

THERMAL DECOMPOSITION OF NEW BRUNSWICK OIL SHALE

DENIZ KARMAN and BLAKE HENDER

Department of Chemical Engineering
University of New Brunswick
P.O. Box 4400, Fredericton, NB E3B 5A3
Canada

ABSTRACT

The oil shale deposits in New Brunswick have been considered as potential SO_2 sorbents in co-combustion with high sulfur coal. In this study the thermal decomposition of shale samples have been studied by thermogravimetry up to 950 C, to cover the decomposition of both organic and inorganic constituents.

Samples from 4 different zones were used in the - 75 μm to +2 mm range with heating rates of 5-20 C/min. Experiments were carried out in N_2 or a simulated combustion gas with N_2 , CO_2 , O_2 and SO_2 .

Total weight loss of the samples reaches up to 30% with differing proportions due to organic and inorganic material for samples from different zones. The rate of mass loss shows 2 or 3 maxima, one in the 400-500 C range, and the others around 700 C. The heating rate in the 5-20 C/min range has a small but noticeable effect on the weight loss characteristics.

Data reduction methods proposed by previous workers have been utilized to obtain kinetic parameters representing the global weight loss rate. The utility of parameters so derived, in describing behaviour in a fluidized bed seems questionable. Current work aimed at obtaining apparent kinetic parameters in a fluidized bed environment is discussed.

1. INTRODUCTION

The oil shale deposits at the Albert Mines site in New Brunswick have been estimated (Macauley, Ball, Powell 1984) to contain 42.8×10^6

cubic metres (270 million barrels) in situ shale oil reserves in an area of 2.6 km² to a depth of 600 m, with average yields of 100 litres/tonne in some areas.

The more recent interest in these deposits has focused on the possibility of using these deposits as SO₂ scavengers during the combustion of high sulfur (6.8%) New Brunswick coal. Direct co-combustion with coal and integrated retort/combustor operations have been considered by the Research and Productivity Council of New Brunswick and experimental work has been carried out on a pilot scale moving bed retort and circulating fluidized bed combustor (Furimsky, Synnott, Boorman, Salter 1984 and Salib, Barua, Furimsky 1986). The New Brunswick Electric Power Commission have constructed a circulating fluidized bed combustor for a 22 MWe generating Station in Chatham, N.B. to demonstrate the combustion of high sulfur coal with low SO₂ emissions using limestone and/or oil shale for SO₂ capture. In such an operation the shale contributes about 4000 kJ/Kg to the thermal generation and is expected to capture an amount of SO₂ proportional to the calcium content in the form of calcite or dolomite.

Although the standard Fischer Assay, Rock-Eval Pyrolysis and the RPC pilot plant tests have provided a gross characterization of the retorting properties of N.B. shale samples, detailed data on thermal decomposition behaviour is rare. This study was undertaken to obtain weight loss and rate of weight loss versus temperature data so that the behaviour of shale in a combustor or retort can be modelled. In a parallel study (Karman and Kresta 1987) a semi quantitative analysis of the sulfation behaviour of spent shale was undertaken.

2. EXPERIMENTAL

The experiments were conducted in a thermogravimetric apparatus built to separate the balance from the gas chamber so that gases containing the corrosive SO₂ could be handled (Kocaeffe, Karman, Steward 1985). 150-200 mg samples of crushed and sieved shale were placed in baskets (1.5 cm diameter, 3 cm high) made of 300 mesh stainless steel, suspended in a quartz tube being flushed with N₂ or simulated combustion gases and were heated at rates in the 5-20 C/min range.

The samples come from the Canadian Occidental Petroleum's #5 hole core archive as well as from material delivered to NB Power's Chatham plant from the open pit in the Albert Mines region. Table 1 identifies the samples according to the zones (Macauley, Ball, Powell 1984) in this deposit.

The Can Oxy #5 hole samples were studied in four different size fractions from - 0.075 to +2 mm and at 4 different heating rates from 5 to 20 C/min.

