

APPLICATION OF THERMAL ANALYTICAL TECHNIQUES TO
 ENHANCED OIL RECOVERY

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INTRODUCTION

The world, especially in Canada and Venezuela, has extensive resource of oil sands and heavy oils. These resources are characterized by high viscosity, low API gravity, i. e., high density, and large sulfur contents (Table I). Recovery of Lloydminster heavy oils in Canada under primary and secondary processes are less than 9% of initial oil-in-place, whereas that of bitumen from oil sands is nil.

TABLE I
 PROPERTIES OF HEAVY OILS AND OIL SANDS^{a-c}

Source	Gravity °API	Viscosity cp(°C)	Sulfur Wt%	Asphaltene Wt%	Conradson Carbon Residue Wt%
<u>Canada</u>					
Lloydminster	10-18	2000-20,000(20)	2.6-3.5	8 - 12	8 - 12
S. E. Alberta	12-18	3000 (T _R) ^d	3.5	12	12.2
Athabasca	8-12	1-5x10 ⁶ (T _R)	4.6	17	13.5
Cold Lake	10-12	1 x 10 ⁵ (T _R)	4.7	15	12.6
Peace River	8-9	1 x 10 ⁵ (T _R)	5.6	20	
Wabasca A	8-13	8 x 10 ⁵ (T _R)	5.5	19	
<u>Venezuela</u>					
Boscan	10-12	26 x 10 ³ (38)	5.2	9 - 17	15.0
Tia Juana	12	37 x 10 ² (38)	2.7	6	11.2
Morichal	12	32 x 10 ² (38)	2.1	11	14.0
Jobo	8.4	62 x 10 ³ (38)	3.7-4.1	9	14.1
<u>U.S.A.</u>					
Asphalt Ridge, Utah	8-13	69 x 10 ⁶ (25)	0.2-0.8	12	9.1

- a. Work done in our laboratory on Lloydminster, Saskatchewan crudes.
- b. "The Future of Heavy Crude Oils and Tar Sands", Ed. R. F. Meyer and C. T. Steele, McGraw-Hill, inc., New York (1981), pp. 168, 187, 237.
- c. "The Oil Sands of Canada - Venezuela 1977", Ed. D. A. Redford and A. G. Winestock, CIM Special Volume 17, The Canadian Institute of Mining and Metallurgy, pp. 146, 178, 284.
- d. Reservoir temperature.

For the development and utilization of these resources, enhanced oil recovery (EOR) processes have to be employed (1-3). EOR refers to all techniques used to increase the amount of oil produced after primary recovery. EOR methods encompass pressure maintenance, water-flooding, gas injection, thermal, miscible displacement and chemical processes. The thermal process is most suitable for recovery of heavy oils and oil sand bitumens. In this process oil displacement results from:

- i) viscosity reduction primarily due to heat and secondly due to carbon dioxide dissolution in oil,
- ii) thermal expansion of the oil resulting in increased relative permeability,
- iii) distillation and thermal cracking of oil,
- iv) a solution gas drive from produced gas which facilitates the flow of fluids within the reservoir toward the production wells, and

v) increased pressure gradient imposed by the injected air.

Heat is transferred to the reservoir either by injection of steam/hot water or by *in-situ* combustion. The latter process, of interest to us at present, consists of injecting air/oxygen/water into an oil reservoir to establish a flow path for the movement of fluids, igniting the crude oil and propagating the combustion front by continued air/oxygen injection (Figure 1).

The important factors required to establish the feasibility of initiating an *in-situ* combustion field test are the fuel (coke) content of the oil being burned, the volume of air/oxygen required to sustain combustion and the efficiency of oxygen utilization. These parameters are usually determined by laboratory experiments employing a combustion tube. A sample of the data obtained is presented in Table II. Most of these parameters could be estimated from TGA/DSC data.

TABLE II
TYPE OF DATA GENERATED FROM COMBUSTION TUBE EXPERIMENTS^{a, b}

Fuel Concentration, Kg/m ³	16-48
Air-Fuel Ratio, m ³ /Kg	10
Oxygen Utilization, %	90+
Combustion Front Velocity, m/h ^c	0.1
Steam Front Velocity, m/h	0.1
Vaporization Front Velocity, m/h	0.1
Fuel Required to Sustain Combustion, Kg/m ³	20
Maximum Peak Temperature, °C	450-700
Hydrogen to Carbon Ratio of Fuel	0.6-2.0
Oil Recovery, %	90
Produced Gas Analysis, Vol. %	CO ₂ , CO, O ₂ , N ₂ , C ₁ -C ₄ , SO ₂ , H ₂

- a. D. W. Bennion et al., "Proceeding II International Conference on Heavy Crude and Tar Sands", Caracas, February 7-17, 1982.
- b. "The Future of Heavy Crude and Tar Sands", Ed. R. F. Meyer and C. T. Steele, McGraw-Hill, Inc., New York, pp. 413-25, 1981.
- c. Meters per hour.

Although combustion tube experiments generate data useful for the design and operation of the field-pilot, it is imperative that the numerical simulation of the *in-situ* combustion process be carried out in making meaningful predictions of the parameters for planning, construction and optimum operation of field pilots.

