

## Correlation Between Arrhenius Kinetic Parameters In Coal Combustion

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### Abstrak

Parameter kinetika Arrhenius pembakaran batubara telah dipelajari menggunakan analisis termogravimetrik. Sampel batubara yang digunakan berperingkat sub-bituminus hingga bituminus yang berasal dari tambang batubara di Sumatra dan Kalimantan Indonesia. Penelitian menggunakan peralatan termogravimetrik dilakukan dengan laju pemanasan tetap sebesar  $10 \text{ K min}^{-1}$  di kondisi udara dengan sampel berukuran partikel 45 to 53  $\mu\text{m}$ . Tujuan dari penelitian ini adalah : (a) mengukur parameter kinetika Arrhenius pembakaran batubara dan (b) menggambarkan korelasi antara energi aktivasi dan faktor pre-eksponensial ( $E$  vs.  $A$ ) untuk sampel batubara yang diteliti. Hasil penelitian ini memperlihatkan bahwa parameter kinetika reaksi pembakaran dipengaruhi oleh sifat analitis batubara. Suatu korelasi yang kuat antara parameter Arrhenius berhasil diperoleh.

**Kata kunci:** Pembakaran batu bara, Parameter kinetika arrhenius, Analisis termogravimetrik dan Korelasi  $E$  vs.  $A$ .

### Abstract

The Arrhenius kinetic oxidation parameters of coal combustion have been investigated using a thermogravimetric analyzer. The coal samples, ranging from sub-bituminous to bituminous coals, were selected from coal fields in Sumatra and Kalimantan Indonesia. The thermogravimetric experiments were carried out at a constant heating rate of  $10 \text{ K min}^{-1}$  in air atmosphere with particle sizes ranging from 45 to 53  $\mu\text{m}$ . The objectives of the present works are to: (a) measure the Arrhenius kinetic parameters of coal combustion and (b) to illustrate the apparent activation energy and pre-exponential factor (the  $E$  vs.  $A$ ) correlation for the range of the studied coal samples. The results show that the values of the kinetic parameters for combustion reactions are affected by the analytical properties of the coals. A strong correlation between Arrhenius parameters is found.

**Keywords:** Coal combustion, Arrhenius kinetic parameters, Thermogravimetric analysis and  $E$  vs.  $A$  correlation.

### 1. Introduction

Solid-fuel combustion processes represents a major segment of modern energy technology, finding their primary applications in large-scale electricity generation, industrial heating and steam generation, thermal waste destruction, and, in many parts of the world, domestic heating and cooking [1]. In Indonesia coal is expected to provide a significant contribution in replacing Indonesia's dependence on oil and natural gas,

particularly, for power generation and industrial sectors. This will be a consequence of the changing pattern of energy production in Indonesia, and a government policy of diversifying domestic energy consumption away from oil in order to preserve Indonesia's oil declining reserves [2].

The combustion of coal in pulverised-coal flame can be divided ideally into the following stages: heat-up and pyrolysis, ignition and volatile combustion, and heterogeneous char burn-out [1,3,4]. For

heterogeneous char oxidation, reaction rates may be controlled by one or more of the three major steps: mass transfer, pore diffusion and chemical reactivity. At low temperature, where the reactivity of the char is low, a molecule of oxygen entering a pore has a high probability of diffusing deeply into the char before reacting with an active site on the char surface. Thus, the rate of combustion will be controlled by chemical reactivity of the char. As the temperature increases, the chemical reactivity increases and the probability of an oxygen molecule penetrating deeply into the char pores before reacting is small. Pore diffusion and bulk diffusion become important in determining the overall rate of coal/char combustion [1,3].

Extensive research work on coal combustion, in particular the burning rate of a char has been carried out experimentally as well as theoretically. Much attention has been paid to the kinetic parameters i.e. the activation energy ( $E$ ) and the pre-exponential factor ( $A$ ) which are derived experimentally from a typical Arrhenius plot of  $\ln(\text{rate})$  against  $1/T$ . For a specified coal, the experimental values of  $E$  and  $A$ , are only useful for the one coal [5]. Of course, different values of  $E$  and  $A$  are obtained for different coals. So far, one still cannot predict the values of  $E$  and  $A$  for any kind of coal.

Formal kinetics predicts that the Arrhenius equation parameters, activation energy and pre-exponential factor, are essentially independent from each other [6]. This is no surprise since the  $E$  and  $A$  are affected by both chemical and physical factors of the coal. However, it has been found that in a number of cases, especially for heterogeneous catalytic reactions, that  $E$  and  $A$  change in the same direction [7]. An establishment of a correlation between  $E$  and  $A$  will be useful particularly in coal flame modelling as this reduces the number of independent kinetic parameters from two to one [6,7].

