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The Mississippi Mineral Resources Institute
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MMRI FINAL REPORT

Hydropyrolysis and Methanolysis Of Mississippi's Lignite

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INTRODUCTION

Vie would like to report here findings of our data analysis/modeling study of the effect of particle sizes and heating rate.

We carried out a kinetic parameter analysis based on the data we collected from our TG experiments. The model assumed pyrolysis occurs by a large number of parallel first-order reactions having a normal distribution of activation energies. The rate of volatiles production by a particular reaction within the coal structure can be distributed in the following manner:

$$dvi/dt = k_{r}(U_{i}^{\circ} - V_{i}) \tag{1}$$

k_i is the rate constant and mav be correlated with temperature bv an Arrhenius expression

$$\kappa_i = k_{0i}\, 1^{E_i/RT} \tag{2}$$

where κ_{oi} = frequency factor

E_i = activation energy

R = gas constant.

If the experiment is carried out non-isothermally and the temperature changes reactilinear with time then equation (1) can be integrated approximately to give:

$$\frac{V_i^{\circ} - V_i}{V_i} = \exp[(-k_{0i}\, RT^2/hr(i) \quad \exp(-E_i/RT)] \tag{3}$$

where hr = dT/dt , the linear heating rate. The κ_i's is assumed to be different only in activation energy and the number of reaction is large enough to permit E to be expressed as a continuous distribution function of (E). A Gaussian distribution function is assumed. Thus

$$f(E) = [\sigma(2\tau)^{1/c}]^{-1} \exp[-(E - E_{0})^2/2c^2] \tag{4}$$

where E_0 = mean activation energy

σ = standard deviation.

The weight loss from a heating process becomes an integral relationship:

$$\frac{V^* - V}{V^*} = \frac{1}{\sigma(2\pi)^{1/2}} \int_0^\infty \exp\left[-k_0 \int_0^t \exp(-E/RT)\, dt - (E - E_0)^2/2\sigma^2\right] dE \qquad (5)$$

This model is called the Anthony-Howard model. It permits correlation of coal decomposition data by using four parameters (V^*, E_0, σ, k_0). We wrote a computer program that involves the search of values for E_0, σ, V^* and calculates weight loss at various temperatures using the integral relationship. These parameters quantify comparisons among process conditions, they describe the global intrinsic kinetics of the devolatilization process.

RESULTS OF DISCUSSION

Table 1 summarizes the model parameter data for gas atmosphere runs in He, H_2, CH_4. The pre-exponential factor is fixed at $1.0 \times 10^{13}\ sec^{-1}$ in the computer program since it gives a more consistent calculated activation energy. The k_0 calculated from transition-state theory is of the order $10^{13}\ sec^{-1}$. This arbitrary choice of k_0 is justified on theoretical ground. The computer determined k_0 in helium is in the order of $1 \times 10^{10}\ sec^{-1}$, which lowers the activation energy by about 30 kJ/mole, but the standara deviation is almost the same in both cases.

In all the figures the lines represent the calculated results and symbols represent experimental data points. Figure 2 shows the heating rate effect in helium atmosphere for 1.0/1.41 min, 0.25/0.59 mm and 44/75 micron. The trend here is that at a slower heating rate the ultimate weight loss is higher due to partial gasification of the char. Also, there is more volatile evolved at lower temperatures if the heating rate is slower.

One well worth mentioning phenomenon happened during these experiments. The weight increases when the temperature raised to 850°C, presumably at the end of the devolatilization stage. It is probably caused by the deposition of carbon from methane in the bulk phase. The weight started to increase at a lower temperature at slower beating rate.

RESULTS

Results show the effect of particle size in Helium atmosphere. Surprisingly the smallest particle size, which is 44/75 micron, gives the loudest ultimate weight loss. The particle size effect in methane atmosphere here is totally reverse from that in He. The smallest particle size gives the highest ultimate weight loss. The effect of particle szie in Hydrogen on a dry and DAf basis respectively shows the smaller particle size gives slightly higher yields.

In general, the Anthony-Howard model works quite well. We are currently doing more test on our lignite. In addition, we acquired some well analyzed Texas and Dakota lignite from Pennsylvania State University Coal Bank to test on for comparison purposes .