Numerical *in-situ* combustion simulation usually requires reservoir description, reservoir fluid properties, thermodynamic, chemical kinetics and well data (4). Experimental data for thermodynamic properties and chemical kinetics required in the area of low temperature oxidation, cracking, combustion and coking reactions are lacking in order to make meaningful predictions of an *in-situ* combustion project (5-7). To this end, we have employed thermal analytical techniques, thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) to generate the required data such as energy of activation, pre-exponential factor, rate constant, and heat of reaction for chemical reactions. Thermal techniques can also provide data on minimum ignition temperature of crude oil to sustain combustion, fuel content of the core, fluid-rock interaction, decomposition of the mineral matter present in the core and residue left after heating.

This paper presents TGA and DSC results obtained for two Lloydminster heavy oil core samples under flow of helium, nitrogen and air.

EXPERIMENTAL

Tests were performed using a DuPont 951 Thermogravimetric Analyzer and a 910 Differential Scanning Calorimeter attached to the 1090 Data Analysis System. A sample size of 25-60 mg and a temperature range of 40° to 900°C for TGA, and 1-3 mg and 40° to 580°C for DSC studies were used. Samples were heated at a rate of 5° or 10°C/min. in air, nitrogen or ultra pure helium flowing at 60 cm³/min. for TGA and 20 cm³/min. for DSC experiments. Thermograms recorded the percentage weight loss as a function of temperature and its derivative for TGA and heat flow in mW versus temperature for DSC runs. The DSC cell constant was determined to be 1.081 using an indium standard. DSC experiments were performed using hermetic pans.

Samples A and B used for this study had an initial oil saturation of 63 and 85%, a porosity of 29 and 33%, and a permeability of 1.9 and 2.3 Darcies, respectively. Gravity and viscosity of crude oils were 16°API and 236 cp at 38°C for sample A and 11°API and 46,000 cp at 38°C for sample B.

RESULTS

Thermograms of weight loss versus temperature for Lloydminster core A are shown in Figure 2. The total weight losses were 6.92% in He, 7.57% in N₂, and 7.79% in air. The higher weight loss under air than under He indicates that the coke produced in the process is oxidized by oxygen, resulting in additional weight loss. The results under N₂ atmosphere imply that N₂ contains oxygen as an impurity.

Figures 3, 4 and 5 show weight loss curves and their derivatives (DTG) against rising temperature for sample A in He, N₂ and air. The derivative curves suggest that there are at least four groups of reactions which can be convoluted in four temperature zones. Kinetics for loss in weight in each temperature zone is described later.

TGA and DTG thermograms are presented in Figures 6 and 7 for core sample B. The total weight loss was 14.8% in He and 15.6% in air in the temperature range 40° to 880°C. The characteristics of the TGA and DTG curves are similar to those obtained for sample A. It should be noted, however, that the oil content of sample B is twice as much as that of A.

For further understanding of reaction kinetics, differential scanning calorimeter experiments were conducted for samples A and B in He and air at a heating rate of 10°C/min. (Figures 8-11). The thermograms produced with He have three peaks, the last one representing the cracking reactions. The large exothermic peak produced under air is attributed to combustion reactions. The peak temperatures for these tests range between 453° and 484°C. Arrhenius and thermal parameters obtained by using the Borchardt and Daniels kinetics data analysis program supplied by DuPont are discussed later (8-10).

DISCUSSION

Derivatives of TGA thermograms for core samples A and B have demonstrated that there are four temperature regimes for weight loss. The temperature ranges and percentage weight loss for the total material and organic components within each range are listed in Table III. The percentage weight loss in the first region (50°-380°C) was approximately the same under He and air for sample A or B. This weight representing 40 to 55% of the total loss is attributed largely to volatilization and to some extent to low temperature oxidation. The weight loss in the second temperature regime (340°-540°C) was 19% in He and 43% in air for sample A and 27% in He and 54% in air for sample B. This indicates that volatilization and thermolysis of heavy oil present in the core is taking place under He whereas more efficient reactions, such as oxidation and subsequent decomposition and volatilization, are involved in the presence of air. The third regime (450°-630°C) is characterized by cracking, volatilization and combustion reactions whereas the last fraction of the weight loss between 550° and 900°C is assigned to coking, decomposition of mineral matter and oxidation. Oxidation and combustion reactions take place when sample is in contact with oxygen.

Weight loss kinetics for pyrolysis and combustion processes is extremely complex for such systems because of the numerous components present and their simultaneous and competing reactions. Kinetic treatment of the data is described below.

Solid phase thermal decomposition is described by the rate expression (11-12):

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad 1)$$

$$\alpha = (\omega_0 - \omega_t) / (\omega_0 - \omega_\infty) \quad 2)$$

$$k = A e^{-E/RT} \quad 3)$$

where k is rate constant; n, order of reaction; ω_0 initial sample weight; ω_t sample weight at time t; ω_∞ final weight; A, pre-exponential factor; E, activation energy; R, gas constant; and T, absolute temperature in K. For a linear heating rate, β , °C/min:

$$\beta = dT/dt \quad 4)$$

By combining Equations 1, 3 and 4, rearranging, integrating and taking the natural logarithm and assuming n = 1, we obtain:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} \left[1 - \frac{2RT}{E} \right] - \left(\frac{E}{R} \right) \frac{1}{T} \quad 5)$$

A plot of $-\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ versus $1/T$ should result in a straight line of slope E/R. The value of E obtained graphically is substituted in Equation 5 to calculate the pre-exponential factor, A. Typical plots to obtain apparent activation energies are shown in Figures 12-15 for reactions

occurring in the four temperature zones for sample A under He flow.