Thermogravimetric analysis (TGA) is commonly used to measure the chemical reactivity of carbonaceous materials

including coal. In TGA technique, a burning profile is produced by heating a coal sample at a constant rate from ambient temperature to about 900°C in an air atmosphere. The burning profiles obtained are useful for predicting relative combustion characteristics and coal combustion performance in boiler [8].

The objectives of the present works are to: (a) measure the Arrhenius kinetic parameters of coal combustion and (b) to illustrate the apparent activation energy and pre-exponential factor (the  $E$  vs.  $A$ ) correlation for the range of the studied coal samples. This paper provides further data on the correlation between Arrhenius parameters and throws additional light on this issue, especially in the case of Indonesian coals.

## 2. Experimental

This section provides details of sample used, characterization, experimental procedure and burning profiles determination.

### 2.1. Coal selection and preparation

Five coals obtained from different coal fields in Sumatra and Kalimantan Indonesia were used in this work. The as-received coal samples were ground and sieved into pulverised size of 45 to 53  $\mu\text{m}$ . The samples were left exposed to air to equilibrate with the room atmospheric condition. Each sample was stored in glass vials for further analysis and tests.

### 2.2. Coal characterisation

The samples were characterised both physically and chemically. Proximate analysis was performed with thermogravimetric method. The ultimate analysis were determined using Perkin Elmer elemental analyser. The data were reported on a dry-as free basis. The surface area were measured by a Quantachrome Quantasorb QS-13 analyser using  $\text{N}_2/\text{He}$  mixture and calculated on the basis of the Brunauer-Emmett-Teller (BET) equation [9]. Table 1 summarises the properties of the coal samples.

**Table 1.**  
Properties of the coal samples

Properties	Coal samples				
	TEC	SBC	ADC	ATC	KPC
<i>Proximate analysis (wt%)</i>					
Moisture:	17.5	6.7	9.8	3.2	5.2
Volatile matter :	39.7	43.7	45.2	44.6	46.8
Fixed carbon :	39.1	37.5	43.0	47.2	49.1
Ash :	3.7	4.6	2.0	5.0	2.9
<i>Ultimate analysis (wt%) daf<sup>b</sup>(*)</i>					
Nitrogen :	1.05	1.25	1.17	1.27	1.76
Carbon :	65.36	62.54	61.67	75.30	76.78
Hydrogen :	4.51	4.20	4.56	5.59	5.50
Combustible sulphur :	0.24	0.39	0.34	0.65	0.30
(*) daf <sup>b</sup> :dry ash free basis					
BET surface area (m <sup>2</sup> gr <sup>-1</sup> ):	6.21	5.32	3.69	2.76	2.94

### 2.3. Determination of burning profiles

The burning profile of coal is determined by heating a sample of coal at a constant heating rate in air atmosphere. The sample in the thermogravimetric analyser (Shimadzu TGA-50H) [9] is heated from 25°C to 900°C. Factors such as sample quantity heating rate and air flow were carefully controlled between runs for comparisons between among samples. Throughout all the experimental runs, the sample weight was kept in a range of 10 ± 0.5 mg. The gas flow rate and heating rate were 50 cm<sup>3</sup> min<sup>-1</sup> and 10 K min<sup>-1</sup>, respectively.

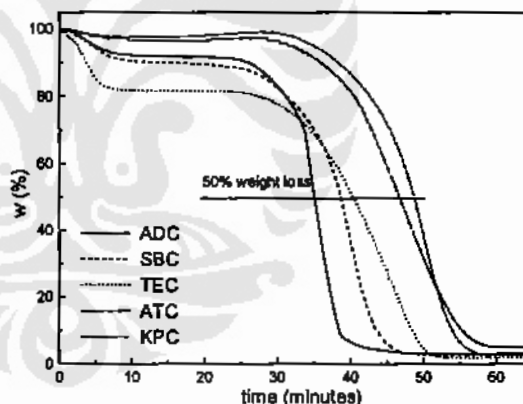
## 3. Results and Discussion

The main outcomes of this work are presented and discussed in the following sections.

### 3.1. Features of thermogravimetric curve

Figure 1 shows thermogravimetric curves for five coal samples with different analytical properties. Taking into account the same heating rate of 10 K min<sup>-1</sup> used in the experiments, this figures clearly show that the combustion reaction of the coal samples took place over different temperature intervals depending upon their analytical properties.

