

Thermolysis and Oxidation of the Alberta Oil Sand Bitumen

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INTRODUCTION

The composition and the rates of evolution of light gases and volatile materials from Athabasca and Cold Lake oil sand bitumen and their separated fractions have been described as a function of temperature.¹⁻³ From the estimation of the Arrhenius parameters for product formation it was concluded that both these reservoirs are currently undergoing a slow but measurable thermal decomposition even at the formation temperature. The activation energies for the formation of products for the whole oil sand system were low, ranging between 6 and 26 kcal/mol, indicating the catalytic effects of mineral matter present in the oil sand. Previous work suggests a common origin for these oils, and our own results¹⁻³ suggested similar thermal diagenetic histories for the Athabasca and Cold Lake oil sand deposits. Similar studies have now been conducted on the Peace River oil sand to gain deeper insight into the relationships between this oil and the other two oil sands.

Preliminary results on the kinetics of consumption of molecular oxygen in the thermolysis of the Athabasca oil sand, extracted bitumen, asphaltene and maltene have shown that the rate of thermolysis of each product was substantially increased in the presence of molecular oxygen and that the rate of depletion of oxygen followed first order reaction kinetics.^{3,4} Exposure of the oil sand to oxygen resulted in a substantial increase in the asphaltene content of the sample.

These studies have been extended to include the effects of oxygen pressure and heating time on the yields of the products from the whole oil sand as a function of temperature in order to clarify geological processes such as the introduction of molecular oxygen into the bitumen via oxidizing ground water and weathering processes occurring at the oil sand outcrops or in piles of mined bituminous sand.

EXPERIMENTAL

The experimental details for the collection and analysis of gases and the volatile materials have been described previously.¹⁻³ The Peace River oil sand was received from Shell Canada Ltd., labeled OBS-5 Shell Cadotte OV, 4-21-85-18 W5 from a depth of 563-573 m. These samples were contained in split cores which had been exposed to air at some stage. The oil sands were manually homogenized before use for most of the experiments in order to obtain reproducible results.

The bituminous sands from the Saline Creek tunnel area of the Athabasca reservoir were used for the oxidation experiments. Bitumen was extracted from this oil sand and separated into asphaltenes and maltenes using standard techniques.⁵ Trace amounts of clay and mineral matter present in these fractions were removed by centrifugation. Non-condensable gases at 77°K were analyzed by gc on a 2.4 m molecular sieve column and the gases volatile at 195°K but condensable at 77°K on a 4.6 m Porapak Q column. Since neopentane, acetone, propionaldehyde and carbon disulfide are unresolved on Porapak Q, this total fraction was trapped from the effluent and further analyzed on a 4.6 m tricresylphosphate column, on which excellent resolution was achieved.

RESULTS AND DISCUSSION

The composition and rates of the light gases evolved from the Peace River bituminous sand at 278, 298, 323, 343, 368, 388, 403 and 423°K are presented in Table I. The volatile material obtained up to 298°K, which is the formation

Table I. Composition of Gases Evolved from the Peace River oil sand as a Function of Temperature

Temperature (°K)	10 ⁻⁸ mol hr ⁻¹ kg ⁻¹ oil sand							
	278	298	323	343	365	388	403	423
Heating Time (hours)	5.5	5.5	5.5	5.2	3.0	2.0	2.0	1.0
Methane	0.62	0.85	1.4	7.6	20.7	80.1	165	577
Ethylene	n.o. ^a	0.10	10.2	12.7	7.9	24.3	35.8	43.4
Ethane	n.o.	0.03	0.58	6.1	3.2	8.9	20.1	50.5
Methanol	n.o.	n.o.	n.o.	0.11	4.3	11.7	11.6	16.1
Acetaldehyde	0.03	0.18	12.2	26.4	80.2	126	101	155
Propylene	0.10	0.11	10.9	11.6	15.6	37.2	62.6	156
Propane	n.o.	n.o.	1.8	4.2	22.2	12.6	34.7	357
i-Butane	n.o.	n.o.	0.09	0.9	11.6	7.9	20.8	151
i-Butene	n.o.	n.o.	6.3	6.2	8.7	27.5	50.3	124.5
n-Butane + Butenes	n.o.	0.13	0.78	3.0	7.4	17.0	21.8	86.7
Pentanes + Pentenes	17.7	26.4	6.7	13.0	65.8	112	170	609
C ₆	7.3	9.8	2.7	6.2	10.9	24.9	38.0	119
Carbon monoxide	0.24	0.54	14.4	20.3	483	261	548	2,050
Carbon dioxide	143	500	3,260	6,820	24,300	13,400	26,800	101,000
Carbonyl sulfide	0.03	0.04	0.59	1.30	11.5	20.3	31.8	105