Equation 3 is used to estimate rate constant at any temperature. Values of E, A, and rate constant at mean temperature for each reaction zone are presented in Table III.

TABLE III
THERMAL DECOMPOSITION PARAMETERS FOR LLOYDMINSTER
HEAVY OIL CORES

Sample (Purge Gas)	Reaction Zone	Temp. Range, °C	Wt. Loss %		E kcal/mol	A s ⁻¹	10 ³ k _{mean} ^b s ⁻¹	Fuel (Coke) Kg/m ³	
			Total	Organic ^a					
A. (He)	1	50-340	3.01	2.94	4.6	1.3 x 10 ⁻¹	0.92)39.2 29.3)	
	2	340-475	1.25	1.08	20.2	3.3 x 10 ³	1.1		
	3	475-550	0.69	0.45	49.9	2.5 x 10 ¹¹	3.3		
	4	550-800	1.62	1.33	18.3	1.5 x 10 ¹	0.91		
	(N ₂)	1	50-360	3.09	3.01	4.9	1.3 x 10 ⁻¹	0.75	
		2	360-450	0.89	0.79	29.3	5.0 x 10 ⁶	1.8	
		3	450-550	1.18	0.88	36.3	3.3 x 10 ⁷	1.8	
		4	550-900	2.32	1.98	14.8	1.8	1.0	
	(Air)	1	50-340	3.17	3.10	4.9	1.2 x 10 ⁻¹	0.62	
		2	340-480	3.26	3.00	23.5	6.7 x 10 ⁴	2.0	
		3	480-550	0.62	0.45	45.5	1.7 x 10 ¹⁰	4.1	
		4	550-800	0.48	0.08	14.2	2.5	1.3	
B. (He)	1	50-380	8.10	8.01	6.2	6.4 x 10 ⁻¹	1.1)49.1 28.8)	
	2	380-500	3.90	3.66	35.3	3.8 x 10 ⁸	5.8		
	3	500-600	1.15	0.92	46.4	1.0 x 10 ¹⁰	4.8		
	4	600-800	1.52	1.31	21.5	1.2 x 10 ²	1.8		
	(Air)	1	50-380	6.85	6.74	6.6	8.8 x 10 ⁻¹	1.0	
		2,3	380-540	8.32	7.95	39.4	1.8 x 10 ⁹	3.2	
		3,4	540-630	0.22	0.10	29.2	2.0 x 10 ⁵	7.3	

a. Contribution from decomposition of mineral matter was subtracted from % total weight loss to get organic weight loss.

b. Mean temperature.

The apparent activation energy obtained for reaction zone 1, E₁, varies between 4.6 and 6.6 kcal/mol for samples A and B under He, N₂ and air. E₁ values being very close to the latent heat of vaporization for hydrocarbons confirms our suggestion that weight loss in this reaction zone is mostly due to volatilization (13). E₂ values for sample A range from 20.2 to 29.3 kcal/mol and for sample B 35.3 to 39.4 kcal/mol. These values are similar to those reported for thermolysis and oxidation of hydrocarbons and crude oils (14-16). E₃ values of 49.9 and 46.4 kcal/mol for samples A and B in He are larger than 45.5 and 29.2 kcal/mol for A and B, respectively, in air. Cracking reactions under inert environment are known to have higher E values than under oxidizing atmosphere (5-6). Hayashitani et al. have postulated a series of cracking reactions in helium involving light oil, heavy oil and asphaltene components in the pyrolysis of bitumen extracted from the Athabasca oil sand (17). Activation energies for cracking reactions reported by them range between 57.4 and 65.2 kcal/mol. Bennion et al. have reported that these values of activation energies were divided by 1.37 to be used in numerical simulation in order to obtain reasonable values of temperature and fuel lay-down (5). These activation energies divided by 1.37 produce an average value of 44.1 kcal/mol which agrees with 49.9 and 45.5 kcal/mol obtained by us for reactions in zone 3 under He atmosphere. This indicates that the results obtained from TGA are more meaningful for use in the numerical simulation than those obtained from pyrolysis experiments in a closed system. Activation energies for reactions in zone 4 ranging between 14.2 and 21.5 kcal/mol are typical of reactions involving either coke formation or its oxidation (6).

The fuel (coke) contents of samples A and B have been determined to check if the minimum amount of fuel required to sustain combustion front is available. Calculation of fuel lay-down was based upon percentage organic loss in He in reaction zone 4 because coke is formed in this region. Since the maximum combustion temperature of the fire front listed in Table II ranges between 450° and 700°C, it is expected that for some fireflood tests, weight loss in zone 3 in He will also contribute to fuel lay-down. The fuel content under both scenarios calculated by assuming the density of the sample 2.2 g/cm³ is included in Table III. Estimated fuel content values under either assumption are greater than the value required (20 kg/m³) to sustain combustion.

