

CHEMICAL COMPOSITION OF GASES IN THE ALBERTA  
BITUMINOUS SAND

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INTRODUCTION

The major bituminous sand formations in Canada are located within the heavy oil belt of northern Alberta. The two largest reservoirs, known as Athabasca and Cold Lake, are known to be interspersed with occasional small gas pockets indicating that secondary thermal or microbial alterations of the bitumen have taken place in the recent past or may still be occurring. The presence of the volatile materials, their composition and origin and their continuous formation and escape into the atmosphere pose challenging problems with regard to the past and current history of the formation and to the air quality of the region.

For the above reasons we have undertaken a detailed study of the composition of gases present in the bituminous sand, of gases produced in the low-temperature pyrolysis of the bituminous sand and of the separated asphaltene and maltene fractions.

The isotopic carbon ratios in two of the components of the gases and in the different fractions of the Athabasca and Cold Lake bituminous sands were measured in order to gain a better understanding of the alteration processes and the extent of maturity of these deposits.

EXPERIMENTAL

The experimental details for the collection and analysis of gases and the conversion of methane and carbon monoxide to carbon dioxide for isotopic measurements have been described before (1). The standard extraction procedures for bitumen, asphaltene and maltene from the Athabasca (2) and Cold Lake (3) oil sands were followed. The isotopic distribution of carbon in bitumen, asphaltene and maltene was determined as follows. Approximately 5 mg of the desired fraction weighed in a narrow quartz tube was pushed into the center of a wider quartz tube maintained at 980°C inside an electric furnace. Oxygen was flowed through the system at a rate of 7 cm<sup>3</sup>/min.

Oxidation of the material was complete within 20 minutes and the oxidized products, mainly carbon dioxide and sulfur dioxide, were condensed into a trap maintained at -161°C. Carbon dioxide was then removed from sulfur dioxide by vacuum distillation at -130°C and collected in a transfer tube. The isotopic ratios were measured with a 25 cm radius 90° sector magnetic mass analyzer equipped with a dual collection system. The digital output was handled with a TI 980 computer.

RESULTS AND DISCUSSION

The composition and yields of gases evolved upon heating the Cold Lake bituminous sand samples at 5°, 70°, 95°, 130°, 170° and 210°C for 5.5 hours each are presented in Table 1. At 5°C the volatile fraction contained CH<sub>4</sub>, CH<sub>3</sub>CHO, C<sub>3</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons. At elevated temperatures the following additional compounds were detected: C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>, 1- and 2-C<sub>4</sub>H<sub>8</sub>, CO, COS and H<sub>2</sub>S. Gases collected at 5°C, which is the formation temperature, are considered to be constituents present in the formation while the others are expected to arise from pyrolysis of the bituminous sand. The yields of all products except acetaldehyde increase with rising temperature, implying that these are pyrolysis products as well.

The same products were obtained by heating Cold Lake maltene and asphaltene samples at 210° and 400°C and the results are given in Table 2. Most of the decomposition products were not detected at 210° because only 100 mg of samples were heated.

The yields of products at 400° are much larger than those at 210°C. The yields of some products are markedly affected by the reaction volume or more likely by the pressure in the system; for example, the yields of ethylene, propylene, propane and butane are enhanced at lower pressures. The total weight loss of asphaltene and maltene at 400°C was 29.9 and 34.5%, respectively, independent of pressure.

From comparison of the results, it is apparent that the amount of saturated hydrocarbons present in the Cold Lake deposit is greater than that in the Athabasca formation (1). On the other hand, the yields of carbon monoxide and carbon dioxide are much smaller in the Cold Lake samples than those in the Athabasca deposits. These results seem to imply that thermal or microbial degradation of the Cold Lake bitumen has occurred to a lesser extent than that in the Athabasca deposits.

Kinetic analysis of the data in Table 1 yielded Arrhenius parameters for the decomposition. They are given in Table 3 along with those obtained from the Athabasca study (1) for comparison. Since the Arrhenius parameters are favorable for a slow but significant rate of product formation at the ambient temperature of the reservoir, it follows that these materials were produced in the formation by the slow pyrolysis of the bituminous sand. The low values of the activation energies estimated for product formation in the Cold Lake samples are similar to those measured for the Athabasca bitumen. These low values may be attributed to the catalytic effect of the mineral matter present in the sample.

The carbon isotope ratios,  $C^{13}/C^{12}$ , of different fractions obtained from Athabasca and Cold Lake bituminous sands have been measured and are reported in Table 4. The  $\delta C^{13}$ \* values are corrected for the  $O^{17}$  contribution and are quoted relative to the Chicago PDB standard.