Table 1. Sample Identification and Zones for the Can Oxy #5 hole

Zone	Depth, m	Sample #	Depth, m
Surface	0 - 190	5 - 17	85
Laminated Marlstone	190 - 280	5 - 47	206
Clay Marlstone	280 - 390	5 - 78	343
Dolomite Marlstone	390 -	5 - 116	557
		"Albert Mines"	surface pit.

The "Albert Mines" sample from the Chatham plant was studied for 1 size range (-1.5/+0.5 mm) and 1 heating rate (10 C/min).

3. RESULTS AND DISCUSSION

Total weight loss of the samples studied is between 20-30 wt.% with differences between samples on the total weight loss and the fractions attributable to organic and carbonate decomposition. Samples 5-47 and 5-116 which represent extremities in terms of organic and carbonate content show the markedly different behaviour in Figures 1 a and b. Although the total weight losses are comparable, most of it occurs at the high temperatures for samples 5-116 while most decomposition for sample 5-47 occurs at lower temperatures. Even though the range of heating rates is modest, some effect on total weight loss is observed in Fig. 1a, mostly at the higher temperatures.

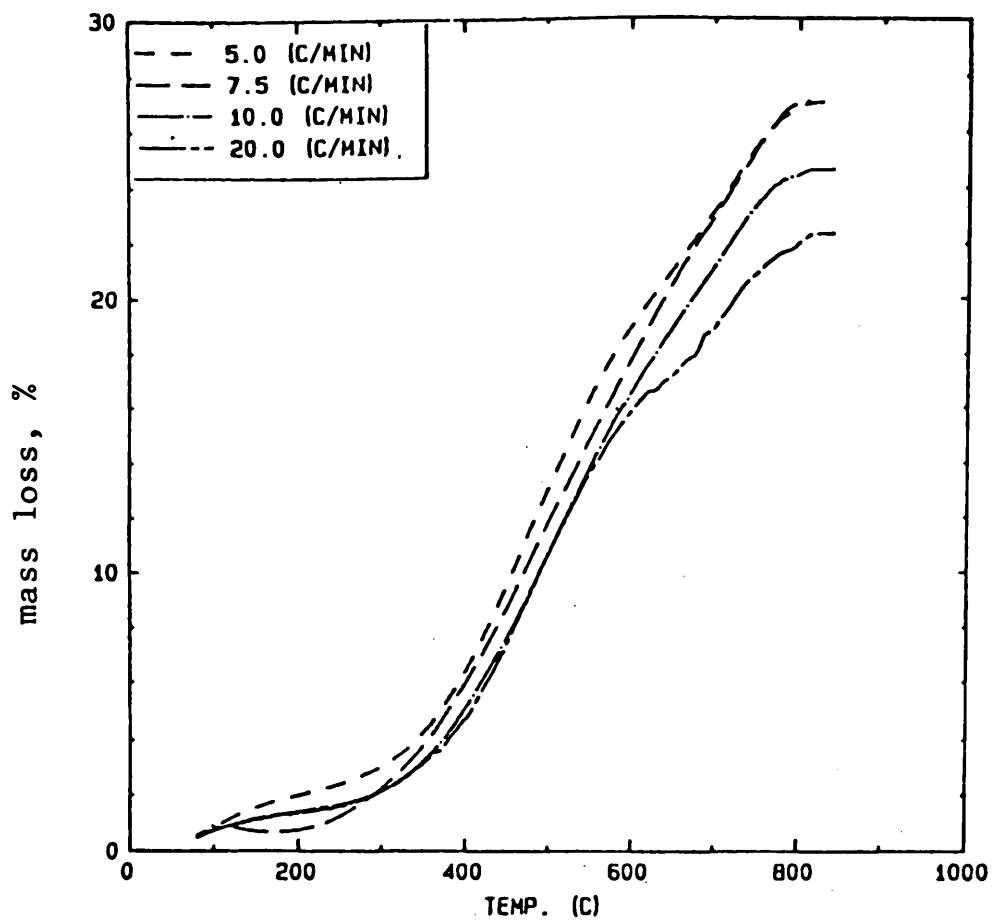
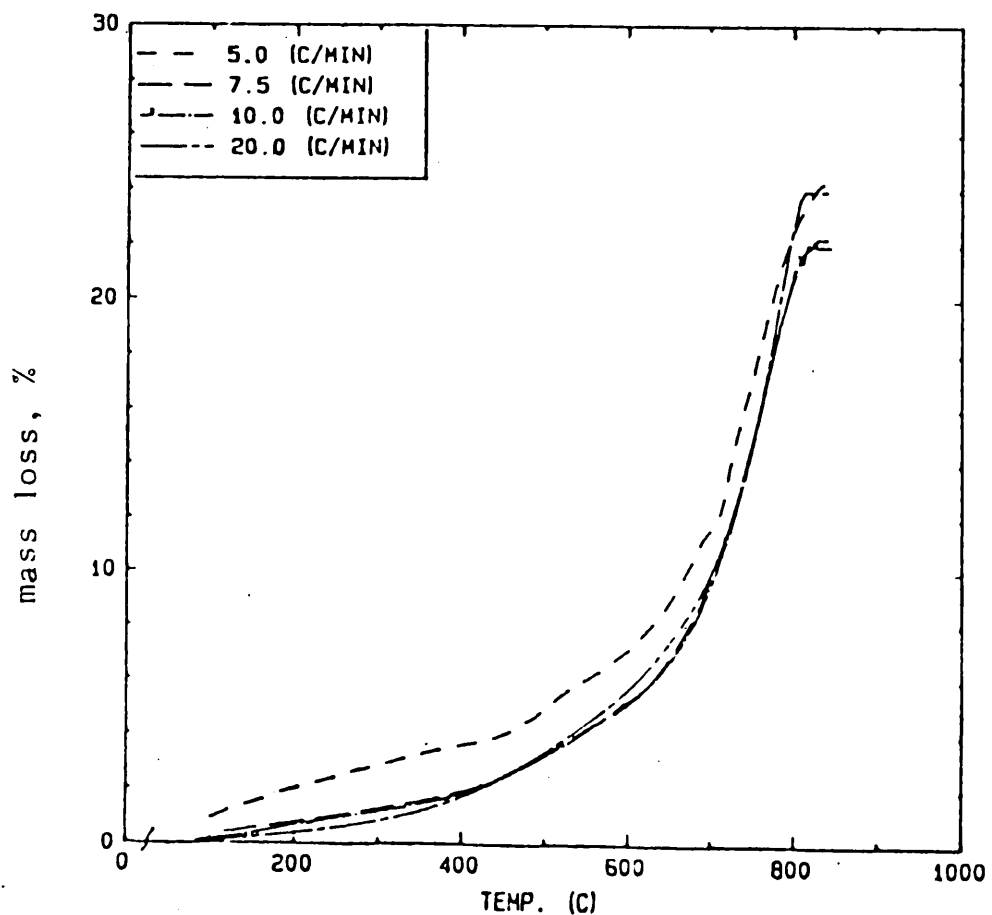
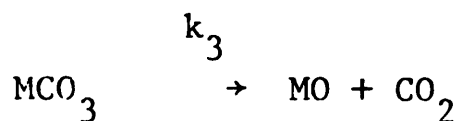
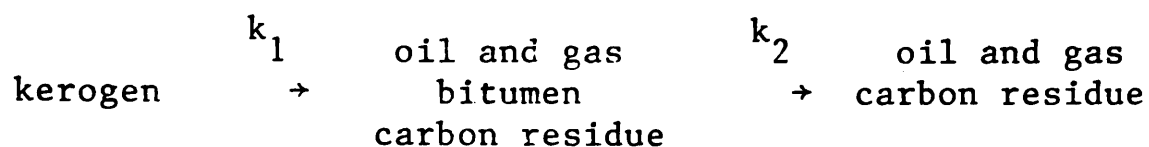
a) Sample 5-47, size $-0.841/+0.500$ mmb) Sample 5-116, size $-0.841/+0.500$ mm

Figure 1 Mass loss for nonisothermal decomposition in nitrogen at different heating rates.

