

Kinetic Compensation Effect in Thermal Decomposition of Cellulosic Materials in Air Atmosphere

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ABSTRACT: The decomposition of wood and leaf of eight species in air atmosphere is examined by nonisothermal means with linear temperature programming, and a simple kinetic description is developed based on the experimental results and integral analysis method. The relation between the apparent activation energy E and preexponential factor A is analyzed, and it is found that the parameters E and A resulted from the variation of the species and the variation

of model functions exhibit kinetic compensation effects. Quantitative and statistical criterion to distinguish between real and false compensation effects is discussed in detail. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 135–141, 2003

Key words: activation energy; cellulosic materials; compensation; decomposition; thermogravimetry

INTRODUCTION

Understanding the thermal decomposition of biomass is of great importance for the modeling of biomass combustion and fire propagation. During the past several decades, it has been found that for polymer decomposition, the kinetic parameters, i.e., the preexponential factor A and the activation energy E , often exhibit the following relationship:

$$\ln A = aE + b \quad (1)$$

where a and b are constant coefficients for a series of related rate process. This relationship is referred to as the “kinetic compensation effect” (KCE), and here the so-called compensation means that the reduction in rate expected to result from an increase in activation

energy does not occur for the set of reactions obeying eq. (1), due to a compensatory increase of A . In traditional kinetic studies involving homogeneous reactions, the evaluation of the kinetic parameters assumed importance because they were considered to be indicative of the reaction mechanism. However, in the case of heterogeneous reactions taking place in the solid state, both these parameters lose their relevance because the concepts of “order of reaction” and “concentration” are not applicable. Hence, E and A values have little physical significance. It is also evident from the literature that the value of E depends heavily on various experimental factors sample size, particle size and its distribution, heating rate, presence of impurities in the sample, and gaseous atmosphere in and around the sample. Thus we may ask whether the experimentally determined Arrhenius parameters have any relevance to their practical application. The KCE in fact provides a possible means to predict the effects of experimental factors on kinetic parameters. According to this relationship, for any change in the experimental activation energy arising from the variation of experimental conditions, a corresponding change in A also occurs, thus we could correlate the different parameters under different experimental conditions.¹ True KCE can prove to be useful in predicting Arrhenius parameters when limited data are available.²

The purpose of this article is to examine the KCE relationship existing in the thermal decomposition of biomass materials. This work is specifically directed toward revealing the KCE for the kinetic parameters due to species variation. Galwey and Brown³ re-

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TABLE I
Features of the Thermogravimetric Curves for Wood and Leaf Samples in Air

Sample	Symbol ^a	T_{m1} (°C) ^b	T_{m2} (°C) ^c	Volatile (%)	Ash (%)
Fir	LF	332	460	87.6	12.4
	WF	312	442	92.7	7.3
Banana shrub	LB	300	492	85.3	14.7
	WB	300	460	93.2	6.8
Tea tree	LT	312	496	90.0	10.0
	WT	312	480	98.8	1.2
Waxberry	LW	316	472	89.8	10.2
	WW	308	448	94.5	5.5
Holm oak	LHO	320	492	94.8	5.2
	WHO	304	484	95.6	4.4
Heath	LH	292	452	90.5	9.5
	WH	276	436	93.0	7.0
Masson Pine	LMP	320	472	91.3	8.7
	WMP	312	456	98.6	1.4
Nammao	LN	303	472	98.1	1.9
	WN	302	472	98.8	1.2

^a The initials "L" and "W" in this column denote leaf sample and wood sample, respectively.

^{b, c} Temperatures of DTG peaks (for each sample there are two peaks).

viewed the compensation behavior in solid-state decomposition extensively and pointed out that compensation has been reported for sets of chemically comparable reactants that decompose in the same temperature interval. Nevertheless, for biomass the KCE relationship due to species variation has been rarely reported so far. For biomass decomposition, the KCE relationship, if available, would help correlate the kinetic parameters under different experimental conditions, and thus be useful for the modeling of biomass combustion. We emphasize on the KCE resulted from the species variation and model variation. The criterion to recognize a real KCE relationship is also investigated.

