PYROLYSIS KINETICS OF THAI LIGNITES

S.TIA *, W. KRITPIPHAT, N. PHUPOKSAKUL AND N. ANANATA-ART

Combustion Research Laboratory
Department of Chemical Engineering
King Mongkut's Institute of Technology Thonburi
Bangkok 10140, Thailand

ABSTRACT

In this study the pyrolysis kinetics of Thai lignites were estimated by using nonisothermal Thermogravimetric Analysis (TGA). The results from TGA showed that the ultimate volatiles of five lignite samples were in the range of 30.41- 46.37 % by weight of dry lignite. Using a two-component model, the average value of estimated activation energy of these samples were 6.36 and 12.87 kcal.gmol $^{-1}$ for the first and second components respectively. For the distributed activation energy model the average values of the activation energy and the standard deviation were 57.95 kcal.gmol^{-1} and 18.45 kcal.gmol^{-1} respectively. The individual volatile product model fits the experimental data quite well when using the set of kinetic parameters for Montana lignite.

NOMENCLATURE

E	activation energy
k_0	frequency factor
q	heating rate
R	universal gas constant
T	absolute temperature
t	time
V^*	ultimate volatile yield
w	weight
χ	fraction of weight loss
σ	standard deviation

Subscripts

f	final
i	component or volatile product i
o	initial

INTRODUCTION

The economically mineable reserves of coal in Thailand, which are mostly lignite and subbituminous coals, was about 800 Mtons in 1987 [1]. The ultilization of this coal is mainly for power generation and industrial boilers/furnaces, and usage is significantly increasing at a rate of about 34% per year[2]. It is estimated that indigenous coal ultilization will increase from 12.5 Mtons/y in 1990 to 38 Mtons/y by 2000 [2]. Therefore, detailed study of the combustion-related properties of these low rank coals is essential for combustor design and improvement.

Pyrolysis is the initial step in coal combustion and the evolved volatiles contribute about 30-40% of the total amount of heat released during combustion of low grade coal. The rate of heat release from the volatiles combustion is determined by the rate at which they can escape from the coal particle and combine with oxygen in the gas phase. The study of pyrolysis kinetics will provide the information for predicting the evolution rate and composition of volatiles. One of the methods that has been widely used for coal pyrolysis study is Thermogravimetric Analysis (TGA). It provides a measurement of the weight loss of the sample as a function of time and temperature. This paper describes the derived kinetics of Thai lignite pyrolysis by using nonisothermal TGA. Results from each pyrolysis model were compared in term of activation energy.

THEORY

The general expression for weight loss rate of coal during pyrolysis can be written as [3]:

$$\frac{dx}{dt} = k_o \exp(-E/RT) f(x) \qquad \text{———} (1)$$

where x = fraction of weight loss$[(w_o-w)/(w_o-w_f)]$, w_o = initial weight of sample, w=sample weight at time t, w_f=sample weight at t approch infinity, k_o =frequency factor, E=activation energy, R=universal gas constant, T=absolute temperature, and $f(x)$=function of x depending on the reaction mechanism.

For linear heating rate, $q=dT/dt$, equation(1) can be expressed as:

$$\frac{dx}{dT} = (k_o/q)\exp(-E/RT) f(x) \qquad \text{———} (2)$$

Two-Component (TC) Model

It has been pointed out that simple first-order kinetic was inadequate to characterize the weight loss of one of the Thai lignite sample during pyrolysis[3]. However, a good correlation was obtained when simple first-order reaction was separately fitted the TGA data in the high and low temperature regions, which has the dividing line at about 730 K. This behaviour, as postulated by the authors[3], corresponds to the two-component constitution medel of coal structure[4]. Verification is therefore essential.

