OXIDATION OF THE ATHABASCA OIL SAND AND ITS FRACTIONS

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INTRODUCTION

The Athabasca oil sand and its fractions are known to be thermally unstable and sensitive to air (1-2). They react with molecular oxygen even at low temperatures. It has been reported that oxidation of bitumen generates high molecular weight material (3). The high susceptibility of the oil sand to aerobic oxidation could have practical relevance with regard to the surface strip mining and processability of the oil sand. Apart from its influence on the quality of the product, the phenomenon is also relevant to the origin, history, thermal and microbial maturation of the deposits and also to the *in situ* fire-flooding recovery technology of the oil sand.

Results of laboratory and field experiments on the production of crude oil by *in situ* forward and reverse combustion have been reported (4-7). However, quantitative studies of the parameters related to the chemical aspects of these processes, such as oxidation kinetics, have not been performed.

The chemical transformations in the oil sand due to oxidation reactions at low temperatures are difficult to detect by analysis of the bulk composition but they can be easily monitored by measuring the gaseous and highly volatile materials which are produced therefrom.

The present study was undertaken in order to gain an insight into the oxidation and weathering processes taking place in the Alberta oil sand.

EXPERIMENTAL

The high vacuum apparatus employed in this study was similar to that used previously (1-2). The experimental details for the collection and analysis of gases and the volatile materials have also been described (1-2). About 130 g Athabasca oil sand was placed in a 500 cm^3 Pyrex vessel fitted with a breakseal and several 1 cm^3 ampoules. The vessel was attached to the vacuum apparatus and degassed at room temperature for one hour. Oxygen was then introduced into the vessel at about 150 torr, the vessel was sealed off and heated to the desired temperature in a silicone oil bath. The vessel was shaken intermittently and the ampoules were sealed at desired time intervals and analyzed for oxygen on a 2.4 m molecular sieve column. The samples heated at 130°C in the absence and presence of oxygen were analyzed for both non-condensable and condensable materials at -196°C. Standard extraction procedures for bitumen and for the separation of asphaltene and maltene from the oil sand samples were followed (8). Elemental analyses for C, H, N, O and S were performed in the Microanalytical Laboratory of the Chemistry Department.

Between 5 and 10 g bitumen, asphaltene or maltene was introduced into a 250 cm^3 Pyrex vessel. The vessel was joined to a Hoke valve fitted with a standard taper joint on the other end through which it was attached to another Hoke valve fixed to the vacuum apparatus. The volume enclosed between the two Hoke valves was used as a sampler. All samples were evacuated uniformly at ambient temperature before introduction of 250 torr oxygen. The oxygen concentration was determined by transferring it from the sampler into the gas burette and injecting it into the *gc*. The silicone oil bath was used to heat samples at 137°C. For higher temperatures, an electric furnace equipped with a 2-mode API Instrument Co. temperature controller and a Hewlett-Packard 3420 A d.c. differential voltmeter was employed. The consumption of oxygen was followed by expanding oxygen from the vessel into the sampler at desired time intervals and measuring the concentration as described above.

RESULTS AND DISCUSSION

The presence of oxygen has an enhancing effect on the rate of the low temperature thermolysis of the Athabasca oil sand, bitumen, asphaltene and maltene. The product yields obtained from heating oil sands at 130°C for 24 hours in the absence and presence of oxygen are presented in Table I. The products include C_1-C_7 hydrocarbons including *neo*pentane, CH_3CHO, CO, CO_2 , COS and H_2S. In the presence of oxygen, CH_3COCH_3 and SO_2 are produced in addition to these compounds. Unfortunately, the acetone peak masked the C_5 hydrocarbon peaks and consequently the latter could not be determined accurately. It is evident that in the presence of oxygen, the rates of production of hydrocarbons are increased by factors ranging from 2 to 70, those of the apparent oxidation products by up to 500, and H_2S is probably converted to SO_2.

