

THE OXIDATION OF A BITUMEN IN RELATION TO ITS
RECOVERY FROM TAR SAND FORMATIONS

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The bitumen present in the Athabasca tar sand is a viscous material with a specific gravity of approximately 1.03, a viscosity at reservoir temperature, i.e., about 5° to 8°C, of several thousand centipoises and is generally located under an overburden ranging in thickness from a few feet to 200 or more feet in depth. The bitumen itself does not generally command a very high price and its separation and recovery must involve a minimum of expenditure in order to be economically attractive for commercial practice. If conventional mining forms one of the primary steps in the process for recovering bitumen from the sand, it is desirable to find locations where the overburden is light, i.e., up to 80 feet, and where the bituminous sand is relatively thick, i.e., about 150 feet. In regions where the overburden is in excess of 150 feet, the conventional strip mining method is impractical, and in situ methods have to be developed to reduce the costs.

Various methods have been attempted and proposed for the in situ extraction and recovery of oil and bitumen from formations such as the Athabasca tar sand but the majority have been found to be either ineffective in actual field operations or require the use of significant amounts of relatively expensive chemicals. Therefore, an in situ recovery method using inexpensive chemicals and simple chemical reactions to modify asphaltenes and resins in the bitumen fractions which would in turn act as emulsifying agents, would be desirable. Previous investigations in this laboratory on the chemical modification of Athabasca asphaltenes, in particular the work dealing with water-soluble derivatives (1,2) and oxidation of the bitumen fractions (3) prompted an investigation into a process for in situ recovery of bitumen from the sand. The results of our previous investigation (3) presented briefly here for convenience and illustrated in the Figure, showed that some fractions of the bitumen are more susceptible to oxidation than others and it was believed that in situ oxidation of the bitumen per se and subsequent treatment with alkali solutions of sulfites and/or bisulfites would result in water-soluble sulfonated derivatives of these fractions which would then act as emulsifying agents for dispersion and emulsification of the remaining bitumen and hence aid in its transportation to a production well.

EXPERIMENTAL

Oxidation of the bitumen with oxygen:

A weighed amount of dry bituminous material (ca. 50 ml) was placed in a 100-ml round bottomed flask, fitted with a reflux condenser, and heated in a metal bath. Oxygen was passed into the bitumen for varying periods of time after which the product was allowed to cool and shaken with 0.1 M aq. NaOH for 24 hr. The alkaline solution was acidified to pH 2.0 and extracted with methyl ethyl ketone; soluble products were recovered by evaporation of the solvent. The results are illustrated in the Figure.

Oxidation of the bitumen on the sand:

(a) With oxygen and air

Athabasca tar sand (50 grams) was placed in each of four columns and oxidized at 4°C with oxygen and/or air (6 cu. ft./hr.) for 240 hours. The oxidized tar sand was then extracted at 4°C for 96 hours with aqueous solutions of sodium hydroxide and sodium sulfite and bitumen was recovered by acidulation and extraction of the resulting solutions with methyl ethyl ketone. The results are presented in Table 1.

(b) With ozone

A horizontal column, 112 cm long and 5 cm internal diameter, equipped with a cooling jacket, was packed with a weighed amount of Athabasca tar sand. Oxygen containing 6-9% by volume of ozone was passed through the column (0.45 cu. ft./hr.) and, after a specified time, air was injected to flush out excess ozone still present in the sand followed by circulation (~125 ml/hr.) of an eluant to produce a dark brown solution. After acidification with concentrated hydrochloric acid, the bitumen was recovered by extraction with methyl ethyl ketone (MEK) and the product isolated by evaporation of the solvent. The results are presented in Table 2 and the analyses in Table 3. In a further experiment, Athabasca tar sand was packed in a column, placed in a vertical position, and oxygen containing ~6% ozone was passed through the column at 4°C for 48 hours. After thorough blending, 50 grams of ozonized tar sand was placed in each of eight columns and treated at 4°C for 96 hours with water, aqueous sodium hydroxide, aqueous sodium sulfite, and aqueous sodium sulfite plus sodium hydroxide solutions. The bitumen from the resulting solutions was recovered by acidulation and extraction with methyl ethyl ketone, as described above; the results are presented in Table 4.