The mechanism of coal pyrolysis based on the TC model was proposed by Essenhigh [4]. The two-component hypothesis has been interpreted in terms of the process of coalification represented by component 1 (parent material) being transformed into component 2 (antracitic structure). The two components are then presumed to pyrolyze as noncompeting independent reactions with different products[4]. The simplified mechanism is:

$$\begin{array}{l} Coal \rightarrow Component\ 1 \rightarrow VM_1\ ,\ T<650\ C \\ \quad \searrow Component\ 2 \rightarrow VM_2{+}char\ ,\ T>650\ C \end{array}$$

Assuming that the decomposition of each component can be represented by first-order reaction, equation (2) can be written as:

$$\frac{dx_i}{dT} = (k_{oi}/q)\exp(-E_i/RT)(1-x_i)\ ,\ i=1,2 \quad \text{—} (3)$$

$$x_1 = (w_o-w_1)/(w_o-w_1^*) = (w_0-w_1)/V_1^* \text{—} (4a)$$

$$x_2 = (w_1^*-w_2)(w_1^*-w_2^*) = (w_1^*-w_2)/V_2^* \text{—} (4b)$$

where w_o is the initial weight of coal sample, w_i is the weight of the coal sample during the decomposition of component i (i=1,2), w_i^* is the weight of the coal sample after decomposition of component i was completed, and V_i^* is the ultimate volatile yield of component i.

Equation (3) can be integrated to yield[5]:

$$\ln[-\ln(1-x_i)/T^2] = \ln\left[\frac{k_{oi}R}{qE_i}\left\{\begin{matrix} 1-2RT/E_i \\ 1-5\ (RT/E_i)^2 \end{matrix}\right\}\right] - \frac{E_i}{RT} \quad (5)$$

By plotting $ln[-ln\,(1-x_i)/T^2]$ vs $1/T$, the activation energy can be determined from the slope, and the frequency factor from the intercept of the resulting straight line.

Distributed Activation Energy(DAE) Model

This model treats the decomposition of coal as a large number of independent, parallel first-order reactions and the activation energy of all reactions can be presented by the continuous Guassian distribution. Assuming the same frequency factor in the Arrhenius rate expression, the nonisothermal weight loss of a coal particle at constant heating rate and zero hold-up time can be approximated as [6]:

$$\begin{aligned} 1-x &= \frac{1}{\sqrt{\pi}}\int_{\infty}^{\infty} \exp(-y^2)dy \\ &= \frac{1}{2}\, erfc\,(y_c) \\ &= \frac{1}{2}\left[1 - erf(y_c)\right] \end{aligned}$$

and

$$y = (z-z_0)/g \quad ,\ y_c = (z_c-z_o)/g \qquad \text{———} (6)$$

where $g=\sigma\sqrt{2}/RT, z=E/RT, z_0=E_0/RT, E_0$ is the mean activation energy, and σ is the standard deviation. The value of z_c is estimated from [6]:

$$\frac{A}{Z_c}\exp(z_c) = 0.5 \qquad \text{———} (7)$$

where $A=k_0/RT$. This approximation gave an error of < 5% for $A = 10^5$-10^{20}, z_o= 10-100, and g = 2-20 [6].

This model, with k_0, E_0, σ, and $V^* = w_0 - w_f$ as the kinetic parameters, is the most commonly used in coal pyrolysis[7]. However, the assumption is essentially empirical and has no particular mechanistic or constitutional basis beyond postulating that production of a range of different products can imply an array of reactions[7].

Individual Volatile Product (IVP) Model

This model uses multiple independent parallel first-order reactions to describe the evolution of volatile products. Assuming the rate constant to be $k_i=k_o \exp(-E_i/RT)$, the contribution of reaction *i* to the amount of the product evolved up to time *t* is, for nonisothermal conditions with constant heating rate and zero hold-up time[8]:

$$1-x_i = \exp\left[-\frac{k_{oi}RT^2}{qE_i}\exp(-E_i/RT)\right] \qquad (8)$$

where $x_i=V_i/V_i^*$, V_i is amount of the product evolved from reaction i up to time *t*, and V_i^* is the value of V_i as *t* approaches infinity. The total yield of the product, therefore, is the sum of the contribution of all *i*.

Not only temperature-time histories are needed in order to use equation (8), one set of parameters (k_{oi}, E_i and V_i^*) for each reaction involved is also necessary. Good agreement was achieved when this model was used to predict the pyrolysis products of Montana lignite[8]and the total weight loss of one Thai lignite[3].

