq 150^\circ\text{F}$ ($\geq 66^\circ\text{C}$)) or by the many more hours of exposure at lower temperatures.

The practical implication of the divergent k^*_F values from the full model implies that wood treated with inorganic phosphate (i.e., PA and MAP) will undergo a measurably greater strength loss than will untreated wood or even wood treated with GUP/B for every hour of exposure at the higher temperatures ($\geq 130^\circ\text{F}$ ($\geq 54^\circ\text{C}$)). This characteristic is of interest because it might partially explain the poor in-service performance of some inorganic-phosphate-based fire-retardant-treated plywood roof sheathing (APA 1989a; NAHB 1990).

While we do not have strength effects data at temperatures $>180^\circ\text{F}$ (82°C), we do have data at 80°F (26°C). To test the three candidate models' abilities to extrapolate to these lower temperatures, we calculated RMSE for only

the 80°F (26°C) data. Parameters were not re-evaluated because the 80°F (26°C) test data did not experience further strength loss over exposure duration and data were tested at only two time periods. The results reported in Table 8 show that for the full model, RMSE is equal to or minimized in five of seven cases. This supports the conclusion that the full model is preferable over either of the best two-stage approaches.

A simulation study was then conducted to compare a single-stage full modeling approach to either the weighted or linear (i.e., non-weighted) least-square fit with the two-stage approach. The results showed that all three models are essentially equivalent in the estimate of initial strength (b), although the single-stage full model approach gave some indication of more precision based on true mean squared error (MSE) (Table 7). The pre-exponential factor ($\ln(A)$) and activation energy (E_a) estimates obtained by the linear approach had a noticeably larger bias and less precision, as indicated by true MSE (Table 7), than did estimates obtained with either the single-stage full model approach or the weighted regression in the two-stage approach. These latter two approaches were essentially equal in most respects in estimated mean trends; however, bias of $\ln A$ was noticeably higher with the two-stage nonlinear-weighted approach than with the single-stage full approach.

This simulation also illustrates that with fu-

TABLE 8. Goodness-of-fit based on RMSE for various two-stage and single-stage model forms when using 80°F (27°C).

| Chemical | Nonlinear-linear ^a | Nonlinear-weighted ^a | Full |
|----------|-------------------------------|---------------------------------|---------|
| PA | 2,415.3 | 2,387.6 | 2,247.9 |
| MAP | 2,101.9 | 2,007.1 | 1,943.3 |
| BBA | 2,731.6 | 2,697.8 | 2,783.3 |
| GUP/B | 1,610.9 | 1,611.3 | 1,612.8 |
| DPF | 1,695.4 | 1,711.7 | 1,689.9 |
| OPE | 1,700.2 | 1,684.1 | 1,720.2 |
| UNT | 1,892.2 | 1,902.9 | 1,892.9 |

^a Two-stage model (first stage-second stage).

ture data analysis (i.e., with the addition of 3- and 4-year data), distributional assumptions will become increasingly important in model development. With the exception of PA, all the data have appeared normal to this point. Finally, it could be expected that the two-stage approach would not fare as well as the full model approach when considering treatments that experience little or no degrade at temperatures near 130°F (54°C).

CONCLUSIONS

Several model types were evaluated using a kinetics-based approach for predicting the strength loss of fire-retardant-treated wood as a function of cumulative thermal exposure. The single-stage full model approach was superior to all others. It fit the data better, and residual error was reduced when compared to any other model form. When considering the more traditional two-stage approaches to predict strength loss over time of exposure, the initial use of a nonlinear model with additive error for each temperature, followed by a weighted regression across temperatures, was selected as the most viable alternative to the single-stage model based on its maximized fit and more random error structure when compared to other simpler and more traditional two-stage models. While previous work suggested that strength loss resulting from thermal degradation of fire-retardant-treated wood might be modeled using classic two-stage kinetic theory (Pasek and McIntyre 1990; Winandy et al. 1991; Woo 1981), our results lead us to support the use of a nontraditional, single-stage

full modeling approach (Eq. (10)) for strength because of reduced residual error and a decidedly better fit to our data. Future work will verify the "best" model form when the 3- and 4-year data become available in late 1996. That verified model form will then be applied to develop a prototype serviceability model for untreated and fire-retardant-treated wood products exposed to elevated in-service temperatures.

DEDICATION

This paper is dedicated to the memory of Dr. Merrill "Mike" A. Millett, friend and Forest Products Laboratory pioneer in modeling the thermal degradation of wood.

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