J. Chin. Inst. Chem. Engrs., Vol. 34, No. 5, 587-593, 2003

Short communication

Modeling Sludge as Continuous Mixture during Thermal Pyrolysis

R. M. Wu [1], **C. P. Chu** [2], **D. J. Lee** [3]
Department of Chemical Engineering, National Taiwan University
Taipei, Taiwan 106, R.O.C.

C. Y. Chang [4]
Institute of Environmental Engineering, National Taiwan University
Taipei, Taiwan 106, R.O.C.

Abstract—Interpretation of thermogravimetric analysis (TGA) data of organic materials usually faces difficulties for distinguishing the weight versus temperature data into a complex reaction scheme. This work proposed a general scheme to converting the TGA data into an Arrhenius-type kinetics that regarded the pre-exponential factor, the activated energy, and the reaction order as functions of conversion. The TGA data of two oily sludges were used as demonstrative examples. Agreement between obtained correlation with the experimental data was satisfactory.

Key Words : Thermal pyrolysis, Continuous mixture, Oil sludge, Kinetics

INTRODUCTION

Pyrolysis process involves heating of organic materials in an inert atmosphere, from which part of the organic matters could be released and recycled (Suzuki *et al.*, 1988; Campbell and Bridle, 1989). Heavy metals (except mercury and cadmium that are going to their salts) could be safely enclosed in the solid residues (Kaminsky and Kummer, 1989). Thermogravimetric analysis (TGA) is capable of providing kinetic data of pyrolyzing organic materials at evaluated temperatures (Caballero *et al.*, 1995). For interpreting the obtained TGA data, literature works commonly adopted a skeleton model, like the parallel scheme proposed by Conesa *et al.* (1997), and then evaluated the model parameters based on regression of pyrolysis data.

Pyrolysis of sewage sludge had been extensively investigated (Kaminsky *et al.*, 1982; Kaminsky and Kummer, 1989; Stammbach *et al.*, 1989; Piskorz *et al.*, 1986; Kasakura and Hiraoka, 1982; Urban and Antal, 1982; Lu and Do, 1991; Jeyaseelan and Lu, 1996; Lu and Lau, 1996; Caballero *et al.*, 1997; Conesa *et al.*, 1997; Conesa *et al.*, 1998; Inguanzo *et al.*, 2002). Various skeleton models had been proposed for sludge pyrolysis kinetics. For instance, Dumpelmann *et al.* (1991) developed a model for pyrolysis of sewage sludge that could predict the maximum weight loss in a fluidized bed. Conesa *et al.* (1997, 1998) proposed a kinetic model for the pyrolysis of anaerobically digested and non-digested sewage sludge. Chu *et al.* (2001) quantitatively investigated the thermal pyrolysis characteristics of an activated sludge sample, with an especial attention to the presence of polyelectrolyte. These authors observed two maxima on their pyrolysis curves, based on which a two-species kinetic model was adopted. Conesa *et al.* (1998) proposed the more complicated kinetic model that contained six species during thermal pyrolysis. Nevertheless, since the skeleton models could not comprehensively incorporate the actual chemical reactions involved, they should be considered as preliminary in nature. Conesa *et al.* (2001) commented the use and the applicable range of different skeleton models. The difficulties faced by researchers are to distinguish the weight versus temperature data into a complex reaction scheme (Boldyreva, 1987).