^aNot observed.

temperature, are CH₄, C₂H₄, C₂H₆, CH₃CHO, C₃H₆, n-C₄H₁₀, 1- or 2-C₄H₈, C₅, C₆, CO, CO₂ and COS, and these are considered to be constituents present in the formation. Neopentane was not detected in these samples, in contrast to the Athabasca and Cold Lake bituminous sand.¹⁻³

It is observed that a considerable similarity exists in the gases found to be present in the Peace River, Cold Lake and Athabasca deposits with the notable exception of neopentane, which is absent in the Peace River reservoir.¹⁻³ The formation temperatures for the Athabasca, Cold Lake and Peace River reservoirs are 278, 293 and 300°K, respectively. The yields of hydrocarbon gases - with the exception of methane - from three reservoirs at 343°K increase with increasing formation temperature.³

The yields of all materials after a given time are enhanced with increasing temperature, indicating that both thermolysis and desorption processes may be involved in determining the yield. The amounts of volatile materials evolved at 278°K are less from the Peace River bituminous sand than those from the Athabasca and Cold Lake samples.¹⁻³ However, the rates of increase of most of the products with rising temperature are higher in the former than in the latter.

The yields of products as a function of reaction time of Peace River oil sand were studied in detail at 423°K using homogenized bituminous sand samples. The homogenization process was done quickly to minimize additional contact of the bituminous sand with air. The results show that although the product yields increase with increasing reaction time, however, the rates of formation of some of the products actually decreased. This is illustrated for the cases of CH₄, C₂H₄, i-C₄H₈, CO and COS in Figure 1 where rates of formation could be estimated from the slopes of the curves. From these plots it appears that CH₄, CO and COS are primary

products while the principal origins of C_2H_4 and $i-C_4H_{10}$ are secondary in nature.

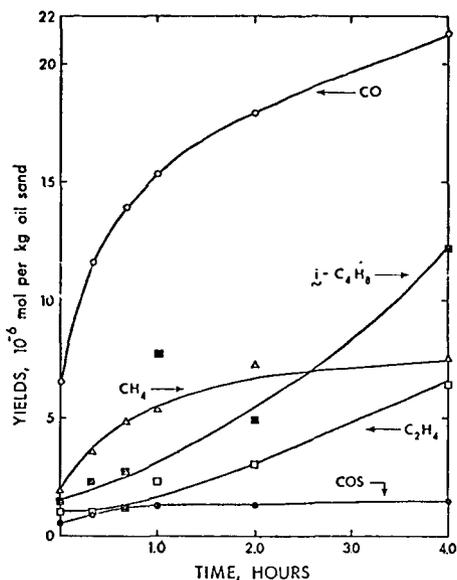


Figure 1. Yields of gases as a function of time in the Peace River oil sand at 423°K.

Kinetic treatment of some of the data in Table I, i.e., plots of the logarithms of rates versus reciprocal temperatures yielded Arrhenius parameters which are listed in Table II. The corresponding values estimated from the Cold Lake and Athabasca data are included in Table II for comparison. The activation energies for the most of the product formation from Peace River oil sand are higher than those from Athabasca or Cold Lake samples. This implies that the former reservoir is more mature than the latter two. It is interesting to note, however, that the activation energy of 4.1 kcal/mol for ethylene formation from Peace River oil sand is much lower than those for Athabasca or Cold Lake, which are 11.8 and 12.4 kcal/mol, respectively. It must be pointed out that all the activation energies measured are very low, indicating that catalytic processes are involved. The rates of product formation at 278°K, calculated by extrapolation of the Arrhenius parameters, are included in Table II. These rates, which are small but significant even at 278°K, indicate that all these oil sand reservoirs of Alberta are presently undergoing similar thermal maturation processes.

The distribution of the products and the values of the Arrhenius parameters for these oil sand formations support our earlier conclusion that these deposits have a common origin and a similar diagenetic history.^{1-3,6}

The yields of the volatile materials collected from Athabasca oil sand at 333°K in the absence and presence of oxygen are listed in Table III. In the absence of oxygen C_1 - C_6 hydrocarbons, CH_3CHO , CO and CO_2 were detected. In the presence of oxygen acetone, propionaldehyde and carbon disulfide are produced in addition to the above compounds. It was observed that oxygen has an enhancing effect on the yields of every product except olefins. These results are in contrast to those

Table II. Arrhenius Parameters for the Thermolysis of Peace River (PR), Cold Lake (CL) and Athabasca (AT) Oil Sands