Samples ADC, SBC and TEC which are ranked as lower rank coals loss 50 % of their initial masses faster than that of the higher rank samples (ATC and KPC).



**Figure 1.**  
Themogravimetric curves for the coals.

Noting that the heating rate was the same, temperatures necessary to achieve 50% conversion of the samples were lower for ADC, SBC and TEC samples.

### 3.2. Calculations of Arrhenius Parameters

The dependence of any chemical reaction on temperature can be represented by the Arrhenius equation [7]:

$$\frac{d\alpha}{dt} = A e^{-E/RT} g(\alpha) f(P_{O_2}) \quad (1)$$

Since the gas flow is large enough to carry over the reaction products, the partial pressure of oxygen can be considered to be constant and included in the pre-exponential factor. Using a linear heating rate  $H = dT/dt$ , or  $d/dT = (1/H) d/dt$ , one can include the heating rate in the pre-exponential factor. The inclusion of the constant partial pressure of oxygen and heating rate into the pre-exponential factor, modifies  $A$  to  $A^*$ .

Thus Eq.1 can be re-written to,

$$\frac{d\alpha}{g(\alpha)} = A^* e^{-E/RT} dT \quad (2)$$

Now, one can choose between differential or integral methods. By using an integral approach Eq. 2 can be transformed into,

$$f(\alpha) = \int_0^\alpha \frac{1}{g(\alpha)} d\alpha = A^* \int_{T_0}^T e^{-E/RT} dT \quad (3)$$

The integral method requires to evaluate the temperature integral. By defining the variable  $x = E/RT$  and modifying the limits between 0 and  $T$ , one arrives at,

$$f(\alpha) = A^* \frac{E}{R} \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (4)$$

Now we define

$$p(x) = \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (5)$$

Eq.5 can be evaluated either by integrating the equation or by numerical calculation methods. By adopting the Schlomich series [7]

$$p(x) = \frac{e^{-x}}{x(x+1)} \times$$

$$\left[ 1 - \frac{1}{(x+2)} + 2 \left( \frac{2}{(x+2)(x+3)} - \frac{4}{(x+2)(x+3)(x+4)} + \dots \right) \right] \dots(6)$$

For simplification we only take the first and second terms of the above series, i.e.

$$p(x) \approx (x-2) \frac{e^{-x}}{x^3} \quad (7)$$

By assuming that  $2RT/E \ll 1$ , and re-submitting Eq. 7 and the variable  $x = E/RT$  into Eq. 4 one can arrive to a simple form of Eq. 4 as

$$\left( \frac{f(\alpha)}{T^2} \right) = A^* \frac{R}{E} e^{\left( \frac{E}{RT} \right)} \quad (8)$$

or

$$\ln \left( \frac{f(\alpha)}{T^2} \right) = \ln \left( A^* \frac{R}{E} \right) - \frac{E}{RT} \quad (9)$$

A plot of  $\ln (f(\alpha)/T^2)$  against the reciprocal  $T$  produces a straight line (or sections of straight lines) with a slope (or slopes) of  $-E/R$  and an intercept of  $\ln (A^*R/E)$ . The apparent activation energy  $E$  can be deduced from the slope and the modified pre-exponential factors  $A^*$  from the intercept.

The applicability of Eq. 9 should be warranted by strong correlation coefficient of the linear regression (0.97 to 0.99). In this case one must be careful in taking the interval of the fraction transformed  $\alpha$ . As shown on Fig. 2, in the case of the TEC coal, the  $0.28 < \alpha < 0.8$  interval was considered to secure the best correlation applied for Eq. 9.

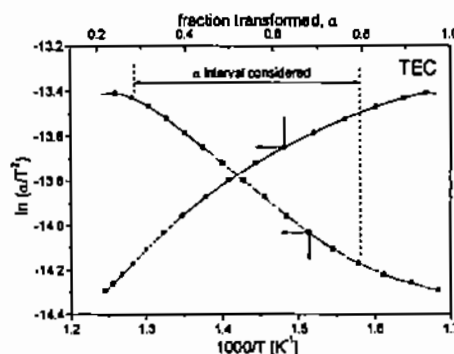


Figure 2.

