

## PHYSICAL PROPERTIES OF CONVENTIONAL AND BIODEGRADED OILS

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### INTRODUCTION

During our studies on the origin and evolution of the Alberta oil sands we studied the bacterial attack on conventional crude oils, and came to the conclusion that the oil sand bitumen was the end product of the biodegradation of a liquid pooled oil (1). The biodegradation of a light, fluid conventional crude oil yielded a heavy, dense bitumen after bacterial attack, (2,3,4) which resembled the naturally occurring bitumen found in the Alberta oil sand formations (1).

The fact that biodegraded oils and oil sand bitumens have such different physical properties from conventional crude oils is of great importance to the petroleum industry. A fluid fossil fuel may be extracted from a reservoir by sinking a well and permitting the fluid to flow out of the ground under its own or assisted hydrostatic pressure, and it may be transported by pipeline or vessel to a remote plant for treatment. The oil sand bitumen, on the other hand, is a heavy tarry material, solid at ambient local temperature, which is held in an adhesive matrix around grains of sand in a solid geological formation underground. This requires difficult, and hence expensive, mining or *in-situ* recovery, and the bitumen released from the sand matrix must be treated and refined on-site since it is not easily transported to a remote refinery.

The three physical criteria of importance in this field of petroleum exploitation are Pour Point: -the temperature above which the oil is a liquid and will flow, Gravity: -the density of the material, and Viscosity: -its ability and resistance to flow.

We have investigated various oils, and bitumens and some of their major component fractions for these criteria, and noted their properties before and after biodegradation in an attempt to rationalize their physical behavior.

### MATERIALS AND METHODS

Samples investigated are shown in Table I. Prudhoe Bay is a conventional crude oil from Alaska, and its incubation for 168 hours with a culture of mixed bacteria yielded sample PB 168 (1). This latter material has been shown to resemble chemically the Alberta oil sand bitumens. Sample PB s.l. is the product of the incubation of Prudhoe Bay oil with a culture of the yeast *Saccharomyces lipolytica*. This organism removes completely the *n*-alkanes (5). Sample At is a typical oil sand bitumen from one of the four major deposits in Alberta. The Lloydminster crude oil is a heavy naphthenic crude oil found in a reservoir system in the Mannville formation in Eastern Alberta. It is thought to be related to the four oil sand formations bitumens (6,7) and is an example of an intermediate biodegradation product (1). The three component fractions, the saturate, aromatic and polar materials of the samples At and PB were isolated from the respective oils by column chromatography (1). Sample PB Sat. A.F. was a sample of PB Sat. from which the *n*-alkanes, *iso*- and *ante-iso* alkanes had been removed by molecular sieve inclusion (8) and urea adduction (9).

The Pour Point was determined by observing the temperature at which the liquid sample ceased to flow on cooling, and also the temperature at which this same sample, when frozen, commenced to flow on heating. The figures quoted are averages of these two values.

The gravity was determined by densitometry at 25°C. The values quoted are A.P.I. gravities calculated according to the formula 
$$\text{A.P.I. gravity} = \frac{141.5}{\text{specific gravity}}$$
 - 131.5. Hence water has a value of A.P.I. 10. More dense materials have lower values, less dense materials have values greater than 10.

Viscosities were measured at 38°C and 99°C with a Brookfield Viscosimeter on 5 ml samples, absolute values being corrected against known standards. Values quoted are in Saybolt Universal Seconds (s.u.s.) and are calculated using the formulae:

$$\frac{\text{Centipoise}}{\text{Specific Gravity}} = \text{Centistokes}$$

and S.U.S. = Centistokes x 4.635. Since oils and bitumens are not homogenous materials, the values quoted should not be regarded as absolute, but rather viewed for comparative purposes.

## RESULTS AND DISCUSSIONS

The chemical analyses of the materials investigated are illustrated in Figure 1. From this it may be seen that sample PB was a conventional crude oil containing a full complement of *n*-alkanes, acyclic isoprenoids, oligo- and polycyclic saturated alkanes, oligo- and polycyclic aromatics and polar materials. Biodegradations by the yeast (sample PB s.l.) removed solely the *n*-alkanes and minor amounts of small-ring aromatic materials. Biodegradation by the bacteria (sample PB 168) had removed all the *n*-alkanes and the acyclic isoprenoids, some mono and dicyclic saturates, and small ring aromatics, leaving the polar material unchanged (1).

