

## A MODEL FOR COAL PYROLYSIS

by

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### INTRODUCTION

Pyrolysis of coal occurs in all coal conversion processes and is perhaps the most difficult to model mathematically. A number of models on coal pyrolysis have been proposed during the past several decades. However, very few of these models address the simultaneous changes in product distribution and particle weight loss (or conversion) over a wide range of operating conditions. Such a mathematical model which could take into consideration the effects of residence time, final temperature, heating rate and pressure is needed for design and scale-up of coal pyrolysis and gasification reactors. The purpose of this study is to develop such a mathematical model for simulation of the pyrolysis phenomena of a coal particle. The model to be developed should be general enough to be applicable to other pyrolysis system such as the pyrolysis of wood.

### MODEL DEVELOPMENT

The assumptions used to formulate the single particle model are as follows:

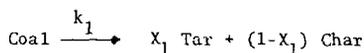
- (a) pseudo-steady state concentration profiles
- (b) negligible increase in internal pressure
- (c) equal binary diffusivities

This model combines the chemical reactions and the transport processes occurring during pyrolysis.

#### 1. Chemical Reactions:

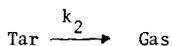
Three chemical reactions are assumed to simultaneously occur within a coal particle which is undergoing pyrolysis in an inert atmosphere. These are devolatilization, cracking and deposition. For convenience, the products of pyrolysis are categorized as char, tar and gas. Char is defined as the undistillable material which remains in the form of a solid. Tar is defined as the distillable liquid which has a molecular weight larger than  $C_6$ . Gas is defined as those components lighter than  $C_6$ , i.e.,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_6$ ,  $H_2O$ , etc. Both tar and gas occur in the form of vapor when coal is pyrolyzed. A similar treatment was applied to the catalytic cracking of petroleum<sup>(11)</sup>. During pyrolysis all of the chemical reactions are assumed to be first order with respect to the concentration of reactants and rate constants are expressed in Arrhenius form. The chemical reactions and the rate expressions for the pyrolysis of a coal particle are formulated as follows:

A. Devolatilization



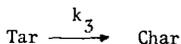
$$\text{Rate} = k_{10} \cdot \exp(-E_1/\overline{RT}) C_{\text{coal}}$$

B. Cracking



$$\text{Rate} = k_{20} \cdot \exp(-E_2/\overline{RT}) C_{\text{tar}}$$

C. Deposition



$$\text{Rate} = k_{30} \cdot \exp(-E_3/\overline{RT}) C_{\text{tar}}$$

The net production rates of tar, gas and inert gas can be obtained as:

$$R_{\text{tar}} = X_1 k_1 C_{\text{coal}} - (k_2 + k_3) C_{\text{tar}} \quad (1)$$

$$R_{\text{gas}} = k_2 C_{\text{tar}}$$

and  $R_{\text{inert gas}} = 0$

While the solid concentrations,  $C_i$ , and the net production rates of coal and char can be obtained as:

$$\frac{dC_i}{dt} = R_i \quad (2)$$

where

$i$  is the coal or char

and

$$R_{\text{coal}} = -k_1 C_{\text{coal}}$$

$$R_{\text{char}} = (1-X_1)k_1 C_{\text{coal}} + \frac{1}{\left(\frac{4}{3} \pi R^3\right)} \int_0^R k_3 C_{\text{tar}} 4\pi r^2 dr$$

2. Transport Processes:

Both mass and heat transfer affect the pyrolysis of a single coal particle. This is particularly significant for large particles.

## 2-1. Mass transfer

### A. Gas phase

The coal particle can be considered as a porous sphere which retains its integrity as the pyrolysis reaction proceeds. The conservation equation for the gaseous species,  $i$ , tar, gas or inert gas, inside the particle having a mass concentration,  $C_i$ , can be formulated as<sup>(8)</sup>:

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 N_i) = R_i \quad (3)$$

where  $R_i$  is the rate of generation of the species  $i$  due to the chemical reactions.