The thermolysis products obtained from heating bitumen at 137°, 172° and 207°C are given in Table II. The product distribution is similar to that from the whole oil sand (Table I), but the ratios of the product yields in the presence and absence of oxygen at 207° are higher than those at 137°C. The rates of production of hydrocarbons at 207°C in the presence of oxygen are increased by factors up to 100 and those of the apparent oxidation products, by up to 170. Oxidation of asphaltene and maltene at 172°C produced similar results.

Although many details of the complex reaction network involved in the oxidation of hydrocarbons by molecular oxygen have not yet been elucidated, it is commonly accepted that a chain mechanism is operative and that one of the first products formed is a hydroperoxide which may be oxidized further or decompose thermally, thereby initiating new chains (9,10). At 100° and 130°C Kovalev and Denisov (11) reported that peroxides, alcohols and carbonyl compounds are intermediate products whose time profile concentrations pass through a maximum (11). It is also known that these intermediates are responsible for the enhanced yields of hydrocarbons and oxygenated compounds in the thermolysis of hydrocarbons in the presence of oxygen (9-11). The enthalpy changes of the oxidation and combustion reactions leading to the observed end products range between 80 and 105 kcal per mol of oxygen (7).

The efficiency of oxygen in the low temperature thermolysis of the oil sand, bitumen, asphaltene and maltene could also be explained by such a general mechanism, where the initial reaction between the organic free radicals formed by thermolysis and molecular oxygen to form a hydroperoxy radical

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad 1)$$

is followed by the chain propagating steps

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot \qquad 2)$$

$$RO_2\cdot + C{=}C \rightarrow ROOC\text{-}\dot{C} \qquad 3)$$

$$ROOH \rightarrow RO\cdot + HO\cdot \qquad 4)$$

Typical chain terminating steps could be

$$\left.\begin{array}{l} R\cdot + R\cdot \\ RO_2\cdot + R\cdot \\ RO_2\cdot + RO_2\cdot \end{array}\right\} \rightarrow \text{molecular products} \qquad \begin{array}{r} 5) \\ 6) \\ 7) \end{array}$$

The combustion type reactions in our system will produce additional amounts of hydrocarbons, carbon monoxide, carbon dioxide and water.

A simple mechanism for the oxidation of hydrogen sulfide to sulfur dioxide could be expressed as follows:

$$H_2S + O_2 \rightarrow H_2O + SO \qquad 8)$$

$$2SO + O_2 \rightarrow 2SO_2 \qquad 9)$$

The overall heat of oxidation is exothermic by about 124 kcal per mol.

The rates of consumption of oxygen by the oil sand were studied at various temperatures between 24° and 130°C. The data obtained are plotted in Figure 1. The semi-logarithmic plots of the concentration of oxygen in the gas phase as a function of time at each temperature follow first order reaction kinetics. The half-lives, i.e., time required for one-half of oxygen to be used up, vary between 111 days at 24° and 0.6 hours at 130°C. The rate constants, k, were estimated from the slopes of these plots and Equation 10 was used for the Arrhenius plot of ln k *versus* 1/T:

$$\ln k = \ln A - E_a/RT \qquad 10)$$

where k is the rate constant, A the preexponential factor, E_a the activation energy, R the gas constant and T is the temperature in °K.

The Arrhenius parameters estimated from the plot are temperature dependent (Table III). Around room temperature, the rate of depletion of oxygen features a lower activation energy and preexponential factor than at the higher temperatures. The temperature dependence of the rate parameters is indicative of changes in the reaction mechanism and suggests a largely surface-catalyzed, i.e., heterogeneous reaction network at the lower temperature, changing over to non-catalytic gas phase reactions at the higher temperatures. It is to be noted that an increase in temperature from 24° to 130°C brings about a 4000-fold rate increase in oxygen uptake. The last column of Table III lists the time required to deplete 99 percent of oxygen added at each temperature and is equivalent to 7 half-lives.