Product	A (mol hr ⁻¹ kg ⁻¹)			E _a (kcal/mol)			R _{278°K} (mol hr ⁻¹ kg ⁻¹)		
	PR	CL	AT	PR	CL	AT	PR	CL	AT
CH ₄	1.8 x 10 ³	3.1	6.5	16.6	12.8	13.6	1.7 x 10 ⁻¹⁰	3.1 x 10 ⁻¹⁰	1.4 x 10 ⁻¹⁰
C ₂ H ₄	5.5 x 10 ⁻⁵	3.8 x 10 ⁻¹	9.5 x 10 ⁻²	4.1	12.4	11.8	3.3 x 10 ⁻⁸	8.0 x 10 ⁻¹¹	5.1 x 10 ⁻¹¹
C ₂ H ₆	5.3 x 10 ¹		1.2 x 10 ⁻³	15.5		8.3	3.2 x 10 ⁻¹¹		3.5 x 10 ⁻¹⁰
C ₃ H ₆	7.1	9.6 x 10 ⁻²	1.4	12.9	11.2	13.8	4.7 x 10 ⁻¹⁰	1.7 x 10 ⁻¹⁰	2.2 x 10 ⁻¹¹
i-C ₄ H ₆	8.8 x 10 ²		2.9 x 10 ⁻⁵	17.3		6.8	2.2 x 10 ⁻¹¹		1.3 x 10 ⁻¹⁰
1-C ₄ H ₁₀	5.5 x 10 ¹	5.5 x 10 ⁻⁶	1.5 x 10 ⁻⁴	14.8	5.1	8.3	1.3 x 10 ⁻¹⁰	5.6 x 10 ⁻¹⁰	4.5 x 10 ⁻¹¹
CO	7.6 x 10 ³	1.4 x 10 ¹	2.0 x 10 ¹	16.7	9.4	8.8	5.5 x 10 ⁻¹⁰	6.5 x 10 ⁻⁹	2.4 x 10 ⁻⁸
CO ₂	1.1 x 10 ²			9.8			2.1 x 10 ⁻⁶		
COS	4.9 x 10 ¹	3.5 x 10 ⁻³	9.1 x 10 ⁻²	14.9	9.0	11.6	1.0 x 10 ⁻¹⁰	3.3 x 10 ⁻¹⁰	7.3 x 10 ⁻¹¹

Table III. Composition of Gases from the Oxidation of the Athabasca Oil Sand at 333°K^a

Product	O ₂		O ₂	
	Nil ^b	6.37 mmol ^c	Nil ^b	6.37 mmol ^c
	Rates, 10 ⁻⁸ mol hr ⁻¹ kg ⁻¹ oil sand		Rates, 10 ⁻⁸ mol hr ⁻¹ kg ⁻¹ oil sand	
Methane	0.18	0.26	Pentanes + Pentenes	0.55
Ethylene	0.41	0.12	C ₆	0.10
Ethane	0.05	0.06	Acetaldehyde	0.06 ^d
Propylene	0.39	0.14	Acetone	n.o.
Propane	0.01	0.04	Propionaldehyde	n.o.
i-Butane	0.01	0.03	Carbon monoxide	0.08
1-Butene	0.27	0.05	Carbon dioxide	38.8
n-Butane	0.03	0.04	Carbon disulfide	n.o.
Neopentane	0.12	0.32		

^a Each sample contained 200 g oil sand. ^b The sample was heated for 1846 hours. ^c The sample had an initial 411 torr pressure of oxygen and was heated for 1822 hours. ^d Not observed.

obtained at 403°K where oxygen has an enhancing effect on the yields of each product.⁴

The rates or ratios of rates of evolution of some of the gases at 403°K for 4 hrs heating time as a function of oxygen pressure are plotted in Figure 2. It is apparent from these plots that the rate of thermolysis increases with increasing pressure of oxygen; however, the rates of some products rise more rapidly than those of others.

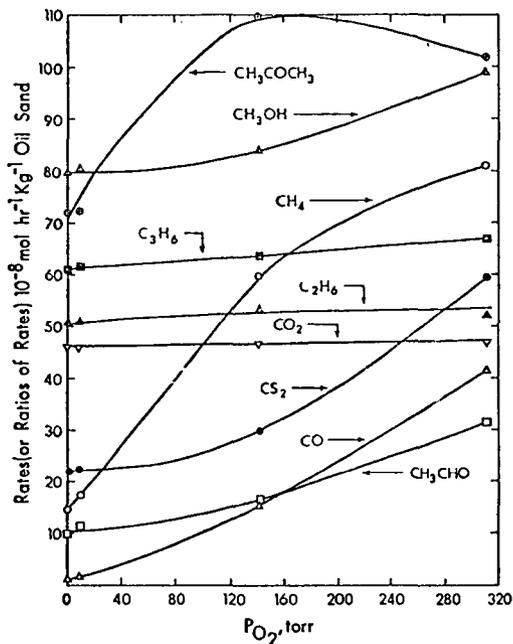


Figure 2. Rates or ratios of rates (based on the rate in the absence of $O_2 = 1.00$) in the thermolysis of Athabasca oil sands at 403°K as a function of oxygen pressure:

- , CH_4 (rates);
- △, CO (rate ratios);
- ▽, CO_2 (rate ratios + 45);
- , CH_3CHO (rate ratios + 10);
- , CS_2 (rates + 20);
- ▲, C_2H_6 (rates + 50);
- , C_3H_6 (rates + 60);
- ⊕, CH_3COCH_3 (rates + 70) and
- △, CH_3OH (rates + 80).

It has been observed that the rates of evolution of CH_4 and CO at 373°K are not appreciably affected in the presence of a few torr oxygen but are markedly enhanced at higher pressures. These results imply that either the product yields are insensitive to trace amounts of oxygen in the system or that the sample was already contaminated with oxygen during storage and handling.

The yields of a few typical products are plotted as a function of time in Figure 3. Those of CH_3CHO , CH_3COCH_3 , C_2H_5CHO and CS_2 initially increase with increasing conversion of the bitumen, then decline, as secondary reactions begin to predominate. The trend in the CO production is not as clearly defined but it is highly improbable that such a stable molecule would undergo secondary reactions; very likely, its yield becomes constant as the precursors become depleted.

CH_3CHO , CH_3COCH_3 and C_2H_5CHO are typical products observed in the thermolysis of hydrocarbons in the presence of molecular oxygen and also have been observed to pass through a maximum with increasing conversion.⁷⁻¹⁰ In these systems, however, CO is a minor product at low conversion and CO_2 is only detected at high conversions, of the order of 30%.¹⁰ In contrast, even at very low conversions, CO and CO_2 are the most abundant products formed upon oxidation of oil sands, and the CO_2 yields are much higher than those of CO . It is tempting to conjecture that these

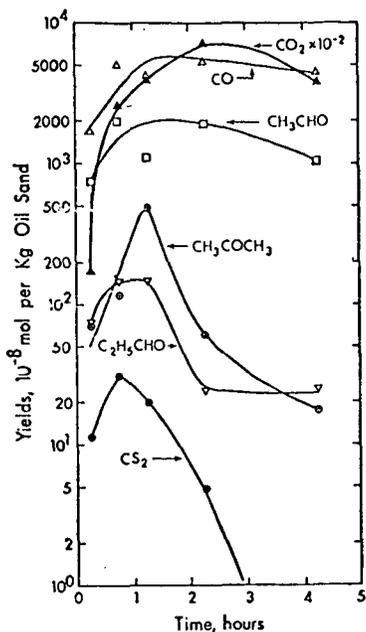


Figure 3. Yields of the thermolysis products of Athabasca oil sand in the presence of oxygen at 403°K as a function of time.

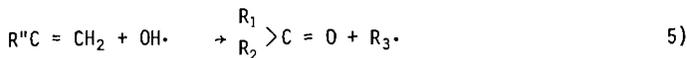
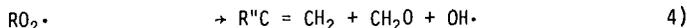
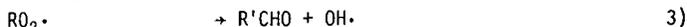
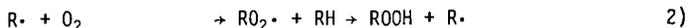
products are formed mainly, if not entirely, from carboxylic acids and aldehydes already present as constituents in the bitumen and that the other identified products are formed *via* oxidation of hydrocarbon precursors; however, we have observed that the CO and CO₂ yields depend to some extent on the nature of the sample and its previous history and therefore much more work is needed before the reaction channels can be elucidated.

The oxidation of hydrocarbons by molecular oxygen involves a complex reaction network; however, 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, initiating new chains.⁷⁻¹²

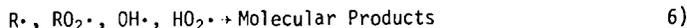
- initiation:



- chain propagation:



- chain termination:



Detailed discussions of this general mechanism have been presented in several publications.^{7,8,10-11} This type of mechanism applies to pure hydrocarbons and its application to a complex system such as Athabasca oil sand is of very limited scope; moreover, it does not account for most of the CO₂ and CO yields evolved in this low temperature region, 278 to 403°K.

It should be noted that the quantities of CO and CO₂ evolved are the most sensitive indicators of the degree of oxidation of the sample and therefore can shed light on its previous history. For example, CO was demonstrably absent among the products evolved upon thermolysis of a fresh oil sand sample from the Athabasca reservoir, strongly suggesting that this deposit has not been exposed to air in the recent past.

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