$N_i$  is the mass flux of the species  $i$  and can be expressed as the sum of the diffusion flux in the radial direction and the bulk flow through the pores. Thus

$$N_i = - D_{\text{eff},i} \frac{\partial C_i}{\partial r} + \bar{W}_i \sum_j N_j \quad (4)$$

$\bar{W}_i$ , the weight fraction of the species  $i$  in the gas phase, can be expressed as:

$$\bar{W}_i = C_i / \sum_j C_j \quad (5)$$

### B. Gas film

The conservation equation for the gaseous species,  $i$  (tar, gas or inert gas) across the gas film can be written as:

$$N_i \Big|_R = k_{gi} [C_{i,s} - C_{i,b}] \quad (6)$$

where,

$C_{i,s}$  and  $C_{i,b}$  are the concentrations of species  $i$  at the particle surface and at the bulk gas stream outside, respectively.

$k_{gi}$  is the mass transfer coefficient across the gas film and can be estimated from an appropriate mass transfer correlation.

## 2-2. Heat transfer

The energy balance equation for the particle is derived by taking into account convective, radiative and conductive heat transfer with the heating devices and the heat of reaction of the pyrolysis process. The temperature gradient which occurs inside of the particle due to the conduction is negligible for small particles and is neglected. (For a 1000  $\mu\text{m}$  particle, the maximum temperature gradient is 20 °C at 0.5 sec and less than 5 °C at 1 sec. This is the case, if the particle at room temperature is dropped into a pyrolyzer maintained at 1000 °C. The heating rate of the particle is 1000 °C/sec which is in the range usually encountered in pyrolyzers or gasifiers). Accordingly,

$$C_{ps} \cdot \rho_s \cdot \frac{dT}{dt} = \frac{3}{R} h_c (T_w - T) + \frac{3\sigma Fe}{R} (T_w^4 - T^4) + \frac{3 k a}{R^2} (T_w - T) + \sum_i (-\Delta H_i) R_i \quad (7)$$

where,  $a$  represents the fraction of the surface area of the particle that comes in contact with the heating elements.  $T_w$ , is the temperature of the heating elements and can be characterized by the following equation:

$$C_{pw} \cdot \rho_w \cdot \frac{dT_w}{dt} = h_{ov}' (T_f - T_w) \quad (8)$$

Since the heating rate of a heating device is specified in the experimental work the wire temperature,  $T_w$ , can be obtained by substituting a relative overall heat transfer coefficient,  $h_{ov}'$ , into Equation 8.

#### DETERMINATION OF PARAMETERS

Sensitivity analysis of each parameter of the model on the weight loss of the particle under different operating conditions shows that the value of  $k_1$  for different types of coal can be estimated by comparing the weight loss history, the value of  $k_2$  can be estimated based on product distribution of tar and gas under different temperatures and the value of  $k_3$  can be estimated based on the pressure effect on the weight loss.

The pyrolysis data of Anthony and Howard<sup>(1,2,3)</sup> for bituminous coal and those of Suuberg et al.<sup>(10)</sup> for lignite coal were used to determine the reaction rate constants for the devolatilization step and the deposition step. For sub-bituminous coal, due to the lack of data on weight loss history and pressure effects, an average value between the rate constant of bituminous coal and that of lignite is used. The cracking reaction rate constants for each type of coal were chosen based on the product distribution data of Solomon et al.<sup>(9)</sup>. The reaction rate constants obtained for different ranks of coals are tabulated in Table 1.

A comparison between the calculated results and the experimental data for the weight loss history and the effect of pressure on bituminous coal is shown in Figure 1 and 2. The effect of pressure on weight loss for lignite has been reported to be negligible for pressures ranging from 0.01 to 100 atmospheres<sup>(3)</sup>. Figure 2 also demonstrates this trend. Figure 3 shows the effect of the heating rate on the weight loss history for lignite. Good agreement between the calculated lines and the experimental data indicates that the proposed model can represent the pyrolysis process successfully. The comparisons of the product distribution of tar and gas are shown in Figures 4, 5, and 6 for bituminous, sub-bituminous and lignite coal, respectively. The calculated tar yield is slightly higher than the observed yield especially in the low temperature range. Figures 7 to 9 show the application of the model with the predetermined reaction rate constants for bituminous, sub-bituminous and lignite coal.  $X_1$ , the amount of tar formed in the devolatilization step, is correlated with the volatile matter content for each type of coal and is shown in Figure 10. The correlation equations for  $X_1$  with different types of coals can be seen to represent this value closely for bituminous coal. This results from the aforementioned lack of data necessary for accurately determining the chemical reaction rate constants. The relation of  $X_1$  with volatile matter content (dry ash free basis) are listed below:

$$\text{Bituminous } X_1 = 1.3 \text{ (V.M.)} + 0.025 \quad (9)$$

$$\text{Lignite } X_1 = 0.95 \text{ (V.M.)} + 0.025 \quad (10)$$

#### DISCUSSION AND CONCLUSIONS

Although the rate of heating affects the weight loss history of lignite coal as shown in Figure 3, it appears that the ultimate weight loss is not affected by the heating rate over the range between 650 to  $10^4$  °C/sec. However, Badzioch and Hawksley<sup>(4)</sup> reported the ultimate weight loss of the particle at a rapid heating rate ( $>2.5 \times 10^4$  °C/sec) may be 1.2 to 1.4 times higher than that at slow heating rate ( $< 1/20$  °C/sec). There is a concern that their results might be attributable to the experimental conditions employed to achieve the rapid heating rate by use of small particles in an entrained reactor. For a slow heating rate, the ultimate weight loss is approximately the same as the proximate volatile matter content of the coal<sup>(5)</sup>. Additional studies are needed to clarify the effect of heating rate on the ultimate weight loss.

The estimation of the amount of tar formed at low temperatures based on the model is higher than those observed experimentally. This is shown in Figures 4 to 6. A minor adjustment was attempted in the cracking reaction rate constants, but this did not improve on the result. Hence, the model cannot adequately represent the pyrolysis at low temperatures ( $< 600$  °C).

The weight loss curves at different temperatures for bituminous, sub-bituminous and lignite coals show that the calculated weight loss of the particle at temperatures higher than 800 °C tends to peak rather than continuously increase as seen in some of the experimental data. The validity of the model above 1000 °C is still undetermined due to the lack of experimental data above this temperature.

The phenomena of coal pyrolysis between bituminous and lignite coals are apparently quite different. Bituminous coal is more pressure dependent and has a lower proportion of gas in the pyrolysis products than lignite. The effect of pressure on the weight loss, according to the model, is primarily related to the rate of tar deposition. Since the rate of tar deposition is higher for the bituminous coal compared to that of lignite, the effect of pressure on the weight loss during pyrolysis is also more appreciable for bituminous coal than lignite. Furthermore, the ratio of the cracking rate to the deposition rate has an important effect on the amount of gas and tar formed. Since this ratio is greater for lignite than bituminous coal, lignite produces more gas than bituminous coal under similar pyrolytic conditions. This implies that the fraction of tar formed during the devolatilization step,  $X_1$ , is smaller for lignite than that for bituminous coal as indicated by Equations 9 and 10.

The model developed is applicable within the operating range of pyrolysis process listed below:

$$\begin{aligned} 400 \text{ }^\circ\text{C} &< \text{Temperature} < 1000 \text{ }^\circ\text{C} \\ 25 \text{ } \mu\text{m} &< \text{Particle size} < 1000 \text{ } \mu\text{m} \end{aligned}$$

$1/180$  °C/sec < Heating rate <  $10^4$  °C/sec

0.01 atm < Pressure < 100 atm

For large particles beyond 1000  $\mu\text{m}$ , temperature gradient within the particle may not be neglected requiring an additional term on heat condition within the particle to be included in Equation 7.