The raw mass vs. temperature data show significant noise but smoothing by cubic spline software enables the calculation of rate of mass loss vs. temperature data.

Data analysis was carried out by following the methods detailed in a study comparing the thermal decomposition of Colorado and Moroccan oil shale samples (Bekri, Baba-Habib, Cha, Edelman 1983). The model assumed is two first order reactions in series for the organic decomposition and first order reaction for carbonate decomposition:



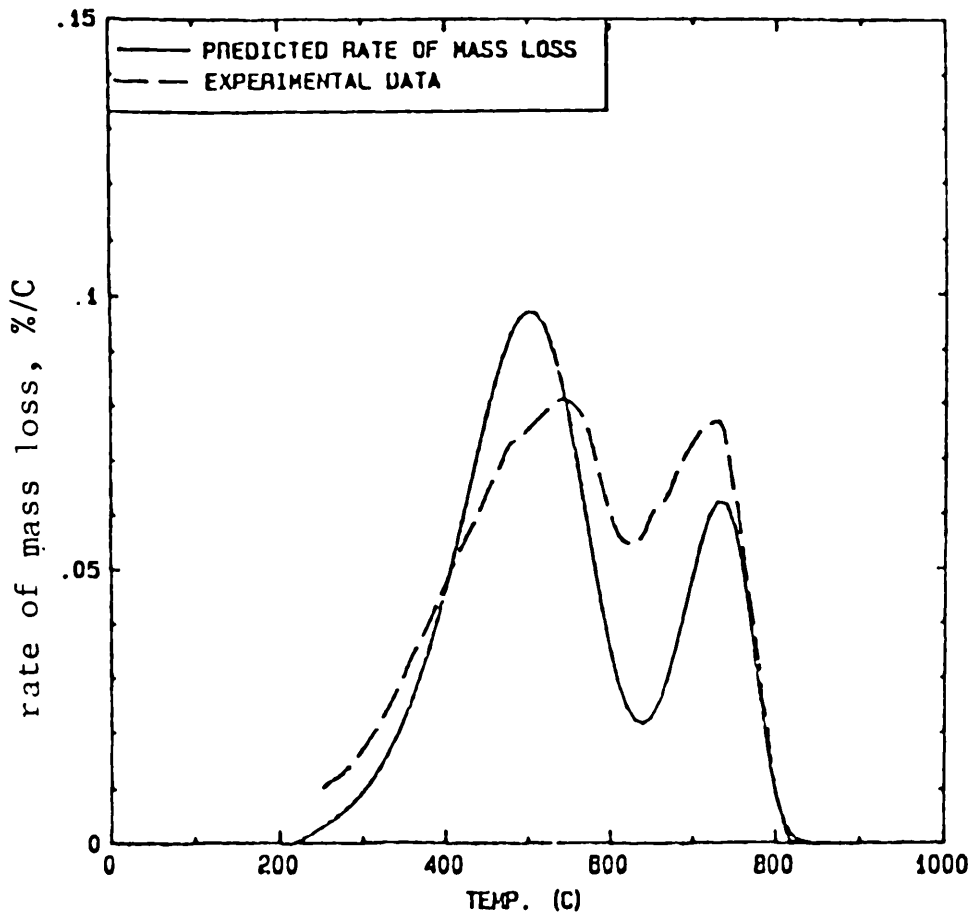
with $k_i = k_{i0} e^{-E_i/RT}$

and

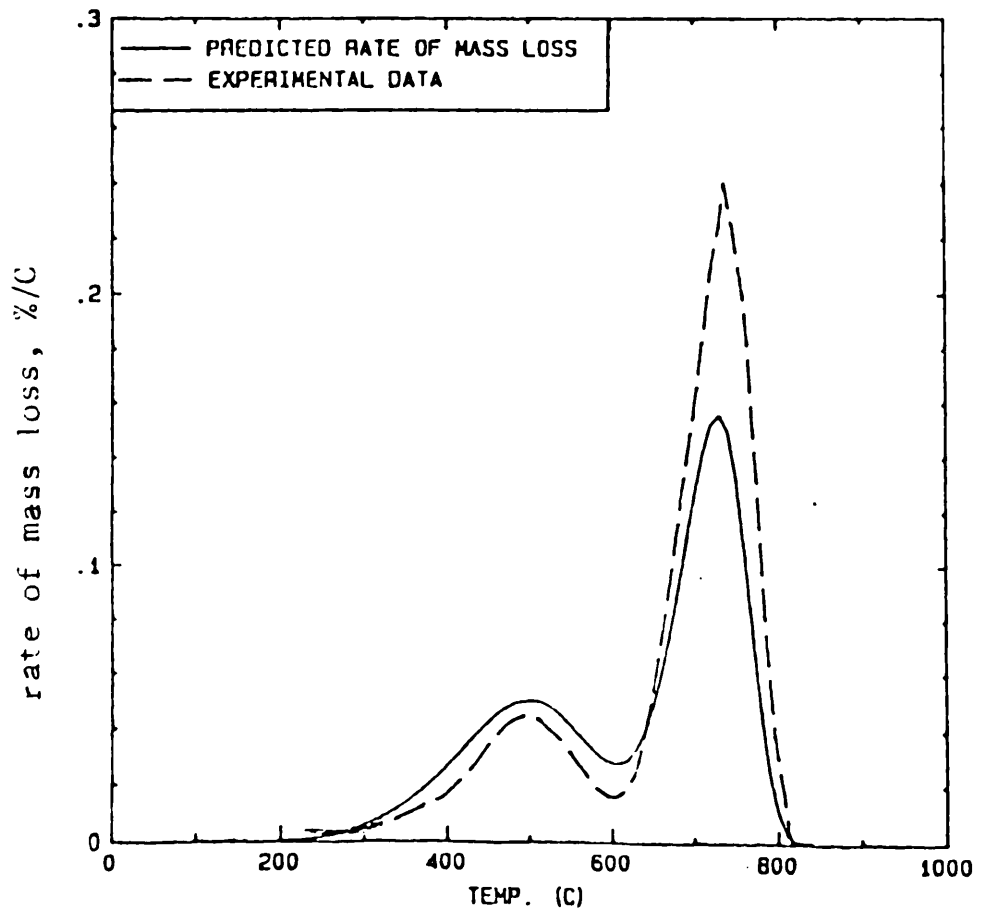
$$-\frac{dX_i}{dt} = k_i X_i \quad i = 1, 2, 3$$

where X_i is the fraction of kerogen, bitumen or carbonate remaining at time t .

It is possible to back out the k_0 and E parameters from the methods outlined in the above reference but the rate of mass loss versus temperature behaviour suggested by the model and parameters is not always in good agreement with the observed behaviour. Figures 2a and b show two examples of rate of mass loss versus temperature behaviour which are reasonably well represented by the above model. It should be noted that Bekri et. al (1984) demonstrate the fit of their model calculations by using mass loss data rather than rate of mass loss. The latter is a more critical test of the adequacy of the model in terms of predicting the behaviour of shale particles which are exposed to a furnace or retort environment. Some of the model predictions and parameters for their runs probably do not give adequate representation on rate vs. temperature co-ordinates just like some of our data were poorly represented by this model. Some general comparisons among the reported parameters may still be made however.



a) Sample 5-47, size $-0.841/+0.500$ mm, heating rate 5 C/min.



b) Sample 5-17, size $-0.841/+0.500$ mm, heating rate 7.5 C/min.