Activation energies, pre-exponential factors, rate constants at peak temperatures, and heats of reactions obtained from treating DSC data for the last peak using the Borchardt and Daniels kinetics program are listed in Table IV. Order of reaction was assumed to be 1.0. Activation energies for cracking under He of sample A was 55.9 and of sample B was 61.7 kcal/mol and for combustion under air of sample A was 20.5 and of sample B was 28.9 kcal/mol. These values are higher for cracking and lower for combustion reactions than those obtained from kinetic treatment of TGA data in temperature zone 3 (Table III). Although inhomogeneity of core samples is always a problem in generating reproducible data, it is believed that more experimental data is needed before such discrepancy can be resolved. Heats of reaction for tests under air are much larger, 147 for A and 240 cal/g for B, than in He, 38 for A and 91 cal/g for B. It is evident that heat of reaction for sample A is lower than that of B. This is because oxidation reactions are much more exothermic than cracking reactions and oil content of sample A is one-half of B. Table IV includes peak and ignition temperatures derived from DSC thermograms. Ignition temperature is defined here as the temperature to which the product must be heated in the presence of air to sustain combustion. Temperature at the onset point of the combustion peak on DSC thermograms has been assigned to this value. Ignition temperature for sample A is 325°C and for sample B is 345°C.

TABLE IV
REACTION PARAMETERS FROM DSC EXPERIMENTS^a

Sample (Purge Gas)	Peak Temp. °C	Activation Energy kcal/mol	A s ⁻¹	10 ³ k s ⁻¹ _{peak}	Heat of Reaction cal/g	Ignition Temp. °C
A. (He)	462	55.9	2.6 x 10 ¹⁴	5.7	38	
	(Air) 453	20.5	6.2 x 10 ³	3.9	147	325
B. (He)	484	61.7	4.2 x 10 ¹⁵	5.2	91	
	(Air) 480	28.9	9.2 x 10 ⁵	3.3	240	345

- a. Order of reaction was assumed to be 1.0 for estimation of activation energy and pre-exponential factor.

SUMMARY

Thermal degradation of Lloydminster heavy oil core samples has been investigated in He, N₂ and air using TGA and DSC techniques. TGA and DTG thermograms demonstrated four distinct types of chemical reactions occurring in four different temperature zones. Reactions in zone 1 are attributed to volatilization and low temperature oxidation; in zone 2 to thermolysis of heavy oil fractions, volatilization and oxidation; in zone 3 to cracking and combustion; and in zone 4 to coking, decomposition of mineral matter and oxidation of the coke produced. Oxidation reactions take place when the sample is in contact with air. Fuel (coke) contents of sample A ranged between 29.3 and 39.2 Kg/m³ and that of B, 28.8 and 49.1 Kg/m³. Arrhenius and thermal parameters obtained for reactions in TGA/DSC studies are listed in Tables III and IV.

Data generated from TGA/DSC experiments are essential for running numerical simulation of the *in-situ* combustion process and verifying their match to the laboratory results. In addition, TGA/DSC data can be manipulated to yield air-fuel ratio, oxygen utilization, combustion front velocity, produced gas composition and hydrogen-to-carbon ratio of the fuel. It is evident that thermal analytical techniques have the potential to produce data which can be used for planning, design and construction of the field *in-situ* combustion tests and for numerical simulation to predict process variables and economics.

ACKNOWLEDGMENTS

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Figure 1. Schematic diagram of in-situ combustion process.

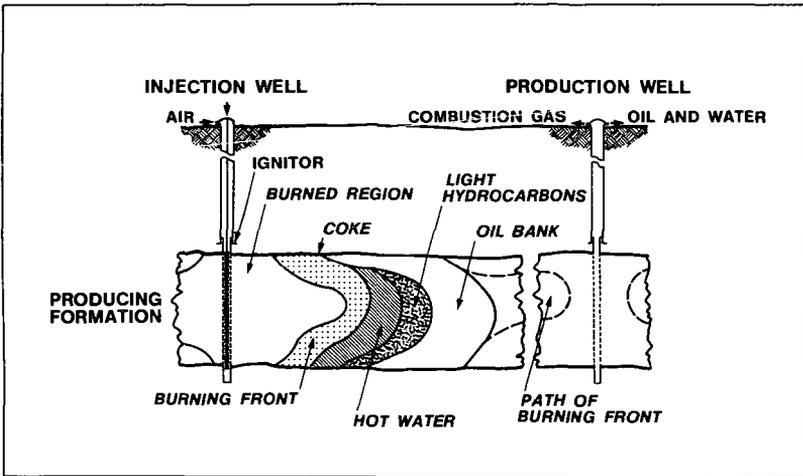


Figure 2. TGA thermograms of core sample A under the flow of He, N₂ and air.

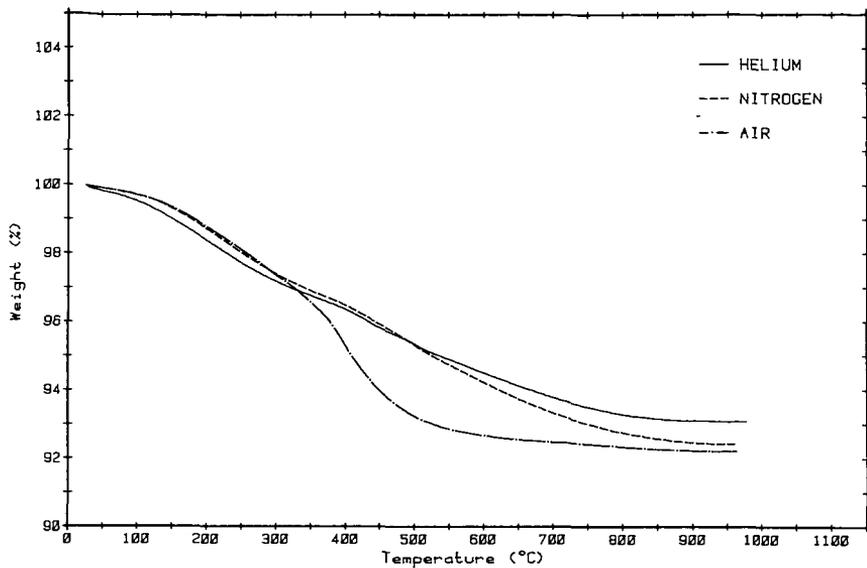


Figure 3. TGA and DTG thermograms of core sample A under He.