Reactions involving a very large number of components are of interest in many processes, like thermal and catalytic cracking, steam reforming, and polymerization reactions (Aris and Cicarelli, 1994). To simplify the analysis a promising approach consists of describing the kinetics in terms of a continu-

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[1] 吳容銘
[2] 朱敬平
[3] 李篤中, To whom all correspondence should be addressed
[4] 張慶源

ous distribution of species rather than a discrete number of components (Astarita and Ocone, 1988, 1990; Aris, 1989; Cicarelli *et al.*, 1992; McCoy, 1993; Amundson and Aris, 1993). Such an approach considers no real chemical scheme that occurs during reaction, but uses some relevant process index (like boiling point of mixture in distillation) to characterize the reaction for engineering application sake. During thermal pyrolysis of complicated organic materials, like sludge, various compounds would be generated and released from the sample surface. Instead of seeking a comprehensive kinetic model, we proposed an alternative approach: to model the organic materials as a continuous mixture of components, with their conversion as an index parameter. This proposal is not totally new. Conesa *et al.* (2001) listed some related works using pyrolysis temperature as the continuous index. However, the use of pyrolysis temperature could not interpret the effects of heating rate on the pyrolysis characteristics. To adopt the conversion as the classification index is based on the knowledge that thermal pyrolysis is mainly a surface reaction and the surface area of sample would change with conversion, hence could be used to characterize the reaction.

KINETIC MODEL

Assuming that the pyrolysis kinetic follows an Arrhenius-type expression:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(\frac{-E}{RT}\right)(1-\alpha)^{n}, \qquad (1)$$

where α is the conversion; E is the activation energy; A, the pre-exponential factor; n, the reaction order; and R, the gas constant. The parameters E, A, and n are taken as (yet to determine) functions of conversion α. Then the distributions of these parameters could be constructed in the following two steps. First, Eq. (1) is arranged into the following form:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln\left[A(\alpha)(1-\alpha)^{n(\alpha)}\right] + \left(\frac{-E(\alpha)}{R}\right)\left(\frac{1}{T}\right). \qquad (2)$$

Apparently the slope of the natural logarithm of pyrolysis rate, $\ln(\mathrm{d}\alpha/\mathrm{d}t)$, versus $1/T$ curves at each specific α estimates the value of $(-E(\alpha)/R)$. The activation energy distribution with respect to α could be subsequently obtained.

Secondly, rearrange Eq. (2) as follows:

$$\ln\left[\frac{\dfrac{\mathrm{d}\alpha}{\mathrm{d}t}}{\exp\left(\dfrac{-(E(\alpha))}{RT}\right)}\right] = \ln A(\alpha) + n(\alpha)\ln(1-\alpha). \qquad (3)$$

Then, together with the $E(\alpha)$-distributions determined using Eq. (2) and the $(\mathrm{d}\alpha/\mathrm{d}t)$ data collected in experiments, the distributions of A and n could be constructed by finding the slopes and intercepts of Eq. (3) at various α's.

SAMPLE DATA

The TGA data for thermal pyrolysis of the oil sludge were extracted from Shie (2001) and were used herein for sample calculation. The oil sludge was taken on Sep. 22, 1997 from the petroleum refinery plant of the northern Taiwan. The thermal analyzer (SETARAM, 77A-92) was employed for recording the thermographs with Ar (sample #1) and CO_2 (sample #2) as the carrying gas. The oil sludge is first drying at 378K for 24 h. The cell temperature was heated at a rate of 0.09K/s, 0.21K/s, or 0.36K/s till 873K, for demonstrating the effects of heating speed. The weight-time (w-t) data represent the TGA curve (Figs. 1(a)-(b)).