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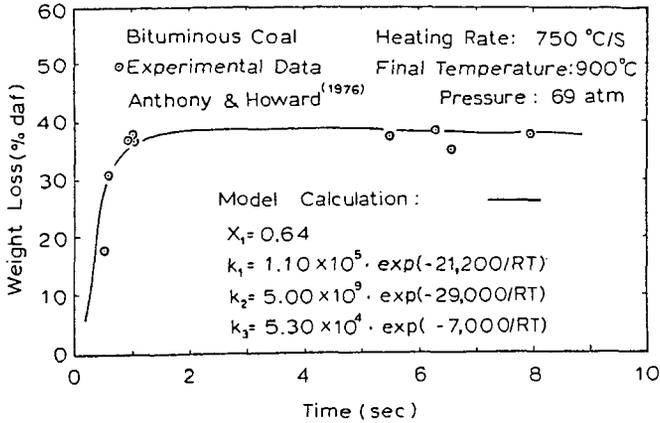


FIG. 1. PYROLYSIS WEIGHT LOSS HISTORY OF BITUMINOUS COAL

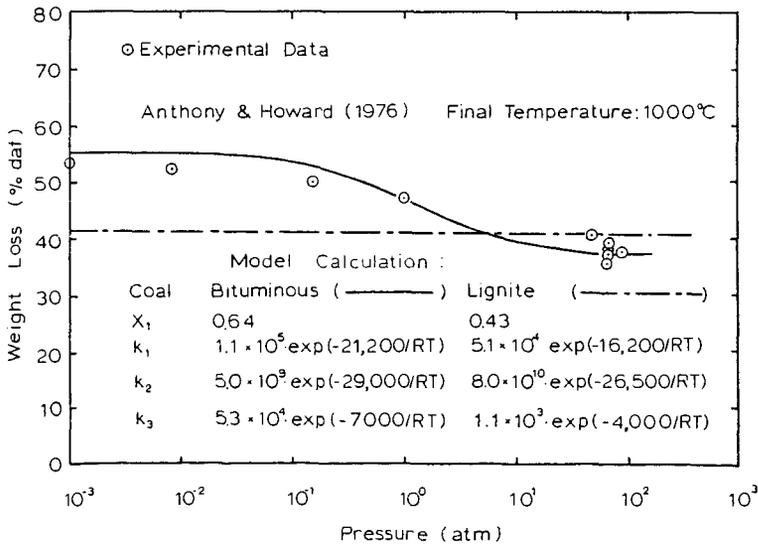


FIG. 2. EFFECT OF PRESSURE ON THE WEIGHT LOSS OF BITUMINOUS AND LIGNITE COALS

Table 1  
Reaction Rate Constants for Coal Pyrolysis Model

Reaction Rate Constants	Coal	Bituminous	Sub-bituminous	Lignite
$k_{10}$ 1/sec		$1.1 \times 10^5$	$7.5 \times 10^4$	$5.1 \times 10^4$
$E_1$ J/mole cal/gmole		88,700 21,200	78,200 18,700	67,800 16,200
$k_{20}$ 1/sec		$9.7 \times 10^9$	$3.5 \times 10^{10}$	$8 \times 10^{10}$
$E_2$ J/mole cal/gmole		121,500 29,000	116,100 27,750	110,900 26,500
$k_{30}$ 1/sec		$5.3 \times 10^4$	$2.5 \times 10^4$	$1.1 \times 10^3$
$E_3$ J/mole cal/gmole		29,500 7,000	23,000 5,500	16,700 4,000