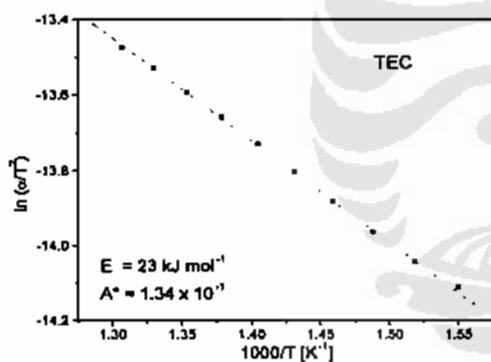
The best interval of fraction transformed,  $\alpha$  for TEC coal to warrant the applicability of Eq. 9.

### 3.3. The $E$ , $A^*$ and $T_{0.5}$ values

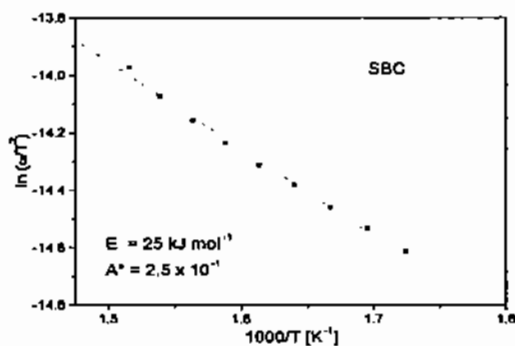
Figure 3 to 7 show the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for all coal samples. The correlation coefficient of the linear regression for all the samples are 0.985 or better. The activation energy  $E$  and the modified pre-exponential factor  $A^*$  for each sample is given on the graph. Table 2 summaries the values of  $E$ ,  $A^*$  and the temperatures necessary to achieved 50% conversion ( $T_{0.5}$ ) or fraction transformed,  $\alpha = 0.5$ .

**Table 2.**  
Summary of the results

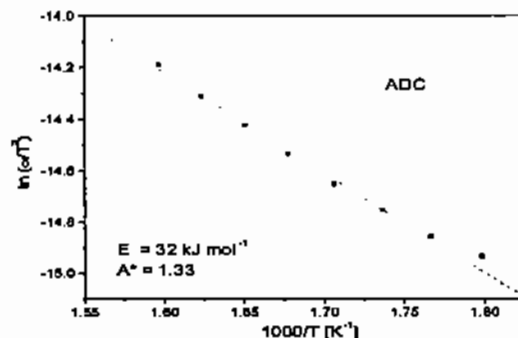
Sample	$T_{0.5}$ [K]	$E$ (kJ mol <sup>-1</sup> )	$A^*$
TEC	698	23	$1.34 \times 10^{-1}$
SBC	679	25	$2.50 \times 10^{-1}$
ADC	645	32	$1.33 \times 10^0$
ATC	762	50	$1.24 \times 10^1$
KPC	777	61	$8.35 \times 10^1$



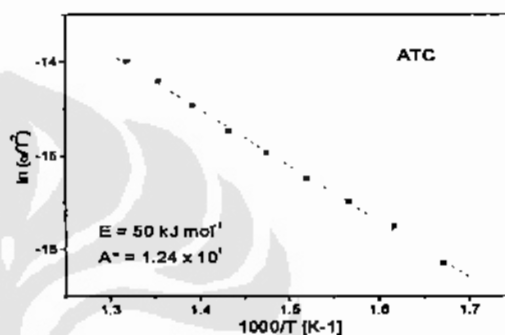
**Figure 3.**  
Shows the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for TEC coal.



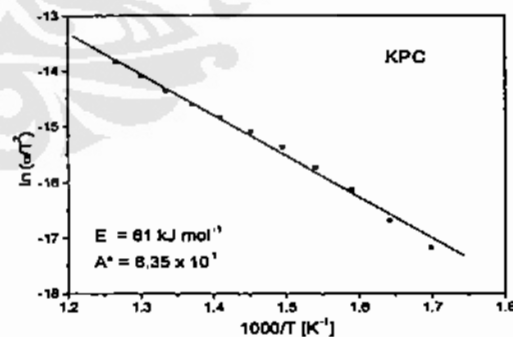
**Figure 4.**  
Shows the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for SBC coal.



**Figure 5.**  
Shows the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for ADC coal.



**Figure 6.**  
Shows the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for ATC coal.



**Figure 7.**  
Shows the Arrhenius plots on  $\ln(f(\alpha)/T^2)$  versus  $1/T$  for KPC coal.

The results for  $T_{0.5}$  as shown on Fig. 1 and in the second column of Table suggest that the lower rank coals (TEC, SBC and ADC) reach 50% transformation at lower temperatures than the higher rank coals (ATC and KPC). This is in agreement with generally accepted views on the trends for reactivity of carbon materials, where the

graphitization (or the coalification) degree are generally considered to play a major role [7]. In other word, it can be said that the sub-bituminous coal are much more reactive toward air than the bituminous coal [5].