EXPERIMENT

Five Thai lignite samples were used in this study. Sample No. 2 was from the southern part, while all others were from the northern part of Thailand. Their proximate analyses are shown in Table 1. The lump coal samples were ground and sieved through a 150 mesh (<105 μm) screen, and then stored in a desiccator.

The experiment was carried out in a NETZSCH STA 409 instrument, using approx. 10 mg of powdered sample. For each sample, nonisothermal TGA curves were achieved over the range of 393-1373 K in N_2 gas (flow rate - 200 ml/min). Since the ultimate yield of volatile was insensitive to the variation of heating rate between 5-50 K/min as reported by Tia et al. [3] for one of the Thai lignite samples, the heating rate was fixed at 10 K/min throughout the study. It was also assumed that the effects of heat and mass transfer are negligible and the pyrolysis rate is controlled by the thermal decomposition kinetics. Before starting each run, the lignite sample

Table 1 Proximate analysis(ASTM D-3172) of Thai lignite samples. (air dried)

Source	Ash %	Moisture %	Fixed carbon %	Volatile matter %
Krabi(S1)	9.54	16.97	34.99	38.50
Li (S2)	35.52	21.19	19.32	23.97
Mae Ta(S3)	22.96	21.20	22.21	33.63
Mae Moe(S4)	11.35	16.36	37.29	35.00
Mae Ramad(S5)	11.27	17.5	39.42	31.81

was dried in N_2 gas at 378 K for 30 minutes in the apparatus.

RESULTS AND DISCUSSION

TGA Curve

The TGA curves from which the sample weight have been plotted as a function of temperature are presented in Fig. 1. All samples show the beginning of weight loss due to thermal decomposition at around 420 K. The ultimate yield of volatiles are found to be in the range of 34.6-51% by weight of dry lignite at about 1373 K(Fig.1). These values are significantly higher than those obtained from proximate analysis (Table 2). This behaviour, however, has been reported in the literature[4], and in this case may be due to the use of higher temperature and longer time of heating when compared to the proximate analysis. Moreover, the relatively small sample mass used in this study compared to proximate analysis will reduce the opportunity for secondary cracking with the neighboring particles[4].

Estimation of Kinetic Parameters

Two Component Model

Based on the TC model, equation(5) has been used to determine the activation energy and frequency factor from nonisothermal TGA data. It was assumed that the pyrolysis of component 1 was completed when the temperature reached 923 K[4]. Good correlation was obtained for all lignite samples as shown in Fig.2. The derived kinetic parameters are presented in Table 2 for components 1 and 2. The percentage of ultimate yield of volatiles contributed by component 1 and 2 are nearly the same for all lignite samples and the average values are 68.5 and 31.5%,respectively. The derived activation energies for components 1 and 2 are 5-8 and 11-14 kca/gmol, respectively, and the frequency factor of both components are in the range of 7-70/s(Table 2). As the decomposition of component 1 and 2 of all samples are very close in activation energy value, it is possible to plot all the data on the same graph

