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THERMOPHYSICAL CHARACTERIZATION OF OIL SANDS. 4. THERMAL ANALYSES

ROBERT J. ROSENVOLD, JOEL B. DuBOW * and KRISHNAN RAJESHWAR **

Department of Electrical Engineering, Colorado State University, Fort Collins, CO 80523 (U.S.A.)

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ABSTRACT

TG and DSC data are presented for oil sand and bitumen extracts selected from four major deposits in the United States and Canada. The specimens were heated in an inert atmosphere. Thermal dissociation of oil sand bitumen takes place in two distinct stages, the first process peaking at temperatures around 350°C and the subsequent step showing a rate maximum at ~475°C. The gross enthalpies for these reactions as measured from the areas under the DSC thermograms, are presented for the various samples.

INTRODUCTION

Much attention has been focussed in recent years on the recovery of hydrocarbon fuels from oil sand deposits. Both in situ as well as above-ground processing schemes are being considered, wherein the formation is heated to lower the viscosity of the indigenous organic matter and to pyrolyze the oil sand bitumen. Obviously, the thermal behavior of oil sands needs to be well characterized in order that these recovery schemes be designed for optimal performance. In this vein, previous papers from this laboratory have addressed aspects related to the thermal, acoustic and electrical characteristics of oil sand samples [1–3]. In this paper, we present a comparative thermal analysis study of four oil sand specimens selected from major deposits in the United States and Canada.

EXPERIMENTAL

Oil sand samples for this study originated from the N.W. Asphalt Ridge, P.R. Spring and Circle Cliffs deposits in Utah and from the Athabasca

* Present address: Polytechnic Institute of New York, 333 Jay Street, Brooklyn, NY 11201, U.S.A.
** To whom correspondence should be addressed.

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TABLE 1

Properties of oil sand samples and composition of extracted bitumen

Property	Sample			
	N.W. Asphalt Ridge (Sample A)	P.R. Spring	Circle Cliffs	Athabasca
Elemental analysis [a] (wt.%)				
C	84.1_5	78.4_9	77.0_2	82.1_3
H	11.1_8	9.8_9	9.1_2	10.3_2
N	1.1_2	1.1_5	0.4_9	0.4_4
S	0.6_9	0.6_5	5.7_2	5.7_3
O	0.7_7	5.8_4	4.7_3	0.9_2
Specific gravity (g cm^{-3})	1.97	1.83	2.27	2.05
Ash content [a] (wt.%)	0.26	4.59	7.52	0.40
Bitumen content [b] (wt.%)	13.0_8 (11.5)	11.2_2 (11.5)	4.0_8 (3.5)	14.3_9 (13.0)

[a] Values refer to extracted bitumen and represent the mean value from duplicate determinations.

[b] Determined by Soxhlet extraction with benzene. Values in parentheses refer to those determined from the TG weight loss at 500°C (cf. Fig. 1).

formation in Alberta. Further details on these samples may be found elsewhere [1].

Procedures for thermal analyses and instrumentation have been described in previous publications from this laboratory [1,4]. All experiments were conducted in a flowing atmosphere (nominal flow rate: 500 cm^3 min^{-1}) of ultrapure N_2.

Experiments were conducted both on whole oil sand samples as well as on bitumen extracts. The latter were prepared by Soxhlet extraction with benzene. Generally, the bitumen yields were in good agreement with those predicted from TG weight loss data at 500°C (cf. Table 1 and vide infra). Relevant properties of oil sand samples and bitumen extracts are assembled in Table 1.

RESULTS AND DISCUSSION

Figure 1 illustrates TG data on the four samples of bitumen extract (cf. Table 1). Also shown for comparison is a TG curve for P.R. Spring oil sand sample (curve B). The weight loss observed in the latter case at temperatures up to ~500°C is attributable almost entirely to thermal alterations in the indigenous bitumen. This is shown by the fact that the weight loss at 500°C correlates within limits of experimental error to the bitumen content as estimated during Soxhlet extraction (cf. Table 1). A similar approach was suggested recently by us [5,6] as an alternative to Fischer assay for oil shales.

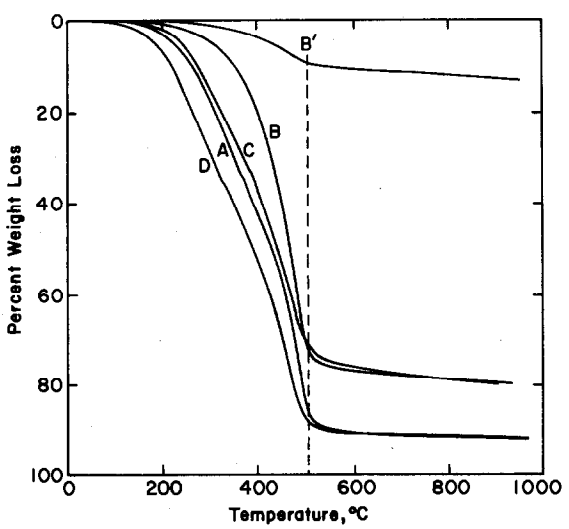

Fig. 1. TG curves (N_2 atmosphere, 20°C min^{-1} heating rate) for oil sand bitumen extracts (A–D) and a whole oil sand sample (B'). A, N.W. Asphalt Ridge; B, P.R. Spring (B', P.R. Spring oil sand sample); C, Circle Cliffs; and D, Athabasca bitumen.

