

APPLICATION OF FIRST-ORDER SINGLE-REACTION MODEL
FOR COAL DEVOLATILIZATION OVER A WIDE RANGE OF HEATING RATES

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INTRODUCTION

The first-order single-reaction model offers a simple but effective mathematical description of coal devolatilization. Under conditions where the effects of physical transport processes and secondary reactions are relatively small but not negligible, the model approximates the complex chemical decomposition and any transport effects by a single global first-order decomposition reaction occurring uniformly throughout the particle. In more complete devolatilization descriptions that explicitly include mass transfer, the model represents only the chemical decomposition.

The model is most useful in applications where minimizing computational effort is important such as in large combustion or gasification models that fully describe fluid mechanics, heat and mass transport, and reaction kinetics; and in comprehensive devolatilization models that explicitly include the complex decomposition and secondary reaction chemistry, and multicomponent mass transfer in a gaseous or liquid phase environment. However, the model has a major weakness in that a different set of rate parameters is required at different heating rates. Thus, for a given set of rate parameters, the applicability of the model is confined to a narrow range of heating rates.

This paper presents a novel method to extend the applicability of the first-order single-reaction model over a wide range of heating rates. The two rate parameters in the model, a pre-exponential factor and activation energy, are derived in the form of heating rate dependent functions. The total weight loss data from devolatilization of a Montana lignite over heating rates from ≈ 0.1 to 10^4 C/s were used to illustrate the derivation procedure, and to test the reliability of this method.

EXPERIMENTAL DATA

The devolatilization weight loss data used in this work were obtained using the thermogravimetric analyzer at low heating rates (0.67-2.67 C/s) (1), and the electrical screen-heater reactor at high heating rates ($650-10^4$ C/s) (2). In both reactors, small samples (<20 mg) of a Montana lignite in the particle size range 50 to 100 μm were used, with reactor conditions of 1 atm pressure and 1000 C maximum temperature.

The maximum volatiles yield, V^* , indicated by the upper asymptotic limit of the time-resolved yield curve, is one of the input parameters in the first-order single-reaction model. For a Montana lignite, V^* can be assumed to be independent of heating rate since the experimentally observed V^* is reported to be constant at ≈ 40 wt% (as-received) between the heating rates of 0.1 and 10^4 C/s (1,2,3). For higher rank coals, e.g., softening HVB coals, this assumption is still valid, but only over a narrower heating rate range. Suuberg et al. (3) observed a constant V^* of 47 wt% (as-received) between the heating rates of 350 and 15,000 C/s for a Pittsburgh Seam HVB coal under 1 atm, whereas Serio(4), and

Weimer and Ngan(5) reported a much lower V^* of 30 to 37 wt% (as-received) between 0.05 and 0.2 C/s for the same type of coal.

MODEL DESCRIPTION

The rate of volatiles evolution in the first-order single- reaction model is represented as,

$$dV/dt = k_{Os} \exp(-E_s/RT) (V^* - V) \quad (1)$$

where V is the cumulative amount of volatiles evolved up to time t , $V \rightarrow V^*$ at large t , and the subscript s denotes single-reaction. The global rate parameters, k_{Os} and E_s , are heating rate specific, and thus a given set is only applicable over a narrow range of heating rates. This limitation restricts the use of the model over the confined heating rate range in which the rate parameters are valid.

Integrating Eq.(1), using the approximation of Agrawal and Sivasubramanian (6), under a constant heating rate, m , up to temperature, T , yields

$$\ln [(V^*-V)/V^*] = \frac{-k_{Os}RT^2}{mE_s} \left[\frac{1-2(RT/E_s)}{1-5(RT/E_s)^2} \right] \exp(-E_s/RT) \quad (2)$$

The above equation was found to be the most accurate integral approximation among different methods reported in the literature (7,8,9). The approximation deviates $< \pm 1\%$ from Simpson's 1/3 numerical method for the ranges of E_s and T typically encountered in coal devolatilization ($E_s > \approx 10$ kcal/mole and $T < \approx 1000$ C).