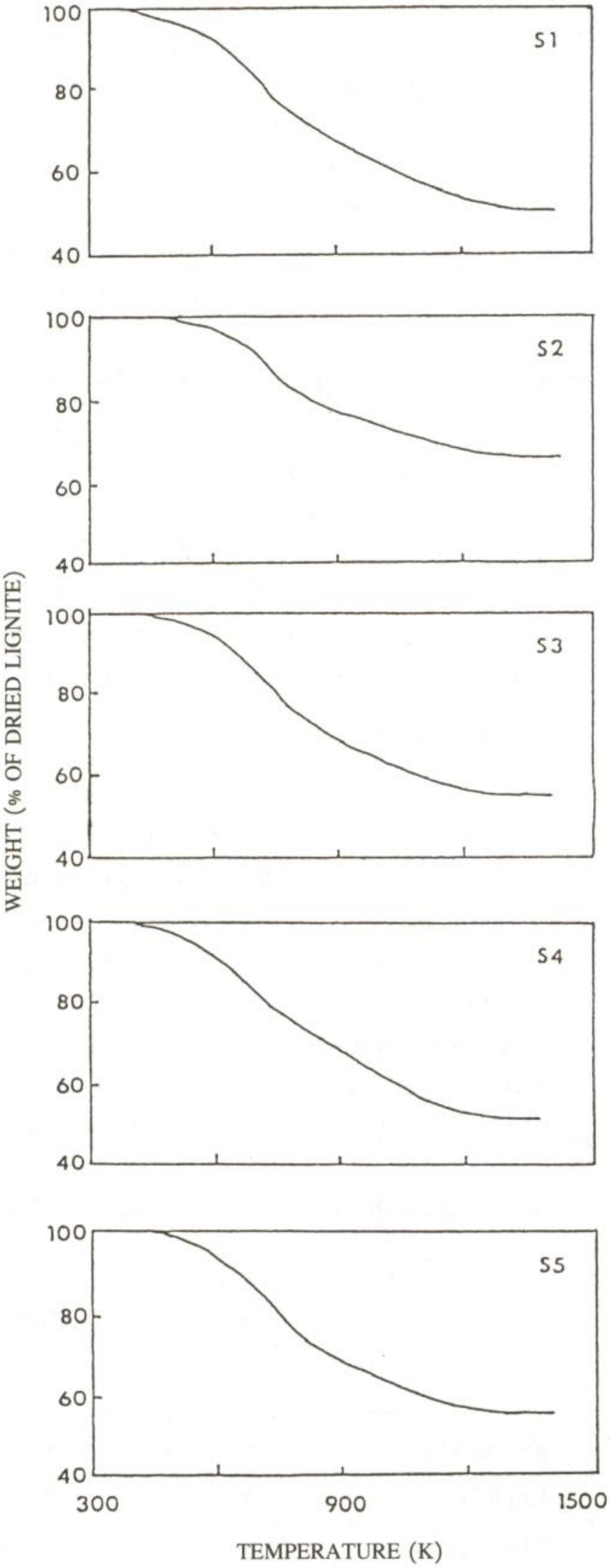

Figure 1 **TGA curves of lignite samples pyrolyzed at 10 K/min.**

Table 2 **Kinetic parameters of lignite pyrolysis obtained from the two-component model.**

Lignite Samples	E_1	E_2	k_{o1}	k_{o2}	Volatile matter(%)^a		V_1^{*b}	$V2^{*b}$
	kcal/gmol	kcal/gmol	/s	/s	TG	ASTM	(%)	(%)
S1	6.07	12.63	13.96	31.00	51.00	46.37	67.16	32.84
S2	8.24	13.23	58.56	40.01	34.60	30.41	68.64	31.36
S3	6.05	13.18	12.89	39.94	47.80	42.68	69.72	30.28
S4	4.94	11.38	7.74	20.14	50.13	39.48	67.01	32.99
S5	6.49	13.92	16.98	69.36	46.67	35.85	69.23	30.77
Average^c	6.36	12.87	16.34	37.01				

a. % by weight of dry lignite

b. % by weight of ultimate volatile obtained from TGA

c. estimated from Fig. 2

as depicted in Fig.3. Good fit was obtained and the average values of activation energy and frequency factor for each component are also shown in Table 2. These results correspond to the TC hypothesis for coal that, for the same rank coal, the contribution of each component in total evolved volatiles should be the same. Also, the activation energy of each component should be insensitive to the coal rank and origin. This model will be more applicable if testing for other coal ranks were included. However, an acceptable method for estimating the amount of each component is still lacking and needs to overcome before the model can be incorporated into coal combustor modelling.

Compared to the decomposition of organic chemicals[9], the activation energy obtained from this model is quite low. This can be attributed to, as discussed by Howard[9], the using of a single first-order model to fit approximately the temperature dependence that actually results from the occurrence of different reactions at different temperature intervals. The intraparticle and external mass transfer also have an effect on pyrolysis rate. To minimize this effect, it is suggested that the sample mass used in the TGA experiment be as amall as possible.