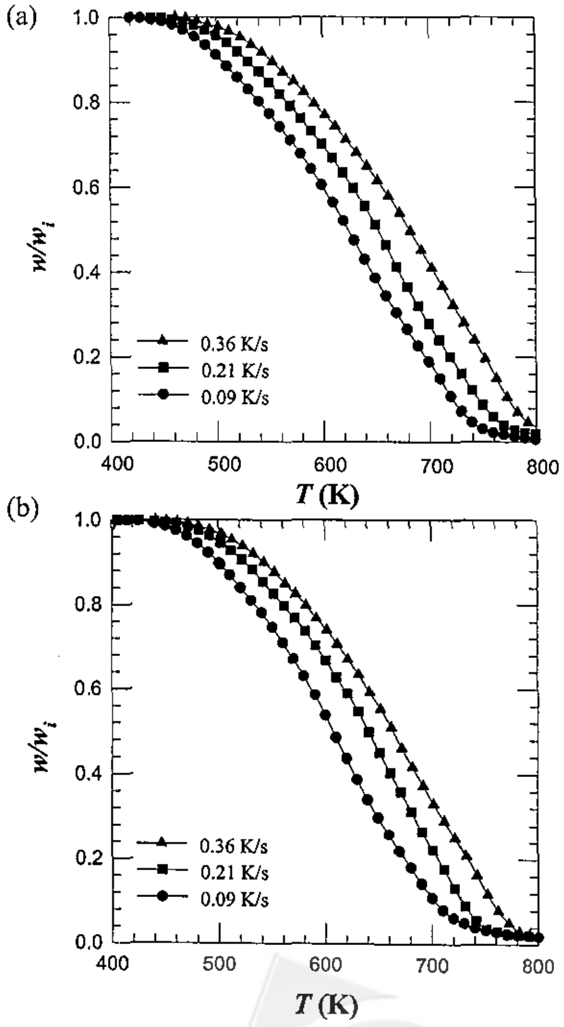

Fig. 1. TGA data with three heating rates, 0.09, 0.21, and 0.36K/s; (a) sample #1; (b) sample #2.

Define the pyrolysis conversion as ratio, $\alpha = (w_i - w)/(w_i - w_f)$, where w, w_i, and w_f are the sample weight at time t, at time zero (initial), and at the end of the test, respectively. Figures 2(a) and (b) depict the $d\alpha/dt$ versus T data for these two samples (samples #1 and #2) at three different heating rates. These curves show a single-peak characteristic, with their peaks occur at higher temperatures and/or at greater heating rates when CO_2 is present.

At each conversion α, there are three ($d\alpha/dt$) values could be obtained at three distinct heating rates. Then the $E(\alpha)$ values could be estimated at each α using linear regression technique. Based on Eq. (2), the $E(\alpha)$-distributions were constructed and demonstrated in Figs. 3(a) and 3(b). As the reaction proceeded, the activation energy generally increased with conversion, with a local minimum occurring at $\alpha = 0.25$ for the sample #2. The range for the E/R for samples #1 and #2 are 8,000-12,600K and 8,700-16,500K, respectively.