TABLE 1

Gas Atmosplier e	Particle Size (Micron)	Fractional Weight loss (wd-wf)/wd$_o$ V ex p	V cal	Eo kJ/mole	o kJ/mole	Fractional Weight loss (DAE) V exp	V C¿l1	Heating rate (°C/min)
He	45/75	47.75	45.17	203.1	29.88	64.06	60.59	200
	2500/5700	55.30	52.52	202.22	26.32	75.36	71.58	200
	10000/]4000	58.49	55.31	203.30	26.39	75.21	71.13	200
	10000/14000	63.27	55.96	203.59	50.14	81.37	73.14	5
	10000/14000	56.17	52.47	187.78	26.88	72.23	67.47	88
UU	44/75	49.6	48.5	188.06	25.65	66.55	85.06	200
	2500/5700	44.87	4 3.57	202.08	27.17	60.00	58.27	200
	10000/14000	47.31	46.1 7	204.67	25.97	60.84	59.38	200
	10000/14000	49.29	51.67	186.27	21.55	63.38	66.44	25
H_2	44/75	59.42	58.35	178.03	27.89	79.71	75.59	1.50
	2500/5700	54.69	52.04	180.8	28.53	73.13	89.58	150
	10000/14000	57.57	53.71	191.08	29.82	74.03	69.07	150
	10000/14000	62.42	59.52	170.06	23.83	80.28	78.54	25

Standard Conditions: (.1) Gas flow rate 200 cc/min
(2) Final Temperature 900°C

TEMPERATURE VS WEIGHT LOSS

LIGNITE (DAP BASIS)