EXPERIMENTAL

The raw materials used in the investigation were respectively the wood and leaf of fir, banana shrub, tea tree, waxberry, holm oak, heath, masson pine, and nanmao collected from the Qimen forest zone of China (Table I). These materials were first cut and then ground, thereby the average particle size was specified to be approximately 40 μm . The grains of the sample were evenly distributed over the open sample pan of 5 mm diameter, loosely, with the initial amounts of the samples all kept to be 10 mg or so. The depth of the sample layer filled in the pan was about 0.5 mm. Thermal decomposition was observed in terms of the overall mass loss by using a STA 409C Thermobalance. Temperature calibration of thermogravimetric analysis (TGA) was carried out with spe-

cial concern, since in this device the thermocouple was not in direct contact with the sample. An air stream was continuously passed into the furnace at a flow rate of 60 mL/min (at normal temperature and atmospheric pressure). The temperature was increased to 750°C at a rate of 10°C/min. The heating rate of this order is generally considered able to ensure that no temperature gap exists between the sample and its surroundings.⁴ In order to test the transport effect under this heating rate and sample mass condition, we especially carried out the experiments using the masson pine as an example with different sample masses for which the least being 4 mg and the most being 10.6 mg. The result indicated that the TG curves for different masses differed from each other only around the upper edge of the domain of evaluation, at temperatures starting around 500°C. We regarded one of the curves as a benchmark curve and evaluated the fit of any other curve (e.g., the j th curve) relative to this benchmark curve according to the following expression:

$$\text{fit (\%)} = \left(\sum_{i=1}^{N_j} [w_{ji} - w_{bi}]^2 / N_j \right)^{0.5} \quad (2)$$

where w is the mass percentage, the subscript b refers to the benchmark curve, and N_j is the number of points on the j th curve. Acceptable agreements were achieved with the most fit being only 2.6%, indicating that the effect of the transport processes is low. This may be partly due to the low heating rate employed in this study. The sample mass loss percentage and its temperature were recorded continuously as a function of heating time. From the sample mass-loss percentage, mass loss due to water evaporation could be recognized and the normalized mass-loss ratio of a sample due to the thermal decomposition can be determined and plotted vs the sample temperature as the TG curve. The derivative thermogravimetric (DTG) curve can then be calculated by differentiating the mass-loss ratio with respect to time or temperature.

RESULTS AND DISCUSSION

Kinetic model of the mass loss process

Following the water evaporation, two distinct DTG peaks are observed for all the samples subjected to experiments in air. When the temperature reaches relatively high, oxidation of the char residue generated in the early stage is likely to occur. The maximum of the first DTG peak occurs at about 300°C. Comparing the present results with those in literature⁵⁻⁷ (at the same or almost the same heating rates but in nitrogen atmosphere) shows that the present first DTG peak tem-

TABLE II
Kinetic Model Functions $f(\alpha)$ and Corresponding $g(\alpha)$ Usually Employed for the Solid State Reactions

Model	$g(\alpha) = kt$	$f(\alpha) = (1/k)(d\alpha/dt)$
Reaction order		
O0	α	1
O1	$-\ln(1 - \alpha)$	$1 - \alpha$
O2	$(1 - \alpha)^{-1} - 1$	$(1 - \alpha)^2$
O3	$0.5[(1 - \alpha)^{-2} - 1]$	$(1 - \alpha)^3$
Phase boundary controlled reaction		
R2	$1 - (1 - \alpha)^{1/2}$	$2(1 - \alpha)^{1/2}$
R3	$1 - (1 - \alpha)^{1/3}$	$3(1 - \alpha)^{2/3}$
Diffusion		
D1	α^2	$1/2\alpha$
D2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	$\{-\ln(1 - \alpha)\}^{-1}$
D3	$[1 - (1 - \alpha)^{1/3}]^2$	$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$
D4	$(1 - 2\alpha/3) - (1 - \alpha)^{2/3}$	$3/2[(1 - \alpha)^{-1/3} - 1]^{-1}$