Another commonly used global devolatilization model, the multiple independent parallel reaction (MIPR) model was used (next section) to represent the experimental weight loss data from different heating rates. With just one set of rate parameters, the MIPR model successfully describes volatiles evolution data with heating rates that span several orders of magnitude (2,5,10,11), but it has a drawback in that it requires more computational effort. The rate of volatiles evolution in the MIPR model is expressed as the sum of the contributions from multiple first-order independent parallel reactions,

$$dV/dt = \sum k_{oi} \exp(-E_i/RT) (V_i^* - V_i) \quad (3)$$

where i denotes one reaction. The same pre-exponential factor is used for all reactions, i.e., $k_{oi} = k_o$, and the activation energies are described by a Gaussian distribution with mean E_o and standard deviation σ . Thus,

$$f(E) = [\sigma(2\pi)^{1/2}]^{-1} \exp[-(E-E_o)^2/2\sigma^2] \quad (4)$$

where $f(E) = V_i^*/V^*$ for a large number of reactions and V^* is the sum of the V_i^* for all i . Integration of Eq.(3) for any temperature history yields

$$(V^*-V)/V^* = \int_0^\infty \exp[-k_o] \int_0^t \exp(-E/RT) dt f(E) dE \quad (5)$$

DERIVATION OF HEATING RATE DEPENDENT KINETIC PARAMETERS

To extend the use of the model over a wider heating rate range, we sought to relate E_s and k_{OS} to the heating rate, m , in the form of

$$E_s = f(m) \quad (6)$$

$$k_{OS} = g(m) \quad (7)$$

where f and g represent mathematical functions derived below.

The combined weight loss data of Ciuryla et al.(1) and Anthony et al.(2) were fitted using the MIPR model. Table 1 gives the best-fitted parameter values from fitting the combined data set, as well as those obtained by Ciuryla et al.(1) and Anthony et al.(2) using only their own data. The two groups of investigators(1,2) have shown that this model has an excellent capability to fit the data over a wide range of heating rates with just one set of parameter values.

An arrhenius plot (Fig.1) was then produced using the rate of total volatiles evolution predicted by the MIPR model at heating rates 0.1, 1, 10, 10^2 , 10^3 , and 10^4 C/s [Eq.s (3) and (5), Table 1(c)]. The lines in the figure are sufficiently straight to assume a first-order single-reaction behavior for each of the heating rates. Table 2 gives the values of E_s and k_{OS} computed from Fig.1, which respectively represent the slope and the y-intercept of the lines in the figure.

Plotting individually the values of k_{OS} and E_s versus $[3+\log_{10}(m)]$ from Table 2 produced the following relationship:

$$\log_{10}k_{OS} = -3.16514 + 0.941867(3+\log_{10}m) \quad (8)$$

$$E_s = 5909.411 + 182.7911(3+\log_{10}m) + 66.80278(3+\log_{10}m)^2 \quad (9)$$

The correlation coefficient exceeded 0.999 in both cases, assuring that the rate parameters computed from the above equations closely agree with those obtained from Fig.1.

RESULTS AND DISCUSSION

Figure 2 shows that the predicted weight loss behavior by the first-order single-reaction model [Eq.s (2), (8) and (9)] agree well with the data represented by the predictions from the MIPR model [Eq.s (3) and (5), Table 1]. Thus, with the heating rate dependent kinetic parameters derived in this study, the single-reaction model can successfully be applied over a wide range of heating rates. Furthermore, the use of the integral approximation of Agrawal and Sivasubramanian(6) allows the volatiles evolution rate equation [Eq.(1)] to be expressed in an analytical form, which considerably reduces the computational effort.

The empirical coefficients in Eq.s (8) and (9) are specific for the data from which they were best-fitted. However, since a given data set can accurately be described by a set of MIPR model parameters, a more general form of Eq.s (8) and (9) may respectively be represented as functions ψ and ϕ

$$\psi(E_s, E_0, \sigma, k_0, m, T) = 0 \quad (10)$$

$$\phi(k_{OS}, E_0, \sigma, k_0, m, T) = 0 \quad (11)$$

V^* also varies for different data, but it has no effect on the rate parameters of either models. Equating $[(dV/dt)/(V^*-V)]/\ln[(V^*-V)/V^*]$ from Eq.s (1) and (2) to that from Eq.s (3) and (5) yields the function ψ in the form of

$$E_s^2 + (QRT^2/m)E_s - [5(RT)^2 + 2QR^2T^3/m] = 0 \quad (12)$$

where Q is $[(dV/dt)/(V^*-V)]/\ln[(V^*-V)/V^*]$ obtained from Eq.s (3) and (5), and is a function of only E_0 , σ , k_0 , m and T . Having obtained E_s from Eq. (12), rearranging Eq. (1) yields the function ϕ

$$k_{0S} - [(dV/dt)/(V^*-V)] \exp(E_s/RT) = 0 \quad (13)$$

where $[(dV/dt)/(V^*-V)]$ is obtained from Eq.s (3) and (5). Although rigorous, the above equations are too complex to readily observe the effect of changing E_0 , σ , or k_0 on E_s and k_{0S} . Also, for the same reason, it is difficult to detect any relationship between Eq.s (8) and (12), and Eq.s (9) and (13).