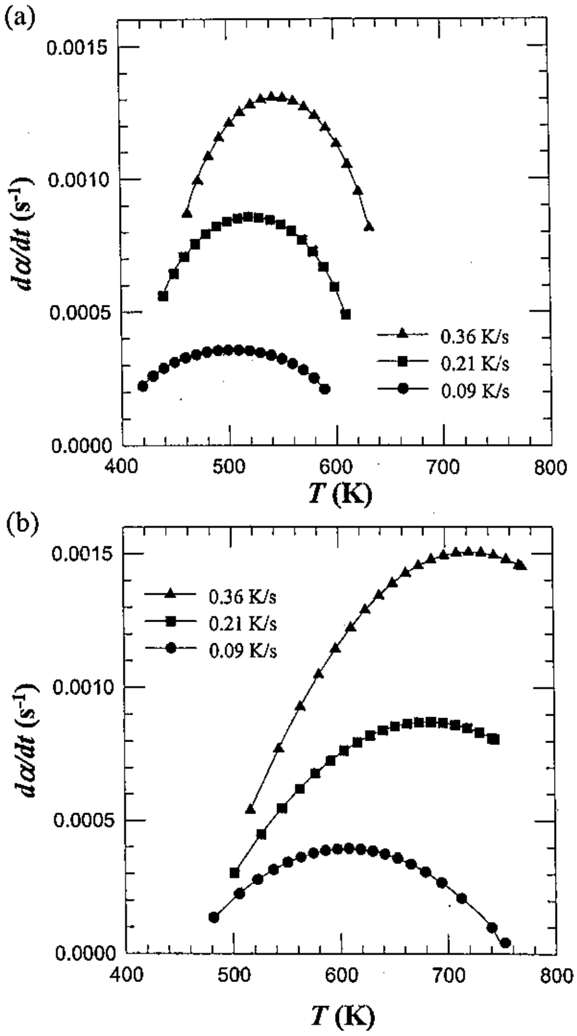

Fig. 2. Conversion rates of oily sludge with temperature and three heating rates, 0.09, 0.21, and 0.36K/s. (a) sample #1; (b) sample #2.

With the $E(\alpha)$-distributions depicted in Fig. 3 and the ($d\alpha/dt$) data in Fig. 2, we can plot Eq. (3) in Figs. 4(a) and 4(b). Then the intercept and the slope estimate the distributions of A and n. Figures 5 and 6 illustrate these distributions. The oily sludge pyrolyzed in Ar-gas would exhibit a frequency factor ranging 1,000-4,000 s, with a local maximum occurring at $\alpha = 0.4$. The addition of CO_2 would instead yielded a very high frequency factor at low α. Meanwhile, the reaction order n for sample #1 ranges −2 to +0.4, and that for sample #2, −12 to +32. Apparently these values are not reasonable for real kinetics, and are merely the fitting parameters to represent the TGA data.

Figure 7 demonstrates the sample data and the fitting. The agreement between the experiments and the correlation based on the distributions of E, A, and n in Figs. 3, 5, and 6 is satisfactory. Notably, despite the Arrhenius-type kinetics in Eq. (1), no complicated kinetic schemes are *a priori* assumed for data interpretation. This proposed scheme is hence skeleton-model free and is general for interpreting all kinds of TGA data.

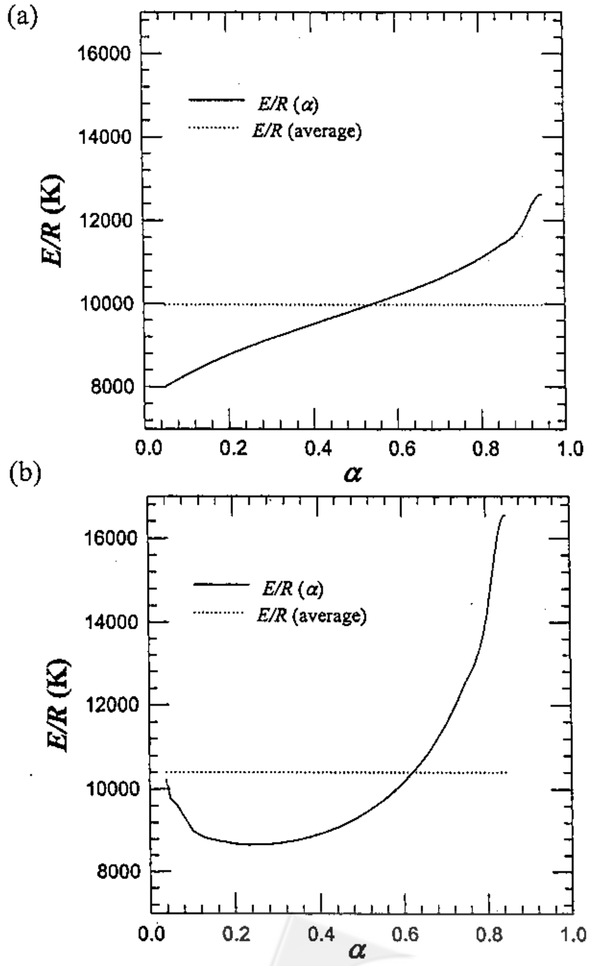

Fig. 3. The distributions of activation energy for the pyrolysis processes determined by data regression using Eq. (2). (a) sample #1; (b) sample #2.