Distributed Activation Energy Model

The set of equations given for the DAE model have been used to evaluate the kinetic parameters from nonisothermal TGA data. The frequency factor, k_o, which has been calculated from transition state theory, was fixed at 1.67×10^{13} /s [10], and the ultimate yield, V^*, of each samples can be taken from experimental data(see Table 2). The number of parameters needed to characterize the pyrolysis weight loss, as a result, can be reduced to two without greatly affecting the fit of the model [10]. The two-parameter, E_o, the mean activation energy, and σ, the standard deviation, were estimated by using nonlinear Hooke and Jeeves optimizing method[11]. Details of the calculation were presented elsewhere[3]. The estimated values of E_o and σ for each sample are shown in Table 3. The consistency of both parameters for the same rank coal is clearly seen. The

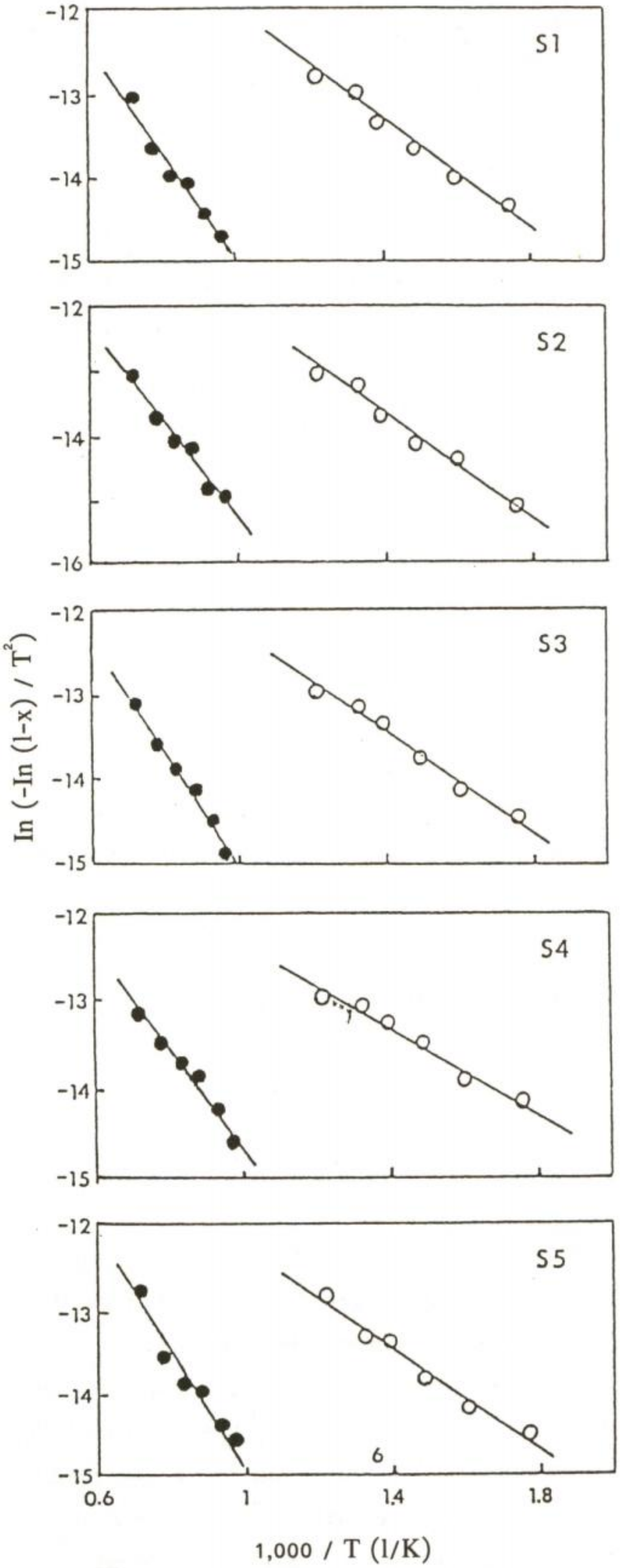

Figure 2 **The plotting of TGA data for kinetic parameter determination of lignite pyrolysis using TC model.**

average values of E_o and σ are found to be 57.95 and 18.45 kcal/gmol, respectively, and are in line which those reported previously for one Thai lignite(E_o=53.04 kcal/gmol and σ =13.36 kcal/gmol) and the same rank coal reported in the literature[3]. The derived activation energy from this model is much higher than that obtained from the TC model (Table 2). The reason has already been discussed in the TC model.