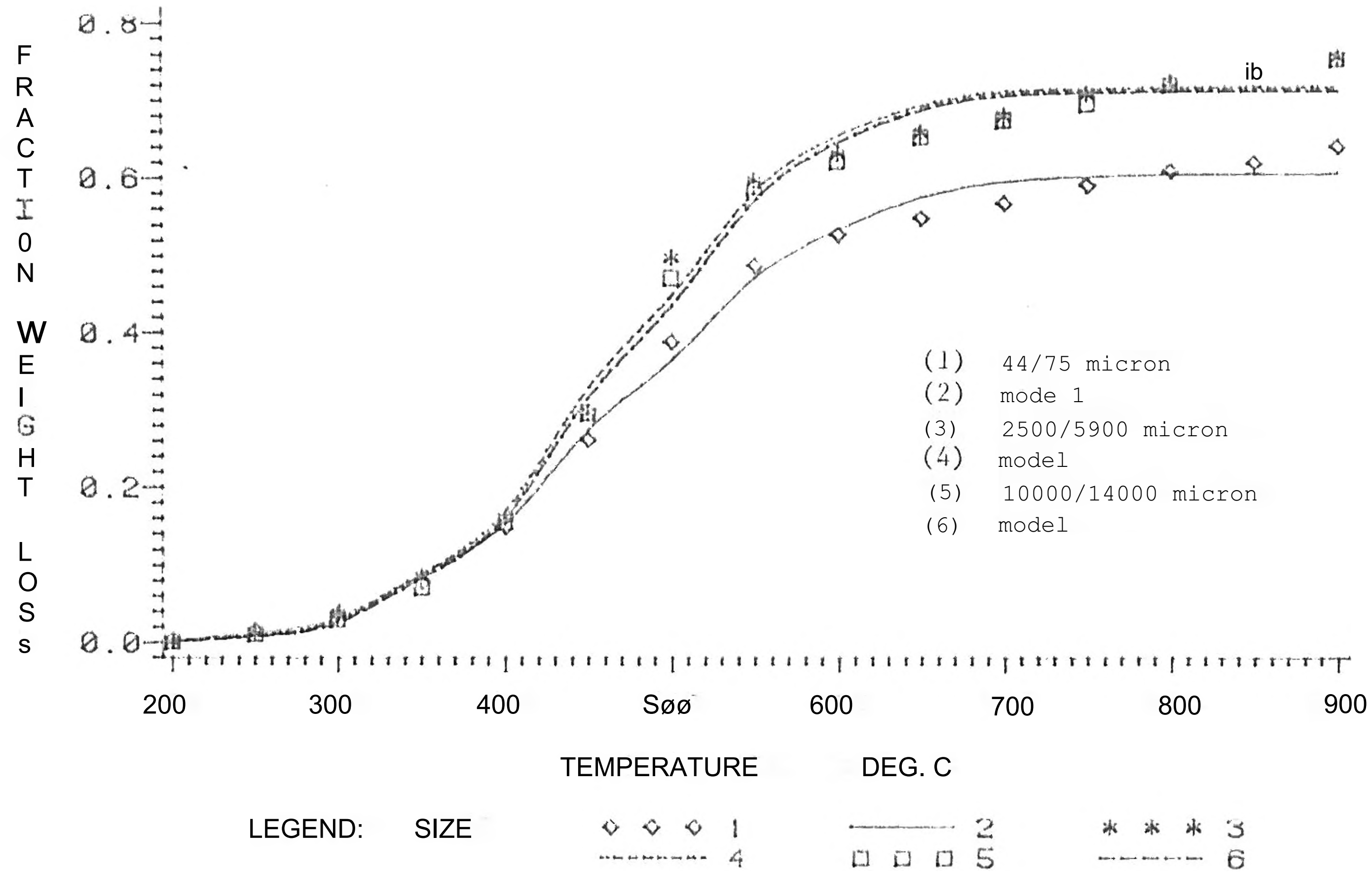


FIGURE 1. EFFECT OF PARTICLE SIZE IM HELIUM

TEMPERATURE VS WEIGHT LOSS

LIGNITE 1.00-1.41 MM (DAF BASIS)