Sample L1 was similar to sample PB s.l. in that the *n*-alkanes were absent, but the acyclic isoprenoids (the pristane and phytane family) were still present. However, as typical of the oils found in the Mannville formation of Alberta, there was a relatively large amount of polar material present. Similarly, sample At, the oil sand bitumen, resembled the fully biodegraded sample PB 168, excepting for, again, the larger amount of polar material present (1).

### a) Pour Point

The values obtained for the pour points of the samples are shown in Table II. The conventional crude oil, sample PB, had a pour point of -2°C. Removing the *n*-alkanes (sample PB s.l.) caused this figure to fall to -12°C; i.e. the oil was still liquid at an even lower temperature. Increasing the amount of polar material (as in sample L1) caused a marked increase in the pour point value to +3°C. Further biodegradation to completion (as in sample PB 168 and At) caused a further rise in the pour point, with the amount of polar material having little additional effect.

Looking at the values for the component fractions, it may be noted that the polar material had a very high pour point, and therefore the proportions present in a mixture had a marked effect on the overall pour point. The more polar material being present, the higher the pour point became.

Biodegradation caused a rise in the pour point values in the aromatic fraction, due to the removal of the lighter components (sample PB Aro, sample At Aro).

The most striking difference was observed in the saturate fractions. Sample PB Sat had a pour point of +1°C, due to the presence of the solid waxy *n*-alkane series. Removal of this (sample PB Sat A.F.) caused a marked fall in the pour point, hence the fall in values observed between samples PB and PB s.l. Further biodegradation (i.e. removal of the acyclic isoprenoids and mono- and di-cyclic saturates) caused a further decrease in the pour point values.

Thus biodegradation by the *Saccharomyces lipolytica* may be said to have "upgraded" the oil, in that its pour point had fallen due to the removal of the *n*-alkanes. Further biodegradation in the saturate and aromatic fractions caused a "downgrading" by increasing the pour point of the oil. The overriding factor involved in the pour point was the quantity of polar material present. The higher the percentage of polar material present, the higher the pour point became.

### b) Viscosity

The Viscosities obtained are tabulated in Table III.

Sample PB had a low viscosity, and thus flowed easily. Removing the *n*-alkanes (sample PB s.l.) increased this value from 208 to 1006. Adding polar material (sample L1) further increased this value to 3610. Complete biodegradation of sample PB increased the viscosity sharply to over five thousand (sample PB 168), and the addition of further polar material (sample At) more than doubled this figure. The values for the component fractions explain this in that biodegradation had only a minor effect on

the viscosity of the saturate and aromatic fractions. Since the polar material was a solid at 38°C, and was extremely viscous even at 99°C, its presence was the most important factor in the determination of the viscosity of an oil. Hence the Mannville oils (samples Ll and At) were all highly viscous at 38°C due to their high content of polar material, and were more viscous than their low-polar counterparts even at 99°C.

c) Gravity

Table IV lists the values obtained for the A.P.I. gravities of the oils. The conventional crude oil sample PB had a relatively high A.P.I. gravity, which fell to close to that of water on complete biodegradation with the bacteria (sample PB 168), and also on biodegradation with the *Saccharomyces lipolytica* (sample PB s.l.). The values for the samples At and Ll were likewise close to that of water. The values for the saturates (samples At Sat, PB Sat, PB Sat A.F.) revealed high values unaffected by biodegradation, and the values for the aromatic fractions fell only to a minor extent. It may thus be surmised that the concentration of polar material was the most important factor involved in the determination of the gravity of an oil (see Figure 1).

CONCLUSIONS

- i) Conventional crude oils are characterised in their physical properties by a high A.P.I. gravity, low pour point and low viscosity. Biodegraded oils and bitumens have low A.P.I. gravities, high pour points and high viscosities.
- ii) The most influential factor involved in the physical properties of oils is the amount of polar material present.
- iii) The selective removal of *n*-alkanes by the yeast *Saccharomyces lipolytica* caused an anomalous "upgrading" of the oil in that the pour point was decreased.