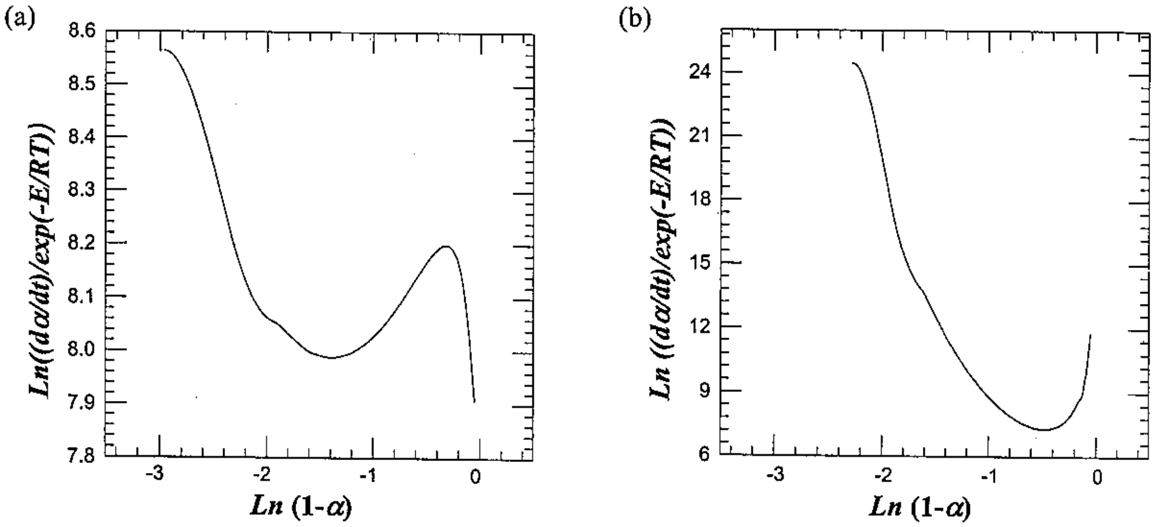

Fig. 4. Graphical construction of Eq. (3) for data regression. (a) sample #1; (b) sample #2.

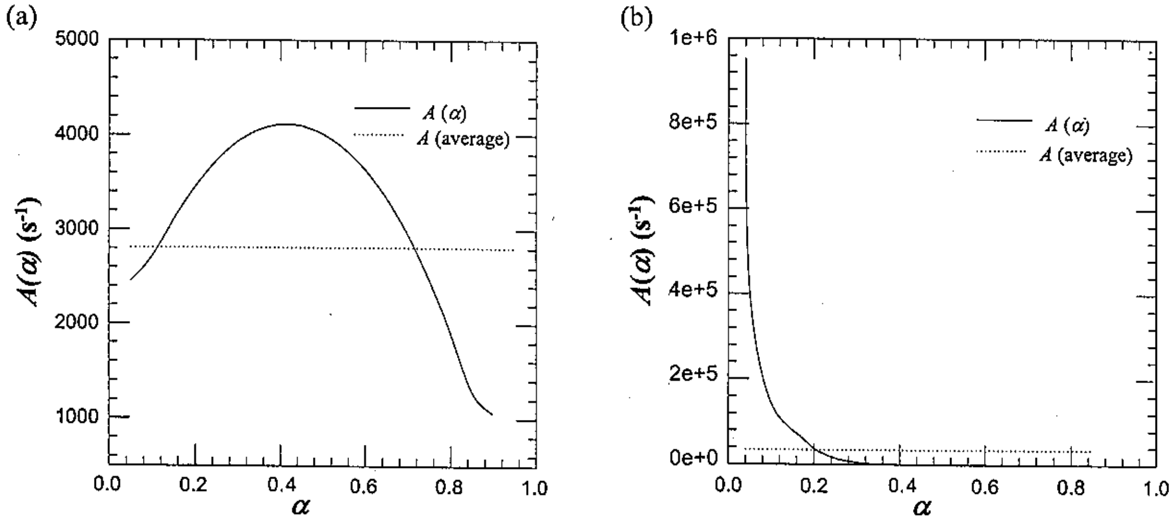

Fig. 5. The distributions of frequency factor for the pyrolysis processes determined by data regression using Eq. (3). (a) sample #1; (b) sample #2.