perature is close to that in literature, indicating that the first major mass loss is little affected by oxidation of char. From this evidence it can be concluded that the mechanism controlling this step is mainly due to the pyrolysis of hemicellulose and cellulose, and partly due to lignin pyrolysis that, however, occurs in a broad temperature range generally. For different sample species, the temperature of the second DTG peak varies between 440 and 500°C, which is much higher than that in nitrogen atmosphere,⁷ implying that the second major mass loss is ascribed to the combined effect of lignin pyrolysis and char oxidation.

The experimental results show that the two DTG peaks appear nearly separate in almost all the cases, indicating that the two controlling mechanisms illustrated above interact little with each other, and they take effect respectively in the lower and higher temperature ranges. This evidence leads to the basic assumption of the kinetic model, i.e., the two major mass losses can be regarded as due to two independent reactions of two pseudo components occurring respectively in the lower and higher temperature ranges. Correspondingly, the initial and residue solid mass fractions for the two separate reactions are defined respectively in the definite lower and higher temperature ranges, and the temperature corresponding to the minimum in the DTG curve is regarded as the point of separation between the two temperature ranges.

Here we use the integral Coats–Redfern method⁸ to perform the kinetic analysis for the TG curves, and the basic equation of this method for component i ($i = 1, 2$) is

$$\ln\left[\frac{g_i(\alpha_i)}{T^2}\right] = \ln\left\{\frac{A_i R}{\beta E_i}\left[1 - \frac{2RT}{E_i}\right]\right\} - \frac{E_i}{RT} \quad (3)$$

where the subscript i refers to the pseudo component i , the variable α is the degree of transformation of the

sample itself defined globally, i.e., $\alpha = (w_0 - w)/(w_0 - w_\infty)$, while α_i refers to the transformation of the component i ($i = 1, 2$), i.e., $\alpha_i = (w_{i0} - w)/(w_{i0} - w_{i\infty})$ ($i = 1, 2$). The w_0 , generally not 100% due to the water evaporation, accounts for about 10% of the total mass loss. R is the ideal gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$). The parameter β is heating rate ($^\circ\text{C/min}$), T is the absolute temperature of the sample, and $g_i(\alpha_i)$ is the integral of the reciprocal of $f_i(\alpha_i)$ between $0 \sim \alpha_i$ ($i = 1, 2$), where the specific form of $f_i(\alpha_i)$ represents the hypothetical model of the reaction mechanism. In general, the term $(1 - 2RT/E_i)$ appears to be reasonably constant for most values of E in the temperature range over which most reactions occur. A plot of $\ln[g_i(\alpha_i)/T^2]$ against $1/T$ should result in a straight line of slope $-E_i/R$ for the correct reaction mechanism. Obviously, the key of this method is the determination of the correct form of $f_i(\alpha_i)$ ($i = 1, 2$) by trial. Based on the correct form of $f_i(\alpha_i)$ ($i = 1, 2$), the activation energy and preexponential factor can be determined respectively from the slope and intercept terms of the regression line.

The calculation results show that the first order function (O1) leads to good linearity with regard to eq. (3) for all the wood and leaf samples without exception. Taking the leaf sample of fir (LF) as an example, with 10 different functions in Table II used, Figure 1 shows the plots of $\ln[g_i(\alpha_i)/T^2] \sim 1/T$ with the kinetic scheme. By observation and the comparison of the correlation coefficients, it can be verified that the O1 function leads to the best linearity for both components 1 and 2. Similar plots are obtained for other samples, and the presentation of these plots is omitted here because of space constraint. The kinetic parameters obtained are listed in Table III. This table also lists the kinetic parameters calculated by selecting the model function to be O0, O2, and O3, respectively. It can be seen from Figure 1 that for the model functions based on “order” of reaction, the plots for the functions of O2 and O3 bend down greatly, while the plot