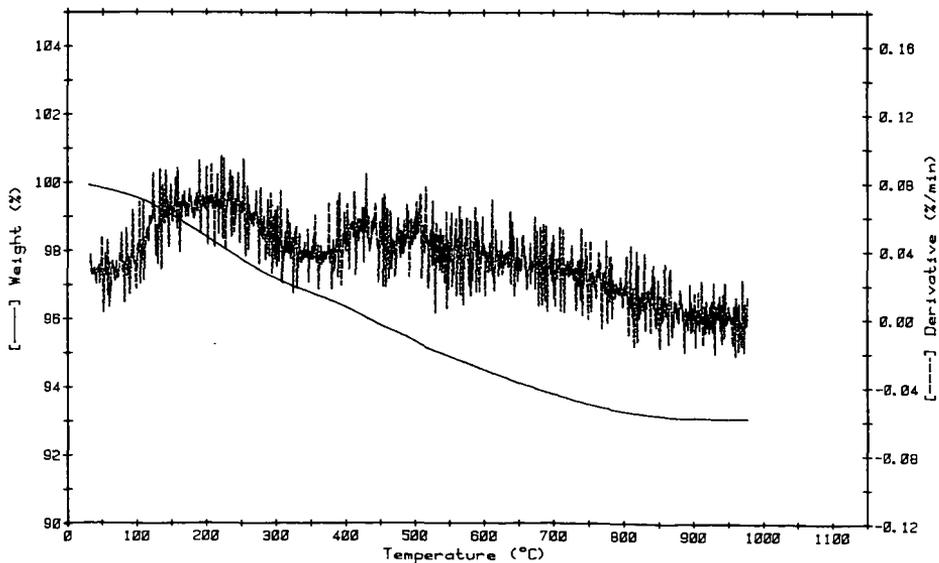


Figure 4. TGA and DTG thermograms of core sample A under N₂.

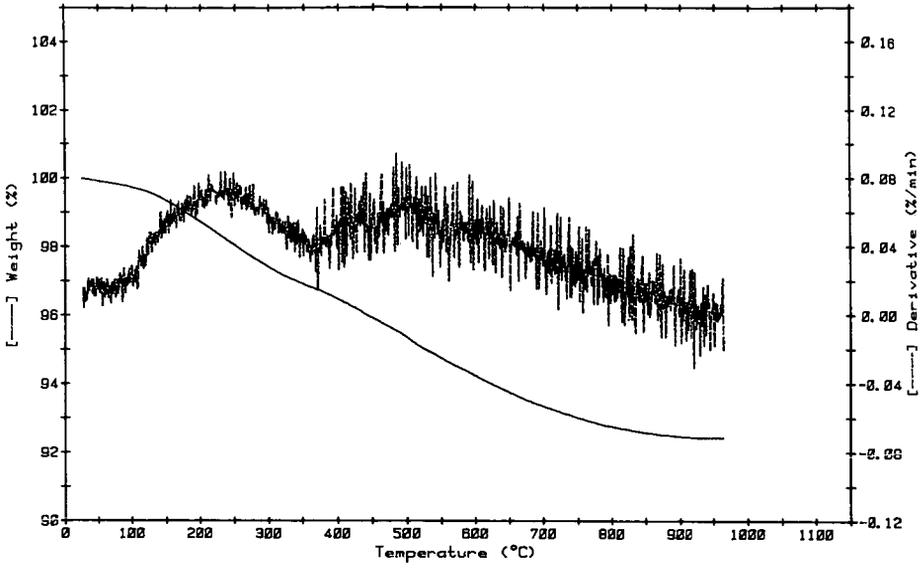


Figure 5. TGA and DTG thermograms of core sample A under air.

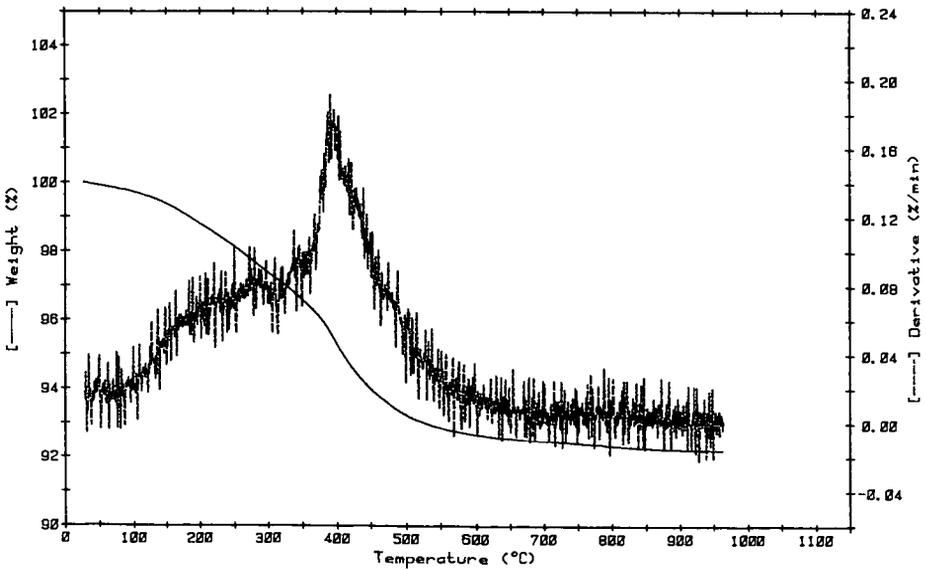


Figure 6. TGA and DTG thermograms of core sample B under He.