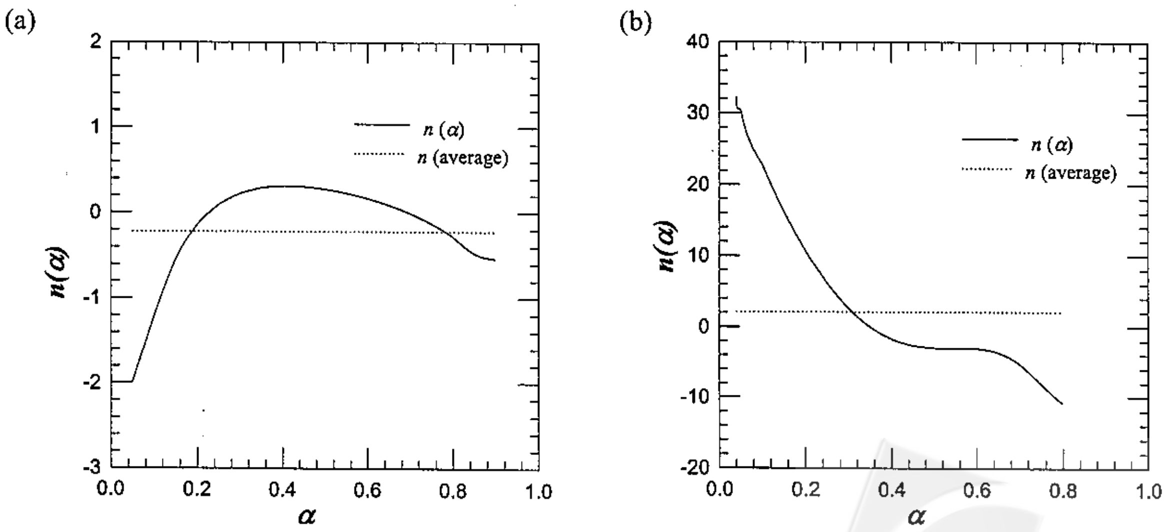

Fig. 6. The distributions of reaction order for the pyrolysis processes determined by data regression using Eq. (3). (a) sample #1; (b) sample #2.