Individual Volatile Product (IVP) Model

This model is much more complex than the TC and DAE models, but its ability to predict the amount of volatile species is its main advantage over the previous two models. In addition, the use of kinetic parameters for Montana lignite[8] with little modification, reasonably predicted the total weight loss of one Thai lignite[3]. Before using IVP model for general kinetic parameters, it is important to test the model with other Thai lignites, as carried out in this study. Following our previous work[3], the activation energy and frequency factor of each volatile product were taken from the work of Suuberg *et al.*[8], while their ultimate yield was modified by multiplying the original value of Montana lignite by the ratio of the total ultimate yield of volatiles between Thai and Montana lignite.

COMPARISONS BETWEEN EXPERIMENT AND MODELS

The predicted weight loss of lignite samples from each model have been compared with the nonisothermal TGA data as shown in Fig.4. Both TC and DAE models are in good agreement with experimental data. The TC model, however,gave slightly better results than the DAE model. The prediction results from the IVP model using the set of parameters of Montana lignite[8] were also presented in Fig.4. As reported by Tia *et al.*[3], fairly good agreement is obtained with no adjustment in the values of activation energy and frequency factor.

Table 3 Kinetic parameters of lignite pyrolysis obtained from the distributed activation energy model.

Lignite samples	E_o kcal/gmol	σ kcal/gmol	V^* %MF
S1	58.12	19.70	51.00
S2	58.64	16.85	34.60
S3	57.71	18.52	47.80
S4	57.36	19.57	50.13
S5	57.95	17.62	46.67
Average	57.95	18.45	