Figure 2 Rate of mass loss for nonisothermal decomposition in nitrogen.

The parameters backed out from the above mentioned procedure are compared to those reported by the same authors in Table 2.

Table 2. Comparison of Kinetic Parameters for the Three Consecutive Reactions Decomposition Model.

Sample	E_1 kJ/mol	k_{10} s^{-1}	E_2 kJ/mol	k_{20} s^{-1}	E_3 kJ/mol	k_{30} s^{-1}
Colorado	18.2	3.0×10^{11}	201	2.5×10^{12}	242	1.7×10^{10}
Moroccan X Zone	111	2.4×10^5	95	1.3×10^3	220	4.8×10^8
T Zone	83	6.1×10^3	77	83	203	9.9×10^7
New Brunswick 5 - 17	55	360	32	1.1×10^4	201	6.0×10^9
5 - 47	55	637	50.5	2.3×10^3	225	1.6×10^{11}

The first thing to note about the derived parameters in Table 2 is that for carbonate decomposition, activation energies are in reasonable agreement and the pre-exponential terms span a range that may be attributed to differences in the rock matrix. On the other hand, the wide variations observed for the organic decomposition parameters raise serious doubts about attaching any physical significance to the mathematical model and/or the data reduction technique. The utility of devising such parameters to characterize other samples from the same geological formation is tested in Figure 3 where the thermal decomposition of the "Albert Mines" sample is compared to the model calculations based on parameters derived for sample 5-47. The "Albert Mines" sample from the Chatham plant comes from an open pit which is an outcrop of the Laminated Marlstone zone of Table 1, i.e. the same zone for sample 5-47. Without a complete characterization of the sample itself, the parameters derived for a "similar" sample clearly do not offer adequate representation of the rate of weight loss vs. temperature behaviour.