Uncertainty of  $E_i$ :  $\pm 100$  J/mole or cal/gmole

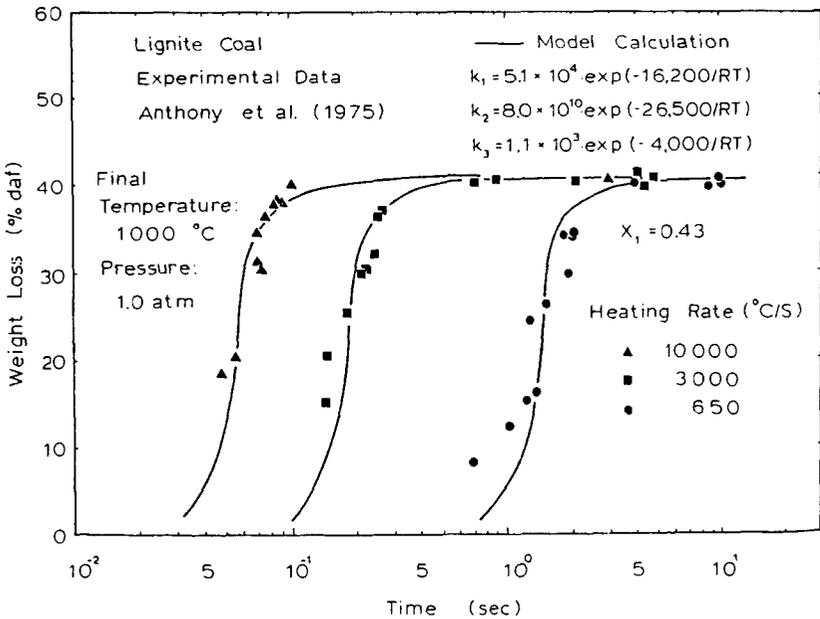


FIG. 3. EFFECT OF HEATING RATE ON THE WEIGHT LOSS HISTORY OF LIGNITE COAL

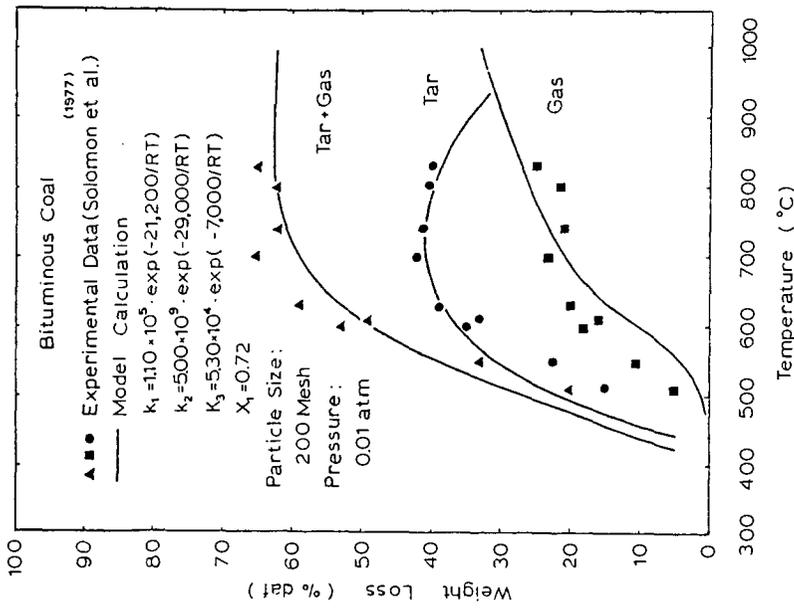


FIG. 4. PRODUCT DISTRIBUTION FROM BITUMINOUS COAL PYROLYSIS

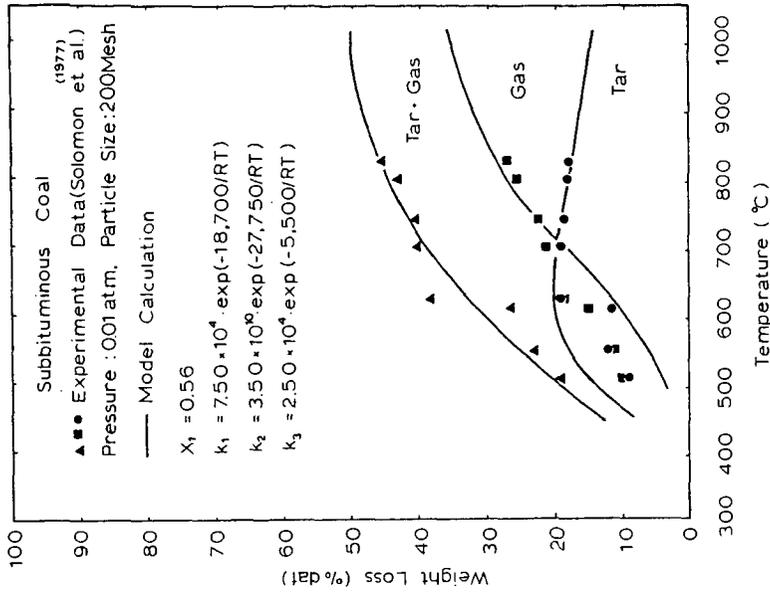