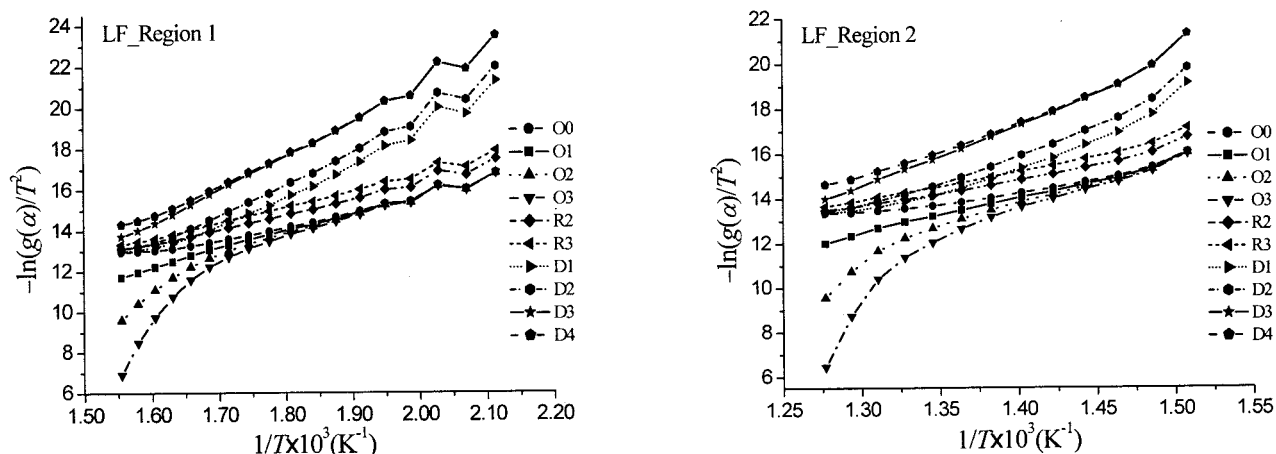


Figure 1 Plot of $\ln[g(\alpha)/T^2] \sim 1/T$ for the sample of LF.

for O0 bends up slightly. It is the function of O1 that shows the best linearity. Therefore the kinetic parameters obtained by O0, O2, and O3 have no kinetic

significance. However, as to be clarified in the later section, KCE can be revealed from these “pseudo” kinetic parameters.

TABLE III
Kinetic Parameters Calculated by the Reaction Order Model Functions^a

Sample	$n = 0$		$n = 1$		$n = 2$		$n = 3$	
	E (kJ/mol)	$\text{Ln}A$ (A, min ⁻¹)	E (kJ/mol)	$\text{Ln}A$ (A, min ⁻¹)	E (kJ/mol)	$\text{Ln}A$ (A, min ⁻¹)	E (kJ/mol)	$\text{Ln}A$ (A, min ⁻¹)
LF	57.10	9.45	72.34	13.08	94.80	18.38	122.72	24.96
	91.39	12.37	133.23	20.38	199.91	31.47	284.19	46.24
WF	60.10	10.20	81.60	15.12	113.19	22.32	152.67	31.28
	72.25	9.85	136.25	21.70	251.09	41.37	399.23	67.35
LB	47.69	7.75	69.10	12.81	105.05	21.22	150.48	31.82
	57.44	6.71	94.08	13.41	148.69	22.56	217.59	34.44
WB	57.14	9.78	79.62	15.07	117.82	23.98	166.04	35.21
	58.92	7.37	112.67	17.18	213.24	34.35	342.12	56.76
LT	42.73	6.34	51.56	8.56	62.79	11.38	76.16	14.72
	86.36	10.55	130.61	18.92	198.82	29.38	284.80	43.70
WT	77.46	14.22	99.43	19.33	132.29	26.94	173.41	36.43
	63.48	8.47	93.95	13.96	136.59	21.74	189.47	31.28
LW	48.91	8.03	67.17	12.33	93.14	18.39	125.33	25.87
	80.02	10.61	122.16	18.81	200.24	32.17	299.17	49.84
WW	82.03	15.26	95.73	18.48	112.54	22.41	132.21	27.02
	62.65	8.21	123.55	19.19	242.87	39.72	396.07	66.35
LHO	54.00	8.91	69.30	12.60	92.31	18.13	121.04	25.01
	70.87	8.74	108.43	15.74	167.35	25.49	241.79	38.35
WHO	65.67	11.46	83.28	15.65	109.56	21.88	142.42	29.65
	37.91	3.71	86.68	12.19	184.02	28.72	309.72	50.06
LH	49.06	8.06	62.89	11.53	83.52	16.67	109.28	23.07
	149.02	21.88	201.50	32.31	287.59	46.28	396.29	65.38
WH	79.52	15.23	95.82	19.15	116.64	24.13	141.51	30.07
	78.90	11.20	113.25	17.69	162.86	26.59	224.78	37.88
LMP	47.97	7.35	66.43	11.57	93.15	17.64	126.47	25.18
	72.19	9.13	136.73	20.92	255.28	40.35	408.03	66.27
WMP	65.85	11.66	84.39	16.04	111.50	22.40	145.28	30.32
	56.55	6.75	101.62	15.43	162.88	25.40	249.25	40.44
LN	53.48	8.88	67.07	12.18	86.56	17.09	111.32	23.21
	124.71	17.70	160.87	24.92	209.29	32.51	268.22	42.79
WN	53.87	8.96	71.90	13.28	100.27	19.98	135.79	28.37
	62.07	7.40	92.75	13.05	136.61	20.45	191.28	29.97