Although qualitative, Table 3 provides a useful means to predict the effect of a new data set on E_s and k_{0S} . For a given heating rate, the new time-resolved rate (or yield) curve is characterized by T_{max} and T_{sig} , where T_{max} represents the temperature at which the maximum rate occurs, and T_{sig} the temperature spread of the curve. The temperature spread is arbitrarily defined as the range of temperatures in which the yield is between two fixed values [e.g., Ko et al. (11) used 15.87 and 84.13% of the final yield]. Some examples will illustrate how to use the table. E.g., 1: for a fixed heating rate, the new data have higher T_{sig} , but no change in T_{max} . Table 3 shows that the newly fitted k_{0S} must be lower to match the increased T_{sig} , and the new E_s must also be lower to off-set the increase in T_{max} caused by the lower k_{0S} . E.g., 2: again for a fixed heating rate, the new data have higher T_{max} , but no change in T_{sig} . The table shows that the newly fitted E_s has to be higher to match the increased T_{max} , and the new k_{0S} is unchanged. Table 3 can also be used to relate qualitatively E_0 , σ , and k_0 to E_s and k_{0S} . For example, the reason why the fitted E_s and k_{0S} for the same data are generally smaller than the E_0 and k_0 , respectively, is that a finite σ requires k_{0S} to be smaller than k_0 to produce to same T_{sig} . Since lowering k_{0S} increases T_{max} , E_s must also be smaller to off-set the increased T_{max} .

The correlation procedure developed here can easily be applied to describe the evolution of total volatiles of other coals, and individual product species. A new set of E_0 , σ , k_0 and V^* , best-fitted using the MIPR model, can be used to represent the new data set. Despite the lack of rigorous proof, the form of the Eq.s (8) and (9) are expected to remain the same, only the coefficients need to be re-fitted using the newly computed values of E_s and k_{0S} at different heating rates.

CONCLUSIONS

This work has demonstrated that the first-order single-reaction model can successfully be applied over a wide range of heating rates using the heating rate dependent kinetic parameters [Eq.s (8) and (9)].

The use of the integral approximation method of Agrawal and Sivasubramanian(6), provides an accurate analytical solution of the single-reaction model rate equation [Eq.(1)] for the ranges of E_s and T typically encountered in coal devolatilization.

The heating rate dependent kinetic parameters combined with this integral approximation are expected to be useful in applications where minimal computational effort is desired.

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Table 1 : Best-Fitted Global Rate Parameters for the Multiple Independent Parallel Reaction Model Using Total Weight Loss Data from Montana Lignite.

	(a)		(b)	(c)	
Fitted By:	Ciuryla et al.(1)		Anthony et al.(2)	This Study	
Data Source:	Ciuryla et al.(1)		Anthony et al.(2)	Ciuryla et al.(1) Anthony et al.(2)	
Heating Rate: (C/s)	0.67	2.67	650-10 ⁴	0.67-10 ⁴	
Cooling Rate: (C/s)	-c	-c	≈200	≈200	
Log(ko/s ⁻¹)	13.22 ^b	13.22 ^b	13.22 ^b	13.22 ^b	8.91 ^a
E _o , kcal/mole	54.3	53.3	56.3	56.8	38.6
σ, kcal/mole	1.32	1.21	1.09	1.16	0.706
V [‡] , wt% as received	41.1	41.2	40.6	41.0	40.0

^a Allowed to vary. This set of parameters was used to produce Fig.1.

^b This parameter was fixed.

^c Continuous heating until all reactions are completed.

Table 2 : Computed E_s and k_{o_s} from the Arrhenius Plot in Fig. 1.

Heating Rate ^a C/s	Pre-Exponential Factor(ko _s) s ⁻¹	Activation Energy(E _s) cal/mole
0.1	0.05076	6528
1	0.4578	7078
10	4.089	7718
10 ²	36.19	8489
10 ³	309.2	9385
10 ⁴	2582.0	10480

^a Continuous heating until all reactions are completed.

Table 3 : The Effect of Changing T_{max} and T_{sig} on the Global Rate Parameters of the First-Order Single-Reaction Model (E_s and k_{os}) and of the Multiple Independent Parallel Reaction Model (E_o , σ and k_o).

The Effect of Increasing(\uparrow) the parameter X on :		
Parameter X	T_{max}	T_{sig}
E_s, E_o	\uparrow	- ^a
k_{os}, k_o	\downarrow	\downarrow
σ	-	\uparrow

^a No change.