The temperature required for reaching half-time  $T_{0.5}$  can also indicate the level of activation energy for the reaction. When the temperature  $T_{0.5}$  is relatively high, the value of  $E$  should be higher. Therefore,  $E$  should be some function of temperature  $T$  which depends on chemical factors. The results for all coal samples given on Figs. 3 to 7 and summarised on Table 2 show that the values of the activation energies  $E$  increase with  $T_{0.5}$ .

The pre-exponential factor  $A$  represents the effective number of collisions between coal (mostly carbon) and oxygen molecules. Consequently, the value of  $A$  is affected by coal properties such as surface area and pore or surface diffusion etc[1,4,5]. One factor related to the specific surface area of the coal is the volatile. After the volatile release, the coal becomes char particle which is porous, resulting in an increase in the specific surface area. During the initial stages of coal combustion process, the intrinsic moisture content is released. The intrinsic moisture behaves like the volatile during the devolatilization of a coal [5]. On the other hand any collisions between ash and oxygen molecules will not contribute to the pre-exponential factor. From this one can conclude that the specific surface area of a coal available for the collision of carbon and oxygen molecules after the heat-up and devolatilization stages must be much higher than the surface area of the original coal. This implies that the actual specific surface area ( $SA$ ) during the combustion processes of each coal char are much higher than the original  $SA$  of the coal as shown on Table 2.

By considering the ideas given in the previous paragraph and by taking the proximate analysis of the sample, one can draw an understanding that the values of pre-exponential factor  $A^*$  should be somehow related to moisture and volatile

content, since their release increase  $SA$  significantly. Now, once again, we consider the values of the pre-exponential factor  $A^*$  on Figs. 3 to 7, Table 2, and the volatile contents summarised in Table 1. It is shown that the values of  $A^*$  increase with volatile matter content of the coal. The higher volatile content and rank for sample ATC and KPC responsible for higher  $A^*$  for these coals.

### 3.4. Correlation of $E$ and $A^*$

Pairs of  $E$  and  $A^*$  values calculated for the coal samples are reported in Table 2. Fig. 8 shows a general correlation pattern drawn by plotting  $\log A^*$  against  $E$ . It is found that both  $E$  and  $A$  change in the same direction. In fact, a linear correlation coefficient of 0.99 between Arrhenius parameters is obtained.

The reason for higher  $E$  and  $A^*$  for bituminous coals relates by the fact that these coals require higher temperature for reaching the half-time ( $\alpha = 0.5$ ) and have increase active areas in char combustion stages due to higher volatile matter content. The correlation between  $E$  and  $A^*$  found in the present work is in agreement with the literatures [6,7].

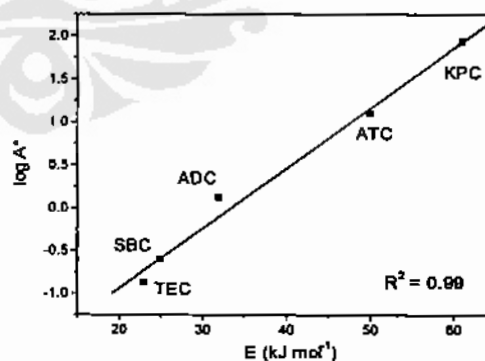


Figure 8.

Correlation between modified pre-exponential factor  $A^*$  and apparent activation energy  $E$  for combustion of the coal samples, fitted to a straight line.

## 4. Conclusions

Five Indonesian coals have been studied for their combustion characteristics using

thermogravimetric method. The five coals can be grouped into the sub-bituminous (TEC, SBC and ADC) and the bituminous coals (ATC and KPC) which have different combustion behaviours. The values of Arrhenius parameters ( $E$  and  $A^*$ ) and  $T_{0.5}$  of the coals are related to their analytical properties. A strong correlation between Arrhenius parameters is found.

### Nomenclatures

$A$	pre-exponential factor, $s^{-1}$
$A^*$	modified pre-exponential factor
$E$	activation energy, $J\ mol^{-1}$
$H$	heating rate, $K\ min^{-1}$
$T$	temperature, $K$
$t$	time, $s$
$P$	pressure, $N\ m^{-2}$
$R$	universal gas constant = $8.314\ J\ mol^{-1}\ K^{-1}$
$SA$	specific surface area, $m^2\ gr^{-1}$
$TGA$	Thermogravimetric analysis
$w$	normalised weight, (%)
$\alpha$	fraction transformed

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