^a For each sample, the upper row denotes the mass loss process in the lower temperature range, and the lower row denotes the mass loss process in the higher temperature range.

Since in the kinetic analysis only a few number of points are used, the TG and DTG curves resulted from the experiment and calculation can be fully compared, and the satisfactory agreements between them may be looked on as an acceptable justification of the model. With this suggestion in mind, in the present work, the obtained apparent kinetic parameters are first substituted into the general integral kinetic equation to obtain the calculated TG curves. The exact value of the temperature integral is calculated numerically by using the 1/3rd Simpsons rule. The calculated TG curve is then substituted into rate equation leading to the calculated DTG curve. By comparing the calculated and experimental TG-DTG curves, the kinetic model may be further tested and verified. Representative plots of comparison are presented in Figure 2 for the nanmao leaf (LN) and nanmao wood (WN) samples. Similar plots are obtained for other samples, and so omitted here for the limitation of space. The results show that the experimental and calculated TG curves have excellent agreements for all the samples.

KCE is often correlated with the concept of isokinetic point (IKP). IKP refers to a common point of intersection of Arrhenius lines [i.e., $\ln k(T)$ vs T^{-1} , where

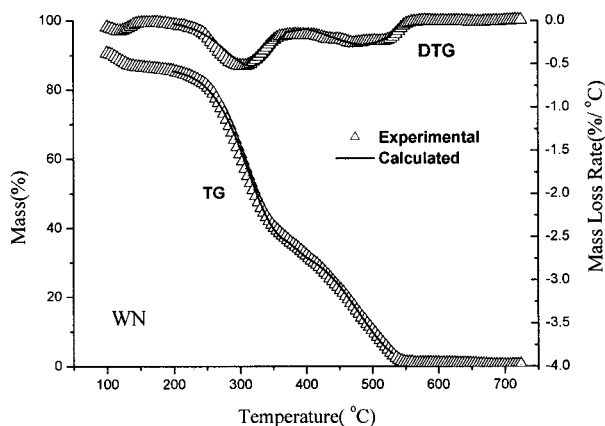
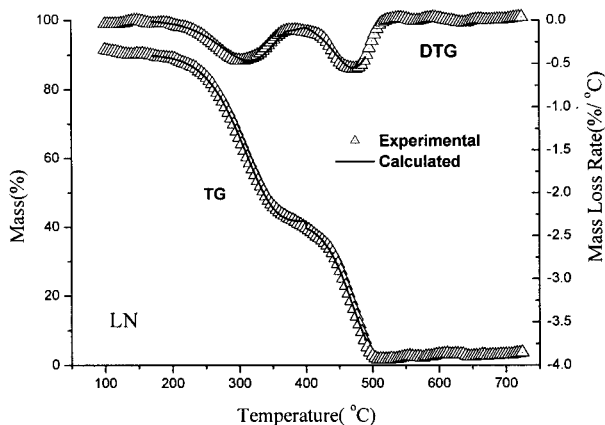