FIG. 5. PRODUCT DISTRIBUTION FROM SUB-BITUMINOUS COAL PYROLYSIS

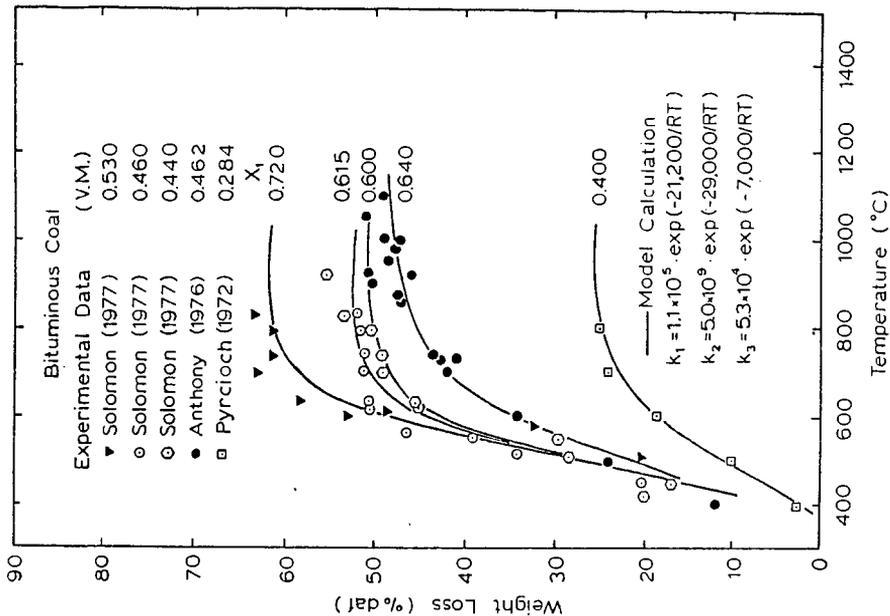


FIG. 7. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF BITUMINOUS COAL

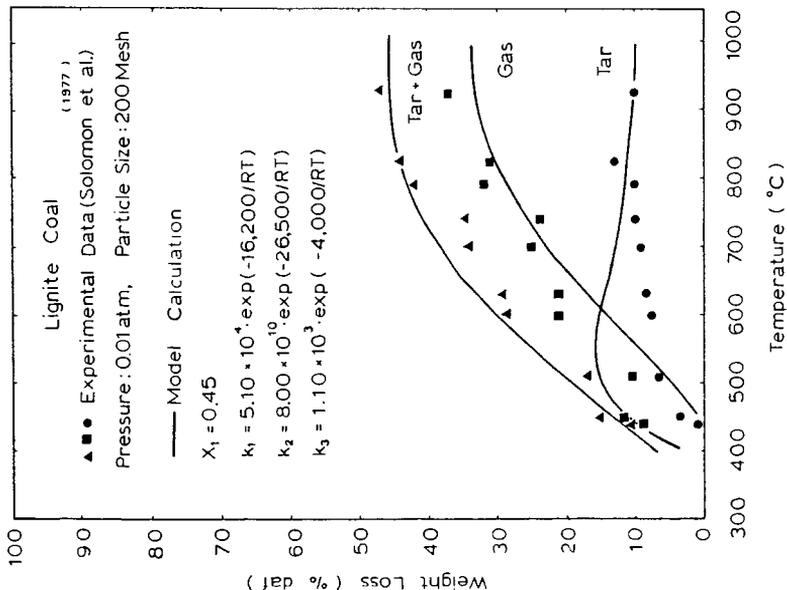


FIG. 6. PRODUCT DISTRIBUTION FROM LIGNITE COAL PYROLYSIS

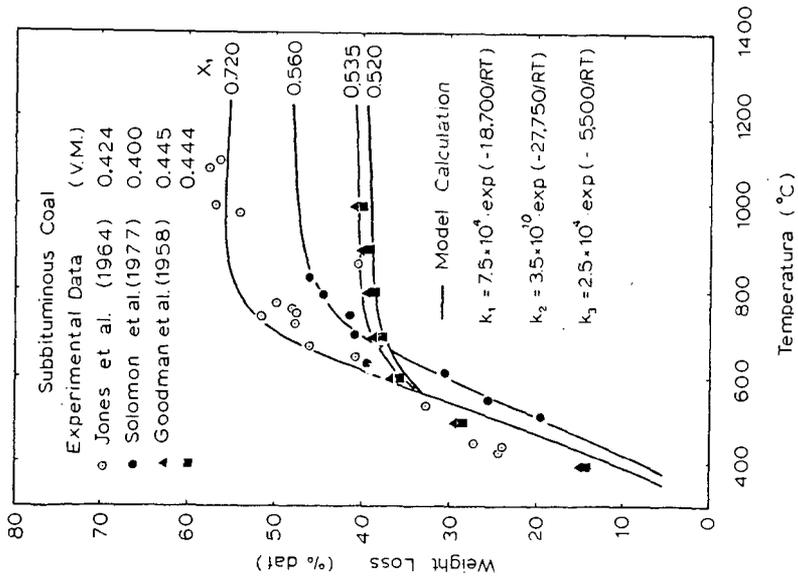