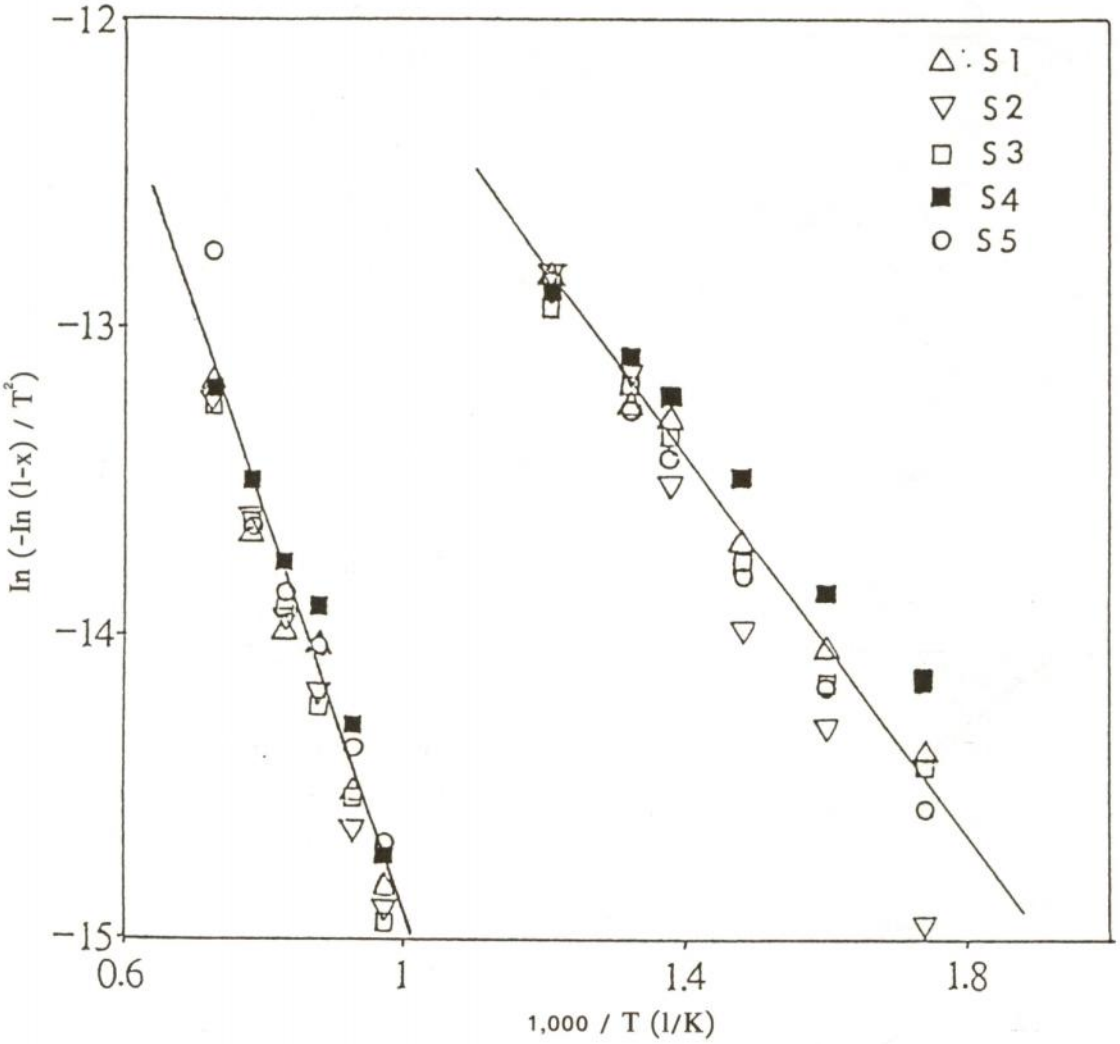

Figure 3 **The plotting of TGA data of all lignite samples for average pyrolysis kinetic estimation using TC model.**