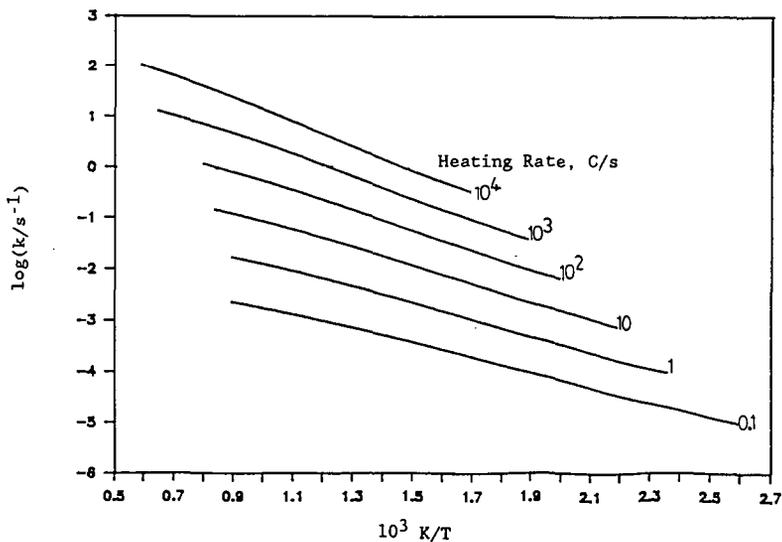


Figure 1 : Arrhenius Plot for Total Volatiles Evolution of Montana Lignite Described by the MIPR Model [Eq.(3) and (5), Table 1(c)]. The lines represent the rates computed between 1 to 99% of total volatiles yield.

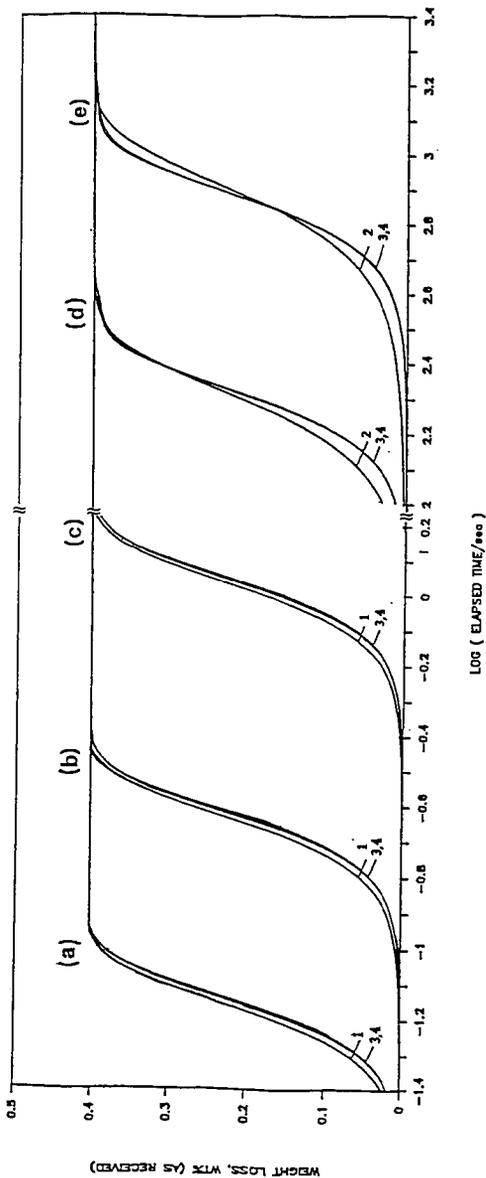


Figure 2 : Comparison of Predicted Total Volatiles Yield from the First-Order Single-Reaction Model [Eq.s (2), (8) and (9)] and from the MIPR Model [Eq.(5) and Table 1].

Heating, cooling rates in C/s (a) 10^6 , 200; (b) 3000, 200; (c) 650, 200; (d) 2.67 continuous heating to T_{max} ; (e) 0.67 continuous heating to T_{max} (≤ 1000 C).

The curves represent model, source of kinetic parameters 1. MIPR, Anthony et al.(1974); 2. MIPR, Ciuryla et al.(1979); 3 MIPR, this study; 4. First-Order Single-Reaction, heating rate dependent kinetic parameters derived in this study. The kinetic parameter values for the curves 1, 2 and 3 are given in Table 1, and those for the curve 4 can be computed from Eq.s (8) and (9). For non-continuous heating cases [curve sets (a), (b) and (c)], let m_b be the equivalent heating rate equal to $m_b m_c / (m_b + m_c)$ where m_b and m_c are heating and cooling rates respectively.