FIG. 8. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF SUB-BITUMINOUS COAL

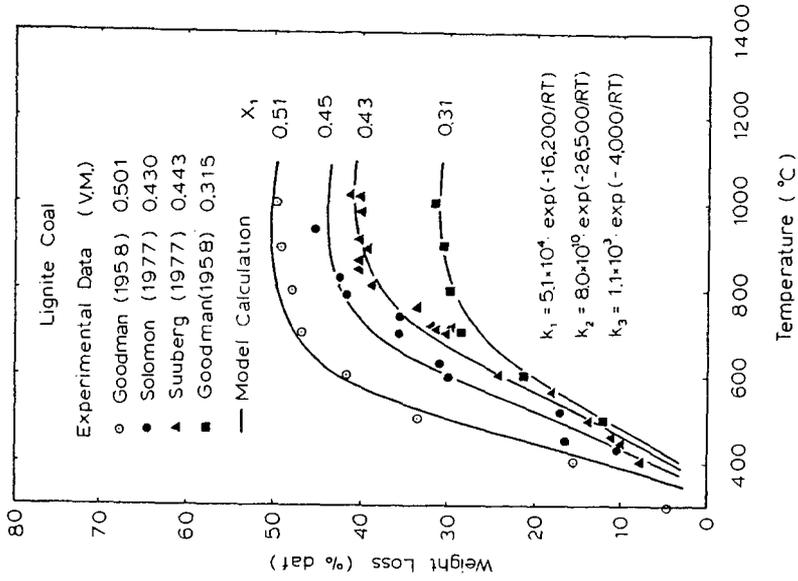


FIG. 9. EFFECT OF TEMPERATURE ON THE WEIGHT LOSS OF LIGNITE COAL

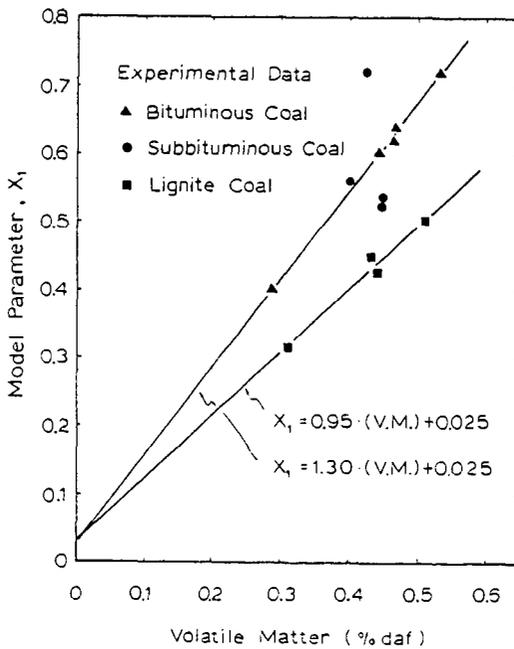


FIG. 10. THE RELATION OF THE MODEL PARAMETER,  $X_1$ , WITH THE VOLATILE MATTER CONTENT FOR BITUMINOUS, SUB-BITUMINOUS AND LIGNITE COALS