RESULTS AND DISCUSSION

The results of our previous work (3), outlined here in the Figure, show that whilst oxidation of the bitumen components, by oxygen, is a feasibility, the temperatures required for conversion to significant amounts of soluble materials are quite high. Nevertheless, after 8 hr., the proportions of the fractions converted to soluble products at 125°C are equivalent to ca. 3% w/w of the original bitumen. However, prolonged oxidation may lead not only to water soluble organic acids but also to extensively degraded materials with low dispersing and/or emulsifying power. To avoid this, and to increase the water solubility, the bitumen was first oxidized at temperatures similar to those that exist in the formation (~4°C). Oxidation by oxygen and air at these temperatures is slow under these conditions (Table 1) but soluble materials were produced by subsequent treatment with aqueous alkaline solutions or aqueous alkaline sulfite solutions.

The successes achieved here prompted further investigations into the use of a somewhat stronger oxidant, i.e. ozone*, in the hope that a more rapid reaction rate would be achieved for the purposes of the current work. Accordingly, treatment of the bitumen on the sand with ozonated oxygen followed by contact with alkaline sulfite solutions did in fact produce the desired effect (Table 2). Elemental compositions and molecular weights of the original Athabasca bitumen and the different reaction products (Table 3) illustrate the pronounced changes in carbon, hydrogen and oxygen concentrations, and also the relative increase of sulfur contents in the ozonized and subsequently sulfite-treated derivatives. Confirmation that reaction (sulfonation) of the oxidized bitumen and alkali sulfite had occurred was derived from several sources.

* Redford (4) has reported that ozone has a pronounced effect on the bitumen and can be used to produce communication paths within a tar sand formation.

In the first instance, sulfur analyses have shown an overall increase of sulfur contents of ozonized and subsequently alkali sulfite-treated derivatives, as compared to the sulfur contents of derivatives obtained by treating ozonized tar sand with water or sodium hydroxide solution (Tables 3 and 4). Secondly, infrared spectra of the oxidized and extracted bituminous derivatives, besides exhibiting the carbon-hydrogen absorptions at frequencies of 2900 to 3000 cm^{-1} and 1450 to 1580 cm^{-1} , exhibited broad absorptions centered at about 3400 cm^{-1} and 1700 cm^{-1} , due to hydroxyl and carbonyl groups. However, an extra absorption of moderate intensity at 1030 to 1050 cm^{-1} appeared only in the spectra of the sodium sulfite-treated derivatives - attributable to the presence of sulfonic group(s) characteristic of this type of sulfonated carbonaceous material, e.g., humic acids (5). Finally, nuclear magnetic resonance spectroscopy indicated significant differences between the two extracts. Alkaline-extracted material had an aliphatic proton distribution similar to that recorded previously for the resins and low molecular weight asphaltenes extracted from the Athabasca bitumen through use of organic solvents (6,7). Material produced by sodium sulfite extraction had a more complex and less well defined aliphatic proton distribution; also evident was a region centered at 9.35 ppm (0.65 τ) and assigned to protons in acidic locations.

The data presented in Table 4 give an indication of the extractive ability of water and aqueous solutions of sodium hydroxide and sodium sulfite on oxidized tar sand, and the surface tension-reducing powers of these bituminous derivatives are illustrated in Table 5. It is apparent that the oxidized and subsequently sulfonated bituminous derivatives have greater surface tension-reducing powers and much greater ability to extract bitumen from the oxidized tar sand than does water or sodium hydroxide solution. We presume that the fractions prone to oxidation are the dark oils and resins (Figure) leaving the bulk of the bitumen relatively unchanged.