Bousaid and Ramey determined the rates of oxygen disappearance in the 13.9° API Athabasca crude at 23°, 38° and 52°C and found them to follow first order reaction kinetics (5). In this temperature range, they estimated an activation energy of 12.7 kcal per mol which is in agreement with our value of 13 kcal per mol. However, the rate constants and preexponential factor estimated from their data are larger than ours by about two orders of magnitude. We have also estimated the activation energies for the oxidation of hexadecane by molecular oxygen in the temperature ranges 100°-120° and 120°-150°C from the rate data of Kovalev and Denisov to be 17 kcal and 40 kcal per mol, respectively (11). These results show trends similar to ours.

The rates of disappearance of oxygen in bitumen at 137°, 172° and 207°C and in asphaltene and maltene at 137° and 172°C obey first order kinetics (Figure 2). The rate constants estimated from these plots are listed in Table IV. It is apparent that the trend in reactivity is oil sand, asphaltene, bitumen and maltene in decreasing order. It should be pointed out that the rate of oxygen uptake is a measure of the oxidizability of the fractions, which in turn is a function of the chemical composition of the sample.

In the oil sand experiment at 130°C, the 6 mmol oxygen added was completely consumed: 9.3% appeared in the volatile oxygen-containing products and 45% in the bitumen as determined by the elemental analysis (Table V). The rest was presumably converted to water and other oxygenated compounds which were lost during the bitumen extraction. Table V shows that the bitumen contents of non-oxygenated and oxygenated oil sand samples are the same, 13.3%. However, the maltene and asphaltene contents of the former were 83.2 and 16.8 while those of the latter were 76.1 and 23.9%, respectively. It should be noted that in these experiments the oxygen was completely consumed and that the alteration effect of oxygen would have been much larger if the oxygen concentration had been maintained throughout the course of the experiment.

The substantial increase in the asphaltene content of the oxygenated sample, at the expense of maltene, demonstrates that exposure of the oil sand to air has an adverse effect on the quality of the bitumen. The increase in asphaltene content would likely lead to an increase in the yield of coke formation and a lowering in the yield of synthetic crude in the upgrading process. The possibility of aerobic oxidation should therefore be taken into consideration in the storage of the mined oil sands, especially during the summer months when sand temperatures could significantly exceed ambient air temperature. It could also be a factor in affecting bitumen quality during storage of liquid bitumen and in the initial stages of the *in situ* recovery processes of the bitumen.

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Table I. Composition of Gases from the Oxidation of the Athabasca Oil Sand at 130°C[a]

Product	10^{-8} mol hr^{-1} kg^{-1} oil sand				
	Nil	6 mmol		Nil	6 mmol
	O_2			O_2	
Methane	4.97	81.8	C_5	34.8	37.0
Ethylene	0.82	57.0	C_6	2.74	148.0
Ethane	1.14	21.6	C_7	3.68	11.5
Propylene	1.95	67.9	CH_3CHO	5.50	1,640
Propane	0.73	20.1	$(CH_3)_2CO$	n.o.[c]	459
i-Butane	0.20	1.74	CO	11.1	5,920
i-Butene	0.72	25.7	CO_2	2,830	56,400
Butane	14.5	29.5	COS	0.41	42.2
Butenes	0.35	7.70	H_2S	35.7	n.o.
Neo-pentane	20.0	n.d.[b]	SO_2	n.o.	23.4

[a]The oxygen pressure was 150 torr and the sample was heated for 24 hours.
[b]Not determined, due to the large interfering peak of acetone.
[c]Not observed.

Table II. Composition of Gases from the Oxidation of the Athabasca Bitumen as a Function of Temperature[a]

Product	10^{-8} mol hr^{-1} per 100 g bitumen				
	137°C		172°C	207°C	
	Nil	3.3 mmol	3.6 mmol O_2	Nil	3.9 mmol
	O_2			O_2	
Methane	2.6	11.0	36.4	114	1,000
Ethylene	1.2	3.4	52.1	21	171
Ethane	n.o.[b]	2.5	68.5	14	234
Propylene	1.8	6.4	59.0	2.0	209
Propane	n.o.	4.5	49.0	17	202
i-Butane	0.6	3.4	41.8	13	41.0
i-Butene	n.o.	2.1	23.4	n.o.	36.0
n-Butane + Butenes	3.5	4.5	476	20	440
Acetaldehyde	2.4	108	494	18	2,920
Acetone	n.o.	2,760	2,830	n.o.	51,100
Carbon monoxide	44.0	392	421	213	12,400
Carbon dioxide	330	1,320	11,700	2,880	33,800
Carbonyl sulfide	1.0	7.7	129	39.0	556
Sulfur dioxide	n.o.	1.8	314	n.o.	28
Hydrogen sulfide	n.o.	n.o.	n.o.	1,270	270

[a]The samples had 250 torr pressure of oxygen.
[b]Not observed.