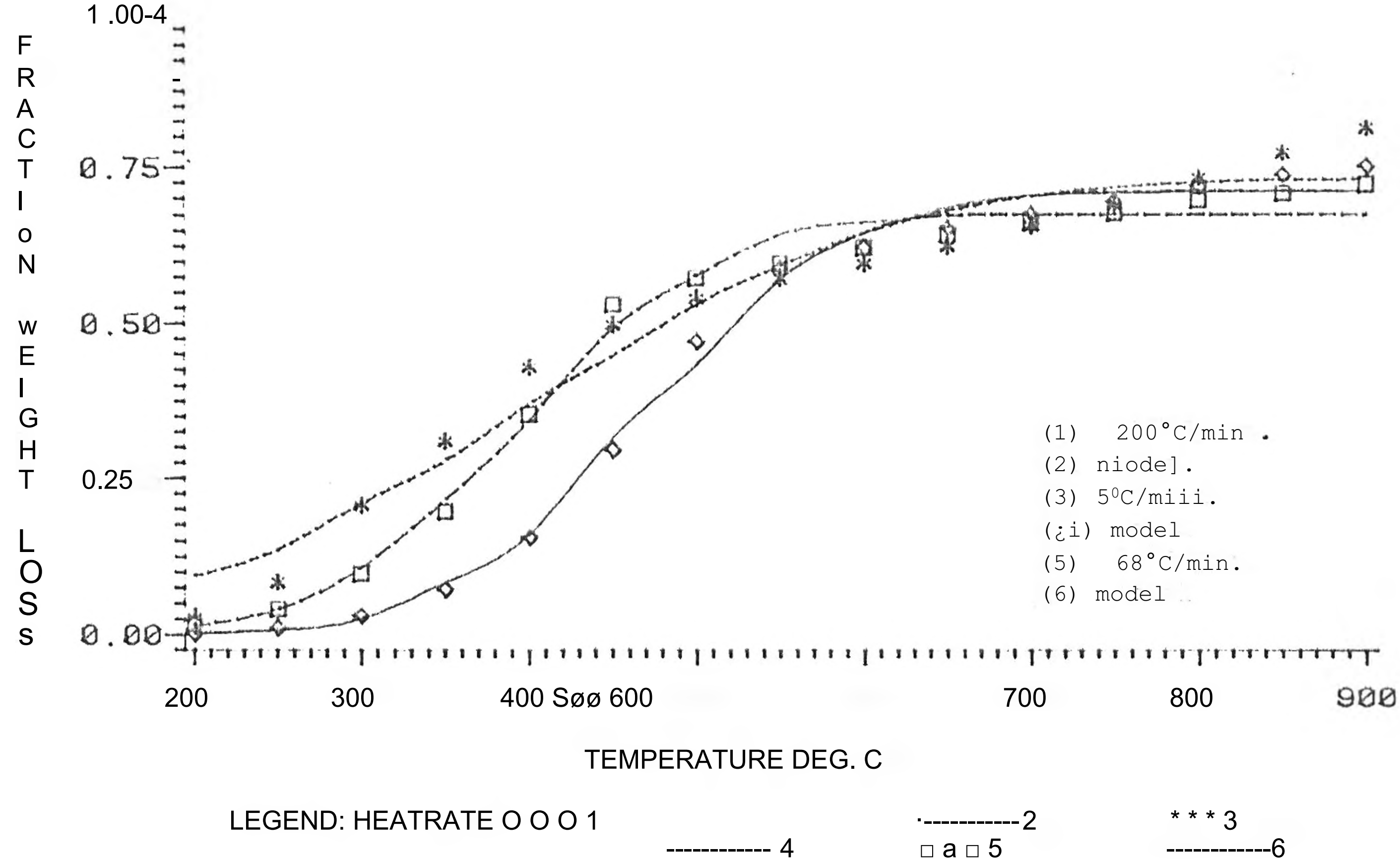


FIGURE 2. EFFECT OF HEATING RAIE DEG. C PER MIN. IN HELIUM

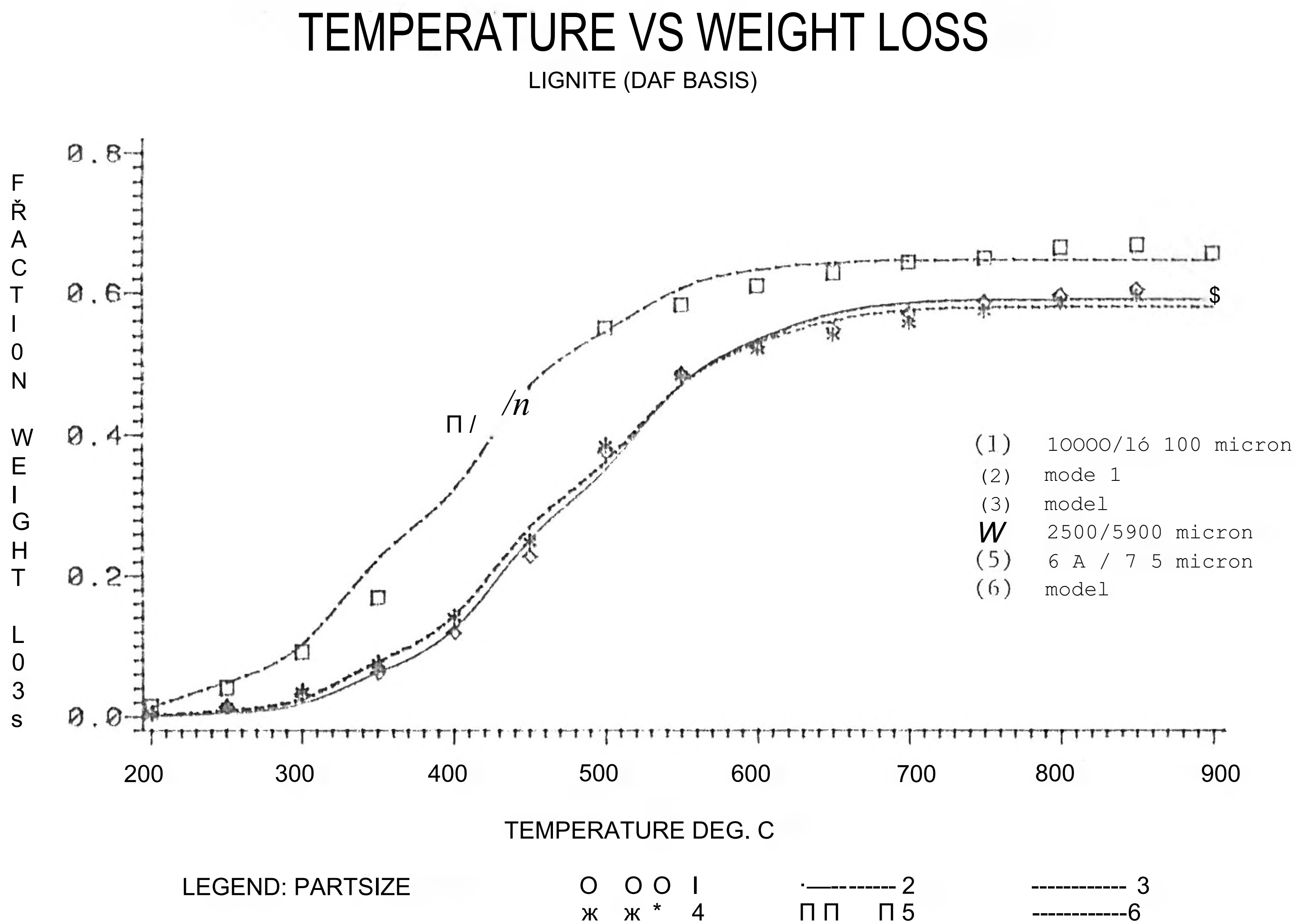