In retrospect, we have shown that oxidation of bitumen on Athabasca sand can occur by means of an oxygen-containing gas. Furthermore, sulfur-bearing group(s) can then be introduced into the molecular structures of the oxidized materials which renders the bituminous materials more hydrophilic, increases their surface tension-reducing power, and also increases their dispersing and emulsifying power. We are of the opinion that the present method therefore provides a plausible means for recovery of bitumen from the tar sand by the following steps: (a) *in situ* oxidation of the tar sand bitumen (e.g. by injecting an oxygen-containing gas into the tar sand formation); (b) injection of an aqueous alkaline sulfite or bisulfite solution into the oxidized tar sand formation to react and form the water-soluble sulfonated asphalt-type bituminous materials; (c) formation of an aqueous emulsion between the soluble sulfonated material and the oil in the tar sand formation; (d) circulation of the emulsion formed *in situ*, with the purpose of extracting oil from the formation, and separation of the oil from the emulsion by any of the known techniques.

It is presumed that the aqueous solution of the water-soluble sulphonated materials would circulate throughout the formation and establish free flow paths. We are also inclined to believe that this process, when combined with other recovery techniques, would afford an easier, more efficient and more economic recovery of bitumen and the oxidation, with subsequent sulfonation, is compatible with other *in situ* recovery techniques, e.g., steam injection, cold emulsification, low- or high-pressure injection of fluids.

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Oxidative Degradation of Bitumen Fractions

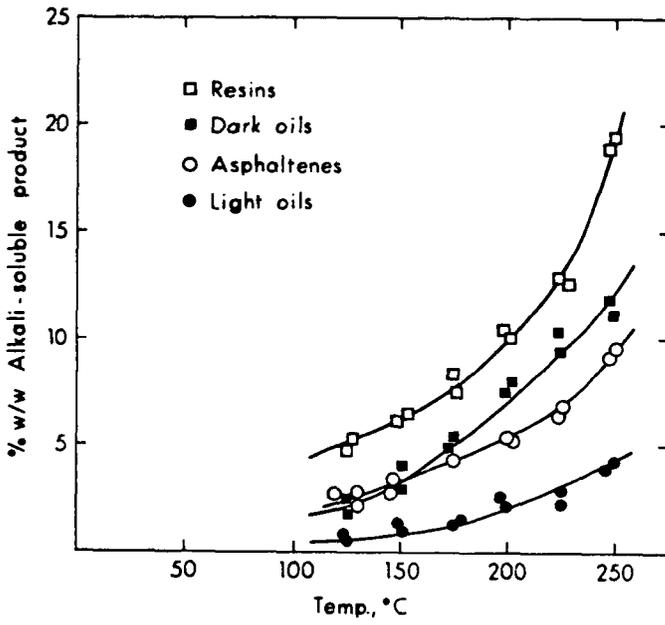


Table 1. Extractive abilities of aqueous solutions on oxidized tar sand

Column	Oxidizing agent	Eluant*	Solution pH	Weight of Extracted Bitumen (g)**	% Extracted Bitumen
1	oxygen	0.2% NaOH recycled	9.9	0.085	1.32
2	oxygen	Na ₂ SO ₃ (0.1M) + NaOH (0.2%) recycled	9.9	0.124	1.92
3	air	0.2% NaOH recycled	9.9	0.023	0.36
4	air	Na ₂ SO ₃ (0.1M) + NaOH (0.2%) recycled	9.9	0.122	1.89