Table III. Arrhenius Parameters for the Uptake of Oxygen by Athabasca Oil Sand

Temp. °C	k hr^{-1} kg^{-1} oil sand	E_a kcal/mol	A hr^{-1} kg^{-1} oil sand	Time required to deplete 99% of O_2 added
24	2.6×10^{-4}			2.0 years
60	2.6×10^{-3}	13	1×10^{6}	0.2 year
85	1.1×10^{-2}			17 days
105	9.8×10^{-2}	29	6×10^{15}	47 hours
130	1.1			4.1 hours

Table IV. Rate Constants for Oxygen Depletion

t°C	Oil Sand	Asphaltene	Bitumen	Maltene
	hr^{-1} kg^{-1} oil sand	hr^{-1} per 100 g		
130	1.1	-	-	-
137	-	0.22	0.076	0.055
172	-	0.22	0.20	0.102
207	-	-	0.36	-

Table V. Elemental Composition of Athabasca Oil Sand[a]

Fraction	$[O_2]$[b]	C	H	N	O	S
		%				
Bitumen						
13.3%	none	82.58	10.26	0.39	1.36	5.22
13.3%	6 mmol	82.21	10.09	0.40	1.99	4.95
Asphaltene						
16.8%	none	79.35	8.14	1.06	1.58	7.39
23.9%	6 mmol	76.68	7.95	0.97	3.30	7.97
Maltene						
83.2%	none	83.74	10.90	0.20	1.03	3.78
76.1%	6 mmol	83.05	11.09	0.09	0.99	3.87

[a]130 g of the Athabasca oil sand was heated at 130°C for 24 hours.
[b]An oxygen pressure of 150 torr was used.

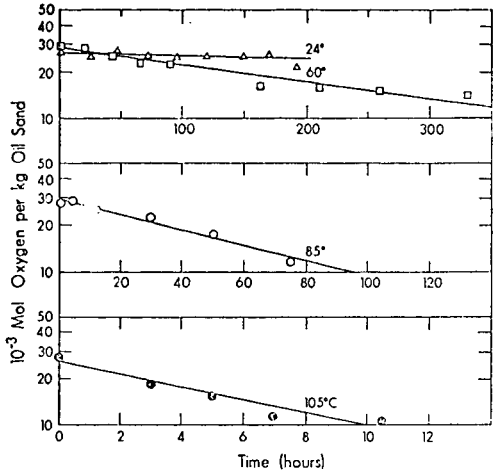

Figure 1. Depletion of oxygen concentration as a function of time in the Athabasca oil sand: Δ, 24°C; □, 60°C; O, 85°C; ●, 105°C.

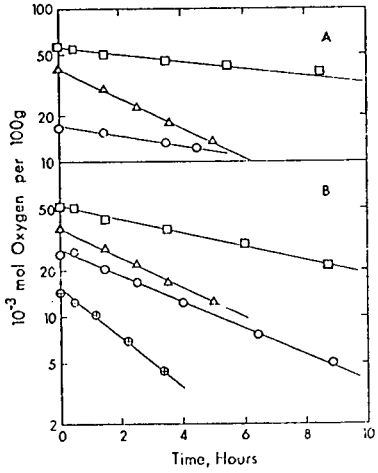

Figure 2. Depletion of oxygen concentration as a function of time in the Athabasca bitumen (O), asphaltene (Δ) and maltene (□): A, 137°C; B, 172°C and ⊕, bitumen at 207°C, abscissa reduced to half.