Figure 2 Comparison of the experimental and calculated TG-DTG curves for the leaf and wood samples of nanmao (LN and WN).

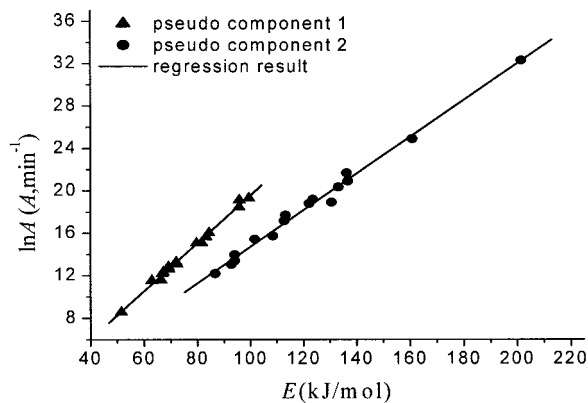


Figure 3 Compensation plot of kinetic parameters for all samples (due to species variation).

k is the rate constant). From the Arrhenius equation we obtain

$$\ln A = \frac{1}{RT} E + \ln k \tag{4}$$

Comparing this expression with (1), we can see that for all the rate processes whose kinetic parameters are in the parameter set that satisfies (1), the corresponding Arrhenius lines have a common point of intersection (T_{iso}^{-1} , $\ln k_{iso}$):

$$T_{iso} = \frac{1}{Ra} \tag{5}$$

$$\ln k_{iso} = b \tag{6}$$

Equation (1) can thus be rewritten as

$$\ln A = \frac{1}{RT_{iso}} E + \ln k_{iso} \tag{7}$$

Using the kinetic parameters listed in Table III for the model function O1, we obtain the plot $\ln A \sim E$ respectively corresponding to the two pseudo components, as shown in Figure 3. The kinetic parameters E and A are indicated to satisfy the KCE relationship, and the two linear relations are respectively:

$$\begin{aligned} \text{Component 1 } \ln A &= -3.0 (\pm 0.4) \\ &+ 0.226 (\pm 0.005) E \quad r = 0.9968 \end{aligned}$$

$$\begin{aligned} \text{Component 2 } \ln A &= -2.5 (\pm 0.5) \\ &+ 0.173 (\pm 0.004) E \quad r = 0.9957 \end{aligned} \tag{8}$$

where r is the correlation coefficient. E is expressed in kJ/mol and A in min^{-1} . The figures in brackets represent errors limits at 95% confidence for the reported

parameters. As indicated above, many factors variation can lead to the KCE relationship. However, the KCE relationship due to species variation has rarely been reported so far.

As indicated previously, the concepts of “order of reaction” and “concentration” are not applicable for the solid-state reaction. In this sense, although the true energy barrier may be related to the calculated value of E in the solid state reaction kinetics, its true relationship will not be clear until a definition or the significance for a “mole of solid” is established. Hence, in order to avoid confusion and to distinguish the difference between gas phase and solid state reactions, A should be called the “preexponential factor” rather than the “frequency factor,” and E should be called the “apparent activation energy.” However, from the present analysis we can see that the two pseudo components respectively satisfy two distinct KCE relations, which is consistent with the fact that the mass losses in these two temperature regions are respectively controlled by two different kinetic processes. This implies that KCE relations, although based on apparent kinetic parameters, in some degree reveal the reaction mechanism from aside. KCE relation to some degree provides a clue to recognize whether or not the obtained parameter set (E, A) fit the same mass loss kinetics: If two parameter sets (E, A) satisfy two different KCE relations, then different kinetics may be correlated with them.