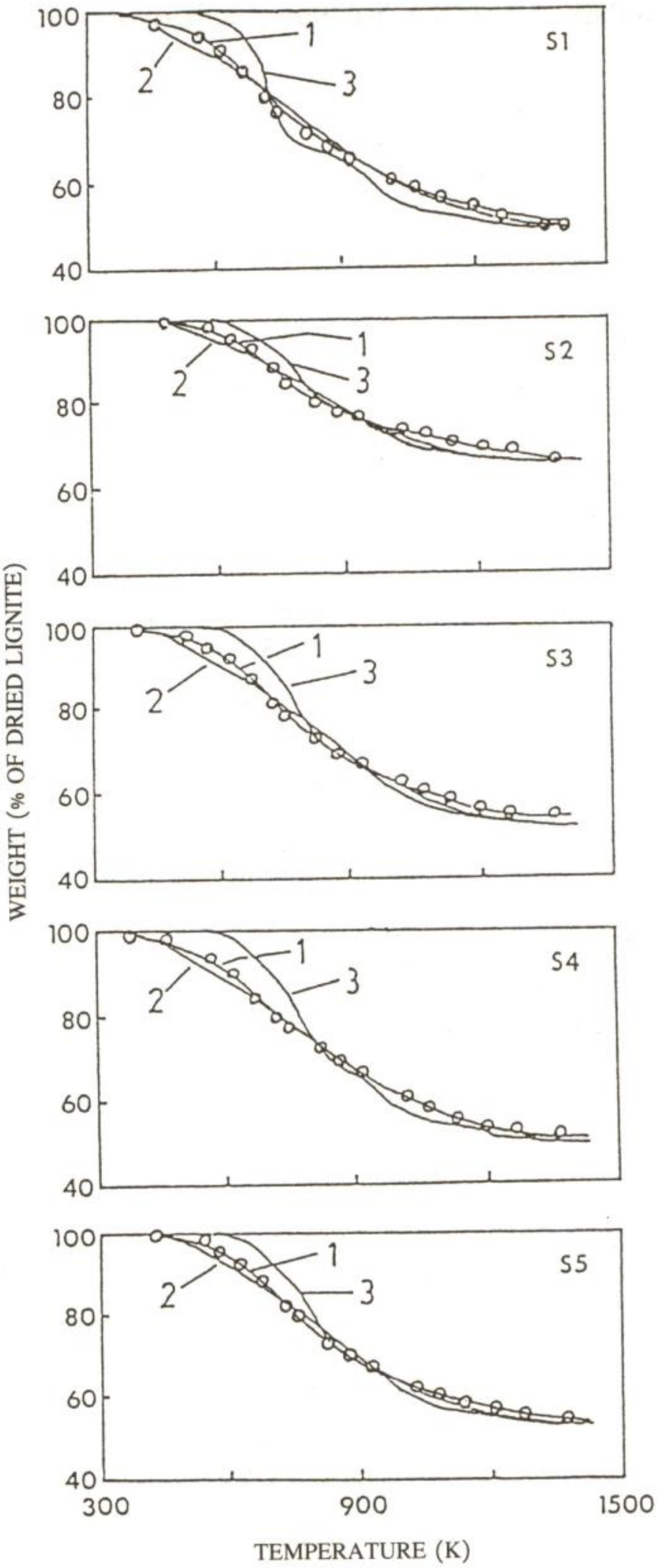

Figure 4 **Comparison between experimental data and model prediction of lignite sample weight during pyrolysis. Data(o); TC model (1); DAE model (2); IVP model (3).**

CONCLUSIONS

a) From TGA all lignite samples showed significantly higher value of ultimate volatile yield than those obtained from proximate analysis. This may be attributed to the use of smaller sample mass, higher pyrolysis temperature and longer exposure time when compared to proximate analysis.

b.) Both the TC and DAE models are applicable for predicting the weight loss of Thai lignites during pyrolysis. The former model which is based on coal constituent and simpler to apply gave slightly better results, but the method to determine the quantity of each component is still lacking.

c.) With little modification of the ultimate yield of volatile products, the calculated results from the IVP model showed fairly good agreement with TGA data when using the kinetic parameters of Montana lignite reported in the literature.

REFERENCES

1. Wibulswas, P.(1987), Energy Resources and Reserves in Thailand, *Thailand Eng.J.*, Vol. 40, p.31(in Thai).
2. ....,Thailand Coal Development and Utilization Study, Joint UNDP/ World Bank/ NEPO Report,1991.
3. TIA,S. et.al.(1991), Thermogravimetri Analysis of Thai Lignite-I. Pyrolysis Kinetics, *Energy Convers. Mgmt.*, Vol. 31, p. 265.
4. Essenhigh, E.H.(1979), Coal Combustion, in *Coal Conversion Technology*, Eds., Wen, C.Y. and Lee, E.S., Academic Press, p. 171.

5. Agrawal, R.K. and Sivasubramanian, M.S. (1987), Integral Approximations for Nonisothermal Kinetics, *AIChEJ.*, Vol. 33, p. 1212.
6. Suuberg, E.M.(1983), Approximate Solution Technique for Nonisothermal Gaussian Distributed Activation Energy Models, *Combust. Flame*, Vol. 50, p.243.
7. Misra, M.K. and Essenhigh, R.H. (1988), Release of Volatiles from Pyrolyzing Coal Particle: Relative Roles of Kinetics, Heat Transfer, and Diffusion, *Energy & Fuel*, Vol. 2, p.371.
8. Suuberg, E.M. et al. (1978), Product Composition and Kinetics of Lignite Pyrolysis, *Ind. Eng. Chem. Process Dev.*, Vol. 17, p.37.
9. Howard, J.B. (1981), Fundamental of Coal Pyrolysis and Hydropyrolysis, in *Chemistry of Coal Utilization*, Ed., Elliott, Wiley, New York, p. 665.
10. Antrony, D.B. and Howard, J.B.(1976), Coal Devolatilization and Hydrogasification, *AIChEJ.*, Vol.22, p.625.
11. Beveridge, G.S.G. and Schechter, R.S.(1970), Optimization: Theory and Practice, McGraw-Hill, pp. 56,384.