The  $\delta C^{13}$  values obtained for methane and carbon monoxide which were collected from bituminous sand, asphaltene and maltene at different temperatures, show a gradual increase with rising temperature. Those values for Athabasca bitumen and the separated asphaltene and maltene fractions are the same,  $\delta C^{13} = -29.6 \pm 0.10/_{\infty}$  at 980° whereas the corresponding values for Cold Lake maltene, asphaltene and bitumen are -31.6, -30.0 and -30.3 respectively. It is worth noting that the  $\delta C^{13}$  values obtained from the Cold Lake samples are slightly smaller than the corresponding ones from the Athabasca bitumen. This may imply that biological and/or chemical degradation of Cold Lake bitumen has occurred to a lesser extent than in the Athabasca bitumen.

The homogenization of the carbon isotope ratios in the bitumen, asphaltene and maltene may be due to mixing through migration and carbon isotope exchange reactions. Our values of  $\delta C^{13} = -29.6$  and  $-30.7$  for the Athabasca and Cold Lake bitumens respectively are very close to those obtained for different fractions of Saskatchewan and Alberta conventional oils (Mississippian and Devonian) which range between -30.6 and -26.6 (4). The sulfur isotope ratios,  $S^{34}/S^{32}$ , of several Saskatchewan crude oils and the Athabasca bitumen are also very similar (5).

The variation of the  $C^{13}/C^{12}$  ratios with temperature for methane, a pyrolysis product, can be explained in terms of the selective breaking of weaker C-C bonds at lower temperatures as a result of the kinetic isotope effect. It has been reported that methane produced by the bacterial degradation of oil has much lower  $\delta C^{13}$  values than those obtained in the present work (6). It is possible that the maturity, reservoir temperature and the strength of the C-C bonds cleaved are the primary factors influencing the isotopic distribution of gases in the bituminous sand.

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\* $\delta C^{13}$  ‰ (per mil) is defined as  $\left\{ \frac{(C^{13}/C^{12})_{\text{sample}}}{(C^{13}/C^{12})_{\text{standard}}} - 1 \right\} 10^3$ .

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TABLE 1

Composition of Gases Evolved from the Cold Lake Oil Sand  
as a Function of Temperature.<sup>a</sup>

	5°C	70°C	95°C	130°C	170°C	210°C
Methane	12.1	37.1	62.5	191.5	570.0	3,800
Ethylene	n.o. <sup>b</sup>	3.17	9.7	39.8	192.7	449.0
Ethane	n.o.	7.16	13.5	26.3	28.4	452.0
Acetaldehyde	9.0	54.5	146.6	84.0	18.8	7.22
Propylene	n.o.	4.13	12.0	68.1	n.d. <sup>c</sup>	494.0
Propane	3.49	10.2	16.7	153.7	n.d.	n.d.
<i>i</i> -Butane	3.49	5.52	6.68	8.42	13.9	n.d.
<i>i</i> -Butene	25.6	34.9	38.2	62.2	127.2	104.0
<i>n</i> -Butane	n.o.	63.8	71.3	79.8	130.5	246.3
Butenes	n.o.	90.0	147.4	152.2	152.4	521.4
Pentanes & Pentenes	1.34	5.34	16.04	36.6	62.1	231.0
C <sub>6</sub>	2,860	3,780	4,120	4,450	4,620	4,950
Carbon monoxide	n.o.	74.2	231.2	879.2	1,840	4,790
Carbonyl sulphide	n.o.	3.63	10.2	27.7	50.5	195.2
Hydrogen sulphide	n.o.	n.o.	n.o.	<85.0	<160	<1,930

<sup>a</sup> The sample was heated for 5.5 hours at each temperature.

Yields are expressed in units of 10<sup>-8</sup> mol/kg oil sand.

<sup>b</sup> Not observed.

<sup>c</sup> Not determined.

TABLE 2

Composition of Gases from Cold Lake Maltene  
and Asphaltene.<sup>a</sup>

	Maltene			Asphaltene		
	210° <sup>b</sup>	400° <sup>c</sup>	400° <sup>b</sup>	210° <sup>b</sup>	400° <sup>c</sup>	400° <sup>b</sup>
Methane	n.o. <sup>d</sup>	140,000	197,000	65.5	167,000	151,000
Ethylene	71.0	5,440	42,100	16.2	10,200	25,900
Ethane	n.o.	115,000	95,000	11.1	104,000	97,000
Acetaldehyde	n.o.	n.o.	n.o.	6.91	n.o.	n.o.
Propylene	n.o.	19,700	82,700	7.60	31,000	44,300
Propane	n.o.	77,800	91,900	9.10	67,200	73,500
<i>i</i> -Butane	n.o.	152.0	n.d. <sup>e</sup>	n.o.	259.0	n.o.
<i>i</i> -Butene	n.o.	17,700	13,900	n.o.	8,600	6,780
<i>n</i> -Butane	n.o.	18,600	52,400	14.3	20,800	33,800
Butenes	n.o.	55,500	61,900	8.13	47,700	49,700
Pentanes & Pentenes	16.0	69,100	75,900	314.0	59,700	58,400
C <sub>6</sub>	769.0	77,300	71,200	38.2	53,500	61,200
C <sub>7</sub>	n.o.	50,900	10,500	n.o.	36,400	6,600
Carbon monoxide	n.d.	n.d.	n.d.	340.0	n.d.	3,990
Carbon dioxide	135.4	529.0	615.0	369.0	2,900	1,850
Carbonyl sulphide	n.o.	60.0	44.0	n.o.	<0.1	24.0
Hydrogen sulphide	n.o.	<47,200	<33,400	<51.1	<86,900	<89,400
Oxygen	8.00	n.o.	438.0	6.94	n.o.	16.5
Nitrogen	17.90	n.o.	107.0	17.9	n.o.	94.6