Then, if two sets (E, A) satisfy the same KCE relation, can it be concluded that they satisfy the same kinetic expressions? The answer seems to be *No*. We shall clarify this point in the following paragraphs.

Although the model function O1 has been verified to be the most reasonable kinetic description of the biomass decomposition in this study, pseudo kinetic parameters can be calculated by different reaction orders. The apparent kinetic parameters corresponding to these reaction orders are listed in Table III. The plots of $\ln A \sim E$ for all the samples are indicated in Figure 4. It is obvious that for the two pseudo components, very high correlation coefficients of the plots are achieved. The regression straight lines are respectively

$$\begin{aligned} \text{Region 1: } \ln A = & -3.5(\pm 0.1) \\ & + 0.233(\pm 0.001)E, r = 0.9978 \end{aligned}$$

$$\begin{aligned} \text{Region 2: } \ln A = & -2.9(\pm 0.2) \\ & + 0.173(\pm 0.001)E, r = 0.9976 \quad (9) \end{aligned}$$

This KCE is derived from the model variation, and so it is believed to be lack of chemical significance. In this sense it can be called “pseudo KCE.” The implication of this pseudo KCE has not yet been realized. However, it can be concluded that, when different param-

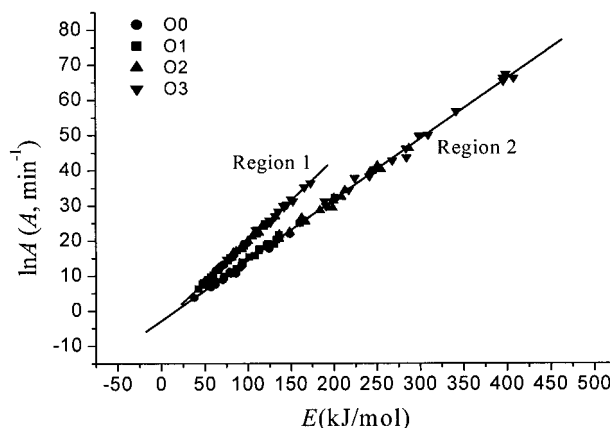


Figure 4 Compensation plot of kinetic parameters for all samples and reaction order models ($n = 0, 1, 2, 3$) (due to species variation and model variation simultaneously).

eter sets (E, A) are found to satisfy a specific KCE relation, it is still possible that they support different kinetic descriptions.

On the criterion to distinguish between true and false kinetic compensation effect

As clarified earlier, the KCE relation is in fact equivalent to the so-called isokinetic effect. In the coordinate of $\ln k - 1/T$, the straight lines corresponding to different kinetic parameters (A, E) satisfying KCE relation have a common intersection point ($1/T_{\text{iso}}, \ln k_{\text{iso}}$). Agrawal⁹ claimed a criterion to recognize the KCE relation, i.e., KCE relation exists only if the plots $\ln k \sim 1/T$ display concurrence at a single point. If a series of reaction displays the linear plot of $\ln A \sim E$ with relatively high correlation coefficient, but fails to display a single point of concurrence, then the system exhibits a false compensation effect. Agrawal used a few examples in the literature to justify his viewpoint. This criterion is correct in theory, but is obviously too restrictive to meet. Later, Agrawal did not persist in his original rigorous procedures. In one of his papers² he clarified that in actual experimental data, there will be experimental errors in measuring temperature T and computational errors in determining the reaction rate constant k . Due to these errors, even if the system exhibits a true KCE, a single point of concurrence may not be observed. Instead, the rates should at least appear to converge at T_{iso} . But in the face of so many straight lines, how can we judge whether or not they have a trend to converge at a single point quantitatively? This is to be clarified as follows.