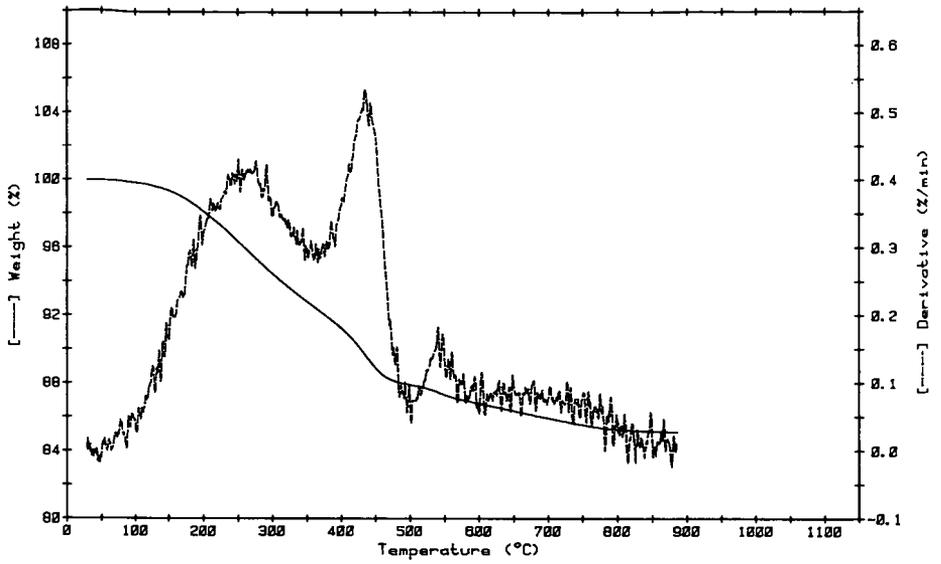


Figure 7. TGA and DTG thermograms of core sample B under air.

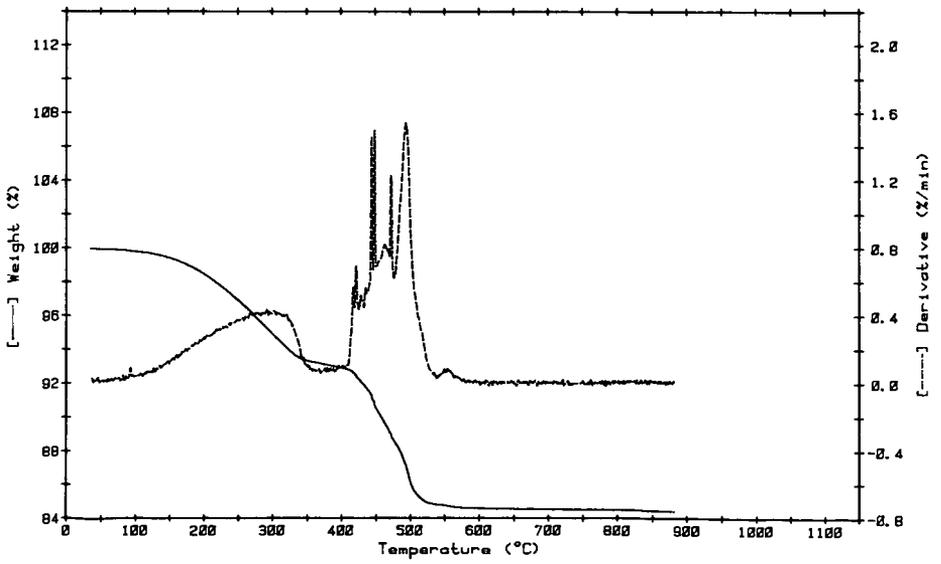


Figure 8. DSC thermograms of sample A under He.

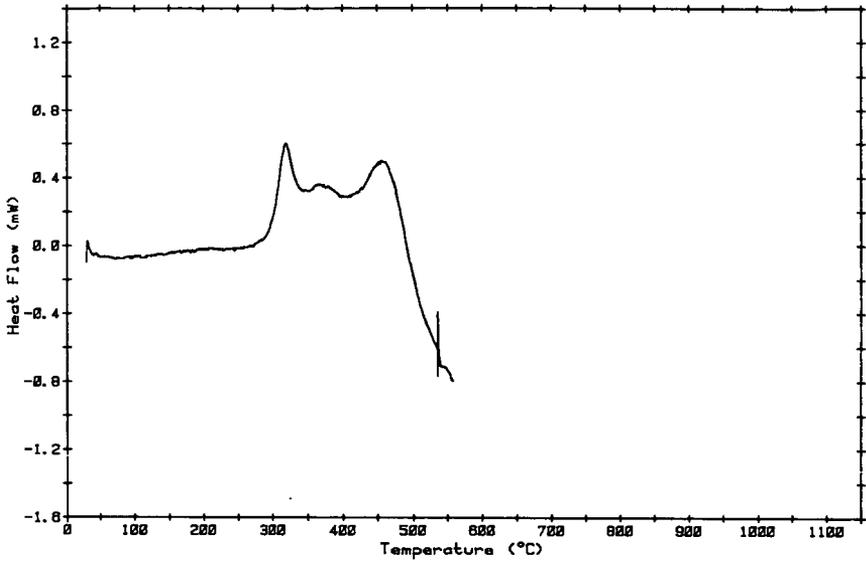


Figure 9. DSC thermograms of sample A under air.