TABLE 2

Parameters from thermal analyses [a] on oil sand bitumen extracts

Sample	Parameter			
	TG wt. loss at 300°C (%)	TG wt. loss at 500°C (%)	TG wt. loss at 800°C (%)	ΔH [b,c] ($J\ g^{-1}$)
N.W. Asphalt Ridge (Sample A)	16	85	91.5	672
P.R. Spring	4	71.5	79	634
Circle Cliffs	13	71	78	406
Athabasca	27	88	91.5	474
	(21) [d]	(87)	(91)	(478)

[a] Heating rate: 20°C, N_2 atmosphere.
[b] Based on starting weight (daf) of sample.
[c] Nominal temperature range of measurement: 25–550°C.
[d] Values refer to duplicate sample.

Of greater relevance to the present study, however, is the thermal behavior of bitumen extracts (Fig. 1, curves A–D). A major portion of the weight loss in these samples is seen to occur at temperatures below 500°C (Table 2). The reaction responsible for this weight loss may be represented by the generalized scheme in eqn. (1)

$$\text{bitumen} \rightarrow \text{solid} + \text{liquid} + \text{gas} \qquad (1)$$

The solid is a carbonaceous residue which may be termed "semi-coke" at temperatures around 500°C. It is quite doubtful whether the coking reaction is entirely complete at this temperature. The gradual weight loss at temperatures >500°C (Fig. 1) suggests progressive dehydrogenation of the semi-coke to compositions approaching that of coke at temperatures around ~ 1000°C [7]. Note that the degree of conversion for the P.R. Spring and Circle Cliffs samples is low relative to the other two specimens (Fig. 1 and Table 2). This trend is consistent with the relative ash content of these samples (cf. Table 1). Furthermore, combustion of the pyrolysis residue in the TG assembly itself yielded values for ash content which were in accord with the analytical data in Table 1.

A pronounced knee is generally observed in the TG weight loss curves althought this discontinuity is less pronounced with the P.R. Spring bitumen sample. That the weight loss is proceeding in two distinct stages is clearly brought about by differentiating these data as shown in Fig. 2. Note that even for the P.R. Spring sample, there is pronounced asymmetry now in the DTG peak. The first reaction peaks around 350°C whereas the subsequent process shows a rate maximum at ~ 475°C. There is controversy on the exact nature of these reactions [8]. Previous authors have concluded from

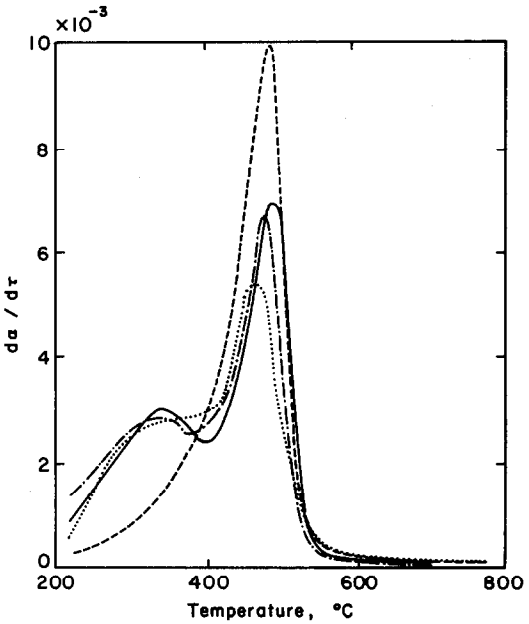

Fig. 2. DTG curves for oil sand bitumen. ——, N.W. Asphalt Ridge; — — —, P.R. Spring; · · · · · ·, Circle Cliffs; and ·–·–·; Athabasca bitumen.

flash pyrolysis studies [8] that the first step is essentially a physical process (distillation of maltene fractions) whereas the second step is believed to be associated with asphaltene decomposition. While further studies would be needed to verify this interpretation, the general scheme represented by eqn.

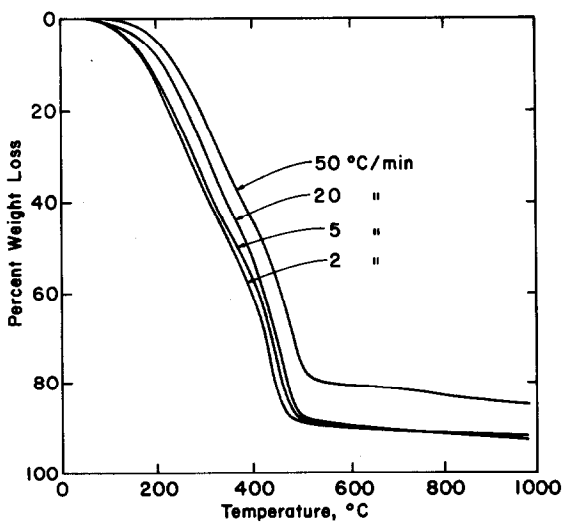

Fig. 3. Effect of heating rate on TG behavior of Athabasca oil sand bitumen.