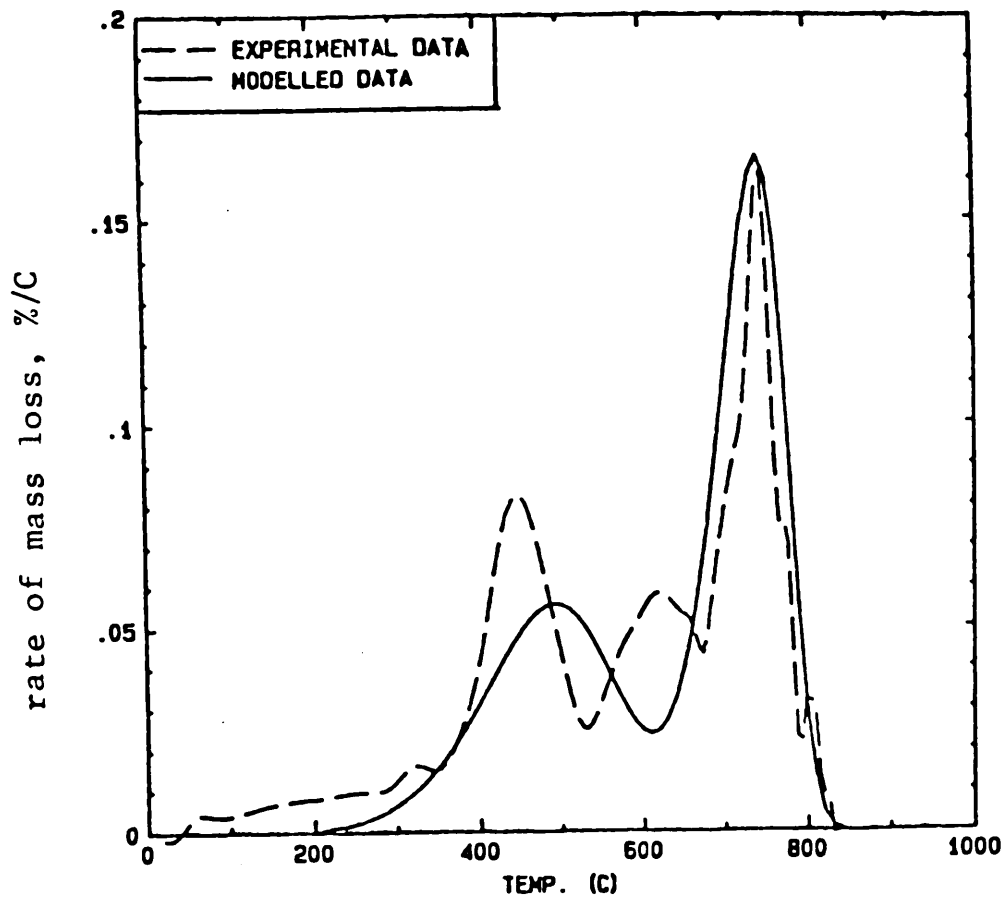


Figure 3 Comparison of rate weight loss data for "Albert Mines" sample (size $-1.5/+0.5$ mm, heating rate 10 C/min) with model and average parameters for sample 5-47.

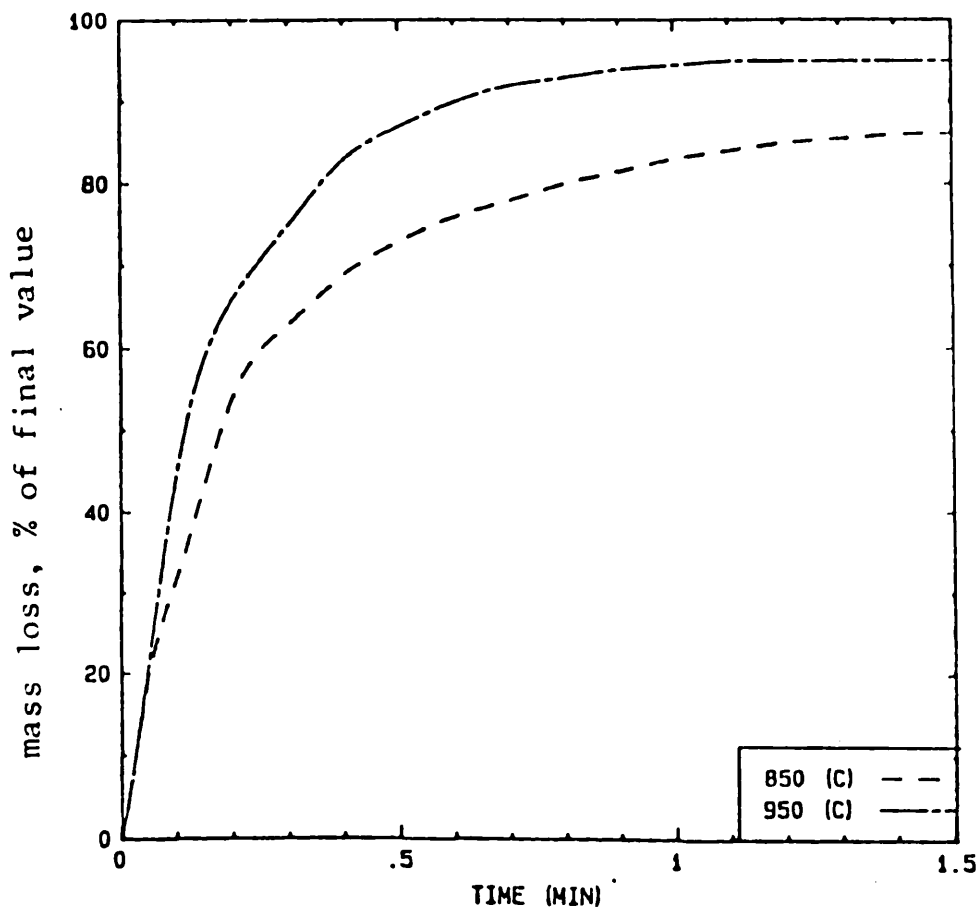


Figure 4 Isothermal decomposition in nitrogen at two different temperatures. Sample 5-47, size $-0.841/+0.500$ mm. (Mass loss is compared to final mass loss for nonisothermal run.)