* Volume = 0.2 litre

** Weight of bitumen in tar sand = 12.9%

Table 2. Ozonization of Athabasca tar sand

Method	Tar sand charged in g.	Bitumen in charge g.	Oxidation Temp. °C	Time hr.	Eluant	Circulation Temp. - Time	Solution pH (approx.)	Product Recovered g.	%	Surface tension ¹ dynes/cm.
I	3190	412	6	48	0.05 M aq. Na ₂ SO ₃ /2 litre	5°C - 24 hr.	2	16.0	4	45.1
II	3530	455	25	48	{ 0.1 M aq. Na ₂ SO ₃ /1 litre 0.1 M aq. NaOH/1 litre	25°C - 96 hr.	2	24.8	5	46.5
						25°C - 24 hr.	9	18.5	4	45.1
III	3450	445	25	48	{ 0.15 M aq. NaOH/1 litre 0.1 M aq. Na ₂ SO ₃ /1 litre water/1.6 litre	a) 25°C - 72 hr.	12	45.2	10	
						b) 60°C - 24 hr.		7.2	2	
						c) 97°C - 5 hr.				
IV	3790	489	25	48	{ 0.2 M aq. NaOH/1 litre 0.2 M aq. Na ₂ SO ₃ /1 litre	a) 25°C - 5 hr.	12	12.5	3 ^a	
						b) 60°C - 48 hr.		63.0	13 ^a	48.0
						c) 97°C - 10 hr.				
V	3900	503	25	96	{ 0.2 M aq. Na ₂ SO ₃ /1 litre 0.2 M aq. NaOH/1 litre	25°C - 72 hr.	12	97.4	19	

¹ 0.1% solution in 0.1 N NaOH

^a Toluene extract

^b MEK extract

Table 3. Analysis of unozonized and ozonized-sulfonated bitumen from Athabasca tar sand

Sample Description	Carbon %	Hydrogen %	Oxygen* %	Sulfur %	Nitrogen %	Ash %	Molecular Weight	Remarks
Unozonized original bitumen	81.3	10.1	1.7	4.1	0.5	2.4	497	Toluene extract
Method I	63.2	7.4	24.4	3.8	0.3	0.8	321	Methyl ethyl ketone extract
Method II Step 1	55.7	6.4	27.9	4.8	0.2	1.7	311	Methyl ethyl ketone extract
Method II Step 2	62.7	7.5	19.1	6.0	0.3	2.6	395	Methyl ethyl ketone extract
Method III Step 1	55.6	6.4	27.7	5.4	0.2	2.7	-	Methyl ethyl ketone extract
Method IV	79.7	10.2	5.0	4.2	0.3	1.5	567	Toluene extract
Method IV	52.6	6.1	26.8	6.4	0.2	8.4	533	Methyl ethyl ketone extract
Method V	50.8	5.8	32.2	4.2	0.2	3.1	229	Methyl ethyl ketone extract
Ozonized depleted bitumen	81.1	10.1	2.2	4.0	0.5	2.0	504	Toluene extract

* Oxygen contents were determined directly.

Table 4. Extractive abilities of aqueous solutions on oxidized tar sand

Column No.	Eluant*	Solution pH	Surface Min.	Tension Max.	Weight of Extracted Bitumen(g)**	% Extracted Bitumen	% Sulfur in Extracted Bitumen
1	H ₂ O	5.5	64.3	68.8	0.168	2.61	0.97
2	H ₂ O recycled	5.5	64.2	68.7	0.157	2.44	1.96
3	Na ₂ SO ₃ (0.1M) passed through	8.5	48.0	54.8	0.194	3.01	0.89
4	Na ₂ SO ₃ (0.1M) recycled	8.0	43.4	49.8	0.440	6.84	4.09
5	Na ₂ SO ₃ (0.1M) + NaOH (0.2%) passed through	-	41.2	50.4	0.610	9.48	6.7
6	Na ₂ SO ₃ (0.1M) + NaOH (0.2%) recycled	adjusted to 12-13.5	36.5	42.0	0.510	7.92	5.69
7	NaOH (0.2%) passed through	-	40.4	54.0	0.237	3.68	2.12
8	NaOH (0.2%) recycled	adjusted to 12-13	40.6	43.2	0.221	3.43	2.06

* Volume: ≈2.2 litres; recycle = 0.2 litre

** Weight of bitumen extracted by toluene from 50 g ozonized tar sand = 6.435 g

Table 5. Surface tensions of ozonized and ozonized-sulfonated bitumen

% Concentration	Ozonized bitumen	Ozonized-Sulfonated bitumen
0.1	62 dynes/cm	48 dynes/cm
0.5	62 dynes/cm	41 dynes/cm
1.0	52 dynes/cm	39 dynes/cm