As indicated earlier, for the lower or high temperature range, the kinetic parameters listed in Table III indicate linear relation between $\ln A$ and E . Here and in the following discussion, we use the mass loss process of the pseudo component 1, which occurs in the lower temperature range as the example to illus-

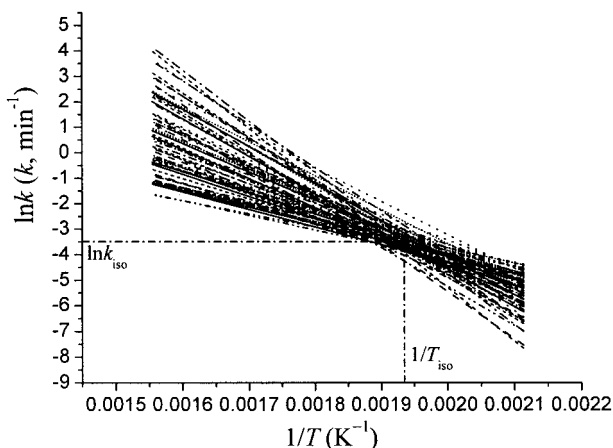


Figure 5 Plot of $\ln k$ vs T^{-1} for all the samples and reaction order models ($n = 0, 1, 2, 3$) (due to species variation and model variation simultaneously).

trate our point. Figure 5 indicates the plot of $\ln k$ vs T^{-1} for all the kinetic parameters listed in Table III. Obviously, these straight lines do not have a common point of intersection; however, they tend to converge at a single point. We now define a measure to characterize this tendency quantitatively.

As we know, whether or not the effect is a real or false compensation effect, the $\ln k_{\text{iso}}$ and $1/T_{\text{iso}}$ can be proximately evaluated from expression (9). For each straight line in Figure 5, $(\ln k)_{T = T_{\text{iso}}}$ can be calculated. In fact, $(\ln k)_{T = T_{\text{iso}}}$ can be looked on as a random variable since the straight lines in Figure 5 are independent to each other. The value of $\ln k_{\text{iso}}$ can be looked on as the predicted value of $(\ln k)_{T = T_{\text{iso}}}$. Thus all the $(\ln k)_{T = T_{\text{iso}}}$ values obtained can be looked as the random samples. When the number of samples is relatively high (generally higher than 50), the mean value of the samples can be used as the estimation. If the estimation of $(\ln k)_{T = T_{\text{iso}}}$ proves to be close to $\ln k_{\text{iso}}$, then the compensation effect obtained is recognized to be a true KCE.

By the above procedure we obtain that the mean value of $(\ln k)_{T = T_{\text{iso}}}$ is -3.49 , which is very close to -3.5 as indicated in expression (9), and the standard deviation of the mean value is 0.04 . This result indicates that the KCE obtained in this article is a real compensation effect, although the implication of the so-called pseudo compensation effects due to model variation is not yet clear.

CONCLUSIONS

1. A simple kinetic scheme consisting of two first-order independent reactions that occur respectively during the lower and higher temperature ranges is suitable to describe the mass loss behaviors of biomass samples.
2. The kinetic parameters E and A of biomass decomposition derived from the species variation the variation of model functions exhibit the kinetic compensation effect.
3. When different parameter sets (E, A) are found to satisfy a specific KCE relation, it is still possible that they support different kinetic descriptions.
4. The $(\ln k)_{T = T_{\text{iso}}}$ can be used a random variable to help distinguish between real and false compensation effect quantitatively by statistical means.

NOMENCLATURE

A	apparent preexponential factor (min^{-1})
E	apparent activation energy (kJ mol^{-1})
n	apparent reaction order
r	correlation coefficient
R	gas constant ($\text{kJ K}^{-1} \text{mol}^{-1}$)
T	absolute temperature (K)
T_0	initial decomposition temperature (K)
T_{m1}, T_{m2}	the temperatures of the DTG peaks (K)
T_f	final decomposition temperature (K)
w	sample mass percentage
w_0	initial sample mass percentage
w_∞	residual sample mass percentage
α	degree of transformation
β	heating rate (K min^{-1})

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