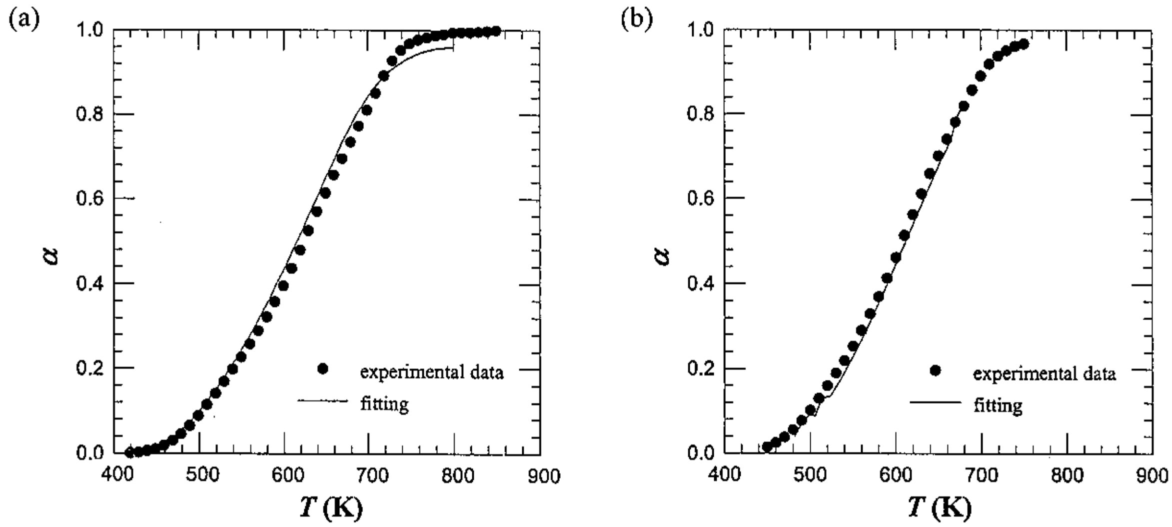

Fig. 7. Comparisons between the fitting results and the experimental data. (a) sample #1; (b) sample #2.

For the sake of comparison, the average activation energy is defined as follows:

$$E_{avg} = \int_0^1 E(\alpha)\,\mathrm{d}\alpha\,. \tag{4}$$

Replace the $E(\alpha)$ by E_{avg} estimated above, the average n and A values could be estimated from the slope and intercept by linearly regressing all data presented in Fig. 4. An average kinetic parameter represents a horizontal line in Figs. 3, 5, and 6. All the demonstrated E-, A-, and n-distributions in these figures are markedly deviated from a constant. The employment of average parameters in reactor design and optimization may lead to erroneous conclusion.

A constraint for the validity of the proposed scheme remains the hidden assumption that the intrinsic kinetics of pyrolysis would not be affected by the applied heating rates. Restated, the $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ should be linearly dependent on $(1/T)$, or the pyrolysis rate should follow an Arrhenius-like behavior. This assumption fails for the flocculated wastewater sludge as demonstrated by Chu *et al.* (2001), whose pyrolysis kinetics shifted when the heating rate increased beyond 20K/min. This occurrence would lead to a poor regression of TGA data using Eq. (2).

CONCLUSION

Lump-parameter kinetic model is commonly adopted in literature for interpreting the thermogravimetric analysis (TGA). A skeleton chemical scheme is normally required for model construction, which limits the accuracy of data fitting and the applicable range for the proposed model. To build up an appropriate kinetic model is a challenging task for related researchers. This work proposed an alternative approach for modeling the sludge as a continuous mixture using an Arrhenius-type kinetic expression. Rather than searching for an average kinetic parameter valid over the entire temperature range investigated, a two-step procedure was employed to construct the distributions of the activation energy, the pre-exponential factor, and the reaction order as functions of sample conversion. Such an approach could be considered as "skeleton model-free" and could be utilized for thermal contactor design without taking into account the detailed structure of the chemical scheme involved.

NOMENCLATURE

A	pre-exponential factor, s^{-1}
E	activation energy, N · m/mol
E_{avg}	average activation energy, N · m/mol
n	reaction order
R	gas constant, N · m/mol · K
T	temperature, K
t	reaction time, s
w	sample weight at time t, kg
w_f	sample weight at the end of test, kg
w_i	sample weight at initial time, kg

Greek symbol

α	conversion

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(Manuscript received Dec. 9, 2002, and accepted Mar. 26, 2003)

視污泥為連續混合物質於熱解處理之模式分析

吳容銘　朱敬平　李篤中
國立台灣大學化學工程學系

張慶源
國立台灣大學環境工程學研究所

摘　要

欲將有機物質熱重分析 (TGA) 數據進行動力學分析時常面臨選擇複雜反應式之困難，本論文提出一基於阿瑞尼斯反應動力之普遍適用之方案，將前指數參數 (pre-exponential factor)、活化能 (activated energy) 及反應級數 (reaction order) 均視爲轉化率 (conversion factor) 之連續函數。此方法不需假設複雜之反應模式，因此爲一泛用方法。本論文中將此方法套用於 2 種油污泥之 TGA 數據，得到之關聯式與實驗數據極爲相近。