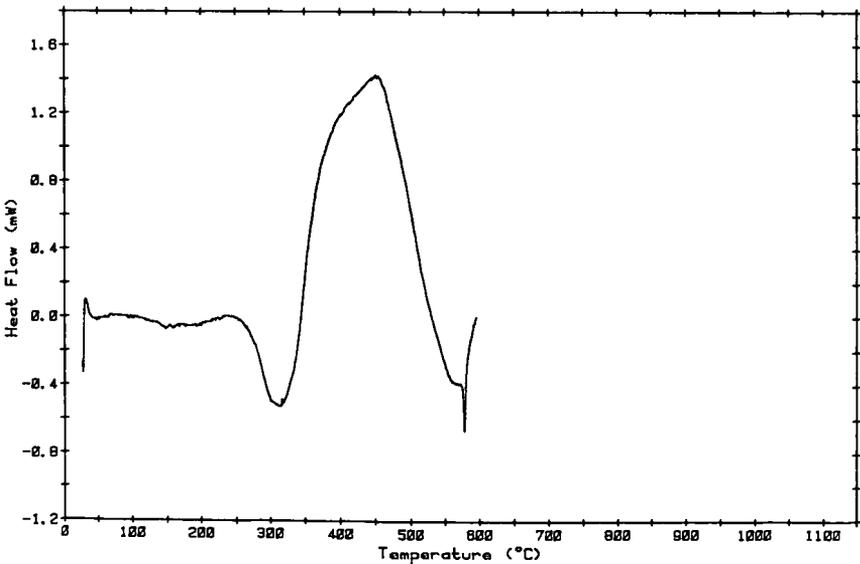


Figure 10. DSC thermograms of sample B under He.

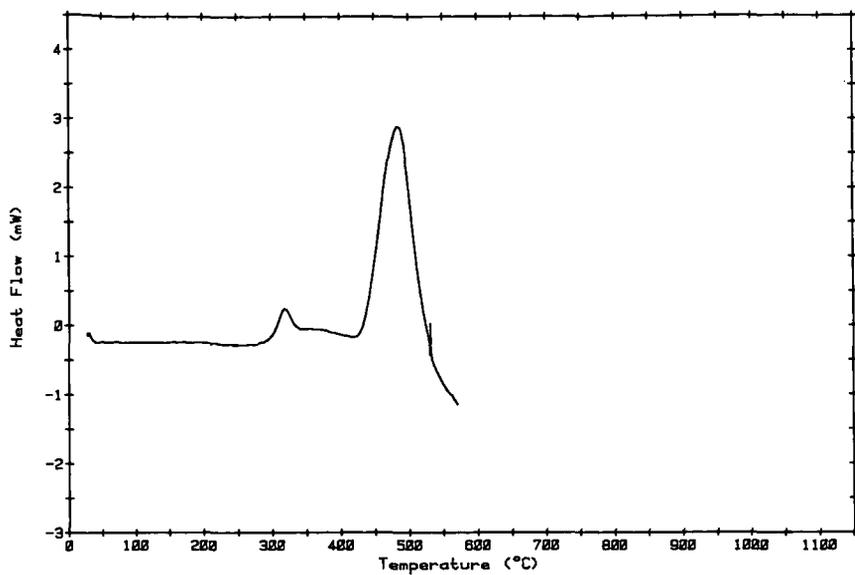


Figure 11. DSC thermograms of sample B under air.

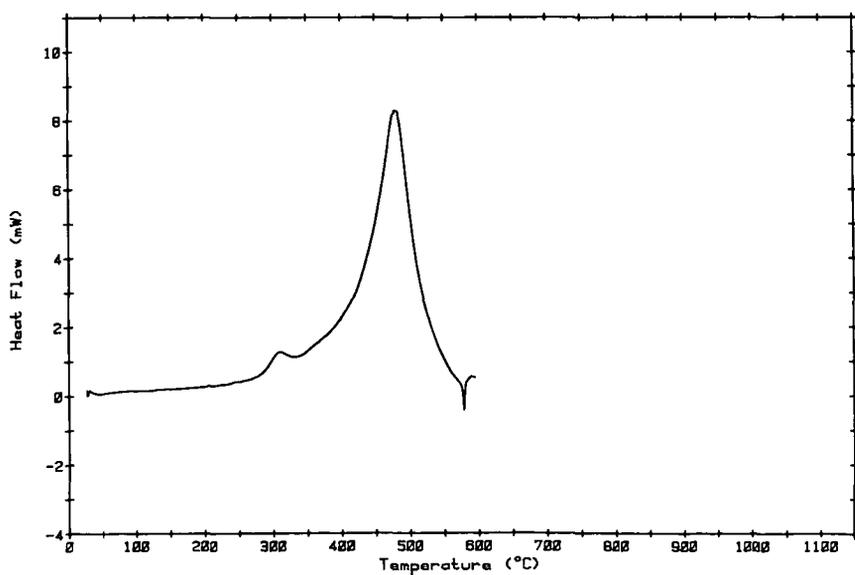


Figure 12. Arrhenius plot for sample A under helium between 50° and 340°C.