<sup>a</sup> The samples were heated for 20 hours. Yields are expressed in units 10<sup>-8</sup> mol/g.<sup>b</sup> The volume of the cell was 155 cm<sup>3</sup> and contained ≈100 mg material.<sup>c</sup> The volume of the cell was 1.0 cm<sup>3</sup> and contained 15 mg of maltene or 5 mg of asphaltene.<sup>d</sup> Not observed.<sup>e</sup> Not determined.

TABLE 3

Arrhenius Parameters for Pyrolysis  
of Bituminous Sand

Product	A		E <sub>a</sub>		k <sub>5°C</sub>	
	[(5.5h) <sup>-1</sup> kg <sup>-1</sup> ]		[kJ/mol]		[(5.5h) <sup>-1</sup> kg <sup>-1</sup> ]	
	Cold Lake	Athabasca	Cold Lake	Athabasca	Cold Lake	Athabasca
CH <sub>4</sub>	1.7x10 <sup>9</sup>	3.6x10 <sup>9</sup>	53.8	56.9	1.7x10 <sup>-1</sup>	7.6x10 <sup>-2</sup>
C <sub>2</sub> H <sub>4</sub>	2.1x10 <sup>8</sup>	5.2x10 <sup>7</sup>	52.0	49.3	4.4x10 <sup>-2</sup>	2.8x10 <sup>-2</sup>
C <sub>3</sub> H <sub>6</sub>	5.3x10 <sup>7</sup>	7.9x10 <sup>8</sup>	46.8	57.7	9.4x10 <sup>-2</sup>	1.2x10 <sup>-2</sup>
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	3.6x10 <sup>5</sup>	1.6x10 <sup>4</sup>	31.0	28.4	6.0x10 <sup>-1</sup>	7.3x10 <sup>-2</sup>
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	3.0x10 <sup>3</sup>	8.2x10 <sup>4</sup>	21.3	34.7	3.1x10 <sup>-1</sup>	2.5x10 <sup>-2</sup>
CO	7.9x10 <sup>7</sup>	1.1x10 <sup>8</sup>	39.3	36.8	3.6	13.2
COS	1.9x10 <sup>6</sup>	5.0x10 <sup>7</sup>	37.7	48.5	1.8x10 <sup>-1</sup>	4.0x10 <sup>-2</sup>

TABLE 4

Isotopic Ratios for C<sup>13</sup>/C<sup>12</sup> in the Fractions  
of Alberta Bituminous Sand

Temperature °C	Bituminous Sand Fraction	δC <sup>13</sup> (per mil)	
		Athabasca	Cold Lake
95	Bituminous Sand, CH <sub>4</sub> + CO <sub>2</sub>	-48.8 (1) <sup>a</sup>	
210	Bituminous Sand, CH <sub>4</sub> + CO <sub>2</sub>	-41.1±2.3(4)	
210	Bituminous Sand, CO + CO <sub>2</sub>	-32.0±2.4(4)	-37.3 (1)
210	Bitumen + Sand <sup>b</sup>		
	CH <sub>4</sub> + CO <sub>2</sub>	-47.8±0.9(3)	
	CO + CO <sub>2</sub>	-29.0 (1)	
400	Maltene, CH <sub>4</sub> + CO <sub>2</sub>	-41.9 (1)	-44.3 (1)
400	Asphaltene, CH <sub>4</sub> + CO <sub>2</sub>	-45.5±0.1(2)	-44.3±0.1(2)
980	Maltene, Total C + CO <sub>2</sub>	-29.7±0.1(3)	-31.6±0.1(3)
980	Asphaltene, Total C + CO <sub>2</sub>	-29.5±0.1(3)	-30.0±0.3(3)
980	Bitumen, Total C + CO <sub>2</sub>	-29.6±0.1(3)	-30.3±0.4(2)

<sup>a</sup> Numbers in brackets indicate number of analyses.

<sup>b</sup> Sand recovered after the extraction of oil from the Athabasca bituminous sand was mixed with bitumen in the proportion estimated in the bituminous sand.