Braun and Burnham (1986) have analyzed the isothermal decomposition of Colorado oil shale by considering one or more simultaneous, independent n^{th} order reactions where the fraction X_i of the i^{th} oil progenitor remaining at time t obeys:

$$-\frac{dX_i}{dt} = k_i X_i^{n_i} \quad i = 1, 2, \dots, I$$

with I being total number of such reactions and the k_i obeying:

$$k_i = k_{i0} e^{-E_i/RT}$$

They conclude:

1. That a single 1.51 order reaction or two parallel first order reactions represent the data equally well for rapid pyrolysis in a fluidized bed,
2. That the single first order reaction model used earlier to interpret data from slow heating rate (2 C/min) experiments is not representative of pyrolysis in a fluidized bed with heating rates of the order of 10^2 C/s.

In our work we have also completed some isothermal runs with the TGA apparatus, quickly lowering the sample baskets into the furnace. Figure 4 shows typical results from such runs at two different temperatures. The time scales for such runs are comparable to the data presented by Braun and Burnham (1986) although the experiments are of a different nature (temperatures, 480-540 C vs 850-950 C, fluidized bed reactor, evolved HC measurement vs TGA weight loss measurement). The differences in total weight loss for the two temperatures cannot be compared directly with nonisothermal runs since the latter were typically terminated around 800-850 C when the rate of weight loss became too slow for differential analysis. The difference seems to develop almost at the start and is probably due to differences in mass loss from both organic and inorganic components.

In light of the above observations our current studies are aimed at:

1. Interpreting the current TGA data with a generalized approach similar to Braun and Burnham's (1986).
2. Characterizing the gas evolution during nonisothermal runs to see if the weight loss from organic and inorganic components have significant overlap.

3. Obtaining evolved gas data in a fluidized bed reactor to check if such data for N.B. oil shale show differences from nonisothermal TGA data as Braun and Burnham (1986) have demonstrated for Colorado oil shale.

REFERENCES

- Macauley, G., Ball, F.D., and Powell, T.G., "A Review of the Carboniferous Albert Formation Oil Shales, New Brunswick", Bulletin of Canadian Petroleum Geology, v. 32, no. 1, p. 27-37, March. 1984.
- Salib, P.F., Barua, S.K., and Furimsky, E., "Retorting of Oil Shale from New Brunswick, Canada", Canadian Journal of Chemical Engineering, v. 64, p. 1001-1007, December 1986.
- Furimsky, E., Synnott, J., Boorman, R.S., and Salter, R.S., "Hydrogen Retorting of Oil Shales From Eastern Canada", Fuel Processing Technology, v. 8, p. 293-306, 1984.
- Karman, D., and Kresta, S., "Sulfation of Mineral Matter in New Brunswick Oil Shale", Energy and Fuels, v. 1, p. 10-16, November 1987.
- Kocaeffe, D., Karman, D., and Steward, F.R., "Comparison of the Sulfation Rates of Calcium, Magnesium and Zinc Oxides with SO_2 and SO_3 ", Canadian Journal of Chemical Engineering, v. 63, p. 971-977, 1985.
- Bekri, O., Baba-Habib, H., Cha, C.Y., and Edelman, M.C., "Study of Moroccan Oil Shale Thermal Decomposition Kinetics", Proc. 16th Oil Shale Symposium, Colorado School of Mines, 1983.
- Braun, R.L., and Burnham, A.K., "Kinetics of Colorado Oil Shale Pyrolysis in a Fluidized Bed Reactor", Fuel, v. 65, pp. 218-222, February 1986.