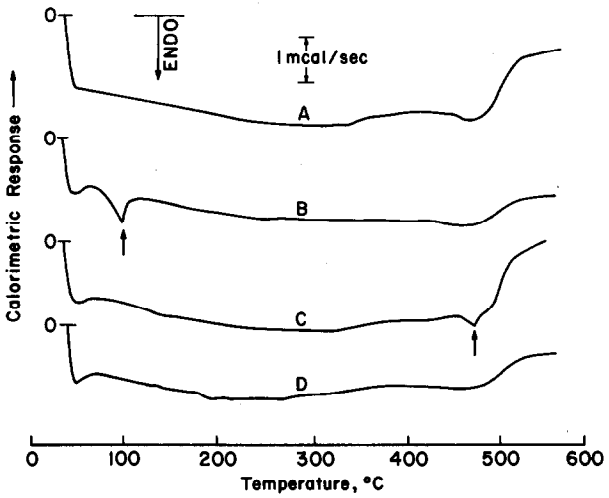

Fig. 4. DSC thermograms (N_2 atmosphere, 20°C min^{-1}) for oil sand bitumen. A, N.W. Asphalt Ridge; B, P.R. Spring; C. Circle Cliffs; and D, Athabasca bitumen.

(1) seems to be consistent with the observed behavior insofar as both physical and chemical processes may be incorporated into it. Indeed, with these complex materials, it is quite possible that both types of reactions occur simultaneously [9].

Figure 3 illustrates the influence of sample heating rate on weight loss characteristics for the Athabasca bitumen extract. The thermal lag at high heating rates between sample and ambient is responsible for the shift in weight loss curves to higher temperatures [4,10]. The lower degree of conversion at the 50°C min^{-1} heating rate (Fig. 3) is consistent with the smaller residence times for the evolving products. There is obviously an optimum value of the heating rate, because at low heating rates secondary polymerization reactions can have a deleterious influence on the product yield [4].

Relevant TG data for the four bitumen samples are assembled in Table 2. Repeatability in weight loss values as noted from replicate measurements (e.g., Athabasca specimen, Table 2) is especially good considering the nonhomogeneous nature of these samples.

Figure 4 illustrates representative DSC thermograms for the four bitumen samples. These thermograms are characterized by broad endothermic effects paralleling the reaction sequence noted in the TG experiments. Additionally, sharp peaks are sometimes superimposed on the broad envelope (denoted by arrows on curves B and C in Fig. 4). Those peaks centered around 100°C are undoubtedly due to loss of free moisture while peaks in the region 400–500°C are attributable to volatilization of the pyrolysis products. The net area encompassed by the two major endotherms are listed in Table 2 for the various samples. For ΔH determinations, the melting enthalpy of indium

(28.45 J g^{-1}), tin (59.25 J g^{-1}), and zinc (113.34 J g^{-1}) were used as standards.

SUMMARY AND CONCLUSIONS

TG and DSC studies on oil sands and bitumen extracts from four major deposits reveal broad similarities in their thermal behavior. Thermal analyses are consistent with a two-step degradation of the oil sand bitumen with the major portion of the pyrolysis being essentially complete at $\sim 500°C$. Aspects related to the kinetics of the pyrolysis process are currently being studied in this laboratory.

REFERENCES

1 K. Rajeshwar, D.B. Jones and J.B. DuBow, Fuel, 61 (1982) 237.
2 T. Mraz, K. Rajeshwar and J. DuBow, Fuel, 61 (1982) 240.
3 M. Das, R. Thapar, K. Rajeshwar and J. DuBow, Can. J. Earth Sci., 18 (1981) 742.
4 R. Rosenvold, J. DuBow and K. Rajeshwar, Thermochim. Acta, 53 (1982) 321.
5 K. Rajeshwar, R. Rosenvold and J. DuBow, to be published.
6 R.J. Rosenvold, K. Rajeshwar and J.B. DuBow, Thermochim. Acta, 57 (1982) 1.
7 R.G.S. Ritchie, R.S. Roche and W. Steedman, Fuel, 58 (1979) 523.
8 R.G.S. Ritchie, R.S. Roche and W. Steedman, Ind. Eng. Chem., Prod. Res. Dev., 17 (1978) 370.
9 K. Rajeshwar, R. Nottenburg and J. DuBow, J. Mater. Sci., 19 (1979) 2025.
10 K. Rajeshwar, Thermochim. Acta, 45 (1981) 253.