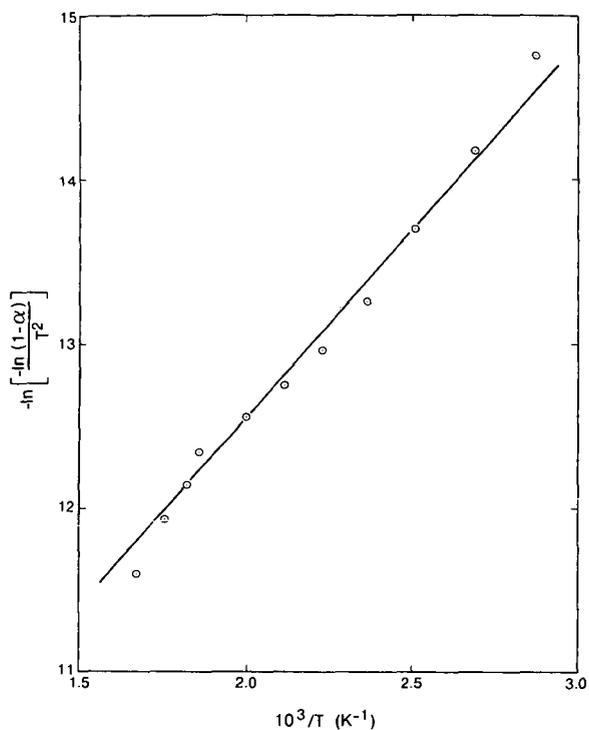


Figure 13. Arrhenius plot for sample A under helium between 340° and 475°C.

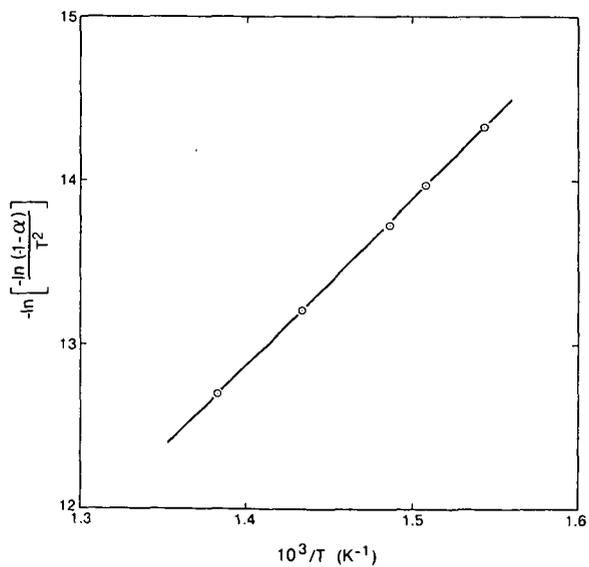


Figure 14. Arrhenius plot for sample A under helium between 475° and 550°C.

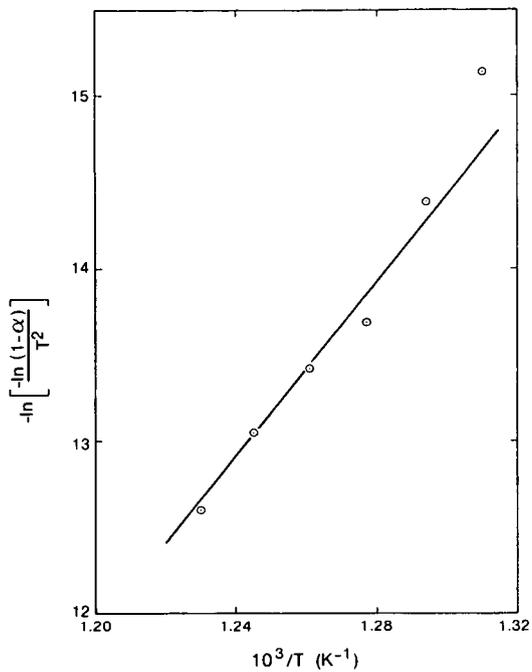
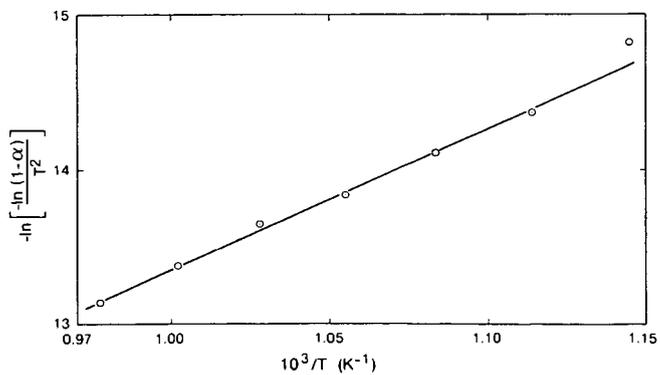


Figure 15. Arrhenius plot for sample A under helium between 550° and 800°C.



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