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Table I  
The Oils Examined

PB	Prudhoe Bay Crude. Location: Alaska (British Petroleum Ltd.)
PB 168	Prudhoe Bay Crude incubated 168 hours, mixed bacterial culture.
PB s.l.	Prudhoe Bay Crude incubated 21 days with <i>Saccharomyces lipolytica</i> culture.
L1	Lloydminster Crude. Location: 16-3-50-1 W4. Well depth 600 m. (Husky Oil Ltd.).
At	Athabasca Oil Sand Bitumen. Location: 24-92-10 W4. Quarry depth 22 m. (Great Canadian Oil Sands Ltd.).
PB Sat	Prudhoe Bay Saturate Fraction
PB Aro	Prudhoe Bay Aromatic Fraction
PB Pol	Prudhoe Bay Polar Fraction
PB Sat A.F.	Prudhoe Bay Saturate Fraction free of <u>n</u> -alkanes.
At Sat	Athabasca Saturate Fraction
At Aro	Athabasca Aromatic Fraction
At Pol	Athabasca Polar Fraction

Table II  
Pour Point Values (°C)

<u>Sample</u>	<u>Pour Point</u>	<u>Sample</u>	<u>Pour Point</u>	<u>Sample</u>	<u>Pour Point</u>
PB	-2	PB Sat	+1	At Sat	-55
PB s l	-12	PB Aro	-55	At Aro	-25
PB 168	+7	PB Pol	+50	At Pol	+45
L1	+3	PB Sat A.F.	-35		
At	+8				

Table III  
Viscosity Values 38°C; 99°C  
(Saybolt University Seconds)

<u>Sample</u>	<u>Viscosity</u>	<u>Sample</u>	<u>Viscosity</u>	<u>Sample</u>	<u>Viscosity</u>
PB	208 ; 131	PB Sat	<50 ; <50	At Sat	<50 ; <50
PB s l	1006 ; 215	PB Aro	<50 ; <50	At Aro	850 ; <50
PB 168	5280 ; 117	PB Pol	solid ; >20000	At Pol	solid ; >20000
L1	3610 ; 260	PB Sat A.F.	<50 ; <50		
At	11680 ; 513				

Table IV  
Gravity Values (°API)

<u>Sample</u>	<u>Gravity</u>	<u>Sample</u>	<u>Gravity</u>	<u>Sample</u>	<u>Gravity</u>
PB	27	PB Sat	36	At Sat	30
PB s 1	12	PB Aro	17	At Aro	4
PB 168	10	PB Pol	-10	At Pol	-10
L1	13	PB Sat A.F.	36		
At	10				

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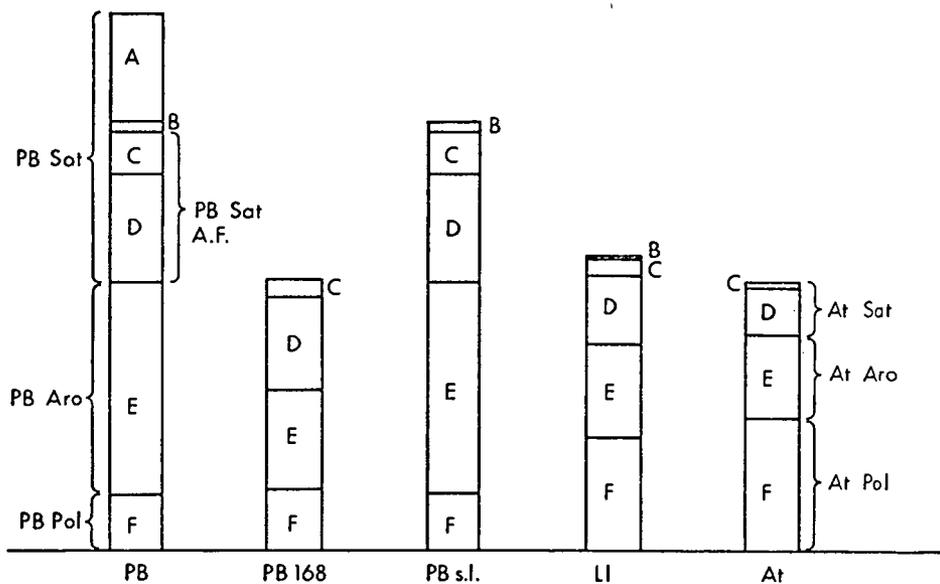


Figure I: Gravimetric analyses of the Oils and bitumens.

- A. Sieve adduct
- B. Urea adduct
- C. Thiourea adduct
- D. Thiourea non-adduct
- E. Aromatic Fraction
- F. Polar fraction

} Saturate fraction