FIGURE 3. EFFECT OF PARTICLE SIZE IN METHANE

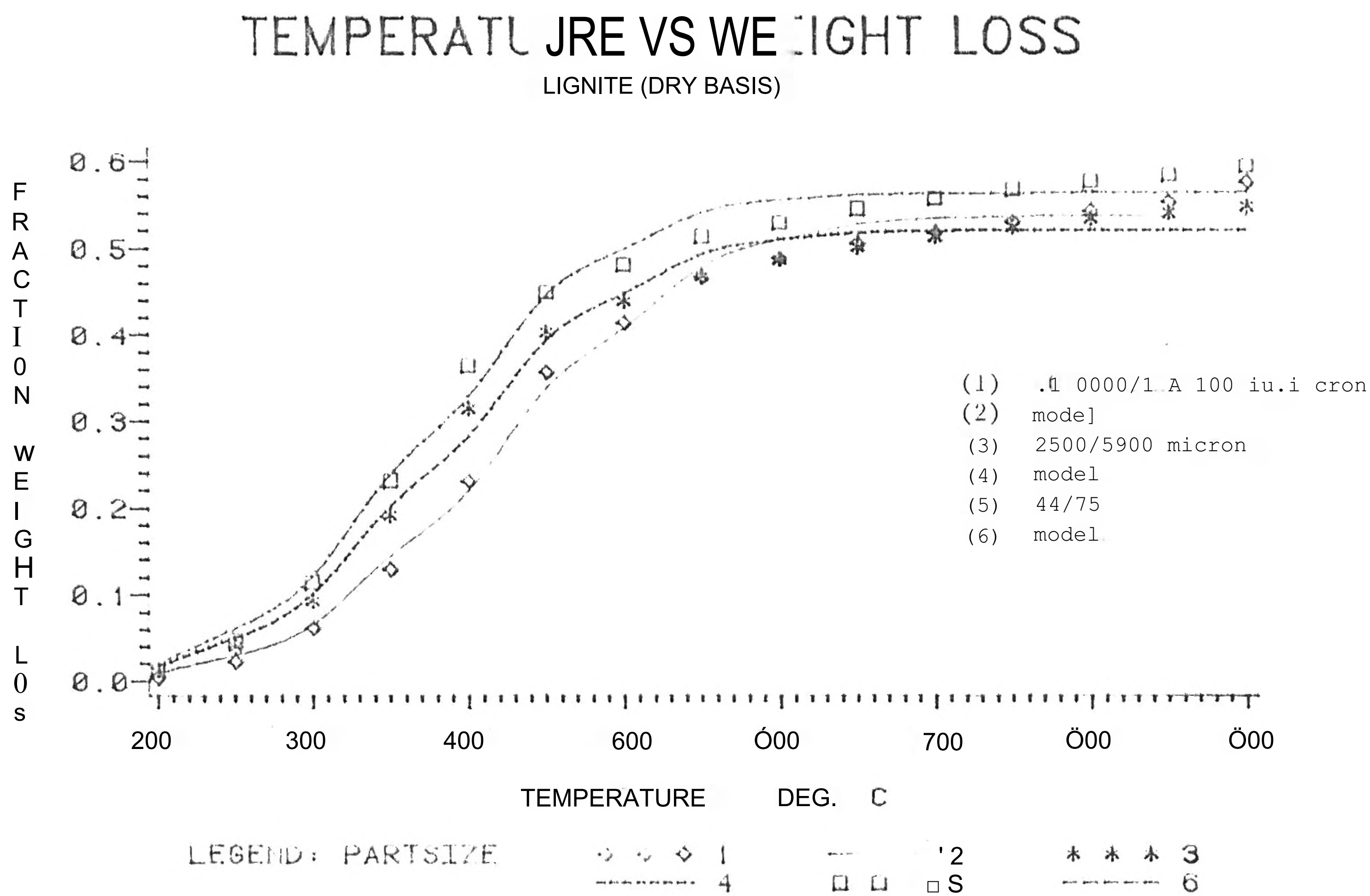
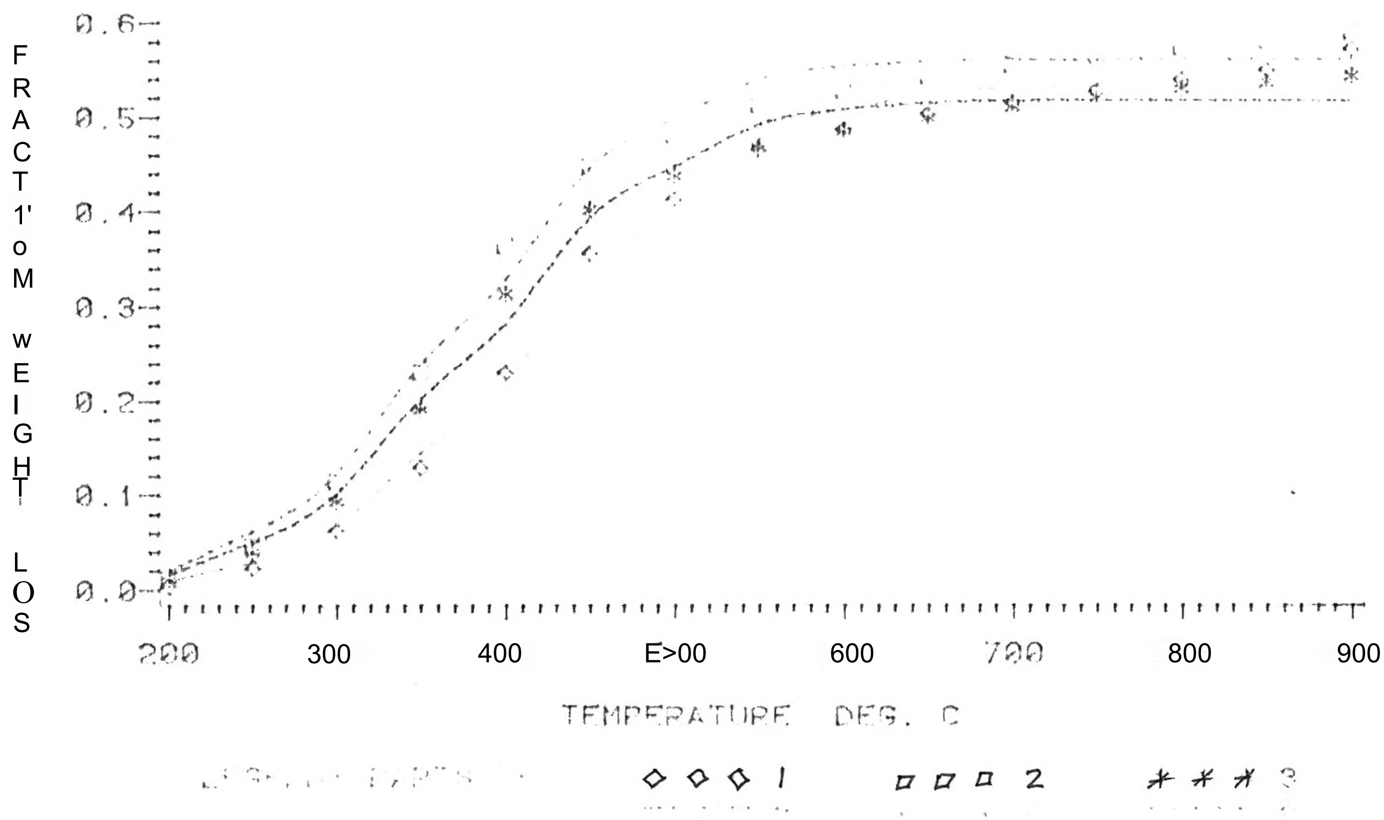


FIGURE 4. EFFECT OF PARTICLE SIZE IN HYDROGEN

TEMPERATURE VS WEIGHT LOSS

URI UTE (DAE BASIS)



FIGURI: 5. EFFECT OF PARTICI,E SIZES IN FTDROGEN